Universitat de Girona

METAL IONS REMOVAL FROM POLLUTED WATERS BY SORPTION ONTO EXHAUSTED COFFEE WASTE. APPLICATION TO METAL FINISHING INDUSTRIES WASTEWATER TREATMENT

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Girona, September 2014

To my parents

致我的父母

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A journey of a thousand miles begins with a single step.

(Laozi)

千里之行，始于足下。

(老子)

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LIST OF ABBREVIATIONS

BFGS	Broyden, Fletcher, Goldfarb and Shanno
CMC	Critical micelle concentration
COD	Chemical oxygen demand
DAF	Dissolved-air flotation
DCM	Dichloromethane
EU	European Union
E1	Industrial effluents 1
E2	Industrial effluents 2
E3	Industrial effluents 3
EC	Exhausted coffee waste
EC1	Exhausted coffee waste extracted by dichloromethane
EC2	Exhausted coffee waste extracted by dichloromethane and ethanol
EC3	Exhausted coffee waste extracted by dichloromethane, ethanol and water
EC4	Exhausted coffee waste extracted by dichloromethane, ethanol, water and 1% sodium hydroxide
ECA	Exhausted coffee waste with particle size between 500 and 1000 µm
ECB	Exhausted coffee waste with particle size between 250 and 500 µm
ED	Electrodialysis
EDTA	Ethylenediaminetetraacetate salts
EDX	Energy dispersive X-Ray
EIMS	Electron impact mass spectra
EtOH	Ethanol
FAAS	Flame atomic absorption spectroscopy
FTIR	Fourier transform infrared ray
GAE	Gallic acid equivalents
GC	Gas chromatography
GFC	Glucose tolerance factor
K_d	Distribution constant
LD_{50}	Median lethal dose
LOD	Limit of detection
MCL	Maximum contaminant level
MEUF	Micellar enhanced ultrafiltration
MS	Mass spectrometer
NF	Nanofiltration
PAA	Polyacrylic acid
PAC	Polyaluminium chloride

PAM	Polyacrylamide
PEI	Polyethyleneimine
PEUF	Polymer enhanced ultrafiltration
PFS	Polyferric sulfate
pH_{pzc}	pH point zero charge
PI	Polarity index
pK_a	Acid dissociation constant
QP	Quadratic programming
R1	Residual effluent of 6.0 mM Cr(VI)-2.0 mM Cu(II) binary mixtures after biosorption by exhausted coffee waste
R2	Residual effluent of 6.0 mM Cr(VI)-4.0 mM Cu(II) binary mixtures after biosorption by exhausted coffee waste
RO	Reverse osmosis
S1	Synthetic solutions 1
S2	Synthetic solutions 2
SDS	Sodium dodecyl sulfate
SEC	Static exchange capacity
SEM	Scanning election microscopy
SIA	Sequential injection system
SRB	Sulfate-reducing bacteria
SRT	Statistical rate theory
SS	Suspended solids
SSR	Sum of Square Residuals
ST	Total suspended solids
TMP	Transmembrane pressures
TMS	Trimethylsilyl
TPC	Total polyphenol content
UF	Ultrafiltration
UL	Upper intake level
USEPA	United States Environmental Protection Agency
WSPs	Water-soluble polymers

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SUMMARY

Wastewaters from metal finishing industries usually contain high amount of toxic metal ions especially hexavalent chromium and pose high risk to the environment and human beings. The traditional technology to treat this kind of wastewaters is based on chromium electrolysis coupled to precipitation and filtration in order to eliminate reduced trivalent chromium and other metal ions from wastewater. Due to the drawbacks associated with traditional methods, such as a quite large consumption of chemical reagents and the frequent requirement of equipment maintenance, there is an urgent need for sustainable technologies in industrial effluent treatment.

Biosorption using agricultural by-products has attracted attention as an effective and economic method for metal ions removal from wastewaters. This thesis focuses on the use of exhausted coffee waste, an abundant by-product from soluble coffee production, as a low-cost biosorbent for the treatment of water and industrial wastewaters containing hexavalent chromium and other metal ions.

First of all, the physical and chemical characteristics of exhausted coffee waste were studied in order to evaluate the potential of this material for biosorption.

In the next step, the sorption mechanisms of exhausted coffee waste towards hexavalent chromium and divalent copper and nickel were investigated through identifying the role of each chemical components, both non-structural (extractives) and structural compounds, in metal ions sorption. The raw material was treated through sequential extraction to remove different components and the material and the extracts were subjected to metal ions sorption. By comparing the sorption efficiency of different treated samples and raw exhausted coffee waste, the chemical components responsible for biosorption were identified: the lignin moieties were actively involved in the hexavalent chromium sorption/reduction and the sorption of formed trivalent chromium; the carboxylic groups were related to divalent metal ions sorption.

After understanding the sorption mechanisms, exhausted coffee waste was used as sorbent for Cr(VI) sorption from Cr(VI)-Cu(II) binary mixtures in a stirred batch reactor. This sorbent was effective for hexavalent chromium removal via sorption/reduction of Cr(VI) and sorption of formed Cr(III). After biosorption, around 85% of chromium was eliminated and the rest remained in solution in its trivalent form. It was found that the presence of copper exerted a synergistic effect on chromium removal. A kinetics model was developed, calibrated and validated by using independent sets of data. The model described and simulated successfully Cr(VI) sorption by EC in the presence of Cu(II).

A suitable post-treatment method was investigated to remove the non-sorbed trivalent chromium and copper ions after biosorption, so as the treated solutions were suitable for discharge.

The effectiveness of biosorption by using exhausted coffee waste and the subsequent post-treatment encouraged us to apply the overall process as a new technology for the treatment of effluents from metal finishing industries. The behavior of this technology was assessed taking into account the Cr(VI) sorption/reduction and the elimination of formed Cr(III) and other metal ions. Exhausted coffee waste biosorption proved to be alternative to current electrolysis method for Cr(VI) reduction from industrial effluents due to its less consumption of reagents and energy. Therefore, our proposed wastewater treatment technology based on biosorption appeared to be sustainable and promising for the detoxification of metal finishing effluents containing hexavalent chromium and other metal ions.

This thesis will be of great importance for metal finishing industries to lower wastewater treatment costs and for coffee manufacturers for re-utilization and possible commercialization of the coffee waste.

RESUM

Les aigües residuals de les industries de recobriment de superfície contenen gran quantitat d' ions metàl·lics tòxics que suposen un gran risc pel medi ambient i pels éssers humans. La tecnologia que s'utilitza tradicionalment per tal de tractar aquest tipus d'aigües residuals està basada en l'electròlisi acoblada a processos de precipitació i filtració per tal d'eliminar el crom trivalent producte de la reducció de crom hexavalent i altres ions metàl·lics. Degut als desavantatges associats a la utilització dels mètodes tradicionals com són el gran consum de reactius químics i el manteniment dels equips, és urgent trobar tecnologies sostenibles per al tractament d'efluents industrials.

La biosorció mitjançant la utilització de sub-productes de l'agricultura té el seu atractiu perquè és un mètode efectiu i econòmic per eliminar metalls de les aigües residuals. Aquesta tesis s'ha centrat en la utilització de marro de cafè, un subproducte molt abundós que resulta de la producció de cafè soluble, com a biosorbent per al tractament d'efluents industrials que contenen crom hexavalent i altres ions metàl·lics.

En primer lloc, el residu de cafè es va caracteritzar física i químicament per tal d'avaluar el potencial d'aquest material per a la seva utilització en processos de bioadsorció.

El següent pas, va ser investigar els mecanismes d'adsorció de crom hexavalent i metalls divalents com el coure i el níquel emprant el residu. La investigació es va dur a terme a través de la identificació del paper en el procés d'adsorció de cadascun dels components químics del residu, tant els components no estructurals (extractius) com estructurals. El material es va sotmetre a una extracció seqüencial per tal d'eliminar alguns dels components i els residus de cada extracció es van posar en contacte amb solucions contenint hexavalent crom, coure o níquel. Per comparació de l'eficiència en l'adsorció de metalls del residu sense extraure cap component amb la dels diferents extractes aïllats es van identificar els components responsables de la biosorció. Es va trobar que els residus de lignina estaven activament involucrats en l'adsorció i reducció de crom hexavalent i adsorció del crom trivalent format i que els àcids carboxílics estaven relacionats amb l'adsorció de metalls divalents.

Un cop entesos els mecanismes d'adsorció, el marro de cafè es va utilitzar per a l'adsorció de Cr(VI) de mescles binàries Cr(VI)-Cu(II) en un reactor de tanc agitat. El sorbent va ser efectiu per a l'eliminació de crom via adsorció/reducció de Cr(VI) i adsorció de part del crom trivalent format. Després de la biosorció, al voltant del 85% del crom va ser eliminat i la resta va romandre en solució en la forma de crom trivalent. Es va trobar que la presència de coure en la mescla binària exerceix un efecte sinèrgic sobre l'eliminació de crom.

Un model cinètic va ser desenvolupat, calibrat i validat amb diferents conjunts de dades experimentals.. El model descriu molt bé el procés d'eliminació de crom en presència de coure.

Es va investigar un possible post-tractament per tal d'eliminar el crom trivalent i el coure que no havia sigut adsorbit durant el procés de bioadsorció de manera que l'aigua fos adequada per al seu abocament.

L'eficàcia de la biosorció utilitzant el marro de cafè seguida d'un post-tractament de precipitació va encoratjar-nos a aplicar el procés global com una nova tecnologia per al tractament d'efluents d'indústries de recobriment de superfícies. El comportament d'aquesta tecnologia va ser avaluat tenint en compte l'adsorció/reducció de crom i l'eliminació del crom trivalent format. El residu de cafè va demostrar ser una alternativa a l'electròlisi que s'utilitza actualment per a la reducció de crom en efluents industrials. La tecnologia proposada estalvia reactius i energia, és sostenible i obre noves expectatives per a la descontaminació de efluents que contenen crom hexavalent i altres ions metàl·lics.

Aquesta tesi contribueix en gran mesura a rebaixar els costos del tractament d'aigües residuals d'indústries de recobriment de superfícies. Així mateix representa una gran oportunitat pels productors de cafè pel que fa a la reutilització del residu i per tant a la seva comercialització.

RESUMEN

Las aguas residuales de las industrias de tratamiento de superficies contienen una gran cantidad de iones metálicos tóxicos que suponen un gran riesgo para el medio ambiente y para los seres vivos. La tecnología que se utiliza tradicionalmente para el tratamiento de este tipo de aguas residuales se basa en la electrolisis acoplada a procesos de precipitación y filtración para eliminar el cromo y les iones metálicos. Debido a las desventajas asociadas a la utilización de los métodos tradicionales como son el gran consumo de reactivos químicos y de energía así como también el coste del mantenimiento de los equipos es urgente encontrar tecnologías sostenibles para el tratamiento de efluentes industriales contaminados con cromo.

La bioadsorció utilizando subproductos de la agricultura son atractivos debido a que es una metodología efectiva i económica para eliminar metales. Esta tesis se centra en la utilización del residuo de café, subproducto abundante que resulta de la producción del café soluble, como adsorbente de cromo y otros metales divalentes.

En primer lugar, se caracterizó física y químicamente el residuo de café con el fin de evaluar el potencial de este material para su utilización en procesos de bioadsorción.

El siguiente paso fue investigar los mecanismos de adsorción de cromo hexavalente y metales divalentes como el cobre y el níquel utilizando como sorbente el residuo de café. La investigación se llevó a cabo mediante la identificación del papel de cada uno de los componentes en el proceso de adsorción, tanto de los componentes no estructurales (extractivos) como estructurales. Para ello, el material se sometió a una serie de extracciones con diferentes disolventes con el fin de ir eliminando componentes. Por comparación de la eficiencia en la adsorción de metales presentada por el residuo y los diferentes extractos sólidos se identificaron los componentes químicos responsables de la bioadsorción. Se encontró que los residuos de lignina estaban activamente involucrados en la adsorción y reducción de cromo hexavalente y la adsorción del cromo trivalente formado y que los ácidos carboxílicos estaban relacionados con la adsorción de metales divalentes.

Una vez conocidos los mecanismos de adsorción, el residuo de café se utilizó para la adsorción de Cr(VI) de mezclas binarias Cr(VI)-Cu(II) en un reactor de tanque agitado. El sorbente fue efectivo para la eliminación de cromo vía adsorción/reducción de cromo hexavalente y adsorción de parte del cromo trivalente formado. Después de la bioadsorción, alrededor del 85% del cromo fue eliminado y el resto permaneció en solución en su forma trivalente. Se encontró que la presencia de cobre en la mezcla binaria ejerce un efecto sinérgico en la eliminación de cromo.

Se desarrolló un modelo cinético, se calibró y se validó con conjuntos de datos independientes. El modelo describió muy bien el proceso de eliminación de cromo en presencia de cobre en solución acuosa.

Se investigó un posible post-tratamiento para eliminar el cromo trivalente y el cobre que no habían sido adsorbidos durante el proceso de bioadsorción con el objetivo de que el agua fuese apta para su vertido..

La eficacia de la bioadsorción utilizando el residuo de café seguida de un post-tratamiento de precipitación nos animó a aplicar el proceso global como una nueva tecnología para el tratamiento de efluentes de industrias de tratamiento de superficies. El comportamiento de dicha tecnología fue evaluada teniendo en cuenta la adsorción/reducción de Cr(VI) y la adsorción de Cr(III) formado. El residuo de café demostró ser una buena alternativa a la electrólisis que se utiliza a menudo para la reducción de cromo de efluentes industriales. La tecnología que se propone ahorra reactivos y energía, es sostenible y abre nuevas expectativas para la descontaminación de efluentes que contienen cromo hexavalente y otros iones metálicos.

Esta tesis contribuye en gran medida a rebajar los costes del tratamiento de aguas residuales de industrias de recubrimiento de superficies. Al mismo tiempo representa una gran oportunidad para los productores de café soluble ya que se reutiliza un residuo y que éste se puede comercializar.

摘要

金属加工业废水通常含有高毒性的六价铬和多种其他金属，给环境和人类健康带来了不可忽视的危害。传统金属加工业废水处理技术基于添加化学试剂来还原六价铬离子，结合后续的絮凝沉淀和分离技术来去除水中还原的三价铬离子和其他金属离子。此种技术需要消耗大量的化学试剂和能量，并产生大量的二次污染物金属污泥，因此，寻求高效环保的处理工艺成为了亟待研究的课题。

利用农产品废弃物进行重金属的生物吸附，因其高效、经济等特点，引起了人们的广泛关注。本篇论文着力于研究速溶咖啡生产过程中产生的咖啡残渣对水体中六价铬和其他金属离子的吸附，建立了一种基于生物吸附的新型污水处理工艺并将其应用于对电镀废水的处理中。

首先，为了判断咖啡残渣的生物吸附潜力，我们对咖啡残渣的物理和化学特性进行了全面地表征。

其次，为了进一步研究咖啡残渣对六价铬和二价金属离子（铜和镍）的吸附机理，我们对咖啡残渣的各个化学组分，包括非结构性组分（提出物）和结构性组分，在吸附中发挥的作用分别进行了鉴定。经过分步萃取，指定的化学组分从咖啡残渣中陆续分离出来。通过比较萃取前后的咖啡残渣样品对金属的吸附效果，从而鉴定出对金属有效的化学组分：木质素在六价铬的吸附/还原和三价铬的吸附中均起到了积极的作用；羧基官能团与二价金属离子的吸附有关。

了解了咖啡残渣对水中金属离子的吸附机理之后，通过搅拌反应器中的动态实验，我们对此种材料对水中六价铬的吸附动力学进行了探讨。结果证明了咖啡残渣对水中六价铬的高效去除。六价铬可逐渐被咖啡残渣吸附/还原，15%左右的铬离子以还原的三价铬形式残留在吸附后的废水中。此外，水中二价铜离子的存在对铬离子的整个吸附过程表现出一定协同作用。基于吸附动态数据而建立的拟合数学模型很好地描述并模拟了二价铜离子存在下咖啡残渣对六价铬的动态吸附。

吸附过程之后，沉淀法可用于去除未被完全吸附的三价铬离子和二价铜离子，从而使处理后的废水远远达到污水排放标准。

基于以上结果，我们提议了一项利用咖啡残渣对金属的生物吸附并结合后续处理过程的污水处理新型工艺。作为本篇论文的最后一项也是最重要的一项任务，这项技术成功地运用在了对含

有六价铬和多种其他成分的电镀工业废水的处理中。与传统处理工艺相比，基于咖啡残渣生物吸附的工业废水处理工艺无需消耗大量的化学试剂和能量，为金属加工业废水的净化提供了经济环保的可替代方案。

本论文从吸附机理，吸附动力学直至工艺设计证实了农作物废弃物——速溶咖啡生产残渣在金属加工业废水处理中的应用价值。在追求可持续发展，提倡绿色能源的当今社会，研究结果对于降低工业废水的处理成本和充分利用农产品加工业的固体废物均具有远大的意义。

CHAPTER I.

GENERAL INTRODUCTION

1. GENERAL INTRODUCTION TO METAL POLLUTION IN WATER RESOURCES

Water is essential for living beings and it is a scarce resource on the Earth. With the development of industries such as surface finishing, metal plating, leather tanning, mining and smelting, paper producing and dyeing, etc., an increasing amount of effluents containing chemical substances especially metal ions is directly or indirectly discharged into the environment, either freshwater or marine environment (Agarwal et al., 2006; Pal and Banat, 2014). The metal pollution has become one of the most serious environmental problems nowadays (Abdulsalam et al., 2014; Samiey et al., 2014). About one fifth of the world's population does not have access to sage water, and two fifths suffer the consequences of unacceptable sanitary conditions (Bhatnagar et al., 2014). In Catalonia, the discharges, waste and leaks resulted from industrial activity act as sources of metal pollution for various water systems, affecting 6.7% of rivers, 2.9% of coastal waters and 64.2% of groundwater (ACA, 2014). Facing with this reality, it has been growing concern about the toxic effects of metal ions in the aquatic environment and the removal of these toxic metals from water and wastewater.

Metal pollution in water resources will be introduced from the following aspects, starting with the origin and toxicity of metal pollutants, then an overview of their treatment techniques, then introduction of a new method using exhausted coffee waste as biosorbent for metal removal from wastewaters.

2. METAL POLLUTANTS

Metal pollutants are among the most toxic and persistent pollutants in aquatic environment (Hsieh et al., 2004). Metal ions can be incorporated into food chains and concentrated in aquatic organisms to a level that affects their physiological state. Due to the non-biodegradable properties and the toxicity and carcinogenicity to living organisms (Bulut and Tez, 2007), many metal ions are regarded as priority pollutants (Hastuti et al., 2013; Hsieh et al., 2004). Among them, the toxic metals of particular concern in treatment of industrial

wastewaters include chromium, copper, nickel, zinc, cadmium, lead, iron, aluminium and mercury. The description of these toxic metals will be presented as following.

2.1. Chromium

Chromium is a first-series transition element from group VIB of the periodic table. It is a brittle, hard, lustrous and silver-grey metal with a melting point at 1907^{o}C, boiling point at 2672^{o}C and density of 7.19 g/cm^{3} at 20^{o}C. Chromium is the 21st most abundant mineral in the Earth's crust at about 100-140 mg/kg (Barnhart, 1997; Pechova and Pavlata, 2007; Saha et al., 2011). It can exist in oxidation states ranging from -2 to +6, however the 0, +2, +3, and +6 forms are commonly encountered. Elemental chromium (0) is not naturally present in the environment and is biologically inert. Cr(II) is a strong reductant (E^{0} = -0.41 V) and can rapidly oxidize and decompose when in contact with air or water, producing trivalent species. Cr(III) is the most stable oxidation state in which chromium is found in living organisms. It is soluble in acidic solutions, forming hexahedral complexes with ligands such as oxalate and sulphate ions. And as a trivalent cation, Cr(III) has a strong affinity for negatively-charged ions and colloids in soils, plants, micro-organisms and animals and as a result, it is relatively immobile (Viti and Giovannetti, 2007). The second most common oxidation state is Cr(VI), with strong oxidizing potential (E^{0} = +1.41 V), particularly in acidic media. Cr(VI) can persist in polyatomic anionic form as CrO_4^{2-} under strong oxidizing conditions (Pechova and Pavlata, 2007; Cohen et al., 1993).

Therefore, chromium normally exists as the relatively immobile chromium (III) under reducing conditions and the highly mobile chromium (VI) under oxidizing conditions.

However, natural chromates are rare. Chromium is derived in influent mainly from industrial sources (Ivaka, 2009), where both chromium (III) and chromium (VI) may occur. Chromium (III) is emitted from oil combustion, sewer sludge incineration, cement production, municipal waste incinerations and refractories. Cr(VI) due to its acidic and oxidant properties, its emissions are from various industries such as chromium plating, lead chromate, pigments, ink manufacture, dyes, tanning, wood preservatives, textiles, etc. (Mishra and Anand, 2012).

Chromium is an essential micro-nutrient in the diet of animals and humans for the metabolism maintenance. It is biologically active in facilitating insulin binding to receptors at the cell surface (Lukaski, 2000; Pechova and Pavlata, 2007). Chromium is also included in the complex named glucose tolerance factor (GFC). If the daily intake is below some minimal level, symptoms of chromium deficiency will occur including impaired glucose tolerance, glycosuria, and elevations in serum insulin, cholestero1, and total triglycerides (Cohen et al., 1993).

On the other hand, elevated levels of chromium are always toxic. Chromium is widely known to cause allergic dermatitis as well as toxic and carcinogenic effects in animals and humans (Stohs and Bagchi, 1995), although the toxicity and fate of chromium in the body varies with its oxidation state. As the main existence of chromium in the environment, Cr(III) seems relatively innocuous because cellular membranes appear to be quite impermeable to most Cr(III) complexes while Cr(VI) exhibits 100 times higher toxicity than Cr(III) (Gómez and Callao, 2006). Cr(VI) toxicity is related to its easy diffusion across the cell membrane in prokaryotic and eukaryotic organisms and subsequent Cr(VI) reduction in cells, which gives free radicals that may directly cause DNA alteration as well as toxic effects (Viti and Giovannetti, 2007). As a result, Cr(VI) affects human physiology, accumulates in the food chain and cause severe health problems ranging from simple skin irritation to lung carcinoma (Khezami and Capart, 2005). In epidemiological studies on cancer in human, elevated lung cancer risks have been clearly and consistently observed in CrO_4^{2-} production, in CrO_4^{2-} pigment production and also in chromium plating using chromic acid (Saha et al., 2011).

Therefore, the maximum contaminant level (MCL) of Cr(VI) in drinking water is proposed at 0.01 mg/L by the California Department of Public Health of United States, and the MCL of total chromium is regulated at 0.1 mg/L by the United States Environmental Protection Agency (USEPA) (CPDH, 2014). The maximum acceptable total chromium in drinking water in Europe Union (EU) is regulated at 0.05 mg/L (EU, 2014).

2.2. Copper

Copper is synthesized in massive stars and is present in the Earth's crust at a concentration of about 50 mg/kg, where it occurs as native copper or in minerals such as the copper sulfides chalcopyrite and chalcocite, copper carbonates azurite and malachite, copper (I) oxide mineral cuprite (Jeong, 2003). Copper is a ductile metal from group IB of the periodic table with very high electrical conductivity (59.6×10^6 S/m), a melting point at 1083^{o}C, boiling point at about 2590^{o}C and density of 8.93 g/cm^3 at 20^{o}C. Pure copper is orange-red and acquires a reddish tarnish when exposed to air, it is one of only four elemental metals with a natural color other than gray or silver. Besides small amounts of metallic copper, copper can form a rich variety of compounds usually with oxidation states +1 and +2, either binary compounds (e.g. oxide, sulfide and halide) or coordination complexes with ligands (e.g. oxyanions form complexes, organocopper complexes) (Karamat et al., 2013).

Due to its high electrical conductivity, copper is widely used in industrial processes (e.g. dyeing, paper, petroleum, copper/brass-plating and copper-ammonium rayon manufacturing) as well as in agriculture (e.g. fungicides) (Rao and Ikram, 2011; Trakal et al., 2014). As a result, copper is massive appeared in industrial effluents, mainly as the soluble form Cu(II), which can travel through the food chain via bioaccumulation (Subbaian et al., 2011)

Although Cu(II) is an essential micronutrient for metabolism of human beings, the high doses can cause anemia, stomach and intestinal disorder and kidney and liver damage, thus bring about serious toxicological concerns, such as vomiting, cramps, convulsions, even death (Paulino et al., 2006). Therefore the MCL of Cu(II) in drinking water is defined at 1.3 mg/L by USEPA (Hossain et al., 2012) and the maximum acceptable copper in drinking water in EU is regulated at 2.0 mg/L (EU, 2014).

2.3. Nickel

Nickel belongs to transition metals from group VIIIB of the periodic table. It is a silvery-white, hard, malleable and ductile metal with a melting point at 1453^{o}C, boiling point at about 2732^{o}C and density of 8.91 g/cm^3 at 20^{o}C. Nickel is thought to compose Earth's inner core in combination with iron (Stixrude et al., 1997). It is one of four elements that are ferromagnetic

around room temperature. It is also corrosion-resistant because of its slow rate of oxidation at room temperature. The most common oxidation state of nickel is +2, which forms compounds with all common anions such as sulfide, sulfate, carbonate, hydroxide, carboxylates and halides.

Nickel is chiefly valuable in the formation of alloys. More than 70% of nickel produced annually is devoted to the production of alloys. It is also widely used in metal finishing industries, in the manufacture of batteries and in welding procedures, as a catalyst in large scale processes, and in the glass and ceramics industry (Nurchi and Villaescusa, 2008).

Humans may be exposed to nickel by breathing air, drinking water, eating food or smoking cigarettes. In small quantities nickel is essential, but the exceeding uptake might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis (Borba et al., 2006). And it is known that nickel is human carcinogen. Thus EU limit for nickel in drinking water is 0.02 mg/L (EU, 2014).

2.4. Zinc

As the 24th most abundant element in the Earth's crust, zinc is a bluish-white, lustrous, diamagnetic metal. Zn is the first element from group IIB of periodic table with a density of 7.14 g/cm^3 at 20^{o}C, relatively low melting point (420^{o}C) and boiling point (907^{o}C). Its only common oxidation state is +2 and sphalerite (ZnS) known as zinc blende is the most frequently found in zinc minerals.

Zinc is the fourth most widely used metal in alloy production, as anticorrosion coating of steel and iron, in electrical devices, in rubber and tyre industries, in paints, in pesticides and as chemical reagents in number of applications (Nurchi and Villaescusa, 2008).

Zinc is the second most abundant trace element for human health. It appears in the active site of variety of enzymes and is important for the physical processes. Thus Zinc is relatively nontoxic, even if daily doses greater than 100 mg during several months may lead to different disorders. However, too much zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia (Oyaro et al., 2007). This feature allows a non strictly regulated zinc value in drinking water.

2.5. Cadmium

Cadmium is a soft, malleable, ductile, bluish-white divalent metal from group IIB of periodic table with a density of 8.65 g/cm^3 at 20^{o}C. Cadmium presents in the Earth's crust with an average concentration between 0.1 and 0.5 mg/kg with low melting point (321^{o}C) and boiling point (767^{o}C). The main oxidation state of cadmium is +2, in the forms greenockite (hexagonal CdS), hawleyte (cubic CdS), otavite ($CdCO_3$) and cadmoselite (CdSe) presented in rare minerals. Normally cadmium occurs as a minor component in most zinc ores and therefore is a byproduct of zinc production.

Cadmium exposes human health to severe risks: chronic exposure of cadmium results in kidney dysfunction and high levels of exposure will result in death (Maret and Moulis, 2013). Thus cadmium is specifically regarded as a human carcinogen (Fu and Wang, 2011). The maximum acceptable cadmium in drinking water is regulated by EU at 0.005 mg/L (EU, 2014).

For a long time, cadmium was widely used in battery production, pigment industry and for corrosion resistant plating on steel. Taking into account its high toxicity, the use of cadmium has decreased generally. Nowadays, the common use is in cadmium telluride solar panels, and the nickel-cadmium batteries are replaced with nickel-metal hydride and lithium-ion batteries (Nurchi and Villaescusa, 2008).

2.6. Lead

Lead is the heaviest non-radioactive element and has the highest atomic number (82) of all of the stable elements. It is a volatile, soft, malleable and silvery metal from group IVA of periodic table with a melting point at 327^{o}C, boiling point at 1749^{o}C and density of 11.34 g/cm^3 at 20^{o}C. Lead occurs in small amounts but widespread on Earth, usually in its oxidation state +2. Galene (PbS) is found to be the most common lead mineral, together with cerussite ($PbCO_3$) and anglesite ($PbSO_4$).

Because of its easiness to be extracted and to work with, in the past two centuries, lead was dominantly applied in producing leaded gasoline production, lead pigment and lead containing pipes (Yavuz et al., 2007). However, lead can be emitted as an atomic vapor when

lead-containing materials are heated to a certain temperature. Lead is also emitted as reactive PbBrCl compounds upon the combustion of leaded gasoline (Boyle et al., 2014). Nowadays, these leaded products have been phased out in many countries in efforts to reduce toxic pollution that affected the environment and humans (Richmond-Bryant et al., 2014).

Environmental contamination by lead probably dates back to Bronze Age (Nurchi and Villaescusa, 2008). Lead is also the metal that has the most damaging effects on human health. Lead can cause central nervous system damage, and is known to damage the kidney, liver and reproductive system, basis cellular processes and brain functions. The toxic symptoms can be anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damage (Naseem and Tahir, 2001). Thus EU restricts the use of lead in many electronics applications if it presents in a homogenous material in amounts exceeding 0.1% by weight. The concentration for nickel in drinking water is limited also by EU at 0.01 mg/L (EU, 2014). Lead is still widely used in the industries including smelting, coal combustion, lead-acid batteries, glassware and ceramics with an increasing production and consumption. Because of its rare occur in nature, its recycling has been a valuable option for sustainability (Wang and Kanter, 2014).

2.7. Iron

Iron is a lustrous silvery-gray metal in the first transition series from group VIII of periodic table with a melting point at 1538^{o}C, boiling point at 2862^{o}C and density of 7.87 g/cm^{3} at 20^{o}C. It is the fourth most common element in the Earth's crust. Elemental iron occurs in low oxygen environments but is reactive to oxygen and water. Of the wide range of oxidation states of iron (-2 to +6), +2 and +3 are most common, where iorn(II) compounds are called ferrous and iron(III) compounds ferric. The iron compounds produced on the largest scale in industry are iron(II) sulfate ($FeSO_4 \cdot 7H_2O$) and iron(III) chloride ($FeCl_3$). The latter is useful in water purification and sewage treatment as a coagulant-flocculant (Sahu and Chaudhari, 2013).

Iron is the most widely used metal for metal-processing industry such as the construction of machinery and machine tools, automobiles, the hulls of large ships, and structural components for buildings.

Iron is a necessary trace element for all living organisms. It plays an important role in biology, forming complexes with molecular oxygen in hemoglobin and myoglobin, which are common oxygen transport proteins in vertebrates. Iron is also the metal used at the active site of many important redox enzymes dealing with cellular respiration and oxidation and reduction in plants and animals (Asliyuce et al., 2010). However, if the ingested iron exceeds the tolerable upper intake level (UL) (45 mg/day for adults, 40 mg/day for children, the excessive levels of iron in the blood can cause cell injury. Iron is low-molecular-weight forms may play a catalytic role in the initiation of free radical reactions. The resulting oxyradicals have the potential to damage cellular lipids, proteins and carbohydrates and result to a wide-ranging impairment in cellular function and integrity (Britton et al., 2002).

2.8. Aluminium

Aluminium is a silvery white, soft, ductile metal from group IIIA of periodic table with a low density of 2.70 g/cm^3 at 20^{o}C and high boiling point at 2470^{o}C, melting point at 660^{o}C. It is the most abundant metal in the Earth's crust, making up about 8% by weight of the Earth's solid surface. Aluminium forms strong chemical bonds with oxygen and the great majority compounds of aluminium is in its oxidation state +3, in the forms of alumina, sulfates, chlorides and niche compounds.

Because of the abundance and relatively low toxicity, aluminium compounds are extensively used in various industries based on food and beverages, drugs, packing materials, and construction, dyeing industries. Considering the difficulty in extracting aluminium from ore, all the aluminium has to be theoretically 100% recyclable without any loss of its natural qualities. Furthermore, aluminum sulfate ($Al_2(SO_4)_3$) known as alum is traditionally used as a coagulant-flocculant in the treatment of municipal waters (Kumari and Ravindhranath, 2012). Despite the fact that aluminum sulfate has an median lethal dose (LD_{50}) of 6207 mg/kg, the undesirable presence of the element in the residue of water treatment and the widespread occurrence in the environment and in commerce can also pose multiple problems to organisms (Madhan et al., 2014; Woodburn et al., 2011). If the accumulation of aluminium exceeds the

body's excretory capacity, chronic toxicity will occurs affecting the bone, the central nervous system and the brain, resulted in morbidity and mortality (Exley and House, 2012).

2.9. Mercury

Mercury is a heavy, silvery-white metal from group IIB of periodic table with a high density of 13.53 g/cm^3 at 20^{o}C, very low boiling point at 357^{o}C and freezing point at -39^{o}C. Being commonly known as quicksilver, is the only metallic element that is liquid at standard conditions for temperature and pressure. Mercury is extremely rarely present in the Earth's crust, having an average crustal abundance by mass of only 0.08 mg/kg, but extremely toxic. It exists most commonly in its oxidation states +2, as the red pigment vermilion mercuric sulfide (cinnabar), and mercuric chloride and methylmercury which can result to mercury poisoning.
Mercury has been found in the wastewaters coming from color-alkali manufacturing industry, oil refinery, paint, pharmaceutical, paper and pulp and battery manufacturing industries (Manohar et al., 2002). it, mercury is used primarily for the manufacture of industrial chemicals or for electrical and electronic applications, such as in thermometers, especially ones which are used to measure high temperatures, and in fluorescent lamps as gaseous mercury, while most of the other applications are slowly phased out due to its high toxicity (Surmann and Zeyat, 2005).
Mercury is a neurotoxin that can cause damage to the central nervous system. The major effects of mercury poisoning manifest as neurological and renal disturbances as it can easily pass the blood-brain barrier and affect the foetal brain. High concentration of Hg(II) cause impairment of function and kidney pulmonary, chest pain and dyspnousea (Namasivayam and Kadirvelu, 1999). The classic example of mercury poisoning is in Minamata Bay, where 887 people were dead by the consumption of seafood contaminated with methylmercury, resulting from the $HgCl_2$ discharge from a chemical plant.
Thereby mercury is defined as the 6th most toxic in a universe at 6 million substances (Nascimento and Chartone-Souza, 2003). Its concentration in drinking water is regulated in EU at 0.001 mg/L (EU, 2014). In summary, the toxic metals from the earth's geological structures such as chromium, copper, nickel, zinc, cadmium, lead, iron, aluminium and

mercury are widely used in modern industry, producing large volumes of metal-rich effluents and posing significant risks for the environment and human health. These metal ions have to be removed from water resources to meet their regulation in drinking water through several technologies.

3. METAL IONS REMOVAL TECHNOLOGIES

A large increasing amount of wastewaters containing metal ions is generated with the progressive development of industry. As a result of the inappropriate discharge or inadequately treatment, metal ions from the contaminated waters have become one of the critical environmental problems. Since metals can persist and accumulated in all the living organisms, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment (Barakat, 2011). For minimizing these hazardous pollutants, various techniques have been employed with varying degree of success for the removal of toxic pollutants from water and wastewater, including chemical precipitation (Oncel et al., 2013), coagulation-flocculation (Zheng et al., 2011), flotation (Veetil et al., 2013), membrane filtration (Liu et al., 2014), ion exchange resin (Wang et al., 2014), solvent extraction (Zoubi, 2013) and adsorption (Keng et al., 2014). The commonly used techniques will be introduced as follow.

3.1. Chemical precipitation

Chemical precipitation is effective and so far the most widely used process for metal removal from inorganic effluent. After pH adjustment to basic conditions, the dissolved metal ions are converted to insoluble solid phase via a chemical reaction.

The forming precipitates can be separated from the water by sedimentation or filtration. And the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation, sulfide precipitation, metal chelating precipitation and electrochemical precipitation.

3.1.1. Hydroxide precipitation

The most widely used chemical precipitation technique is hydroxide precipitation due to its relative simplicity, low cost and ease of pH control. The solubility of the various metal hydroxides are minimized in the pH range of 8.0-11.0. The conceptual mechanism of metal removal by hydroxide precipitation is presented in Equation 1.1:

$$M^{n+}_{(aq)} + n(OH)^{-}_{(aq)} \leftrightarrow M(OH)_{n\,(s)}\downarrow \qquad (1.1)$$

where M^{2+} and OH^- represent the dissolved metal ions and the precipitant, respectively, while $M(OH)_n$ is the insoluble metal hydroxide, and n is the coefficient of the reaction component, depending on the oxidation state of metal ions.

A variety of hydroxides has been used to precipitate metal from wastewater, such as CaO (lime), $Ca(OH)_2$ and NaOH. Based on the low cost and ease of handling, lime is the preferred choice of base used in hydroxide precipitation at industrial settings. Lime precipitation can be employed to effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/L. In hydroxide precipitation process, the addition of coagulants such as alum, iron salts, and organic polymers can enhance the removal of heavy metals from wastewater (Oncel et al., 2013).

3.1.2. Sulfide precipitation

Sulfide precipitation is also an effective process for the treatment of toxic metal ions. Compared with hydroxide precipitation, the solubility of the metal sulfide precipitates are dramatically lower, and hence the sulfide precipitation process can achieve a high degree of metal removal over a broad pH range. Metal sulfide sludge also exhibits better thickening and dewatering characteristics than the corresponding metal hydroxide sludge.

The mechanism governing metal removal by pyrite and synthetic ion sulfides was determined as chemical precipitation at low pH (<3) due to H_2S generation (Equations. 1.2 and 1.3) and adsorption at high pH (in the range of 3-6).

$$FeS_{(s)} + 2H^{+}_{(aq)} \rightarrow H_2S_{(g)} + Fe^{2+}_{(aq)} \qquad (1.2)$$

$$2M^{n+}_{(aq)} + nH_2S_{(g)} \rightarrow M_2S_{n\,(s)}\downarrow + 2nH^{+}_{(aq)} \quad (1.3)$$

where M^{n+} and H_2S represent the dissolved metal ions and the precipitant, respectively, while M_2S_n is the insoluble metal sulfade, and n is the coefficient of the reaction component, depending on the oxidation state of metal ions.

Recently, new sulfide precipitation process has been developed based on sulfate-reducing bacteria (SRB) (Kousi et al., 2007). SRB oxidize simple organic compounds under anaerobic conditions and the SRB transform the sulfates into hydrogen sulfide (Equation 1.4)

$$3SO_4^{2-} + 2CH_3CH(OH)COOH \rightarrow 3H_2S + 6HCO_3^{-} \quad (1.4)$$

where $CH_3CH(OH)COOH$ stands for simple organic compounds. Hydrogen sulfide reacts with soluble metals to form insoluble metal sulfides (Equation 1.3).

However, there are potential dangers in the use of sulfide precipitation process. As we know, metal ions often in acid conditions and sulfide precipitants in acidic conditions can result in the evolution of toxic H_2S fumes. It is essential that this precipitation process is performed in a neutral or basic medium. Moreover, metal sulfide precipitation tends to form colloidal precipitates that cause some separation problems in either settling or filtration processes.

3.1.3. Chelating precipitation

In spite of that the conventional precipitation processes are effective for water purification; it is difficult to meet the increasing stringent environmental regulations at present. As an alternative, many companies use chelating precipitants (e.g., trimercaptotriazine, potassium/sodiumthiocarbonate and sodiumdimethyldithiocarba- mate to precipitate heavy metals from contaminated waters. Since the commercial metal precipitants either lack the necessary binding sites or pose too many environmental risks, some new and more effective precipitants have been synthesized to meet the discharge regulation, such as 1,3-benzenediamidoethanethiol ($BDET^{2-}$) dianion, N,N'-bis-(dithiocarboxy) piperazine (BDP), dithiocarbamate-type supramolecular heavy metal precipitants, chelator-dipropyl

dithiophosphate and 1,3,5-hexahydrotriazinedithiocarbamate (HTDC) (Fu and Wang, 2011). The new synthesized chelators have been tested to remove metal ions up to 99.9%.

3.1.4. Electrochemical precipitation

To improve the removal of metal ions from contaminated water, electrical potential is used as an alternative to the conventional chemical precipitation technique. Electrochemical precipitation is based on the precipitation of metal ions as hydroxides. The hydroxide ion results from the cathodic reduction of water, following the process expressed in Equation 1.5:

$$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^- \quad (1.5)$$

then the hydroxide ion reacts with metal ions in the medium to form the precipitation, as presented in Equation 1.1.

In general, electrochemical precipitation process can treat inorganic effluent with a metal concentration higher than 2000 mg/L, at either acidic or basic conditions, depending on the characteristics of the electrodes (Subbaiah et al., 2002). Without a continuous feeding of redox chemicals, electrochemical precipitation reduces the amount of sludge, which could be a remarkable advantage.

Furthermore, chemical precipitation processes have also been successfully used for metal ions removal in combination with other methods, followed by nanofiltration (Gonzalez-Munoz et al., 2006) and ion exchange process (Papadopoulos et al., 2004) as a second step.

Generally speaking, chemical precipitation processes are relatively simple and convenient to operate. However, they have also some limitations. Firstly, conventional chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Secondly, the precipitation generates large volumes of relatively low density sludge, which can prevent metal precipitation, thus requires further treatment and could have long-term environmental impacts.

3.2. Coagulation-flocculation

Coagulation-flocculation is one of the most important physico-chemical operations used in wastewater treatment which can be achieved by chemical and electrical ways. Principally, the process destabilizes colloidal particles by adding a coagulant and results in sedimentation. To increase the particle size, coagulation is followed by the flocculation of the unstable particles into bulky floccules. The general approach for this technique includes pH adjustment and involves the addition of ferric/alum salts as the coagulant to overcome the repulsive forces between particles (Zheng et al., 2011).

Specifically, coagulation is the addition of a positively charged ion of metal salt or catalytic polyelectrolyte that results in particle destabilization and charge neutralization. Coagulation targets the colloid particles of size 10^{-7} to 10^{-14} cm in diameter. The colloid particles exhibit Brownian movement through the water; their surface is negatively charged so they repel one another, and from a stable dispersed suspension. If colloid particles or ions of positive electric charge are added it neutralizes the electric negative charge. Flocculation refers to the successful collision that occurs when destabilized particles are driven toward each other by the hydraulic shear force in the rapid mix and flocculation basin. Flocculation is the action of polymers to form bridges between the flocs and bind the particles into large agglomerates or clumps. It agglomerates of a few colloids then quickly bridge together to form microflocs, which is turned into visible floc masses (Sahu and Chaudhari, 2013). The process can be seen in Figure 1.1.

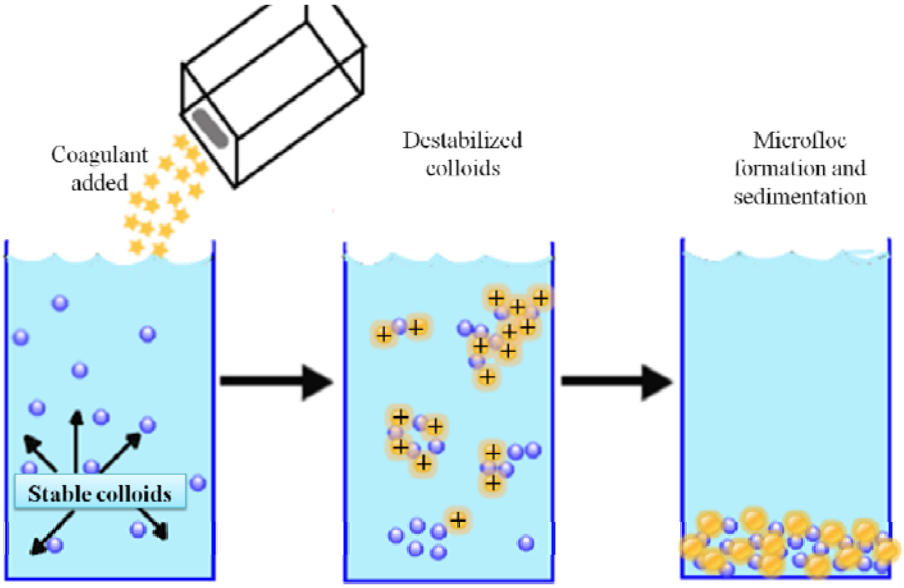


Figure 1.1 Coagulation-flocculation process

Coagulation-flocculation can treat inorganic effluents with a metal concentration of less than 100 mg/L or higher than 1000 mg/L. pH around 11.0 has been found to be effective to improve the metal removal. Today many kinds of coagulants-flocculants, such as polyaluminium chloride (PAC), polyferric sulfate (PFS) and polyacrylamide (PAM), are widely used in the treatment of wastewater. Improved sludge settling, dewatering characteristics, bacterial inactivation capability, sludge stability are the major advantages of coagulation-flocculation. However, the high operational cost due to chemical consumption and the potential hazardous of the toxic sludge is still the drawbacks of this technique.

In the two recent decades, electrocoagulation has been improved as a better alternative to the conventional coagulation (Jung and Pyo, 2008; Keerthi et al., 2013). In electrocoagulation the flocculating agent is generated by electro-oxidation of a sacrificial anode, generally made of iron or aluminium. In this process, the treatment is done without adding any chemical coagulant or flocculant, thus reducing the amount of sludge which must be disposed.

3.3. Flotation

Flotation originated in mineral processing is extensively employed to separate metal ions from a liquid phase using bubble attachment. The attached particles are separated from the suspension of metal ions by the bubble rise. The conventional flotation can be classified into

five categories: dispersed-air flotation, dissolved-air flotation (DAF), vacuum air flotation, electroflotation, and biological flotation. Among the various types of flotation, DAF is most commonly used for the treatment of metal-contaminated wastewater since 1990s. In the last decade, it has been a trend of the combination of flotation and other physico-chemical treaments, ions flotation and precipitate flotation are two successful alternatives widely applied in metal ions removal from wastewaters.

DAF allows micro-bubbles of air to attach to the metal ions in the water, develops agglomerates with lower density than water, and causes the flocs to rise through the water and accumulating at the surface where they can be removed as sludge (Waters, 1990). Ion flotation is based on imparting the ionic metal species in wastewaters hydrophobic by the use of surfactants and subsequent removal of these hydrophobic species via air bubbles (Polat and Erdogan, 2007). And precipitate flotation is based on the formation of precipitate and subsequent removal via attachment to air bubbles (Capponi et al., 2006).

Flotation can be employed to treat inorganic effluent with a metal concentration of less than 50 mg/L or higher than 150 mg/L. It has big potential for industrial application due to the low cost materials and effective removal efficiency especially for small particles.

3.4. Membrane filtration

Membrane filtration technology is another process with considerable attention for the treatment of metal-contaminated effluent, because of its high removal efficiency, easy operation and space saving. Depending on the type of membrane, it can be classified as: ultrafiltration, nanofiltration, reverse osmosis and electrodialysis.

3.4.1. Ultrafiltration (UF)

UF is a membrane technique working at low transmembrane pressures (TMP) for the removal of dissolved and colloidal material. Since the pore sizes of UF membranes (5-20 nm) are larger than dissolved metal ions in the form of hydrated ions or as low molecular weight complexes, these ions would pass easily through UF membranes. To obtain high removal efficiency of

metal ions, the micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) was proposed.

MEUF has been proved to be an effective separation technique to remove metal ions from wastewater (Landaburu-Aguirre et al., 2009). This separation technique is based on the addition of surfactants to wastewater. When the concentration of surfactants in aqueous solutions is beyond the critical micelle concentration (CMC), the surfactant molecules will aggregate into micelles that can bind metal ions to form large metal-surfactant structures. The micelles containing metal ions can be retained by a UF membrane with pore sizes smaller than micelle membrane. To obtain the highest retentions, surfactants of electric charge opposite to that of the metal ions have to be used, such as the anionic surfactant sodium dodecyl sulfate (SDS). Metal removal efficiency by MEUF depends on the characteristics and concentrations of the metals and surfactants, solution pH, ionic strength and parameters related to membrane operation. The retentate is the concentrated solution of surfactants and metal ions retained by membrane, which has to be disposed afterwards in avoid of secondary pollution.

PEUF has been proposed as another feasible method to separate a great variety of metal ions from aqueous streams. It can achieve high removal efficiency, high binding selectivity and high concentrated metal ions for reuse (Fu and Wang, 2011). PEUF uses water-soluble polymer to complex metallic ions and form a macromolecular, having a higher molecular weight than the molecular weight cut off the membrane. The macromolecular will be retained when they are pumped through UF membrane. After that, retained metals can be treated in order to recover metallic ions and reuse polymeric agent. Complexing agents such as polyacrylic acid (PAA), polyethyleneimine (PEI), diethylaminoethyl cellulose and humic acid have been proved to achieve selective separation and recovery of metal ions with low energy requirements. The main parameters affecting PEUF are metal and polymer type, the ratio of metal to polymer, pH and existence of other metal ions in the solution.

3.4.2. Reverse osmosis (RO)

RO is one of the popular techniques able to remove a wide range of dissolved species from water. It accounts for more than 20% of the world's desalination capacity. In metal removal

treatment, RO is a pressure driven membrane process which uses a semi-permeable membrane with pore size down to 0.1 nm, allowing purified water to pass through it, while cationic compounds are retained (Coman et al., 2013). RO can be used for solutions with low amounts of dissolved metal (micromolar to millimolar range).

3.4.3. Nanofiltration (NF)

NF is a pressure-driven separation process employing semipermeable membranes with the pore size between those of UF and RO membranes. It has gained much interest in the field of water purification for its unique separation characteristics and advantages of lower energy consumption and higher permeation flux compared with RO. The separation mechanism involves both steric (pore size) and electrical effects (negatively charged surface groups), using low-pressure membranes which are typically polymeric, asymmetric and consist of a low resistance support layer with a functionally active porous top layer. (Liu et al., 2014). The technique is applied at ambient temperatures in a large pH range and can be used for solutions with metal concentrations in the millimolar range (Coman et al., 2013). NF is an extremely complex process and is dependent on the micro-hydrodynamic and interfacial events occurring at the membrane surface and within the membrane nanopores.

3.4.4. Electrodialysis (ED)

ED is another membrane process for the separation of metal ions across charged membranes from one solution to another using an electric field as the driving force. Ion-exchange membranes either cation-exchange and anion-exchange membranes are usually applied in this process. When a solution containing ionic species passes through the cell compartment, the anions migrate toward the anode and the cations toward the cathode, crossing the anion exchange and cation-exchange membrane (Barakat, 2011). It was found that the separation performance of ED cell is almost independent on the type of ions and only depends on the cell structure and the operating conditions, as can be improved by increasing voltage and temperature, be decreased with an increasing flow rate (Fu and Wang, 2011). Moreover, the

valuable metals such as chromium and copper can be recovered. As limitations, it requires clean feed, careful operation, periodic maintenance to prevent any stack damages.

Integrated technologies combing different processes of membrane filtration and other purification techniques have been developed for advanced treatment of drinking water (Fan et al., 2014). It is important to note that the selection of the appropriate membrane depends on a number of factors such as the characteristics of the wastewater, the nature and concentration of materials present in the wastewater, pH and temperature. In addition, the membranes should be compatible with the feeding solution and cleaning agents to minimize surface fouling.

3.5. Ion exchange resin

Ion-exchange resin is another process widely used in metal removal systems. In ion exchange, a reversible interchange of ions between the solid and liquid phases occurs, where an insoluble substance (resin) removes ions from an electrolytic solution and releases other ions of like charge in a chemically equivalent amount without any structural change of the resin.

Ion-exchange resin, either natural solid or synthetic resin, has the specific ability to exchange its cations with metals in the wastewaters. Natural zeolites and naturally occurring silicate minerals have been widely used as natural solid resins to remove metal ions from aqueous solutions due to their low cost and high abundance. Besides natural solid resins, synthetic resins are more commonly used as they are effective to nearly completely remove the metal ions from solution, for example the strongly acidic resins with sulfonic acid groups ($-SO_3H$) and weakly acid resins with carboxylic acid groups (-COOH) (Kurniawan et al., 2006a). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. The physicochemical interactions that occur during metal removal by these two types of synthetic resins can be expressed as Equations 1.6 and 1.7:

$$\underset{\text{(resin)}}{n\text{RSO}_3^-\text{-H}^+} + \underset{\text{(solution)}}{\text{M}^{n+}} \leftrightarrow \underset{\text{(resin)}}{n\text{RSO}^{3-}\text{-M}^{n+}} + \underset{\text{(solution)}}{n\text{H}^+} \quad (1.6)$$

$$\underset{\text{(resin)}}{n\text{RCOO}^-\text{-H}^+} + \underset{\text{(solution)}}{\text{M}^{n+}} \leftrightarrow \underset{\text{(resin)}}{n\text{RCOO}^-\text{-M}^{n+}} + \underset{\text{(solution)}}{n\text{H}^+} \quad (1.7)$$

where ($-RSO_3^-$) and ($-RCOO^-$) represent the anionic group attached to the ion exchange resin and the metal cation, and *n* is the coefficient of the reaction component, depending on the oxidation state of metal ions.

Ion exchange technique is also useful in recovering valuable metals from inorganic effluent. After separating the loaded resin, the metal is recovered in a more concentrated form by elution with suitable reagents (Dabrowski et al., 2004).

In general, ion exchange shows many advantages such as fast kinetics and high treatment capacity. Unlike chemical precipitation and coagulation-flocculation, it does not present any sludge disposal problems, thus lowering the operational costs for the disposal of the residual metal sludge. Despite these advantages, ion exchange also has some limitations in treating wastewater laden with metal ions, mainly reflected in the corrosion, nonselectivity and high sensitivity to the pH of the solution. (Kurniawan et al., 2006a).

3.6. Solvent extraction

Solvent extraction (liquid-liquid extraction) is also recommended as a suitable technique to selectively extract metal ions from polluted aqueous solutions. In this technique, the aqueous phase containing a metal salt is mixed with an organic phase containing an extraction agent. The metal ion forms a hydrophobic complex with the extraction agent and migrates to the organic phase. The separation of metals is based on the different affinities of complexes for different metals in the organic phase, as well as on the relative solubility of the complexes in the aqueous and organic phase (Hoogerstraete et al., 2013).

Common extracting agents are volatile and flammable organic solvents, mainly made from petroleum, for instance, kerosene, toluene, dichloromethane and diethyl ether. Recently, solvents such as vegetable oil were exploited as alternatives to replace the commonly used petroleum-based organic solvents (Chang et al., 2010).

Once the metal of interest has been removed, the metal ions can be recovered from the solvents, afterwards the organic solvents have to be recycled. The high selective metal recovery from aqueous solution is the great advantage of the solvent extraction technique. However, the

requirement of expensive equipment and monitoring systems, high energy requirements and possible pollution of organic solvents pose significant disadvantages.

3.7. Adsorption

Basically, adsorption is a mass transfer process by which a substance (adsorbate) is transferred from the liquid or gas phase to the surface of a solid (adsorbent), and becomes bound by physical and/or chemical interactions. A number of different metal-binding mechanisms have been postulated to be active in adsorption. According to the strength of the interaction adsorbate-adsorbent, it can be divided into physisorptive and chemisorptive mechanisms, where physisorption (e.g. physical adsorption and microprecipitation) is reacted by weak interactions such as London or Van Der Waals forces, while chemisorption (e.g. ion exchange, complexation, coordination and chelation) involves the net formation of chemical bonds adsorbent-adsorbate. Based on the fact that the structural complexity might be reflected in the presence of different types of sorption sites in the adsorbents, it is possible that various mechanisms would participate at different extent in the metal ion uptake (Volesky, 2003). Under these mechanisms, there are three main steps involved in metal adsorption onto solid adsorbents: (i) the transport of the metal ions from the bulk solution to the sorbent surface; (ii) adsorption on the particle surface; and (iii) transport within the sorbent particle (Demirbas, 2009).

Various types of adsorbents, derived from commercial activated carbon and low-cost materials including natural mineral materials, natural biomasses, industrial by-products and agricultural wastes, have been recently developed and applied for metal ions adsorption from aqueous solutions.

3.7.1. Activated carbon

Activated carbon is the most commonly used commercial adsorbent for industrial applications due to its richness in micropores (< 2 nm) and mesopores (2-50 nm) and the resulting large surface area (500-1500 m^2/g) and surface reactivity (Satyawali and Balakrishnan, 2008). Any carbon-containing organic materials can be used to produce activated carbon. The selection of

suitable precursor is mainly conditioned by its availability and cost, although it also depends on the main applications of the manufactured carbon and the type of installation available. Thus commercial activated carbon is manufactured from those who have some original porosity and are easy to activate, such as coal, petroleum coke, wood, sawdust, nutshells, fruit stones, peat, lignite, etc. (Marsh and Reinoso, 2006). With the effort to reduce costs, various kinds of activated carbon have been prepared from agro-byproducts, such as pinewood, rice hull, palm shell, seed husks, coconut shell palm fruit for metal ions sorption (Kurniawan et al., 2006b).

Despite the high adsorptive capacity, the high costs of activated carbon and 10-15% loss during regeneration limit its development all over the world. Moreover, activated carbon also shows high affinity towards organic molecules. As a result, these high molecular weight organic compounds will block the heavy metal ions from reaching the adsorbents bed. Due to these drawbacks, searching for alternative adsorbent from abundant and inexpensive sources is of extensive concern (Keng et al., 2014).

3.7.2. Low-cost adsorbent

Adsorption using low-cost adsorbent has attracted increasing attention of numerous researchers mainly due to its cost-efficiency, effectiveness, technical flexibility and regenerability of used adsorbents (Keng et al., 2014). Apparently, utilization of naturally occurring materials or industrial by-products or locally available agricultural waste materials as the adsorbents in removing heavy metals from wastewaters is not only cost-effective in metal ion removal, but it also contributes to a zero waste situation in the environment (Barakat, 2011; Coman et al., 2013; Demirbas, 2008; Dhir, 2014; Fu and Wang, 2011; Keng et al., 2014).

3.7.2.1. Natural mineral materials

As natural occurring minerals, zeolites have been widely applied in metal ion separation systems (Babel and Kurniawan, 2003; Bianchi et al., 2013) due to their valuable properties as cation-exchange capability. Among the most frequently used natural zeolites, clinoptilolite

was shown to have high selectivity for certain metal ions such Cu(II), Pb(II), Cd(II) and Zn(II). Several clay minerals such as kaolinite clay (Jiang et al., 2010) and montmorillonite clay (Bhatnagar and Minocha, 2006; Crini, 2006) were also proved to play an important role in metal ion removal by taking up cations either through ion exchange or physisorption or both.

3.7.2.2. Industrial by-products

Industrial by-products such as fly ash (Gupta et al., 2003), waste iron (Lee et al., 2004), iron slag (Feng et al., 2004), hydrous titanium oxide (Barakat, 2005) and metal (hydr)oxide waste (Escudero et al., 2009a) have been reported as no expensive sorbents for metal removal from wastewater.

3.7.2.3. Natural biomasses

Natural biomasses, either algal and microbial biomass or non-living biomass, are available in bulk and regular quantities and possess large surface area and various chemical compounds (Keng et al., 2014) that are essential requisite for an adsorbent (Demirbas, 2009). They are also much cheaper than commercial activated carbon and even natural mineral materials, being regarded as suitable alternatives for metal ions cost-effective sorption. These biological material employed in adsorption processes is defined as "biosorbent". The adsorption process involves the use of biosorbent that form complexes with metal ions using their functional groups is thus, defined as "biosorption" (Gadd, 1993).

(1) Algae

Algae, a renewable natural biomass proliferates ubiquitously and abundantly in the littoral zones of world has attracted the attention of many investigators as organisms to be tested and used as new adsorbents to adsorb metal ions. Algae has been proved to possess high metal binding capacities, due to the presence of polysaccharides, proteins or lipid on the surface of their cell walls containing some functional groups such as amino, hydroxyl, carboxyl and sulfate, which can act as binding sites for metals (Das and Guha, 2007; Gupta and Rastogi, 2009). Green alga macroalga *Caulerpa lentillifera* (Pavasant et al., 2006), *Cladophora fascicularis* (Deng et al., 2007), *Ulva lactuca* (El-Sikaily et al., 2007), *Chaetomorpha linum*

(Ajjabi and Chouba, 2009), red algae *Ceramium virgatum* (Sari and Tuzen, 2008) and brown alga *Fucus serratus* (Ahmady-Asbchin et al., 2008) all exhibit high uptake values for chromium and many other metal ions.

(2) Microbial biomasses

Microbial removal of metal ions from wastewater by bacteria, fungi and yeast has also been indicated as being highly effective. Recently years, metal-bearing bacteria such as *Bacillus cereus* (Pan et al., 2007), *Pseudomonas aeruginosa* (Gabr et al., 2008; Tuzen et al., 2008), *Escherichia coli* (Souiri et al., 2009; Quintelas et al., 2009), etc. have possessed biosorption/bioaccumulation performance to metal ions. As to fungi and yeasts, because they are easy to grow, thus can produce high yields of biomass continuously used for metal uptake. *Rhizopus* biomass is the most commonly reported fungi involved in metal ion removal, such as *Rhizopus arrhizus* (Aksu and Balibek, 2007; Bahadir et al., 2007) and *Rhizopus oryzae* (Bhainsa and D'Souza, 2008). Metal ions could be adsorbed by complexing with negatively charged reaction sites on the cell surface. A variety of ligands including carboxyl, amine, hydroxyl, phosphate and sulfhydryl groups located on the fungal walls are known to be involved in metal chelation (Barakat, 2011).

(3) Non-living biomasses

Besides the living organics, non-living biomasses are also naturally and abundant occurring biopolymeric materials containing variety of organic compounds could be involved in metal ion physical and/or chemical adsorption. Depending on the origin, non-living biomasses can be generally classified as agricultural products and by-products two categories.

Agricultural products including chitin and chitosan (Zhou et al., 2004), black gram husk (Saeed et al., 2005), sawdust (Kaczala et al., 2009), peat (Demirbas, 2009), wood (Boving et al., 2008), cork (Sen et al., 2012) and lignin (Liu et al., 2010) have been investigated.

As to agricultural by-products produced in astronomical quantities from various agriculture industries, the tested agricultural by-products are mainly in the following aspects: (i) crop residues, such as wheat and rice waste (Dupont et al., 2005; Mohan and Sreelakshmi, 2008); (ii) fibers, for instance spruce, coconut coir, kenaf bast, kenaf core, coir, jute, and cotton (Lee et al., 2008; Shukla and Roshan 2005); (iii) fruit residues, including potato peels (Aman et al., 2008),

citrus peels (Schiewer and Patil, 2008), eggshell (Jai et al., 2007), seed shells (Amudaa et al., 2009), tea and coffee waste (Fiol et al., 2008a; Prabhakaran et al., 2009; Kyzas, 2012; Pujol et al., 2013a), coffee husks (Oliveira et al., 2008), coconut waste (Olayinka et al., 2007; Gowda et al., 2012), sugar-beet pectin gels (Mata et al., 2009a), etc.; (iv) wood and tree residues, as grape stalk waste (Escudero et al., 2009a).

In general, the biosorption process has been proved to be an excellent strategy, for the obvious advantages of low-cost, availability, convenient operation and efficiency (Patel, 2012). Unfavorably, these researches were still in the theoretic and experimental phase. Moreover, the separation of biosorbents would be difficult after adsorption.

3.7.3. Modified adsorbent

Up to now, various commercial and low-cost adsorbents have been investigated intensively for adsorption of individual or multiple heavy metals in an aqueous solution. Low-cost biosorbents possess significant advantages over currently available expensive commercially activated carbons, and in addition contribute to an overall waste minimization strategy. It is evident that most of these biosorbents have shown their potential in metal removal without any modifications. But it is interesting to note that their removal capabilities can generally be improved through properly physical or chemical modifications (Barakat et al., 2011; Patel, 2012).

In order to enhance the sorption properties, physical modification such as suitable sizing of the adsorbents by chopping and grinding, thermal treatment (steam and microwave), ultrasonic irradiation, stirring, freeze drying and high pressure (autoclaving) can be performed prior to sorption process. Chemical modification involves a treatment of the biosorbents with an array of chemicals for washing, enhancement of binding groups, elimination of inhibiting groups and graft copolymerization (Park et al. 2010).

Some low-cost biosorbents have been modified as activated carbon to enhance their metal removal efficiency, such as rice husk (Bishnoi et al., 2003), spent coffee (Kante et al., 2012), etc.

Besides biomass-based activated carbon, immobilization of the bio-materials in hydrogel polymers, thus forming hybrid polymers is also proposed. Hydrogels, which are cross-linked hydrophilic polymers synthesized by either algae or chemicals, are capable in the purification of wastewater due to the polymerization/crosslinking reaction that results in three-dimensional network formation of cationic hydrogel (Crini, 2005). In some case, small particle size of biosorbents can cause practical problems such as column and pipe clogging. By entrapping them in hydrogel polymers, not only the clogging problems can be avoided, but also the sorption behavior can be enhanced. In recent decades, calcium alginate, polyacrylamide, polysulfone, polyethylenimine and covalent cross-linking are the common approaches towards entrapment (Samiey et al., 2014). Chitosan immobilized in crosslinked membranes (Liu et al., 2003) to adsorb transition metal ions, thiacrown ethers immobilized into sol-gel matrix (Saad et al., 2006), *Fucus vesiculosus* immobilized in calcium alginate xerogels (Mata et al., 2009b), grape stalks waste and metal (hydr)oxide waste entrapped into calcium alginate beads (Fiol et al., 2006; Escudero et al., 2009b) as well as alginate, pectate and polygalacturonate calcium gel beads (Cataldo et al., 2013) have been reported.

3.8. Remarks of metal treatment techniques

Although all the metal wastewater treatment techniques can be employed to remove heavy metals, they have their inherent advantages and limitations.

Metals removal from aqueous solutions has been traditionally carried out by chemical precipitation for its simplicity process and inexpensive capital cost. However, chemical precipitation is not economical and can produce large amount of sludge to be treated with great difficulties.

Using coagulation-flocculation technique, the produced sludge has better sludge settling and dewatering characteristics than chemical precipitation process. But this technique involves higher chemical consumption and increased sludge volume generation.

Flotation offers several advantages over the more conventional methods, such as high metal selectivity, high removal efficiency, high overflow rates, low detention periods, low operating

cost and production of more concentrated sludge. But it also rise to disadvantages such as high initial capital cost, high maintenance and operation costs.

In membrane filtration wastewater treatment process, in spite of the high removal efficiency, the cleaning and maintenance of membranes also increase the cost, and could possess secondary pollution.

Ion exchange resin has been widely applied for the removal of heavy metal from wastewater. However, ion-exchange resins must be regenerated by chemical reagents when they are exhausted and the regeneration can cause serious secondary pollution. And it is expensive, especially when treating a large amount of wastewater containing metal in low concentration, so they cannot be used at large scale.

Through solvent extraction, metal ions can be selectively separated from wastewaters. However, the expensive equipment and operation, the potential pollution of organic solvents limit its industrial application.

Adsorption is a recognized method for the removal of metal ions from wastewater in a more environmental friendly way. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process. The alternative of high cost activated carbon to varieties of low-cost biosorbents has promoted its development in practical application. However, biosorption of metal ions from aqueous solutions is a relatively new process that has not been widely applied at large scale. The mechanisms of metal ion biosorption and its application at pilot-scale or industrial-scale are required to be further studied to meet the sustainable reality.

In a word, the conventional techniques used for metal ions removal from wastewaters including chemical precipitation, coagulation-flocculation, flotation, membrane filtration, ion exchange resin, solvent extraction and adsorption by activated carbon are all facing a drawback with reference to the operation and maintenance (O&M) costs. Thus biosorption using low-cost sorbent has been regarded as an economical and sustainable alternative to be applied in industry effluent decontamination. Taking into account that sorption efficiency is strongly depended on the type of biosorbent and the sorption mechanisms are complicated, there will be a necessary to introduce the biosorbent which will be used in our study.

4. EXHAUSTED COFFEE WASTE AS A BIOSORBENT FOR METAL IONS REMOVAL

As talked in the last section, biosorption has become a cost-effective technique for metal ions removal from aqueous solution. Being a kind of agricultural by-product, exhausted coffee waste, the solid residue from soluble coffee manufacturer, can be used for metal biosorption.

4.1. Coffee and exhausted coffee waste

Coffee has been consumed for over 800 years since the Arabs brought *Coffea arabica* seeds from Ethiopia to Yeman (Arabian Peninsula) during the 13th century and established the first plantation (Monaco et al., 1977). The province of Kaffa in Ethiopia is considered to be the original habitat of Arabica coffee and Central Africa is reckoned to be the native of robusta coffee. With extensive and wide spread cultivation of coffee across the globe during the last 150 years (Daglia et al., 2000), at present coffee is the most popular beverages in the world (more than 400 billion cups yearly) (Sobésa Café, 2008) and is the second largest trade commodity after petroleum (Murthy and Naidu, 2012). According to the International Coffee Organization (ICO), output of coffee brew in 2012-2013 seasons is estimated at 145 million bags (ICO, 2014).

In the last years, the soluble coffee industry has experienced a constant growth as soluble coffee has become one of the most popular kinds of coffee drunk by millions of people around the world. Almost 50% of coffee production is processed for soluble coffee preparation (Ramalakshmi et al., 2009). Soluble coffee processing initiates with the conversion of coffee cherries into green coffee beans; and follows by roasting, grinding, extraction and concentration of water soluble. The coffee cherries are the raw fruit of the coffee plant, which are usually harvested after 5 years of coffee trees plantation and when the bear fruit turns red (Arya and Rao, 2007).

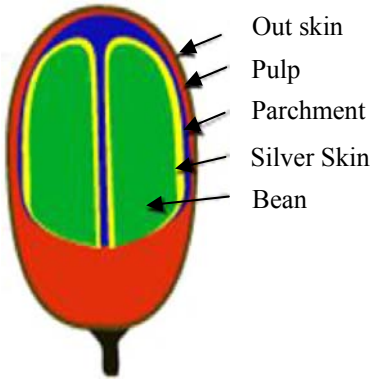


Figure 1.2 Cross-section of the coffee cherry (Murthy and Naidu, 2012)

As shown in Figure 1.2, coffee cherries are composed of two coffee beans covered by a thin parchment like hull and further surrounded by pulp. Using either a wet or dry method, both the pulp and hull are removed, the green coffee beans are subjected to the roasting processing to develop the specific organoleptic properties (flavors, aromas and color). This process is time-temperature dependent and leads to several changes in the chemical composition and biological activities of coffee as a result of the transformation of naturally occurring polyphenol constituents in a complex mixture of Maillard reaction products, as well as the formation of organic compounds resulting from pyrolysis. After the roasting process, the roasted beans are ground, usually by multi-stage grinders and pass to soluble coffee production. The soluble solids and volatile compounds that provide aroma and flavor are extracted from the coffee beans using water. Water heated to about 175^{o}C under pressurized conditions is used to extract all of the necessary soluble contents from the coffee beans. Following extraction, the concentrated extracts are dried by freeze drying or spray drying to produce the soluble coffee (Mussatto et al., 2011b).

As a consequence, large amounts of exhausted coffee waste (EC), which are the solid residues obtained from soluble coffee production, have been generated worldwide (6 million tons per year) (Mussatto et al., 2011b). On an average one ton of green coffee beans generates about 650 kg of EC, and about 2 kg of wet EC are obtained to each kg of soluble coffee produced

(Pfluger, 1975). Considering this huge amount of EC produced all over the world, the disposal of this waste could bring severe contamination and pollution if it is not discharged in an

environmentally friendly way (Fan et al., 2000; Leifa et al., 2000). The picture of roasted coffee beans and exhausted coffee waster can be seen in Figure 1.3.

Figure 1.3 Roasted coffee beans and exhausted coffee waste

4.2. Re-use of exhausted coffee waste

Nowadays the organic properties of EC have aroused people's interests in its reutilization. Instead of being sent to landfill or flushed down the sink, EC has been used as a natural fertilizer, a compost feedstock, a horticultural amendment and a mushroom growing medium (Liu and Price, 2011; Nogueira and Costa, 1999) due to its high nutrient and energy materials. Other attempts have been made for the reuse of EC as a bioresource for biodiesel and fuel pellets (Caetano et al., 2012; Silva et al., 1998; Jenkins et al., 2014; Limousy et al., 2013), for polysaccharide, polyhydroxyalkanoates (Mussatto et al., 2011a; Cruz et al., 2014) and for antioxidant (Panusa et al., 2013) owing to its rich in lipids and polyphenolic compounds. In addition, EC has been explored as a low-cost sorbent for the removal of organic components such as dyes (Roh et al., 2012; Safarik et al., 2012) and phenolic compounds (Hernandez-Remirez and Holmes, 2008). Its potential in metal ions sorption has also been tested by our group and some other researches for the removal of Cr^{6+} (Fiol et al., 2008a; Kyzas, 2012; Mulani et al., 2013; Pujol et al., 2013a), Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+} (Impellitteri et al., 2008; Utomo and Hunter, 2009; Kumaraswamy et al., 2014) and Hg^{2+} (Giraldo and Moreno-Pirajan, 2012) from aqueous solution. The adsorptive property of EC is attracting more and more attention, however the sorption mechanism is not very clear, simply generalized to the lignocellulosic substrate (Fiol et al., 2008a; Pujol et al., 2013a) of EC.

Therefore, the sorption mechanisms and sorption behaviors of EC for different metal ions will be studied in this thesis.

5. METAL FINISHING INDUSTRIES EFFLUENT AND TREATMENT PROCESS

Metal finishing is one of the important metal working processes aimed to increase the durability of metal products. Recent years, with the development of metal finishing industry, the effluent of this industry is also one of the major sources of wastewater containing metal ions (Wei et al., 2013). The generation of metal finishing industry effluent and its main composition will be described, as well as the conventional treatment technique for this effluent.

5.1. Metal finishing industries effluent

As one of the major metal working processes, metal finishing is used to treat the exterior of metal products by coating or plating a thin complementary layer to its surface, in order to provide corrosion protection, wear or erosion resistance, anti-frictional characteristics or for decorative purposes. The metal finishing process involves the deposition of a thin protective layer (usually metallic) onto a prepared surface of metal, using a wide variety of chemical processes, such as pretreatment (cleaning, degreasing and other preparation), plating, rinsing, passivation and drying (Cavaco et al., 2007). The common metals include chromium, copper, nickel, zinc, tin, lead, cadmium, iron and aluminium. Among them, chromium has withstood the competitive challenges due to its unmatched aesthetics as well as its superior technical capabilities, and is widely used in the metal finishing industry for both decorative and hard-chrome plating.

Thus a large amount of effluents containing hexavalent chromium and other various metal ions are generated from surface operations and rinsing process (Ismail et al., 2014; Li et al., 2008; Suksabye et al., 2008). Particularly, the highly toxic hexavalent chromium can reach hundreds milligram per liter (Park et al., 2006), posing a high risk to human, animals and the environment.

Apart from metals, anions are another pollutants contained in the metal finishing industry effluent. The largest proportion comes from the metallic salts contained in the processing and

etching baths. These are chlorides, fluorides, cyanides, nitrates and nitrites, phosphates and sulfates.

Furthermore, the metal finishing industry use a growing number of organic chemical products to enhance the quality of coating (brighteners) or complexing agents such as tertiary amines, quaternary ammonium salts, ethylenediaminetetraacetate salts (EDTA), etc. to promote deposition, especially in the case of co-deposits. These chemicals have negative effects on the environment because they significantly increase the chemical oxygen demand (COD) of the effluent and are difficult to eliminate.

5.2. Treatment of metal finishing industries effluent

Due to the serious hazard of metal finishing industry effluent, it has to be strictly regulated and must be treated before being discharged (Adhoum et al., 2004). Many efforts are made for metal ion separation from the effluent. Meanwhile, if the metal ions can be effectively removed, both the filtered effluent and the metals have a great possibility of being recycled (Wei et al., 2013).

Most traditional technique have been employed by the metal finishing industries to remove metal ions from their effluents is combination of physico-chemical methods, such as chemical reduction of hexavalent chromium followed by precipitation, coagulation-flocculation, ion exchange, membrane filtration or reverse osmosis (Adhoum et al., 2004; Li et al., 2008; Velazquez-Peña et al., 2012; Wei et al., 2013). The typical method to reduce and remove soluble metals from metal finishing effluent follows the procedure shown in Figure 1.4.

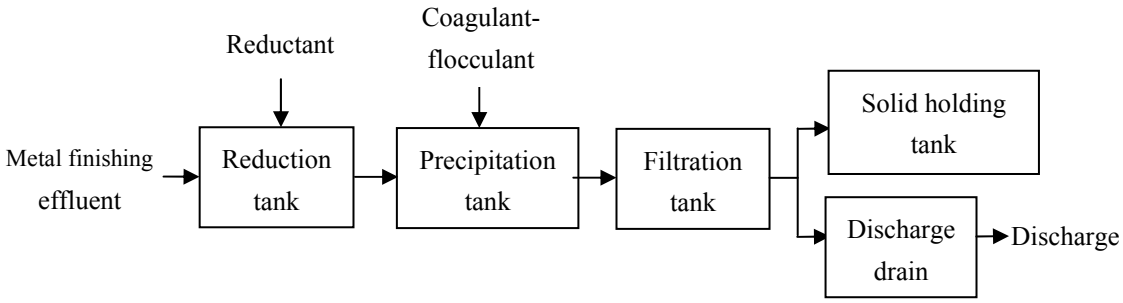


Figure 1.4 Flowchart of typical process of metal finishing effluent treatment

As seen in Figure 1.4 the typical technique used for metal control is based on chemical reduction coupled to post-precipitation followed by filtration in order to separate the metal ion contaminants from wastewater. After hexavalent chromium reduction, precipitation is most applicable and considered to remove the metal ions (Zeng et al., 2014). Precipitation is based on chemical coagulation-flocculation by adding lime to raise the pH and agent to remove colloidal matter as gelatinous hydroxides (Adhoum et al., 2004).

Nowadays, this physico-chemical treatment system is used in more than 80% of the metal finishing industries in Europe. Despite the broad application and the high removal efficiency, conventional technique suffers from serious drawbacks (Gutpa et al., 1999; Park et al., 2006) including:

(1) reagent consumption, in particularly an excess of expensive reducing reagents;

(2) increase of effluent salinity due to the added reagents;

(3) possible secondary pollution of the solid residues (sludges) containing toxic compounds;

(4) treatment and disposal of the residual metal sludge;

(5) high capital and operational costs.

In Catalonia most of the industries dealing with metal finishing are family business run by parents and their children and few workers. During the last years their income has diminished due to the economic crisis, accompanying with the increasing reagents and material price and the more and more exigent environmental requirements. For all these reasons there exists the need to find out a less costly alternative to the traditional wastewater treatment. The use of biosorbents considered low cost sorbents is one of these alternatives.

6. BACKGROUND

The present thesis is framed in the project "Desarrollo de tecnologia a escala piloto para depuración de aguas contaminadas con iones metalicos mediante residuos agroalimentarios" (CTM2012-37215-C02-01) from Ministry of Science and Innovation of Spain. The project is centered in the development of metal-contaminated water detoxification techniques by the use of agricultural by-products and in the design of the metal ion biosorption technique at a pilot scale for its application to industrial effluent treatment.

In our research group, Metals and Environment from the University of Girona, several types of agricultural by-products have been investigated as biosorbents for metal ions removal, such as olive stone, cork, yohimbe bark, grape stalk and exhausted coffee waste. As concern to exhausted coffee waste, it resulted to be effective for hexavalent chromium and other metal ions elimination at little scale (Fiol et al., 2008a; Pujol et al., 2013a). For further industrial application, the sorption mechanisms and the large-scale sorption behavior of this material have to be investigated.

7. OBJECTIVES

The objective of the present thesis is the development of a sustainable technology for hexavalent chromium and divalent metal ions removal based on biosorption using exhausted coffee waste.

To attain this objective it is necessary the achievement of different specific objectives.

(1) Physical and chemical characterization of exhausted coffee waste, in order to get information about the potential of this material as a biosorbent for metal ions sorption.

(2) Identification of the role of exhausted coffee chemical components, both structural compounds and extractives, in hexavalent chromium and divalent metal ions sorption so as to explore the sorption mechanisms.

(3) Study of the kinetics of hexavalent chromium removal by exhausted coffee waste in the presence of divalent copper ions in a stirred batch reactor.

(4) Development of a kinetic model to describe kinetics of Cr(VI) sorption onto exhausted coffee from Cr(VI)-Cu(II) binary mixtures.

(5) Investigation of a suitable post-treatment of the residual metal ions in solution after biosorption so as the treated water meets the wastewater discharging standard.

(6) Study of the behavior of the proposed technology based on biosorption for the treatment of wastewater from metal finishing industries in a pilot plant.

CHAPTER II.

CHARACTERIZATION OF EXHAUSTED COFFEE WASTE

1. INTRODUCTION

Exhausted coffee waste (EC) as one kind of agricultural by-product hugely generated from soluble coffee manufacturer, possesses great potential in its reutilization such as biodiesel production, precursor for production of activated carbon and sugars, compost, and metal ions and other compounds sorption, due to its rich in organic compounds (i.e. fatty acids, lignin, cellulose, hemicellulose and other polysaccharides (Mussatto et al., 2011b; Pujol et al., 2013b). The employment of EC as a low cost sorbent aroused interests in our study of Cr(VI) and divalent metal ions removal from aqueous solutions. As mentioned in General Introduction EC has proved to be a good sorbent for these metal ions (Fiol et al., 2008a; Pujol et al., 2013a).

The biosorption process is a very complicated process, which involves the interaction between the solid phase (sorbent or biosorbent; biological material) and the liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate) (Ahmad et al., 2014; Das et al., 2012). The sorbent affinity for the sorbate which determines the distribution between the solid and liquid phases will judge the biosorption capacity of the sorbent (Volesky, 2003). The sorbent affinity for the sorbate is related to the physico-chemical properties of the sorbent, especially the relative amount of the mineral and organic materials and their respective composition with associated physical characteristics (Hubbe et al., 2011). Hence the knowledge about the composition and structure of EC in our case is equally important to its availability at its point of use.

The composition of EC is very complex as a wide variety of chemical compounds are present. After being extracted in water, most of the hydrophobic compounds, including lipids, triglycerides and fatty acids could remain in the EC as well as insoluble carbohydrates like lignin, hemicellulose, cellulose and various indigestible sugars (Murthy and Naidu, 2012; Mussatto et al., 2011b). In general, EC is a kind of lignocellulosic material (Protásio et al., 2013) which contains a great variety of structural compounds (lignin, cellulose and hemicellulose) and non-structural compounds (extractives) (Mussatto and Texeira, 2010). Lignin is a heterogeneous phenolic compound that lacks primary structure and consists of an irregular array of variously bonded hydroxy- and methoxy-substituted phenylpropane units. Cellulose is a rigid, linear polymer of glucose subunits and is the structural component of

primary cell wall of plants. Hemicelluloses are branching polymers of C-5, C-6 found along with cellulose in almost all plant cell walls that include the polysaccharides xylan, glucuronoxylan, arabinoxylan, glucomannan and xyloglucan which are formed of many different sugar monomers (Boeriu et al., 2004; Chakar and Ragauskas, 2004). Lignin fills the spaces in the cell wall between cellulose, and hemicellulose and is covalently linked to hemicellulose forming crosslinks between polysaccharides conferring mechanical strength to the cell walls (Chabannes et al., 2001). The structural compounds of lignocellulosic materials is depicted in Figure 2.1.

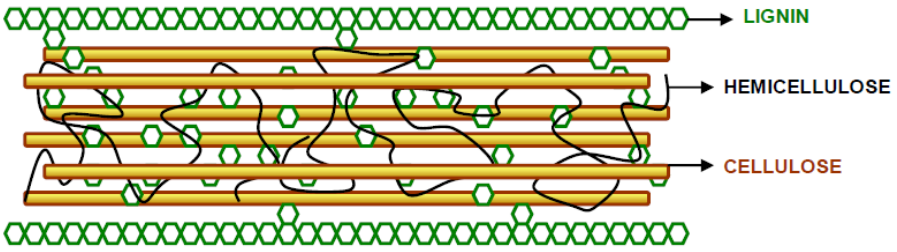


Figure2.1 Representation of lignocellulose structure showing cellulose, hemicellulose and lignin fractions (Mussato and Texeira, 2010)

Besides structural compounds, extractives are a group of non-structural cell walls compounds that can be solubilised by solvents of different polarity. These chemicals exist as monomers, dimers and polymers and their role in the cell wall is to provide protection against pathogen invasion. Extractives are a large variety of organic compounds that include hydrocarbons, fatty acids, polyphenolic compounds and condensed tannins (Rowe and Conner, 1979). Chlorogenic acids, an important group of phenolic compounds which contribute to coffee flavor and are of potential biopharmacological importance for humans, are included in the water-soluble fraction (Farah et al., 2006).

The properties of EC also vary within the plants from different geographic locations, ages, climate, and soil conditions and within the producing process from different roasting, extraction condition. An overall knowledge of the physical and chemical properties of the EC will lead to better understanding of the metal-binding mechanism that governs the adsorption process.

For instance, particle size and pore size are related to EC surface condition, they are important factors not only influencing the sorption capacity but also the sorption rate of metal ions onto EC surface (Krishna and Swamy, 2012; Shi et al., 2014). The protonation-desprotonation behavior of EC in aqueous media will determine a positively or negatively charged EC surface in solution at different pH values, thus also plays a crucial role in the sorption of metal cations and ions (Fiol and Villaescusa, 2009). The elemental analysis will determine some major elements of the material which could be involved in metal ions sorption. Moreover, the polarity index (PI: (O+N)/C) can be obtained through elemental analysis. This is proved to be inversely correlated with material aromatic character which could be related to sorption capability for metal ions sorption (Wang and Xing, 2007). The polarity of EC can be also reflected by their acidic functional groups, which are based on carboxyl and phenolic hydroxyl groups (Liu et al., 2014).

A characterization of EC from these above-mentioned aspects could be very useful to understand its application in metal removal. However, it has not been clearly established a complete physico-chemical characterization of EC. For this reason, the integrated features of EC and its overall chemical composition were carried out with an integrated approach in this chapter, in order to better predict the potential of this material as a biosorbent for metal ions and further explore the mechanisms of metal ions sorption.

The physico-chemical characterization includes humidity, particle size distribution, density and porosity, pH of point zero charge (pH_{pzc}) determination, determination of acidic surface functional groups, summative chemical composition, ash composition, analysis of total polyphenols, condensed tannins, and lipids in the extracts. Among them the overall chemical composition of EC was determined through sequential extractions by solvents with different polarity. Furthermore, elemental analysis, Fourier transform infrared ray (FTIR) spectroscopy analysis and scanning election microscopy (SEM) coupled to energy dispersive X-Ray (EDX) analysis were performed as well to describe the properties of the material surface.

2. MATERIALS AND REAGENTS

2.1. Reagents and Solutions

- Analytical grade KNO_3 (Panreac) were used to pH_{pzc} determination under N_2 (Praxair) atmosphere.
- Analytical grade NaOH in pellets (Panreac), analytical grade $NaHCO_3$ (Panreac), analytical grade Na_2CO_3 (Panreac) and 37% HCl (Panreac) were used to determine acid groups.
- 99.99% dichloromethane (Fisher), 96% ethanol (Aga), Milli-Q water, analytical grade NaOH in pellets (Panreac) and ice were applied in solvent extraction and alkaline lixiviation.
- 72% sulphuric acid (Merck) was used to Klason and acid-soluble lignin, and carbohydrates content determination.
- Gallic acid (Panreac) was used to total polyphenol determination.
- Methyl cellulose (BDH Chemicals) and sodium ammonium (Panreac) were used to condensed tannins determination.
- Pyridine (Panreac) and Bis(trimethylsily)-trifluoroacetamide (Panreac) were used to lipophilic extractives composition determination.
- FTIR grade KBr (Acros Organics) was use to prepare pellets for Fourier Transform Infrared Ray (FTIR) analysis.

2.2. Equipment

- Atomic absorption spectroscopy (Pye Unicam SP-9 equipped with a graphite furnace GF95) was used to determine the elemental composition of ash content.
- Elemental analyzer (Perkin Elmer EA2400 series II, the scales Sartorius 2MP with a ENAC calibration) was used for elemental analysis.
- Fourier transform spectrometer (Galaxy Series FTIR 5000, Mattson Instrument Co., Madison, WI) was used for FTIR analysis.
- Gas chromatography (GC) (HP5890A) was used to analyse polysaccharides.
- Gas chromatography (GC) (Agilent 5973 MSD) coupled to a mass spectrometer (MS) (Agilent 5975C) was applied to determine lipophilic extractives.

- Scanning election microscopy (Zeiss DSM 960A, Germany), with energy dispersive X-Ray analyser (Bruker AXS Microanalysis GmbH, Germany) was used for SEM-EDX analysis.
- VIS/UV spectrophotometer (Hitachi U-2000) was used to determine acid-soluble lignin and total polyphenol.

3. METHODOLOGY

3.1. Humidity

As soon as EC arrived from the industry, around 200 g of EC weighted by an analytical balance (Cobos precision, J. Touron, s.a.) were placed into an aluminium tray and put in the oven (J.P. Selecta, s.a.) at 105°C until constant weight. Then the humidity was calculated as:

$$\text{Humidity} = \frac{w_1 - w_2}{w_1 - w_0} \times 100 \qquad (2.1)$$

where w_0 is the weight (g) of the empty aluminium tray, w_1 is the weight (g) of the aluminium tray with EC before it was put in the oven, w_2 is the weight (g) of the aluminium tray with EC after drying in the oven until constant weight. All determinations were made in duplicate.

3.2. Particle size distribution

Before sieving EC for particle size characterisation most of the EC received from the industry was dried in the oven at 105°C and then well mixed for homogenisation. The particle size distribution was determined using a set of standard sieves (1000 µm, 500 µm, 250 µm, 100 µm, 50 µm, 25 µm nominal aperture). About 200 g of certain amount of sample were placed on the largest sieve and then sieved by an electromagnetic sieve shaker (CISA BA 200N) for 4 times, each time 10 minutes. The weight of samples retained on each sieve after final shaking was recorded. The particle size was expressed as the percentage of particles retained on each sieve. All determinations were made in triplicate.

3.3. Density and porosity

The particle density of EC refers to the mass of exhausted coffee in a given volume of particles (mass/volume). Particle density focuses on just the coffee particles and not the total volume of the particles and pore spaces occupied in the particles. Particle density differs from bulk density because bulk density includes the volume of the solid (mineral and organic) portion of the coffee along with the spaces where air and water are found (Huerta-Pujol et al, 2010). The difference between particle density and bulk density can be visible in Figure 2.2.

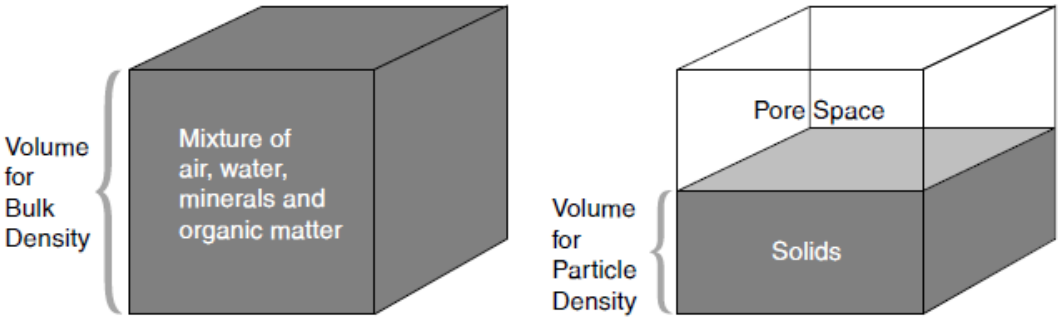


Figure 2.2 Bulk density and particle density (GLOBE, 2005)

Particle density data is not only used to better understand the physical and chemical properties of EC, but also used with bulk density data to calculate the pore space (porosity) occupied by air and water in the EC sample. In order to determine EC particle density, bulk density and porosity the protocols from GLOBE (2005) were followed.

3.3.1. Particle density

For calculating the particle density of EC, the mass and the volume of the solid particles were both measured. Pay attention, there should not be air between the particles. The measurement was done by placing the sample in an Erlenmeyer flask with distilled water, then boiling the mixture to remove any air that may remain. After cooling, some water was added to obtain the specific volume. The mass of the mixture was then measured. The mass of the water was the difference between the mass of the mixture and the sample. The density of the particles was calculated from the mass of the solid particles and the specific volume.

The steps of the experimental procedure are as follows (GLOBE, 2005): 10 g of dried and sieved EC sample were weighted (w_{EC}) and placed in a 100 mL Erlenmeyer flask carefully. 50 ml distilled water were added in the Erlenmeyer flask to make the sample immersed in the water. Then the EC/water mixture was boiled gently for 10 minutes to remove air bubbles by placing the Erlenmeyer flask on a heater (Agimatic-N, J.P. Selecta, s.a.). Note that the flask was swirled gently for 10 seconds each minute to keep the EC/water mixture from foaming over. Afterwards, the Erlenmeyer flask was removed from the heater to be cooled. Once the mixture was cooled, the Erlenmeyer flask was covered with parafilm and allowed to sit for 24 hours. After 24 hours, an empty 100 ml volumetric flask without its cap was weighted (w_O) (g). Then the mixture was transferred into the volumetric flask very carefully, the volumetric flask was filled with distilled water so that the volume of the mixture and water was 100 mL (v_V). Weight the volumetric flask containing the mixture without its cap (w_{EC}+w_O+w_W); where w_W is water weight (g). Finally, the temperature of the sample was measured by placing the bulb of the thermometer in the volumetric flask for 2-3 minutes until the temperature was stable. The test was done induplicate.

The particle density of EC was calculated as the ratio between the mass and the volume (air removed) of the solid. The volume (air removed) of the solid was the difference between the volume of the volumetric flask and the volume of water. The calculation is as:

$$\text{Particle density} = \frac{w_{EC}}{v_V - \frac{w_W}{\partial_W}} \quad (2.2)$$

where ∂_W is the density of distilled water at the measured temperature (g/mL).

3.3.2. Bulk density and porosity

For calculating the porosity of EC, the bulk density must be measured. The methodology is as follows (GLOBE, 2005): An empty measuring cylinder was weighted, then a quantity of solid particles was placed in the measuring cylinder and the volume (V_S) (mL) and weight (w_S) (g) of the solid particles were recorded. The step was repeated for different amount of samples. The calculation is as follows:

$$\text{Bulk density} = \frac{w_S}{V_S} \quad (2.3)$$

The porosity of EC is calculated from the particle density and bulk density:

$$\text{Porosity} = 1 - \frac{d_B}{d_P} \times 100 \quad (2.4)$$

where d_B and d_P represent the bulk density of the particle density of the EC samples, respectively.

3.4. Elemental analysis

The carbon, hydrogen and nitrogen elements of dried EC waste were determined by an elemental analyzer in the Chemical and Structural Analysis Unit - Technical Services of University of Girona. The detection limit of the instrument for carbon, hydrogen and nitrogen is 0.72%, 0.20% and 1.20%, respectively. Oxygen content was calculated by difference. All determinations were made in duplicate.

3.5. pH of point zero charge (pH_{pzc})

The pH is a very important parameter influencing on metal ions sorption due to its influence on chemical speciation of the metal in solution and also on the ionization of chemically active sites on the sorbent surface. Thus, the net charge of sorbent surface may play a crucial role in sorption processes, and the characterization of protonation-deprotonation behavior of sorbent material in aqueous media could be useful to explain sorption mechanism (Fiol and Villaescusa, 2009).

The pH at which the sorbent surface charge takes a zero value is defined as point of zero charge (pH_{pzc}). At this pH, the charge of the positive surface sites is equal to that of the negative ones. At solution pHs higher than pH_{pzc}, sorbent surface is negatively charged and could interact with metal positive species while at pHs lower than pH_{pzc}, solid surface is positively charged and could interact with negative species.

According to the protocol described by Fiol and Villaescusa (2009) mass titrations (MT) were performed to determine the pH_{pzc} of EC. By looking at the distribution of EC particle size, two

kinds of particles which were the largest portions of EC were analyzed. Different masses of each particle size within the concentration range 0.2 -100 g/L were put into contact with a 50 mL 0.03 M KNO_3 solution. The aqueous suspensions were agitated for 24 hours in an orbital shaker (SSL2, Stuart Scientific) at a speed of 250 rpm until equilibrium pH was reached. The pH_{pzc} is the pH at which a plateau is achieved when plotting equilibrium pH versus sorbent mass. The same treatment and procedure was used for blank solution (50 mL 0.03 M KNO_3). All experiments were performed in Anaclin plastic bottles at room temperature (20±2^{o}C) under N_2 atmosphere and in duplicate.

3.6. Determination of acidic groups

Acidic surface properties of the coffee samples were determined by the Boehm method (Psareva et al., 2005). The Boehm method consists of a selective neutralization of the surface acidic groups with various strengths, using bases that have conjugate acids with a wide range of acid dissociation constants. According to Boehm (Boehm, 2002), surface oxides creat with liquid oxidants or with oxygen at elevated temperatures (or by ageing) are acidic in character and cause cation exchange properties. The acidic surface properties are caused by the presence of carboxyl groups (also in the form of their cyclic anhydrides), lactones or lactols, enolic, and hydroxyl groups of phenolic character. These groups differ in their acidities and can be selectively determined by neutralization with 0.1 M solutions of NaOH, Na_2CO_3 and $NaHCO_3$: all the acidic groups can be neutralized by NaOH; weakly acidic groups (i.e. both strong and week carboxylic, lactonic and enolic) are neutralized by Na_2CO_3; strong carboxylic groups are neutralized by $NaHCO_3$. Thus, the difference between Na_2CO_3 and $NaHCO_3$ consumption is the weakly acidic groups including weak carboxylic groups, lactonic and enolic groups; the difference between NaOH and Na_2CO_3 consumption corresponds to the weakly acidic phenolic groups.

According to the protocol (Psareva et al., 2005), 1.0 g of EC was placed into an Anaclin plastic bottle containing 0.1 L 0.1 M NaOH, $NaHCO_3$ or Na_2CO_3 and placed into the orbital shaker (SSL2, Stuart Scientific) at the speed of 250 rpm until equilibrium. Blanks were also prepared. Afterwards, the suspensions were filtered and 0.01 L of the filtrate of each investigated

solution (NaOH, $NaHCO_3$ and Na_2CO_3) were titrated using an automatic titrator (Orion 960) with 0.1 M HCl down to pH 4.3 (pH was measured permanently). The procedure was performed in duplicate. The cation exchange capacity on Na^+ from 0.1M solutions of NaOH, $NaHCO_3$ and Na_2CO_3 was then calculated as:

$$q = \frac{V \times (C_0 - C_{\mathrm{eq}})}{m} \tag{2.5}$$

$$C_{\mathrm{eq}} = \frac{V_{\mathrm{h}} \times C_{\mathrm{h}}}{V_{\mathrm{f}}} \tag{2.6}$$

where q is the cation exchange capacity (mequiv/g), C_o the initial concentration of NaOH, $NaHCO_3$ or Na_2CO_3 (mequiv/L), C_{eq} the equilibrium concentration of NaOH, $NaHCO_3$ or Na_2CO_3 (mequiv/L) obtained by titration, V the volume of the initial solution in the Anaclin plastic bottle (0.1 L in this case), V_h and C_h the volume and the concentration of the HCl (L) consumed in the titration, V_f the volume of the filtrate used in the titration (0.01 L in this case) and m the mass of EC (1.0 g).

3.7. Chemical summative composition

The chemical summative analysis of EC included the determination of extractives soluble in solvents with different polarity, Klason and acid-soluble lignin and monomeric composition of polysaccharides. These analyses were explored in the Forest Research Centre, imbedded in Institute Superior of Agronomy in the Technical University of Lisbon, together with ash content and composition, total polyphenol and condensed tannins determination and lipophilic extractives composition analyses. Some chemical components were extracted from EC during the sequential extraction with organic and inorganic solvents, and to be determined with specific methods. The procedure of extraction and determination will be introduced below.

3.7.1. EC sequential extraction

The overall flowchart of sequential extraction procedure is shown in Figure 2.3. The extractives were obtained by successive extraction with a series of solvents with different polarity (dichloromethane, ethanol and water) in a Soxtec extractor for 1.5 hours with each

solvent. Each solvent removes different amounts and types of extractives as well as other cell wall components (Pereira, 2007). Dichloromethane (DCM) solubilizes non-polar aliphatic compounds such as n-alkanes, n-alkanols and fatty acids. Ethanol (EtOH) and water solubilise phenolic compounds including simple phenols, benzoic acids, cinnamic acids and polymeric phenols. Then, the free-extractive samples were subjected to aqueous alkaline extraction (1% NaOH) to remove tannins and other polyphenols insoluble in ethanol and water. After all these extraction processes, the remaining solid extract should contain essentially lignin and polysaccharides. However, it is reported that under drastic conditions (concentrated NaOH solutions and high temperature) a significant amount of hemicelluloses and lignin may be extracted and solubilized (Fradinho et al., 2002). It is obvious that the successive extraction processes provokes changes of the material structure that may result in an enhanced or restricted accessibility of metal ions to cell wall components (Lee and Rowell, 2004).

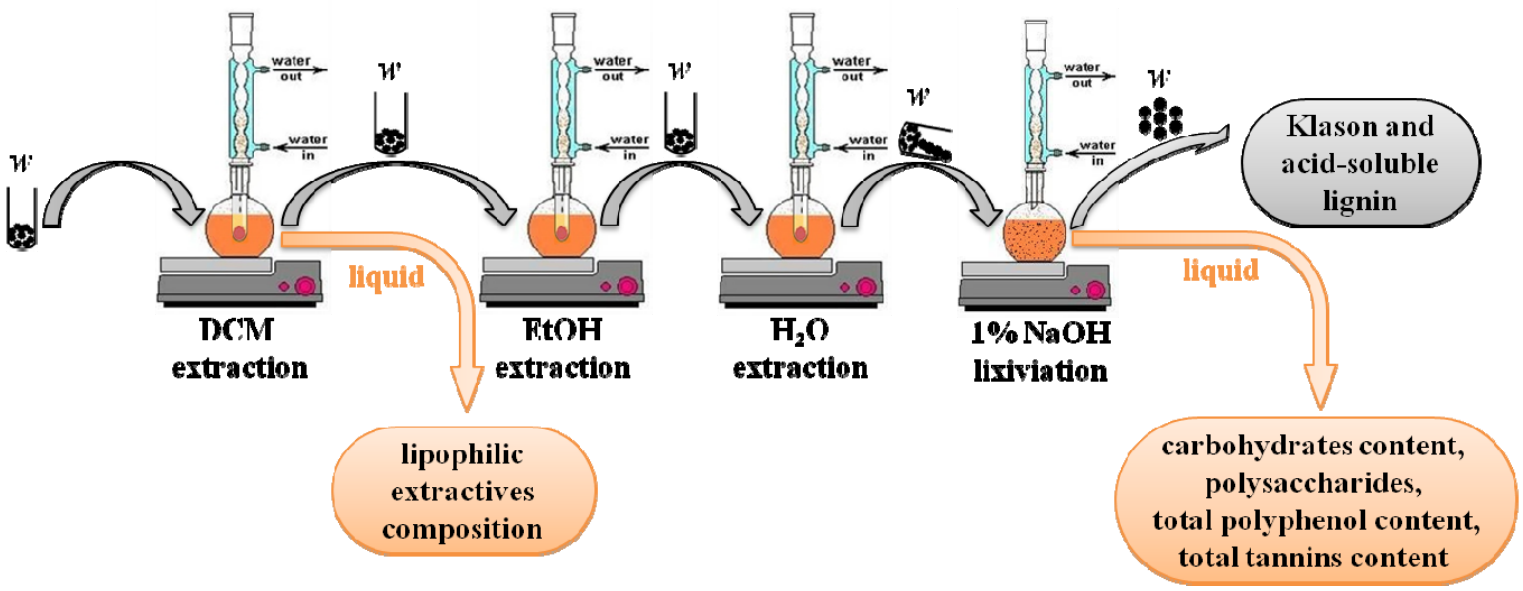


Figure 2.3 Flowchart of chemical summative composition, total polyphenol, condensed tannins and lipophilic extractives composition determination

The weight of extractives solubilized by each solvent was determined by the difference between the initial mass of dry coffee sample (2.2 g) and the mass of the solid residue obtained after extractions dried at 105°C. Results are reported as a percentage of original samples.

The alkaline lixiviation with 1% NaOH of the extractive-free EC samples was performed in a stirred glass reactor with reflux using 1.0 g of material with a 1:50 solid: liquid ratio (g/mL), at 100°C during 1 hour.

Klason (TAPPI 13 m-54) and acid-soluble (TAPPI UM 250) lignin, and carbohydrates content were determined after 1% NaOH extraction. Sulphuric acid (72%, 3.0 mL) was added to 0.35 g of extracted sample and the mixture was placed in a water bath at 30°C for 1 hour. Afterwards, the sample was diluted to a concentration of 3% H_2SO_4 and hydrolysed for 1 hour at 120°C. The sample was vacuum filtered through a crucible and washed with boiling purified water. Klason lignin was determined by the mass residue after drying at 105°C. Acid-soluble lignin was determined on the combined filtrates by measuring the absorbance at 205 nm using a UV-VIS spectrophotometer. Measurements of Klason and acid-soluble lignin were combined to give the total lignin content.

The polysaccharides were calculated based on the amount of the neutral sugar monomers released by total hydrolysis. The hydrolysed carbohydrates were derivatized as alditol acetates and separated by gas chromatography (GC) equipped with a FID detector, using helium as carrier gas (1 mL/min) and a fused silica capillary column S2330 (30 m x 0.32 mm ID; 0.20 μm film thickness). The column program temperature was 225-250°C, with 5°C/min heating gradient, and the temperature of injector and detector was 250°C. For quantitative analysis the GC was calibrated with pure reference compounds and inositol was used as internal standard in each run (method adapted from TAPPI 249 cm-00). All determinations were made in duplicate.

3.7.2. Ash content and composition

Ash content was determined according to TAPPI Standard T 15os-58. 1 g dry exhausted coffee wasted was placed in an oven 500^{o}C for 24 hours. The ashes were extracted with three successive extractions with 3 M HCl (10 mL). Elemental composition was determined by Atomic Absorption Spectroscopy.

3.7.3. Total polyphenol and condensed tannins determination

The total polyphenol content (TPC) was determined in the liquid extracts after the extractions with ethanol, water and 1% NaOH. TPC was determined by spectrophotometry, using gallic acid as standard according to the Folin-Ciocalteu assay. The method was adapted from Pereira (1981). The calibration curve was obtained by preparing different concentrations of gallic acid within the range 0.1-0.6 mg L^{-1}. Briefly, a 100 µL aliquot of extracts, the gallic acid standard solutions (0.1-0.6 mg L^{-1}) and a blank (deionized water) were put in different tubes. Then, 4 mL of the Folin-Ciocalteu's phenol reagent diluted 1:10 were added to each tube, the tubes were shaken and allowed to react for 5 minutes. After this time, 4 mL of 7.5% Na_2CO_3 solution was added. After incubation of the mixture in a thermostatic bath for 15 minutes at 45^{o}C, the absorbance against a blank was determined spectrophotometrically at 765 nm. Total phenolic content was expressed as milligrams of gallic acid equivalents (GAE) per 100 g dry mass. All samples were analysed in triplicate.

The total tannins content was determined in the same extract used for the total polyphenolic compounds determination. The method was also adapted from Pereira (1981). Condensed tannins were separated from the liquid extract by precipitation with a 0.04% methyl cellulose solution in deionized water. To precipitate the condensed tannins, 1 mL of extract was put into contact with 1 mL of 0.04% methyl cellulose, 0.8 mL of saturated sodium ammonium solution and 2.5 mL deionized water. After 20 minutes, the solution was filtered and total polyphenol content in the filtrates was determined by following the same procedure as described in last paragraph. The difference between total polyphenols content and polyphenols determined after precipitation with methyl cellulose corresponds to the condensed tannins. The samples were analysed in triplicate.

3.7.4. Lipophilic extractives composition

Aliquots of the dichloromethane extracts (1-5 mL) were filtered through Anatop 10 membranes (pore dimensions 0.2 μm, Merck). The filtrate was evaporated under N_2 flow and dried under vacuum at room temperature. The residues were dissolved in 250 μL of pyridine per mg of dry mass and the compounds containing hydroxyl and carboxyl groups were trimethylsilylated into trimethylsilyl (TMS) ethers and esters, respectively, by adding 250 μL of bis(trimethylsily)-trifluoroacetamide. The reaction mixture was carried out for 30 minutes in an oven heated at 60°C.

The final extracts were analyzed by GC performed with an Agilent 5973 MSD coupled to a mass spectrometer. The separation was achieved using a DB5-MS column (30 m length, 0.25 mm I.D., 0.25 μm film thickness), injector temperature 320°C, oven temperature program, 100°C (5 min), rate of 8°C/min up to 250°C, rate of 2.5°C/min up to 320°C (20 min). The MS source was kept at 220°C and the electron impact mass spectra (EIMS) taken at 70 eV of energy.

The compounds were identified as TMS derivatives by comparing their mass spectra with data from a GC-MS spectral library (Wiley, NIST), and their fragmentation profiles with published data (Eglinton and Hunneman, 1968; Kolattukudy and Agrawal, 1974). For semi-quantitative analysis, peak area integration with total area detected normalized to 100% was used to calculate the different components content, expressed as percentages. All the experiments and GC-MS analysis were performed in duplicate and the average results are presented in this work.

3.8. Fourier Transform Infrared Ray (FTIR) analysis

FTIR analysis was used to identify the functional groups on exhausted coffee waste surface. Spectra were recorded in KBr pellets using a FTIR spectrometer. To prepare the pellets, 2 mg of exhausted coffee waste was finely grinded for 1 to 2 minutes together with 200 mg of KBr. The FTIR spectra were recorded in the spectral range 3600 to 600 cm^{-1} by co-addition of 32 scans with a resolution of 4 cm^{-1}.

3.9. SEM – EDX analysis

Scanning Election Microscopy (SEM) coupled to energy dispersive X-Ray (EDX) analysis was carried out to obtain topographical and elemental information of exhausted coffee particles (GLOBE, 2005) Samples were mounted on a stainless stub using a double-stick tape coated with a thin layer of carbon. Digital images were processed by using Quartz PCI program.

4. RESULTS AND DISCUSSION

4.1. Humidity

The mean value of exhausted coffee waste humidity tested in duplicate was 57.01%. This humidity was lower than that reported by Mussatto (80-85%) of spent coffee grounds (Mussatto et al., 2011b), could due to the different drying processes of the soluble coffee residue.

4.2. Particle size distribution

Three set of samples with similar weight of exhausted coffee (S_1: 191.495 g, S_2: 175.844 g, S_3: 191.104 g) were used to determine particle size distribution. Results are shown in Table 2.1.

Table 2.1 Particle size distribution of EC

	S_1		S_2		S_3		Average
Nominal aperture (µm)	**weight (g)**	**weight fraction (%)**	**weight (g)**	**weight fraction (%)**	**weight (g)**	**weight fraction (%)**	**weight fraction (%)**
>1000	36.441	19.03	32.245	18.34	34.077	17.83	18.40
500-1000	51.212	26.74	46.070	26.20	49.342	25.82	**26.25**
250-500	39.015	20.37	37.895	21.55	41.386	21.66	**21.19**
100-250	38.148	19.92	34.787	19.78	38.360	20.07	19.93
50-100	25.710	13,43	24.832	14.12	25.175	13.17	13.57
25-50	0.969	0.51	0.015	0.01	2.764	1.45	0.65
Total	191.495	100.00	175.844	100.00	191.104	100.00	100.00

It is evident that the two largest portions of the exhausted coffee waste were 500 - 1000 µm and 250 - 500 µm particles, accounted to 26.25% and 21.19%, respectively. These two portions were used in some of following characterizing experiments: density and porosity, pH of point zero charge, determination of acidic groups and morphological analysis. In short, the 500 - 1000 µm and 250 - 500 µm particle size of exhausted coffee were named as ECA and ECB, respectively. The smallest portion of exhausted coffee waste (25 - 50 µm) was used for elemental analysis, determination of chemical summative composition and ash content and Fourier transform infrared ray analysis.

4.3. Density and porosity

The results analyzed from ECA and ECB were summarized in Table 2.2. The particle density of different particle sizes was similar; the porosity increased and hence the bulk density was decreasing with the decrease in particle size, which was contrary to the previous report by other authors. According to Ouchlyama (1986), Nimmo (2004) and Manickam (2011), the porosity has a relationship with the particle size: the larger the particle size, the higher the porosity.

Table 2.2 Density and porosity of two largest portions of EC (ECA: 500-1000 µm and ECB: 250-500 µm)

	Particle Density (g/ml)	**Bulk Density (g/ml)**	**Porosity (%)**
ECA	1.20	0.51	57.05
ECB	1.23	0.39	68.12

This reverse trend could be explained by the alteration of pore structure of coffee beans affected by roasting conditions. During the hot-air roasting of coffee beans, not only the colors and flavor compounds are formed, but also the pore structure of coffee beans is completely altered (Tsai and Liu, 2013; Schenker et al., 2000). When coffee is roasted at temperatures above 200ºC, drying takes place, water is redistributed, then complex chemical reactions such as Maillard reaction and pyrolysis are induced. Loss of water and organic mass leads to large

amounts of gases and causes high internal pressure hence result in a complete alteration of the bean macropores and micropores.

Compared to other biosorbents, the porosities of these EC samples were higher than those of coconut shell (55%), *Penicillium* biomass (44%), chitosan-coated perlite beads (43%) and moringa oleifera seeds (34%), which have been used for divalent metal ions biosorption (Acheampong et al., 2011; Zhang et al., 2011; Swayampakula et al., 2009), also higher than those of chitosan coated with silica (46%) and *Parthenium hysterophorus* weed (42%) to remove Cr(VI) from aqueous solutions (Vijaya et al., 2010; Venugopal and Mohanty, 2011), even higher than those of acid treated tamarind fruit nut cover (31%) and tamarind nut fruit cover (22%) for defluoridation of water (Kumar et al., 2012), lower than the porosities of coconut hust (72%) and sawdust (77%) (Acheampong et al., 2011).

The adsorption capacity depends greatly on the porosity of the adsorbent material (Weber et al., 2013), which is due to the porous structure may facilitate the diffusion of metal ions through the porous networks of adsorbent particles, making the adsorption process more efficient. According to the high porosity (>50%) of exhausted coffee waste, this material has strong capacity of adsorption and could be widely used in the metal ions removal.

4.4. Elemental analysis

Exhausted coffee with particle size at 25-50 μm was used to elemental analysis. The percentage of the different elements (on average C: 57.56, H: 7.86, N: 2.48, O: 32.10) was within the range of values reported in the literature for spent coffee (Caetano et al., 2012; Bizzo, 2003; Nogueira and Costa, 1999), resulting in the H/C, O/C and C/N ratio at 1.64, 0.42 and 27.07. Compared to other materials, EC samples showed a higher carbon content (>50%) and a slight higher nitrogen content (>2%) and consequently a higher C/N ratio (Droussi et al., 2009; Preethu et al., 2007). This will limit the use of this material as compost although it would be possible to add inorganic nitrogen (ammonium phosphate) or other organic sources of nitrogen such as green weeds, forest litter, or micronutrients to improve the quality of compost (Preethu et al., 2009; Pazhanivelan et al., 2006).

The polarity index (PI: (O+N)/C) is an important parameter inversely correlated with the aromatic character of the sample. PI found for EC sample (0.46) were closer to the polarity range of some commercial lignins (0.33-0.65) than to that of cellulose and chitin (0.84-1.94) (Wang and Xing, 2007; Xing et al., 1994). A negative correlation between this coefficient and the hydrophobic pollutants sorption was also reported (Rutherford et al., 1992; Xing et al., 1994). Lignins have predominantly aromatic carbons and their affinity for hydrophobic pollutants is much higher than that of chitins and celluloses (Wang and Xing, 2007).

These results suggest that exhausted coffee waste due to their high aromatic character could be an effective sorbents for the removal of hydrophobic pollutants. PI of the studied EC samples found in this work were higher than those of the humic-acid-like compounds during composting of olive mill by-products (i.e. 0.19-0.34) (Droussi et al., 2009) and similar to those found for raw cork by-products (i.e. 0.33-0.61) (Olivella et al., 2013) that also showed high affinity for polycyclic aromatic hydrocarbons sorption (Olivella et al., 2011).

4.5. pH of point zero charge (pH_{pzc})

ECA and ECB within the concentration ranged from 0.2 to 100 g/L were used for pH_{pzc} determination. Two curves by plotting equilibrium pH after treatment versus sorbent mass are shown in Figure 2.4. The pH_{pzc} is the pH at which a plateau is achieved in the curve. As can be seen, two experimental curves corresponding to ECA and ECB were overlapped. A plateau was achieved at pH 4.3 for both of them, which means the pH_{pzc} for the exhausted coffee waste was at pH 4.3. This result was close to what found for another exhausted coffee waste (pH 3.9) (Fiol et al., 2008a). At solution pHs higher than 4.3, EC surface is negatively charged and could interact with metal positive species while at pHs lower than 4.3, its surface is positively charged and could interact with negative species. Thus, exhausted coffee waste has the capacity to adsorb divalent or trivalent metal ions in slight acidic solutions.

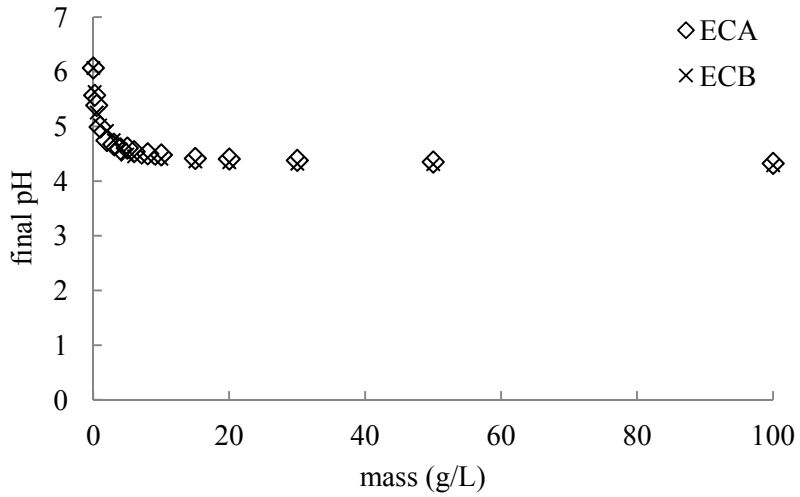


Figure 2.4 Experimental mass titration curves corresponding to two largest portions of EC (ECA: 500-1000 μm and ECB: 250-500 μm)

4.6. Determination of acidic groups

The static exchange capacity (SEC) (here only cation exchange) examined for ECA and ECB can be seen in Figure 2.5. The Na^+ cation exchange for NaOH solution (1.30 and 1.35 mequiv/g for ECA and ECB, respectively) that corresponds to the full cation exchange capacity, is equal to the concentration of total acidic groups. The Na^+ cation exchange for Na_2CO_3 solution (0.37 and 0.42 mequiv/g for ECA and ECB, respectively) is equal to the concentration of weakly acidic groups (i.e. both strong and week carboxylic, lactonic and enolic) groups. The Na^+ cation exchange for $NaHCO_3$ solution (both 0.30 mequiv/g for ECA and ECB) is equal to the concentration of strong carboxylic groups. Thus, the difference between the cation exchange values for Na_2CO_3 and $NaHCO_3$ is the concentration of weakly acidic groups including weak carboxylic groups, lactonic and enolic groups, 0.07 and 0.12 mequiv/g for ECA and ECB, respectively. The concentration of the phenolic groups is the difference between the cation exchange values for NaOH and Na_2CO_3, both 0.93 mequiv/g for the two particle sizes of exhausted coffee. The phenolic groups of exhausted coffee are mostly located in lignin and extractives.

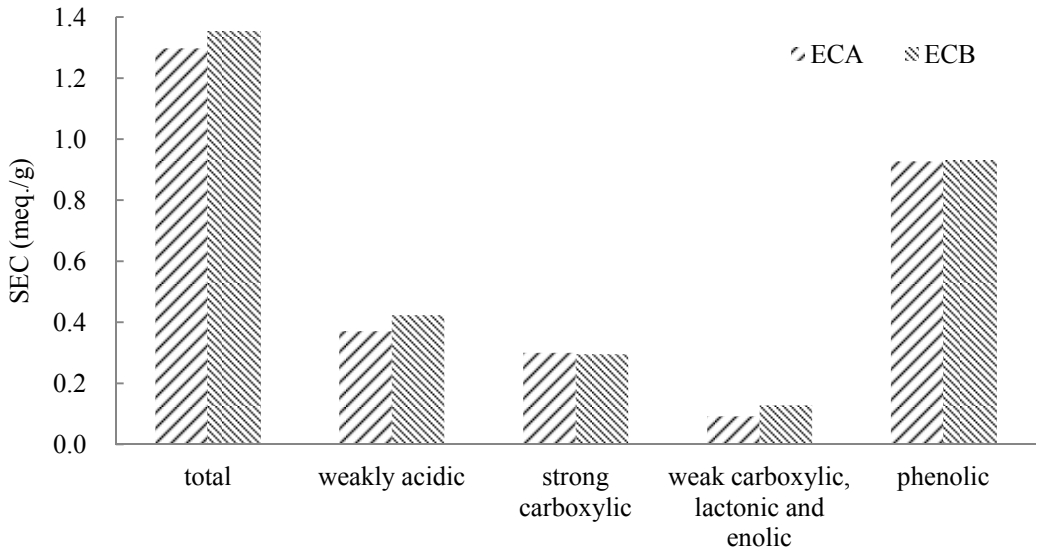


Figure 2.5 Acidic groups of exhausted coffee waste

As seen, the sum of total acid groups in ECB was a little higher than in ECA. The difference only lied in the 0.05 mequiv/g higher possess of weakly acidic groups (i.e. strong and weak carboxylic, lactonic and enolic) in ECB than in ECA. The main acidic compounds of exhausted coffee were phenolic groups (0.93 mequiv/g). The amounts of total acidic groups of exhausted coffee samples were in the range of values reported for mango pit husk (1.38 mequiv/g) (Elizalde-González and Hernández-Montoya, 2007), slightly lower than those for *Quercus suber* cork samples which ranged from 1.10 to 1.80 mequiv/g (Olivella et al., 2013) and much lower than that for mango pit/seed (3.15 mequiv/g) (Elizalde-González and Hernández-Montoya, 2007).

4.7. Chemical summative composition

4.7.1. EC sequential extraction

The chemical summative composition obtained from the EC portion (25 - 50 μm) are shown in Table 2.3. As seen, the total content of extractives which are soluble in DCM, EtOH, water and 1% NaOH was very high (55.78%). A large proportion (25.41%) of the extractives corresponds to non-polar compounds that are soluble in dichloromethane. The content of lipids in EC was higher than oil content in maize seeds (3.75%) (Ali el al., 2010) and in cherry

seeds (8.70%) (Duman et al., 2011), similar to the percentage of oil in *Parkia biglobbossa* (26.52%) and lower than that in *Jatropha curcas* seeds (47.25%) (Akintayo, 2004).

Polar compounds extracted by ethanol and water, which include especially phenolic and polyphenolic compounds (Miranda et al., 2013), corresponded to a lower proportion of the extractives total content, and amounted to 4.3% in EC.

The solubilization by 1% NaOH represented a significant proportion of the exhausted coffee waste (26.06%). As regards to the extraction with 1% NaOH, it must be remarked that not only tannins and other polyphenols insoluble in water and ethanol are extracted but molecules of high molecular weight such as lignin and polysaccharides can be also found in the extract. In this case the more chemically labile moieties are either cleaved or solubilized in this alkaline medium especially when more drastic alkaline conditions (i.e. 100^{o}C) are used (Fradinho et al., 2002). The percentage of alkaline bark extract obtained of a maritime pine from Portugal using the same temperature but different time and NaOH concentration (2% NaOH, 0.5 h) was lower (11%) than that obtained in this study (Fradinho et al., 2002).

Table 2.3 Summative chemical composition and monosaccharide composition (% oven dry mass) of EC (25 - 50 μm)

Composition	**% w/w**
Tatal extractives	55.78
Dichloromethane	25.41
Ethanol	3.42
Water	0.89
1% NaOH	26.06
Total lignin	19.84
Klason lignin	16.67
Soluble lignin	3.17
Polysaccharides [a]	24.38
Glucose	15.44
Mannose	8.94

[a] Polysaccharides include only the neutral monosaccharides.

The high content in exhausted coffee waste of such extractives of phenolic character opens expectations for applications like the production of wood adhesives, biocides, pharmaceuticals or leather tanning (Atanassova et al., 2011; Fernandes et al., 2009; Mazimba et al., 2011; Pizzi, 1991). It is clear that for such specific applications the components in the alkaline extracted material should be deeply investigated.

The total lignin content was 19.84% in exhausted coffee waste. Klason lignin content was higher than soluble lignin that showed a lower lignification of the cell wall. In the literature, 31.9% and 1.7% Klason lignin and soluble lignin, respectively, were reported for spent coffee grounds (Caetano et al., 2012); 39.4% total lignin for exhausted coffee residue (Tsai et al. 2012), and 38.6 and 39.4% total lignin for coffee pulp and coffee husk, respectively (Preethu et al. 2009).

It should be noted that in this work lignin determination was made on the alkali extracted material, which otherwise would increase the lignin values. In other materials, such as barks of different species, Klason lignin values were reported within the range 23.4 to 27.1% (Kofugita et al., 1999), for *Picea abies* and *Pinus sylvestris* barks as 26.8 and 32.9%, respectively (Miranda et al., 2012) for *Quercus suber* cork from 21 to 23% (Pereira, 2007) and 27% for *Quercus cerris* cork (Şen et al., 2010).

The polysaccharides were calculated based on the amount of total neutral sugar monomers released by total hydrolysis and resulted to be 24.38% in exhausted coffee waste. The carbohydrate composition was reduced to only two monomers: glucose (15.44%) and mannose (8.94%) for exhausted coffee waste. Glucose is the building monomer of cellulose. As regards to hemicelluloses, the results obtained in this study contrast with those reported in the bibliography that showed that galactose and arabinose were also present in the exhausted coffee waste (Mussatto et al., 2011a; Simoes et al., 2009). These two monomers were not present in the studied exhausted coffee samples and a possible explanation is that these monosaccharides, that are more easily hydrolyzed, were dissolved in the alkali extraction.

4.7.2. Ash content and composition

The ash content of exhausted coffee waste was lower compared to range of values reported for spent coffee (0.4-1.6%) (Caetano et al., 2012; Lago et al., 2001; Mussatto et al., 2011b). The low amount of ashes together with the high content of carbon and hydrogen made these EC samples suitable as energy source. The calorific values calculated following the method reported by Van Loo and Koppejan (2008) were relatively high, up to 26 MJ/kg dry weight basis. This value was similar to the reported values by Bizzo (2003) (i.e. 21.8-26.9 MJ/kg) and lower than the one reported by Caetano et al. (2012) (46.29 MJ/kg) for spent coffee grounds. The calorific values found for EC in this study was also comparable to those reported for other agricultural by-products (Gravalos et al., 2010). The quite high calorific value suggests a good potential for bioenergy.

The concentration of major mineral elements (i.e. Ca, K, Mg) in the exhausted coffee waste ashes is presented in Table 2.4. Calcium and sodium are the most abundant elements in the sample. The reported trends for the major constituents of exhausted coffee grounds were: K>P>Mg (Mussatto et al., 2011b) and K>Mg>P>Ca (Tsai et al., 2012), while Na>Ca>K>Fe was the trend found in the present study. Differences of exhausted coffee mineral composition must be attributed to the soil and the fertilizers used in the cultivation of coffee varieties (Hombunaka and Rowell, 2002; Laviola et al., 2007). This diversity should be taken into account when assessing the potential of the exhausted coffee wastes as a feedstock.

Table 2.4 Elemental constituents of ashes of EC (25 - 50 μm)

Elements	g/kg
Ca	0.498
Mg	0.073
K	0.215
Na	0.627
Fe	0.147
Cu	0.039
Zn	0.010
Mn	0.029

4.7.3. Total polyphenol and condensed tannins determination

The content of total polyphenolic compounds and of condensed tannins was analyzed in the ethanol, water and 1% NaOH liquid extracts of exhausted coffee waste. The results, expressed as percent of gallic acid equivalent (GAE), are presented in Table 2.5. It must be pointed out that about 80%, 100% and 60% of the total polyphenolic compounds found in the EtOH, H_2O and 1% NaOH extracts, respectively, were condensed tannins. The condensed tannins are a source for tanning chemicals of hides or for wood adhesives (Vázquez et al., 1992).

The polyphenols content found in the exhausted coffee samples was low compared to green tea (14-21% GAE) (Anesini et al., 2008). This content was found at 1.09 mg/g for peas (Chavan et al., 2001). The tannin content of other plants such as leaves of *K. candel* and *R. mangle* was reported at 106 mg/g and 219 mg/g, respectively (Zhang et al., 2010). The extraction yields of polyphenolic compounds found for the exhausted coffee samples in relation to the total extracted material open a path for further studies on EC valorization as natural source of antioxidant.

Table 2.5 Total polyphenols content and condensed tannins expressed in percentage of mass of acid gallic equivalents (GAE) in different extracts of EC (25 - 50 μm)

	%GAE w/w
Polyphenolic compounds	
EtOH	0.75
H_2O	0.17
NaOH	4.54
Condensed tannins	
EtOH	0.61
H_2O	0.17
NaOH	2.93

4.7.4. Lipophilic extractives composition

The results of the GC-MS analysis of the dichloromethane extracts are shown in Table 2.6.

Table 2.6 Composition of dichloromethane extracts of exhausted coffees, in % of the chromatographic peak areas compounds detected by GC-MS

Compound	**%**
Hydrocarbons	3.14
n-Tetracosane	1.76
n-Nonadecane	1.38
Saturated fatty acids	62.57
n-Hexadecanoic acid	37.97
n-Octadecanoic acid	9.92
n-Eicosanoic acid	5.51
9,10-dihidroxioctadecanoic acid	2.49
2,3-dihidroxihexadecanoic acid	4.66
n-Docosanoic acid	2.02
Unsaturated fatty acids	12.61
octa-9,12-dienoic acid	6.04
n-oleic acid	5.55
2-Butenedioic acid	1.02
Benzoic acids	1.27
1,4-Benzenedicarboxylic acid	1.27
Sterols	3.11
Stigmasterol	1.35
b-Sitosterol	1.76
Other compounds [a]	17.30

[a]Components that are present in the extract in a percentage lower than 1%.

As seen, the extracted components included hydrocarbons, fatty acids, a benzoic acid and sterols. The predominant compounds in the lipidic fraction of exhausted coffee waste were fatty acids that account for 75.18%. The fatty acids are within the range from C_{16} to C_{22}, and the predominant component is n-hexadecanoic acid (C_{16}) followed by 9,12-octadienoic acid ($C_{18:2}$), n-octadecanoic acid (C_{18}) and oleic acid ($C_{18:1}$). It is important to remark that the most common fatty acids in biodiesel are those of C_{16} and C_{18}. Therefore, the results found in this work for lipids composition are a starting point to evaluate the use of coffee waste for biodiesel production in the future. Caetano et al. (2012) evaluated the quality of biodiesel produced from spent coffee grounds and found that the oil parameters did not comply with the standard limits set by the European Standard NP EN 14214:2009.

Minor amounts of n-alkanes (< 3%), benzoic acids (< 1.5%) and sterols (< 3%) were also identified in the sample. There is no bibliography on chemical composition of lipophilic extractives of exhausted coffee waste. Martín et al. (2001) who studied the fatty acid profiles in the lipid fraction of green and roasted coffee beans of several coffee varieties reported that linoleic acid (9,12-octadienoic acid) and palmitic acid (n-hexadecanoic acid) were the most predominant components, followed by oleic ($C_{18:1}$) and stearic ($C_{18:0}$) acids. These results are in agreement with the trend found in the present study.

4.8. Fourier Transform Infrared Ray (FTIR) analysis

The FTIR spectra obtained for the exhausted coffee sample are shown in Figure 2.6. The characteristics of the most representative peaks can be seen in Table 2.7. The broad band at about 3400 cm^{-1} included many vibration modes is mainly attributed to -OH groups with a minor contribution of -NH functional groups (Kante et al., 2012). The presence of methyl and methylene groups are confirmed by the two sharp peaks at 2925 cm^{-1} and 2855 cm^{-1} attributed to asymmetric and symmetric stretching of C-H bonds in aliphatic chains. These peaks have been previously identified in roasted coffee and attributed to the presence of caffeine (Craig et al., 2012). The same peaks have been attributed to the presence of lipids in corn and corn flour (Cremer and Kaletunç, 2003). Given that the exhausted coffee waste is the residue from coffee extraction in which most of the caffeine has been already extracted, these peaks can likely be

attributed to lipids which are present in the coffee samples in a large amount. The sharp band at 1742 cm^{-1} is associated to the carbonyl vibration (C=O) in aliphatic esters (Lyman et al., 2003) or in triglycerides (Kemsley et al., 1995). Therefore, this band can be attributed to lipids. The low intensity bands at 1665 cm^{-1} and 1523 cm^{-1} are due to C=C vibration of lipids and fatty acids, and C=C vibration of aromatic rings from lignin moieties, respectively (Wang and Lim, 2012). The band at 1665 cm^{-1} can be also ascribed to the carbonyl stretching from lignin moieties (Herbert, 1971). The band at 1461cm^{-1} corresponds to C-H bending of CH_3 groups. The peak at 1319 cm^{-1} is associated to CO- stretching of syringyl ring from lignin moieties (Fiol et al., 2008b; Martínez et al., 2006) and to OH bending of phenolic groups (Nezahuatl-Muñoz et al., 2012). The bands of exhausted coffee spectrum at 1065, 1113, 1163, 1245, 1376 cm^{-1} could be attributed to chlorogenic acids which are a large family of esters formed by quinic acid and certain trans-cinnamic acids (Clifford et al., 2008). Axial C-O deformation of the quinic acid occurs in the range 1085-1050 cm^{-1}, O-H angular deformation occurs between 1420 and 1330 cm^{-1} and C-O-C ester bond absorbs in the 1300-1000 cm^{-1} range (Silverstein et al., 2005). According to Nezahuatl-Muñoz et al. (2012), the peak at 1163 cm^{-1} can be also attributed to C-H in plane bending of guaiacyl ring from lignin moieties. The region 900-1400 cm^{-1} also exhibit several types of vibrations including C-H, C-O-C, C-N and P-O characteristic of polysaccharides (Haussard et al., 2003). FTIR spectroscopy cannot distinguish the bands corresponding to chlorogenic acids from those of polysaccharides, and a chromatographic analysis should be applied to detect the presence of chlorogenic acids. Chlorogenic acids are an important group of phenolic compounds which contribute to coffee flavor and are of potential biopharmacological importance for humans (Farah et al., 2006).

Table 2.7 Characteristic IR peaks of exhausted coffee waste

Frequancy (cm^{-1})	Compound	Bond	Assignment
3470 (s, b)	polysaccharides, lignin, extractives (aliphatic -OH)	stretching	γ O-H, N-H
3379 (s, b)	polysaccharides, lignin, extractives (phenolic -OH)	stretching	γ O-H, N-H
2925 (s, sh)	extractives (lipids, caffeine)	asymmetrical stretching	γass C-H
2855 (m, sh)	extractives (lipids, caffeine)	symmetrical stretching	γs C-H
1742 (m, sh)	extractives (lipids (ester groups in triglicerids))	stretching	C=O: 
1665 (w)	extractives (lipids, fatty acids), lignin	stretching	C=C
1635 (w)	extractives (caffeine)	stretching	γ C=O
1523 (m)	lignin, extractives (aromatic ring)	skeletal vibrations	C=C
1461 (m)	extractives (fatty acids)	asymmetrical deformation	C-H Deformations
1376 (m)	polysaccharides (cellulose)	stretching	Symmetric-COO-, aromatic CO-
1319 (w)	lignin (syringyl), tannins	stretching, bending	CO-, O-H
1163 (m)	lignin (guaiacyl), extractives (esters (chlorogenic acid))	stretching	C-H, C-O-C ester bond
1113 (w)	extractives (esters (chlorogenic acid))	stretching	CO
1065 (w)	polysaccharides (carboxylic acid)	stretching	C-O
1033 (w)	polysaccharides (cellulose)	deformation	C-O Deformations

s= strong, m=medium, w=weak, b=broad,sh=sharp.

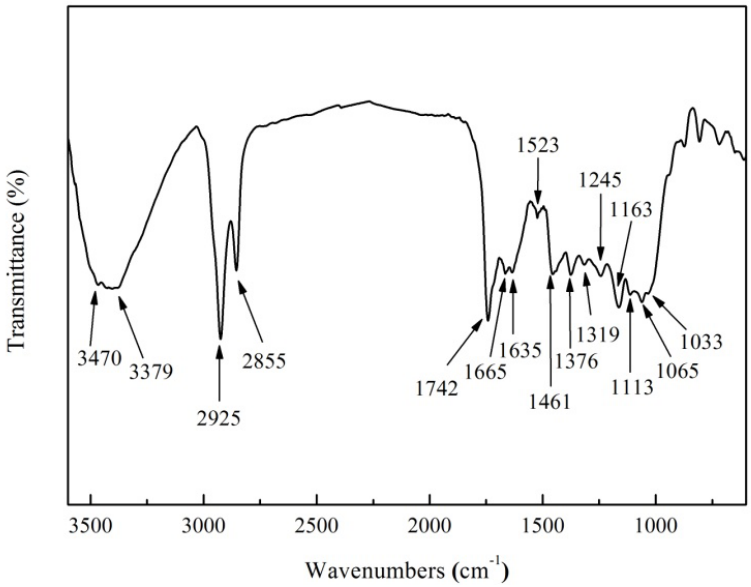


Figure 2.6 FTIR spectra of exhausted coffee waste

4.9 SEM – EDX analysis

The electron micrographs and EDX spectra of exhausted coffee samples ECA and ECB are shown in Figure 2.7 with different magnification. The atomic percentages of C, O, S and Ca elements were calculated averagely by 5 samples. The micrographs shows the non smooth heterogeneous morphology of the EC surface with distributed abrasions. It is clear to see a macroporous and microporous structure of the EC samples with different particle size, which is similar to the observation by Fiol et al. (2008a) and Tsai and Liu (2013). More pores seem can be observed on the ECB surface which is of smaller particle size than ECA, confirming the higher porosity of ECB. This trend can be attributed to an alteration and rearrangement of the polysugar structures present in the terrified biomass under high temperature (Tsai and Liu, 2013). The local composition evaluated by the EDX spectra, indicates that C and O are the main element remaining in exhausted coffee waste. The result of C is similar to elemental analysis results. Note that the much higher percentage of C is due to the carbon coating of the samples.

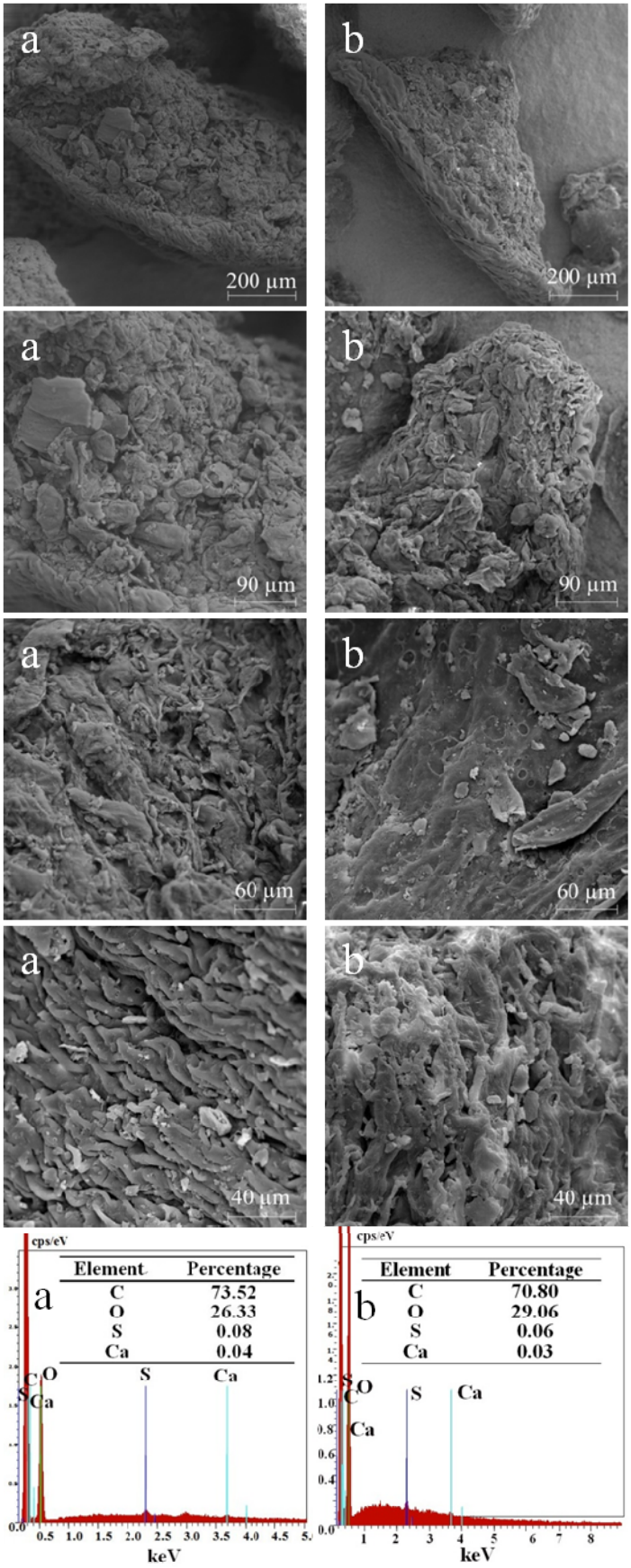


Figure 2.7 SEM-EDX analysis of exhausted coffee waste samples (a. ECA: 500 - 1000 µm, b. ECB: 250 - 500 µm)

CHAPTER III.

THE ROLE OF CHEMICAL COMPOUNDS OF EXHAUSTED COFFEE WASTE IN METAL IONS SORPTION

1. INTRODUCTION

In Chapter II, a complete physical and chemical characterization of exhausted coffee waste has been performed to assess the potential of exhausted coffee waste as sorbent. As mentioned in Chapter II, the high amount of EC chemical components, including non-structural and structural compounds, possess plenty of functional groups that could be of great potential for their sorption towards metal ions and other matters. Therefore, the investigation of the role of chemical components of EC in sorption process becomes of high importance for study of sorption mechanism.

Up to now, the adsorptive property of EC is attracting more and more attention. As mentioned before, EC has been investigated as a versatile biosorbent for hexavalent chromium (Fiol et al., 2008a; Kim et al., 2012; Prabhakaran et al., 2009; Pujol et al., 2013a), divalent metal ions (Kyzas, 2012; Oliveira et al., 2008; Rao et al., 2010; Tokimoto et al., 2005; Utomo and Hunter, 2006; 2010) and dyes (Ahmad and Rahman, 2011; Franca et al. 2009; Hirata et al., 2002). However the sorption mechanism is not very clear. Lignin is known to adsorb many metal ions and organic matters from aqueous solutions (Demirbas, 2008; Guo et al., 2014; Haven and Jorgensen, 2013; Nuhu, 2014; Zhou et al., 2014). Among EC sorption studies, lignin moieties were reported to contain electron donor groups for Cr(VI) reduction to Cr(III) (Fiol et al., 2008a; Prabhakaran et al., 2009; Pujol et al., 2013a). Lignin was also resulted to be responsible for divalent metal ion sorption together with ion exchange between metal ion and the light metals on the sorbent surface (Oliveira et al., 2008; Rao et al., 2010; Tokimoto et al., 2005). Nevertheless, a great variety of functional groups i.e. alcohol, ketone and carboxylic groups as well as alkaline and alkaline earth metals as counterions possessed by the surfaces of EC can be involved in complexation reactions and ion-exchange processes (Nurchi and Villaescusa, 2008; Turanov et al., 2013). Up to our knowledge, besides lignin, the influence of the non-structural components (extractives) on sorption of metal ions onto EC has not been investigated. The real challenges in the field of biosorption are to identify the chemical components responsible for the sorption behavior and the mechanisms governing the different sorption processes. In view of the EC characterization obtained in Chapter II, the extractives

form a significant fraction of EC. In this case the investigation of the influence of extractives of EC on metal ions sorption is of extremely importance.

The aim of the study presented in this chapter is to give some insight into the role of both extractives and structural components of EC in metal ions sorption. For this purpose, EC samples were treated by the same series of sequential extraction as being treated in the characterization process (see Chapter II section 3.7.1). The treated materials (free-extractives) with particular losing of non-structure and structure compounds from EC were collected and subjected to Cr(VI) and divalent metal Cu(II) and Ni(II) sorption. The sorption features of the treated EC samples were compared to the ones presented by raw EC. Through the enhanced or restricted sorption effect, the role of each chemical composition in metal ions sorption can be elucidated. Thus the sorption mechanism of EC involves chemical reaction between functional groups on the biosorbent and the metal ions can be explored.

2. MATERIALS AND REAGENTS

2.1. Reagents and Solutions

- 99.99% dichloromethane (Fisher), 96% ethanol (Aga), Milli-Q water, analytical grade NaOH in pellets (Panreac) and ice were applied in solvent extraction and alkaline lixiviation.
- Analytical grade potassium dichromate (Scharlau), analytical grade copper chloride dehydrate (Merck) and analytical grade nickel chloride 6-hydrate (Panreac) were used as metal ions salts for metal sorption study.
- 0.1 M HCl (Panreac) and 0.1 M NaOH (Panreac) were prepared to adjust pH.
- 1000 mg L^{-1} chromium, copper and nickel standard solutions (Panreac) were employed in standard preparation for metal ions analysis in flame atomic absorption (FAAS).
- Analytical grade potassium dichromate (Panreac) was employed in standard preparation for hexavalent chromium analyses in sequential injection system (SIA). Analytical grade 1,5-diphenylcarbazide (Panreac), reagent grade ethanol (Scharlau) and reagent grade sulfuric acid 95-97% (Scharlau) were also used for hexavalent chromium analyses in sequential injection system (SIA).

- FTIR grade KBr (Acros Organics) was use to prepare pellets for Fourier Transform Infrared Ray (FTIR) analysis.

2.2. Equipment

- Flame atomic absorption spectroscopy (FAAS) (Varian Absorption Spectrometer SpectraAA 220FS) was used to determine the total concentration of chromium, i.e., Cr(VI)+Cr(III) and copper and nickel concentrations.
- Sequential injection system (SIA) recently developed in our laboratory was applied to hexavalent chromium analyses.
- Elemental analyzer (Perkin Elmer EA2400 series II, the scales Sartorius 2MP with a ENAC calibration) was used for elemental analysis.
- Fourier transform spectrometer (Galaxy Series FTIR 5000, Mattson Instrument Co., Madison, WI) was used for FTIR analysis.

3. METHODOLOGY

3.1. Sequential extraction of exhausted coffee waste

This section was carried out in the Forest Research Centre, imbedded in Institute Superior of Agronomy in the Technical University of Lisbon during my stay there. The procedure of sequential extraction of EC follow the same series as has been carried out in EC characterization, by dichloromethane (DCM), ethanol (EtOH), water (H_2O) and 1% NaOH solution. In order to obtain enough amount of treated materials (free-extractives), the Soxtec extraction used in characterization was replaced by Soxhlet extraction. The percentage of extractives removed by each of the solvents was compared with the results obtained in Chapter II in order to assess the extraction procedure.

In order to get enough treated biomass at each of the different extraction level, batches of 16.2 g of raw EC were placed inside a glass fiber thimble. In the first batch, EC was extracted by DCM to get treated sample EC1. In the second batch, EC sample was extracted by DCM then followed by EtOH to get treated sample EC2. In the third batch, EC sample was extracted sequentially by DCM, EtOH and water to get treated sample EC3. In the last batch, EC sample

was treated by DCM, EtOH, water and then followed by aqueous alkaline extraction with 1% NaOH (1:50 solid: liquid ratio) obtaining the EC4 sample. The flowchart of the extraction process can be seen in Figure 3.1.

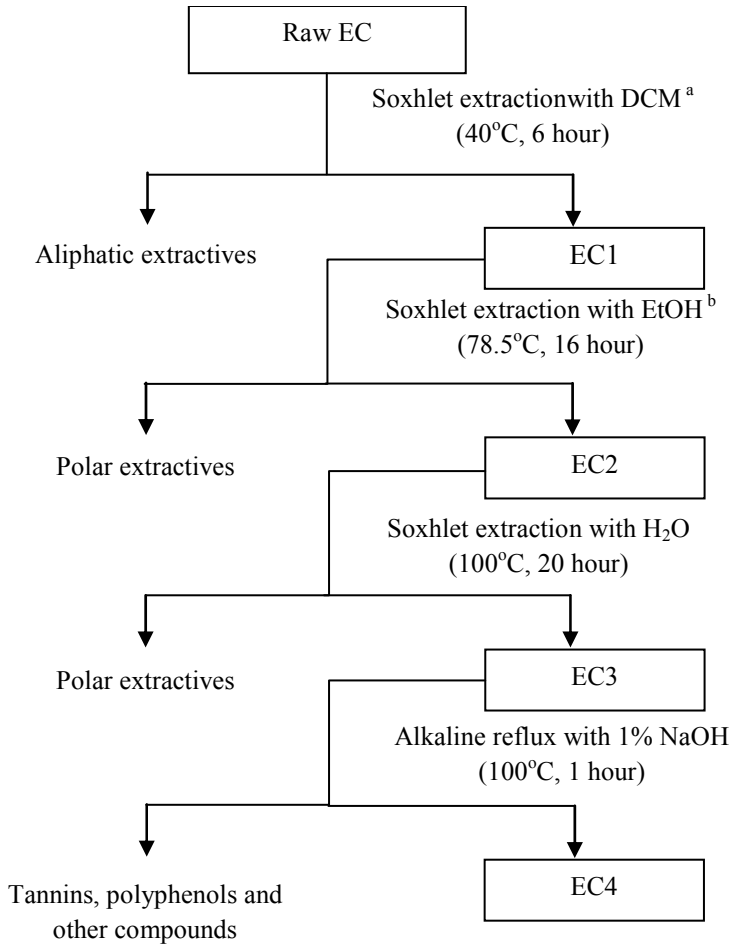


Figure 3.1 Flowchart of the extraction process of exhausted coffee waste (EC).

[a]DCM: dichloromethane; [b] EtOH: ethanol.

The extraction with organic solvents and water was performed in a Soxhlet extractor. The conditions of DCM, EtOH and water extraction were at 40°C for 6 hours, at 78.5°C for 16 hours and at 100°C for 20 hours, respectively. The solvents were recovered afterwards. Each thimble containing treated sample was dried in a fume hood at room temperature if it was needed to be subjected to next extraction step. Otherwise, the thimble was dried in the fume hood, after that, the free-extractive samples inside were rinsed with Milli-Q water until neutral pH then dried in an oven at 60°C until constant weight. The alkaline lixiviation with 1% NaOH of the

free-extractive samples was carried out in a flat bottom flask under reflux at 100^{o}C for 1 hour. Afterwards, the flask was cooled with ice, the solution was filtered by a sand core funnel using a vacuum pump and the solid rinsed with Milli-Q water until neutral pH. The sand core funnel was put in the oven at 60^{o}C until constant weight. All the treated samples were washed thoroughly with water to remove the remaining solvents and specially to remove NaOH in the case of EC4 sample.

As mentioned in section 3.7.1 of Chapter II, each solvent removes different amounts and types of extractives as well as other cell wall components (Pereira, 2007). The obtained treated samples (EC1-4) were kept in a desiccator before used for metal sorption and Fourier Transform Infrared Spectroscopy (FTIR) analysis.

3.2. Metal sorption procedure

Batch experiments were carried out at 20±2^{o}C in stoppered glass tubes by shaking 0.1 g of either raw material (EC) or treated biomass (EC1-4), with 15 mL of metal ions solution in a rotary stirrer (Rotator drive STR4, Stuart Scientific) at 40 rpm. After agitation, the solid was removed by filtration through a 0.45 mm cellulose filter paper (Millipore).

Cr(VI) in single solutions with two different concentrations at 98.09 mg L^{-1} and 304.89 mg L^{-1} was subjected to sorption onto raw and treated EC samples. The selection of pH and contact time for Cr(VI) removal using raw EC was made on the basis of the results obtained in our previous study (Fiol et al., 2008a) in which maximum Cr(VI) sorption by EC was attained at pH 2.0 after 4 days agitation. Therefore, this condition was selected to carry out Cr(VI) sorption onto raw and treated biomass fractions. With the aim to monitor the process of Cr(VI) reduction to Cr(III) two contact times were considered, half-time equilibrium ($t_{e½}$) and equilibrium time (t_e). Meanwhile, Cu(II) and Ni(II) in single solutions with concentrations at 124.66 mg L^{-1} and 124.89 mg L^{-1}, respectively were subjected to sorption onto raw and treated EC samples. Their optimal conditions which at pH 5.0 and one hour contact time were decided based on the result of Cu(II) sorption kinetics using EC (see Chapter IV) and the result obtained by Pujol et al. (2013a). All sorption experiments were carried out in duplicate and the average results are presented.

3.3. Analysis of metal ions

The total concentration of chromium, i.e., Cr(VI)+Cr(III) and copper and nickel concentration in the remaining solution after sorption were determined by flame atomic absorption spectroscopy (FAAS). Hexavalent chromium was analyzed by the standard colorimetric 1,5-diphenylcarbazide method (Clesceri et al., 1998) by using a sequential injection system (SIA). The concentration of trivalent chromium was determined as the difference between total chromium and hexavalent chromium concentrations, respectively. For comparison sake, the Cr(VI) standard used in diphenylcarbazide method was analysed by FAAS. Analytical measurements made by the two techniques were comparable within 5%.

3.4. Elemental analysis

Elemental contents (C, H and N) of raw materials (EC) and treated biomass (EC1-4) were determined using an Elemental Analyzer. C, H and N detection limits were the same as shown in Chapter II. Oxygen content was calculated by difference. The elemental ratios H/C, O/C, C/N, (O + N)/C were computed for all the samples.

3.5. FTIR analysis

To give a qualitative and preliminary analysis of the main surface functional groups on raw materials and treated biomass solid fractions, a Fourier Transform Infrared (FTIR) analysis in solid phase was performed using a Fourier Transform Spectrometer. Solid phase FTIR analysis was used to investigate changes in the absorption bands corresponding to the functional groups of the adsorbents as a consequence of the summative extraction and chromium, copper and nickel loading. Spectra of the samples before and after contact with Cr(VI) of high concentration (304.89 mg L^{-1}), Cu(II) (124.66 mg L^{-1}) and Ni(II) (124.89 mg L^{-1}) were recorded on a FTIR spectrometer. For FTIR analysis, 200 mg KBr disks containing 2 mg of finely ground sample were prepared. Spectra were recorded in the spectral range 3600 to 600 cm^{-1} by co-addition of 32 scans with a resolution of 4 cm^{-1}.

4. RESULTS AND DISCUSSION

4.1. Isolation and characterization of EC and treated biomass samples

The mass of each solid (raw EC and treated biomass) together with the percentage of extractives removed after the successive extractions are presented in Table 3.1.

Table 3.1. Exhausted coffee waste (EC) mass loss after successive extractions and percentage of extractives removed. The cumulative removal of extractives is indicated in brackets. DCM: dichloromethane, EtOH: ethanol, mass of raw EC: 16.2 g.

Solvent	Treated samples	Mass loss (g)	Extractives removal (%)
DCM	EC 1	3.87	23.89 (23.89)
EtOH	EC 2	0.60	3.70 (27.59)
H_2O	EC 3	0.15	0.93 (28.52)
1% NaOH	EC 4	4.85	29.94 (58.46)

As seen in Table 3.1, the percentage of total extractives removed from EC was very high (58.46%). The amount of apolar compounds solved in DCM was also high, which is expected because coffee beans contain high percentages of fatty acids that partially pass to the brewed coffee (Mussatto et al., 2011b). The low content of compounds solved in H_2O (0.93%) is probably due to the process of the brewed coffee extraction with hot water. The alkaline lixiviation with 1% NaOH provoked a remarkable loss of EC mass (4.85 g) and 30% extractives removal. Miranda et al. (2013) found that the amounts of extractives of tree barks solubilized in the alkaline solution were related to the hemicelluloses and suberin content. In the results of raw EC characterization, polysaccharides content was reported to account for 24% of raw EC (see Chapter II section 4.7.1). The values of extractives solubilized by alkaline solution were also reported for the maritime pine bark from Portugal (11%) (Fradinho et al., 2002) and various pine barks (17.2-39.1%) (Fengel and Wegener, 1984). The percentage of extractives removed by each of the solvents is comparable to the results obtained in raw EC

characterization (see Chapter II section 4.7.1), where Soxtec extractor was used for the extraction of less amount of EC by DCM, EtOH and H_2O. The expected results can validate the sorption procedure performed in this chapter for the obtaining of treated EC samples.

Elemental composition and elemental ratios of raw EC and treated biomass are given in Table 3.2. According to the characterization of raw EC reported in Chapter II, the raw EC were mainly composed by some polar and non-polar atoms C, O, N and H. The elemental ratios (O+N)/C named polarity index (PI) is an important index indicating the polarity of the material and is an important parameter inversely correlated with the aromatic character of the sample (Pujol et al., 2013b).

Table 3.2 Elemental analysis and elemental ratios H/C, O/C and (O+N)/C of raw exhausted coffee (EC) and treated samples.

	%C	%H	%N	%O[a]	H/C	O/C	(O+N)/C
EC	57.56	7.86	2.48	32.10	1.64	0.42	0.46
EC1	51.87	7.07	2.68	38.38	1.64	0.55	0.60
EC2	51.25	6.93	2.71	39.11	1.62	0.57	0.62
EC3	50.87	6.90	2.67	39.56	1.63	0.58	0.63
EC4	48.41	6.65	2.69	42.25	1.65	0.65	0.70

[a] oxygen was calculated by mass difference.

As seen in Table 3.2, EC samples polarity index (O+N)/C showed a trend to increase (from 0.46 to 0.70) with the successive extractions. The highest increase of polarity was found after aliphatic extractives removal by DCM (EC1).

4.2. Sorption studies

4.2.1. Cr(VI) sorption

The results obtained for Cr(VI) sorption onto raw EC and the different EC treated samples at $t_{e½}$ (2 days) and at t_e (4 days) are presented in Table 3.3. In the same table the pH values and the percentage of total chromium removed at equilibrium are also shown. As seen, Cr(VI) has been totally eliminated by all EC and treated biomass after two days contact time ($t_{e½}$) in the

case of the low Cr(VI) initial concentration (98.09 mg L^{-1}); chromium in the remaining solution was in its trivalent form and a larger contact time did only enhance sorption by about 2%. Conversely, when a three folds higher Cr(VI) concentration was contacted with the studied EC samples both Cr(VI) and Cr(III) were found in the remaining solution at both studied contact times. Note that for both Cr(VI) initial concentrations doubling the contact time had no effect on Cr(III) concentration in solution. The increase of pH denoted the amount of protons consumed and was consistent with chromium reduction.

Table 3.3 Cr(VI) sorption onto raw exhausted coffee (EC) and treated samples. Initial pH 2.01, half-time equilibrium ($t_{e½}$) time: 2 days and time at equilibrium (t_e): 4 days.

Sample	$Cr(VI)_{te½}$ (mg L^{-1})	$Cr(III)_{te½}$ (mg L^{-1})	$pH_{te½}$	$Cr(VI)_{te}$ (mg L^{-1})	$Cr(III)_{te}$ (mg L^{-1})	pH_{te}	Removal (%)
Initial Cr(VI) 98.09 mg L^{-1}							
EC	< LOD[a]	11.69	2.29	< LOD	11.24	2.33	88.54
EC1	< LOD	11.36	2.30	< LOD	10.84	2.35	88.95
EC2	< LOD	9.87	2.30	< LOD	9.60	2.36	90.21
EC3	< LOD	10.03	2.31	< LOD	9.63	2.33	90.18
EC4	< LOD	13.38	2.34	< LOD	13.12	2.39	86.63
Initial Cr(VI) 304.89 mg L^{-1}							
EC	6.94	33.62	2.48	1.39	35.43	2.60	87.93
EC1	1.51	28.11	2.61	0.20	29.14	2.64	90.38
EC2	1.34	25.14	2.6	0.23	26.53	2.68	91.22
EC3	2.02	26.18	2.58	0.52	26.28	2.62	91.21
EC4	5.28	45.84	2.81	1.88	46.75	2.90	84.05

[a] LOD = Limit of detection of SIA.

A glance on the percentage of total chromium removed by EC leads to deduce that the best results were obtained when aliphatic and polar compounds were removed (treated biomass EC1, EC2 and EC3). These results suggest that: (i) these two families of compounds did not participate in the chromium reduction/sorption process and (ii) the removal of these compounds favored Cr(VI) interaction with the sorbent active sites where chromium reduction and sorption took place. The same observation was found by Olivella et al. (2013) that the removal of apolar extractives of cork favored the interaction between lignin and phenanthrene.

A deeper examination of Cr(VI) and Cr(III) concentration values shown in Table 3.3 allows observing differences between raw material and treated samples sorption behavior. For the highest Cr(VI) concentration tested (304.89 mg L^{-1}) it is observed that reduction took place more effectively with EC1, EC2 and EC3 compared to raw EC and EC4 samples. Notice that EC4 was slightly more effective for Cr(VI) reduction but quite less effective to sorb chromium in its trivalent form than raw EC. Moreover, the equilibrium pH after Cr(VI) sorption onto EC4 was very high compared to the one of the systems in which reduction reaction was more effective. The reason for the high ΔpH (0.89) (calculated as the difference between initial pH (2.01) and equilibrium pH (2.90)) could be attributed to the fact that EC4 could have on its surface more active sites to be protonated. Thus, under the action of NaOH, the functional groups of EC structural compounds moieties (i.e. lignin, hemicellulose) could be hydrolyzed resulting in EC4 whose structure and chemical composition differs from the one of EC3. The lower chromium sorption exhibited by EC4 at both studied chromium concentrations may be explained by considering that the moieties hydrolyzed by the action of the alkaline solution are presumably involved in chromium reduction/sorption processes.

4.2.2. Cu(II) and Ni(II) sorption

The results obtained when investigating Cu(II) and Ni(II) sorption onto raw EC and treated biomass at pH 5.0 are presented in Table 3.4. In this table, metal concentration and solution pH after 60 minutes contact time are shown. As can be seen EC and treated biomass were more efficient to sorb copper than nickel. Note that among the EC treated biomass the best results for both metals sorption were obtained for EC4. This would be consistent with the formation of new active sites for copper and nickel sorption after the alkaline treatment. Jorge et al. (1999) found that the oxidation process with dichromate, even of an alkyl aromatic side chain, will end in a carboxyl group. The formation of acidic sites might be the reason why EC4 exhibits the best sorption rates. Like it was found for chromium removal it seems that the removal of polar and apolar extractives favors the interaction of copper and nickel with the exhausted coffee matrix.

Table 3.4 Cu(II) and Ni(II) in solution at equilibrium and percentage of metal ions removed after contacting with raw EC and treated samples. Initial Cu(II) and Ni(II) concentration: 124.66 mg L^{-1} and 124.89 mg L^{-1}, respectively, initial pH: 5.00, contact time: 1 hour.

Sample	Cu(II) (mg L^{-1})	Cu(II) removal (%)	Ni(II) (mg L^{-1})	Ni(II) removal (%)	$pH_{Cu(II)}$	$pH_{Ni(II)}$
EC	104.27	16.36	124.89	0.00	4.24	4.58
EC1	102.21	18.01	115.29	7.69	4.38	5.39
EC2	95.07	23.74	116.31	6.87	4.62	6.10
EC3	98.82	20.73	115.34	7.65	4.46	5.92
EC4	74.48	40.25	94.58	24.27	3.97	5.72

4.3. Relationship between sorption affinities and sorbent characteristics

In an attempt to explain the sorption yields obtained by the studied samples (Tables 3.3 and 3.4), the sorption affinity which describes the equilibrium distribution of the sorbate (metal ion) between sorbed and dissolved phase is represented by the distribution constant K_d (Lyngsie et al., 2014; Volkov et al., 2013). K_d (in L g^{-1}) is a quantitative characteristic of the measure of interactions between sorbate and the sorbent. It was calculated for each metal and each of raw EC and treated biomass and defined by the equation

$$K_d = [Metal]_{sorbent} / [Metal]_{solution} \quad (3.1)$$

where $[Metal]_{sorbent}$ is the concentration of the metal ions in the sorbed phase and $[Metal]_{solution}$ the concentration in the dissolved phase of a system in equilibrium (Stuer-Lauridsen and Pedersen, 1997).

The sorbent characteristics, for example, polar and non-polar atoms have shown to be correlated with the sorption behavior (Kile, 1999; Rutherfore et al., 1992; Site, 2001). As mentioned in section 4.1, the amount of polar atoms, especially oxygen and nitrogen, compared to the content of non-polar atoms, especially carbon, is expressed as the term polarity index (PI) for the molar mass ratio (O+N)/C (Xing et al., 1994). PI is an important parameter to predict sorption. This parameter was shown to be negatively correlated with the sorption capacity of biopolymers for organic matter (Stuer-Lauridsen and Pedersen, 1997) and

hydrophobic pollutants (Wang et al. 2007), and has been related with heavy metal ions sorption.

In the effort to see the relationship between sorption affinities and sorbent characteristics, K_d was plotted versus elemental ratios PI (O+N)/C and H/C.

4.3.1. Relationship between Cr(VI) sorption affinities and sorbent characteristics

K_d values for Cr(VI) onto EC samples plotted versus PI and elemental ratios H/C are presented in Figure 3.2(a) and (b), respectively.

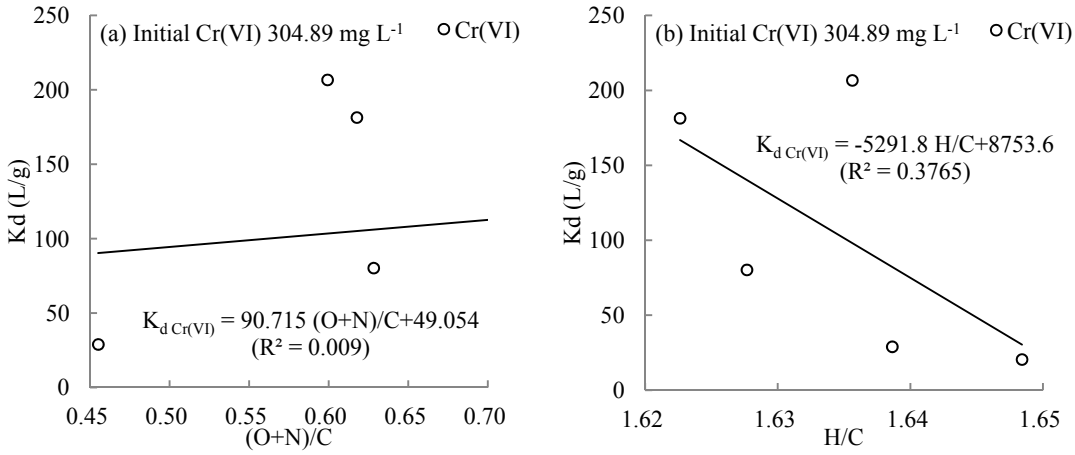


Figure 3.2 Exhausted coffee (EC) distribution constant (K_d) for Cr(VI) vs elemental ratios (a) PI and (b) H/C. Initial Cr(VI): 304.89 mg L^{-1}.

The lack of linear correlation between Cr(VI) K_d values and PI and elemental ratios H/C of EC puts into evidence that Cr(VI) sorption followed a complex mechanism that was not directly related to these elemental ratios. Indeed, Cr(VI) sorption process onto EC includes different steps: Cr(VI) sorption, Cr(VI) reduction and sorption of the formed Cr(III) (Fiol et al., 2008a; Pujol et al., 2013a; Shen et al., 2010).

With the purpose of evaluating the affinity of sorbent on the formed Cr(III) species, K_d values for Cr(III) were also plotted versus PI and elemental ratio H/C and presented in Figure 3.3, respectively. Under the assumption that all the chromium on the sorbent at equilibrium was in the form of Cr(III) species, thus the amount of Cr(III) on EC surface was considered as the difference between initial Cr(VI) concentration and the final Cr(VI) concentration in solution and minus the final Cr(III) concentration in solution.

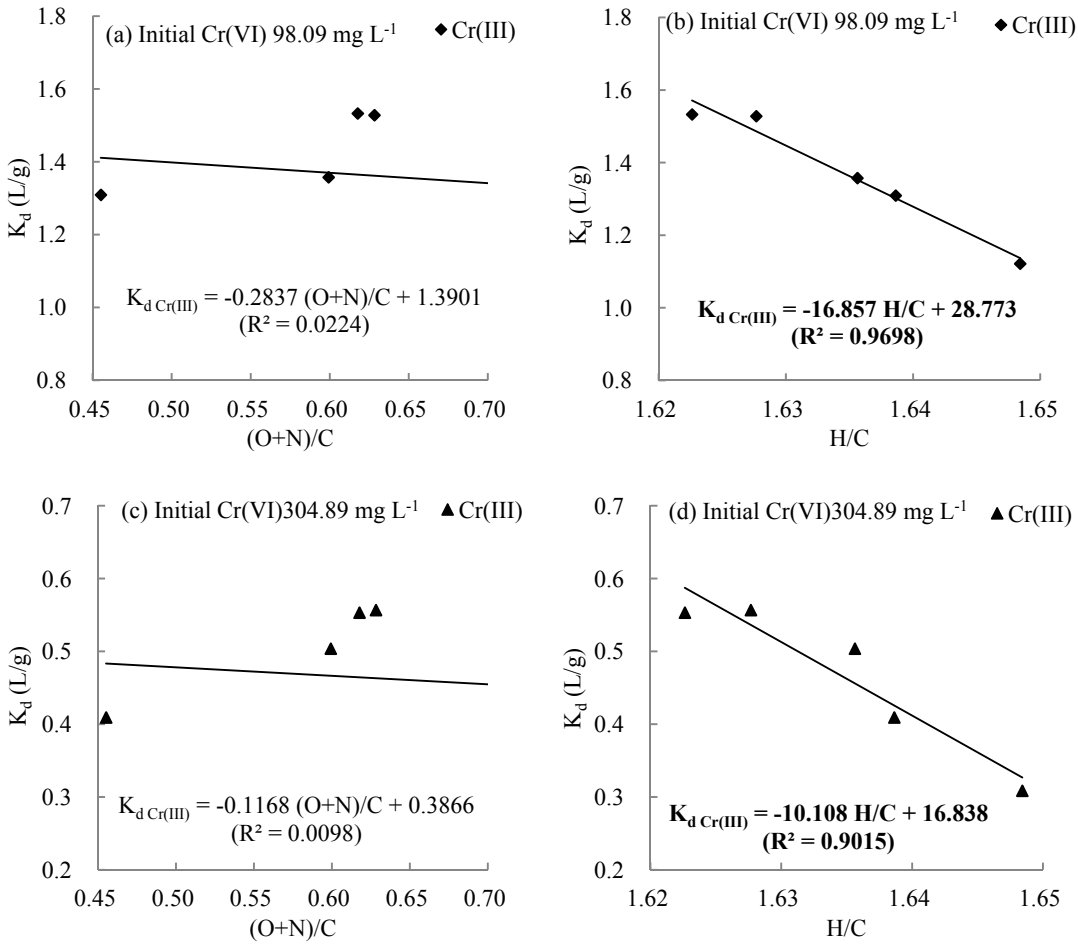


Figure 3.3 Exhausted coffee (EC) distribution constant (K_d) for Cr(III) vs elemental ratios (a) (c) PI and (b) (d) H/C.

It is worthwhile noting that the plot of Cr(III) K_d vs H/C values obtained for EC shows a significant negative correlation either when initial Cr(VI) was at 98.09 mg L^{-1} or at 304.89 mg L^{-1}. Therefore, these results could confirm the ability of EC in Cr(VI) reduction and suggest a dominate binding form Cr(III) on EC. Furthermore the results seem to indicate that EC binding affinity for Cr(III) is not favored by the presence of aliphatic carbon structures (e.g. aliphatic hydrocarbons).

4.3.2. Relationship between Cu(II) and Ni(II) sorption affinities and sorbent characteristics

K_d values for Cu(II) and Ni(II) onto EC samples plotted versus PI and elemental ratios H/C are presented in Figure 3.4(a) and (b), respectively.

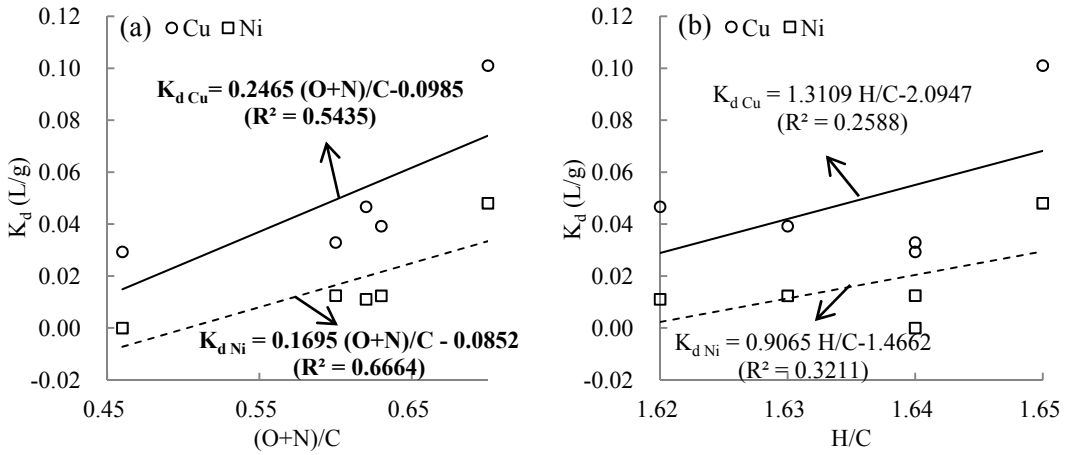


Figure 3.4 Exhausted coffee (EC) distribution constant (K_d) for Cu(II) and Ni(II) vs elemental ratios (a) PI and (b) H/C. Initial Cu(II): 124.66 mg L^{-1}, initial Ni(II): 124.89 mg L^{-1}.

Regarding K_d values for Cu(II) and Ni(II) sorption onto EC samples, they were found to have a weak positive correlation (R^2 = 0.54 for copper and R^2 = 0.66 for nickel) with the PI value of raw EC and treated biomass and while less significant correlation with the elemental ratios H/C. This result suggests that the oxygen functional groups (i.e. carboxylic COOH and phenolic OH groups) on EC surface could be involved in Cu(II) and Ni(II) binding.

The acid dissociation constant (pK_a) values for carboxylic groups range between 3 and 5, and those for phenolic groups are between 9.5 and 10.5. In the literature, some authors using sorbents based on natural organic matter found that copper sorption was strongly influenced by the carboxylic groups content (Sun et al., 2012) while some others by that of the phenolic groups (Rey-Castro et al., 2009). When looking at Table 3.4 pH values ranged between 3.97-4.62 and 4.58-6.10 after copper and nickel sorption, respectively. Within these pH ranges strong carboxylic groups are fairly deprotonated while phenolic groups remain protonated. The lower pHs obtained after copper sorption seems to indicate that the sorption of this metal ion causes a larger release of protons in solution favoring copper sorption onto EC biomass matrix and its binding to decarboxylic acids (i.e. $-COO^-$). This fact would explain the higher copper removal compared to nickel.

4.4. Fourier Transform Infrared Ray (FTIR) analysis

The most representative transmittance peaks of raw EC and treated samples spectra before and after Cr(VI), Cu(II) and Ni(II) sorption were assigned and are reported in Table 3.5, where the shift in wavenumber of the peaks can be observed and the increase in intensity of the peaks is presented with symbol "*".

As far as all the unloaded EC samples, the comparison of the spectra between raw EC and treated biomass allows to observe the modifications due to the removal of aliphatic structures (i.e. long-chain n-alkanes and fatty acids) after DCM extraction, such as: the peak attributed to C-H vibrations shifted from 2855 to 2863 cm^{-1}, the peak corresponding to C=O stretching shifted from 1742 to 1710 cm^{-1}. The intensity of both mentioned peaks was also reduced. Moreover, the peak at 1461 cm^{-1} attributed to CH deformation (asymmetry in methyl groups $-CH_3$ and $-CH_2$) was shifted to 1439 cm^{-1} (Herbert, 1971). As a consequence of the extraction with 1% NaOH some polysaccharides were structurally modified, denoted by the shift of the peak from 1033 (EC3) to 1027 cm^{-1} (EC4) attributed to C-O deformation from polysaccharides. Other significant changes after alkaline hydrolysis were observed: the peaks attributed to CH vibrations of $-CH_3$ and $-CH_2$ groups were shifted from 2925 (EC3) to 2918 cm^{-1} (EC4) and from 2863 (EC3) to 2870 cm^{-1} (EC4), which could be due to the partial removal of cellulose, hemicellulose and lignin components (Haussard et al., 2003).

Table 3.5 Wavenumbers (cm^{-1}) of the most representative bands of raw EC and treated samples spectra before and after Cr, Cu and Ni sorption.

EC/ state	γ O-H/N-H	γass C-H	γs C-H	C=O	C=C	C-H Deformations	-COO-, CO-	C-O-C	C-O
Raw									
unloaded	3470, 3379	2925	2855	1742, 1635, 1065	1665, 1523	1461	1376, 1319, 1245	1163	1033
Cr loaded	3470, 3379	2925*	2855*	1742*, 1635*, 1065*	1665*	1439*	1376*, 1319*, 1245*	1163*	1033
Cu loaded	3470, 3379	2925	2855	1742, 1635, 1065	1665, 1523	1461	1376, 1319, 1245	1163	1033
Ni loaded	3470, 3379	2925	2855	1742, 1635, 1065	1665, 1523	1461	1376, 1319, 1245	1163	1033
EC1									
unloaded	3470, 3379	2925*	2863*	1710*, 1635, 1065	1665, 1523	1439	1376, 1319, 1245	1163	1033
Cr loaded	3470*, 3379*	2925*	2863*	1710*, 1635*, 1065*	1665*	1439*	1376*, 1319*, 1245	1163*	1033
Cu loaded	3470, 3379	2925	2863	1710, 1635, 1065	1665, 1523	1439	1376, 1319, 1245	1163	1033
Ni loaded	3470, 3379	2925	2863	1710, 1635, 1065	1665, 1523	1439	1376, 1319, 1245	1163	1033
EC2									
unloaded	3470, 3379	2925*	2863	1710, 1635, 1065	1665, 1523	1439	1376, 1319, 1245	1163	1033
Cr loaded	3470*, 3379*	2925	2863	1710*, 1635, 1065*	1665*	1439*	1376*, 1319*, 1245*	1163*	1033
Cu loaded	3470, 3379	2925	2863	1710, 1635, 1065	1665, 1523	1439	1376, 1319, 1245	1163	1033
Ni loaded	3470, 3379	2925	2863	1710, 1635, 1065	1665, 1523	1439	1376, 1319, 1245	1163	1033
EC3									
unloaded	3470, 3379	2925*	2863	1710, 1635, 1065	1665, 1523	1439	1376, 1319, 1245	1163	1033
Cr loaded	3470*, 3379*	2925*	2863*	1710*, 1635*, 1065*	1665*	1439*	1376*, 1319*, 1245*	1163*	1033
Cu loaded	3470, 3379	2925	2863	1710, 1635, 1065	1665, 1523	1439	1376, 1319, 1245	1163	1033
Ni loaded	3470, 3379	2925	2863	1710, 1635, 1065	1665, 1523	1439	1376, 1319, 1245	1163	1033
EC4									
unloaded	3470, 3379	2918*	2870	1710, 1635, 1065	1665, 1523	1439	1376, 1319, 1245	1163	1027
Cr loaded	3470, 3379	2918*	2870*	1710*, 1635*, 1065*	1665*	1439*	1376*, 1319*, 1245*	1163*	1027
Cu loaded	3470, 3379	2918	2870	1700, 1635, 1065	1665, 1523	1439	1376, 1319, 1245	1163	1027
Ni loaded	3470, 3379	2918	2870	1700, 1635, 1065	1665, 1523	1439	1376, 1319, 1245	1163	1027

"*" indicates the decrease of the peak intensity .

When comparing unloaded and chromium loaded spectra the most important changes were the absence of the peak at 1523 cm^{-1} in all EC samples and the shift of the peak from 1461 cm^{-1} (EC) to 1439 cm^{-1} (EC1) attributed to asymmetric C-H deformations from cellulose and lignin (Herbert 1971). Spectra of EC and treated materials unloaded and Cr(VI) loaded were recorded and are shown in Figure 3.5.

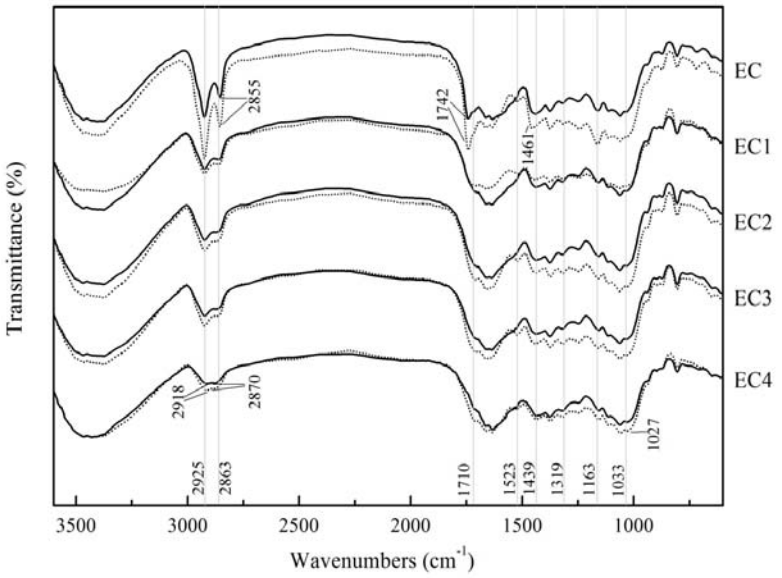


Figure 3.5 FTIR spectra of EC and treated samples unloaded and loaded with chromium. The dotted and solid line represented unloaded and chromium loaded spectra for each sorbent, respectively.

The disappearance of the peak at 1523 cm^{-1} that is attributed to C=C vibration of the aromatic ring of lignin (Fiol et al., 2008a; Djilani et al., 2012), in conjunction with the intensity decrease of the peak at 1163 cm^{-1}, attributed to C-H in plane bending of guaiacyl ring, confirm the involvement of lignin in chromium sorption (Nezahuatl-Muñoz et al., 2012). The lower intensity of the peak at 1319 cm^{-1} associated to CO- stretching of syringyl ring from lignin moieties (Fiol et al., 2008a; Martínez et al., 2006) and OH bending of phenolic groups (Nezahuatl-Muñoz et al., 2012) indicates that phenolic groups of lignin and tannins are also taking part in chromium sorption. Moreover, the peaks in the region 2950-2850 cm^{-1} corresponding to CH stretching vibration in methyl/methylene groups (Kante et al., 2012) were reduced by the effect of chromium sorption, indicating that apart from lignin, cellulose and hemicellulose could be also involved in chromium sorption.

As shown in Table 3.5 and Figure 3.5, the shift and decrease in intensity of some peaks after Cr(VI) sorption can be observed. Whereas concerning Cu(II) and Ni(II), the change of peaks after Cu(II) and Ni(II) sorption was not embodied. As shown in Figure 3.6, the non observed change between unloaded spectra and Cu(II) and Ni(II) loaded spectra is probably due to the low metal loading onto all the studied samples.

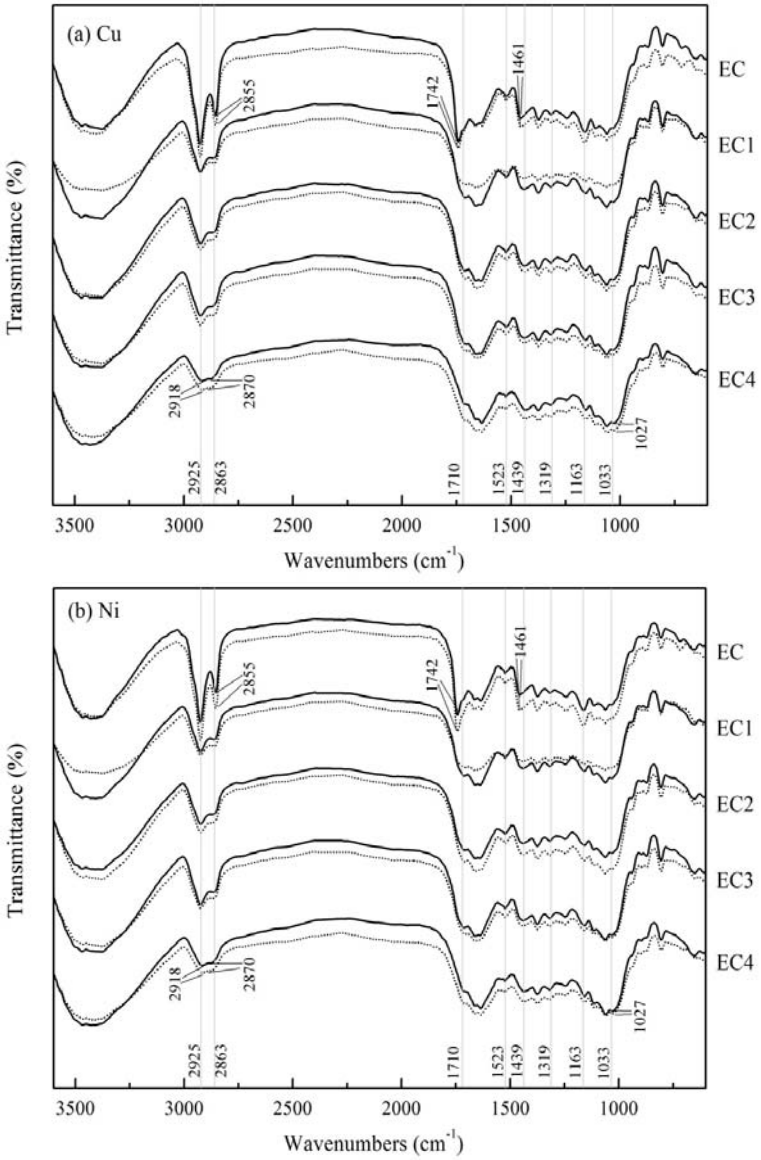


Figure 3.6 FTIR spectra of EC and treated samples unloaded and loaded with copper (a) and nickel (b). The dotted and solid line represented unloaded and metal loaded spectra for each sorbent, respectively.

CHAPTER IV.

KINETICS STUDY OF CHROMIUM SORPTION ONTO EXHAUSTED COFFEE WASTE IN A STIRRED BATCH REACTOR

1. INTRODUCTION

In Chapter III, the role of chemical compounds of exhausted coffee waste (EC) in metal ions sorption was discussed through comparing the metal ions sorption by using raw EC sample and the samples treated through sequential extraction to remove desired chemical compounds. The difference in sorption behavior confirmed the active involvement of lignin moieties in chromium reduction/sorption and divalent metal ions sorption. In addition, carboxylic groups were found to be related to divalent metal ions sorption, whereas the aliphatic carbon structures do not favor the binding affinity of the sorbent for metal ions.

Sorption affinity of EC towards hexavalent chromium (Fiol et al., 2008; Kim et al., 2012; Kyzas, 2012; Oliveira et al., 2008; Prabhakaran et al., 2009) and divalent metal ions (Tokimoto et al., 2005; Utomo and Hunter, 2006; 2010) has been proved separately using single metal solution. As we know, metal ions scarcely exist alone in the environment. Cr(VI) is usually found in mixtures with Cu(II), Ni(II), Fe(III) and other metal ions in real industrial wastewaters. Therefore it is very important to study the simultaneous sorption of Cr(VI) and other metals because the sorption behavior of EC for each metal could be varied due to the interaction between them. However, up to our knowledge, only one study concerning this has been done (Pujol et al., 2013a) where a synergistic effect of Cr(VI)-Cu(II) and Cr(VI)-Ni(II) was found. Whereas normally a competitive sorption between Cr(VI) and other metals was regarded when activated carbon or several other kinds of biomasses were used as sorbent (Ahalya et al., 2007; Aksu et al., 2002; Hussein et al. 2004; Narasimhulu and Setty, 2012; Park et al., 2008; Sag and Kutsal, 1995; Thilagavathy and Santhi, 2013; Wu et al., 2013; Zhong et al., 2013).

The synergistic effect observed by Pujol et al. (2013a) when using EC for the removal of Cr(VI) and other metal ions from aqueous solution is quite exciting. It suggests that EC can be a good biosorbent for metal removal from multi-metal systems. Nevertheless, this study, together with other sorption studies above-mentioned were performed at small-scale batches, either in tubes (Ahalya et al., 2007; Fiol et al., 2008; Pujol et al., 2013a), Erlenmeyer flasks (Kyzas, 2012; Oliveira et al., 2008; Prabhakaran et al., 2009; Utomo and Hunter, 2006; 2010)

or amber bottles (Kim et al., 2012). As we know, at small scale, biosorption is more sensitive to the change of working parameters in comparison with large scale (Pospisil et al., 2009). With the progress of biosorption study, nowadays one of the biggest challenges in this field is to evaluate the feasibility of the biosorptive process for big amount of pollutants at large scale (Park et al., 2010). From this point of view, the biosorption study using EC as sorbent has to be engaged predominantly in reactors.

Meanwhile, most of the aforementioned researches emphasized on the sorption isotherms and focused on the adsorptive metal ions when equilibrium was reached. However, the rate at which the reduction and sorption of metal ions take place cannot be reflected through the equilibrium study, has to be explored by kinetics study. The kinetics of sorption are of great significance to evaluate the performance of a given sorbent and gain insight into the underlying mechanisms (Qiu et al., 2009). The sorption kinetics also describe the solute uptake rate which in turn governs the residence time at the solid-solution interface in a given system. Moreover by doing kinetics simulation, the sorption kinetics are considered as an essential part for operability study and play an important role in the prediction of sorption reaction (Rengaraj and Moon, 2002). It is also a powerful tool for plant optimization, both the operational and at the design stage.

Modelling of sorption kinetics is generally designed considering that the sorption process takes place in four consecutive steps: (i) solute transport in the solution (bulk solution); (ii) diffusion of the solutes across the liquid film surrounding the sorbent particles (film diffusion); (iii) diffusion of the solute along the porous of the sorbent (intraparticle diffusion); (iv) solute sorption/desorption onto the sorbent surface. The global rate of the process can be controlled by any of these steps or a combination of two of them (Haerifar and Azizian, 2013). If the rate limiting step is supposed to be the intraparticle diffusion the intraparticle diffusion model (Haerifar and Azizian, 2013; Plazinski, 2013) or the Weber-Morris equation (Sharma and Goyal, 2009) is used to model the experimental data. In the case that the rate limiting step is the sorption/desorption of the solute molecules onto the sorbent surface the following models are mostly used: pseudo-first order, pseudo-second order, Langmuir, Langmuir-Freundlich or statistical rate theory (SRT) models (Haerifar and Azizian, 2013; Plazinski et al., 2009; Plazinski, 2013; Sharma and Goyal, 2009).

However, these models were frequently employed to fit the kinetic data in an unsuitable or improper manner. This is mainly because the boundary conditions of the associated models were, to a considerable extent, ignored for data modelling. In the case of Cr(VI) sorption kinetics, most of the researches were using classical kinetic models as pseudo-first, pseudo-second and Elovich to model the obtained kinetic data (Kyzas, 2012; Oliveira et al., 2008; Pehlivan et al., 2012; Prabhakaran et al., 2009; Thilagavathy and Santhi, 2013). It must be remarked that these models do not include explicitly the process of Cr(VI) reduction to Cr(III). At present, the kinetics sorption models have to take into account every reaction that occurs in the sorption process in order to improve the authenticity of simulation and description. Recently years, there are specific models that include the step of Cr(VI) reduction to Cr(III) developed in our group (Escudero et al., 2009a; Poch and Villaescusa, 2010).

The effect of the presence of Cu(II) on Cr(VI) sorption kinetics at different pHs by using EC as a sorbent will be assessed by comparing Cr(VI) biosorption from single and Cr(VI)-Cu(II) binary mixtures. The effect of Cu(II) will be also evaluated through several sorption experiments carried out in different Cr(VI)-Cu(II) mixtures ranging concentration of them.

A model that includes Cr(VI) reduction and adsorption will be developed to simulate and describe both Cr(VI) and Cr(III) kinetics profiles in the presence of Cu(II).

2. MATERIALS AND REAGENTS

2.1. Reagents and Solutions

- Analytical grade potassium dichromate (Scharlau) and analytical grade copper chloride dehydrate (Merck) were used as metal ions salts for metal sorption study.
- 0.1 M HCl (Panreac) and 0.1 M NaOH (Panreac) were prepared to adjust pH of sorption solutions.
- 1000 mg L^{-1}chromium and copper standard solutions (Panreac) were employed in standard preparation for metal ions analysis in flame atomic absorption (FAAS).
- Analytical grade potassium dichromate (Panreac) was employed in standard preparation for hexavalent chromium analyses in sequential injection system (SIA). Analytical grade1,5-diphenylcarbazide (Panreac), reagent grade ethanol (Scharlau) and reagent grade sulfuric acid 95-97% (Scharlau) were also used to hexavalent chromium analyses in sequential injection system (SIA).

2.2. Equipment

- pH meter (Crison Basic 20, Spain) was used to measure the solution pH before and after sorption process.
- Flame atomic absorption spectroscopy (FAAS) (Varian Absorption Spectrometer SpectraAA 220FS) was used to determine the total concentration of chromium, i.e., Cr(VI)+Cr(III) and copper, iron and aluminium.
- Sequential injection system (SIA) recently developed in our laboratory was applied for hexavalent chromium analyses.

3. METHODOLOGY

3.1. Experimental set-up

The kinetics study of Cr(VI) and Cu(II) sorption was carried out in a 5 L stirred batch reactor at room temperature (20±2^{o}C) under continuous agitation by using EC with particle size ranged from 0.5 to 1.0 mm. The set-up for kinetics study is presented in Figure 4.1.

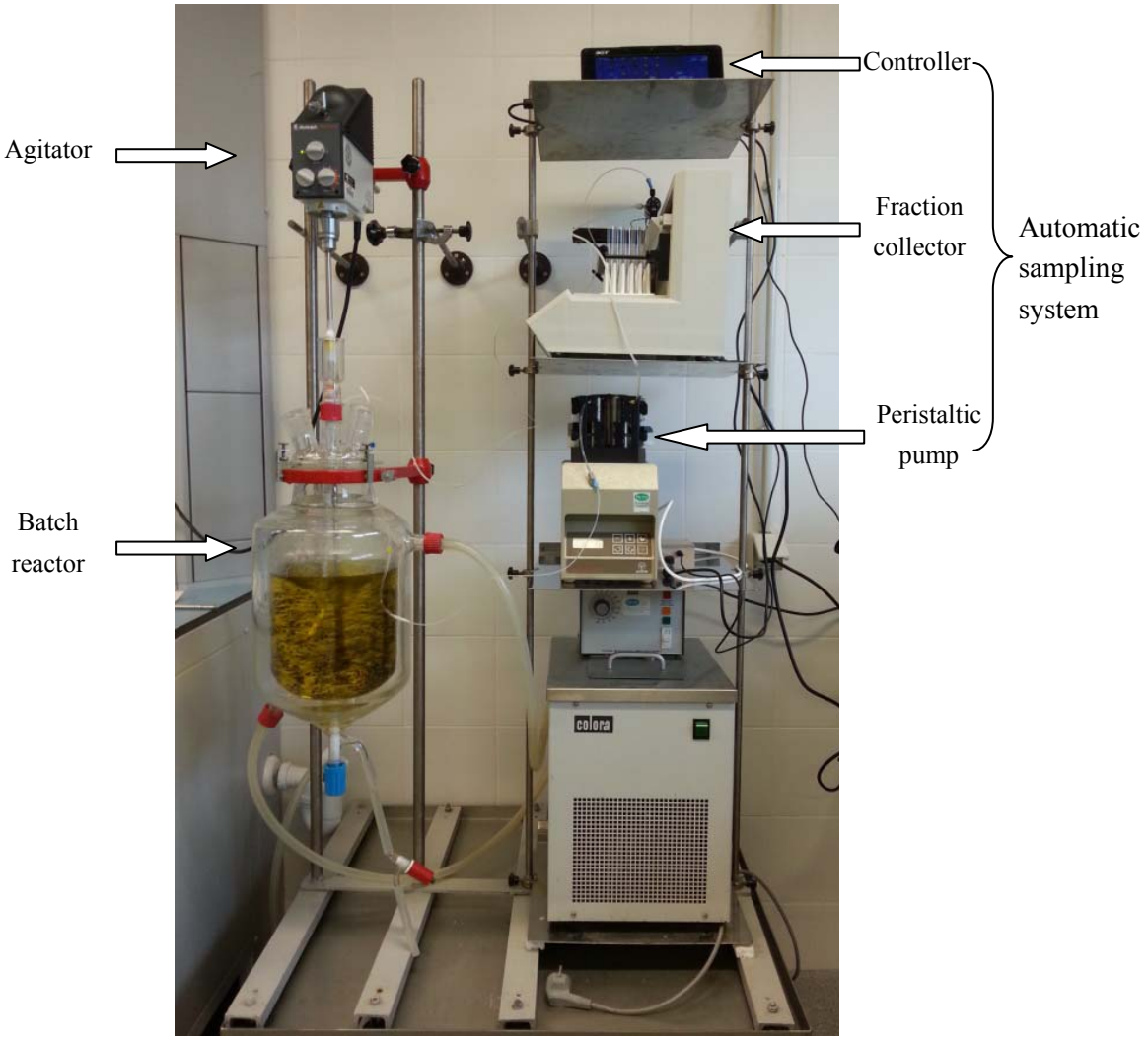


Figure 4.1 Installation of kinetic sorption in a 5 L batch reactor

3.1.1. Description of the control elements

As seen from Figure 4.1, a 5 L batch reactor made by Pyrex glass was used for kinetics sorption study. The reactor is closed by a detachable glass cap with different openings that enable the introduction of the sorbent, the paddle agitator and the sampling tube.

In order to obtain homogeneous mixture of sorbent and solution, the agitating speed was at 350 rpm for all the experiments.

With the aim of acquiring the profiles of metal ions concentration during the sorption process, an automatic sampling system recently developed in our group was used for sampling. A peristaltic pump (Gilson, Minipls 3) and a fraction collector (Gilson, FC203B) were programmed. A sampling tube was connected to the automatic sampling system, approximately 7 mL of sample were collected at the programmed time. The sampling tube was always rinsed by sample before sample collecting. The end of sampling tube was posited in the reactor for circulation. During the first half an hour, sampling was taken frequently (every 5 minutes) so as to get as much as possible information about the sorption rate at the beginning of the process. In order to avoid the little particles of EC reaching the fraction collector and thus damaging it, the bottom of the sampling tube was covered with glass wool acting as a filter.

A drain valve posited at the bottom of reactor was used for discharging the effluent and sorbent out of the reactor when the sorption process was finished.

3.1.2. General operation procedure

3.1.2.1. Solution introduction and conditioning

First of all, the time for sample collection was programmed in the automatic sampling system in advance. The sampling tube was introduced to its position and connected with the sampling system. 4 L of solution at the desired pH were introduced in the reactor from the top, followed by the introduction of 26.67 g of EC. The corresponding sorbent dose was 6.67 g L^{-1}. Agitation was switched on and set at a speed of 350 rpm. Once EC was homogeneous in solution, the programmed sampling system was clicked to start.

3.1.2.2. Sorbent filtration, effluent draining and cleaning of reactor and tubes

When the biosorption process was stopped, the sorbent loaded with metals was filtered, the effluent was collected and the reactor and the entire plumbing device were cleaned. In a first step, the solid and liquid from the reactor were drained through the drain valve of reactor and a

cellulose filter was used to separate the metal-loaded EC and the liquid. In a second step, the sampling tube was removed from its fixed position with its glass wool filter detached, then placed in deionized water. The sampling and recirculation devices were cleaned by running peristaltic pump for a while. In the last step, the reactor walls, the stirred blade and the drain valve were washed with deionized water.

3.2. Effect of Cu(II) on Cr(VI) sorption by EC

In order to evaluate the effect of Cu(II) on Cr(VI) sorption, Cr(VI) removal from Cr(VI) single solution and Cr(VI)-Cu(II) binary mixtures was compared. EC samples were put into contact with 0.4 mM Cr(VI) solution and 0.4 mM Cr(VI)-0.4 mM Cu(II) binary mixture in a stirred batch reactor until sorption equilibrium was reached or nearly reached. A preliminary study of the pH effect on Cr(VI) and Cu(II) removal by EC presented in Annex I showed that pH 2.0 and pH 3.0 were the most favourable conditions for Cr(VI) removal. Therefore, the effect of copper was studied at both pH 2.0 and 3.0.

3.3. Kinetics study of Cr(VI) sorption from Cr(VI)-Cu(II) binary mixtures

The kinetics study of Cr(VI) sorption from binary mixtures was carried out at pH 2.0 which resulted the pH that provided a faster removal of chromium from the solution. In order to obtain fully information of Cr(VI) sorption kinetics in the presence of Cu(II), Cr(VI) sorption experiments were performed using different Cr(VI)-Cu(II) binary mixtures. Two sets of experiments differing 10 folds in metal ions concentration range were carried out. In the first set of experiments Cr(VI) and Cu(II) mole ratios in the binary mixtures (Cr(VI):Cu(II) were 1:2, 1:3, 2:1, 2:2, 2:3, 3:1 and 3:2 and the concentration range of 0.2 to 0.6 mM. In the second one, mole ratios were the same and the metal ions concentration range of 2.0 to 6.0 mM. Each set of experiments includes 7 series of experiments. The initial concentration of Cr(VI) and Cu(II) of the seven experiments corresponding to the two sets is presented in Figure 4.2.

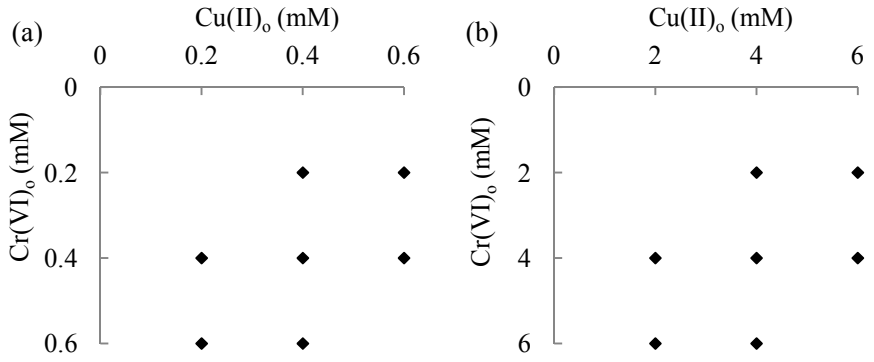


Figure 4.2 Initial concentration of Cr(VI) and Cu(II) in the experiments for the kinetics sorption study

3.4. Analytical methods

The pH value was measured by a pH meter. The concentration of total chromium and Cu(II) were determined by flame atomic absorption spectroscopy (FAAS). Hexavalent chromium was analysed by the standard colorimetric 1,5-diphenylcarbazide method by using a sequential injection system (SIA) recently developed in our laboratory. The concentration of trivalent chromium was determined as the difference between total chromium and hexavalent chromium concentration. The Cr(VI) standard used for obtaining the calibration curves in the diphenylcarbazide method was analysed by FAAS. Analytical measurements made by the two techniques were comparable with 5%. After pH record, samples were acidified by adding 0.1 M HCl to avoid possible metal ions precipitation, and then analysed.

4. RESULTS AND DISCUSSION

4.1. Effect of Cu(II) on Cr(VI) sorption by EC

The results presented in Annex I show that Cr(VI) removal was favourable at both pH 2.0 and 3.0. A slight higher removal of total chromium was found at pH 3.0 nevertheless the sorption process was faster at pH 2.0. The effect of Cu(II) on Cr(VI) removal was investigated by comparing Cr(VI) sorption from single solution (0.4 mM) and from 0.4 mM Cr(VI)-0.4 mM Cu(II) binary mixture. Experiments were carried out at pH 2.0 and pH 3.0 for comparison sake.

4.1.1. Effect of Cu(II) on Cr(VI) sorption kinetics at pH 2.0

The results of Cr(VI) removal from single solution and Cr(VI)-Cu(II) binary mixture are presented in Tables 4.1 and 4.2.

Table 4.1 Cr total, Cr(VI), Cr(III) concentration and pH values as a function of time at 0.4 mM Cr(VI) solution. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

t (h)	total Cr (mM)	Cr(VI) (mM)	Cr(III) (mM)	pH
0.00	0.3756	0.3756	0.0000	2.00
0.08	0.3013	0.3013	0.0000	2.04
0.25	0.2790	0.2786	0.0003	2.03
0.50	0.2635	0.2631	0.0005	2.03
0.75	0.2585	0.2580	0.0005	2.04
1.00	0.2470	0.2456	0.0014	2.03
1.50	0.2286	0.2119	0.0167	2.04
2.00	0.2142	0.1893	0.0249	2.05
5.00	0.1284	0.0732	0.0553	2.06
8.00	0.0980	0.0437	0.0542	2.05
11.0	0.0748	0.0148	0.0600	2.06
14.0	0.0646	0.0027	0.0619	2.07
20.0	0.0603	< LOD[a]	0.0603	2.08
24.0	0.0580	< LOD	0.0580	2.08
27.0	0.0579	< LOD	0.0578	2.08

[a] LOD=Limit of detection of SIA.

As seen in Table 4.1, the concentration of hexavalent chromium started to decrease when contacting with EC in Cr(VI) single solution at pH 2.0. All the hexavalent chromium

disappeared via sorption and reduction to its trivalent form after 20 hours. Trivalent chromium appeared in solution little by little until its concentration arrived at 0.06 mM and kept constant. It is also noticed that Cr(III) concentration achieved equilibrium at the same time that Cr(VI) disappeared.

As regards to Cr(VI) removal from 0.4 mM Cr(VI)-0.4 mM Cu(II) binary mixture at the same pH (Table 4.2), Cr(VI) was also reduced/sorbed after contacting with EC. The concentration of Cr(VI) decreased with time and almost disappeared after 27 hours. As a result of Cr(VI) reduction Cr(III) concentration appeared in solution after 1.5 hours and continuously increased up to 0.06 mM. Note that the results presented in section 4.3.1 of Chapter III showed the capacity of EC to sorb part of the Cr(III) formed as a result of the reduction reaction. Therefore, Cr(III) in the remaining solution did account for the difference between the Cr(III) formed as a result of Cr(VI) reduction and the Cr(III) adsorbed on EC. It is not surprising that Cu(II) was not sorbed on EC at this so acidic pH 2.0. Similar results were observed when Cu(II) was sorbed from single solution in the same experimental conditions (see Annex I).

Table 4.2 Cr total, Cr(VI), Cr(III), Cu(II) concentration and pH values as a function of time at 0.4 mM Cr(VI)-0.4 mM Cu(II) binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2^{o}C.

t (h)	total Cr (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	pH
0.00	0.3865	0.3865	0.0000	0.3986	2.00
0.08	0.3585	0.3585	0.0000	0.3959	2.08
0.17	0.3383	0.3383	0.0000	0.3948	2.05
0.25	0.3272	0.3269	0.0003	0.3921	2.06
0.33	0.3191	0.3191	0.0000	0.3964	2.08
0.50	0.3122	0.3122	0.0000	0.3953	2.06
0.75	0.3048	0.3048	0.0000	0.3986	2.05
1.00	0.3009	0.3009	0.0000	0.3968	2.05
1.50	0.2946	0.2946	0.0000	0.3986	2.05
2.00	0.2695	0.2687	0.0009	0.3986	2.07
3.50	0.2388	0.2319	0.0069	0.3862	2.09
5.00	0.2170	0.1962	0.0209	0.3950	2.08
8.00	0.1734	0.1458	0.0276	0.3953	2.06
11.0	0.1285	0.0840	0.0445	0.3909	2.06
14.0	0.0929	0.0429	0.0501	0.3986	2.09
24.0	0.0709	0.0085	0.0625	0.3953	2.09
27.0	0.0621	0.0010	0.0611	0.3903	2.10

The increase of pH with time observed in both Tables 4.1 and 4.2 can be explained by the consume of protons for the reduction reaction and for sorbent protonation (Fiol et al., 2008; Liang et al., 2014). Same effect was observed in the preliminary study presented in Annex I. With the aim to assess the effect of Cu(II) in Cr(VI) sorption from Cr(VI)-Cu(II) binary mixtures, the profiles of chromium and copper from the two solutions at pH 2.0 are plotted together in Figure 4.3. Seen from this figure, total chromium followed a quite similar decreasing trend with time in both solutions. Only a little slower removal was found in binary mixture at the first 2 hours.

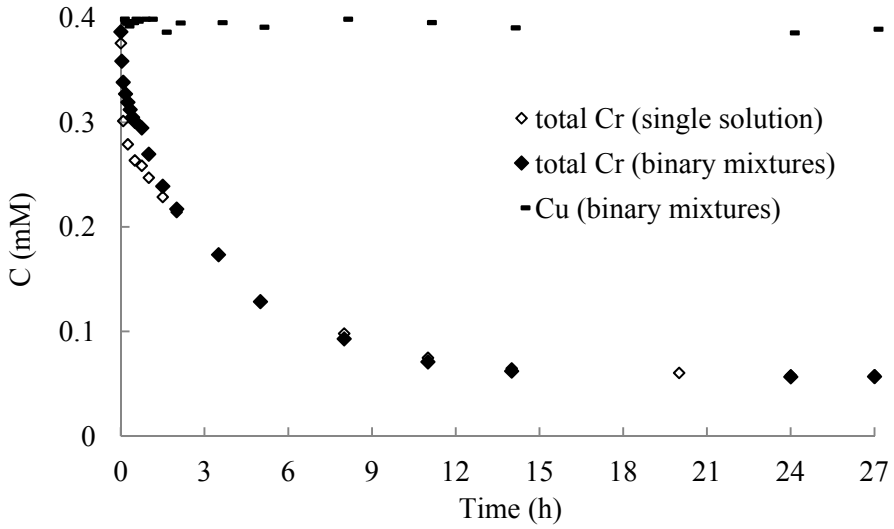


Figure 4.3 Total chromium and Cu(II) concentration in solution as a function of time. Single solution: 0.4 mM Cr(VI). Binary mixture: 0.4 mM Cr(VI)-0.4 mM Cu(II) binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2^{o}C.

As mentioned before, chromium is present in solution in both forms (hexavalent and the reduced trivalent forms. In order to see the effect of Cu(II) on Cr(VI) reduction/sorption and Cr(III) sorption, the profiles of the two forms of chromium in single solution and binary mixture are compared in Figure 4.4. A slight difference between kinetics was only presented in the first hours of chromium sorption. A little higher Cr(VI) concentration was found in metal sorption from the Cr(VI)-Cu(II) binary mixture compared to Cr(VI) sorption from single solution in the beginning of the process. It might be due to the higher ionic strength of the binary mixture by the presence of copper cations that could decrease the adsorption of metal

ions (Borrok and Fein, 2005). Afterwards the decrease of Cr(VI) concentration followed a quite similar trend in both solutions and achieved zero as time progressed. The concentration of Cr(III) increased and had the same value in both solutions. Therefore, it seems that at pH 2.0 the process was not affected by the presence of Cu(II).

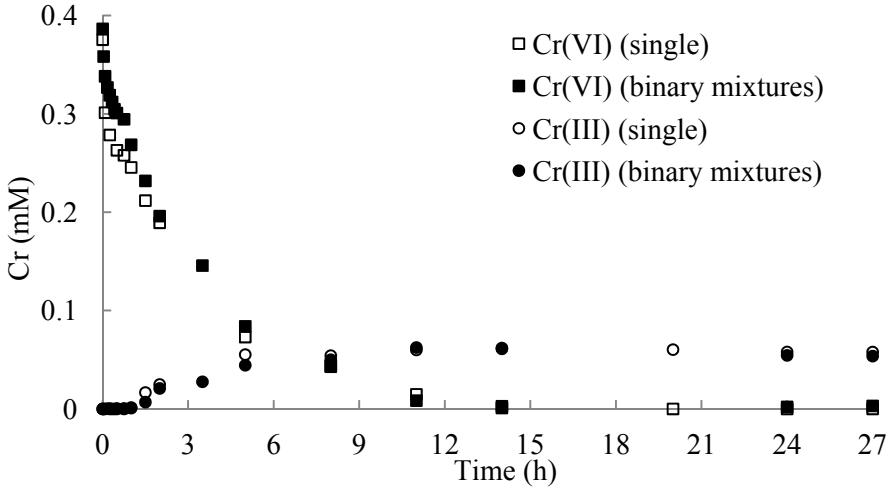


Figure 4.4 Cr(VI) and Cr(III) concentration in solution as a function of time. Single solution: 0.4 mM Cr(VI). Binary mixture: 0.4 mM Cr(VI)-0.4 mM Cu(II). Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2^{o}C.

The evolution of pH value in the two solutions is presented in Figure 4.5.

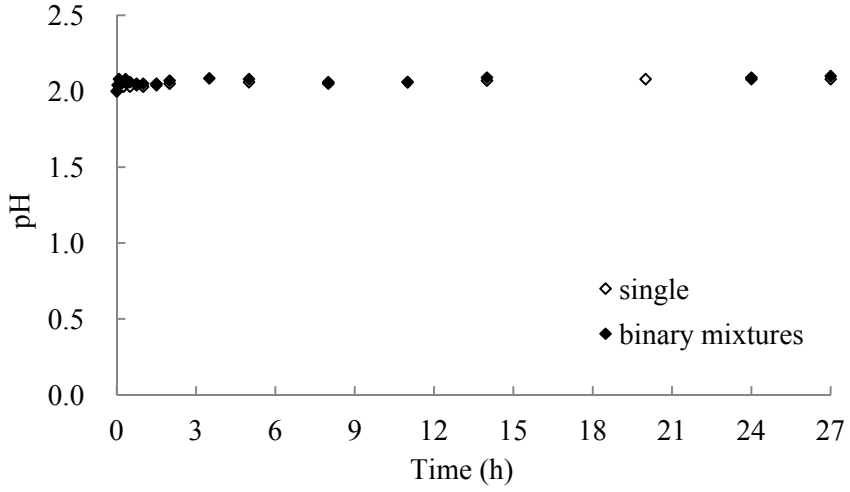


Figure 4.5 pH of the solution as a function of time. Single solution: 0.4 mM Cr(VI). Binary mixture: 0.4 mM Cr(VI)-0.4 mM Cu(II). Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2^{o}C.

Seen from **Figure 4.5**, any significant differences can be observed between Cr(VI) sorption from single solution and from Cr(VI)-Cu(II) binary mixture. The increase of pH values in both solutions put into evidence the protonation of EC and the protons consumed for Cr(VI) reduction.

The observed results corroborate that the presence of Cu(II) in the Cr(VI)-Cu(II) binary mixture at pH 2.0 did not affect neither Cr(VI) sorption/reduction nor Cr(III) sorption.

4.1.2. Effect of Cu(II) on Cr(VI) sorption kinetics at pH 3.0

The results of Cr(VI) sorption at pH 3.0 from single solution and Cr(VI)-Cu(II) binary mixture are shown in Tables 4.3 and 4.4, respectively.

As expected, the concentration of Cr(VI) decreased with time after contacting with EC in both Cr(VI) single and Cr(VI)-Cu(II) binary mixture kinetics profile at pH 3.0. After 80 hours, Cr(VI) disappeared from both solutions. Cr(III) was present in both solutions after 5 hours in Cr(VI) single solution and 8 hours in the case of the binary mixture solution. The formation of Cr(III) also achieved equilibrium after 80 hours. The pH values in these two solutions increased as soon as contacting with EC. It indicates the protonation of EC and the proton-consuming reaction of Cr(VI) reduction. The pH value arrived at equilibrium in both solutions when the concentrations of Cr(VI) and Cr(III) were almost constant. When equilibrium was achieved, a little lower pH was found in Cr(VI)-Cu(II) binary mixture solution compared to the pH found in Cr(VI) single solution. Concerning copper uptake, 15% of Cu(II) was removed as soon as the solution was in contact with EC. This uptake gradually increased with the increase of pH of the solution. As mentioned before Cu(II) sorption is favoured with the increase of pH.

Table 4.3 Cr total, Cr(VI), Cr(III) concentration and pH values as a function of time. Single solution: 0.4 mM Cr(VI) solution. Initial pH 3.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

t (h)	total Cr (mM)	Cr(VI) (mM)	Cr(III) (mM)	pH
0.00	0.3727	0.3727	0.0000	3.03
0.08	0.3417	0.3417	0.0000	3.35
0.25	0.3356	0.3356	0.0000	3.41
0.50	0.3281	0.3281	0.0000	3.53
1.00	0.3192	0.3192	0.0000	3.45
1.50	0.3098	0.3098	0.0000	3.54
2.00	0.2917	0.2917	0.0000	3.60
3.50	0.2634	0.2634	0.0000	3.71
5.00	0.2506	0.2439	0.0068	3.79
8.00	0.2175	0.2036	0.0138	3.89
11.00	0.1902	0.1680	0.0222	3.97
24.00	0.1144	0.0767	0.0377	4.10
36.00	0.0804	0.0465	0.0339	4.36
48.50	0.0593	0.0231	0.0362	4.42
54.00	0.0541	0.0182	0.0359	4.37
60.00	0.0488	0.0162	0.0327	4.43
67.00	0.0429	0.0112	0.0317	4.33
74.00	0.0404	0.0104	0.0300	4.33
80.00	0.0400	0.0100	0.0300	4.33

Table 4.4 Cr total, Cr(VI), Cr(III), Cu(II) concentration and pH values as a function of time. Binary mixture solution: 0.4 mM Cr(VI)-0.4 mM Cu(II). Initial pH 3.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2^{o}C.

t (h)	total Cr (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	pH
0.00	0.3891	0.3891	0.0000	0.3860	3.02
0.08	0.3572	0.3572	0.0000	0.3306	3.63
0.17	0.3477	0.3477	0.0000	0.3283	3.32
0.25	0.3501	0.3501	0.0000	0.3357	3.52
0.33	0.3477	0.3477	0.0000	0.3382	3.48
0.50	0.3474	0.3474	0.0000	0.3327	3.48
0.75	0.3423	0.3423	0.0000	0.3346	3.49
1.00	0.3403	0.3403	0.0000	0.3351	3.50
1.50	0.3314	0.3314	0.0000	0.3318	3.57
2.00	0.3287	0.3287	0.0000	0.3372	3.51
3.50	0.3135	0.3133	0.0002	0.3271	3.74
5.00	0.2993	0.2993	0.0000	0.3257	3.75
8.00	0.2699	0.2600	0.0099	0.3251	3.80
10.25	0.2460	0.2304	0.0156	0.3262	3.88
14.00	0.2054	0.1810	0.0244	0.3318	3.95
24.42	0.1814	0.1531	0.0283	0.3320	4.05
30.00	0.1480	0.1121	0.0359	0.3208	4.04
48.50	0.0922	0.0546	0.0376	0.3213	4.07
56.50	0.0747	0.0354	0.0393	0.3211	4.06
60.00	0.0483	0.0040	0.0443	0.3128	4.04
74.50	0.0422	0.0025	0.0397	0.2981	4.06
80.00	0.0429	0.0012	0.0417	0.2986	4.04

The concentration of total chromium and copper ions in Cr(VI) single solution and Cr(VI)-Cu(II) binary mixture at pH 3.0 was plotted as a function of time and is presented in Figure 4.6.

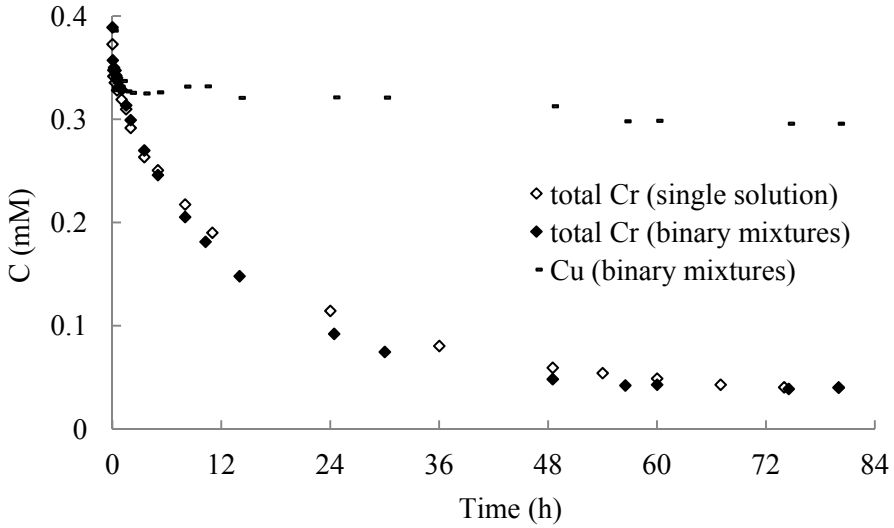


Figure 4.6 Total Cr and Cu(II) concentration in solution as a function of time. Single solution: 0.4 mM Cr(VI). Binary mixture solution: 0.4 mM Cr(VI)-0.4 mM Cu(II). Initial pH 3.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2^{o}C.

Taking into account the reaction of Cr(VI) reduction, the two forms of chromium (hexavalent and trivalent) are plotted separately as a function of time in single and binary mixture solutions in Figure 4.7.

As seen from Figure 4.7, lower concentration of Cr(VI) and higher presence of the formed Cr(III) were found in the solution of binary mixture. This indicates that reduction of Cr(VI) was in a higher extent in binary mixture compared to Cr(VI) single solution.

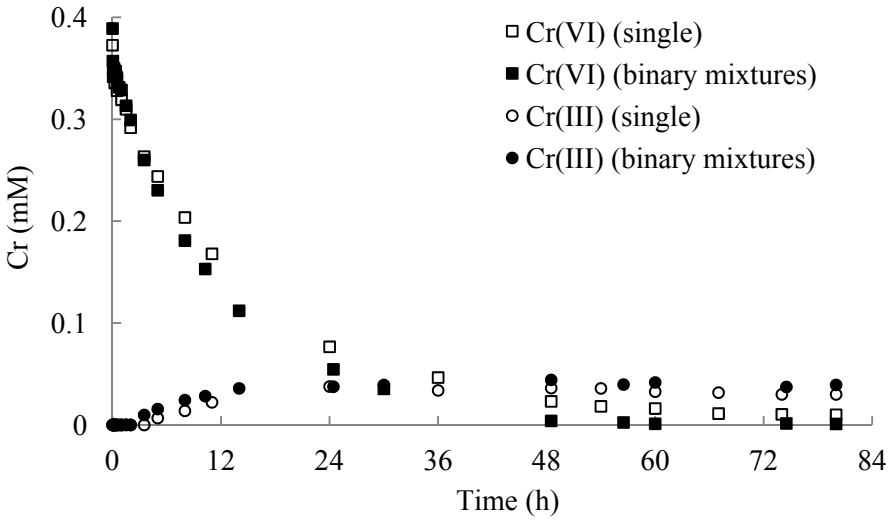


Figure 4.7 Cr(VI) and Cr(III) concentration in solution as a function of time. Single solution: 0.4 mM Cr(VI). Binary mixture solution: 0.4 mM Cr(VI)-0.4 mM Cu(II). Initial pH 3.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2^{o}C.

The effect of Cu(II) on Cr(VI) sorption at pH 3.0 can be also put into evidence by the evolution of pH values during the process, which is shown in Figure 4.8.

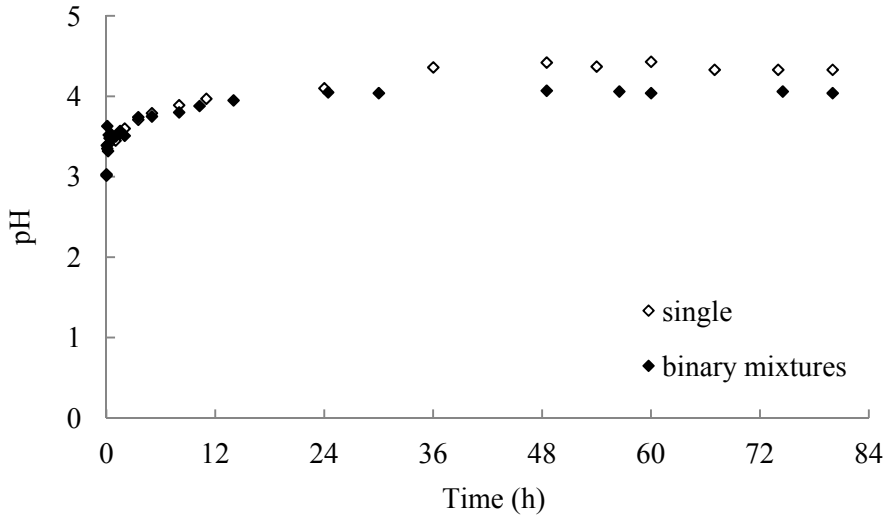


Figure 4.8 pH of solution as a function of time. Single solution: 0.4 mM Cr(VI). Binary mixture solution: 0.4 mM Cr(VI)-0.4 mM Cu(II). Initial pH 3.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2^{o}C.

The pH value increased with time in both solutions, being the increase of pH higher in Cr(VI) single solution. Cu(II) species can exhibit competition with protons for the active sites of the sorbent and result in a greater amount of protons in solution. This situation is favorable for Cr(VI) reduction to its trivalent form. In both solutions pH increased until the reduction reaction was fully accomplished.

As a conclusion, the study shows that Cr(VI) sorption/reduction by using EC as a biosorbent is favored by the presence of Cu(II) in Cr(VI)-Cu(II) binary mixture at pH 3.0. This fact may be mainly attributed to the fact that at this pH the sorption of copper on EC is preferred to protonation and therefore more protons are available in solution for the reduction of Cr(VI). In the case of pH 2.0 due to the presence of much more protons from the initial steps the effect of the presence of copper cannot be appreciated.

4.2.Kinetics study of Cr(VI) sorption from Cr(VI)-Cu(II) binary mixtures

The results of kinetics will be discussed in two sections. In the first section, the results of Cr(VI) kinetics sorption by EC from two sets of Cr(VI)-Cu(II) binary mixtures with varied metal ions concentration and mole ratios are presented. In the second section a kinetic model including Cr(VI) reduction reaction, Cr(VI) and Cr(III) sorption/desorption and the effect of the presence of Cu(II) is developed to simultaneously describe Cr(VI) sorption process in the presence of Cu(II).

4.2.1. Experimental results of Cr(VI) sorption from Cr(VI)-Cu(II) binary mixtures

The kinetic profiles of total, hexavalent and trivalent chromium and copper in the first set of experiments where metal ion concentration ranged from 0.2 to 0.6 mM are summarized in Figure 4.9. The kinetic profiles of these metal ions in the second set of experiments where the concentration was 10 folds higher and ranged from 2.0 to 6.0 mM are summarized in Figure 4.10. Each set of experiments includes 7 series of data. The experimental data as a function of time for each set of sorption experiments are attached in Annex II Tables A2.1-A2.7 and A2.8-A2.14, respectively.

Figures 4.9 and 4.10 clearly show the kinetic profiles of all the metal ions in solution. In all the figures, Cr(VI) concentration decreased gradually and Cr(III) slowly appeared in solution until equilibrium was reached. Cr(VI) species were completely or about completely eliminated and the non sorbed Cr(III) which accounted for 12%-16% of the initial Cr(VI) concentration remained in solution.

When looking at Figure 4.9 it can be remarked that the time needed to achieve equilibrium increased when increasing Cr(VI) concentration and slightly decreased when increasing copper concentration in the binary mixture. For the binary mixtures of Cr(VI) and Cu(II) with a higher concentration range (Figure 4.10) it can be noticed a quite large delay of reaching equilibrium due to the high values of Cr(VI) initial concentration. Nevertheless, no effect on equilibrium time achievement can be noticed by the increase of copper concentration in the binary mixtures.

Comparing the results shown in Figures 4.9 and 4.10, some differences in the kinetics of Cr(VI) and Cr(III) between the two binary mixtures Cr(VI)-Cu(II) concentration ranges can be observed. When the metal ions concentration was within the range 2.0 to 6.0 mM (Figure 4.10), Cr(VI) disappearance and Cr(III) appearance rates were significantly slower than those found for the binary mixtures with 10 folder less metal ions concentration (Figure 4.9).

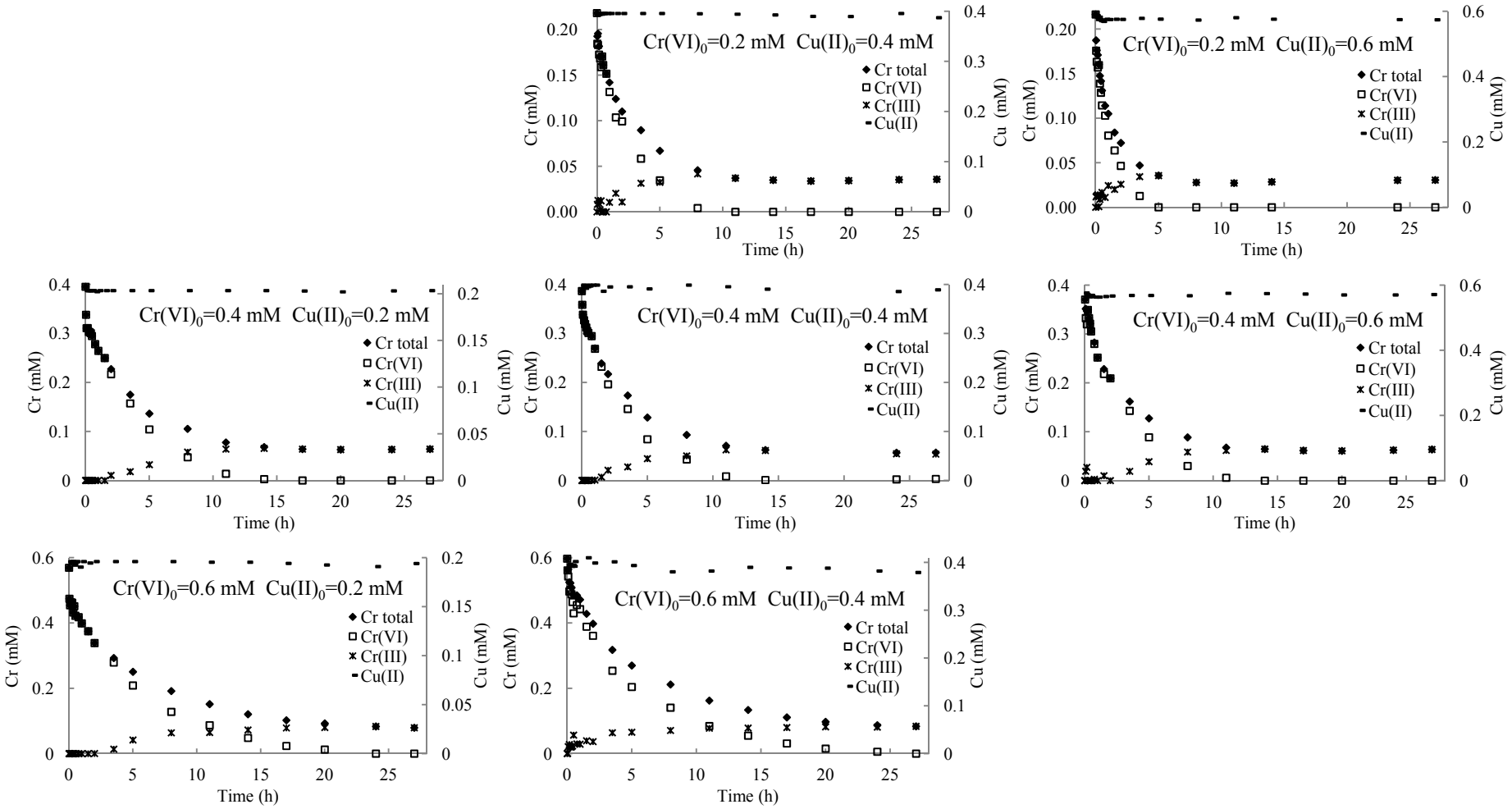


Figure 4.9 Kinetics of Cr(VI) and Cu(II) sorption from Cr(VI)-Cu(II) binary mixtures of 0.2-0.6 mM concentration range. Sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, pH 2.0, temperature: 20±2°C.

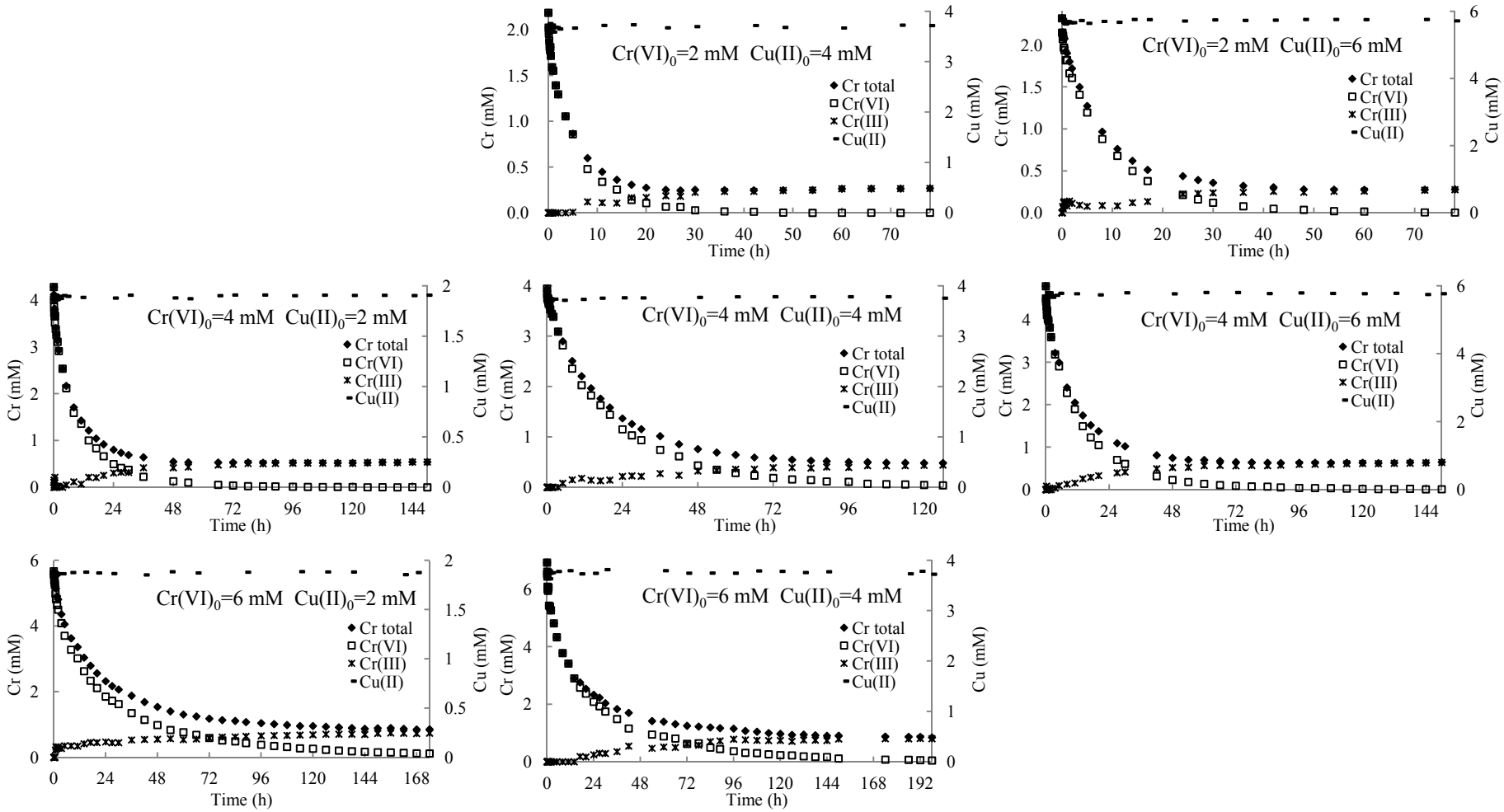


Figure 4.10 Kinetics of Cr(VI) and Cu(II) sorption from Cr(VI)-Cu(II) binary mixtures of 2.0-6.0 mM concentration range. Sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, pH 2.0, temperature: 20±2^{o}C.

The ratio of total chromium removed after 27 hours (binary mixtures of 0.2-0.6 mM concentration range) and 78 hours (binary mixtures of 2.0-6.0 mM concentration range) expressed as C/C_0 can be observed in Table 4.5.

Table 4.5 Concentration of total chromium expressed as C/C_0 ratio after 27 hours (binary mixtures of 0.2-0.6 mM concentration range) and 78 hours (binary mixtures of 2.0-6.0 mM concentration range).

		$C_{o\,Cu}$ (mM)		
	C/C_0	**0.2**	**0.4**	**0.6**
$C_{o\,Cr}$ (mM)	**0.2**		0.157	0.141
	0.4	0.162	0.160	0.158
	0.6	0.169	0.165	
	C/C_0	**2.0**	**4.0**	**6.0**
	2.0		0.122	0.121
	4.0	0.145	0.139	0.133
	6.0	0.189	0.176	

As seen in Table 4.5 the increase of Cu(II) in the binary mixtures resulted in a decrease of total chromium concentration ratio in the remaining solution. This suggests a slight synergistic effect of copper on chromium sorption/reduction when chromium is forming binary mixtures. And this synergistic effect was less in the case of the binary mixtures of high concentration range. Further discussion will be done by simulating the sorption process in a kinetics model for describing the overall sorption process.

Generally speaking, some analogies can be stated with independence of the concentration range and the metals mole ratios of the binary mixtures: (i) Cr(VI) disappeared or tended to disappear from the solution with time and chromium in the remaining solution was mainly in its trivalent form; (ii) the formed Cr(III) progressively appeared with time until it attained a certain concentration value proportional to the initial Cr(VI) concentration; (iii) the presence of Cu(II) had a little synergistic influence on Cr(VI) adsorption and reduction processes.

4.2.2. Kinetics model

Taking into account the results obtained in our previous work (Pujol et al., 2013a), a model was developed in basis to (i) irreversible reduction of Cr(VI) to Cr(III) reaction, whose reaction rate is assumed to be proportional to the concentration of Cr(VI) adsorbed and to the difference between the maximum amount of Cr(III) formed that can be found in solution; (ii) adsorption and desorption of Cr(VI) and formed Cr(III) assuming that all the processes follow Sips type kinetics (Plazinski et al., 2009).

A scheme of Cr(VI) sorption/desorption, chromium reduction and Cr(III) sorption/desorption in the presence of Cu(II) and protons is presented in Figure 4.11. Note that as a consequence of the reduction process the active sites on EC represented by bold triangles (▲) are chemically modified (blank triangles (Δ)) and protons are consumed.

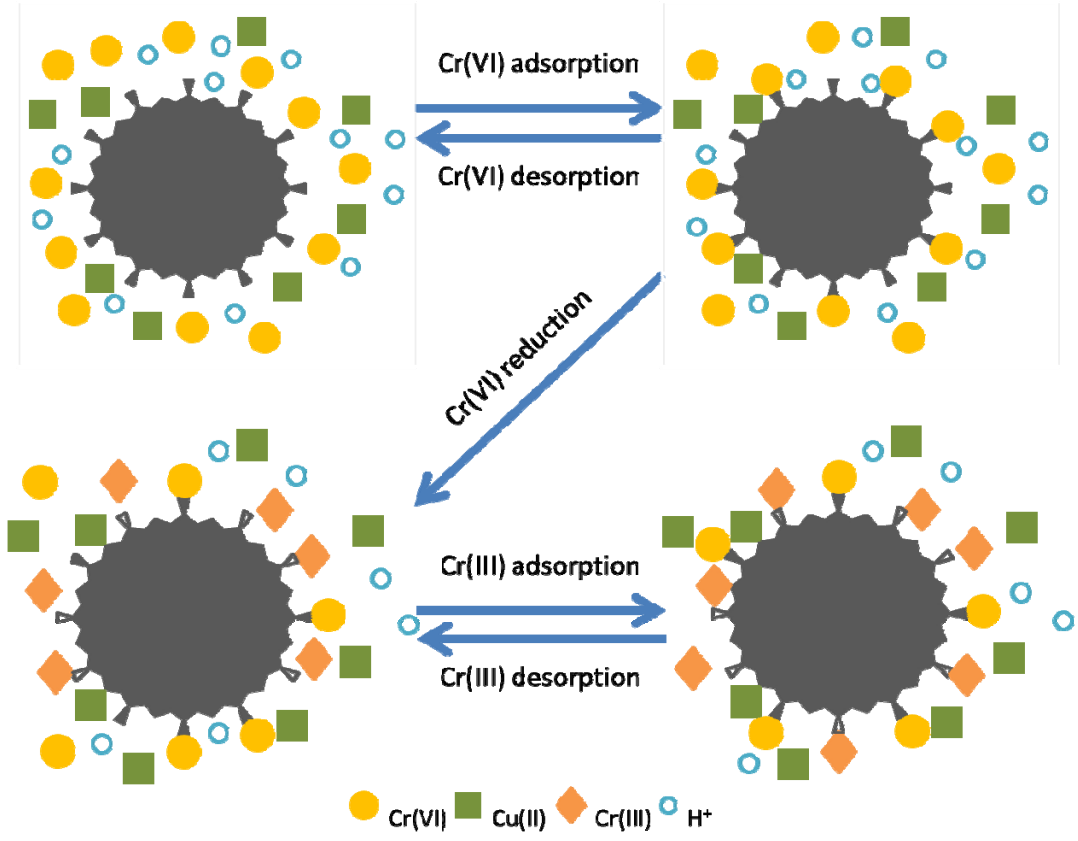


Figure 4.11 A scheme of Cr(VI) sorption/desorption, Cr(VI) reduction and Cr(III) sorption/desorption in the presence of Cu(II) and protons.

The different phenomena can be included in the following system of Equations 4.4-4.7:

$$\frac{dC_{Cr(VI)}}{dt} = -k_2 C_{Cr(VI)}\left[p\, q_{max,Cr}\left(1 + k_7\, C_{Cu(II)}\right) - q_{Cr(VI)}\right]^n + k_3\left(q_{Cr(VI)}\right)^n \quad (4.4)$$

$$\frac{dC_{Cr(III)}}{dt} = k_1 q_{Cr(VI)}\left(k_9 - C_{Cr(III)}\right)\left(1 + k_6\, C_{Cu(II)}\right) - k_4 C_{Cr(III)}\left[(1-p) q_{max,Cr}\left(1 + k_8\, C_{Cu(II)}\right) - q_{Cr(III)}\right]^n + k_5\left(q_{Cr(III)}\right)^n \quad (4.5)$$

$$\frac{dq_{Cr(VI)}}{dt} = k_2 \frac{V}{W} C_{Cr(VI)}\left[p\, q_{max,Cr}\left(1 + k_7 C_{Cu(II)}\right) - q_{Cr(VI)}\right]^n - k_3 \frac{V}{W}\left(q_{Cr(VI)}\right)^n - k_1 q_{Cr(VI)} k_{10} \frac{V}{W}\left(k_9 - C_{Cr(III)}\right)\left(1 + k_6\, C_{Cu(II)}\right) \quad (4.6)$$

$$\frac{dq_{Cr(III)}}{dt} = k_4 \frac{V}{W} C_{Cr(III)}\left[(1-p) q_{max,Cr}\left(1 + k_8\, C_{Cu(II)}\right) - q_{Cr(III)}\right]^n - k_5 \frac{V}{W}\left(q_{Cr(III)}\right)^n \quad (4.7)$$

where $C_{Cr(VI)}$ is Cr(VI) concentration in solution (mmol·L^{-1}), $C_{Cr\ (III)}$ is the concentration of Cr(III) formed (mmol·L^{-1}), $q_{Cr(VI)}$ and $q_{Cr(III)}$ are the amount of Cr(VI) and Cr(III) adsorbed per unit mass (mmol·g^{-1}), $C_{Cu(II)}$ is Cu(II) concentration in solution (mmol·L^{-1}). The model constant $q_{max,Cr}$ represents the maximum amount of total chromium adsorbed per sorbent unit mass (mmol·g^{-1}). Its value was determined in a previous work for Cr(VI) sorption in single metal system (Pujol et al., 2013a). The exponent *n* that is a Sips constant was also determined in the same work.

Concerning the constants of the model, k_1 is the rate constant for the irreversible reaction of Cr(VI) reduction to Cr(III); k_2 and k_4,k_3 and k_5 are the sorption and desorption rate constants respectively, for Cr(VI) and Cr(III); k_6, k_7 and k_8 are the constants that state for the synergistic effect of Cu(II) on Cr(VI) reduction and sorption, and sorption of the formed Cr(III), respectively. The parameter *p* is the ratio between the amount of Cr(VI) adsorbed and the total chromium adsorbed. The constants k_9 represents the maximum amount of Cr(III) formed that can be found in solution and k_{10} the available active sites after the release of Cr(III).

The results of the model were calculated by integration of the differential equations system by means of the function ode15s of Matlab R2013a. The calculation of the parameters were performed by applying a non-linear optimization method based on Numerical Differentiation Formulas. Specifically, the optimisation was performed using fmincon that uses a sequential

quadratic programming (QP) sub problem at each interaction. Fmincon updates an estimate of the Hessian of the Lagrangian at each iteration using the Broyden, Fletcher, Goldfarb and Shanno (BFGS) formula (Powell, 1978a; 1978b). BFGS update is a quasi-Newton method that has been most successful in published studies (Nocedal and Wright, 2006).

The constants of the model were determined by minimizing the Sum of Square Residuals (SSR) (see Equation 4.8). The function is described as the sum of the relative square errors for Cr(VI) and Cr(III).

$$SSR = \sum_{i=1}^{N} \left(\frac{C_{Cr(VI),exp}(t_i) - C_{Cr(VI),calc}(t_i)}{C_0} \right)^2 + \left(\frac{C_{Cr(III),exp}(t_i) - C_{Cr(III),calc}(t_i)}{C_0} \right)^2 \quad (4.8)$$

where $C_{\mathrm{Cr(VI),exp}}(t_i)$ and $C_{\mathrm{Cr(III),exp}}(t_i)$ are the experimental date at time t_i and $C_{\mathrm{Cr(VI),calc}}(t_i)$ and $C_{\mathrm{Cr(III),calc}}(t_i)$ represent the predicted values by the model.

4.2.3.Kinetic modeling of Cr(VI) sorption process in presence of Cu(II)

The experimental results in 27 hours (binary mixtures of 0.2-0.6 mM concentration range) and 78 hours (binary mixtures of 2.0-6.0 mM concentration range) were submitted to this kinetic model. The experimental data corresponding to the binary mixtures 0.2 mM Cr(VI)-0.4 mM Cu(II), 0.4 mM Cr(VI)-0.6 mM Cu(II) and 0.6 mM Cr(VI)-0.2 mM Cu(II) and the experimental data corresponding to the binary mixtures 2.0 mM Cr(VI)-4.0 mM Cu(II), 4.0 mM Cr(VI)-6.0 mM Cu(II) and 6.0 mM Cr(VI)-2.0 mM Cu(II) were used to calibrate the model proposed for the kinetics data of Cr(VI) sorption from binary mixtures of 0.2-0.6 mM and 2.0-6.0 mM concentration ranges, respectively. The rest of the data were used to validate the respective model.

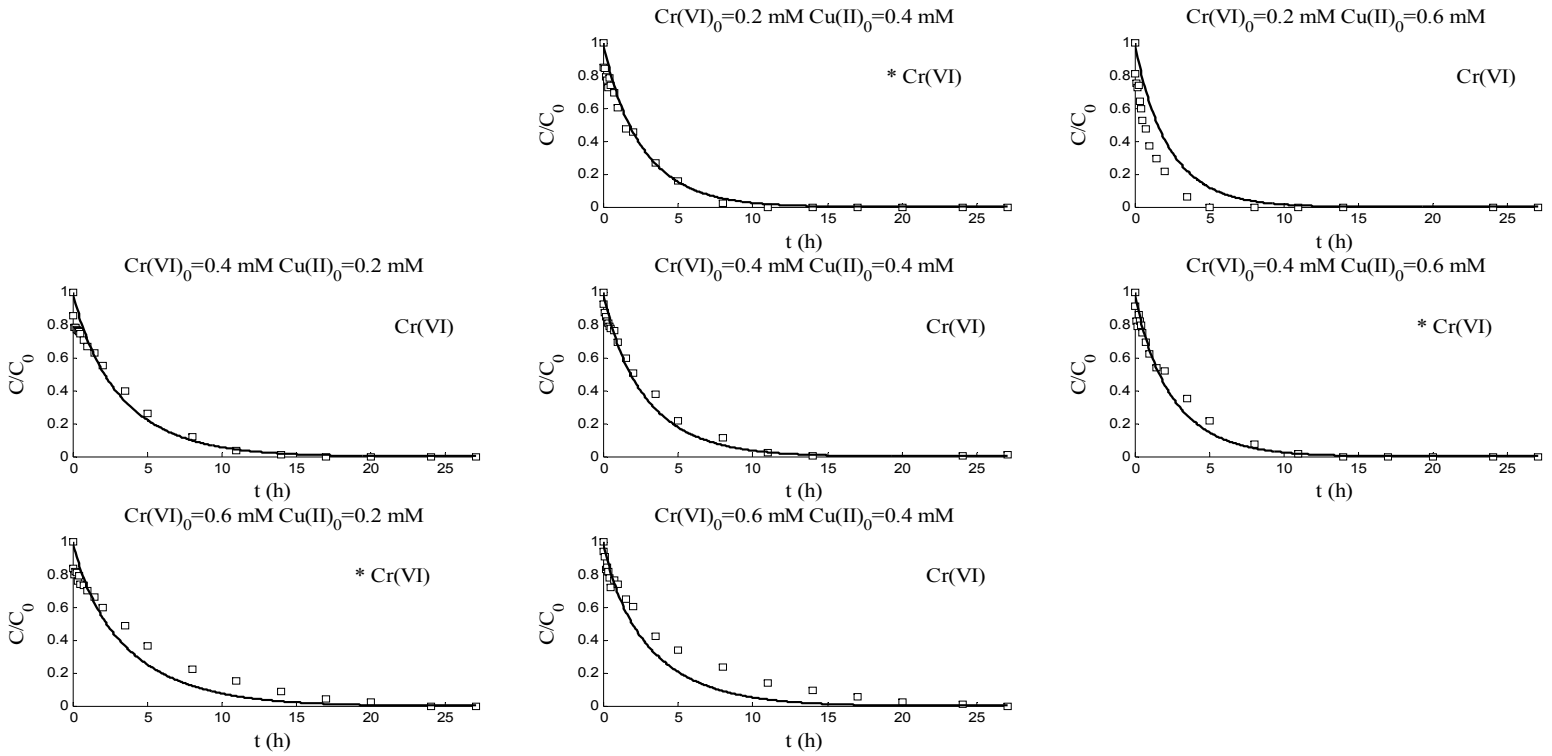
The obtained model parameters are presented in Table 4.6.

Table 4.6 Kinetics model parameters for Cr(VI) sorption onto exhausted coffee from Cr(VI)-Cu(II) binary mixtures.

Concentration range	k_1 g $mmol^{-1}$ h^{-1}	k_2 g^n $mmol^{-n}$ h^{-1}	k_3 g^n $mmol^{-n+1}$ L^{-1} h^{-1}	k_4 g^n $mmol^{-n}$ h^{-1}	k_5 g^n $mmol^{-n+1}$ L^{-1} h^{-1}	k_6 L $mmol^{-1}$	k_7 L $mmol^{-1}$	k_8 L $mmol^{-1}$	k_9 mmol L^{-1}	k_{10} Dimen-sionless	p Dimen-sionless	n Dimen-sionless	q_{max} mmol g^{-1}	SSR
0.2-0.6 mM	0.867	6.891	0.000	2.934	20.992	0.414	0.262	0.000	0.341	1.766	0.522	2.814	0.644	0.584
2.0-6.0 mM	0.666	4.594	0.000	4.401	20.990	0.000	0.000	0.115	0.511	2.649	0.624	2.814	0.644	0.631

The zero value of k_3 constant indicates that the model does not predict any chromium desorption in the hexavalent oxidation state. The presence of Cu(II) seems to have no effect on the reduction reaction rate and on the Cr(VI) sorption in the binary mixtures range 2.0-6.0 mM (k_6=0, k_7=0) while some synergistic effect on both processes is observed in the case of binary mixtures range 0.2-0.6 mM (k_6≠0, k_7≠0). The value of k_8 denotes a slight synergistic effect on Cr(III) sorption due to the presence of copper in solution in the binary mixtures range 2.0-6.0 mM. Synergistic effects were already observed in our previous work (Pujol et al, 2013a). The constant *p* value indicates that 52-62% of Cr(VI) is adsorbed in the hexavalent form. Calculated values obtained from the model have been superimposed on the kinetics experimental data in Figures 4.12 and 4.13 in which it can be observed that the model describes quite well the sorption kinetics profile of Cr(VI) and Cr(III) of the series of data of both metal ions concentration ranges considered in this study.

(a)


Cr(VI)0=0.2 mM Cu(II)0=0.4 mM
* Cr(VI)
Cr(VI)0=0.2 mM Cu(II)0=0.6 mM
Cr(VI)
Cr(VI)0=0.4 mM Cu(II)0=0.2 mM
Cr(VI)
Cr(VI)0=0.4 mM Cu(II)0=0.4 mM
Cr(VI)
Cr(VI)0=0.4 mM Cu(II)0=0.6 mM
* Cr(VI)
Cr(VI)0=0.6 mM Cu(II)0=0.2 mM
* Cr(VI)
Cr(VI)0=0.6 mM Cu(II)0=0.4 mM
Cr(VI)
C/C0
t (h)

(b)

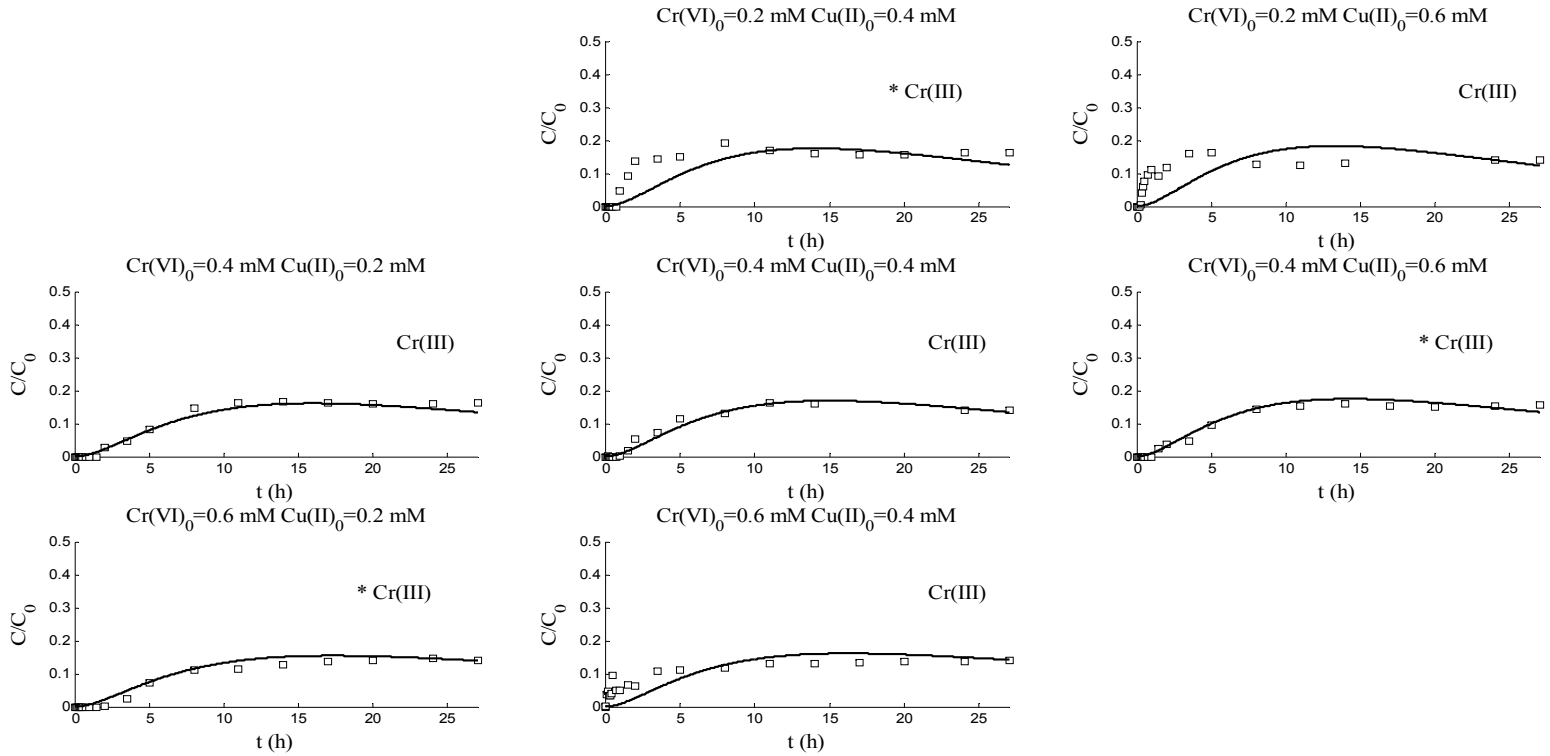
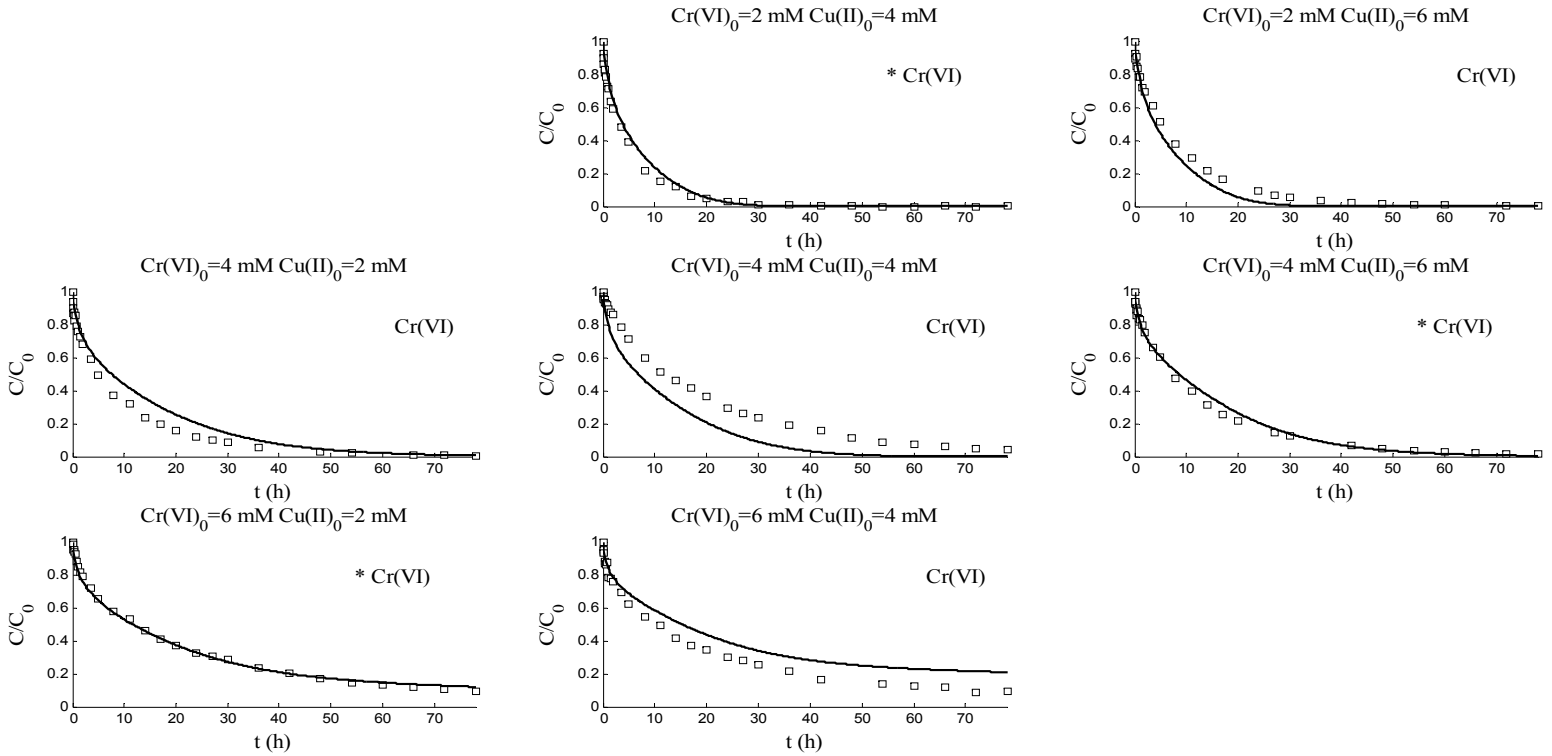


Figure 4.12 Kinetics of Cr(VI) sorption onto exhausted coffee waste of Cr(VI)-Cu(II) binary mixtures of 0.2-0.6 mM concentration range (a) Cr(VI) disappearance kinetics, (b) Cr(III) appearance kinetics. Solid lines represent predicted data by the proposed model, open symbols the experimental data. Sorbent dose: 6.67 g L^{-1}, sorbent particle size: 0.5-1.0 mm, pH 2.0. Sorption kinetics data marked with an asterisk (*) were used for model calibration, the rest of the data for model validation.

(a)


Cr(VI)0=2 mM Cu(II)0=4 mM
* Cr(VI)
Cr(VI)0=2 mM Cu(II)0=6 mM
Cr(VI)
Cr(VI)0=4 mM Cu(II)0=2 mM
Cr(VI)
Cr(VI)0=4 mM Cu(II)0=4 mM
Cr(VI)
Cr(VI)0=4 mM Cu(II)0=6 mM
* Cr(VI)
Cr(VI)0=6 mM Cu(II)0=2 mM
* Cr(VI)
Cr(VI)0=6 mM Cu(II)0=4 mM
Cr(VI)
C/C0
t (h)

(b)

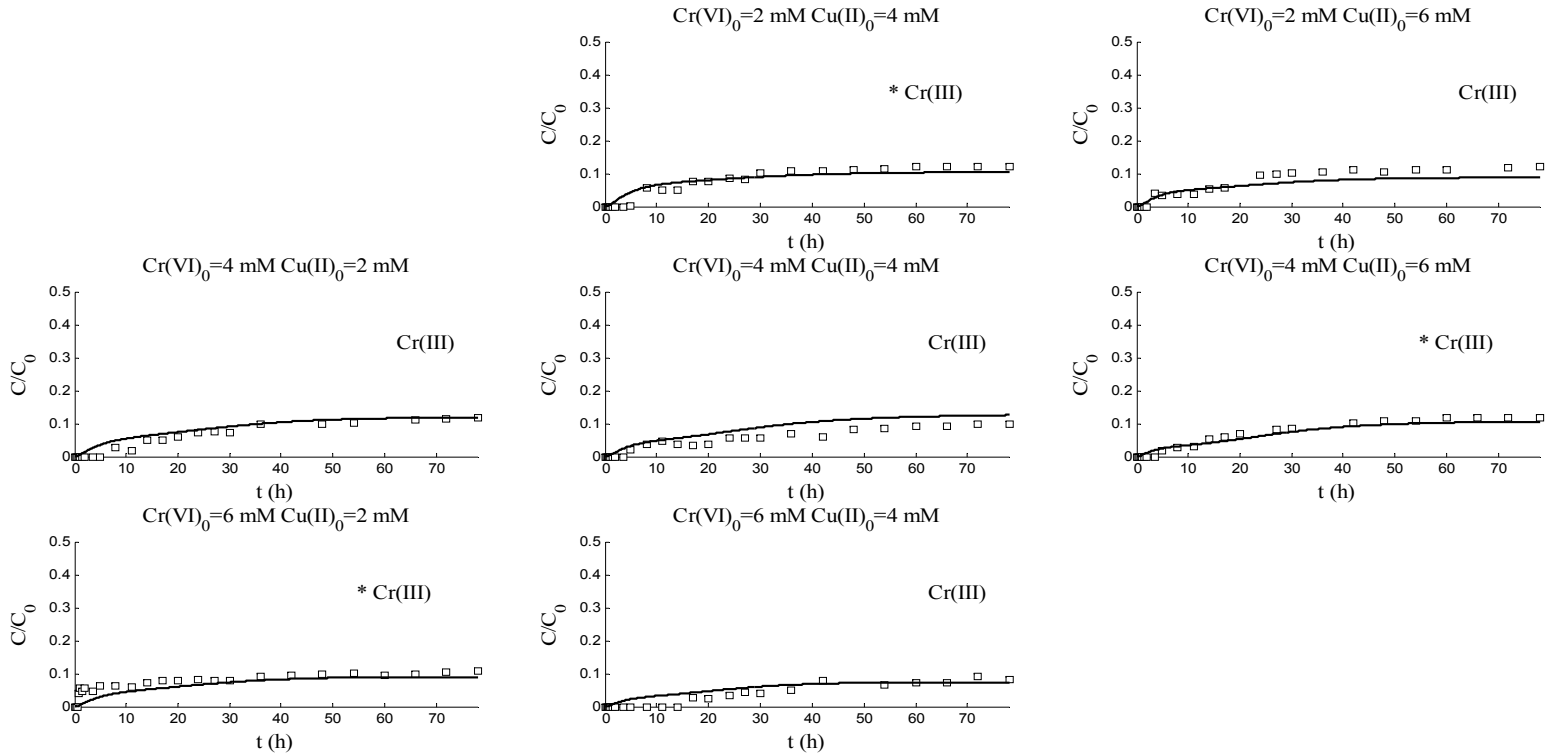


Figure 4.13 Kinetics of Cr(VI) sorption onto exhausted coffee waste of Cr(VI)-Cu(II) binary mixtures of 2.0-6.0 mM concentration range (a) Cr(VI) disappearance kinetics, (b) Cr(III) appearance kinetics. Solid lines represent predicted data by the proposed model, open symbols the experimental data. Sorbent dose: 6.67 g L^{-1}, sorbent particle size: 0.5-1.0 mm, pH 2.0. Sorption kinetics data marked with an asterisk (*) were used for model calibration, the rest of the data for model validation.

A more detailed analysis of the fitting indicates that the model perfectly describes the seven kinetic profiles of Cr(VI) sorption (both the used for model calibration and validation) from the binary mixtures of 0.2-0.6 mM concentrations range (Figure 4.12(a)). The fit of Cr(III) kinetics data corresponding to the same concentrations range is in general very good for all the studied binary mixtures though some discrepancies can be observed between the model prediction and the experimental data when initial Cr(VI) concentration is 0.2 mM and the binary mixtures concentration ranges are 0.2 Cr(VI) mM-0.4 Cu(II) mM and 0.2 Cr(VI)-0.6 Cu(II) mM (Figure 4.12(b)), used for model calibration and validation, respectively. The model fits adequately the experimental data of three of the four kinetic series used to validate. This fact confirms the validity of the model.

Concerning kinetics data from binary mixtures in the 2.0-6.0 mM concentration range, the fit of the model is in general quite acceptable for Cr(VI) kinetics experimental data (Figure 4.13(a)). The main differences between predicted and experimental data can be noticed for 4.0 mM Cr(VI)-4.0 mM Cu(II) and 6.0 mM Cr(VI)-4.0 mM Cu(II) binary mixtures. In the case of Cr(III) sorption kinetics (Figure 4.13(b)) the prediction of the model is very good although some slight differences are observed during the first hours of the sorption process. In general, it can be said that the model responds adequately even though for the binary mixtures of high concentration range.

The effect of Cu(II) on Cr(VI) sorption observed in Table 4.5 also confirms the synergistic effect of Cu(II) on Cr(VI) reduction/sorption taken into account when formulating the model. And the less synergistic effect in the case of the binary mixtures of high concentration range is consistent with the values obtained for k_6, k_7 and k_8 (Table 4.6).

As a conclusion, a model was developed to describe kinetics of Cr(VI) sorption onto EC from two sets of binary mixtures of Cr(VI)-Cu(II) with different metal concentration range. For each binary mixtures concentration range three sets of experimental data have been used to calibrate the model and four independent sets to validate it. The proposed model which includes, Cr(VI) reduction reaction, Cr(VI) and Cr(III) sorption/desorption and the effect of the presence of Cu(II) fits adequately the experimental data obtained with both binary mixtures concentration ranges studied.

CHAPTER V.

POST-TREATMENT OF THE SOLUTIONS CONTAINING METAL IONS AFTER THE BIOSORPTION PROCESS

1. INTRODUCTION

In Chapter IV, kinetics sorption of Cr(VI) onto exhausted coffee waste (EC) from Cr(VI) single solution and Cr(VI)-Cu(II) binary mixtures was studied. With the aim to eliminate Cr(VI) from aqueous solutions, the kinetics sorption was performed at acidic conditions which resulted to be the favorable conditions for Cr(VI) removal. After biosorption, Cr(VI) was eliminated in a great deal but about 15% of the Cr(III) formed as a consequence of the reduction reaction remained in solution together with a high concentration of copper which was not sorbed due to the low pH used in the biosorption process. Therefore, this chapter will be devoted to find out an efficient method for the clean-up of the metal ions that remain in solution after the biosorption process.

According to our findings in Chapter III, lignin moieties of EC are involved in not only Cr(VI) reduction but also in Cr(III) sorption. In the same chapter, oxygen functional groups resulted to be involved in the sorption of divalent metals such as Cu(II). Moreover, a preliminary study about pH effect on Cu(II) sorption (Annex I) demonstrated that the most favorable pH for Cu(II) sorption onto EC is pH 5.0. Based on all of these statements, it was regarded as a possible post-treatment a second biosorption step by using fresh EC and adjusting the pH to pH 5.0 in order to eliminate metal cations and reduce the residual Cr(VI).

On the other hand, coagulation-flocculation coupled with filtration has been widely used in industries to separate metal ions from wastewaters because of its simplicity (Zheng et al., 2011). Salts of Al(III) and Fe(III) are commonly used as coagulants in water and wastewater treatment. When Al(III) or Fe(III) salt is added to water, it dissociates to yield trivalent ions, which hydrate to form metal aquo complexes $Al(H_2O)_6^{3+}$ or $Fe(H_2O)_6^{3+}$ (Licsko, 1997). These complexes then pass through a series of hydrolytic reactions in which H_2O molecules in the hydration shell are replaced by OH^- ions to form a variety of soluble species such as $Al(OH)^{2+}$ and $Fe(OH)^{2+}$. These products are quite effective as coagulants as they adsorb very strongly onto the surface of most negative colloids (Lekhlif et al., 2014; Sorokina and Dresvyannikov, 2014).

Therefore, two methods, one based on biosorption using fresh EC and the other based on a traditional coagulation-flocculation will be both evaluated in this chapter for removing the

metal ions remaining in solution after the biosorption process. The most effective method will be recommended as post-treatment of solutions containing Cr(VI) and other metal ions after the biosorption process by using EC.

2. MATERIALS AND REAGENTS

2.1. Reagents and Solutions

- 1.5% HCl (Panreac), 1.5% and 10% NaOH (Panreac) were prepared to adjust pH of residual solution for post-treatment assays.
- 1000 mg L^{-1} chromium, copper, iron, aluminum and iron standard solutions (Panreac) were employed in standard preparation for metal ions analysis in flame atomic absorption (FAAS).
- Analytical grade potassium dichromate (Panreac) was employed in standard preparation for hexavalent chromium analyses in sequential injection system (SIA). Analytical grade 1,5-diphenylcarbazide (Panreac), reagent grade ethanol (Scharlau) and reagent grade sulfuric acid 95-97% (Scharlau) were also use to hexavalent chromium analyses in sequential injection system (SIA).
- Pure grade $Al_2(SO_4)_3 \cdot 18H_2O$ (Panreac) and $FeCl_3$ (Acros Organics) were used for coagulant-flocculant preparation.

2.2. Equipment

- pH meter (Crison Basic 20, Spain) was used to measure the solution pH.
- Flame atomic absorption spectroscopy (FAAS) (Varian Absorption Spectrometer SpectraAA 220FS) was used to determine the total concentration of chromium, i.e., Cr(VI)+Cr(III) and copper, iron and aluminium.
- Sequential injection system (SIA) recently developed in our laboratory was applied for hexavalent chromium analyses.

3. METHODOLOGY

With the aim of removing the metal ions remaining in solution after the biosorption two possible post-treatment i) biosorption using fresh EC and (ii) coagulation-flocculation using two types of coagulants were investigated. The selected samples from the 14 residual effluents after biosorption performed at pH 2.0 were the ones corresponding to two binary mixtures whose initial chromium and copper concentrations were: 6.0 mM Cr(VI)-2.0 mM Cu(II) (named as R1) and 6.0 mM Cr(VI)-4.0 mM Cu(II) (named as R2). For each residual effluent, the results obtained after each treatment were compared. The reason of selecting these two effluents was that they contained a relatively high amount of Cr(III) and Cu(II) ions compared to the rest of effluents. The methodology of each assay will be presented in the following sections.

3.1. Biosorption using fresh EC

The post-treatment based on using fresh EC as biosorbent was carried out in stoppered glass tubes. Fresh EC samples with the same particle size (0.5-1.0 mm) used for kinetics studies (chapter IV) were put into contact with 15 mL of residual effluents (R1 and R2) adjusted to pH 5.0. The tubes were kept under agitation (40 rpm) for 6 days. The selected contact time was made on the basis of the results obtained in previous studies (Fiol et al., 2008; Pujol et al., 2013). Different amount of EC samples ranged from 0.1 - 1.0 g were used to obtain the optimal sorbent dose for metal ions removal from residual effluents. Sorbent-free blank experiments were performed with R1 and R2 in the same conditions. After agitation, the solutions were filtered through cellulose filter and acidified using 0.1 M HCl. The concentration of metal ions in solution was analyzed.

3.2. Coagulation-flocculation

Two different coagulants were used for the coagulation-flocculation treatment: $Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3$. The coagulation-flocculation followed the procedure reported by Mañunga et al. (2010). Volumes of 50 mL of biosorption treated solutions (R1 and R2) were put into Anaclin plastic containers of 100 mL. The pH of the solutions was adjusted to pH 9.0

by adding dropwise 10% NaOH solution. In each Anaclin different volumes of coagulating solutions (20 g L^{-1} $Al_2(SO_4)_3 \cdot 18H_2O$ or 6 g L^{-1} $FeCl_3$) were added. After the addition of coagulant the pH of the solution was readjusted to pH 9.0. The solutions were kept stirring at 60 rpm for 20 minutes, and after this time they were let to stand for 1 hour for flocs precipitation. The supernatants were filtered through a cellulose filter and then the solutions acidified using 0.1 M HCl before the analysis of metal ions. The added volumes of coagulating solutions were in the range of 0.05 - 4.00 mL. Coagulant-free blank experiments were performed with R1 and R2 following the same procedure.

4. RESULTS AND DISCUSSION

4.1. Metal analysis of residual effluents

The effluents after biosorption (R1 and R2) were subjected to the post-treatment after a month of storage at pH 2.0. The concentration of metal ions remaining in the effluents was analysed before performing the post-treatment and is presented in Table 5.1. In the same table, the concentration of these metal ions determined at the end of the biosorption process is also presented.

Table 5.1 Concentration of metal ions in residual effluents

Solution	Cr total (mg L^{-1})	Cr(VI) (mg L^{-1})	Cr(III) (mg L^{-1})	Cu(II) (mg L^{-1})
(a) At the end of the biosorption process				
R1	44.45	6.13	38.32	120.08
R2	43.89	2.26	41.63	238.31
(b) When performing the post-treatment process				
R1	40.16	4.70	35.46	120.47
R2	41.42	1.97	39.45	238.98

As seen in Table 5.1(a), at the end of the biosorption process, the residual effluents (R1 and R2) contained Cu(II), Cr(III) and a small amount of Cr(VI). After a month of storage, just before the post-treatment the analysis of total chromium and hexavalent chromium shows that the concentration of chromium in R1 and R2 was lower (Table 5.1(b)). The decrease of chromium concentration is probably due to the reduction reaction continuously occurred in the effluent in the absence of EC by some organic compounds such as water-soluble polymers (WSPs) of EC released into the solution (Chowdhury, 2014; Szycher, 1991; Wang and Chen, 2009). These WSPs could still play a role in metal removal due to the interactions between metal ions and WSPs, such as the electrostatic forces, the formation of coordinating bonds and metal ions trapping in the bulk of the polymer phase (Rivas et al., 2003). The formation of metal nanoparticles in the cross-linking matrix of WSPs could also result in the metal removal from solution (Umeda et al., 2003). And some compounds responsible for Cr(VI) reduction in the WSPs might be involved in Cr(VI) elimination as well. The reduction of Cr(VI) during sample storage stage was reported by Park et al. (2008) after using banana skin powder for Cr(VI) reduction.

The post-treatment by fresh EC biosorption and coagulation-flocculation was carried out immediately after checking metal ions concentration. The results of two treatments are presented in the following sections.

4.2. Biosorption using fresh EC

As mentioned before, the biosorption with fresh EC was carried out at pH 5.0. The concentration of Cr(VI), Cr(III) and Cu(II) in solution after contacting with different dose of fresh EC within the range 0.1-1.0 g are presented in Tables 5.2 and 5.3 for R1 and R2, respectively. Results of sorbent-free blank experiments are also presented.

Table 5.2 Post-treatment of R1 using fresh EC as sorbent. pH: 5.0, sorbent dose: 6.67-66.67 g L^{-1}, temperate: 20±2°C. Cr(VI): 4.70 mg L^{-1}, Cr(III): 35.46 mg L^{-1}, Cu(II): 120.47 mg L^{-1}.

Sorbent dose (g)	Sorbent dose (g L^{-1})	pH	Cr(VI) (mg L^{-1})	Cr(III) (mg L^{-1})	Cu(II) (mg L^{-1})
0.0	0.00	5.00	4.70	18.59	74.74
0.1	6.67	4.61	< LOD[a]	22.07	69.98
0.2	13.33	4.35	< LOD	24.31	68.60
0.3	20.00	4.20	< LOD	26.45	65.61
0.4	26.67	4.10	< LOD	28.33	62.88
0.5	33.33	4.01	< LOD	25.96	58.07
0.6	40.00	3.91	< LOD	25.49	55.86
0.7	46.67	3.89	< LOD	25.57	53.01
0.8	53.33	3.88	< LOD	25.29	49.06
0.9	60.00	3.83	< LOD	26.24	47.30
1.0	66.67	3.85	< LOD	26.37	43.58

[a] LOD=Limit of detection of SIA.

Table 5.3 Post-treatment of R2 using fresh EC as sorbent. pH: 5.0, sorbent dose: 6.67-66.67 g L^{-1}, temperate: 20±2°C. Cr(VI): 1.97 mg L^{-1}, Cr(III): 39.45 mg L^{-1}, Cu(II): 238.98 mg L^{-1}.

Sorbent dose (g)	Sorbent dose (g L^{-1})	pH	Cr(VI) (mg L^{-1})	Cr(III) (mg L^{-1})	Cu(II) (mg L^{-1})
0.0	0.00	5.00	1.97	8.34	151.70
0.1	6.67	4.56	< LOD[a]	18.91	153.57
0.2	13.33	4.37	< LOD	23.09	150.96
0.3	20.00	4.09	< LOD	24.89	152.97
0.4	26.67	4.07	< LOD	24.44	138.95
0.5	33.33	3.96	< LOD	25.43	147.24
0.6	40.00	3.78	< LOD	26.39	139.47
0.7	46.67	3.72	< LOD	26.55	135.14
0.8	53.33	3.68	< LOD	26.64	129.84
0.9	60.00	3.67	< LOD	26.56	121.56
1.0	66.67	3.57	< LOD	27.72	121.37

[a] LOD=Limit of detection of SIA.

Before starting the biosorption post-treatment, R1 and R2 solutions were adjusted to pH 5.0. It is worth mentioning that a blue-green colloidal suspension was visualized after the pH adjustment. Taking as reference the concentration of Cr(III) and Cu(II) in both R1 and R2 effluents shown in Table 5.1(b) and comparing the values with the ones presented by the blank shown in Tables 5.2 and 5.3, it can be observed that the concentration of these two cations was lower in the filtered solutions at pH 5.0. The decrease of concentration suggests that the adjustment of pH in the residual solution after the biosorption onto EC provoked the precipitation of Cr(III) and Cu(II).

Theoretically, Cr(III) and Cu(II) present in R1 and R2 should start to precipitate at pH higher than 5.0 in the case of trivalent chromium and 5.5 in the case of divalent copper, according to MEDUSA species distribution diagram presented in Annex I Figures A1.3 and A1.5. In fact, the precipitation of these two cations occurred at pH 5.0.

As discussed in the last section, in the residual effluents, the dissolved polymers could interact with the residual metal ions such as forming metal complexation. When increasing the pH, the metal-organic complexes due to their high molecular mass and consequently low solubility might precipitate prior to the metal hydroxides (Du et al., 2013). In literature, the precipitation of lignin polymers has also been reported to be achieved through lowering solution pH in the range of pH 2.0-6.0 instead of increasing the temperature (Helander et al., 2013; Koljonen et al., 2004).

When fresh EC was added in the residual effluents (R1 and R2) after adjusting pH to 5.0, Cu(II) removal improved. As higher amount of fresh EC, as higher removal of Cu(II) in R1 and R2. This result confirms the involvement of EC functional groups in Cu(II) sorption in the residual effluent after the biosorption process.

In the case of Cr(III), its removal was weakened by the addition of fresh EC at pH 5.0. A big weakening can be found when contacting with 6.67 g L^{-1} of fresh EC. It might be due to the redissolution of the Cr(III) precipitate in solution. The solubility of Cr(III) in the presence of some organic compounds was found to be pH-dependent and favored in less acidic solution due to the higher solubility of Cr(III)-organic complexes at lower pH value (Remoudaki et al., 2003; Walsh and O'halloran, 1996).

The pH value of R1 and R2 samples after contacting with different sorbent dose of EC is also presented in Tables 5.2 and 5.3. The pH was found to be lower with the increase of sorbent addition. The decrease of pH confirms the sorption of Cu(II) in the residual effluents. Based on the results presented in Chapter III section 4.3.2, the binding of copper cations to carboxylic acids (i.e. $-COO^-$) of EC causes the release of protons into the solution. Consequently, the more acidic condition after contacting with EC resulted in less precipitation of trivalent chromium, where the precipitation of Cr(III) in organic polymers is highly pH dependent (Avudainayagam et al., 2003).

Concerning the removal of hexavalent chromium, the residual Cr(VI) can be totally removed by contacting with fresh EC, even though at pH about 5.0 which resulted to be less favorable for Cr(VI) reduction (Annex I). This result suggests that a simple way to remove Cr(VI) from the residual effluent is to make a second contact with fresh material.

As a conclusion of the biosorption post-treatment at pH 5.0, it can be said that this method is quite efficient for Cr(VI) removal, however is not effective enough to remove Cr(III) and Cu(II) so as the concentration of these metal ions meet the authorized discharge limits.

4.3. Coagulation-flocculation

The coagulation-flocculation post-treatment was carried out through jar test with 50 mL R1 and R2 samples at pH 9.0. $Al_2(SO_4)_3 \cdot 18H_2O$ (20 g L^{-1}) and $FeCl_3$ (6 g L^{-1}) were used as two types of coagulating solutions. In Table 5.4(a), metal ions concentration in R1 before (C_i) and after (C_f) the coagulation-flocculation using different volumes of $Al_2(SO_4)_3 \cdot 18H_2O$ solution is presented. In Table 5.4(b), the C_i and C_f of metals obtained by using different volumes of $FeCl_3$ is presented. The results concerning R2 by using $Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3$ are shown in Table 5.5(a) and (b), separately. The results of coagulant-free blank experiments are also presented in Tables 5.4 and 5.5 for R1 and R2, respectively.

Table 5.4 Coagulation-flocculation post-treatment of R1 adding different dosages of (a) $Al_2(SO_4)_3 \cdot 18H_2O$ and (b) $FeCl_3$. pH: 9.0, temperature: 20±2°C. Cr(VI): 4.70 mg L^{-1}, Cr(III): 35.46 mg L^{-1}, Cu(II): 120.47 mg L^{-1}.

(a)	$Al_2(SO_4)_3 \cdot 18H_2O$		Al(III)		Cr(VI)		Cr(III)		Cu(II)	
	(mL)	(mg 50mL^{-1})	C_i(mg L^{-1})	C_f(mg L^{-1})	C_i(mg L^{-1})	C_f(mg L^{-1})	C_i(mg L^{-1})	C_f(mg L^{-1})	C_i (mg L^{-1})	C_f(mg L^{-1})
	0.00	0.00	0.00	0.00	4.70	4.70	35.46	0.00	120.47	0.19
	0.05	0.02	1.75	0.34	4.69	4.69	35.42	0.00	120.35	0.13
	0.20	3.98	6.99	1.02	4.68	4.68	35.32	0.00	119.99	0.16
	0.30	5.96	10.47	1.65	4.67	4.67	35.25	0.00	119.75	0.12
	0.50	9.90	17.38	2.81	4.65	4.65	35.11	0.00	119.28	0.14
	1.00	19.61	34.42	4.88	4.60	4.60	34.76	0.00	118.11	0.14
	1.50	29.13	51.13	3.23	4.56	4.56	34.43	0.00	116.96	0.09
	2.00	38.46	67.52	4.15	4.52	4.52	34.10	0.00	115.84	0.09
	2.50	47.62	83.60	5.82	4.47	4.47	33.77	0.00	114.74	0.09
	3.00	56.60	99.37	4.64	4.43	4.43	33.45	0.00	113.65	0.07
	3.50	65.42	114.85	5.41	4.39	4.39	33.14	0.00	112.59	0.08
	4.00	74.07	130.04	6.57	4.35	4.35	32.83	0.00	111.55	0.09
(b)	$FeCl_3$		Fe(III)		Cr(VI)		Cr(III)		Cu(II)	
	(mL)	(mg 50mL^{-1})	C_i(mg L^{-1})	C_f(mg L^{-1})	C_i(mg L^{-1})	C_f(mg L^{-1})	C_i(mg L^{-1})	C_f(mg L^{-1})	C_i (mg L^{-1})	C_f(mg L^{-1})
	0.00	0.00	0.00	0.00	4.70	4.70	35.46	0.00	120.47	0.12
	0.05	0.30	1.89	0.01	4.69	4.69	35.42	0.00	120.35	0.11
	0.20	1.20	7.55	0.01	4.68	4.68	35.32	0.00	119.99	0.11
	0.30	1.79	11.31	0.01	4.67	4.67	35.25	0.00	119.75	0.09
	0.50	2.97	18.77	0.08	4.65	4.65	35.11	0.00	119.28	0.09
	1.00	5.88	37.18	0.21	4.60	4.60	34.76	0.00	118.11	0.08
	1.50	8.74	55.23	0.06	4.56	4.56	34.43	0.00	116.96	0.09
	2.00	11.54	72.93	0.04	4.52	4.52	34.10	0.00	115.84	0.10
	2.50	14.29	90.29	0.02	4.47	4.47	33.77	0.00	114.74	0.09
	3.00	16.98	107.33	0.01	4.43	4.43	33.45	0.00	113.65	0.08
	3.50	19.63	124.05	0.00	4.39	4.39	33.14	0.00	112.59	0.07
	4.00	22.22	140.46	0.00	4.35	4.35	32.83	0.00	111.55	0.08

Table 5.5 Coagulation-flocculation post-treatment of R2 adding different dosages of (a) $Al_2(SO_4)_3 \cdot 18H_2O$ and (b) $FeCl_3$. pH: 9.0, temperate: 20±2°C. Cr(VI): 1.97 mg L^{-1}, Cr(III): 39.45 mg L^{-1}, Cu(II): 238.98 mg L^{-1}.

(a)	$Al_2(SO_4)_3 \cdot 18H_2O$		Al(III)		Cr(VI)		Cr(III)		Cu(II)	
	(mL)	(mg 50mL^{-1})	C_i(mg L^{-1})	C_f(mg L^{-1})	C_i(mg L^{-1})	C_f(mg L^{-1})	C_i(mg L^{-1})	C_f(mg L^{-1})	C_i(mg L^{-1})	C_f(mg L^{-1})
	0.00	0.00	0.00	0.00	1.97	1.97	39.45	0.00	238.98	0.37
	0.05	0.02	1.75	0.60	1.97	1.97	39.41	0.00	238.74	0.26
	0.20	3.98	6.99	0.81	1.96	1.96	39.29	0.00	238.03	0.30
	0.30	5.96	10.47	0.85	1.96	1.96	39.21	0.00	237.55	0.32
	0.50	9.90	17.38	1.52	1.95	1.95	39.06	0.00	236.61	0.54
	1.00	19.61	34.42	2.45	1.93	1.93	38.68	0.00	234.29	0.29
	1.50	29.13	51.13	5.18	1.91	1.91	38.30	0.00	232.02	0.25
	2.00	38.46	67.52	7.49	1.89	1.89	37.93	0.00	229.79	0.20
	2.50	47.62	83.60	5.34	1.88	1.88	37.57	0.00	227.60	0.30
	3.00	56.60	99.37	7.49	1.86	1.86	37.22	0.00	225.45	0.32
	3.50	65.42	114.85	5.78	1.84	1.84	36.87	0.00	223.35	0.26
	4.00	74.07	130.04	6.43	1.82	1.82	36.53	0.00	221.28	0.28
(b)	$FeCl_3$		Fe(III)		Cr(VI)		Cr(III)		Cu(II)	
	(mL)	(mg 50mL^{-1})	C_i(mg L^{-1})	C_f(mg L^{-1})	C_i(mg L^{-1})	C_f(mg L^{-1})	C_i(mg L^{-1})	C_f(mg L^{-1})	C_i(mg L^{-1})	C_f(mg L^{-1})
	0.00	0.00	0.00	0.00	1.97	1.97	39.45	0.00	238.98	0.28
	0.05	0.30	1.89	0.01	1.97	1.97	39.41	0.00	238.74	0.45
	0.20	1.20	7.55	0.00	1.96	1.96	39.29	0.00	238.03	0.32
	0.30	1.79	11.31	0.04	1.96	1.96	39.21	0.00	237.55	1.09
	0.50	2.97	18.77	0.01	1.95	1.95	39.06	0.00	236.61	0.29
	1.00	5.88	37.18	0.04	1.93	1.93	38.68	0.00	234.29	0.38
	1.50	8.74	55.23	0.01	1.91	1.91	38.30	0.00	232.02	0.23
	2.00	11.54	72.93	0.03	1.89	1.89	37.93	0.00	229.79	0.19
	2.50	14.29	90.29	0.04	1.88	1.88	37.57	0.00	227.60	0.31
	3.00	16.98	107.33	0.02	1.86	1.86	37.22	0.00	225.45	0.17
	3.50	19.63	124.05	0.14	1.84	1.84	36.87	0.00	223.35	0.39
	4.00	22.22	140.46	0.01	1.82	1.82	36.53	0.00	221.28	0.28

As seen in Tables 5.4 and 5.5, Cr(III) was completely precipitated at pH 9.0 with the absence of coagulants. In these conditions Cu(II) ion was precipitated in a great deal and its concentration met the discharge limit of sewage treatment plant < 3 mg L^{-1}. The addition of coagulants slightly improved Cu(II) ions precipitation.

As expected Cr(VI) was not precipitated in spite of both the increase of pH and the addition of the coagulants and its concentration remained invariable after the coagulation-flocculation process.

When comparing the results obtained by using both types of coagulants ($Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3$) the latter appeared to have the advantage that iron was precipitated as the same time that were the target metal ions. Note that a percentage of aluminium remained in solution after the coagulation-flocculation process performed with the coagulant based on an aluminium salt. In spite of this, in all the assays the concentration of both iron and aluminium ions were under the permit limits 10 and 20 mg L^{-1} for iron and aluminium, respectively.

The better performance of iron than the one of aluminum can be explained by the properties of these two coagulants. The addition of $Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3$ to the wastewater results in insoluble aluminum hydroxide and ferric hydroxide that consequently forms gelatinous sweeping floc precipitates responsible for colloid removal. The ferric hydroxide which precipitates in a stronger gelatinous sweeping form would gives more aggregates than aluminum hydroxide due to the faster rate of precipitation with Fe(III) and the formation of larger flocs under 20±2^{o}C (Duran and Gregory, 2003). It has been proved by other authors that iron floc is significantly stronger than the aluminum floc and hence a better performance of iron over aluminium for turbidity and color removal (Haarhoff, 1988; Hanson and Cleasby, 1990). The stronger formation of iron floc could have higher ability for the precipitation of iron by itself.

As a conclusion of coagulation-flocculation, the efficient removal of positively charged Cr(III) and Cu(II) from R1 and R2 can be achieved by adjusting pH to pH 9.0, at which condition Cr(III) can be completely removed and Cu(II) is almost totally eliminated. If the addition of coagulant is necessary, $FeCl_3$ is recommended due to the better performance of iron salt than aluminium salt in metal removal.

CHAPTER VI.

APPLICATION OF EXHAUSTED COFFEE WASTE-BASED TECHNOLOGY FOR THE TREATMENT OF INDUSTRIAL EFFLUENTS

1. INTRODUCTION

In Chapter IV, results of sorption showed that 85% of chromium was to be efficient eliminated by EC. Moreover, the residual chromium in solution was in its trivalent form as a result of Cr(VI) reduction. In Chapter V, precipitation at pH 9.0 was found to be a suitable post-treatment to eliminate the rest of metal cations from the remaining solutions after biosorption. In case Cr(VI) was not totally reduced, the residual Cr(VI) can be removed through another step of biosorption by using fresh exhausted coffee waste. These promising results encouraged us to apply this overall process (biosorption + precipitation) for the treatment of industrial waters contaminated with metal ions.

Metal finishing industry uses many toxic metal compounds. Hence a substantial amount of effluent containing hazardous material especially hexavalent chromium and many other metal ions is generated. In a metal finishing industry located in Catalonia region of Spain, a huge amount of wastewater are produced weekly from the rinsing baths. These effluents have to be treated prior to their discharge to sewage treatment plant, in order to meet the regulation developed by the Government of Catalonia where the allowed limits are: less than 0.5 mg L^{-1} for hexavalent chromium, whereas total chromium, copper, iron, nickel and aluminum must be found in lower concentrations than 3 mg L^{-1}, 3 mg L^{-1}, 10 mg L^{-1}, 5 mg L^{-1} and 20 mg L^{-1}, respectively (DOGC, 2003).

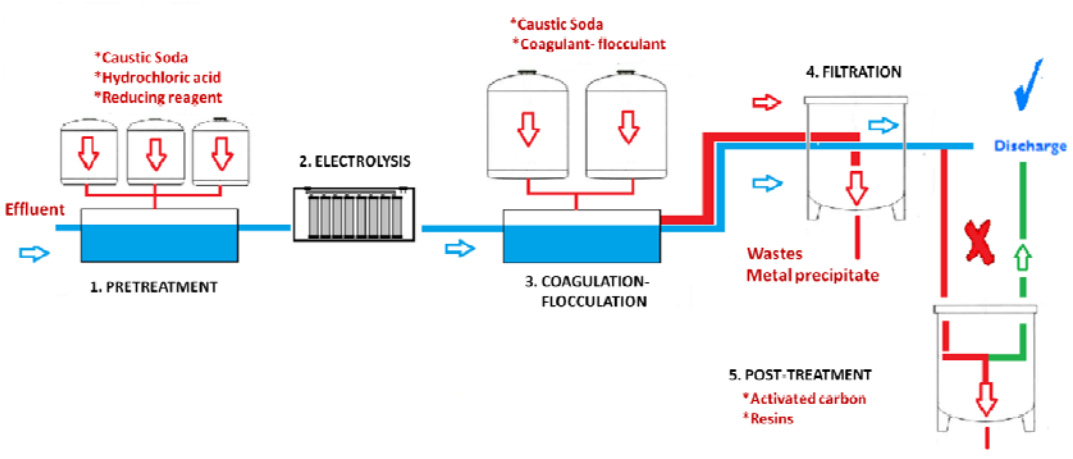


Figure 6.1 Current technology for the treatment of metal finishing industrial effluents

Current technology for the treatment of metal finishing industrial effluents based on Cr(VI) electrochemical reduction and metal ion coagulation-flocculation is presented in Figure 6.1.

As seen in Figure 6.1, the effluent containing hexavalent chromium is pretreated by adding a reducing reagent then subjected to an electrolytic process for Cr(VI) reduction. Metal ions in solution are precipitated by adding caustic soda to raise the pH and coagulant reagent to remove colloidal matter as gelatinous hydroxides. Afterwards, if metal ions concentrations are below the discharge regulation, the treated water can be sent to sewage treatment plant. Otherwise, post-treatment is needed. The most used post-treatment are generally based on metal ions sorption by active carbon or metal ions exchange by ionic resins.

This described conventional technology in Figure 6.1 is effective for the treatment the wastewater from metal finishing industry, nevertheless, it generates big amounts of sludge caused by the addition of a chemical reducing reagent and high amount of coagulant (Gutpa et al., 1999; Park et al., 2006). This drawback, together with the high energy cost due to electrolysis operation and equipment maintenance (Rajemahadik et al., 2013, Chai et al., 2014), calls for the need to develop alternative technology to treat effluent in an environment gently way. In this sense, the technology based on Cr(VI) biosorption by EC could be a good option, not only due to the effective Cr(VI) reduction, but to the ability of the sorbent for formed Cr(III) sorption, which results to less amount of sludge when metals are precipitated.

Therefore, as a final work of this PhD study, the objective of this work is to apply the technology based on EC biosorption for the treatment of metal finishing industrial effluents in a pilot plant. The treatment of the industrial effluents will be performed in two steps: biosorption and coagulation-flocculation. In the former Cr(VI) sorption/reduction will be the main process. In the second step all metal ions in solution will be eliminated by precipitation. The mentioned steps will be performed following the methodology stated in chapter IV and V. The only difference is the volume of the batch reactor. In this chapter a 10 L volume batch reactor was used. This change in scale required to check the sorbent performance in the new conditions by using synthetic Cr(VI) and Cr(VI-Cu(II) binary mixtures solutions. Concerning the step of coagulation-flocculation, proper dosages of coagulant were specifically determined for each effluent to be treated.

2. MATERIALS AND REAGENTS

2.1. Reagents and Solutions

- 1.5% HCl (Panreac), 1.5% and 10% NaOH (Panreac) were prepared to adjust pH.
- 3 M KCl solution was used to store electrode of multiparameter when it is not used.
- Analytical grade potassium dichromate (Scharlau) and analytical grade copper chloride dehydrate (Merck) were used as metal ions salts for synthetic solution preparation.
- Pure grade $Al_2(SO_4)_3 \cdot 18H_2O$ (Panreac) and $FeCl_3$ (Acros Organics) were used for coagulating-flocculating agents preparation.
- 1000 mg L^{-1} chromium, copper, iron, nickel and aluminum standard solutions (Panreac) were employed in standard preparation for metal ions analysis in flame atomic absorption (FAAS).
- Analytical grade potassium dichromate (Panreac) was employed in standard preparation for hexavalent chromium analyses in sequential injection system (SIA). Analytical grade 1,5-diphenylcarbazide (Panreac), reagent grade ethanol (Scharlau) and reagent grade sulfuric acid 95-97% (Scharlau) were also use to hexavalent
chromium analyses in sequential injection system (SIA).
- A kit of chromium hexavalent RGT powder (Lovibond) was used as reagent for Cr(VI) fast determination in a Spectrophotometer (Lovibond).

2.2. Equipment

- Portable multiparameter (HANNA HI 9828) was applied to measure pH and conductivity of the wastewater during treatment.
- Flame atomic absorption spectroscopy (FAAS) (Varian Absorption Spectrometer SpectraAA 220FS) was used to determine the total concentration of chromium, i.e., Cr(VI)+Cr(III) and copper, nickel, iron and aluminum concentrations.
- Sequential injection system (SIA) recently developed in our laboratory was applied for hexavalent chromium analyses.
- Spectrophotometer (Lovibond SpectroDirect) was applied for hexavalent chromium fast analysis (kit) with the concentration ranged from 0.02 to 2.00 mg/L.

2.3. Metal finishing effluents

The chemical and physical characterization of three samples of metal finishing effluents (named as E1, E2, E3) collected from the rinsing baths of an metal finishing industry in different days of January, 2014 are presented in Table 6.1. Determination of metal ions concentration, conductivity and pH were carried out in our laboratory. Determination of anions concentration, total suspended solids (ST) and suspended solids (SS) were performed in the laboratory of "Water Analysis" from the Chemical Engineering Department of our University. As seen from Table 6.1, these three effluents were acid and the main pollutant was hexavalent chromium. In addition to chromium, various ions existed at concentrations lower than 10 mg L^{-1}.

Table 6.1 Metal finishing effluents characterization

Properties	**E1**	**E2**	**E3**
Metal (mg L^{-1})			
Cr(VI)	112.49	108.50	147.18
Cr(III)	0.00	0.00	0.00
Cu	5.04	8.20	8.01
Ni	1.04	0.93	1.23
Fe	4.24	8.54	5.51
Al	0.90	0.66	0.99
Anions (mg L^{-1})			
SO_4^{2-}	93.84	98.81	132.49
PO_4^{3-}	ND[a]	ND[a]	ND[a]
Conductivity (mS cm^{-1})	3.46	3.38	3.29
pH	3.02	3.05	3.01
ST [b] (mg L^{-1})	677	653	820
SS [c] (mg L^{-1})	16	17	19

[a] Not detected. [b] ST: total suspended solids. [c] SS: suspended solids.

2.4. Preparation of synthetic solutions

As mentioned in introduction, in order to check the effectiveness of sorption performed in the 10 L reactor, biosorption was applied for the treatment of two synthetic solutions, one was Cr(VI) single solution and the other was a Cr(VI)-Cu(II) binary mixture. The concentration of Cr(VI) and Cu(II) of the real effluents was taken into account when preparing the synthetic solutions. Cr(VI) was prepared at similar concentration as the one of industrial effluents E1 and E2. Cu(II) was lower than Cr(VI) concentration in the binary mixture. Therefore, Cr(VI) single solution (named as S1) containing 108.15 mg L^{-1} Cr(VI) and Cr(VI)-Cu(II) binary mixtures (named as S2) with 103.04 mg L^{-1} Cr(VI) and 12.96 mg L^{-1} Cu(II) were prepared with deionized water.

3. METHODOLOGY

The study started by applying biosorption to the two prepared synthetic solutions (S1: and S2) first and then to the three samples of metal finishing industrial effluents E1, E2 and E3 shown in Table 6.1.

3.1. Biosorption

Synthetic solutions and industrial effluents were subjected to biosorption with the main objective to reduce hexavalent chromium to its trivalent form. The scheme of the installation implemented to carry out this process is shown in the next section.

3.1.1. Installation scheme

In Figure 6.2 the installation scheme is presented. Biosorption was carried out in a 10 L stirred batch reactor made by Pyrex glass. Detailed description of the individual elements is presented in the next section.

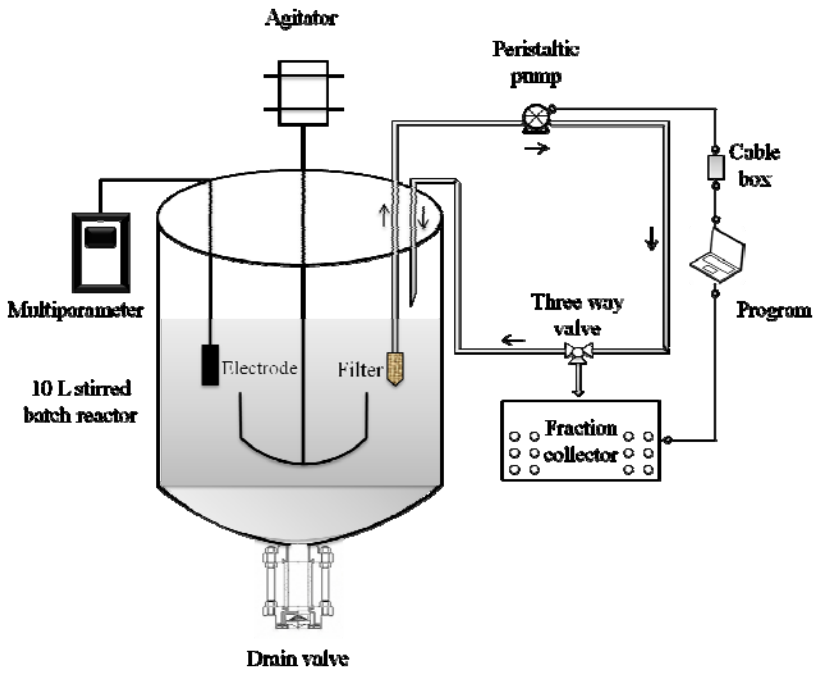


Figure 6.2 Installation scheme of biosorption in a 10 L stirred batch reactor

3.1.2. Description of the control elements

3.1.2.1. Multiparameter

A portable multiparameter was used for measuring conductivity and pH of solution while biosorption process was taking place. The electrode of multiparameter was positioned inside the solution to monitor the values of conductivity and pH in a continuous mode. The values can be read from the screen of the portable multiparameter at any time. At programmed periods of time, the data were collected and stored in the multiparameter. Data were recorded every 5 minutes in the first hour in order to get as much as possible information about sorption at the beginning of the process. After this time, data were recorded every 30 minutes until the process was finished. All the data collected in the multiparameter were transferred to a computer for further treatment.

3.1.2.2. Sampling system

In order to obtain the profiles of metal ions concentration as a function of time during the sorption process, a sampling tube was placed into the solution to take samples at the same interval times as the multiparameter device made measurements. The sampling tube was connected to an automatic sampling system, composed of a peristaltic pump (Gilson, Minipls

3) and a fraction collector (Gilson, FC203B) to take samples at interval times during the sorption process. In order to avoid that the little particles of EC reached the three way valve of the fraction collector and damage the valve, the bottom of the sampling tube was covered with glass wool as a filter. The automatic sampling system and the way of sampling filtration were the same used in the work presented in Chapter IV.

3.1.2.3. Drain valve

A drain valve at the bottom of the reactor was used for discharging the effluent and the sorbent out of the reactor when the biosorption process was finished.

3.1.3. General operation procedure

3.1.3.1. Solution introduction and conditioning

First of all, the electrode of multiparameter for conductivity and pH measurement was washed with Milli-Q water and introduced to its position. The time for data collection was programmed in the multiparameter in advance. The sampling tube was also introduced to its position and connected to the programmed automatic sampling system. Afterwards, 8 L of solution at pH 2.0 were introduced in the reactor from the top, followed by the introduction of 53.33 g of EC which were proposed at the same particle size (0.5-1.0 mm) and sorbent dose (6.67 g L^{-1}) as the ones used in the work presented in Chapter IV. Agitation was switched on and set at a speed of 200 rpm which was found to keep the mixture of sorbent and solution homogenous. Once EC was homogeneous in solution, the programs in multiparameter and in automatic sampling system were clicked to start.

3.1.3.2. Determination of the end of biosorption process

As soon as conductivity and pH values measured by the multiparameter reached almost a constant value at the last stages of the process, samples were taken and a kit was used for Cr(VI) analysis in a fast way (see section 3.3.1). If the concentration of Cr(VI) was below the discharge limit 0.5 mg L^{-1}, the biosorption process was stopped.

3.1.3.3. Sorbent filtration, effluent draining and cleaning of reactor and tubes

When the biosorption process was finished, the sorbent loaded with metals was filtered, in the meanwhile the filtered effluent was collected and the reactor and the pipes were cleaned. In a first step, the solid and liquid from the reactor were drained through the drain valve of reactor and a cellulose filter was used to separate the metal-loaded EC and the liquid. In a second step, the electrode of multiparameter was removed from its fixed position, washed with Milli-Q water and stored in a 3 M KCl solution. In a third step, the sampling tube was also removed from its fixed position with its glass wool filter detached, then placed in deionized water. The sampling and recirculation devices were cleaned by running peristaltic pump for a while. In the last step, the reactor walls, the stirred blade and the drain valve were washed with deionized water.

3.2. Coagulation-flocculation

When the concentration of hexavalent chromium was below the discharge limit, the filtered solution was subjected to coagulation-flocculation process by adjusting the pH to pH 9.0 and adding a certain amount of coagulant. In our previous work (Chapter V), we found that metal ions precipitation is quite good without adding any coagulant. In spite of this, as the characteristics of the metal finishing effluents have a different matrix; there was the need to investigate the effect of the coagulants addition. Therefore, a jar test was carried out for each industrial effluent, with the aim of assessing the performance of two types of coagulant ($Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3$) and optimizing the coagulant dosages. The jar test followed the same procedure presented in Chapter V. The best conditions obtained in the jar test were used for water treatment in a 10 L batch reactor. Concentration of metal ions from supernatant was analyzed.

3.3. Metal ions analysis

3.3.1. Cr(VI) fast analysis

As mentioned in section 3.1.3.2, with the aim to decide the end of biosorption, a kit was used for Cr(VI) fast analysis in the last stages of biosorption. The concentration of hexavalent chromium was determined in a spectrophotometer at 542 λ/nm wavelength using chromium hexavalent RGT powder as reagent. The analysis procedure is the following: 10 mL of sample after filtering by cellulose filter was taken from solution and put in a test tube. The test tube was placed in a spectrophotometer, and signal was reset to zero. Afterwards, the test tube was removed out of the spectrophotometer and one pack of chromium hexavalent RGT powder was added into the test tube. As soon as the reagent was solved, the test tube was put back into spectrophotometer and the determination started. In 5 minutes, the concentration of Cr(VI) can be read on the screen of the spectrophotometer. Note that the detection range of this fast test is between 0.02 and 2 mg L^{-1}. Analytical measurements made by fast test method, Cr(VI) sequential injection system (SIA) and total chromium flame atomic absorption spectroscopy (FAAS) were comparable with 5%.

3.3.2. Analysis of total, hexavalent chromium and other metal ions

Apart from Cr(VI) fast analysis during the last stages of biosorption, Cr(VI) concentration of the samples taken during all the biosorption and coagulation-flocculation processes was analyzed by the sequential injection system (SIA) using diphenylcarbazide method. The Cr(VI) standard used for obtaining the calibration curves in the diphenylcarbazide method was analyzed by flame atomic absorption spectroscopy (FAAS).

The concentration of total chromium, copper, iron, nickel and aluminium of the liquid samples were determined by flame atomic absorption spectroscopy (FAAS). The concentration of Cr(III) was determined as the difference between total chromium and hexavalent chromium concentration.

4. RESULTS AND DISCUSSION

The results obtained when applying the technology based on EC as a biosorbent for the treatment of synthetic solutions and metal finishing effluents are presented in the following sections.

4.1. Biosorption

4.1.1. Biosorption of metal ions from synthetic solutions

In order to evaluate the sorption behavior, treatment of two synthetic solutions (S1: Cr(VI) single solution and S2: Cr(VI)-Cu(II) binary mixtures) were carried out. Results of kinetics of metal removal from S1 and S2 are presented in Figure 6.3(a) and (b), separately, in which kinetic profiles of total, hexavalent, trivalent chromium and copper have been plotted. In the same figure the evolution of conductivity and pH values are also presented. The experimental data as a function of time are shown in Annex III Tables A3.1 and A3.2.

As seen in Figure 6.3 total chromium concentration decreased with time until it reached a plateau at 13.56 and 13.16 mg L^{-1} for S1 and S2, respectively. These concentrations accounted for 12.54% and 12.77% of initial chromium concentration, respectively. In both solutions (S1 and S2), Cr(VI) concentration decreased until it is lower than 0.5 mg L^{-1} with simultaneous appearance of Cr(III) in solution. The trivalent chromium concentration increased with time and tended to reach equilibrium when Cr(VI) concentration was close to zero. Moreover, the percentage of Cr(III) remaining in solution was found at the same level as the results obtained in Chapter IV where 4 L Cr(VI)-Cu(II) binary mixtures were treated by EC with the same sorbent dose (6.67 g L^{-1}) and at the same pH value (pH 2.0). It confirms the efficiency of EC for Cr(VI) removal when a large volume of effluent is used. It must be remarked that Cu(II) was not sorbed from Cr(VI)-Cu(II) binary mixture.

The same as found in the previous work presented in Chapter IV, Cu(II) concentration did not change as a function of time due to the low pH used in the biosorption process.

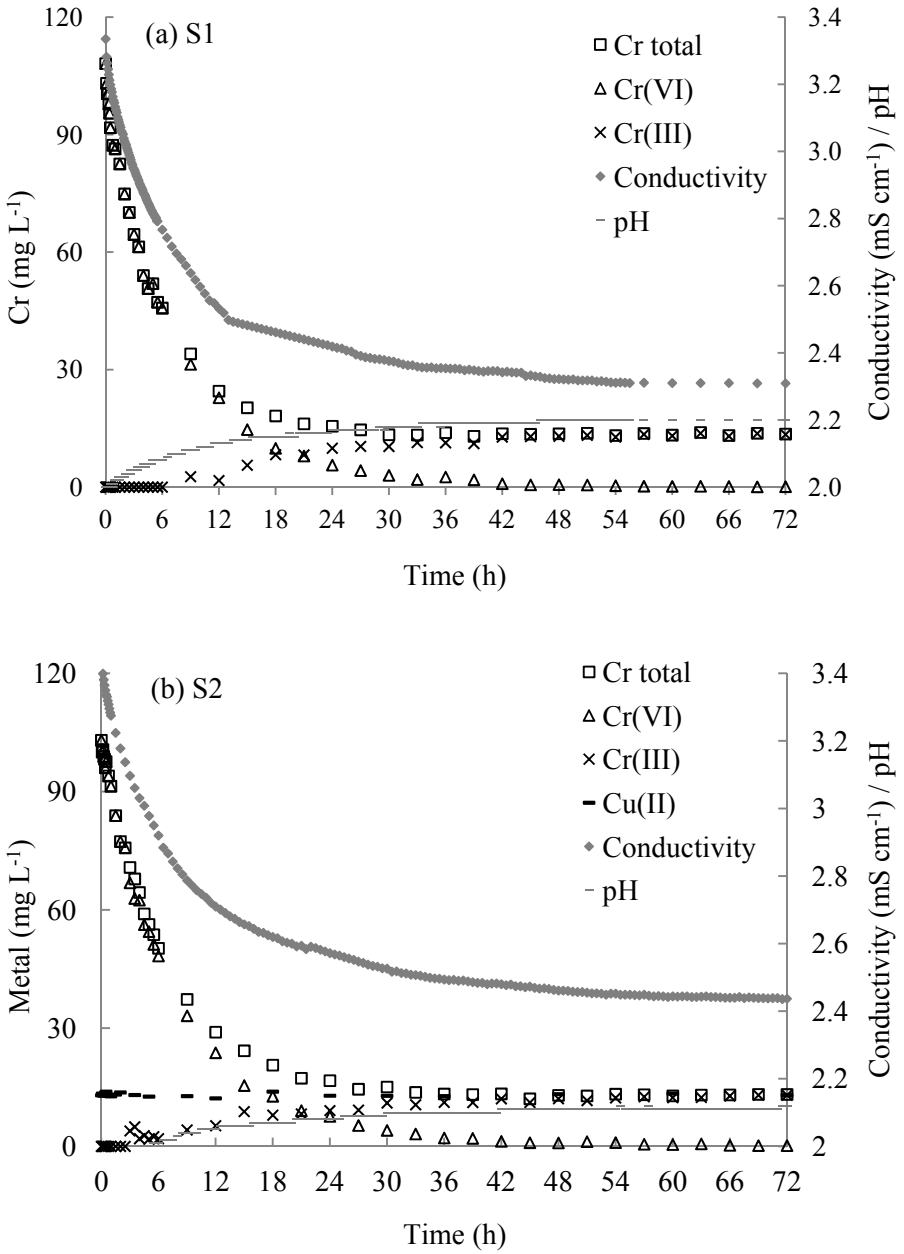


Figure 6.3 Metal ions removal by EC from synthetic solutions in a 10 L stirred batch reactor. Sorbent dose: 6.67 g L^{-1}, pH 2.0, temperature: 20±2^{o}C. (a): S1 108.15 mg L^{-1} Cr(VI), (b): S2 103.04 mg L^{-1} Cr(VI)-12.96 mg L^{-1} Cu(II) binary mixtures.

An increase of pH during the sorption process is observed in Figure 6.3(a) and (b). The pH increase indicates that protons are consumed in Cr(VI) reduction. The pH curve become flattened when Cr(VI) almost disappeared and Cr(III) concentration almost arrived at equilibrium. The evolution of pH value followed Cr(VI) sorption/reduction and formation of Cr(III). Therefore, the stability of pH value of the solution could be an indicator for the end of Cr(VI) reduction reaction.

Conductivity is a parameter for ionic content in solution (Gray, 2004). The value of conductivity decreased with time and tended to be stable when total chromium reaches equilibrium. Whenever the concentration of copper was zero (S1) or stable with time (S2), the decrease of conductivity of these two solutions indicates the removal of total chromium species from both solutions. The removal of total chromium is mainly considered as hexavalent chromium sorption/reduction and sorption of the formed trivalent chromium. Moreover, the stable concentration of total chromium normally was achieved when hexavalent chromium was completely reduced/sorbed from solution and the formed Cr(III) was going to reach a constant concentration. As a result of this, when the removal of total chromium reached equilibrium, the conductivity value of solution remained stable. Therefore, the measurement of conductivity could also be used as indicator of the end of chromium sorption process.

In summary, stability of both pH and conductivity values can indicate the end of biosorption process.

The use of the multiparameter for recording pH and conductivity measurements will have a great advantage for biosorption industrial applications. There is no need of neither sampling nor metal ions analysis during the biosorption process. The process can be stopped as soon as pH and conductivity reach a constant value. Once the process is over a kit for fast Cr(VI) analysis can be used to check whether hexavalent chromium concentration is less than 0.5 mg L^{-1}. In case Cr(VI) concentration is higher than this value a second biosorption step by using fresh EC is recommended.

4.1.2. Biosorption of metal ions from industrial effluents

After confirming behavior of EC for Cr(VI) sorption by using two synthetic solutions, three industrial effluents (E1, E2 and E3) containing Cr(VI) and other metal ions were contacted with EC in the reactor. The kinetic profiles of total, hexavalent and trivalent chromium are plotted in Figure 6.4(a), (c) and (e) for E1, E2 and E3, separately. In the same figures the evolution of conductivity and pH of these three effluents is also presented. Kinetic profiles of the other metal ions also present in the industrial effluents have been plotted in Figure 6.4 (b), (d) and (f) for E1, E2 and E3, respectively. The corresponding experimental data are presented in Annex III Tables A3.3-A3.5.

As shown in Figure 6.4 (a), (c) and (e), concentration of total chromium decreased with time from 112.49 to 33.34 mg L^{-1} in E1 after 72 hours, from 108.50 to 35.33 mg L^{-1} in E2 after 96 hours, from 147.18 to 45.77 mg L^{-1} in E3 after 168 hours. The remaining chromium concentration was higher in E3 than in the other two effluents due to its higher initial chromium concentration. However, the percentage of chromium in the remaining solution was found to be similar for all the three effluents: 29.64%, 32.56% and 31.10% for E1, E2 and E3, respectively. At the end of the process Cr(VI) concentration in the three effluents (0.50, 0.13 and 0.24 mg L^{-1}) met the discharge limit.

Simultaneously to Cr(VI) removal Cr(III) increased in the three effluents. When Cr(VI) was likely to disappear, Cr(III) tended to achieve equilibrium. These results show that EC has the ability to reduce Cr(VI) to its trivalent form from metal finishing industrial effluents. As a result of Cr(VI) reduction, Cr(III) was found in solution and it was the dominant species of chromium in solution.

The performance of the multiparameter soaked in the reactor when treating the three effluents was good and very similar to the one obtained when synthetic solutions were treated. The stability of both pH and conductivity values indicated the end of the process.

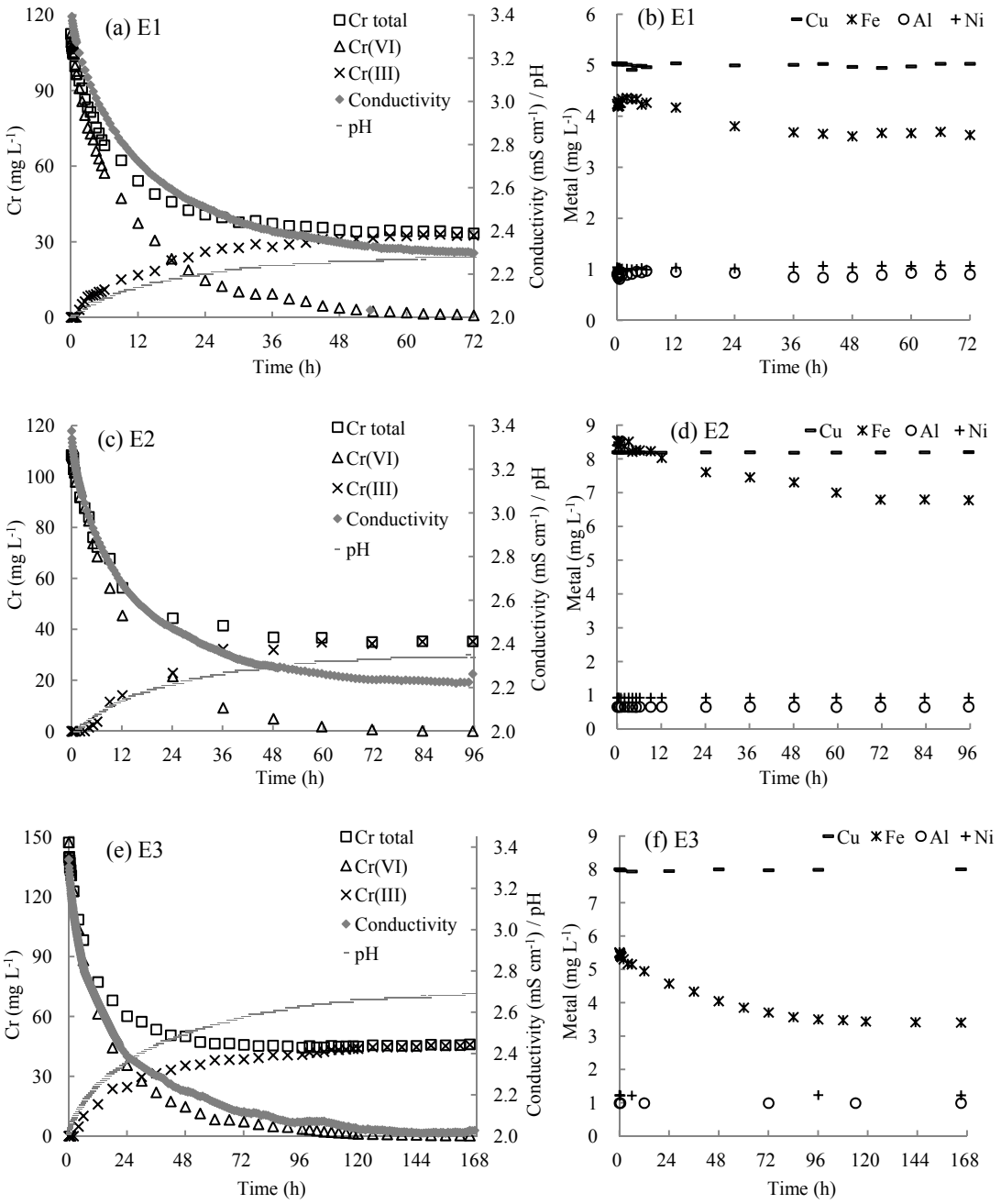


Figure 6.4 Metal ions removal by EC from three metal finishing industrial effluents in a 10 L stirred batch reactor. Sorbent dose: 6.67 g L^{-1}, pH 2.0, temperature: 20±2°C. (a) and (b): E1, (c) and (d): E2, (e) and (f): E3.

Results presented in Figure 6.4 (b), (d) and (f) show the non-efficiency of the sorbent for copper, nickel and aluminum removal at the present experimental conditions which apparently are not the most favorable conditions for the removal of these metal ions. Conversely, a part of the iron present in the effluents was removed. Some researchers also found that Fe(III) and Fe(II) can be removed by the polyphenols and tannins of biosorbents due to the richness in hydroxyl, carbonyl and amine functional groups (Karamac, 2007; Quan et al., 2013). Furthermore, some others found that Fe species can exert a fully competition in the biosorption of Cr(VI) from Cr(VI) and Fe(III) mixtures solutions by microbial biomass (Aksu et al., 1997; Sag & Kutsal, 1996; Yag & Akcael, 2002) or fungus (Bayomi et al., 1998).

In order to compare Cr(VI) reduction/sorption in both synthetic solutions and industrial effluents, profiles of total, hexavalent and trivalent chromium kinetics are plotted in Figures 6.5, 6.6 and 6.7, respectively.

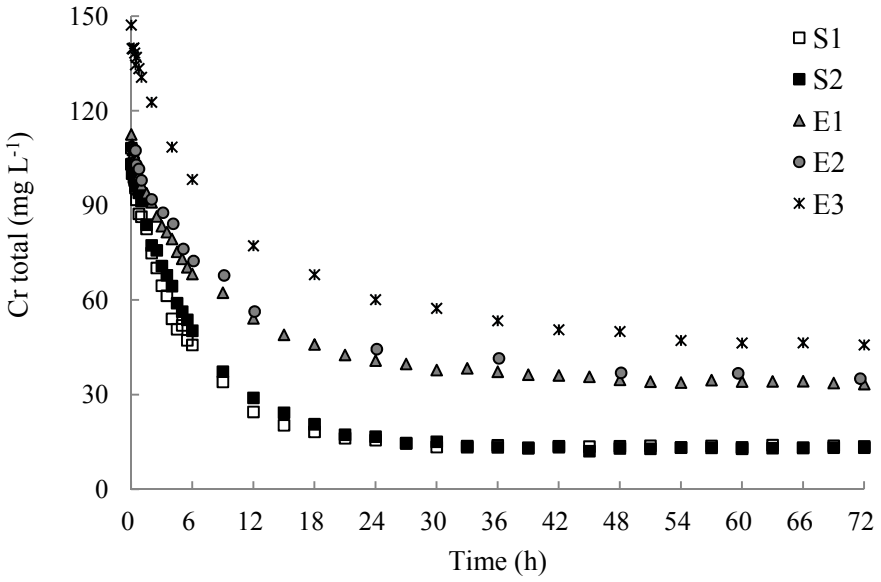


Figure 6.5 Total Cr concentration in solution as a function of time for the synthetic solutions (S1, S2) and metal finishing effluents (E1, E2, E3). Sorbent dose: 6.67 g L^{-1}, pH 2.0, temperature: 20±2^{o}C.

As seen in Figure 6.5, after 72 hours sorption, total chromium concentration in the industrial effluents was higher than in the synthetic solutions. Although, Cr(VI) concentration in S1, S2, E1 and E2 is similar, total chromium concentration in the remaining solutions of these industrial effluents was higher which means that the sorbent was less efficient to remove chromium. E3 presented the highest concentration of total chromium. This was expected as E3 effluent contained the highest initial Cr(VI) concentration. The different sorbent performance must be attributed to the matrix of the industrial effluents (see Table 6.1). The presence of copper, nickel and aluminium were not expected to interfere in chromium reduction/sorption as they were not sorbed onto EC. The sole ion from the industrial effluents that was sorbed onto EC was iron. Iron can be found in both oxidation states Fe(II) and Fe(III) and therefore these ions could compete with Cr(III) for the sorbent active sites.

In order to clarify this point the profiles of Cr(VI) and Cr(III) sorption were examined (Figures 6.6 and 6.7). When looking at the profiles of Cr(VI) sorption presented in Figure 6.6, similar concentration of Cr(VI) is found in S1, S2, E1 and E2 after 72 hours sorption. Cr(VI) was completely eliminated from these solutions though it must be remarked that Cr(VI) disappearance rate was slower in industrial effluents than in the synthetic solutions. Therefore, the industrial effluents matrix seems to influence only on the reduction reaction rate. In the case of the industrial effluent E3 there was some Cr(VI) in solution after 72 hours presumably due to the fact that this effluent contained higher initial Cr(VI) than the other four solutions. From the profiles of Cr(VI) it can be deduced that the differences in total chromium observed in Figure 6.5 must be attributed to different Cr(III) concentration in the solutions.

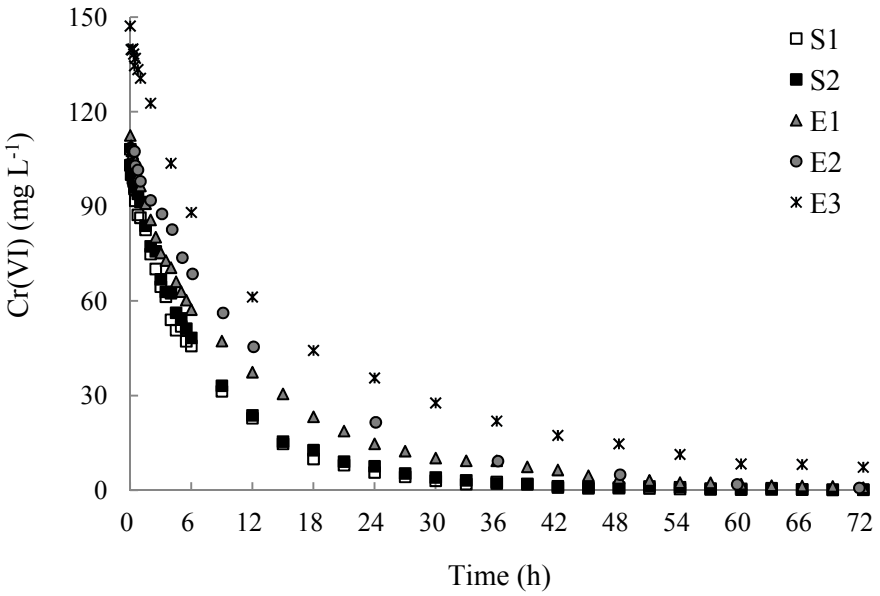


Figure 6.6 Cr(VI) concentration in solution as a function of time for the synthetic solutions (S1, S2) and metal finishing effluents (E1, E2, E3). Sorbent dose: 6.67 g L^{-1}, pH 2.0, temperature: 20±2°C.

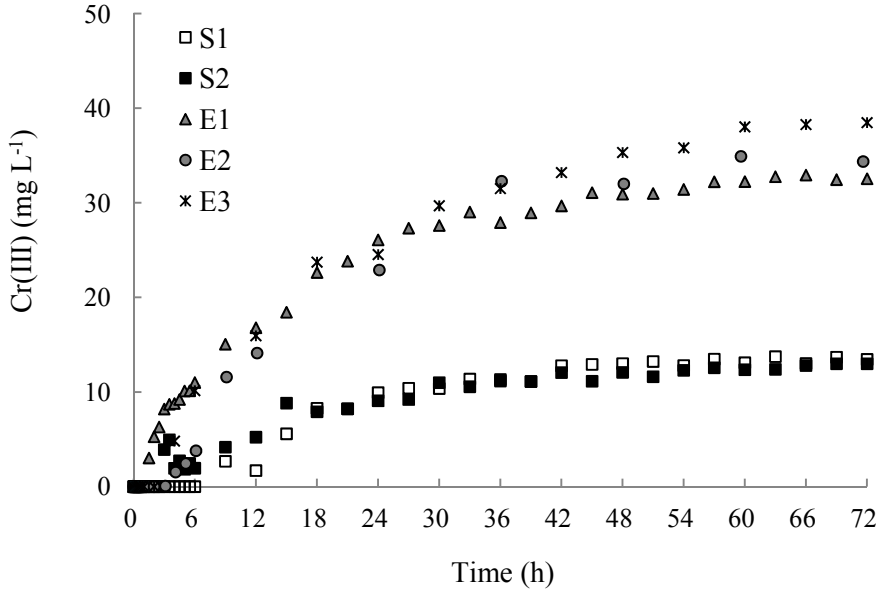


Figure 6.7 Cr(III) concentration in solution as a function of time for the synthetic solutions (S1, S2) and metal finishing effluents (E1, E2, E3). Sorbent dose: 6.67 g L^{-1}, pH 2.0, temperature: 20±2°C.

Indeed, when comparing Cr(III) concentration after 72 hours in S1, S2, E1 and E2, it can be observed a higher Cr(III) concentration in industrial effluents than in synthetic solutions. Concentration of Cr(III) was 13.45 and 12.99 mg L^{-1} in S1 and S2, and 32.84 and 34.36 mg L^{-1} in E1 and E2, respectively, that represents 60% higher trivalent chromium concentration in industrial effluents than in synthetic solutions. This difference could be due to the competition between iron and Cr(III) for sorption onto EC. Lugo-Lugo et al. (2012) also found a competitive biosorption between Cr(III) and Fe(III) from binary mixtures of these cations when using orange peel as sorbent. In that study Cr(III) removal was 30% lower when iron was present.

Though iron-trivalent chromium competition could take place, the high difference of Cr(III) concentration between synthetic and industrial effluents cannot be explained by the little amount of iron sorbed onto EC. Therefore, the rest of components of the industrial effluents matrix must contribute to the less trivalent chromium removal. Additional experiments should be necessary.

The important point is that in spite of the iron and complex matrix of the industrial effluents, EC was effective in Cr(VI) elimination and so the goal of biosorption was successfully achieved. Moreover the concentration of the rest of metal ions except Cr(III) and Cu(II) met the discharge limits of sewage treatment plant. In the next section, coagulation-flocculation process will be performed for the elimination of Cr(III) and Cu(II) ions in solution.

4.2. Coagulation-flocculation

Coagulation-flocculation was performed with the aim of removing Cr(III) and Cu(II) from the industrial effluents. A jar test was carried out to know the performance of the two types of coagulant (20 g L^{-1} $Al_2(SO_4)_3 \cdot 18H_2O$ and 6 g L^{-1} $FeCl_3$) and the optimal coagulant dosage. The results of jar test for E1 solution after biosorption are presented in Table 6.2, where the results obtained by using $Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3$ can be seen in Table 6.2(a) and (b), separately.

Table 6.2 Results of coagulation-flocculation jar test for E1 solution after biosorption by using (a) $Al_2(SO_4)_3.18H_2O$ and (b) $FeCl_3$.

(a) $Al_2(SO_4)_3 \cdot 18H_2O$		Al		Cr(VI)		Cr(III)		Cu		Fe		Ni	
(mL)	(mg 50mL^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})
0.00	0.00	0.90	0.00	0.50	0.50	32.84	0.00	5.38	0.08	3.64	0.07	1.07	0.01
0.05	0.02	2.59	0.12	0.50	0.50	32.81	0.00	5.37	0.09	3.64	0.09	1.07	0.01
0.20	3.98	7.63	0.40	0.50	0.50	32.71	0.00	5.36	0.07	3.63	0.05	1.07	0.00
0.30	5.96	10.98	0.78	0.50	0.50	32.64	0.00	5.35	0.09	3.62	0.06	1.06	0.01
0.50	9.90	17.64	1.80	0.50	0.50	32.51	0.00	5.33	0.09	3.60	0.05	1.06	0.01
1.00	19.61	34.04	2.50	0.49	0.49	32.20	0.00	5.27	0.10	3.57	0.05	1.05	0.01
1.50	29.13	50.13	3.17	0.49	0.49	31.88	0.00	5.22	0.11	3.53	0.06	1.04	0.02
2.00	38.46	65.91	3.15	0.48	0.48	31.58	0.00	5.17	0.12	3.50	0.05	1.03	0.01
2.50	47.62	81.39	3.11	0.48	0.48	31.28	0.00	5.12	0.12	3.47	0.05	1.02	0.01
3.00	56.60	96.58	3.42	0.47	0.47	30.98	0.00	5.08	0.11	3.43	0.05	1.01	0.01
3.50	65.42	111.48	3.71	0.47	0.47	30.69	0.00	5.03	0.11	3.40	0.05	1.00	0.01
4.00	74.07	126.11	3.71	0.46	0.46	30.41	0.00	4.98	0.12	3.37	0.05	0.99	0.01
(b)	$FeCl_3$	Fe		Cr(VI)		Cr(III)		Cu		Al		Ni	
(mL)	(mg 50mL^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})
0.00	0	3.64	0.07	0.50	0.50	32.84	0.00	5.38	0.08	0.90	0.00	1.07	0.01
0.05	0.30	5.51	0.12	0.50	0.50	32.81	0.00	5.37	0.07	0.90	0.14	1.07	0.01
0.20	1.20	11.11	0.07	0.50	0.50	32.71	0.00	5.36	0.08	0.90	0.22	1.07	0.02
0.30	1.79	14.83	0.08	0.50	0.50	32.64	0.00	5.35	0.05	0.89	0.21	1.06	0.00
0.50	2.97	22.21	0.07	0.50	0.50	32.51	0.00	5.33	0.07	0.89	0.26	1.06	0.01
1.00	5.88	40.42	0.03	0.49	0.49	32.20	0.00	5.27	0.10	0.88	0.30	1.05	0.01
1.50	8.74	58.28	0.03	0.49	0.49	31.88	0.00	5.22	0.11	0.87	0.30	1.04	0.01
2.00	11.54	75.79	0.06	0.48	0.48	31.58	0.00	5.17	0.08	0.87	0.41	1.03	0.01
2.50	14.29	92.97	0.06	0.48	0.48	31.28	0.00	5.12	0.09	0.86	0.39	1.02	0.01
3.00	16.98	109.82	0.07	0.47	0.47	30.98	0.00	5.08	0.08	0.85	0.47	1.01	0.01
3.50	19.63	126.36	0.06	0.47	0.47	30.69	0.00	5.03	0.08	0.84	0.56	1.00	0.01
4.00	22.22	142.60	0.05	0.46	0.46	30.41	0.00	4.98	0.10	0.83	0.65	0.99	0.01

As seen in Table 6.2, by adjusting the pH of sample E1 to pH 9.0, total precipitation of Cr(III) can be achieved, copper ions were also almost completely precipitated, only 0.08 mg L^{-1} was remaining in solution. Aluminium, iron and nickel ions were also nearly totally removed. Conversely, Cr(VI) concentration before and after treatment was the same. It means that the alkaline condition is not favorable for hexavalent chromium removal and confirms that the removal of chromium in this oxidation state needs of a previous step, the reduction to its trivalent form.

As seen in the same table, the increase of coagulant dosage did not result in any important improvement of metal ions removal. This observation is similar to the one presented in Chapter V where synthetic solutions were post-treated by coagulation-flocculation after biosorption onto EC. Similar results were obtained when making the jar test using samples E2 and E3 (see Tables 6.3 and 6.4).

Table 6.3 Results of coagulation-flocculation jar test for E2 solution after biosorption by using (a) $Al_2(SO_4)_3.18H_2O$ and (b) $FeCl_3$.

(a) $Al_2(SO_4)_3 \cdot 18H_2O$		Al		Cr(VI)		Cr(III)		Cu		Fe		Ni	
(mL)	(mg 50mL^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})
0.00	0.00	0.90	0.00	0.13	0.13	35.20	0.00	8.20	0.04	6.78	0.06	0.93	0.04
0.05	0.02	2.59	0.02	0.13	0.13	35.16	0.00	8.19	0.04	6.77	0.06	0.93	0.03
0.20	3.98	7.63	0.55	0.13	0.13	35.06	0.00	8.17	0.03	6.75	0.06	0.93	0.03
0.30	5.96	10.98	0.62	0.13	0.13	34.99	0.00	8.15	0.04	6.74	0.06	0.92	0.03
0.50	9.90	17.64	1.21	0.13	0.13	34.85	0.00	8.12	0.04	6.71	0.05	0.92	0.04
1.00	19.61	34.04	1.96	0.13	0.13	34.51	0.00	8.04	0.04	6.65	0.05	0.91	0.04
1.50	29.13	50.13	2.90	0.13	0.13	34.17	0.00	7.96	0.04	6.58	0.05	0.90	0.04
2.00	38.46	65.91	2.48	0.13	0.13	33.85	0.00	7.88	0.03	6.52	0.05	0.89	0.04
2.50	47.62	81.39	2.43	0.12	0.12	33.52	0.00	7.81	0.04	6.46	0.04	0.89	0.04
3.00	56.60	96.58	1.73	0.12	0.12	33.21	0.00	7.74	0.03	6.40	0.04	0.88	0.04
3.50	65.42	111.48	1.81	0.12	0.12	32.90	0.00	7.66	0.04	6.34	0.03	0.87	0.04
4.00	74.07	126.11	1.55	0.12	0.12	32.59	0.00	7.59	0.04	6.28	0.04	0.86	0.04
(b)	$FeCl_3$	Fe		Cr(VI)		Cr(III)		Cu		Al		Ni	
(mL)	(mg 50mL^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})
0.00	0	3.64	0.06	0.13	0.13	35.20	0.00	8.20	0.04	0.66	0.00	0.93	0.04
0.05	0.30	5.51	0.07	0.13	0.13	35.16	0.00	8.19	0.05	0.66	0.00	0.93	0.03
0.20	1.20	11.11	0.07	0.13	0.13	35.06	0.00	8.17	0.05	0.66	0.00	0.93	0.03
0.30	1.79	14.83	0.07	0.13	0.13	34.99	0.00	8.15	0.04	0.66	0.00	0.92	0.04
0.50	2.97	22.21	0.06	0.13	0.13	34.85	0.00	8.12	0.04	0.65	0.00	0.92	0.04
1.00	5.88	40.42	0.06	0.13	0.13	34.51	0.00	8.04	0.05	0.65	0.00	0.91	0.04
1.50	8.74	58.28	0.05	0.13	0.13	34.17	0.00	7.96	0.04	0.64	0.00	0.90	0.04
2.00	11.54	75.79	0.05	0.13	0.13	33.85	0.00	7.88	0.05	0.63	0.00	0.89	0.03
2.50	14.29	92.97	0.05	0.12	0.12	33.52	0.00	7.81	0.04	0.63	0.00	0.89	0.04
3.00	16.98	109.82	0.05	0.12	0.12	33.21	0.00	7.74	0.04	0.62	0.00	0.88	0.04
3.50	19.63	126.36	0.05	0.12	0.12	32.90	0.00	7.66	0.03	0.62	0.00	0.87	0.04
4.00	22.22	142.60	0.06	0.12	0.12	32.59	0.00	7.59	0.03	0.61	0.00	0.86	0.04

Table 6.4 Results of coagulation-flocculation jar test for E3 solution after biosorption by using (a) $Al_2(SO_4)_3.18H_2O$ and (b) $FeCl_3$.

(a) $Al_2(SO_4)_3 \cdot 18H_2O$		Al		Cr(VI)		Cr(III)		Cu		Fe		Ni	
(mL)	(mg 50mL^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})
0.00	0.00	0.90	0.11	0.24	0.24	45.53	0.00	8.01	0.04	3.39	0.07	1.23	0.00
0.05	0.02	2.59	0.13	0.24	0.24	45.48	0.00	8.00	0.21	3.39	0.08	1.23	0.00
0.20	3.98	7.63	0.30	0.24	0.24	45.35	0.00	7.97	0.05	3.38	0.06	1.23	0.00
0.30	5.96	10.98	0.38	0.24	0.24	45.26	0.00	7.96	0.01	3.37	0.07	1.23	0.00
0.50	9.90	17.64	0.58	0.24	0.24	45.08	0.00	7.93	0.03	3.36	0.06	1.22	0.00
1.00	19.61	34.04	1.71	0.24	0.24	44.64	0.00	7.85	0.16	3.32	0.05	1.21	0.00
1.50	29.13	50.13	3.80	0.23	0.23	44.20	0.00	7.77	0.11	3.29	0.04	1.20	0.00
2.00	38.46	65.91	4.77	0.23	0.23	43.78	0.00	7.70	0.04	3.26	0.05	1.19	0.00
2.50	47.62	81.39	4.09	0.23	0.23	43.36	0.00	7.62	0.04	3.23	0.05	1.17	0.00
3.00	56.60	96.58	5.18	0.23	0.23	42.95	0.00	7.55	0.05	3.20	0.05	1.16	0.00
3.50	65.42	111.48	4.74	0.22	0.22	42.55	0.00	7.48	0.06	3.17	0.05	1.15	0.00
4.00	74.07	126.11	5.35	0.22	0.22	42.16	0.00	7.41	0.03	3.14	0.05	1.14	0.00
(b)	$FeCl_3$	Fe		Cr(VI)		Cr(III)		Cu		Al		Ni	
(mL)	(mg 50mL^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})	Initial (mg L^{-1})	Final (mg L^{-1})
0.00	0	3.64	0.07	0.24	0.24	45.53	0.00	8.01	0.04	0.99	0.00	1.23	0.00
0.05	0.30	5.51	0.17	0.24	0.24	45.48	0.00	8.00	0.02	0.99	0.00	1.23	0.00
0.20	1.20	11.11	0.08	0.24	0.24	45.35	0.00	7.97	0.02	0.99	0.00	1.23	0.00
0.30	1.79	14.83	0.10	0.24	0.24	45.26	0.00	7.96	0.01	0.98	0.00	1.23	0.00
0.50	2.97	22.21	0.08	0.24	0.24	45.08	0.00	7.93	0.02	0.98	0.00	1.22	0.00
1.00	5.88	40.42	0.09	0.24	0.24	44.64	0.00	7.85	0.02	0.97	0.00	1.21	0.00
1.50	8.74	58.28	0.06	0.23	0.23	44.20	0.00	7.77	0.03	0.96	0.00	1.20	0.00
2.00	11.54	75.79	0.07	0.23	0.23	43.78	0.00	7.70	0.03	0.95	0.00	1.19	0.00
2.50	14.29	92.97	0.06	0.23	0.23	43.36	0.00	7.62	0.04	0.94	0.00	1.17	0.00
3.00	16.98	109.82	0.06	0.23	0.23	42.95	0.00	7.55	0.02	0.93	0.00	1.16	0.00
3.50	19.63	126.36	0.05	0.22	0.22	42.55	0.00	7.48	0.01	0.93	0.00	1.15	0.00
4.00	22.22	142.60	0.06	0.22	0.22	42.16	0.00	7.41	0.01	0.92	0.00	1.14	0.00

Due to the effectiveness of precipitation taking place at pH 9.0 when using the jar test, elimination of the metal ions was carried out by precipitation at pH 9.0. The transparent supernatant of an industrial effluent after metal precipitation is shown in Figure 6.8.

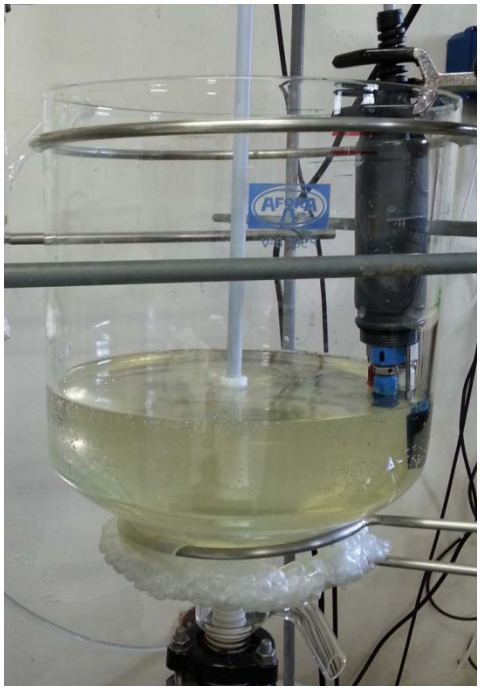


Figure 6.8 Metal finishing effluent treated after biosorption and precipitation

The technology based on EC biosorption was successfully applied for the treatment of wastewaters from metal finishing industry. Biosorption process was effective for hexavalent chromium sorption/reduction and partial removal of iron and the subsequent precipitation process carried out at pH 9.0 eliminated almost all the rest of residual cations, including trivalent chromium formed by chromium reduction, iron, copper, nickel and aluminium.

After the overall treatment, concentration of all the metal ions was far below the regulated discharge limits (see Table 6.5); therefore, the treated effluent is suitable for discharge to sewage treatment plant.

Table 6.5 Metal ion removal from metal finishing industrial effluents.

Metal	**E1**	**E2**	**E3**
	mg/L	**mg/L**	**mg/L**
Cr(VI)	112.49	108.50	147.18
Cr(III)	0.00	0.00	0.00
Cu	5.04	8.20	8.01
Ni	1.04	0.93	1.23
Fe	4.24	8.54	5.51
Al	0.90	0.66	0.99
Biosorption			
Cr(VI)	0.50	0.13	0.24
Cr(III)	32.84	35.20	45.53
Cu	5.03	8.20	8.01
Ni	1.04	0.93	1.23
Fe	3.64	6.78	3.39
Al	0.90	0.66	0.99
Precipitation			
Cr(VI)	0.50	0.13	0.24
Cr(III)	0.00	0.00	0.00
Cu	< LOD	0.04	0.02
Ni	0.04	< LOD	< LOD
Fe	0.10	0.12	0.21
Al	0.09	< LOD	< LOD

[a] LOD=Limit of detection of FAAS.

A scheme of the proposed treatment for metal finishing industries effluents is depicted in Figure 6.9. As an altertive to electrolysis which is currently used for hexavalent chromium reduction (see Figure 6.1), the biosorption by using exhausted coffee waste does not need the addition of chemical reducing agents and is performed in a stirred batch reactor that avoid the frequent equipment mainenance. The subsequent precipitation at pH 9.0 generates less amount of metal sludge compared to traditional technology as part of metal ions have been sorbed onto the biosorbent. Depending on the characteristics of treated effluent, a certain amount of coagulants might be needed to achieve the sufficient metal cations precipitation. Note that hexavalent chromium cannot be removed throught precipitation or coagulation-flocculation, while biosorption is effective for Cr(VI) removal. Therefore, in

case Cr(VI) concentration does not meet the discharge limit after the biosorption process, further step of biosorption can be carried out by using fresh exhausted coffee waste as sorbent.

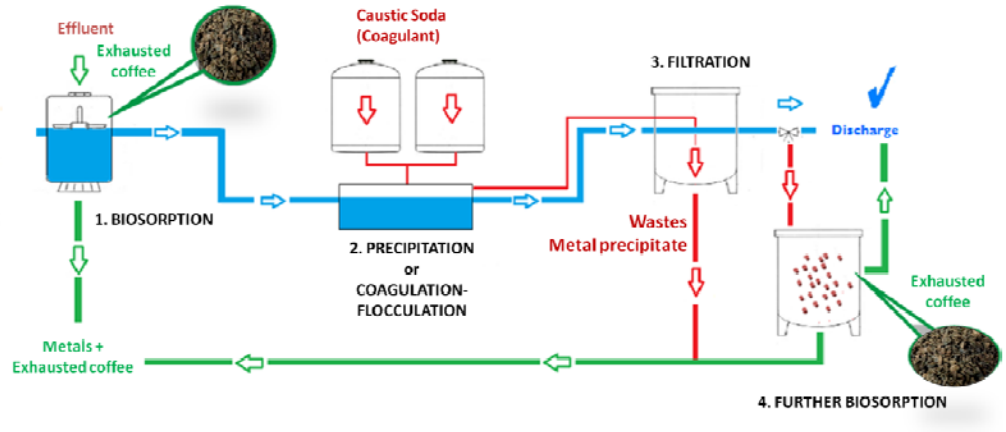


Figure 6.9 A technology based on EC biosorption for the treatment of metal finishing industrial effluents

The effectiveness of this technology for removal of metal finishing industries effluents made it an ideal alternative to other treatment options. The major advantages of this technology over conventional technology are listed below:

- Cheap: exhausted coffee waste is an abundant byproduct from soluble coffee industry; chemical reducing agents are not needed.
- Less sludge generation: since a majority of chromium is sorbed on the biosorbent, less sludge occurs after the overall treatment process.
- Easy operation: exhausted coffee waste loaded with metal ions can be easily filtered from reactor.

CHAPTER VII.

CONCLUSIONS

A sustainable technology for Cr(VI) and divalent metal ions removal has been developed. This technology that consists on a process of biosorption by exhausted coffee waste followed by precipitation has been applied for the treatment of wastewater from a metal finishing industry. The following conclusions can be drawn from the present study.

A physical and chemical characterization of exhausted coffee waste was performed. From the obtained results potential applications of this waste including biosorption may be suggested：

- The high content of extractives (>50%) opens new expectations for industrial applications. The lipophilic extractives accounted for over 20% of the material which would justify further investigation on biodiesel production base on exhausted coffee waste. The high ratio of polyphenolic compounds in relation to the total extracted material also envisages a source of antioxidants. The quite high calorific value (26 MJ/kg) suggests a good potential for bioenergy.
- The high porosity of exhausted coffee waste opens expectation for its use in biosorption. The high aromatic character and the low polarity index suggest the potential use of exhausted coffee waste as sorbent for hydrophobic pollutants.
- Lignin moieties of exhausted coffee waste can provide electron donor groups for reduction reactions.
- Carboxylic groups of exhausted coffee waste provide sites for complexation reactions and ion-exchange processes.

The role of chemical compounds of exhausted coffee waste in metal ions sorption was investigated. From the obtained results the mechanism of Cr(VI) and divalent metals can be drawn:

- The sequential extraction proved to be useful to show the different exhausted coffee waste features related to sorption towards metal ions and the role of extractives and structural compounds involved.
- The removal of aliphatic and polar compounds favored the interactions between metal ions and the sorbent matrix and resulted in an increase of metal sorption.
- Lignin moieties were found to be responsible for Cr(VI) sorption/reduction and sorption

of the formed Cr(III).

- Oxygen functional groups mainly carboxylic groups were responsible for divalent metals sorption.

A kinetic study of Cr(VI) removal from Cr(VI)-Cu(II) binary mixtures was carried out in a batch reactor. In the experimental conditions used in this study:

- Cr(VI) was gradually sorbed/reduced by exhausted coffee waste until being completely or almost completely removed. Simultaneously the formed Cr(III) was in part sorbed.
- Cr(III) in the remaining solution after biosorption was around 15% of the initial Cr(VI) concentration.
- Cu(II) was hardly sorbed on exhausted coffee waste but this metal ion exerted a synergistic effect on the overall process of chromium removal.
- Acidic conditions favored Cr(VI) reduction. Removal of Cr(VI) was faster and pH 2.0 though higher sorption yields were obtained at pH 3.0 in both single solution and binary mixtures. Conversely, pH 5.0 provided the best results of Cu(II) sorption.

A model was developed in basis to (i) irreversible reduction of Cr(VI) to Cr(III) reaction (ii) adsorption and desorption Cr(VI) and formed Cr(III) sorption and desorption (iii) effect of Cu(II) on Cr(VI) sorption.

- The model fitted adequately Cr(VI) kinetics sorption from two sets of binary mixtures of Cr(VI)-Cu(II) of different metal concentration range.
- For each binary mixtures concentrations range the model was calibrated by using three sets of experimental data and validated by four independent sets.
- The values of model parameters showed that from all the processes considered in the formulation of the model Cr(VI) desorption did not occur but desorption of Cr(III) must be taken into account.
- The synergistic effect of Cu(II) in Cr(VI) sorption was more remarkable in the case of the binary mixtures of the lowest concentration range.

Post-treatment after biosorption to eliminate residual metal ions was investigated. The efficiency of biosorption using fresh exhausted coffee waste and precipitation by using coagulants was evaluated.

- Cr(VI) was effectively removed via biosorption by using fresh exhausted coffee waste while Cr(III) and Cu(II) was only partially removed.
- Adjustment of pH to pH 9.0 resulted to be efficient for metal cations precipitation while Cr(VI) concentration did not vary.
- The addition of coagulant slightly improved metal ions precipitation. From both coagulants tested, $FeCl_3$ was recommended.

Biosorption followed by precipitation has been applied for the treatment of wastewater from a rinsing bath of a metal finishing industry.

- Biosorption by using exhausted coffee was efficient for Cr(VI) removal from the industrial effluents though removal rates were slower as compared to the rates obtained with synthetic water.
- Cr(III) in the remaining solution after biosorption was around 30% of the initial Cr(VI) concentration.
- Biosorption was able to eliminate part of the iron present in the industrial effluents.
- Adjustment of pH to pH 9.0 assisted almost total precipitation of the remaining metals cations after biosorption and the effluents fulfilled the discharge limits.
- Measurement of conductivity and pH in continuous mode can be used as indicators of the end of the biosorption process.

The proposed technology based on biosorption using exhausted coffee waste proved to be a technically feasible and economically viable sustainable technology for the detoxification of metal finishing industries effluents. The application of this technology will not only reduce wastewater treatment cost for metal finishing industries and also promote waste re-utilization and possible commercialization for coffee manufacturers.

CHAPTER VIII.

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ANNEX I--Preliminary study of effect of pH on Cr(VI) and Cu(II) sorption onto exhausted coffee waste

The pH value of the solution is of great importance in both anion and cation biosorption. The optimal pH of biosorption is determined based on the characteristics of the biomass as well as considering the speciation of metals in the solution. From this point of view, the effect of pH on Cr(VI) and Cu(II) kinetics sorption from single metal solution was investigated preliminarily, in order to obtain the favorable pH for their removal.

The effect of pH on Cr(VI) sorption was evaluated by adding 10.0 g of EC samples (particle size: 0.5-1.0 mm) into 4 L of 0.2 mM Cr(VI) solution at different pH values ranged from pH 2.0 to 5.0 in a stirred batch reactor under continuously agitation (350 rpm) and 20±2^{o}C (sorbent dose 2.5 g L^{-1}) for 96 hours. Samples were taken through a 0.45 μm cellulose filter at interval times during the biosorption. All the samples were acidified by adding 0.1 M HCl to avoid possible metal ions precipitation, and then subjected to metal ions analyses. The effect of pH on Cu(II) sorption was investigated following the same methodology under 60 minutes agitation.

The concentration of total chromium and copper were determined by flame atomic absorption spectroscopy (FAAS). Hexavalent chromium was analysed by the standard colorimetric 1,5-diphenylcarbazide method by using a sequential injection system (SIA) recently developed in our laboratory. The concentration of trivalent chromium was determined as the difference between total chromium and hexavalent chromium concentration. The Cr(VI) standard used for obtaining the calibration curves in the diphenylcarbazide method was analysed by FAAS. Analytical measurements made by the two techniques were comparable with 5%. The results are shown in this annex.

1. Effect of pH on Cr(VI) kinetics sorption

Results of kinetics of Cr(VI) sorption at four different initial pH are presented in Figure A1.1 in which kinetic profiles of total, hexavalent and trivalent chromium are plotted separately.

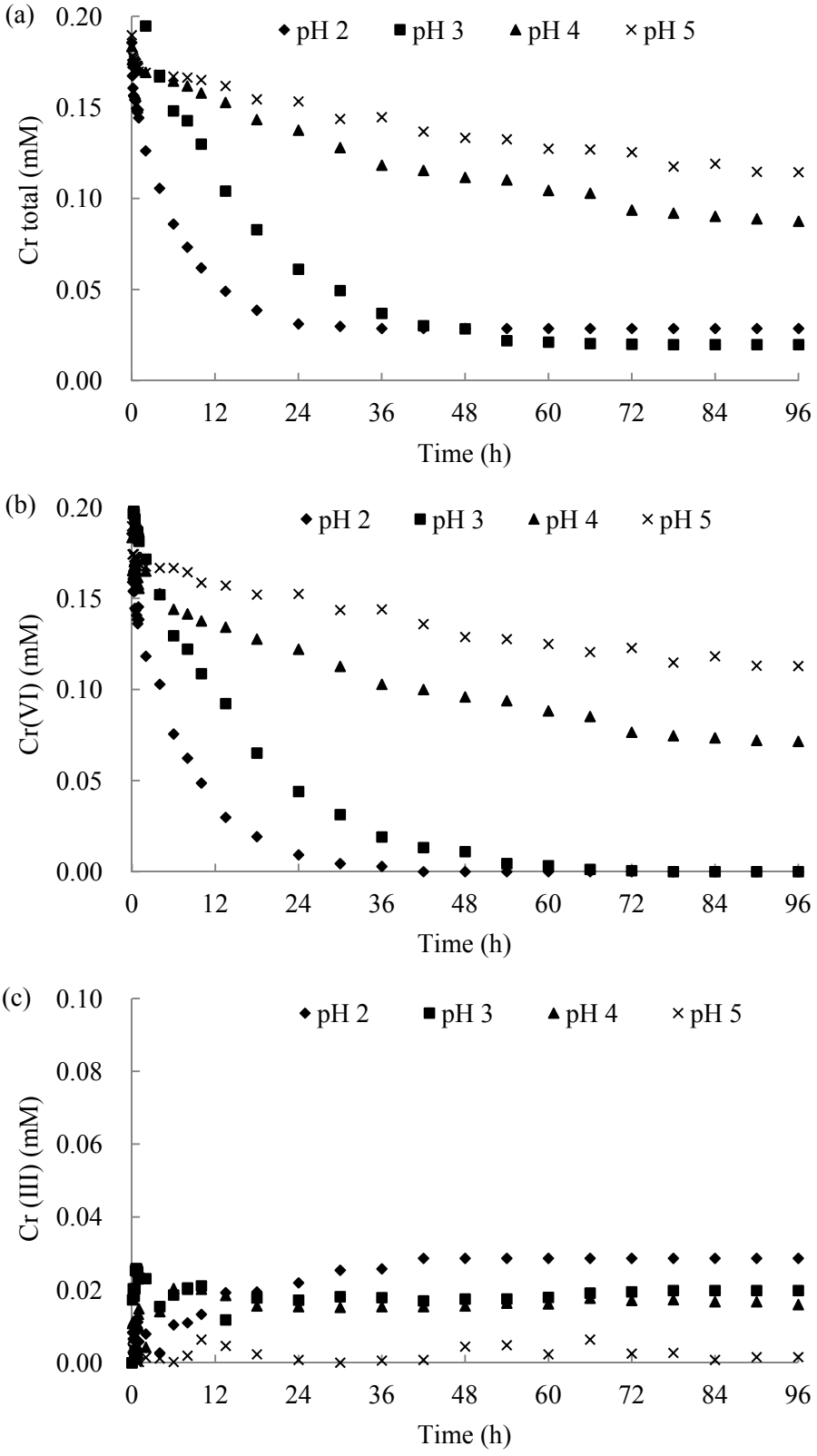

Figure A1.1 Kinetics profiles of total (a), hexavalent (b) and trivalent (c) chromium at different initial pHs (2.0-5.0). Initial Cr(VI) concentration: 0.2 mM, sorbent dose: 2.5 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2^{o}C.

As seen from Figure A1.1(a), the elimination of total chromium species took place when contacting the solution with EC. The concentration of total chromium was still decreasing in the two less acidic conditions (pH 5.0 and 4.0) after 96 hours, whereas it had reached equilibrium at the more acidic conditions (66 hours at pH 3.0 and 36 hours at pH 2.0). It suggests a fastest removal of total chromium species at pH 2.0. On the other side, 40%, 52%, 91% and 85% of total chromium was eliminated after 96 hours from the solutions at pH 5.0, pH 4.0, pH 3.0 and pH 2.0, respectively, where highest removal was found in pH 3.0 solution. The faster removal of total chromium species could be due to the more rapid elimination of hexavalent chromium at lower pH (Figure A1.1(b)). The complete removal of Cr(VI) can be achieved in pH 2.0 and 3.0 solutions, and less time was required at lower pH (pH 2.0). Hexavalent chromium can be reduced to its trivalent form by EC, therefore, the slight higher amount of chromium species at pH 2.0 than pH 3.0 observed in Figure A1.1(a) must be attributed to the higher presence of trivalent chromium in solution.
Indeed, generally speaking, higher concentration of Cr(III) was found at more acidic condition after 24 hours (Figure A1.1(c)). It could be as the result of higher Cr(VI) reduction and/or less Cr(III) sorption by EC at the more acidic condition.

As regards to Cr(VI) sorption/reduction by EC, it is based on the fact that Cr(VI) mainly exists as $HCrO_4^-$ species in the four studied solutions (pH 2.0-5.0), according to the species distribution diagram of Cr(VI) shown in Figure A1.2 obtained by using the MEDUSA (make equilibrium diagrams using sophisticated algorithms) program (Puigdomènech, 2004). The negatively charged $HCrO_4^-$ can be sorbed onto EC surface at pH lower than pH_{pzc} (pH 4.3) of the sorbent (see Chapter II section 4.5) by the electrostatic attraction (Fiol et al., 2008a). Therefore the low acidic conditions would cause the surface of the sorbent to be protonated to a higher extent, which results in a strong attraction between the negatively charged Cr(VI) species and positively charged biomass surface (Prabhakaran et al., 2009).

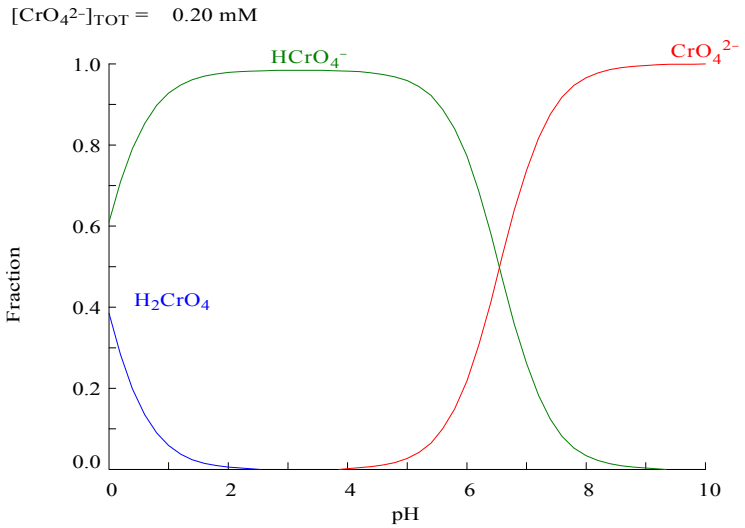

Figure A1.2 The species distribution diagram of Cr(VI) (0.20 mM) as a function of pH.

Moreover, the protonation of the sorbent also helps the reduction of Cr(VI) to its trivalent form. The reduction of Cr(VI) is known to be a proton consuming reaction which can be summarized in Equation A1.1:

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \qquad (A1.1)$$

The electron-donor groups of lignin moieties from some biomaterials have found to be largely responsible for Cr(VI) reduction to Cr(III) (Fiol et al., 2008a; Liang et al., 2014). Hence the reduction of Cr(VI) by EC is also favorable at low pH.

With respect to the formed Cr(III) species that present as Cr^{3+}, $Cr(OH)^{2+}$ and $Cr_3(OH)_4^{5+}$ in the tested solutions (see Figure A1.3), these cationic Cr(III) in solution can be attracted by the negatively charged surface of EC when pH is higher than pH_{pzc} of EC (pH 4.3) by electrostatic attraction. Moreover, these Cr(III) species could be also sorbed onto EC by the functional groups, in which reaction the protons could compete with cationic chromium for active sites of EC. Therefore, the removal of Cr(III) drops off at low pH.

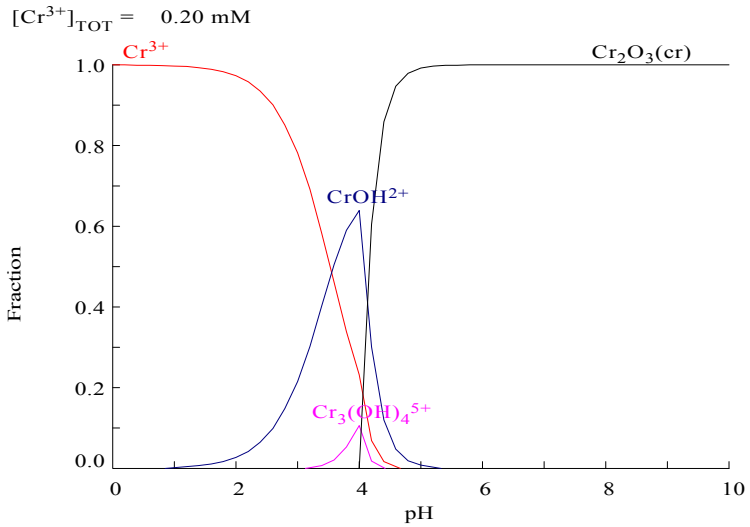

Figure A1.3 The species distribution diagram of Cr(III) (0.20 mM) as a function of pH.

As a conclusion, the optimal pH for Cr(VI) removal by sorption onto EC lies in the region where two mechanisms overlap: (a) the favorable sorption/reduction of Cr(VI) at low pH and (b) the unfavorable sorption of the formed Cr(III) at low pH in aqueous solutions. From pH 2.0 to pH 5.0, these simultaneous mechanisms result in a fastest Cr(VI) sorption at pH 2.0 and a highest Cr(VI) sorption at pH 3.0.

2. Effect of pH on Cu(II) sorption kinetics

Results of kinetics of Cu(II) sorption at four different initial pHs (pH 2.0-5.0) are presented in Figure A1.4 in which kinetic profiles of copper are plotted.

As seen from Figure A1.4, copper sorption onto EC arrived at equilibrium in 5 minutes at all the pHs (pH 2.0-5.0). Higher removal was found at lower pH. The sorption was nearly null at pH 2.0 and up to 50% at pH 5.0.

The results of Cu(II) sorption at different pHs can be explained by considering the surface charge on the sorbent and the speciation of Cu(II).

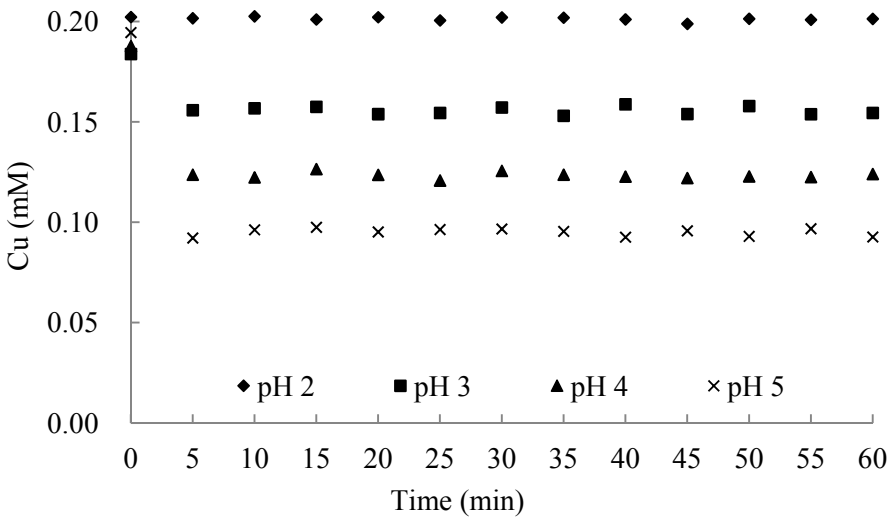

Figure A1.4 Kinetics profiles of copper at different initial pHs (2.0-5.0). Initial Cr(VI) concentration: 0.2 mM, sorbent dose: 2.5 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

The species distribution diagram of Cu(II) shown in Figure A1.5 indicates that the divalent Cu^{2+} is the only specie of copper in solution. It starts to precipitate at pH higher than pH 5.5.

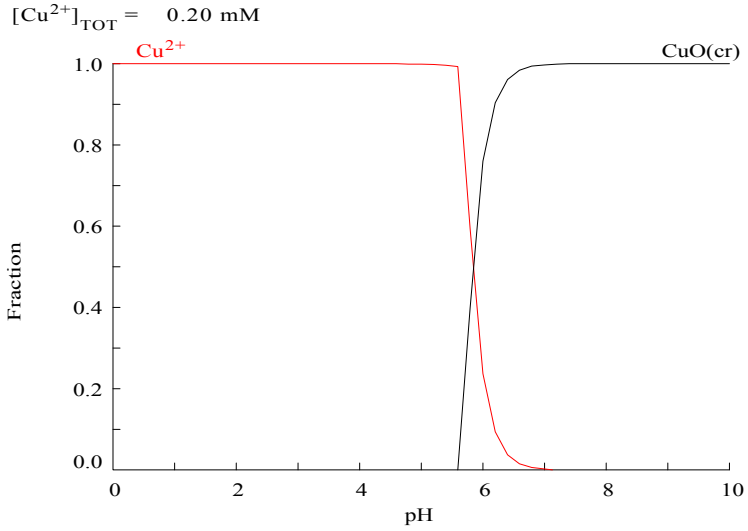

Figure A1.5 The species distribution diagram of Cu(II) (0.20 mM) as a function of pH.

On one hand, the cationic copper can be sorbed onto oxygen functional groups (i.e. carboxylic COOH) of EC (see Chapter III). At acidic pH, the protonation of these functional groups will result in a positively charged surface and consequently compete with Cu(II) cations for binding sites of the sorbent and therefore lead to less Cu(II) sorption.

On the other hand, the positively charged Cu(II) species can be sorbed onto EC surface via electrostatic attraction when pH is higher than pH_{pzc} of EC (pH 4.3). This is another reason for the higher copper removal at less acidic condition.

And when pH is higher than pH 5.5, the precipitation of Cu^{2+} will also contribute to its elimination from aqueous solutions.

Therefore, when the solution pH is ranged between pH 2.0 and 5.0, Cu(II) sorption onto EC is favorable at pH 5.0.

To summarize, the sorption of hexavalent chromium and divalent copper both are strongly pH dependent. More acidic condition favors Cr(VI) sorption while on the contrary, less acidic condition favors Cu(II) sorption. When pH is ranged from pH 2.0 to 5.0, the fastest Cr(VI) removal is at pH 2.0 and the highest sorption can be obtained at pH 3.0; Cu(II) removal by EC is better at pH 5.0.

ANNEX II--The experimental sorption data of Chapter IV

Table A2.1 The data of kinetics sorption using EC for **0.2 mM Cr(VI)-0.4 mM** Cu(II) binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

time (h)	Cr total (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	pH
0.00	0.2180	0.2180	0.0000	0.3957	2.01
0.03	0.1926	0.1845	0.0081	0.3939	2.06
0.08	0.1955	0.1830	0.0125	0.3943	2.03
0.17	0.1816	0.1725	0.0091	0.3948	2.02
0.25	0.1704	0.1682	0.0022	0.3943	2.05
0.33	0.1708	0.1587	0.0121	0.3956	2.01
0.42	0.1704	0.1704	0.0000	0.3956	2.01
0.50	0.1610	0.1610	0.0000	0.3955	2.01
0.75	0.1515	0.1515	0.0000	0.3957	2.01
1.00	0.1419	0.1315	0.0105	0.3957	2.03
1.50	0.1239	0.1035	0.0203	0.3956	2.02
2.00	0.1100	0.0992	0.0108	0.3956	2.04
3.50	0.0896	0.0583	0.0313	0.3956	2.01
5.00	0.0670	0.0345	0.0324	0.3956	2.03
8.00	0.0457	0.0041	0.0416	0.3950	2.03
11.0	0.0370	< LOD[a]	0.0370	0.3941	2.03
14.0	0.0348	< LOD	0.0348	0.3926	2.03
17.0	0.0338	< LOD	0.0338	0.3897	2.03
20.0	0.0343	< LOD	0.0343	0.3896	2.03
24.0	0.0353	< LOD	0.0353	0.3956	2.03
27.0	0.0357	< LOD	0.0357	0.3871	2.03

[a] LOD=Limit of detection of SIA.

Table A2.2 The data of kinetics sorption using EC for **0.2 mM Cr(VI)-0.6 mM** Cu(II) binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

time (h)	Cr total (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	p H
0.00	0.2164	0.2164	0.0000	0.5866	1.97
0.03	0.1873	0.1757	0.0117	0.5821	2.09
0.08	0.1761	0.1633	0.0129	0.5745	2.08
0.17	0.1709	0.1569	0.0140	0.5819	2.04
0.25	0.1603	0.1596	0.0008	0.5737	2.04
0.33	0.1476	0.1388	0.0088	0.5710	2.03
0.42	0.1417	0.1286	0.0131	0.5732	2.01
0.50	0.1310	0.1143	0.0166	0.5689	2.03
0.75	0.1139	0.1028	0.0111	0.5756	2.04
1.00	0.1049	0.0805	0.0244	0.5747	2.02
1.50	0.0838	0.0638	0.0201	0.5755	2.05
2.00	0.0723	0.0464	0.0258	0.5750	2.02
3.50	0.0471	0.0127	0.0344	0.5782	2.02
5.00	0.0356	< LOD[a]	0.0356	0.5760	2.04
8.00	0.0278	< LOD	0.0278	0.5730	2.02
11.0	0.0272	< LOD	0.0272	0.5802	2.05
14.0	0.0285	< LOD	0.0285	0.5757	2.03
24.0	0.0304	< LOD	0.0304	0.5745	2.04
27.0	0.0306	< LOD	0.0306	0.5740	2.04

[a] LOD=Limit of detection of SIA.

Table A2.3 The data of kinetics sorption using EC for **0.4 mM Cr(VI)-0.2 mM** Cu(II) binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

time (h)	Cr total (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	p H
0.00	0.3952	0.3952	0.0000	0.2035	2.00
0.03	0.3381	0.3381	0.0000	0.2034	2.03
0.08	0.3108	0.3108	0.0000	0.2034	2.04
0.17	0.3110	0.3110	0.0000	0.2034	2.03
0.25	0.3034	0.3034	0.0000	0.2034	2.02
0.33	0.3023	0.3023	0.0000	0.2034	2.04
0.42	0.3004	0.3004	0.0000	0.2034	2.03
0.50	0.2947	0.2947	0.0000	0.2034	2.01
0.75	0.2782	0.2782	0.0000	0.2022	2.04
1.00	0.2645	0.2645	0.0000	0.2034	2.01
1.50	0.2498	0.2498	0.0000	0.2034	2.00
2.00	0.2273	0.2168	0.0105	0.2034	2.02
3.50	0.1751	0.1572	0.0179	0.2034	2.00
5.00	0.1363	0.1041	0.0322	0.2034	2.00
8.00	0.1053	0.0474	0.0579	0.2034	2.00
11.0	0.0776	0.0137	0.0639	0.2034	2.04
14.0	0.0682	0.0027	0.0655	0.2034	2.03
17.0	0.0639	< LOD[a]	0.0639	0.2029	2.02
20.0	0.0630	< LOD	0.0630	0.2021	2.03
24.0	0.0632	< LOD	0.0632	0.2031	2.04
27.0	0.0641	< LOD	0.0641	0.2034	2.04

[a] LOD=Limit of detection of SIA.

Table A2.4 The data of kinetics sorption using EC for **0.4 mM Cr(VI)-0.4 mM** Cu(II) binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2^{o}C.

time (h)	Cr total (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	p H
0.00	0.3865	0.3865	0.0000	0.3986	2.00
0.03	0.3585	0.3585	0.0000	0.3959	2.04
0.08	0.3383	0.3383	0.0000	0.3948	2.08
0.17	0.3272	0.3269	0.0003	0.3921	2.05
0.25	0.3191	0.3191	0.0000	0.3964	2.06
0.33	0.3122	0.3122	0.0000	0.3953	2.08
0.42	0.3048	0.3048	0.0000	0.3986	2.06
0.50	0.3009	0.3009	0.0000	0.3968	2.06
0.75	0.2946	0.2946	0.0000	0.3986	2.05
1.00	0.2695	0.2687	0.0009	0.3986	2.05
1.50	0.2388	0.2319	0.0069	0.3862	2.05
2.00	0.2170	0.1962	0.0209	0.3950	2.07
3.50	0.1734	0.1458	0.0276	0.3953	2.09
5.00	0.1285	0.0840	0.0445	0.3909	2.08
8.00	0.0929	0.0429	0.0501	0.3986	2.06
11.0	0.0709	0.0085	0.0625	0.3953	2.06
14.0	0.0621	0.0010	0.0611	0.3903	2.09
24.0	0.0566	0.0021	0.0545	0.3855	2.09
27.0	0.0568	0.0031	0.0538	0.3891	2.10

Table A2.5 The data of kinetics sorption using EC for **0.4 mM Cr(VI)-0.6 mM** Cu(II) binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

time (h)	Cr total (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	p H
0.00	0.4047	0.4047	0.0000	0.5758	2.00
0.03	0.3705	0.3705	0.0000	0.5703	2.00
0.08	0.3516	0.3325	0.0192	0.5705	2.03
0.17	0.3470	0.3198	0.0272	0.5651	2.00
0.25	0.3491	0.3491	0.0000	0.5643	2.00
0.33	0.3326	0.3326	0.0000	0.5673	2.01
0.42	0.3213	0.3213	0.0000	0.5688	2.03
0.50	0.3054	0.3054	0.0000	0.5645	2.03
0.75	0.2826	0.2798	0.0028	0.5632	2.03
1.00	0.2518	0.2518	0.0000	0.5632	2.04
1.50	0.2282	0.2182	0.0100	0.5650	2.04
2.00	0.2094	0.2093	0.0001	0.5666	2.05
3.50	0.1619	0.1428	0.0190	0.5684	2.06
5.00	0.1274	0.0886	0.0388	0.5681	2.05
8.00	0.0886	0.0300	0.0586	0.5673	2.01
11.0	0.0677	0.0059	0.0618	0.5749	2.00
14.0	0.0645	< LOD[a]	0.0645	0.5741	2.00
17.0	0.0616	< LOD	0.0616	0.5727	2.00
20.0	0.0609	< LOD	0.0609	0.5698	2.00
24.0	0.0624	< LOD	0.0624	0.5700	2.01
27.0	0.0638	< LOD	0.0638	0.5713	2.02

[a] LOD=Limit of detection of SIA.

Table A2.6 The data of kinetics sorption using EC for **0.6 mM Cr(VI)-0.2 mM** Cu(II) binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

time (h)	Cr total (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	p H
0.00	0.5690	0.5690	0.0000	0.1959	2.07
0.03	0.4741	0.4741	0.0000	0.1954	2.15
0.08	0.4541	0.4541	0.0000	0.1959	2.16
0.17	0.4634	0.4634	0.0000	0.1959	2.15
0.25	0.4619	0.4619	0.0000	0.1954	2.15
0.33	0.4320	0.4320	0.0000	0.1923	2.17
0.42	0.4511	0.4511	0.0000	0.1956	2.15
0.50	0.4222	0.4222	0.0000	0.1959	2.18
0.75	0.4178	0.4178	0.0000	0.1904	2.17
1.00	0.3988	0.3988	0.0000	0.1959	2.16
1.50	0.3748	0.3748	0.0000	0.1945	2.16
2.00	0.3387	0.3385	0.0003	0.1959	2.19
3.50	0.2927	0.2788	0.0138	0.1959	2.18
5.00	0.2504	0.2087	0.0418	0.1959	2.19
8.00	0.1916	0.1279	0.0637	0.1959	2.18
11.0	0.1516	0.0870	0.0646	0.1953	2.14
14.0	0.1206	0.0481	0.0725	0.1953	2.15
17.0	0.1022	0.0236	0.0786	0.1941	2.17
20.0	0.0926	0.0125	0.0801	0.1925	2.16
24.0	0.0832	< LOD[a]	0.0832	0.1909	2.22
27.0	0.0793	< LOD	0.0793	0.1940	2.15

[a] LOD=Limit of detection of SIA.

Table A2.7 The data of kinetics sorption using EC for **0.6 mM Cr(VI)-0.4 mM** Cu(II) binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

time (h)	Cr total (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	p H
0.00	0.5968	0.5968	0.0001	0.4149	2.01
0.03	0.5618	0.5611	0.0007	0.3949	2.05
0.08	0.5639	0.5424	0.0215	0.3963	2.09
0.17	0.5245	0.4965	0.0280	0.4150	2.13
0.25	0.5224	0.5022	0.0202	0.3918	2.17
0.33	0.5082	0.4878	0.0204	0.3940	2.15
0.42	0.4876	0.4640	0.0236	0.3920	2.10
0.50	0.4863	0.4296	0.0567	0.4017	2.11
0.75	0.4846	0.4549	0.0296	0.4149	2.10
1.00	0.4714	0.4423	0.0291	0.4149	2.12
1.50	0.4280	0.3886	0.0394	0.4098	2.10
2.00	0.3976	0.3608	0.0368	0.3988	2.13
3.00	0.3176	0.2537	0.0639	0.4012	2.17
5.00	0.2696	0.2041	0.0656	0.3936	2.17
8.00	0.2117	0.1407	0.0709	0.3803	2.17
11.0	0.1623	0.0845	0.0778	0.3821	2.19
14.0	0.1337	0.0551	0.0785	0.3898	2.10
17.0	0.1111	0.0312	0.0799	0.3884	2.08
20.0	0.0975	0.0154	0.0821	0.3880	2.10
24.0	0.0870	0.0059	0.0812	0.3821	2.10
27.0	0.0835	< LOD[a]	0.0835	0.3790	2.17

[a] LOD=Limit of detection of SIA.

Table A2.8 The data of kinetics sorption using EC for **2.0 mM Cr(VI)-4.0 mM Cu(II)** binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

time (h)	Cr total (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	p H
0.00	2.1839	2.1839	0.0000	3.7568	2.00
0.03	2.0220	2.0220	0.0000	--	2.00
0.08	1.9584	1.9584	0.0000	--	2.00
0.17	1.8786	1.8786	0.0000	3.6604	2.01
0.25	1.8114	1.8114	0.0000	3.6955	2.01
0.33	1.7749	1.7749	0.0000	--	2.01
0.42	1.8084	1.8084	0.0000	3.6556	2.01
0.50	1.7137	1.7137	0.0000	3.7268	2.02
0.75	1.5902	1.5902	0.0000	3.5887	2.02
1.00	1.5514	1.5514	0.0000	3.6844	2.02
1.50	1.3923	1.3923	0.0000	3.6774	2.03
2.00	1.2937	1.2937	0.0000	3.6503	2.03
3.50	1.0534	1.0534	0.0000	--	2.04
5.00	0.8644	0.8577	0.0067	3.6672	2.06
8.00	0.5977	0.4776	0.1200	--	2.08
11.0	0.4482	0.3380	0.1102	3.7193	2.10
14.0	0.3609	0.2543	0.1066	--	2.11
17.0	0.3065	0.1408	0.1656	3.7336	2.12
20.0	0.2743	0.1055	0.1687	--	2.14
24.0	0.2522	0.0665	0.1856	3.6725	2.15
27.0	0.2441	0.0644	0.1797	--	2.15
30.0	0.2515	0.0279	0.2236	3.6963	2.15
36.0	0.2478	0.0154	0.2324	--	2.15
42.0	0.2458	0.0121	0.2337	3.7188	2.15
48.0	0.2469	0.0028	0.2442	3.6813	2.15
54.0	0.2486	< LOD[a]	0.2486	--	2.15
60.0	0.2627	0.0001	0.2626	3.6687	2.13
66.0	0.2642	0.0004	0.2639	--	2.15
72.0	0.2646	< LOD	0.2646	3.7258	2.15
78.0	0.2673	0.0008	0.2665	3.7181	2.14

[a] LOD=Limit of detection of SIA, -- not determined.

Table A2.9 The data of kinetics sorption using EC for **2.0 mM Cr(VI)-6.0 mM Cu(II)** binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2^{o}C.

time (h)	Cr total (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	p H
0.00	2.3166	2.3166	0.0000	5.7578	2.00
0.03	2.1454	2.1454	0.0000	5.6668	2.00
0.08	2.1452	2.1452	0.0000	5.6855	2.00
0.17	2.1459	2.0688	0.0771	5.6395	2.00
0.25	2.1457	2.0929	0.0528	5.6941	2.00
0.33	2.0979	1.9712	0.1267	5.6332	2.00
0.42	2.0783	1.9654	0.1129	5.6227	2.00
0.50	2.0734	1.9390	0.1344	5.6855	2.00
0.75	1.9272	1.8166	0.1106	5.6906	2.01
1.00	1.9015	1.8195	0.0821	5.6887	2.01
1.50	1.8012	1.6613	0.1398	5.6580	2.01
2.00	1.7189	1.6065	0.1124	5.6623	2.02
3.50	1.4986	1.4068	0.0917	5.7254	2.03
5.00	1.2722	1.1948	0.0774	5.6426	2.05
8.00	0.9658	0.8785	0.0873	5.6996	2.07
11.0	0.7611	0.6782	0.0829	5.6746	2.09
14.0	0.6195	0.4988	0.1207	5.7578	2.11
17.0	0.5123	0.3780	0.1343	5.7512	2.11
24.0	0.4373	0.2133	0.2241	5.7117	2.13
27.0	0.3903	0.1594	0.2309	--	2.13
30.0	0.3586	0.1205	0.2381	5.7453	2.14
36.0	0.3214	0.0781	0.2433	5.7305	2.14
42.0	0.3044	0.0487	0.2557	5.7359	2.15
48.0	0.2799	0.0360	0.2439	5.7563	2.15
54.0	0.2765	0.0201	0.2564	5.7578	2.15
60.0	0.2742	0.0155	0.2587	5.7527	2.15
72.0	0.2759	0.0053	0.2705	5.7578	2.15
78.0	0.2800	0.0033	0.2766	5.7156	2.15

-- not determined.

Table A2.10 The data of kinetics sorption using EC for **4.0 mM Cr(VI)-2.0 mM Cu(II)** binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

time (h)	Cr total (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	p H
0.00	4.2721	4.2721	0.0000	1.9078	2.00
0.03	4.1121	4.0059	0.1062	1.8973	2.01
0.08	4.0073	3.8524	0.1549	1.9063	2.01
0.17	3.7635	3.7160	0.0475	1.8789	2.06
0.25	3.8158	3.7262	0.0895	1.8625	2.05
0.33	3.7883	3.6486	0.1397	1.8975	2.05
0.42	3.7267	3.5126	0.2141	1.8981	2.06
0.50	3.6527	3.6527	0.0000	1.8863	2.06
0.75	3.3998	3.3733	0.0265	1.8631	2.06
1.00	3.2550	3.2492	0.0058	1.8755	2.09
1.50	3.1287	3.1046	0.0240	1.8946	2.09
2.00	2.9221	2.9059	0.0162	1.8736	2.09
3.50	2.5304	2.5304	0.0000	1.9023	2.10
5.00	2.1638	2.1138	0.0500	1.8945	2.11
8.00	1.7046	1.5869	0.1177	--	2.13
11.0	1.4252	1.3556	0.0696	1.8841	2.17
14.0	1.2125	0.9999	0.2126	--	2.20
17.0	1.0410	0.8323	0.2087	--	2.23
20.0	0.9179	0.6628	0.2551	--	2.24
24.0	0.8023	0.4965	0.3058	1.8775	2.29
27.0	0.7381	0.4153	0.3227	--	2.29
300	0.6900	0.3738	0.3162	1.9063	2.29
36.0	0.6425	0.2248	0.4177	--	2.29
48.0	0.5467	0.1304	0.4163	1.8794	2.33
54.0	0.5319	0.1003	0.4316	1.8709	2.33
66.0	0.5296	0.0536	0.4760	1.9017	2.35
72.0	0.5298	0.0394	0.4904	1.9081	2.36
78.0	0.5325	0.0246	0.5079	--	2.37
84.0	0.5244	0.0219	0.5025	1.9078	2.37
89.0	0.5277	0.0199	0.5078	--	2.38
96.0	0.5269	0.0128	0.5142	1.9013	2.39
102	0.5248	0.0081	0.5167	--	2.40
108	0.5223	0.0067	0.5156	1.9069	2.38
114	0.5212	0.0083	0.5129	--	2.39
120	0.5213	0.0068	0.5145	1.9047	2.40
126	0.5267	0.0008	0.5260	--	2.41
132	0.5340	0.0021	0.5319	1.9053	2.40
138	0.5292	< LOD[a]	0.5292	--	2.41
144	0.5440	0.0036	0.5405	1.9025	2.43
150	0.5392	0.0003	0.5390	1.9072	2.41

[a] LOD=Limit of detection of SIA, -- not determined.

Table A2.11 The data of kinetics sorption using EC for **4.0 mM Cr(VI)-4.0 mM Cu(II)** binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

time (h)	Cr total (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	p H
0.00	3.9460	3.9460	0.0000	3.7866	2.01
0.03	3.8362	3.8362	0.0000	3.7774	2.01
0.08	3.7686	3.7686	0.0000	3.6796	2.01
0.17	3.7431	3.7431	0.0000	3.7015	2.02
0.25	3.7255	3.7255	0.0000	3.6984	2.02
0.33	3.7469	3.7469	0.0000	3.7352	2.01
0.42	3.6872	3.6872	0.0000	3.7356	2.02
0.50	3.6458	3.6458	0.0000	3.7509	2.02
0.75	3.6238	3.6238	0.0000	3.7039	2.03
1.00	3.5335	3.5335	0.0000	3.7247	2.05
1.50	3.4423	3.4423	0.0000	--	2.05
2.00	3.3868	3.3868	0.0000	3.7371	2.05
3.50	3.0912	3.0912	0.0000	--	2.06
5.00	2.8980	2.8163	0.0817	3.7137	2.06
8.00	2.5063	2.3566	0.1497	--	2.06
11.0	2.2060	2.0268	0.1792	3.7319	2.08
14.0	1.9662	1.8237	0.1425	--	2.10
17.0	1.7615	1.6308	0.1308	3.7546	2.13
20.0	1.5845	1.4415	0.1429	--	2.16
24.0	1.3686	1.1517	0.2169	3.7634	2.17
27.0	1.2586	1.0317	0.2269	--	2.18
30.0	1.1558	0.9360	0.2198	3.7601	2.18
36.0	1.0168	0.7431	0.2737	--	2.21
42.0	0.8555	0.6160	0.2395	--	2.23
48.0	0.7587	0.4349	0.3238	3.7708	2.25
54.0	0.6907	0.3502	0.3405	--	2.26
60.0	0.6439	0.2850	0.3589	3.7822	2.26
66.0	0.5933	0.2325	0.3608	--	2.28
72.0	0.5762	0.1855	0.3906	3.7844	2.28
78.0	0.5483	0.1566	0.3917	--	2.29
84.0	0.5285	0.1457	0.3828	3.7844	2.31
89.0	0.5196	0.1165	0.4032	--	2.31
96.0	0.5043	0.1100	0.3943	3.7844	2.32
102	0.5014	0.0711	0.4303	--	2.32
108	0.4908	0.0632	0.4276	3.7844	2.32
114	0.4875	0.0580	0.4295	--	2.33
120	0.4828	0.0466	0.4362	--	2.34
126	0.4819	0.0394	0.4425	3.7538	2.34

-- not determined.

Table A2.12 The data of kinetics sorption using EC for **4.0 mM Cr(VI)-6.0 mM Cu(II)** binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

time (h)	Cr total (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	p H
0.00	4.7901	4.7901	0.0000	5.8055	2.00
0.03	4.5032	4.5032	0.0000	5.7410	2.00
0.08	4.4224	4.4224	0.0000	5.7688	2.03
0.17	4.4829	4.4829	0.0000	5.7469	2.02
0.25	4.3934	4.3142	0.0792	5.7555	2.04
0.33	4.2339	4.2339	0.0000	5.7426	2.05
0.42	4.1077	4.1077	0.0000	5.6961	2.07
0.50	4.2058	4.2058	0.0000	5.7844	2.05
0.75	4.0440	4.0118	0.0322	--	2.07
1.00	3.9750	3.9750	0.0000	5.7953	2.06
1.50	3.8140	3.8140	0.0000	5.7090	2.06
2.00	3.5902	3.5902	0.0000	5.6617	2.08
3.50	3.2164	3.1823	0.0341	5.7223	2.06
5.00	2.9945	2.9018	0.0927	5.7809	2.09
8.00	2.4024	2.2753	0.1271	--	2.13
11.0	2.0477	1.8949	0.1528	5.7664	2.16
14.0	1.7456	1.4922	0.2535	--	2.18
17.0	1.5169	1.2284	0.2885	--	2.22
20.0	1.3733	1.0463	0.3270	5.7336	2.23
27.0	1.0918	0.6975	0.3942	--	2.27
30.0	1.0188	0.6053	0.4134	5.7961	2.29
42.0	0.8078	0.3166	0.4913	--	2.32
48.0	0.7454	0.2265	0.5189	5.7648	2.34
54.0	0.6998	0.1776	0.5223	--	2.35
60.0	0.6954	0.1336	0.5618	5.8043	2.35
66.0	0.6722	0.1042	0.5680	--	2.36
72.0	0.6449	0.0878	0.5571	5.8020	2.37
78.0	0.6389	0.0729	0.5660	--	2.38
84.0	0.6308	0.0684	0.5623	5.7711	2.38
89.0	0.6237	0.0505	0.5732	--	2.39
96.0	0.6294	0.0380	0.5914	5.7926	2.39
102	0.6314	0.0351	0.5962	--	2.41
108	0.6269	0.0330	0.5939	5.7762	2.43
114	0.6294	0.0217	0.6077	--	2.43
120	0.6295	0.0157	0.6139	5.7695	2.44
126	0.6225	0.0106	0.6119	--	2.44
132	0.6288	0.0103	0.6185	5.7789	2.44
138	0.6391	0.0175	0.6216	--	2.45
144	0.6332	0.0049	0.6283	5.7457	2.45
150	0.6446	0.0067	0.6379	5.7672	2.46

-- not determined.

Table A2.13 The data of kinetics sorption using EC for **6.0 mM Cr(VI)-2.0 mM Cu(II)** binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

time (h)	Cr total (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	p H
0.00	5.6680	5.6680	0.0000	1.8784	2.01
0.03	5.5745	5.5745	0.0000	1.8604	2.03
0.08	5.5643	5.5643	0.0000	1.8427	2.03
0.17	5.3947	5.3947	0.0000	1.8530	2.03
0.25	5.3938	5.3938	0.0000	1.8717	2.03
0.33	5.3853	5.3853	0.0000	1.8587	2.03
0.42	5.3031	5.3031	0.0000	1.8602	2.03
0.50	5.2432	5.2432	0.0000	1.8631	2.06
0.75	5.2070	4.9851	0.2219	1.8530	2.08
1.00	5.1410	4.8167	0.3243	1.8549	2.08
1.50	4.9077	4.6378	0.2699	--	2.10
2.00	4.8117	4.4956	0.3160	1.8636	2.12
3.50	4.3585	4.0869	0.2716	--	2.17
5.00	4.0556	3.7028	0.3528	1.8643	2.22
8.00	3.6268	3.2772	0.3497	--	2.23
11.0	3.3609	3.0174	0.3435	1.8762	2.23
14.0	3.0366	2.6235	0.4131	--	2.24
17.0	2.7896	2.3345	0.4550	1.8800	2.26
20.0	2.5611	2.1103	0.4508	--	2.28
24.0	2.3185	1.8488	0.4696	1.8715	2.31
27.0	2.1698	1.7249	0.4449	--	2.36
30.0	2.0678	1.6217	0.4461	1.8657	2.38
36.0	1.8772	1.3475	0.5297	--	2.38
42.0	1.6864	1.1419	0.5445	--	2.41
48.0	1.5360	0.9835	0.5525	1.8518	2.46
54.0	1.4026	0.8328	0.5699	--	2.50
60.0	1.3054	0.7656	0.5399	1.8844	2.51
66.0	1.2462	0.6864	0.5598	--	2.54
72.0	1.1771	0.5906	0.5865	1.8721	2.55
78.0	1.1335	0.5163	0.6172	--	2.57
84.0	1.1101	0.4878	0.6224	--	2.55
89.0	1.0747	0.4341	0.6405	--	2.59
96.0	1.0413	0.3848	0.6565	1.8793	2.59
102	1.0130	0.3463	0.6667	--	2.62
108	0.9873	0.3183	0.6689	--	2.63
114	0.9547	0.2749	0.6798	--	2.64
120	0.9555	0.2658	0.6896	1.8848	2.66
126	0.9343	0.2303	0.7039	--	2.67
132	0.9131	0.2073	0.7058	1.8820	2.68
138	0.8920	0.1871	0.7049	--	2.70
144	0.8689	0.1715	0.6974	1.8817	2.70
150	0.8872	0.1572	0.7300	--	2.70
156	0.8934	0.1510	0.7424	--	2.70
162	0.8714	0.1373	0.7341	--	2.70
168	0.8479	0.1217	0.7262	1.8549	2.71
174	0.8547	0.1178	0.7369	1.8762	2.72

-- not determined.

Table A2.14 The data of kinetics sorption using EC for **6.0 mM Cr(VI)-4.0 mM Cu(II)** binary mixture. Initial pH 2.0, sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, temperature: 20±2°C.

time (h)	Cr total (mM)	Cr(VI) (mM)	Cr(III) (mM)	Cu(II) (mM)	p H
0.00	6.9190	6.9190	0.0000	3.7987	2.00
0.03	6.5169	6.5169	0.0000	3.7831	2.04
0.08	6.6052	6.6052	0.0000	3.7866	2.02
0.17	6.4310	6.4310	0.0000	3.7955	2.01
0.25	6.0819	6.0819	0.0000	3.7627	2.06
0.33	5.9905	5.9905	0.0000	3.7523	2.02
0.42	5.9925	5.9925	0.0000	3.7781	2.03
0.50	5.9394	5.9394	0.0000	3.6328	2.07
0.75	6.0580	6.0580	0.0000	3.7568	2.05
1.00	5.4245	5.4245	0.0000	3.7444	2.06
1.50	5.3937	5.3937	0.0000	--	2.05
2.00	5.2604	5.2604	0.0000	3.7548	2.08
3.50	4.8084	4.8084	0.0000	--	2.07
5.00	4.3258	4.3258	0.0000	3.7774	2.12
8.00	3.7760	3.7760	0.0000	--	2.15
11.0	3.4108	3.4108	0.0000	3.7937	2.19
14.0	2.8973	2.8973	0.0000	--	2.24
17.0	2.7577	2.5752	0.1825	3.7294	2.25
20.0	2.5341	2.3671	0.1670	--	2.27
24.0	2.3267	2.0830	0.2438	3.7399	2.31
27.0	2.2269	1.9279	0.2990	--	2.31
30.0	2.0342	1.7457	0.2885	3.8147	2.34
36.0	1.8329	1.4830	0.3499	--	2.38
42.0	1.6999	1.1569	0.5430	--	2.41
54.0	1.4143	0.9461	0.4682	--	2.46
60.0	1.3936	0.8810	0.5125	3.7927	2.50
66.0	1.3082	0.8083	0.4999	--	2.53
72.0	1.2499	0.6222	0.6277	3.7430	2.54
78.0	1.2211	0.6437	0.5774	--	2.57
84.0	1.1934	0.4919	0.7014	3.7453	2.58
89.0	1.1671	0.4424	0.7247	--	2.58
96.0	1.1513	0.3687	0.7825	3.7432	2.60
102	1.0731	0.3111	0.7619	--	2.62
108	1.0448	0.3009	0.7439	3.7888	2.62
114	0.9961	0.2604	0.7357	--	2.64
120	0.9713	0.2305	0.7407	3.7793	2.63
126	0.9320	0.2211	0.7109	--	2.66
132	0.9433	0.1880	0.7553	3.7559	2.67
138	0.9190	0.1690	0.7500	--	2.67
144	0.9040	0.1662	0.7378	3.7716	2.68
150	0.9049	0.1142	0.7907	--	2.70
174	0.8752	0.0735	0.8017	--	2.72
186	0.8651	0.0683	0.7968	3.7317	2.74
192	0.8654	0.0564	0.8090	3.7814	2.74
198	0.8440	0.0434	0.8006	3.7235	2.74

-- not determined.

ANNEX III--The experimental sorption data of Chapter VI

Table A3.1 The data of kinetics sorption using EC for synthetic Cr(VI) solution (S1). Sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, pH 2.0, temperature: 20±2°C.

time (h)	Cr total (mg/L)	Cr(VI) (mg/L)	Cr(III) (mg/L)	pH	Conductivity (mS/cm)
0.00	108.15	108.15	0.00	2.00	3.335
0.08	103.12	103.12	0.00	2.00	3.282
0.17	100.46	100.46	0.00	2.00	3.263
0.25	100.44	100.44	0.00	2.00	3.245
0.33	97.85	97.85	0.00	2.00	3.229
0.42	95.48	95.48	0.00	2.00	3.212
0.50	91.78	91.78	0.00	2.01	3.199
0.75	87.31	87.31	0.00	2.00	3.163
1.00	86.39	86.39	0.00	2.02	3.133
1.50	82.54	82.54	0.00	2.03	3.079
2.00	74.87	74.87	0.00	2.03	3.031
2.50	70.15	70.15	0.00	2.04	2.989
3.00	64.53	64.53	0.00	2.05	2.947
3.50	61.34	61.34	0.00	2.06	2.913
4.00	54.04	54.04	0.00	2.07	2.877
4.50	50.71	50.71	0.00	2.07	2.846
5.00	51.95	51.95	0.00	2.08	2.816
5.50	47.21	47.21	0.00	2.08	2.792
6.00	45.73	45.73	0.00	2.08	2.767
9.00	34.03	31.35	2.68	2.11	2.638
12.0	24.50	22.81	1.69	2.13	2.532
15.0	20.27	14.69	5.58	2.14	2.482
18.0	18.18	9.90	8.28	2.15	2.461
21.0	16.16	7.95	8.22	2.16	2.440
24.0	15.55	5.62	9.94	2.17	2.419
27.0	14.63	4.23	10.40	2.17	2.391
30.0	13.37	3.00	10.37	2.18	2.376
33.0	13.31	1.93	11.37	2.18	2.359
36.0	13.91	2.59	11.32	2.19	2.354
39.0	12.98	1.88	11.11	2.19	2.348
42.0	13.64	0.86	12.78	2.19	2.342
45.0	13.50	0.58	12.92	2.19	2.333
48.0	13.62	0.62	13.00	2.20	2.322
51.0	13.76	0.54	13.22	2.20	2.318
54.0	13.16	0.37	12.80	2.20	2.311
57.0	13.70	0.23	13.47	2.20	2.311
60.0	13.28	0.19	13.10	2.20	2.310
63.0	13.96	0.21	13.74	2.20	2.310
66.0	13.19	0.17	13.01	2.20	2.310
69.0	13.76	0.07	13.68	2.20	2.309
72.0	13.56	0.11	13.45	2.20	2.309

Table A3.2 The data of kinetics sorption using EC for synthetic Cr(VI)-Cu(II) binary mixtures (S2). Sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, pH 2.0, temperature: 20±2°C.

time (h)	Cr total (mg/L)	Cr(VI) (mg/L)	Cr(III) (mg/L)	Cu(II) (mg/L)	pH	Conductivity (mS/cm)
0.00	103.04	103.04	0.00	12.96	1.96	3.452
0.08	100.06	100.06	0.00	13.39	1.96	3.419
0.17	100.66	100.66	0.00	13.02	1.96	3.399
0.25	98.91	98.91	0.00	12.88	1.96	3.381
0.33	98.26	98.26	0.00	13.05	1.96	3.365
0.42	96.05	96.05	0.00	13.63	1.96	3.350
0.50	97.61	97.61	0.00	13.88	1.96	3.337
0.75	93.98	93.98	0.00	12.77	1.96	3.308
1.00	91.39	91.39	0.00	12.72	1.96	3.275
1.50	83.89	83.89	0.00	13.15	1.97	3.224
2.00	77.34	77.34	0.00	13.67	1.97	3.178
2.50	75.73	75.73	0.00	--	1.98	3.137
3.00	70.76	66.85	3.91	--	1.98	3.097
3.50	67.85	62.89	4.95	13.03	1.99	3.061
4.00	64.40	62.47	1.94	--	1.99	3.031
4.50	58.98	56.25	2.73	--	2.00	3.008
5.00	56.30	54.48	1.83	12.62	2.00	2.978
5.50	53.70	51.24	2.46	--	2.01	2.950
6.00	50.24	48.30	1.94	--	2.01	2.920
9.00	37.28	33.12	4.17	12.74	2.04	2.787
12.0	28.97	23.74	5.23	12.19	2.05	2.710
15.0	24.25	15.43	8.83	--	2.06	2.657
18.0	20.60	12.69	7.91	13.89	2.07	2.620
21.0	17.28	9.05	8.23	--	2.08	2.594
24.0	16.67	7.60	9.07	12.85	2.08	2.572
27.0	14.50	5.29	9.21	--	2.09	2.547
30.0	15.05	4.06	10.99	12.81	2.10	2.526
33.0	13.69	3.14	10.56	--	2.10	2.507
36.0	13.28	2.13	11.16	12.74	2.10	2.494
39.0	13.14	2.03	11.11	--	2.10	2.486
42.0	13.32	1.26	12.06	--	2.11	2.480
45.0	12.06	0.92	11.14	--	2.11	2.473
48.0	12.94	0.86	12.08	13.25	2.11	2.461
51.0	12.80	1.19	11.62	--	2.11	2.455
54.0	13.25	0.96	12.29	--	2.11	2.452
57.0	13.10	0.54	12.57	--	2.11	2.449
60.0	12.80	0.45	12.35	13.38	2.11	2.444
63.0	13.02	0.62	12.40	--	2.11	2.443
66.0	13.06	0.26	12.79	--	2.11	2.440
69.0	13.19	0.20	12.99	--	2.11	2.439
72.0	13.16	0.18	12.99	12.98	2.12	2.437

-- not detected.

Table A3.3 The data of kinetics sorption using EC for metal finishing effluent (E1). Sorbent dose: 6.67 g L^{-1}, particle size: 0.5-1.0 mm, pH 2.0, temperature: 20±2°C.

time (h)	Cr total (mg/L)	Cr(VI) (mg/L)	Cr(III) (mg/L)	Cu(II) (mg/L)	Fe(III) (mg/L)	Al(III) (mg/L)	Ni(II) (mg/L)	pH	Conductivity (mS/cm)
0.00	112.49	112.49	0.00	5.04	4.24	0.90	1.04	1.99	3.459
0.08	109.22	109.22	0.00	4.92	4.21	0.93	1.01	1.99	3.410
0.17	107.58	107.58	0.00	5.03	4.19	0.87	1.04	1.99	3.393
0.25	106.68	106.68	0.00	4.75	4.30	0.84	1.02	2.00	3.373
0.33	105.12	105.12	0.00	4.94	4.26	0.87	1.01	2.00	3.360
0.42	104.54	104.54	0.00	5.02	4.21	0.93	1.00	2.00	3.348
0.50	104.46	104.46	0.00	5.03	4.27	0.81	1.04	2.01	3.334
0.75	99.66	99.66	0.00	5.03	4.27	0.93	1.01	2.01	3.302
1.00	96.47	96.47	0.00	5.10	4.34	0.89	1.02	2.01	3.273
1.50	93.88	90.85	3.02	--	--	--	--	2.03	3.224
2.00	90.98	85.72	5.27	5.01	4.36	0.89	1.01	2.03	3.181
2.50	86.51	80.21	6.29	--	--	--	--	2.04	3.145
3.00	83.41	75.21	8.20	4.91	4.34	0.91	1.00	2.05	3.111
3.50	81.52	72.82	8.70	--	--	--	--	2.07	3.076
4.00	79.33	70.55	8.78	5.19	4.34	0.96	1.01	2.06	3.046
4.50	75.29	66.08	9.21	--	--	--	--	2.07	3.015
5.00	73.06	62.95	10.11	4.99	4.23	0.94	1.03	2.07	2.987
5.50	70.38	60.25	10.13	--	--	--	--	2.08	2.963
6.00	68.26	57.25	11.00	4.97	4.27	0.97	1.00	2.09	2.943
9.00	62.32	47.26	15.05	--	---	--	--	2.12	2.813
12.0	54.20	37.41	16.79	5.09	4.17	0.95	1.04	2.14	2.723
15.0	48.96	30.53	18.43	--	--	--	--	2.16	2.650
18.0	45.89	23.26	22.63	--	--	--	--	2.18	2.594
21.0	42.56	18.74	23.82	--	--	--	--	2.19	2.544
24.0	40.78	14.70	26.08	4.90	3.81	0.93	1.02	2.20	2.510
27.0	39.70	12.38	27.32	--	--	--	--	2.21	2.475
30.0	37.79	10.19	27.60	--	--	--	--	2.22	2.445
33.0	38.33	9.31	29.02	--	--	--	--	2.23	2.419
36.0	37.25	9.33	27.91	5.11	3.69	0.85	1.05	2.24	2.398
39.0	36.32	7.39	28.93	--	--	--	--	2.24	2.383
42.0	36.07	6.40	29.67	5.03	3.66	0.84	1.07	2.25	2.376
45.0	35.65	4.58	31.08	--	--	--	--	2.25	2.360
48.0	34.69	3.78	30.91	5.17	3.61	0.85	1.04	2.26	2.347
51.0	34.10	3.12	30.98	--	--	--	--	2.26	2.336
54.0	33.82	2.40	31.42	4.95	3.68	0.89	1.07	2.26	2.327
57.0	34.58	2.36	32.22	--	--	--	--	2.27	2.319
60.0	34.15	1.91	32.24	5.18	3.67	0.93	1.07	2.27	2.316
63.0	34.19	1.43	32.76	--	--	--	--	2.27	2.310
66.0	34.25	1.32	32.93	5.36	3.70	0.90	1.08	2.28	2.306
69.0	33.66	1.21	32.45	--	--	--	--	2.28	2.305
72.0	33.34	0.50	32.84	5.38	3.64	0.90	1.07	2.28	2.298

-- not detected.

Table A3.4 The data of kinetics sorption using EC for metal finishing effluent (E2). Sorbent dose: 6.67 $g \cdot L^{-1}$, particle size: 0.5-1.0 mm, pH 2.0, temperature: 20±2°C.

time (h)	Cr total (mg/L)	Cr(VI) (mg/L)	Cr(III) (mg/L)	Cu(II) (mg/L)	Fe(III) (mg/L)	Al(III) (mg/L)	Ni(II) (mg/L)	pH	Conductivity (mS/cm)
0.00	108.50	108.50	0.00	8.20	8.54	0.66	0.93	1.95	3.376
0.08	108.35	108.35	0.00	--	8.54	--	--	1.96	3.340
0.17	107.90	107.90	0.00	8.20	8.52	0.659	0.93	1.96	3.322
0.25	107.76	107.76	0.00	--	8.54	--	--	1.97	3.304
0.33	107.27	107.27	0.00	8.20	8.38	0.656	0.93	1.97	3.290
0.42	107.41	107.41	0.00	--	8.54	--	--	1.97	3.277
0.50	102.89	102.89	0.00	8.19	8.52	0.66	0.93	1.98	3.264
0.75	101.56	101.56	0.00	--	8.47	--	--	1.99	3.233
1.00	97.95	97.95	0.00	8.20	8.46	0.655	0.93	1.99	3.205
2.00	91.91	91.91	0.00	8.19	8.38	0.66	0.93	2.01	3.119
3.12	87.67	87.61	0.06	8.20	8.51	0.655	0.93	2.03	3.045
4.12	84.18	82.64	1.54	8.20	8.22	0.655	0.93	2.05	2.985
5.12	76.19	73.74	2.45	8.19	8.26	0.65	0.93	2.06	2.930
6.12	72.37	68.58	3.79	8.20	8.25	0.66	0.93	2.08	2.883
9.12	67.80	56.22	11.58	8.19	8.23	0.656	0.93	2.11	2.768
12.12	56.34	45.46	14.12	8.19	8.04	0.66	0.93	2.14	2.674
24.12	44.41	21.52	22.89	8.20	7.61	0.655	0.93	2.21	2.470
36.12	41.50	9.21	32.28	8.20	7.46	0.66	0.93	2.26	2.359
48.12	36.90	4.90	32.00	8.19	7.31	0.66	0.93	2.30	2.297
59.62	36.74	1.83	34.91	8.19	7.01	0.65	0.93	2.32	2.265
71.62	35.06	0.70	34.36	8.20	6.80	0.66	0.93	2.33	2.237
83.62	35.35	0.16	35.19	8.20	6.80	0.65	0.93	2.34	2.232
95.62	35.33	0.03	35.30	8.20	6.78	0.66	0.93	2.34	2.263

-- not detected.

Table A3.5 The data of kinetics sorption using EC for metal finishing effluent (E3). Sorbent dose: 6.67 $g \cdot L^{-1}$, particle size: 0.5-1.0 mm, pH 2.0, temperature: 20±2°C.

time (h)	Cr total (mg/L)	Cr(VI) (mg/L)	Cr(III) (mg/L)	Cu(II) (mg/L)	Fe(III) (mg/L)	Al(III) (mg/L)	Ni(II) (mg/L)	pH	Conductivity (mS/cm)
0.00	147.18	147.18	0.00	8.01	5.51	0.99	1.23	1.96	3.290
0.08	139.74	139.74	0.00	8.01	5.50	--	1.22	1.97	3.255
0.17	139.62	139.62	0.00	8.01	5.49	--	1.22	1.97	3.238
0.25	139.95	139.95	0.00	--	5.48	--	--	1.98	3.221
0.33	138.32	138.32	0.00	--	5.46	--	--	1.98	3.206
0.42	134.57	134.57	0.00	--	5.42	--	--	1.98	3.190
0.50	136.95	136.95	0.00	7.98	5.41	0.99	1.22	1.99	3.177
0.75	133.37	133.37	0.00	--	5.40	--	--	2.00	3.151
1.00	130.62	130.62	0.00	7.97	5.37	--	--	2.01	3.119
2.00	122.71	122.71	0.00	--	5.31	--	--	2.03	3.029
4.00	108.49	103.68	4.81	--	5.17	--	--	2.07	2.885
6.00	98.22	88.07	10.15	7.94	5.15	--	1.22	2.11	2.772
12.00	77.21	61.26	15.95	--	4.95	0.99	--	2.20	2.597
18.00	68.04	44.31	23.73	--	--	--	--	2.26	2.453
54.10	47.16	11.34	35.82	--	--	--	--	2.47	2.142
60.10	46.37	8.33	38.03	--	3.85	--	--	2.49	2.114
66.10	46.44	8.17	38.27	--	--	--	--	2.51	2.084
72.10	45.75	7.27	38.48	7.98	3.71	0.99	--	2.53	2.069
78.10	45.18	5.93	39.25	--	--	--	--	2.54	2.059
84.10	45.42	4.86	40.56	--	3.57	--	--	2.55	2.041
90.10	45.09	4.51	40.58	--	--	--	--	2.57	2.020
96.10	44.39	3.58	40.80	7.99	3.50	--	1.23	2.58	2.018
99.10	45.14	3.20	41.94	--	--	--	--	2.58	2.023
102.1	44.49	2.75	41.74	--	--	--	--	2.59	2.022
105.1	44.49	2.20	42.29	--	--	--	--	2.59	2.023
108.1	45.27	2.01	43.26	--	3.48	--	--	2.60	2.013
111.1	44.94	1.70	43.24	--	--	--	--	2.60	2.005
114.1	45.02	1.60	43.41	--	--	0.99	--	2.60	1.994
117.1	45.11	1.35	43.76	--	--	--	--	2.61	1.990
119.1	44.97	1.14	43.83	--	3.44	--	--	2.61	1.984
125.1	45.57	0.99	44.58	--	--	--	--	2.61	1.979
131.1	45.38	0.84	44.53	--	--	--	--	2.62	1.975
137.1	45.28	0.67	44.61	--	--	--	--	2.62	1.970
143.1	45.23	0.59	44.63	--	3.42	--	--	2.62	1.967
149.1	45.85	0.43	45.42	--	--	--	--	2.63	1.967
155.1	45.56	0.35	45.20	--	--	--	--	2.63	1.964
161.1	45.59	0.29	45.30	--	--	--	--	2.63	1.968
165.1	46.01	0.22	45.78	8.01	3.41	0.99	1.23	2.64	1.978
170.1	45.77	0.24	45.53	8.01	3.39	0.99	1.23	2.64	1.988

-- not detected.

ANNEX IV--Publications

LIST OF PUBLICATIONS

Pujol D., **Liu C.**, Gominho J., Olivella M.À., Fiol N., Villaescusa I., Pereira H., 2013. The chemical composition of exhausted coffee waste. Ind. Crop Prod., 50: 423-429.

Pujol D., **Liu C.**, Fiol N., Olivella M.À., Gominho J., Villaescusa I., Pereira H., 2013. Chemical characterization of different granulometric fractions of grape stalks waste. Ind. Crop Prod., 50: 494-500.

Liu C., Pujol D., Fiol N., Olivella M.À., de la Torre F., Poch J., Villaescusa I., 2014. New insights into the role of chemical components on metal ions sorption by grape stalks waste. Water Air Soil Pollut., in press.

Liu C., Pujol D., Olivella M.À., de la Torre F., Fiol N., Poch J., Villaescusa I., 2014. Metal ions sorption on sequential extracted exhausted coffee. Submitted to Int. J. Environ. Sci. Technol.

Pujol D., Liu C., Gominho J., Olivella M.À., Fiol N., Villaescusa I., Pereira H. “The chemical composition of exhausted coffee waste”. *Industrial Crops and Products*. Vol. 50 (october 2013) : 423-429

http://dx.doi.org/10.1016/j.indcrop.2013.07.056

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Abstract

The chemical composition of exhausted coffee waste generated in a soluble coffee industry was investigated. The chemical characterization included elemental analysis, mineral composition and ash content, summative composition; acidic functional groups, lipophilic extractives, total polyphenols, condensed tannins determination and FTIR analysis. The spent coffee samples showed high carbon (>58%), low nitrogen (<2%), and low ash (<1%) contents and low polarity coefficient (O + N)/C (<0.5). The summative composition reveals that extractives are the main components of exhausted coffee wastes (54%). This percentage includes lipophilic fractions (24%), ethanol and water soluble compounds (5%), and compounds solubilized in 1% NaOH (26%). Lignin and polysaccharides were found in a similar proportion between 20 and 26%. The GC analysis of monosaccharide showed about 60% glucose and 40% mannose. The main components in the lipophilic extractives are free fatty acids (>60%) of which more than 30% was identified to be n-hexadecanoic acid. Total polyphenols and tannins represent <6% and <4% of the exhausted coffee wastes, respectively. Assignments of the bands of the obtained FTIR spectra confirm the presence of lipids, polysaccharides and chlorogenic acid. Exhausted coffee wastes showed characteristics for various potential applications such as biodiesel production, as a source of antioxidants and as a biosorbent of hydrophobic pollutants.

Keywords

Exhausted coffee; Chemical composition; Extractives; Polyphenols; Tannins; FTIR

Pujol D., Liu C., Fiol N., Olivella M.À., Gominho J., Villaescusa I., Pereira H. “Chemical characterization of different granulometric fractions of grape stalks waste” . *Industrial Crops and Products* . Vol. 50 (october 2013) : 494-500

http://dx.doi.org/10.1016/j.indcrop.2013.07.051

http://www.sciencedirect.com/science/article/pii/S0926669013003889

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Abstract

The chemical composition of exhausted coffee waste generated in a soluble coffee industry was investigated. The chemical characterization included elemental analysis, mineral composition and ash content, summative composition; acidic functional groups, lipophilic extractives, total polyphenols, condensed tannins determination and FTIR analysis. The spent coffee samples showed high carbon (>58%), low nitrogen (<2%), and low ash (<1%) contents and low polarity coefficient (O + N)/C (<0.5). The summative composition reveals that extractives are the main components of exhausted coffee wastes (54%). This percentage includes lipophilic fractions (24%), ethanol and water soluble compounds (5%), and compounds solubilized in 1% NaOH (26%). Lignin and polysaccharides were found in a similar proportion between 20 and 26%. The GC analysis of monosaccharide showed about 60% glucose and 40% mannose. The main components in the lipophilic extractives are free fatty acids (>60%) of which more than 30% was identified to be n-hexadecanoic acid. Total polyphenols and tannins represent <6% and <4% of the exhausted coffee wastes, respectively. Assignments of the bands of the obtained FTIR spectra confirm the presence of lipids, polysaccharides and chlorogenic acid. Exhausted coffee wastes showed characteristics for various potential applications such as biodiesel production, as a source of antioxidants and as a biosorbent of hydrophobic pollutants.

Keywords

Exhausted coffee; Chemical composition; Extractives; Polyphenols; Tannins; FTIR

Liu C., Pujol D., Fiol N., Olivella M.À., de la Torre F., Poch J., Villaescusa I. “New insights into the role of chemical components on metal ions sorption by grape stalks waste”. *Water, Air, & Soil Pollution*. In press (2014)

http://link.springer.com/journal/11270

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Abstract

In this work, metal sorption onto grape stalks waste structural compounds and extractives has been studied for determining their role in Cr(VI), Cu(II) and Ni(II) metal sorption. For this purpose, a sequential extraction of extractives and other compounds from the lignocellulosic material has been carried out. The resulting solid samples obtained in the different extraction processes were used as sorbents of Cr(VI), Cu(II) and Ni(II). Sorption results were discussed taking into account the elemental composition and polarity of the solid extracts. Results indicated that tannins and polyphenols are involved in chromium reduction and sorption. Lignin and celluloses are involved in chromium, Cu(II) and Ni(II) sorption. FTIR analysis confirmed the involvement of lignin moieties in the studied metal ions sorption by grape stalks waste. This study presents a new approach on metal sorption field as the knowledge of the role of the sorbent chemical compounds is essential to determine the key sorbent compounds in the sorption process.

Keywords

Grape stalks waste; Polarity; Chromium; Divalent metals

Liu C., Pujol D., Olivella M.À., de la Torre F., Fiol N., Poch J., Villaescusa I. “Metal ions sorption on sequential extracted exhausted coffee”. *International Journal of Environmental Science and Technology*. Submitted (2014)

http://www.springer.com/environment/journal/13762

Abstract

In the present work, the role of chemical compounds of one abundant vegetable waste, exhausted coffee, on Cr(VI), Cu(II) and Ni(II) sorption has been investigated. For this purpose, exhausted coffee was subjected to sequential extractions by using dichloromethane (DCM), ethanol (EtOH), water and NaOH 1%. The raw and treated biomass resulting from the extractions were used for metal ions sorption. Sorption results were discussed taking into consideration polarity and functional groups of raw and treated biomass. In general, the successive removal of extractives led to a slight increase in the studied metal ions sorption after DCM, EtOH and water. A different trend was observed after alkaline hydrolysis, chromium removal slightly decreased while a significant increase of copper and nickel sorption was observed. The determination of elemental ratios of exhausted coffee and all treated biomass evidenced the involvement of oxygen functional groups in copper and nickel sorption. FTIR analysis confirmed the involvement of lignin moieties in the chromium sorption by exhausted coffee. As a final remark, this study shows that the extraction of extractives does not cause any significant loss of exhausted coffee sorption capacities and opens new expectations for the valorisation of lignocellulosic-based waste materials used as bioresource of valuable compounds.

Keywords

exhausted coffee; polarity; chromium; divalent metals