CONVERSION OF SLUDGE BIOMASS INTO CATALYSTS: ENVIRONMENTAL TREATMENT APPLICATIONS.

Sunil Athalathil Ramankutty

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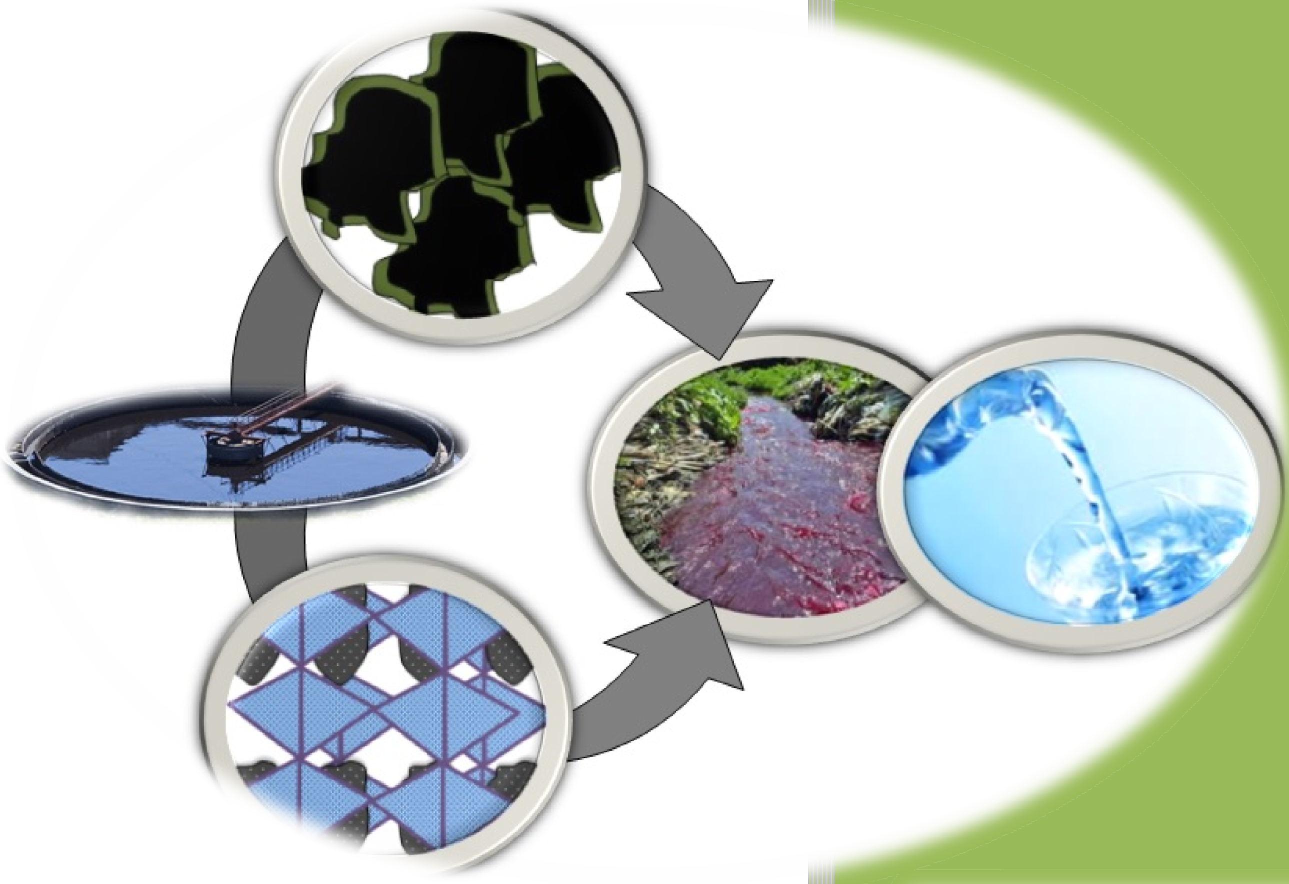
DOCTORAL THESIS

Sunil Athalathil Ramankutty

2014

Conversion of sludge biomass into catalysts: Environmental treatment applications



UNIVERSITAT
ROVIRA I VIRGILI

SUNIL ATHALATHIL RAMANKUTTY

CONVERSION OF SLUDGE BIOMASS INTO CATALYSTS: ENVIRONMENTAL TREATMENT APPLICATIONS

DOCTORAL THESIS

supervised by Dr. **Azael Fabregat Llangostera** and Dr. **Agustí Fortuny Sanromà**

Department of Chemical Engineering

UNIVERSITAT
ROVIRA I VIRGILI

Tarragona

2014

Escola Técnica Superior d'Enginyeria Química

Departament d'Enginyeria Química

Avinguda dels Països Catalans, 26

43007 Tarragona (Spain)

Tel.: 977 559700

I, Dr. **Azael Fabregat Llangostera**, professor in the Department of Chemical Engineering of the Universitat Rovira i Virgili,

Certify:

that the present study, entitled "**Conversion of sludge biomass into catalysts: Environmental treatment applications**", presented by **Sunil Athalathil** for the award of the degree of Doctor, has been carried out under my supervision at the department of chemical engineering of this university, and that it fulfills all the requirements to be eligible for the European Doctorate Award.

Tarragona, October 2014

Prof. Dr. Azael Fabregat Llangostera

Escola Técnica Superior d'Enginyeria Química

Departament d'Enginyeria Química

Avinguda dels Països Catalans, 26

43007 Tarragona (Spain)

Tel.: 977 559700

I, Dr. **Agusti Fortuny Sanromà**, Professor in the Department of Chemical Engineering of the Universitat Politècnica de Catalunya

Certify:

that the present study, entitled **"Conversion of sludge biomass into catalysts: Environmental treatment applications**", presented by **Sunil Athalathil** for the award of the degree of Doctor, has been carried out under my supervision at the department of chemical engineering of this university, and that it fulfills all the requirements to be eligible for the European Doctorate Award.

Tarragona, October 2014

Prof. Dr. Agusti Fortuny Sanromà,

EXAMINATION BOARD MEMBERS

1. Dr. Fidel Cunill García
   Professor

   Dept. de Ingineria Química
   Universidad de Barcelona
   Marti y Franques, 1
   Barcelona, SPAIN

2. Dr. Carine Julcour-Lebigue
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   Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques
   INP-ENSIACET
   France

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   Universitat Rovira i Virgili, Av. Paisos Catalans-26
   Tarragona, Spain

4. Dr. Javier Tejero Salvador

   Professor

   Dept. de Ingineria Química
   Universidad de Barcelona
   Marti y Franques, 1
   Barcelona, SPAIN

5. Dr. Henry Delmas

   Professor

Institut National Polytechnique de Toulouse
Laboratory of Chemical Engineering - LGC
France

6. Dr. Frank Stuber

Professor

Departament d'Enginyeria Quimica, ETSEQ,
Universitat Rovira i Virgili, Av. Paisos Catalans-26
Tarragona, Spain

External evaluators:

1. Dr. Albin Pintar

Head
Laboratory for Environmental Sciences and Engineering,
National Institute of Chemistry,
Hajdrihova 19, SI-1001
Ljubljana, Slovenia

2. Dr. Henry Delmas

Professor
Institut National Polytechnique de Toulouse
Laboratory of Chemical Engineering - LGC
France

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¨ We shall require a substantially new manner of thinking if mankind is to survive ¨

Albert Einstein

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With sincerely,

SUNIL ATHALATHIL RAMANKUTTY

TARRAGONA

…to my beloved parent

Contents

Nomenclature

ace	acetic acid
ASTM	american standard testing methods
AOPs	Advanced oxidation process
ACs	activated carbons
AOII	acid orange II
A_t	external area (m^2/g)
BPA	bisphenol -A
BAC	biological activated carbon
C	concentration in the effluent (mg of compound/L)
CMs	carbonaceous materials
CT	chemical treatment
CWAO	catalytic wet air oxidation process
d_{p}	diameter size (mm)
DS	dried sludge
FTIR	Fourier transforms infra-red
GAC	granular activated carbon
HD	hydrothermal deposition
HPLC	high pressure liquid chromatography
K	Langmuir constants
M	molar
N	normality
n	Freundlich constants

P	pressure (atm)
Q	flow rate (mL/min)
Qm	adsorption capacity
rpm	rotation per minutes
SEM	scanning electron microscopy
S_{BET}	specific surface area (m^2/g)
SBCs	sludge based carbons
SGS	sol gel solution
STP	standard temperature and pressure (273 K and 1 atm)
ST	system type
T	temperature (°C)
TEM	transmission electron microscopy
TOC	total organic carbon
TGA	thermal gravimetric analysis
UPBR	up flow packed bed reactor
V_R	reactor volume (cm^3)
W	catalyst weight (g)
WWTPs	wastewater treatment plants
X	conversion
XRD	x- ray diffraction

Greek Letters

P	density (g/m)
τ	space time (min)

Subscripts

C	relative to carbon
i	relative to a compound
F	relative to adsorption
L	relative to liquid stream
0	relative to initial conditions
N_2	nitrogen
O_2	oxygen
He	helium

SUMMARY OF THE THESIS

The availability of fresh water is essential for development, disease free and quality of life but because to the human activity, population growth and industrialization, environment becomes highly threatened.

At the present situation, environment suffers mainly two kinds of problems, which are related to harmful waste materials and wastewaters; those are harmful to environment also disturbing our socio-economical life.

Firstly, textiles, pharmaceuticals, radioactive and chemical wastes are part of wastewaters. In developing countries, textile industries are one of the best economic growth engines, but now they present a global pollution problem. It is well known, wastewater pollution is a major environmental problem, but still controlling tasks are difficult for several countries. Until now, there is no proper treatment available for the complete removal of wastewaters, especially from textile industries.

Secondly, sewage sludge biomass is one of the biggest contributors of waste materials. It is abundantly available in domestic and municipal wastewater treatment plants all around the world. The amount of harmful sewage sludge rapidly increases day by day in the wastewater treatment plants (WWTPs), and huge amounts of these materials will rise unexpectedly on coming years.

Handling of waste materials and wastewaters is a difficult task for many wastewater treatment plants. Nowadays, traditional sludge disposal and wastewater treatment practices are under stress, and challengeable, become more difficult to treating them in a smooth and cost-effective way. Using this treatment practices is high expensive and also facing many environmental consequences. In this concern, plenty of research group are working for cost-effective and innovative techniques for that. As it is mentioned above, the problems now need a better and fruitful solution.

For a better treatment of these problems there are several laws and regulations implemented by the European Union but, unfortunately, most of them such as sea dumping, incineration and agricultural uses are under crisis.

If the solid wastes are converted and used as low cost adsorbents (LCAs), they will provide a twofold advantage in reducing the environmental pollution. Firstly, the amount of harmful sewage biomass gets partly reduced and secondly the low-cost adsorbent, if developed, can remove the contaminants from wastewaters at a reasonable cost.

In this circumstance, this research can help the scientific community using sludge-derived materials or catalysts for environmental treatment practices in order to safely clean the environment. This research work aims to solve the problem related to waste materials and wastewaters.

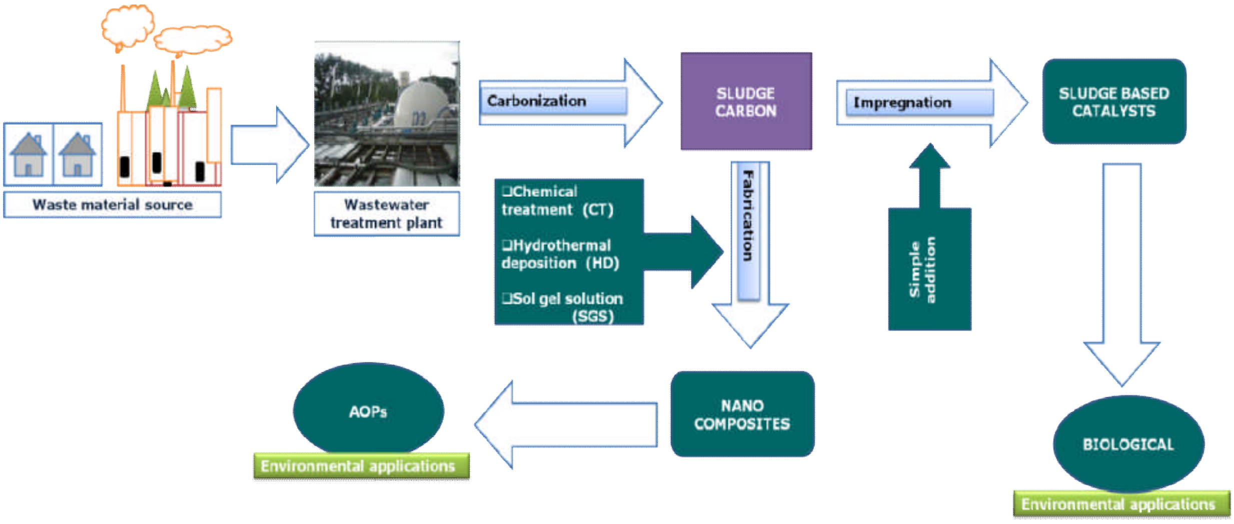
The strength of this research approach is to use sludge-based catalysts (SBCs) for the treatment of wastewaters in the biological and chemical treatment methods at environmentally acceptable conditions. This research presents an alternative way to reuse waste materials from wastewater treatment plants and the performance of new catalysts in the environmental treatment applications, especially in the biological and advanced oxidation processes (AOPs) such as ozonation, photo reaction and catalytic wet air oxidation. This study includes important features such as carbonisation, metal impregnation, surface characterization, and degradation mechanism of pollutants on the biological and oxidative reaction processes. The sludge carbon/TiO_2 nanocomposites were synthesized by different classical methods and the study of the design and fabrication of advanced photocatalytic materials in the framework of nanoscience is presented.

The experimental results show that better conversion were achieved for the newly produced sludge catalysts even though at short space time (τ) when compared to commercial active carbons (AC) in continuous anaerobic UPBR reactor. About 99% removal of azo dye acid Orange II (AOII) was obtained with both SBC600 and SBC800 carbonaceous materials (CMs) at a space time of 4.0 min operation. High values of AOII dye reduction for different metal impregnating to sludge materials SBCZn600, SBCFe600, and SBCNi600 were 78 %, 57 % and 55 % respectively, at a space time of 1.0 min. 97 % of AOII conversion was achieved for SBCFe600 catalyst at 4.0 min of space time, during 100-days continuous operation without loss of catalytic activity. The removal of tartrazine dye for SBCPC800 materials was 74 % at a short space time (τ) of 2.0 min. The result of oxidative (ozonation, photoreaction and catalytic wet oxidation) removal of Bisphenol-A (BPA) in presence of different sludge nanocomposites obtained high results compared to reference materials. The addition of Ti nanoparticles on the sludge carbon (SC) surface increases the crystallinity, electro negativity and surface textures which are able to provide better catalytic activity. The experimental results can boost in the

current environmental applications, especially in the emerging field of advanced catalysts production from other waste sources. This thesis also highlights the major issues related to environmental problems that should be addressed in future research activities.

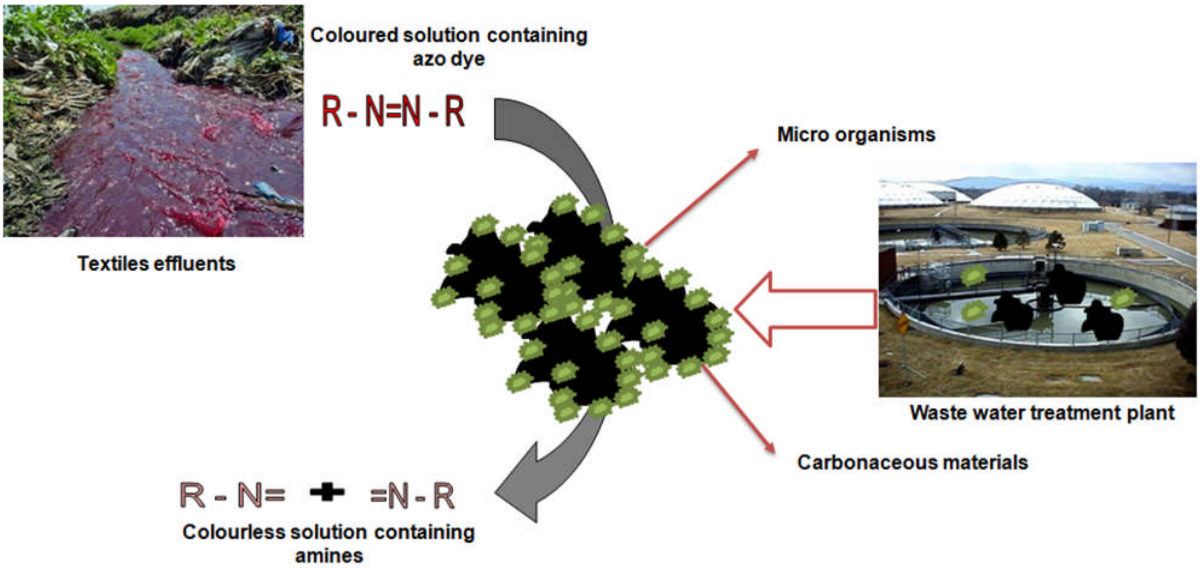
THESIS STRUCTURE

Overall thesis work structure is below:



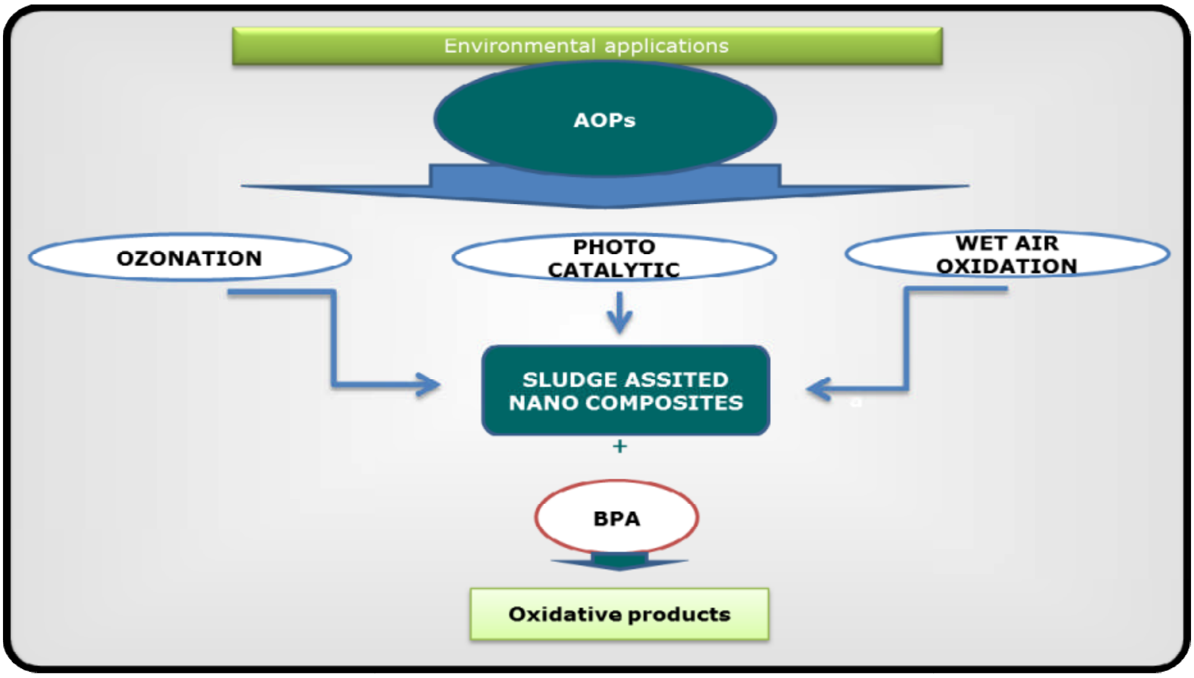
AIM OF THE THESIS WORK

This research is aimed to investigate the performance of new carbonaceous materials based on exhausted sludges from waste-water treatment plant. The catalytic activity of sludge based catalysts was tested in the heterogeneous anaerobic process of biodecolourization of wastewaters containing azo dye in a continuous up flow packed bed reactor (UPBR) (Scheme 1).



Scheme 1. Biological removal of azo dyes using sludge based catalysts from wastewater treatment plants.

Also, various sludge carbon/TiO_2 nano composites were synthesized by different classical methods such as chemical treatment, hydrothermal deposition, sol-gel solution and their potential catalytic activity have evaluated in advanced oxidation processes (AOPs) such as ozonation, photo reaction and catalytic wet air oxidation for treating wastewaters containing an endocrine disrupting chemical as bisphenol-A (Scheme 2).



Scheme 2. Oxidative removal of endocrine disruptive chemical as Bisphenol-A using nano composites.

The level of remotion of azo dyes (acid orange II and tartrazine), and bisphenol-A were measured by High Pressure Liquid Chromatography (HPLC) technique. Surface chemistry of the new solid materials/nano composites was characterized by Environmental Scanning Electron Microscopy (ESEM), Energy Dispersive Spectrometry (EDS), Transmission Electron Microscopy (TEM), Thermal Gravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), CHNOS analysis, Diffuse Reflectance UV–Vis spectra, BET area measurement, and X-ray diffraction (XRD) in order to reveal the surface textures. The ash content of the solid materials was also determined. The adsorption capacities of the new solid materials were thoroughly described by two different isotherm's models such as Langmuir isotherms and Freundlich isotherms in order to determine their adsorption activity.

The objectives of this research work are described in different chapters:

Chapter 1. This review aims to discuss about the sludge derived catalysts, including current status, preparation methods, surface characterization techniques and finally uses in the environmental wastewater treatment applications.

Chapter 2. Performance of new carbonaceous materials obtained from exhausted sludges for the anaerobic removal of the azo dyes acid orange II in continuous up flow packed bed reactor has been investigated in this chapter. The catalytic activity of the new materials is compared with that obtained with commercial activated carbons. The effect of the use of zinc chloride and the effect of carbonization temperature on the activation process are also studied. The batch adsorption equilibrium isotherm studies of the new solids are also developed.

Chapter 3. The effect of zinc chloride and potassium chloride as agglomerators and catalytic agents on the sludge carbonaceous material is studied in this chapter. The surface chemistry and morphology of the new solid materials is subjected to various characterizations in order to obtain the fundamental information for the anaerobic reduction mechanism of tartrazine dye in the packed bed reactor system. The adjustment of the experimental results to a first-order kinetic model is included.

Chapter 4. The effect of transition metal (Zn, Fe, Ni and Cu) on the sludge carbonaceous material is described in this chapter. The catalytic activity of some metal factors on the anaerobic removal of azo dyes is performed in the UPBR system. Different metal impregnated solid materials were also tested in an isotherm batch adsorption experiment with acid orange II dye. The solid materials were characterized using different analytical tools in order to describe the proper route of the degradation mechanism of azo dye molecule. The catalytic stability of the solid material (SBCFe600) is checked during the 100 days continuous experiment in the UPBR reactor system.

Chapter 5. This chapter is devoted to describe the behaviour of various sludge derived nano composites. These materials were synthesized and characterized using various analytical techniques. The performance of Ti incorporated on the surface of sludge carbons was studied. Oxidative removal of endocrine disruptive chemicals as Bisphenol-A on the sludge carbons/TiO_2 nano composites was performed in different oxidative reactions such as ozonation reaction, photo reaction and catalytic wet air oxidation reaction. The catalytic stabilities of nano composites were checked in the catalytic wet air oxidation process (39 h). The photo catalytic activity of new solid materials was compared with commercial titanium oxide (P25).

INTRODUCTION

1. Introduction

This introduction presents an overall view of the thesis, which gives the strength of this research and the aim, scopes and methodology that will contribute to an innovative approach to environmental wastewater applications. The thesis covers different aspects of the waste treatment, including the conversion of exhausted sludge biomass into solid materials that can be used as catalysts and their environmental wastewater applications, which are the main topics of this thesis.

1.1 Background and purpose

The purpose of this research work is mainly stressed on the environmental treatment applications. The use of traditional methods still has disadvantages due to the operational costs and treatment efficiency. Waste solid materials (exhausted sludge) and wastewaters are two main problems in the wastewater treatment plants around the world. This situation needs a proper environmentally acceptable solution and cost-effective methods. The strong aspect of this thesis is to produce sludge-based catalysts from sewage sludge materials and its use in environmental treatment applications, including biological and advanced oxidation processes. The major contribution of this work is of scientific and engineering significance and it is devoted to the re-use of sludge materials as adsorbents or supported catalysts.

2. Approach to literature review

The literature review starts with general aspects of environmental problems. This is the most critical part of this thesis research work. In this section we will provide the basic tools for the treatment of solid waste and wastewaters. This literature review keenly searches on the various issues related to waste materials and wastewaters and also how they impact in the environment. More details are included in the Chapter 1.

2.1 Waste materials

Waste materials: The disposal of sewage sludge is one of the greatest problems in many wastewater treatment plants. The annual amount of sewage sludge production in the European Union is 9.8 million tons and the expected amount will tremendously increase in the future [1] The available sludge disposal methods such as incineration, agricultural uses, sea dumping and land fillings are no more acceptable practices. Generally, waste materials from sewage sludge contain plenty of organic, inorganic, nutrients, and bacteria with different physicochemical properties. The relative abundance of carbon make them an attractive material as supporting catalysts or adsorbents. The synthesis of catalysts has produced intense research during the past decades, thus resulting in 25% of the catalysts used in the chemical industry, 40% in petroleum & petrochemical industry, 30% in environmental protection and 5% in the pharmaceuticals [2]. For the last two decades, solid catalysts have been used for the removal of pollutants from water and wastewater. It has been reported that sludge-based catalysts can enhance the catalytic reactions and also can play an important role for the production of chemicals and other auxiliary products.

2.2 Wastewaters

Wastewaters: The wastewaters object of this study come from textile industries, chemical industries and meat processing units. Among the wastewaters, the textile wastes make the biggest problems to environment. The coloured and complex dye compounds have turned into hazardous to human, aquatic, and marine living organisms. The availability of fresh water is essential for development, disease free and quality of life. In Europe, 108 million tons of wastewaters are produced on a yearly basis; from that, about 36 million tons come from the textile industry [3]. In developing countries textile industries are one of the economic growth engines, but now it presents a global pollution problem due to the discharge of dye containing wastewaters into fresh water. Currently, the control of pollution is one of the most difficult tasks for many countries. Carliell and co-workers have reported that azo dyes account for 60 to 70% of all textile dyestuffs produced and are the most common chromophore of reactive textile dyes [4]. The Essawy group has reported that 20 % of dyes are discharged into industrial wastewaters, but the exact data of dyes discharged into the environment are not available [5]. The European Union has introduced several strict laws and regulations for controlling or preventing the water pollution but still have several limitations. Now, researchers looked for environmentally friendly methods in order to clean up safely the contaminated waters.

2.3 Environmental wastewater applications

Environmental treatment methods: During the past decades, many reviews have been published on several oxidative and biological processes for treating wastewaters, but these classical treatment methods still have many serious problems due to the secondary by-products and operational costs. Until now, most of the researchers focused on the conventional physico-chemical techniques, including the coagulation, ozonation, flocculation, membrane separation, nanofiltration and advanced oxidation processes for the removal of pollutants from the water and wastewaters [6-7]. However, these oxidative practices have obtained poor efficiency for the removal of hazardous pollutants. Even though, the nature of the treatment, experimental protocol and cost of operation are the major key points while considering the efficiency of the treatment practices. The conventional wastewater treatment plants (WWTPs) are not successfully designed for completely removal of pollutants [8-9].

Adsorption: Activated carbon is a solid material with good adsorptive, electrochemical and catalytic properties. Currently, plenty of articles have been published about the adsorption on activated carbons for treating environmental pollutants [10]. Many researchers showed that activated carbon is one of the best-suited materials for cleaning of wastewaters, but unsuitable for many developing countries, for economic reasons.

Advanced oxidation processes (AOPs): The advanced oxidation processes have been extensively used for removing of pollutants from water and wastewater [11]. The AOPs show better yields for the treatment of low concentration aqueous pollutants from the industrial effluents. AOPs use oxidizing agents, mainly hydroxyl-free radicals, to oxidize the pollutants. The ozonation, photocatalytic reaction and catalytic wet air oxidation are the most common AOPs.

Ozonation: In recent years, it has been reported that ozonation treatment can remove the colored compounds from the water and wastewaters [12] and the general mechanism of ozonation reaction has been suggested. The main advantage of ozonation is that it eliminates odors, reduces the chemical oxygen demand containing matters, and increases the suspended solids reduction. It has also several disadvantages such as high investment capital cost, high electric consumption and is highly corrosive. In a study reported on the use of ozone over activated carbon for the removal of biodegradable organic compounds from aqueous solution pollutants [13]. Activated carbons-metal assisted ozonation reaction for the removal of pollutants has also been reported [14-15].

Photocatalytic reaction: The titanium dioxide (TiO_2) has been successfully applied in many environmental treatment applications. TiO_2 has a great practical importance due to its high stability, no toxicity, biocompatibility and its photochemical activity offers potential applications for photoreactions, semiconductors, solar cells, and electro-chemical, but still suffers due to the low efficiency, high cost and short irradiation range. Various research groups have developed photo-catalyst and successfully applied them to photocatalytic reactions [16-18]. There are plenty of research reports of titanium (TiO_2). Nanomaterials such as, nanotubes, nanowires, nanorods, nanofibres and nanoclusters and claimed that to have high surface area, good surface textures, and excellent catalytic activities [19-20].

Catalytic wet air oxidation (CWAO)*:* This method is one of the most economical and environmental friendly wastewater treatment methods. Many researchers have reported the complete mineralization of organic compounds into CO_2, N_2, water and mineral salts [21-22] and some authors have reported the oxidative removal of phenol using various noble metal catalysts [23]. A recent trend in the field of nanocomposites, fabricated from sludge carbon through the hydrothermal, chemical process and sol gel solution, they offer a new attractive option.

Biological treatment: The biological treatment is one of the best tools and cost effective methods for removing the pollutants. The biological treatment can be anaerobic, aerobic or a combination of both. In the current scenario, the use of biomass (fungi, algal and bacteria) in the biologic anaerobic treatment of textile effluents has proven to be a better alternative option compared to the conventional methods. The Fabregat group has recently reported the anaerobic degradation of azo-dyes using commercial active carbon under up-flow packed bed reactor system as one of the environmentally safer and inexpensive methods [24-26].

In this circumstance, several research works have been reported on the removal of wastewater containing dyes with different type of anaerobic reactor configurations, including sequential batch reactor (SBR), fluidized beds, up-flow anaerobic sludge blanket reactor (UASB), rotating biological contactor (RBC) and fixed/packed bed reactor [27-28]. The different studies for treating dye-contaminated wastewaters using these techniques fail to the complete removal of the secondary products. Until now, there is no proper treatment available for the complete removal of wastewaters from the industrial effluents.

3. Conclusion

This thesis mostly devotes to the production of catalysts from exhausted sewage sludge biomass, their surface chemistry characterization and their uses in various environmental wastewater applications. Huge amount of sewage sludge can be used to produce highly porous sludge based carbons, which can replace the commercial activated carbons for the removal of various pollutants from wastewater. The state-of-the-art of the scientific and technological knowledge gives a better idea of the current challenges and the potential applications in the wastewater treatments. From the above-mentioned literature survey, it can be seen how to face the environmental problems and the necessity of its awareness in the social community.

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CHAPTER 1

Utilization of Sludge Based Catalysts for Environmental Wastewater Treatment Applications- A Review

In recent years, conversion of exhaust sludge biomass into catalysts appears to have growing demand to produce cost-effective, environmentally friendly and potential application for the removal of pollutants from water and wastewater. Until now, most of the environmental applications that incorporate solids have been carried out through the adsorption process over activated carbons (AC). Recently, many researchers have studied the sludge-based catalysts (SBCs) from harmful sewage exhaust sludge biomass and utilized them in different environmental applications. This review covers diverse aspects of sludge biomass, including preparation methods, surface textures and their emerging environment applications. This review paper consists of four sections. ***1.*** *This section provides an overall view of sewage biomass, current status, available disposal methods and environmental legislation.* ***2.*** *This section gives an account of production of sludge-based catalysts from sewage exhaust sludge biomass, with the main emphasis placed on various activation techniques.* ***3****. This section discusses the surface chemistry as well as morphological and physicochemical properties.* ***4.*** *Final section describes the environmental treatment applications, namely, adsorption, advanced oxidation processes and biological processes.*

Key words: Sewage sludge, sludge disposal, carbonaceous materials, surface characteristics, environmental treatment, nanocomposites.

1. Introduction

¨Sustainable sludge handling may be defined as a method that meets requirements of efficient recycling of resources without supply of harmful substances to humans or the environment¨ described by the Commission of European Communities in the year of 1991 [1].

1.1 Sewage biomass

Sewage biomass is a suspended solid that comes from households, chemical industries, and hospitals. Most of the wastewater treatment plants (WWTPs) are receiving a wide variety of chemicals and heavy-metal fractions. The chemicals and heavy-metal fractions are one of the important parameters while considering the ultimate disposal and the liquid wastes partially removed during the primary, secondary and tertiary treatment steps. Handling with harmful sludge biomass is one of the most complicated tasks for wastewater treatment plants everywhere in the world. Basically, the sewage sludges are divided into two categories:

1. Primary sludge
2. Secondary sludge.

Primary sludge: The primary sludge is usually collected from the primary settler and contains a huge amount of fats, greases and oils matters, and is further transferred to secondary treatment steps.

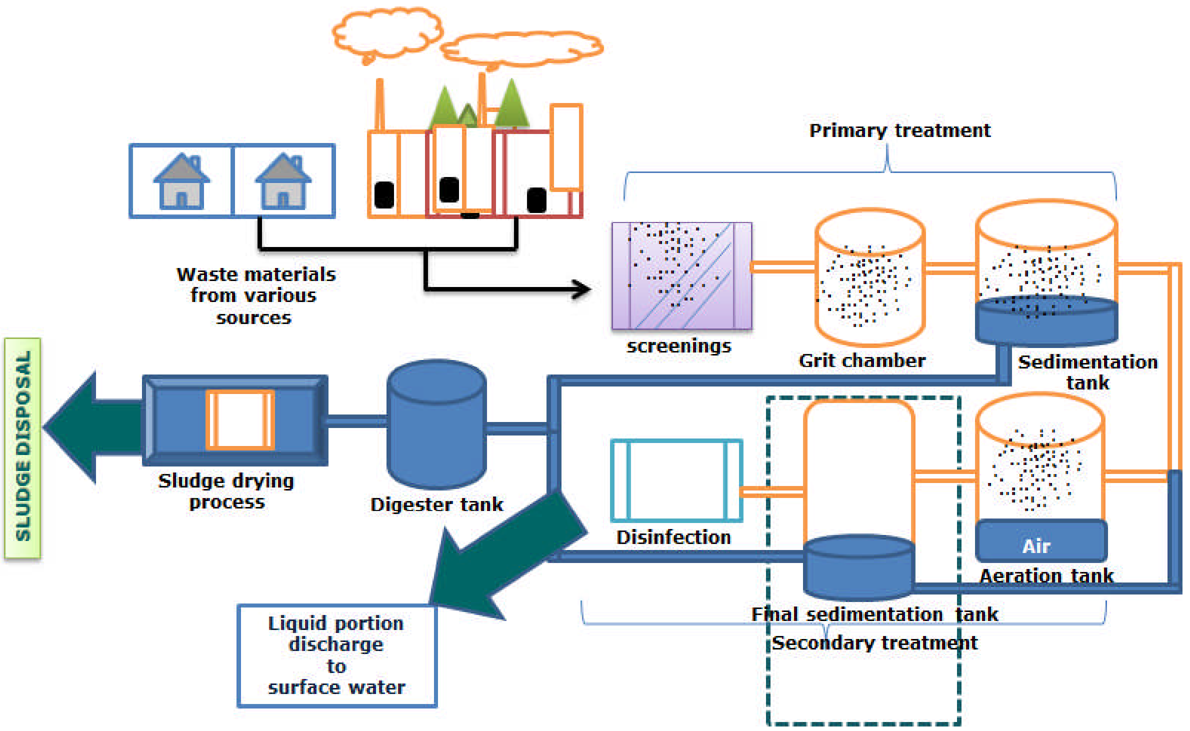
Secondary sludge: The secondary sludge is mainly generated from the different biological processes, including, aerobic, anaerobic or combined aerobic/anaerobic treatment process. This secondary sludge is also called exhausted sludge, because it mainly contains biological organisms and exhausted solid residues.

1.2. Composition of sludge biomass

The composition of sludge biomass depends on several factors, including different location, type of treatment plant, operation conditions and density of population. Basically, sludge biomass contains a variety of plant nutrients, toxic substances, heavy metals and pathogenic substances. Turovskiy and Mathai [2] have reported the composition of metal fractions in the sludge biomass, and the heavy metals accumulated in the plant tissues can directly enter the food chain system causing several health problems [3]. Identification of metal composition and bioavailability of the sludge biomass using various extraction schemes has been reported [4].

1.3. Origin of sewage biomass

The amount of sewage sludge has rapidly increased day by day in the domestic and industrial wastewater treatment plants in the last decades. Due to the industrialization, human activity and population growth, the amount of sludge increases in the wastewater treatment plants. The production of sewage sludge was around 9 million tons in 2005 [5] and the amount will tremendously increase in the coming years. **Figure 1** shows the schematic diagram of production of sewage sludge coming from different treatment lines.



Currently, the data about the amounts of sludge biomass are unavailable. The traditional sludge disposal practices are usually very expensive and are also producing several environmental consequences. In fact, most of the disposal practices are still under stress and show that it is very difficult to treat this harmful material.

1.4. Environmental laws

The waste material is considered one of the biggest environment pollutions; the control of pollutant is one of the most difficult tasks for the developing countries in the world. The majority of the solid waste materials come from wastewater treatment plants. For a smooth operation and eco-friendly waste disposal, several laws and regulations are implemented by the European Union. The European Union has decided to reduce the waste biomass materials by 50 % by 2050 [6]. New regulatory laws are introduced for sludge producers and users in order to improve the quality as well as the standard principles of the wastewater treatment [7].

1.5. Waste management

The waste management is primarily related to collection, processing, transport and monitoring of sewage biomass. The basic strategies of waste management priorities are: (1) prevention of sewage biomass, (2) reuse and (3) advanced disposal practices. The waste management of waste materials from the different localities is a responsibility of the local and international agencies. The government authority is trying to implement new protocols for reducing the sewage biomass in order to clean our environment. For the past two decades, the EU has restricted the disposal practices of urban sewage biomass [8].

1.6 Strategic sludge disposal management

Landmark reviews have been published on sewage sludge, both dealing with variety of disposal practices and their potential impact in the environment [9-10]. The disposal of sewage biomass means reducing the amount, smell, water content and pathogenic (bacteria, yeast, fungi and virus) substances and improving the technical aspects of disposal practices [11]. Over the past decades, sewage biomass disposal has been one of the key issues in the various wastewater treatment plants. Many researchers have focused on the design of innovative treatment systems, especially in the quality, safety and cost-efficiency. A review has been published on the goodness of the disposal practices including the fertilization, incineration and pyrolysis [12]. At the present situation, plenty of sludge disposal practices are available, but some of them are prohibited by European Union, for example, sea dumping [13]. The latest trends of sludge disposal methods including the combustion, wet air oxidation and gasification are also facing environmental problems e.g. air pollution.

Agriculture: The agricultural disposal practice has been used since 1960s. The sludge biomass consists of organic matters, and metal fractions as it is above mentioned. The rich nutrients of sludge can be used as fertilizes. However, some chemical substances that come to agricultural lands may be harmful for crops and vegetables. Review articles have been published on sludge disposal practices for fertilization [14-16]. The sludge biomass usage for agriculture takes 60% of the sludge produced in France, 54% in Denmark, 50% in Spain, 44% in UK and 26% in USA [17].

Incineration: This is one of the best disposal options but still has some drawbacks, mainly air pollutants. In this process, sewage biomass is thermally converted into several products like, ash, flue gas and also generates heat energy. About 30 % of solids still remain after the incineration as ashes [18]. Incineration is performed at high temperature and the byproducts solid ashes contain inorganic maters, such as, quartz, dolomite, calcite and other substances.

Land filling: This method is used to spreading waste materials on the land space, and this practice is followed many countries. Land filling is one of the best ways to recycling the sewage biomass and creating a new land area for agricultural purposes. Usually the liquid and solid biomass is used to spreading on the land. In the WWTPs, the sewage biomass constantly produced can be stored up to six months on the lands. The land-filling methods are performed in different ways, including the lining of clay and plastic materials [19].

Gasification: Gasification is a thermal process, which converts organic matter into various gases such as, carbon dioxide, hydrogen and carbon monoxide. The gasification of sludge biomass produces clean combustible gas (syngas) at temperatures above 700 ^{o}C, which can be used for fuel purposes. Many researchers studied the energy production from sewage biomass and the reduction of the energy problems [20-21]. Hamilton [21] has reported the effect of the combustible gas and the heavy metals (Cs, Cd, As, Zn, Cu and Co) during the gasification process. In the gasification process, many gases are produced, such as H_2, CO and methane (CH_4), which can be used for electricity production. Some literature has dealt with the production of hydrogen gas from the sewage biomass [23-24].

Pyrolysis: The conversion of sludge biomass into useful solid materials using the pyrolysis technique is one of the best options. During the pyrolysis process, several gas fractions are generated including hydrogen, carbon monoxide, methane, acetic acid, acetone and methanol from the sewage biomass [25]. The volatile fractions and chemical compounds are identified in the sludge biomass with the help of various analytical tools such as, TGA, DSC, GC-MS and HNMR [26]. Many researchers have successfully produced sludge-derived catalysts or adsorbents from the sewage biomass using pyrolysis [27-30].

1.6 Cost of treatment and disposal practices

As it was mentioned above, the sewage biomass disposal practices become a problematic task for many WWTPs and are highly expensive. To estimate the cost of sludge treatment it is necessary to consider the characteristics of sewage biomass, re-reuse, quantity of sewage biomass, treatment methods, EU regulations and operational costs. The costs of treatment methods are influenced by several factors, including: salary, fuel, electrical, transportation, and marketing of sludge compost [31-32]. Unfortunately, still there is no healthier solution for the proper sludge biomass disposal methods. Since dewatering and drying of sewage biomass is costly practices, the conversion into useful supporting catalysts or adsorbents can solve a huge amount of sludge problems. More details are discussed in the next section.

2. CONVERSION OF SLUDGE BIOMASS INTO CATALYSTS

For the last two decades, most of the researchers have reported the production of solid catalysts and their potential environmental applications for the removal of pollutants from water and wastewaters. These sludge-derived catalysts can enhance various catalytic reactions, and play an important role in the production of chemicals and other auxiliary products. The synthesis of catalysts has generated intense research studies during the past decades, resulting in 25% of the catalysts have been used in the chemical industry, 40% in petroleum & petrochemical industry, 30% in environmental protection and 5% in the pharmaceuticals [33]. This section devotes mostly on the production of sludge-derived catalysts from various sewage sludge lines.

2.1. Activated carbon

Activated carbon (AC) is an amorphous form of carbon with high surface area, microporous structure, and good adsorption capacity [34-36]. The surface area of the activated carbons commonly ranges from 400 m^2/g to 1800 m^2/g. The activated carbons are used as a solid catalyst or supporting materials for the potential application of various catalytic reactions associated with gas and liquid phase catalytic reactions. Many research articles have studied the sludge-derived carbon production from various waste biomass sources. Usually, adsorption capacity of a catalyst increases with the surface area and it depends on the type of biomass. **Table 1** presents the activated carbons obtained from various non-conventional waste materials.

Table 1. Application of sludge carbons obtained from municipal and industrial wastes.

Raw material	**Contaminants**	**Related matter**	**Reference**
Sewage sludge	Anionic dyes	Contrary to commercial carbons, for pH values between 5 and 9, the adsorption capacity of the AC for dyes is altered	[37]
Industrial waste	Dyes (Rhodamine-B)	Ion exchange was the predominant dye adsorption mechanism; 100 % removal rate	[38]
PET	Dyes and phenol	High adsorption capacity of ethylene blue. Adsorption depends on pH	[39]
Leather industries	Dyes (Acid brown)	Adsorption capacities greater than commercial AC	[40]
Tires	Dyes (Methylene blue, Brilliant red)	Adsorbents developed have good surface characteristics	[41]
Fertilizer	Mercury (II)	Adsorption of mercury II increases with increasing pH	[42]

Generally, activated carbons are originated from two sources: (1) conventional and (agricultural and wood industry wastes) and (2) non-conventional (municipal wastes). Low cost adsorbent materials are usually produced from conventional and non-conventional wastes [43]. The agricultural raw materials such as oil palm trunk fibre, wood, fly ash, rice straw-derived char and rice husk are mostly used to produce activated carbon [44-45]. The non-conventional sources are basically originating from various places such as hospitals, households and factories. These wastes are highly polluted must be eliminating from the environment.

2.2. Catalysts produced from sludge biomass

First sludge carbon from dried sludge was produced in 1971 by Kemmer et al [46]. Smith et al. recently reviewed various aspects of sludge-derived carbon materials, including, production, surface textures and ultimate uses in the environmental applications [47]. Today, there are plenty of research reports on the sludge derived catalysts and their environmental wastewater applications, but all of them have not been covered in the depth study. In the European Union alone, the annual production of dry solid sludge exceeds 10 million tons [10]. This huge amount of waste solid materials, consequently, causes major handling and disposal problems [9]. Usually these waste materials are reutilized in agriculture, incineration, land filling, compost manufacture, biogas production, manufacture of adsorbents, etc.; but some of the disposal methods will be forbidden in the coming days. If the solid wastes are converted into low cost adsorbents (LCAs), it can provide twofold environmental advantages. Firstly, the amount of waste materials is partially reduced, and secondly the low-cost adsorbent can eliminate the contaminants from the environment at a low cost. **Figure 2** shows the schematic route of sludge-derived catalysts from sewage sludge [48].

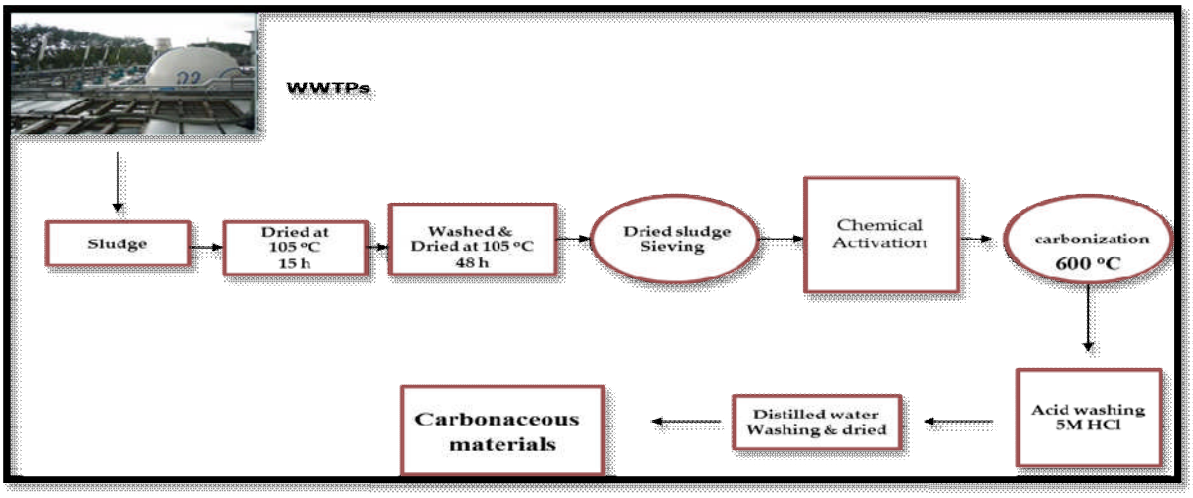


Figure 2 Schematic route of sludge derived catalysts from sewage sludge.

There are various factors such as surface area, pore volume, ashes, crystalline content, and functional groups that can stimulate the adsorption capacity of the sludge-derived catalysts. Thus, small molecules such as phenol can access to the micropores; natural organic matters can access to the mesopores; and bacteria can access to the macropores, as it has been reported by Dias et al [43].

Generally, two types of the activation processes are used to produce sludge-derived catalysts from sewage biomass: chemical activation and physical activation [49-51].

2.2.1. Chemical activation

The sewage biomass is a good source of carbonaceous matters containing organic and inorganic rich materials. Therefore, it is possible to convert it into carbonaceous material, using thermal processes under controlled conditions with the addition of some chemical substances, in order to increase the surface area, porosity and chemical textures. Martin et al. have reported the obtaining of some modified sludge derived catalysts and used them to treat a variety of pollutants, especially dye molecules [52]. The chemical activation process was carried out through thermal decomposition of the sludge biomass impregnated with suitable chemical reagents, such as NaOH, KOH, H_2SO_4, $ZnCl_2$, and H_3PO_4 [53-57]. Most of the authors use $ZnCl_2$ for the chemical activation. The $ZnCl_2$ is a dehydrating reagent that may form a tar-formation suppressant to promote the aromatization of the carbon skeleton and also enhances the porous textures. The addition of chemical reagents on the sludge carbons promotes the formation of a rigid matrix structure. The chemical activation process depends on the type of chemical agents, reagents ratio and activation duration. The sludge-derived catalysts produced from various biomass sources are presented in **Table 2**.

Table 2. Sludge derived catalysts produced from the various biomass sources

Entry	Sludge origin	Activation agents or conditions	Temperature ºC	Dwell time and rate	Post treatment	Gases condition	Adsorption application	Reference
1	Coal/biomass	K_2CO_3& KOH	600& 800	1 h	Hot distilled water /cold water		Hazardous materials	[58]
2	Sewage sludge	---	300, 450, 600 &750	30 min, 10 ºC /min	Distilled water	N_2, 100 NmL/min	4-Chlorophenol	[55]
3	Paper mill sewage sludge	carbonization	850	40 min	---	Steam atmosphere	Methylene blue & reactive Red (RR 24)	[59]
4	Surplus biological sludge WWPTs	H_2SO_4	700	30 min, 15 ºC/min	3M HCl	N_2	Acid brown 283, Direct Red 89 & Direct Black 168)	[60]
5	Sewage sludge	Air	450	1 h, 10 ºC /min	---	N_2, 150 ml/nin	---------	[61]
6	Urban and industrial residues	K_2CO_3	700	1 h	Distilled water		Removal of acetaminophen	[62]
7	Sludge from food processing	$ZnCl_2$, KOH and KCl,	200-400	1-2 h, 20 ºC/min	1.2 M HCl& hot distilled	N_2, 70 mL/min	Methylene blue	[63]

	industry				water			
8	Sludge from municipal treatment plants	KOH, $ZnCl_2$& H_3PO_4 Micro wave	105-110	2 D	3 M HCl	N_2, 5 L/min	Copper, Lead metal from aqueous solutions	[64]
9	Sludge from urban treatment plant	$ZnCl_2$ & H_2SO_4	650	30 min, 40 ºC/min	10 wt % HCl	----	Methylene blue	[42]
10	Biological, chemical and hybrid sludge	H_2SO_4	550	1 h, 18 ºC/min	3 M HCl	N_2	------	[65]
11	Industrial waste oil sludge	---	650-950	--	----	N_2	Antibiotics	[66]

2.2.2. Physical activation

Physical activation is a thermal heating (300-800 ^{o}C) in presence of suitable gases such as oxygen, nitrogen, argon, carbon dioxide or helium. Usually this process is performed by one or combination of different gases and deals with carbonization and oxidation process.

Carbonisation: In this process, sludge biomass is subjected to pyrolysis at different temperatures in absence of oxygen. Some authors have also efficiently produced sludge-derived catalyst with addition of inert gases. This process leads to evaporate the water, and the carbon contents from the dried and charred product then becomes hard, brittle and its catalytic stability is also improved [67].

Oxidation: In this process, the sludge biomass is subjected to heating in presence of oxygen gas. Usually, operational temperature is higher than the carbonization process. Heating at high temperatures, the organic and other inorganic substances are released as volatile substances. The carbon constituents are converted into tar and the materials become hard and develop porous textures. The sludge-derived catalysts produced using steam activation give better adsorptive capacity, as reported Rio et al. [68]. Some researchers have reported that washing with hydrochloric acid (HCl) improves the BET surface area and the surface chemistry [69-70].

2.2.3. Advanced deposition process

Many authors have reported the obtaining of sludge-derived catalysts using different procedures, including, microwave assisted consecutive impregnation and incipient wetness impregnation [71-76]. Recently, titanium mediated heterogeneous catalysts has been proven as a good choice for environmental treatment applications. Generally, TiO_2 nanomaterials can be fabricated using different surface modifications, including hydrothermal deposition, chemical treatment, sol-gel solution and vapor phase deposition. A landmark review has been reported on the carbon-titanium based photocatalysts that are fabricated with various supporting materials, including activated carbon, fullerene [60] and graphene [77]. Among them, activated carbon (AC) has received much attention in the present days, because it has a good performance in several environmental treatment applications such as photoreaction, ozonation and heterogeneous catalyzed reactions. Due to their economic benefits, many researches have been devoted to the development of cost-effective and low toxicity catalysts from waste biomass, but only few studies have reported TiO_2 deposit on the activated carbons for the removal of hazardous pollutants from water and wastewaters [78-81]. This activated carbon assisted nanomaterials have vouched for this cost-effective and good treatment method to many environmental treatment applications. The advanced techniques of carbon surface modification can be mainly categorized into three types: (1) hydrothermal deposition, (2) sol-gel-solution, and (3) chemical processes.

Hydrothermal deposition

Hydrothermal deposition is one of the best methods to deposit chemical reagents, as zinc oxide and titanium oxide on the supporting materials surface (activated carbon, graphite and zeolite). Jitianu and co-workers [72] have produced nanotubes of good quality with better surface chemistry. Until now, no research has been published on the sludge based nanocomposites fabrication and its surface textures studies.

Sol-gel solution

Sol-gel solution process is widely used in the material science engineering for the fabrication of advanced solid materials. This process is used to obtain metal oxides, especially oxides of titanium, zinc and silicon. Metal alkoxides such as, silicon tetraethoxide and titanium tetraethoxide are used as the precursor. Multi walled nanotubes have been successfully fabricated using the sol-gel solution process [72].

Chemical process

This process is frequently cited in several literatures, being the best method for deposition of metal particles on the supporting materials surface. Titanium nanotubes using chemical process were first obtained by Kasuga [82]. The titanium nanotubes fabricated using chemical treatment have been tested in the catalytic wet air oxidation process for the removal of Bisphenol-A (BPA) solution [83]. The chemical process is a new type of fabrication process that can produce good quality materials with remarkable surface chemistry and catalytic activity.

3. SURFACE TEXTURES OF SLUDGE DERIVED CATALYSTS

This section combines the surface chemistry and physicochemical properties of sludge derived catalysts. This combination of parameters is a great help for elucidating the fundamental characteristics and structural identification of the sludge derived catalysts. Most of the reactions occur on the surface of catalysts and, therefore, special consideration is required in the analysis of the characteristic data and the interpretation of the surface. Thus, the identification of surface textural of sludge-derived catalyst is one of the challengeable tasks. There is no general rule to determine the quality of the catalysts and, to date, many researchers have dealt with the surface identification of sludge-derived catalysts and few and poor information is available. This section is dedicated to the surface chemistry of sludge-derived catalysts.

3.1.1. Surface area and porosity

The surface area and porosity are the more important physical properties of the materials and, in fact, can determine the quality of the catalysts. The **BET** method (Brunauer, Emmett and Teller) is the most widely accepted to determine the surface area of a catalyst that is calculated by nitrogen gas uptake over the solid material at particular analysis conditions. The BET technique also gives information about micro, meso and macroporosity of the materials. Higher surface area and better surface porosity can produce higher catalytic activity. Zhai et al. [84] reported the production sludge-based catalysts with large surface area from sewage sludge). High temperature of activation can destroy the micropores, as reported Chiang et al. [85]. The surface area of some sludge-derived catalysts is presented in Table 3.

Table 3. Surface area of some sludge-derived catalysts.

Sources	Type of dye /compounds	Ratio	Activation agent	Pyrolysis temperature °C	Gas Medium	BET area m^2/g	References
Dewatered sewage	Formaldehyde	1:1	$ZnCl_2$	750	---	509	[59]
Aerobic sewage sludge	4-chlorophenol	1:1	KOH	750	--	950	[55]
Paper mill sewage	Methylene blue	--	--	850	Steam atm	140	[59]
Waste newspaper	Methylene blue	1:1	K_2CO_3	850	N_2	1260	[86]
Wastewater treatment plant	Dyes	1:2	H_2SO_4	700	N_2	253	[60]
Wastewater treatment plant	Waste water	1:3	H_2SO_4	550	N_2	89	[65]
Dewatered surplus sludge	Cu^+ and Pd^+		$ZnCl_2$ KOH H_3PO_4	600	N_2	82 130 118	[64]

3.1.2. Surface morphology

The **SEM** (scanning electron microscopy) is a type of electron microscopy technique that can obtain the microstructure image of a catalyst with the help of a high-energy beam of electrons. Zhai et al. [84] determined the grooves and changes in the carbon frame structure while preparing sludge catalysts at high temperatures of activation. The identification of surface micro images of sludge-derived catalysts using SEM techniques permits to reveal the internal surface of the materials [64, 65, 87, 88].

3.1.3. Chemical groups

FTIR (Fourier Transform Infrared Spectroscopy) technique is used to determine the quantity and composition of surface functional groups of an unknown material. Many authors have successfully studied and identified the chemical groups of sludge-derived catalysts [59, 66, 70, 89]. Usually, sludge-derived catalysts contain a variety of chemical groups and it is necessary to identify such groups in order to draw the clear mechanism of the catalytic reaction. The presence of major functional groups in the sludge derived catalysts is Si, OH, NH, C=C, C-C, and C-O bonds. The chemical groups are mostly due to aromatic and aliphatic compounds. The chemical groups of sludge-derived catalysts obtained from sewage biomass are presented in Table 4.

Table 4. The chemical groups of sludge derived catalysts

Entry	Sludge origin	Wavenumber (cm^{-1})	Assignments	Reference
1	Sewage sludge	1650 1385	C—O; —CH.	[59]
2	Sewage sludge	1040	Si–O–C or Si–O–Si	[56]
3	Various sewage sludge	3500	O–H band/stretch	[65]
4	Sewage sludge	1020 700 and 900	C–O Aromatic hydrogen	[90]
5	Metal	2200	CN− groups,	[91]

	sludge/waste oil derived	800	Si–O(Si)	
6	sewage sludge	1330	nitrates (NO_3^-)	[89]
8	Organic solid wastes	2926	C–H symmetric	[91]
9	Sludge from food processing industry	1550 700–610	N–O stretching C–H bending	[63]
10	sewage sludge	800 and 450	Si–O–Si or Si–O–X, X — Al, Fe, Ca, Mg, and Na	[92]
11	Industrial sludge	564	P–O and O–P–O stretching	[93]

3.1.4. Crystalline content

The XRD (X-ray diffraction) technique is used to determine the crystalline content of the materials and also give the information about the crystallographic structure, chemical composition, and physical properties. The sludge-derived catalysts contain, mostly, quartz, albite, calcite, and dolomites. Zhi-hui et al. [65] have identified the inorganic content or crystalline content such as FeC and Al_2O_3 in the sludge catalysts. Many researchers have identified the inorganic composition in the sludge catalyst [91, 94, 95]. Table 5 summarizes the crystalline content of sludge-derived catalysts obtained from sewage biomass.

Table 5, Crystalline content of sludge derived catalysts.

Entry	Sludge origin	Inorganic contents	Reference
1	Metal sludge/waste oil derived	$LiNaSO_4$,FeNi-Kamacite, SiO_2, AlNi	[91]
2	Different sewage sludge	FeC and Al_2O_3	[65]
3	Sludge from food processing industry	Quartz, calcite, alumohydrocalcite, kaolinite 1A, albite, graphite, and carbonate–fluorapatite	[63]
4	Sewage sludge	Quartz (SiO_2), Na_2SiO_3 and Kyanite (Al_2SiO_5)	[92]

5	Sewage sludge	Quartz, calcite, kaolinite, Na-Ca feldspars (albite, anorthite) and micas (illite-type)	[70]
6	Sewage sludge- and waste oil sludge-derived materials	hunite ($Mg_3Ca(CO_3)_4$), sapphirine ($(Mg_4Al_4)Al_4Si_2O_2$), barringerite (Fe_2P), goethite ($FeO(OH)$) and almandine ($Fe_3Al_2SiO_4$)	[66]

3.1.5. Thermal reduction

TGA/DSC (thermal gravimetric analysis and the differential scanning calorimetry) technique is used to analyze the weight loss of a catalyst at 100-900 ^{o}C. In this temperature range, most of the compounds decompose. Several compounds have been identified during the thermal analysis reduction in the sludge-derived catalysts [92]. Many compounds such as, water, volatile substances, calcium carbonate, calcium sulfate, and gases, including carbon dioxide and sulphur dioxide have been reported [96]. Thermal reduction of the material occurred in three different stages, that is, dehydration (80–180 ºC), volatilization (180–500 ºC) and fixed carbon burning (500–850 ºC) and most of the impurities and ashes can be dislodged at 500 ºC [84]. About 80 % of the ashes consist of inorganic oxides such as Al_2O_3, SiO_2, and Fe_2O_3 [94].

3.1.6. EDX elemental composition

EDX (*Energy-dispersive X*-ray *spectroscopy***)** analysis permits to determine the elemental composition of the catalyst materials. Using this technique, coupled with the scanning electron microscopy technique, Fitzmorris et al. identified metals such as As, Cd, Cr, Cu, Ni, Pb, Se and Zn particles in the sludge-derived catalysts [69]. Several metals have been determined in the sludge materials obtained from surplus sewage sludge prepared by physical activation and chemical activation [75].

The **CHNS** elemental analysis is a classical tool to complete the analysis of the sludge derived catalysts.

3.1.7. X-ray photoelectron spectroscopy

XPS technique is a non-destructive surface technique used to determine the electron binding energies of atoms in the materials surface. This technique is also used to determine the elemental composition and chemical states of the materials. Using this technique, it has been determined the binding energies of the silicon (Si 2p), sodium (Na 1s), oxygen (O 1s), and carbon (C1 s) of sludge-derived catalysts [92]. The XPS cannot detect hydrogen directly; this is one of the main drawbacks of XPS technique. Today, many researchers have eagerly used the XPS analysis in order to drawing the exact mechanism of heterogeneous catalytic reactions [97].

3.1.8. Ashes

Ashes are an important factor while considering the quality of sludge-derived catalysts. Ashes are composed of minerals such as silica, aluminium, iron, magnesium, and calcium. The presence of ashes in a sludge material is considered as an impurity, which inhibited the adsorption capacity. Ash content and fixed carbon in the sludge-derived catalysts, and commercial carbons are presented in Table 6.

Table 6. Ash content and fixed carbon of sludge derived catalysts and commercial carbons

Sl	Sources	Temperature ºC	Ash (%)	Fixed carbon (%)	References
1	Anaerobically digested and dewatered sewage sludge	103	37.39	38.94	[56]
2	Aerobic granular sludge	105	23	48.7	[55]
3	Secondary sludge viscous liquid sludge	105	22.0	39.4	[68]
4	Anaerobic ally digested sewage sludge (DS) and undigested sewage sludge (US)	103	29.9 34.62	36.53 32.04	[98]
5	Dried sewage sludge	105	6.4	32.9	[99]
6	Sewage sludge	110	13.9	30.7	[59]
7	Sewage sludge	105	47.15	6.88	[100]

3.2. Modeling of adsorption studies

Adsorption is an inexpensive technique used for the removal of pollutants from waters and wastewaters. Dyes and metals have been successfully removed from water through the adsorption process [101-110]. For this purpose, activated carbon is widely used. The adsorption isotherm is usually known as equilibrium data in order to design the adsorption systems. The depth of the adsorptive activities of the catalysts depend on the several factors such as concentration of adsorbate, pH, temperature and time. Adsorption capacity of catalysts is determined using different isotherm models such as Langmuir, Freundlich, Redlich-Peterson, Dubinin-Radushkevich, Temkin and BET isotherms. These models have been frequently used to describe the physical and chemical adsorption properties of solid materials [111-115]. The Langmuir and Freundlich isotherms are the most accepted models for the adsorption studies of solid materials.

Isotherm models serve to determine the equilibrium adsorption of catalysts [116]. The surface heterogeneity and type of adsorption can be roughly estimated by the Freundlich parameters. Adsorption equilibrium can be also described by other isotherms such as, Brunauer-Emmett-Teller (BET) model [117]. The Dubinin-Radushkevich isotherm is used to calculate the mean adsorption free energy [118]. Temkin isotherm model is used to determine the effect of temperature [119]. To determine the adsorption capacity of sludge-derived catalysts is nowadays an attracting scope in the wastewater treatment field.

4. ENVIRONMENTAL WASTEWATERS TREATMENT APPLICATIONS

Since the availability of fresh water is getting scarce, it is necessary to start designing new protocols for treating pollutants from water and wastewaters. In Europe, 108 million tons of wastewaters are produced on a yearly basis. About 36 million tons of chemicals and other auxiliary substances must be removed from the textile wastewaters [120]. The majority of the textile industries use 60–70 % of synthetic azo dyes throughout the textile processing steps [121] and ~20 % of dyes are discharged into the industrial wastewaters [122]. The total amount of dyes discharged into the environment is not available. Pollutants come from textile, paper and cosmetic industries and most of the dye pollutants are coloured and highly toxic in nature. They are discharged into the open-water reservoirs and may produce hazardous health problems and limit the photosynthesis in the aquatic living organisms. This section is mostly devoted to various environmental treatment applications.

4.1 Dye wastewaters

The first synthetic dye, the Mauveine compound, was discovered by Perkin in 1856. The synthetic dyes are extensively used mainly in textile industries, pigment units, paper production units and leather industries. Generally, dyes have complex structure with conjugated double bonds, and they are classified in the basis of its structural configuration and physico-chemical properties [123]. Synthetic dyes are classified into acidic, basic, disperse, azo, diazo, and anthra-quinone. The synthetic dye classes and their chemical application in various fields are presented in **Table 7**. Textile industry is one of the most economic growth engines, particularly in the developing countries and azo dyes are the chief constituents of the textile wastewaters. The textile industry presents a global pollution problem owing to the discharge of dye contaminated waters into water bodies, which are having a major impact on the quality and hazardous of water resources. The worldwide annual production of dyes is more than $7{\cdot}10^5$ tons [124].

Table 7. Synthetic dye classes and chemical application

Classes	Characteristics and uses	Chemical types
Acid	Water soluble dyes and applied to fibers (silk, wool, nylon and modified acrylic fibers) using neutral to acid dye baths To affix to fibers by hydrogen bonding and ionic bonding.	Azo anthraquinone, nitro and nitroso.
Basic	Water-soluble dyes and mainly applied to acrylic fibers, and are also used in the coloration of paper.	Azo, cyanine, and anthraquinone.
Reactive	Used on cotton, nylon and wool. This dye have low utilization degree compared to other dyes	Azo, anthraquinone, oxazine and basic.

Direct	Used on cotton, paper, leather, wool, silk and nylon To affix by neutral or slightly alkaline dye bath.	Azo, phthalocyanine, and oxazine.
Disperse	Water insoluble and used to dye nylon, cellulose triacetate, and acrylic fibers.	Azo, anthraquinone, and nitro
Vat	Insoluble in water. Used on cotton and stability of the color in the fiber is excellent.	Anthraquinone and indigoids

4. 2 Available wastewater treatment methods

During the past decades, many reviews have been published on several chemical, physical and biological wastewater treatment processes. Among these treatments some of them are facing many serious problems regarding the secondary by-products and operational costs [125,126,127]. Among the various treatment techniques, adsorption process is the best choice that can provide good results for removing colour and related compounds from water and wastewaters. Until now, most of the researches have been focused on the conventional physico-chemical techniques, including coagulation, ozonation, flocculation, membrane, nanofiltration and advanced oxidation processes for removal of pollutants from the water and wastewaters [128,129]. However, these oxidative reaction practices greatly suffer in terms of poor efficiency. Even though, the nature of these treatment practices, experimental protocol and cost of operation will be the major key points while considering the efficiency of the treatment applications.

4.2.1. Adsorption

Activated carbon is adsorptive, electrochemical and catalytic in nature. The specific properties of activated carbon include the surface functionality, electrochemical, good catalytic capacity, thermal stability and low environmental impact. Many researchers think that the activated carbon material is the best-suited solid for purification of wastewaters, but from the economic point of view, it is unsuitable for many developing countries. The removal of organic pollutants through the granular activated carbon (GAC) with support of microorganisms has been reported

[130]. There are plenty of articles published on adsorption over the activated carbons for treating environmental pollutants [105-107].

4.2.2. Advanced oxidation processes

The advanced oxidation process is a chemical process to remove especially organic compounds in wastewaters and water by oxidation reaction. Advanced oxidation processes (AOPs) are extensively used for the treatment of pollutants from water and wastewater, because the conventional methods are not efficient to the complete mineralization of compounds. AOPs can be able to oxidize the pollutants by oxidizing agents, mainly hydroxyl-free radicals. The ozonation, photoreaction and catalytic wet air oxidation are the main oxidative processes.

4.2.2.1. Ozonation

The ozone is a strong oxidant used for drinking water purification since 1893. In recent years, it has been reported the ozonation treatment of colored compounds from the water and wastewaters [131]. The ozone molecule can oxidize the organic molecules by two possible degradation routes. The presence of organic or inorganic compounds involves direct reaction with the ozone molecule and the indirect reaction with the secondary oxidants formed by the decomposition of O_3 in aqueous solution witch produces highly efficient hydroxyl radicals. The ozonation reaction is used to remove the organic substrate mainly because (i) removal occurs in a single step; (ii) less toxicity (iii) less sludge production (iv) oxidative products decomposed into oxygen and water; (v) simple laboratory set up and (vi) very short time operation [132]. The main advantages of ozonation are that eliminates odors, reduces the chemical oxygen demand containing matters, and increases the suspended solids reduction. This process has several disadvantages such as high investment capital cost, high electric consumption and it is highly corrosive. In a study reported the use of ozone over activated carbon for the removal of biodegradable organic compounds from the aqueous solution [133].

Wen and coworkers investigated the catalytic ozonation with support of sludge-based catalysts for removal of oxalic acid [134]. Some works have been published on the metal-assisted ozonation [135, 136]. Many researchers investigated on catalytic ozonation systems such as, O_3/Fe (III), O_3/Mn (II), O_3/Co (II) and O_3/Ni (II) [137, 138, 139, 140, 141]. The catalytic ozonation for removal organic pollutants under various conditions is presented in Table 8.

Table 8. Catalytic ozonation removal of organic pollutants under various conditions

Type of reaction	Model compound and concentration	Operation conditions	Type of Catalysts & catalyst amount	TOC %	Removal %	References
Ozonation	M_C : Reactive Blue 5 C_c :50 mg/L	S_T: batch ; T: rt ; V: 700 ml ; R_T: 120 O_3: 50 g/Nm^3.	C: Ceria-activated carbon composite C_D: 350 mg	100	--	[142]
	M_C : Sulfanilic acid C_c :1 mM	S_T: batch ; T: 25; V: 1 L; pH: 3.0; R_T: 120 $O_{3\ genrator}$: BMT 802X	C: Ce–Mn–O C_D: 350 mg	63	--	[142]
	M_C : Methylene blue (MB) C_c :0.3 g/L	S_T: batch ; T: rt ; V: ;pH. 11; R_T: 10 min O_3: 2.5 g/h $O_{3\ genrator}$: DHX-SS-03C,	C: MnO_2/O_3 with kaolin C_D :MnO_2: 5g C_D :kaolin:10 g	--	98.9	[143]
	M_C : Acid Red B (ARB) C_c :200 mg/L,	S_T: batch ; T: rt ; V:500 ml; pH: 6.36; R_T: 60 O_3: flow 6 mg/min, $O_{3\ genrator}$: CF-G-3-10	C: Fe–Cu–O powder C_D :1 g/L,	70	90	[144]

S_T: System conditions; T: Temperature; P: pressure; V: Volume S_{BET}: surface area; M_C: Model compound; C_c: compound concentration; C: catalysts; $C_{D:}$ catalysts dose

4.2.2.2. Photo catalytic reaction

In recent years, titanium dioxide (TiO_2) has been successfully applied in many environmental treatment applications, mainly in photocatalysis, and used for different environmental applications [145, 146, 147]. The photocatalysis reactions can be homogeneous and heterogeneous. In **homogeneous photocatalysis** the reactants and photocatalyst are in the same phase. The most commonly used homogeneous photocatalysts include ozone, transition metal oxide and photo-Fenton systems. In this reaction, the reactive species is the radical $^{\bullet}OH$. The efficient hydroxyl radical is produced from ozone. In **heterogeneous photocatalysis** the catalyst and the reactants are in a different phase and photocatalysis reaction occurs in different phases such as, dehydrogenation, metal deposition, water detoxification, and gaseous phase. There are plenty of articles describing the mechanism of photocatalytic reaction. Briefly, the energy of the light is absorbed by the photoactive catalyst materials. The photoactivity of catalyst depends on the ability of the catalyst to create the electron-hole pairs. This active site can generate the free radicals ($^{\bullet}OH$) and further undergo the secondary reactions. Many authors have studied photocatalytic reactions using TiO_2 as catalyst and used them in different environment applications. In the photocatalytic reaction mechanism, hydroxyl radicals ($^{\bullet}OH$) are generated from photocatalyst and radical anions ($O_2^{\bullet-}$) are generated under photoelectron-hole reaction. Some authors have reported the energy of $^{\bullet}OH$ (E_o= 2.72 V) [148, 149] a strong oxidant, and $O_2^{\bullet-}$ (E_o= − 0.33 V) [150] a weak reductant, both produced during the photocatalytic redox processes. A few authors reported the use of TiO_2 deposited on AC for the removal of organic pollutants [151, 152]. The photocatalytic removal of organic pollutants under various conditions is presented in **Table 9.**

Table 9. Photo catalytic removal of organic pollutants under various conditions

Type of reaction	Model compound and concentration	Operation conditions	Type of Catalysts and amount of catalyst	TOC %	Removal %	References
Photo catalytic	M_C : Amaranth C_c :8×10^{-5} mol dm^{-3},	S_T: batch ; T:30 ; V: 150 mL; R_T:100 min pH: 4.3 UV_{Lamp}: 6W UV lamp	C: UV + TiO_2 + H_2O_2 $C_{D:}$: 0.16 g/L		64	[153]
	M_C : Acid Orange II : C_c :0.2mM C_{H2O2} : 10mM	S_T: batch ; T: ; V:. 0.5 L. ; R_T: 90: pH. 3.0 UV_{Lamp}:: 1X8W UVC	C: Bentonite clay-based Fe nanocomposite C_D: 1.0 g/L	50	100	[154]
	M_C : Acid Black 1 C_c : 0.1mM C_{H2O2} : 6.4 mM.	ST: batch ; T:30 ; V:.. ; R_T: 120 UV_{Lamp}: 1 × 8W UV-C	C: Bimetallic Cu/Fe clay catalyst C_D.: 0.5 g/L.	93	--	[155]
	M_C : Orange G dye: C_c :50mg/L C_{H2O2} : 130 mmol/L	S_T: batch ; T: 24 ; V:.. ; pH: R_T:30	C: Cu(II) ions with diethylene triamine: $C_{D:}$ 0.06 g	30	100	[156]

S_T: System conditions; T: Temperature; P: pressure; V: Volume S_{BET}: surface area ; M_C : Model compound ; C_c: compound concentration ;C: catalysts ; $C_{D:}$ catalysts dose

4.2.2.3. Catalytic wet air oxidation

Catalytic wet air oxidation (CWAO) is one of the most economical and environmental-friendly wastewater treatment methods and, besides, this oxidative reaction process is used to treat refractory pollutants from water and wastewaters. Usually, this operation performs at high pressure (0.5–20 MPa) and high-temperature range at 175–320 ^{o}C [157]. This reaction process is a thermal aqueous phase reaction; mainly organic and inorganic compounds are oxidized in presence of oxygen or air. The catalytic wet air oxidation reaction is influenced by parameters, such as, reaction temperature, oxygen partial pressure, reactant concentration, solution pH, and reactor type. For the heterogeneous catalytic oxidation of aqueous organic pollutants, the apparent kinetic model is expressed in terms of either a simple power law or a more complex equation based on an adsorption–desorption mechanism using the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model.

Many researchers have reported the complete mineralization of organic compounds to CO_2, N_2, water and mineral anions [158,159, 160]. Noble metals such as Ru, Rh, Rd, and Pt have been used in the catalytic reaction. The phenol oxidation using various noble metal catalysts has been reported [161]. The catalytic wet air oxidation of organic pollutants over different catalysts is presented in **Table 10**.

Table 10. Catalytic wet air oxidation of organic pollutants over different catalysts

Entry	Reactor conditions	Characteristics of catalysts and compounds	Concluding remarks	References
1	S_T: batch; T: 100 to 180 ºC; P: 25 bar; RT: 80 h liquid flow rate: 0.1 to 0.7 mL/min *Air flow*: 300 mL/min	T_M: Co precipitation & Incipient wetness impregnation; C: Nickel(7wt%) with Mg–Al S_{BET}: 182; M_C: Chromotrope 2R C_c; 50 mg/L C_D: 0.5 g	Removal rate not decrease after two generation cycle. 82 % TOC removal achieved at 150 ^{o}C & 50 bar. No loss of catalytic activity,	[162]
2	S_T: batch; T:260 ºC;P: 5.7 bar; V: 250 mL V_{liquid}:0.33 mL/min, V_{gas}:40 mL/min RT: 410 h	T_M: Impregnation *C:* Ru/TiZrO4 S_{BET}: 52.38 M_C: Isophorone C_c; 5000 mg/L C_D: 10 mg	95 % of TOC removal achieved, and formation of free-radical chemical reactions.	[163]
4	S_T: continuous RT: 42 h T: 200 ºC *P:* 25.5 bar Air Flow rate: 60 mL/min Liquid flow: 0.5 mL/min	T_M:: Alkaline hydrothermal synthesis *C:* Titanate nanotube-based catalysts $S_{BET:}$: M_C: Bisphenol-A C_D 300 mg C_c: 10 mg/L	70 % of conversion achieved and no catalyst deactivation occurred	[164]

5	S_T: batch *RT*: 420 h *T*: 150 *P:* 30 Air Flow rate: 30 NL/h	T_M: Carbonization *C:* Carbonaceous materials $S_{BET:}$: 985 M_C: :Phenol C_D : 2 g C_c: 0.05 mol/L	90 % of phenol conversion achieved, the materials adsorptive properties and metal contents influenced the oxidation process	[165]

S_T: System conditions; T: Temperature; P: pressure ; V: Volume S_{BET}: surface area ; M_C : Model compound ; C_c: compound concentration ;C: catalysts ; $C_{D:}$ catalysts dose

4.3 Biological treatment

The biological treatment has been frequently considered, in the scientific literature, as the best method for the complete mineralization of the organic pollutants, also leading to complete detoxification, and avoiding the problems of sludge disposal and maximizing the catalytic reactions. The biological treatment can be anaerobic, aerobic or a combination of both. The use of biomass (fungi, algal and bacteria) in the biologic anaerobic treatment of textile effluents has been proven to be a better option compared to the conventional methods. The biological treatment may occur due to microbial enzymes, which are adsorbed on the activated carbon micropores [166,167]. Aerobic bacteria adapt very well to produce azo reductase under specific controlled conditions but, on the other hand, anaerobic bacteria reduction under specific conditions is relatively unspecific [168].

The anaerobic sequential UASB/aerobic CSTR reactor treatment has recently proved to be effective in the complete biodegradation and decolourization of mixed dyes at a very short residence time [169]. Most of the biological reactions are non-specific extra-cellular processes and there is interaction between the cellular enzymes and the dye molecules [170]. To date, several studies have been conducted on the use of biological methods for the treatment of dye containing water and wastewaters [171]. Beach and co-workers studied the biological and chemical treatment of wastewater effluents [172] and Fabregat group has recently reported the anaerobic degradation of azo-dye using sludge-based catalysts using up flow packed bed reactor system methods [48]. The effective degradation of azo-dyes in wastewater has been reported by Coughlin et al., [173] and Khehra et al., [174]. Forgacs and co-workers have reported the decolorization of azo dyes under aerobic/anaerobic conditions [175]. Some of the biological treatment applications are summarized in Table 11.

Table 11. Biological wastewater treatment of organic pollutants over different catalysts

Sl	Dyes/Type of samples	Biological organism	Type of reactor	Time (Duration)	% of removal	References
				(Res)		
			SBBR	24	Dye: 75 %	
1	Reactive Red 3.1	Anaerobic mixed culture	PBR	24	Dye: 90 %	[176]
				(Res)		
			STR	27	Dye: 93 %	
			SBBR	24	Dye: 90 %	
2	Acid Oragnge 7	Anaerobic microbes living and dead	SBCR	24 cycle	Dye : 100 % COD: 88 %	[177]
3	Acid Orange 7	Anaerobic Methanogenic	Fed- batch and continues UASB	0.4 HRT	Dye : 92 %	[178]
4	Congo Red	Mesophilc anaerobic	Two stage Anaerobic system UASB	HRT 8 h	Dye: 95 – 99 %	[179]
5	Acid Orange 7	Anaerobic sludge	USPBR	0.5 space time	Dye : 90- 96 %	[180]
6	Acid Orange 7 Reactive Black 3HN	Anaerobic – sewage primary stage	Semi continues	HRT 10 D	Dye : 99 % COD : 95 %	[181]
7	Reactive Black 5	Aerobic acclimated	Sequential		Dye: 90 %	[182]

			Anaerobic and aerobic	48 h		
8	Tectilon Red 2B Tectilon Orange 3 G	Activated sludge	STR	24 h	Dye: 80 %	[183]
9	Acid Oragnge 7	Anaerobic sludge	UASB and SBR	HRT 48 h	Dye: 97 % Dye : 95 %	[184]
10	Direct Red 80 Mordant Blue 9	Phanerochaete chrysosporium	Batch	24 h	Dye: 92 – 94 %	[185]
11	Acid Red 151	Aspergillus fumigatus fresenius	Batch	7 D	Dye :84.8 %	[186]
12	Methyl violet Congo Red, Acid Orange Acid Red 114,Acid green	Phanerochaete chrysosporium	Batch	7 D	Dyes: 72- 95 %	[187]
13	Reactive Red	Bacillus cereus	Batch	72 h	Dye : 97 %	[188]
14	Basic Blue 3 Basic Red 2 Acid Yellow 17	Anaerobic and aerobic sludge	UASB	12 h HRT	Dye : 20 – 78 %	[189]
15	Acid Orange Direct Red 254	Mixed anaerobic	UASB	24 HRT	Dye : 88 %	[190]
16	Acid Orange	Methanogenic	Batch	20 D	Dye :10-20 %	[178]
17	Reactive Red 141	Mixed Bacterial	Semi continus	10 D	Dye: 98-99 %	[191]

	Reactive Blue 13			HRT		
18	Synthetic waste water	Anaerobic inoculums	Multi stage biofilm	24 to 16 HRT	COD : 88.3- 91.6 %	[192]
19	Synthetic waste water	Mesophilic	AFBR	30 D	COD. 80 %	[193]
20	Acid Red 1 Reactive Black 5	Rhodopsedomonas paustris	PRBC MBBR	5-10 h HRT	Dye: 62.9- 91.0 %	[194]
21	Reactive dark Blue	Fungus Penicillium sp. QQ and bacterium Exiguobacterium sp. TL	Batch	24 h	Dye: 97 %	[195]
22	Methyl Red	Sphingomonas paucimobilis	Batch	5-10 h	Dye: 99.63 %	[196]
23	Reactive Black	Two stage	RDR	15-7.7 h HRT	Dye: 65 %	[197]
24	Cibacron Red FNR	Mesophilic	Batch	24 h- 50 Days	Dye: 92-97 %	[198]
25	Methylene Blue	Activated sludge microbes	UASB	24 h	Dye: 90 %	[184]

SBBR: Sequencing batch biofilm *reactor; PBR: packed bed reactor; STR: Stirred tank reactor; SBCR:* Slurry Bubble Column *Reactor; UASB:* Upflow anaerobic sludge blanket*; CSTR:* Continuous flow stirred-tank *reactor; PRBC: photo-rotating biological contactor; USPBR: Upflow packed bed reactor; MBBR: Moving Bed Biofilm Reactor;* AFBR: anaerobic fluidized bed *reactor; RDR: Rotating Disc Reactor; HRT: hydrolytic retention time; h: hour; D: days.*

6. Conclusions

This review paper gives a broad approach to the current status of sewage sludge, production of sludge-based catalysts methods, surface chemistry and the ultimate uses in various wastewater applications. Huge amount of sewage sludge can be used to produce sludge-based catalysts highly porous, which can replace commercial activated carbons for the removal of various pollutants from water and wastewaters. Moreover, a recent trend in the field of sludge carbon assisted nanocomposites, through the production and study of these nanomaterials is also discussed.

At the present, many research articles have been published on the topic of low cost catalysts from waste materials and its application in various wastewater treatments, but very little evidences have been reported. In this regards, this collection of evidences and data gives a better idea about the low cost adsorbents production from sludge biomass to scientific community.

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CHAPTER 2

Characterization and performance of carbonaceous materials obtained from exhausted sludges for the anaerobic biodecolorization of the azo dye Acid Orange II

This work presents the preliminary study of new carbonaceous materials (CMs) obtained from exhausted sludge, their use in the heterogeneous anaerobic process of biodecolorization of azo dyes and the comparison of their performance with one commercial active carbon. The preparation of carbonaceous materials was conducted through chemical activation and carbonization. Chemical activation was carried out through impregnation of sludge-exhausted materials with $ZnCl_2$ *and the activation by means of carbonization at different temperatures (400, 600 and 800 °C). Their physico chemical and surface characteristics were also investigated. Sludge based carbonaceous (SBC) materials SBC400, SBC600 and SBC800 present values of 13.0, 111.3 and 202.0* m^2/g *of surface area. Biodecolorization levels of 76 % were achieved for SBC600 and 86 % for SBC800 at space time (τ) of 1.0 min, similar to that obtained with commercial activated carbons in the continuous anaerobic up-flow packed bed reactor (UPBR). The experimental data fit well to the first order kinetic model and equilibrium data are well represented by the Langmuir isotherm model. Carbonaceous materials show high level of biodecolorization even at very short space times. Results indicate that carbonaceous materials prepared from sludge-exhausted materials have outstanding textural properties and significant degradation capacity for treating textile effluents.*

Keywords: Azo dye; Biological carbonaceous material; Biodecolorization; Sewage exhausted materials.

1. Introduction

Sewage sludge is an unavoidable byproduct of the treatment of wastewaters and exists in a huge amount around the world. In the European Union alone, the annual production of dry solid sludge exceeds 10 million tons [1]. These huge amounts of waste materials, consequently, cause major handling and disposal problems [2], and are hence available almost free of cost to be used in other forms for various applications. Usually these materials are reutilized in agriculture, incineration, land filling, compost manufacture, bio gas production, manufacture of adsorbents, etc.; some of which will be forbidden in the next future. If the solid wastes are used as low cost adsorbents (LCAs), it will provide a twofold environmental advantage. First, the amount of waste materials is partially reduced and secondly the low-cost adsorbent, if developed, can reduce the contaminants in wastewater at a reasonable cost.

The sludge-exhausted material is carbonaceous in nature and rich in organic materials. Hence, it has the potential to be converted into carbonaceous material if it is pyrolyzed under controlled conditions or through the addition of some chemical agents like zinc chloride and potassium hydroxide in order to increase the surface area and pore volume [3-5]. Activated carbon has been reported to be adsorptive, electrochemical and catalytic in nature. They have the important characteristic property of adsorbing organic compounds in their porous structure, depending on their surface functionality and the content of mineral matter [6-7]. Although many efforts have successfully been devoted to obtaining activated carbons from sewage sludge, even with a very large surface area, the high cost associated with their preparation has pushed researchers to focus their attempts on developing novel efficient, low cost adsorbent materials from sewage sludge [8-20]. Even, a research work patented the preparation of low cost adsorbent from sludge materials [21]. Usually, $ZnCl_2$ is used as a dehydrating reagent [22] and as a tar-formation suppressant [23] as it essentially promotes the aromatization of carbon skeleton and helps to develop a well porous structure [24]. For $ZnCl_2$ activation and carbonization, the reported optimum procedure involves dwell times of 650 °C for 2 h and 550 °C for 1 h respectively [25]. Depending on the conditions of chemical activation involved in the various mechanisms for $ZnCl_2$ activation, good textural properties of porosity and surface area could be developed [26-27]. Since the carbon constituents are converted to tar at high temperatures while burning them off, the sludge material becomes hard and porous in nature. The carbonaceous material is then activated with $ZnCl_2$ and is finally washed with hydrochloric acid solution to remove the extraneous reaction products and un-reacted $ZnCl_2$ particles. Even after the acid-washing of activated carbon, zinc content is still 10 times higher than that in the raw sludge [28]. The adsorption capacity of any carbonaceous material depends on the type of its organic molecule and its micro porosity. However, certain experimental studies reveal that small molecules such as phenol can access micro pores; natural organic matter can access mesopores; and bacteria can access macro pores [29].

On the other hand, textile wastewater pollution mainly comes from the textile processing unit, pigments units, paper industries, and waste water treatment plant. The textile industry presents a global pollution problem owing to the dumping discharge of dye contaminated water into water bodies, which is having a major impact on the quality and hazardous of water resources. The worldwide annual production of dyes is more than 7×10^5 tonnes reported by Joo et al., 2001 [30]. In the past years, many researchers have reported various physico-chemical methods for removing colored compounds from textile wastewater. These methods include coagulation, adsorption, oxidization, electro-chemical and ultra-filtration [31-32]. In fact, all these methods are costly and need additional set up or arrangement to remove the byproducts. Most physicochemical methods can remove dyes efficiently but are not feasible due to their high cost and limited versatility [33]. Alternately, biological treatment methods may present a relatively inexpensive way to remove the effluents from wastewater [34-35]. Biologically activated carbons (BAC), explored in recent researches, encourages anaerobic degradation resulting in improved efficiency of wastewater treatment process [36-37]. The effective degradation of azo dyes in wastewater effluents have already been successfully studied with selected microorganisms [38-39]. Many bacterial, fungal and algal species can absorb or degrade azo-dye molecules. Some studies have demonstrated that the bacterial biodecolorization of azo dyes can take place under aerobic or anaerobic conditions [40-41]. Biodecolorization of water-soluble azo-dyes from dye house effluents, which can influence the environmental parameters, have been achieved with bacterial cultures [42]. These biological methods are friendly from an environmental point of view, which can complete mineralization of organic pollutants at low cost. However, treatments of wastewater containing dyes are still a technical challenge.

Our previous work demonstrated the feasibility of the anaerobic, catalytic reductive azo-dye degradation mechanism using commercial active carbons, so it offers an effective and promising treatment in the reduction of azo dyes. It was also reported that the biological consortia present in this BAC yielded high biodecolorization rates at short space times [43]. In this work, we focus on the preparation, characterization and catalytic performance of carbonaceous materials from exhausted-sludge materials. The strength of this new approach is to use these new materials for the reaction of azo dyes in anaerobic conditions in which biology, chemistry and physics act in a synergistic way to obtain the reactive biodecolorisation at environmental acceptable conditions. The effective biodecolorization of Acid Orange II (AOII) was carried out in a continuous anaerobic (UPBR) system. Thus, this work describes for a comparison of different carbonaceous materials with commercial activated carbon (CAC) in the biodecolorization of AOII. This work also highlights the significance of chemical activation agents, carbonaceous materials yield, ash content and chemical compositions. The adjustment of the experimental results to a first order kinetic model and the batch adsorption equilibrium isotherm studies are included. In addition, surface area, pore size distribution, thermal gravimetric analysis, functional groups and surface images are shown.

2. Methods and materials

2.1. Dye and chemicals

Acid Orange II (dye content 87 %) and sulfanilic acid (min. 99%), sodium acetate (99 %,), zinc chloride (min. 99%), acetic acid (99.8%) and hydrochloric acid (> 37 %,) were purchased from Sigma-Aldrich Company. Activated carbon (Merck, 1.5 mm granules, ref. 1025141000) was crushed and sieved into 0.5 to 0.7 mm in size. Carborundum granule obtained from Carlo Erba Reagents Company was used as inert diluents for the supporting catalyst. The basal media contained the following chemical compounds (mg L^{-1}): $MnSO_4.\cdot H_2O$ (0.155), $CuSO_4\cdot 5H_2O$ (0.285), $ZnSO_4\cdot 7H_2O$ (0.46), $CoCl_2\cdot 6H_2O$ (0.26), $(NH_4)\cdot 6MO_7O_{24}$ (0.285), $MgSO_4\cdot 7H_2O$ (15.2), $CaCl_2$ (13.48), $FeCl_3\cdot 6H_2O$ (29.06), NH_4Cl (190.9), KH_2PO_4 (8.5), $Na_2HPO_4\cdot 2H_2O$ (33.4), and K_2HPO_4 (21.75). These chemicals were obtained from Sigma–Aldrich Company.

2.2. Preparation of carbonaceous material

Anaerobic sludge materials, obtained from the municipal wastewater treatment plant of Reus (Spain), were used to prepare the carbonaceous materials. Slurry sludge was first dried in an oven at 105 ± 1 °C for 24 h and, then solid material was soaked in distilled water for 2 h. The filtered solid material was dried at 105 ± 1 °C for 48 h. The recovered dried material was subsequently crushed and sieved into 0.5 to 0.7 mm in size. 10 g of dried sample was impregnated into 25 mL (deionized water) of 1 M (Molar) zinc chloride solution stirred (300 rpm) for 2 h at room temperature. The $ZnCl_2$ impregnated solid separated from the solution and the sample was dehydrated in an oven at 105 ± 1 °C for 15 h. The impregnated solid material was placed in a quartz reactor (AFORA, Ref no: V59922) and carbonized in a furnace at different stages of temperatures (400, 600 and 800 °C) with a fixed dwell time for 2 h. After the carbonization, the material was washed three times with 5 M hydrochloric acid solution and finally with distilled water until the solution reached to pH 6-7. After that, the material was dried at 105 ± 1 °C in an oven for 15 h and weighed to calculate the yield. The $ZnCl_2$ impregnated material was placed in a plastic bottle at a room temperature for further studies and materials were designated as SBC400, SBC600 and SBC800.

The yield was calculated for the carbonaceous materials hence produced. The carbonaceous material yield (X) was estimated by eq. 1.

$$X = \left(\frac{C_m}{S_m}\right) \times 100 \tag{1}$$

where C_m is the weight of produced carbonaceous materials and S_m is the weight of sludge material.

2.3. *Experimental setup and methods*

The laboratory experimental set up for anaerobic continuous upflow packed-bed reactor (UPBR) with biological carbonaceous material is shown in Fig. 1.

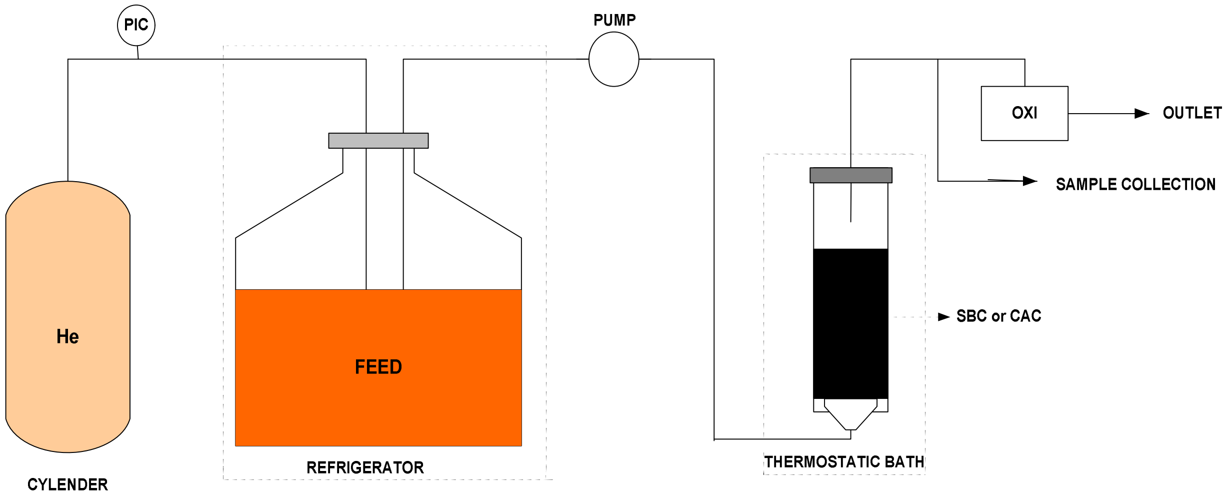


Figure 1. Schematic diagram of the experimental setup of continuous anaerobic upflow

packed-bed bio reactor, UPBR.

The reactor of 15 mm in diameter with an available working volume of about 8 mL was filled with a mixture of 10 g of carborandum granules and 1 g of carbonaceous material used as catalyst. To prevent the washing out of CMs, filters were placed onto the top and bottom of the reactor. To prepare the mixed culture, filtered anaerobic sludge was continuously pumped through the reactor for five days. One reactor outlet is serially connected to other two reactors so that maintained the same culture for all. During this period, mixed culture grown immobilized on the carbonaceous material surface. Through this reactor, a solution containing AOII, basal media and sodium acetate as the carbon source was then fed continuously. The mixed culture within the reactor was maintained at a temperature of 35 ± 1 °C. In the feed bottle, helium gas was continuously bubbled to maintain the anaerobic condition and the pH was adjusted between 6.8 and 7.4 (with acetic acid 10 %). The outlet of the reactor was connected to a redox meter to monitor the redox potential, which was maintained below -500 mV. Experimental points were taken as the average values from triplicate tests for each space time operation. All the experiments were run during, at least, 50 days in order to check the life of the catalysts. In all cases, the conversion obtained was kept constant all over the time.

2.4. Characterization of carbonaceous materials

Surface images of samples were obtained with the electronic scanning microscopy (ESEM)(FEI Quanta 600) using an accelerating voltage of 15 to 20 kV, the elemental composition was obtained by energy dispersive spectrometer (EDS) (Inca system, Oxford instruments) the functional groups of samples were determined using a Fourier transform infrared spectrometer (FT-IR), X-ray diffraction (XRD) spectra were obtained using a D/max-ra X–ray diffract meter (Bruker-AXS D8- Discover diffractometer) with CUk radiation at 40 kV and 40 mA over the 2θ range of 5-70^{o}, the thermal analysis using a TGA analyzer (Perkin-Elmer TGA7) was carried out to investigate the weight loss of the materials and the porosity of the carbonaceous materials was characterized by nitrogen adsorption isotherm. In the N_2 physisorption analysis, adsorption/desorption isotherms at 77 K were measured using a Quadrasorb^{TM} SI (Quantachrome Instruments). The surface area was determined by the BET (Brunauer-Emmett-Teller) method.

2.5. Dye biodecolorization analysis

Acid Orange II, sulfanilic acid (main product of biodecolorization of the AOII), and sodium acetate were analyzed by High Pressure Liquid Chromatography (HPLC) using an Agilent (USA) system equipped with a gradient pump, which impulsed a methanol–water mobile phase at a flow rate of 1 ml min^{-1} through a C18 Hypersil ODS column. A DAD (Diode Array Detector) detector was used to identify the compounds. The analysis for specific wavelengths of each compound yielded 487 nm for Acid Orange II, 252 nm for sulfanilic acid and 210 nm for acetate.

2.6. Adsorption isotherm experiments

Adsorption tests were conducted on a set of six 250 mL Erlenmeyer flasks containing 0.100 g of adsorbent and 50 mL of AOII solutions within the initial concentrations starting range of 12.5 to 400 mg/L. The adsorption experiment was kept for 15 days at ambient room temperature (20 °C) and, each day, 30 s of shaking allowed to maintain a uniform contact between materials and dye solutions. The pH of the solutions was left without any control. The amount of adsorbed dye was measured from the concentrations in the dye solution initial and final adsorption. The amount of adsorbed dye at equilibrium q_e ($\text{mg}_{\text{AOII}}/\text{g}_{\text{CM}}$) was calculated using eq. 2.

$$q_e = \frac{(C_o - C_e)\,V}{W} \tag{2}$$

where, C_o and C_e (mg/L) are the initial and the equilibrium concentrations of dye, respectively. q_e is the amount of adsorbent adsorbed per unit mass of adsorbent (mg/g), V is the volume of the solution (L) and W is the mass of carbonaceous adsorbent used (g). The experiment results reported the average values from duplicate runs.

2.7. Adsorption isotherms modeling

The equilibrium data were then fitted using two different isotherm models, namely the Langmuir and Freundlich models. Langmuir isotherm assumes monolayer adsorption on the catalyst surface. The Langmuir isotherm equation (3) gave accurate information of the experimental data.

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where Q_m (mg_{AOII}/g_{CM}) is the maximum adsorption capacity corresponding to complete monolayer coverage, C_e (mg/L) is the final equilibrium dye solution concentrations, and K_L (L/mg) is the equilibrium constant. The experimental data were also analyzed by using Freundlich isotherm equation (4). It is well described about the non-ideal adsorption process.

$$q_e = K_F C_e^{1/n} \tag{4}$$

where, C_e is the equilibrium concentration of the dye solution (mg/L), K_F and n are Freundlich constants. K_F (mg/g (L/mg) $^{1/n}$) is the adsorption capacity of the adsorbent which can be defined as the absorption coefficient.

3. Results and discussion

3.1. Textural characterization of carbonaceous materials

The physical properties of anaerobic mesophilic sludge were tested according to standard methods [44]. The result of sewage sludge was consisted of 22.7 ± 0.3 of volatile matter, 7.60 ± 0.49 of total carbon, 8.34 ± 0.14 of ashes and the pH range of 7.75 ± 0.34, respectively.

The carbonization yields of the CMs were 83.4 ± 0.1, 69.7 ± 0.5 and 60.4 ± 0.6 wt % for the SBC400, SBC600 and SBC800, respectively. The carbonization temperature does have much influence on the weight loss. The overall weight loss was found to increase with higher carbonization temperature. Increase of temperature also enhances the shrinkage of carbon constituents present in the material, which results in a decrease of the yield of CMs.

Infrared spectroscopy was used to obtain the information on the chemical structure and functional groups on the surface of the dried sludge (DS) and the CMs and the results are shown in Fig. 2.

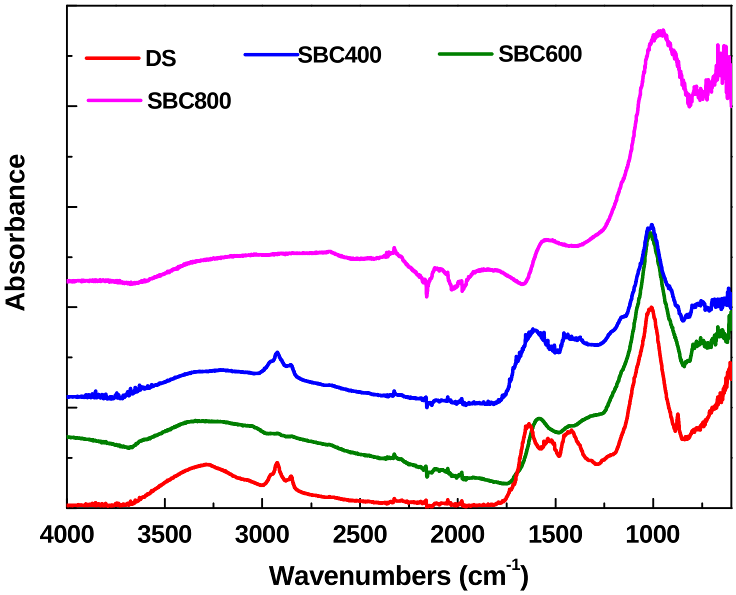


Figure 2. FTIR spectra of DS and the CMs.

Significant changes have occurred in the different carbonization conditions, and some peaks appeared as slightly deviated. The major adsorption bands of dried sludge appears at 3286, 2924, 2853, 2051, 1980, 1635, 1539, 1419, 1022 and 873 cm^{-1}. These peaks correspond to alkenes, ester, aromatic, ketones, alcohol, hydroxyl and carboxyl bonds. The carbonaceous materials prepared at 400 °C and the dried sludge did not give any significant difference in the peak positions. Consequently, the dried sludge and SBC400 material present the same functional groups on the surface. The band frequency at 3286 cm^{-1} is due to the adsorption of water molecules. The band appearing at 2924 cm^{-1} corresponds to ethyl and methylene groups [45] and those at 3200 and 3381 cm^{-1} are attributed to alcohols and phenols. The band range 1981 to 1920 cm^{-1} is assigned to the vibration of C≡N. In the band range of 1400 to 1750 cm^{-1} appears the amides. The band at 1539 cm^{-1} is due to the vibration of aromatic-carbon stretching. The peaks between 1100 to 1200 cm^{-1} are related to alcoholic, phenolic and carboxylic groups [46]. The peaks describe either the Si-O or C-O stretching in alcohol and ether groups [47].

The XRD technique measures the presence of inorganic materials, like quartz and calcite, and also metal oxides (ashes) on the surface of DS and CMs and Fig. 3 shows the experimental results obtained.

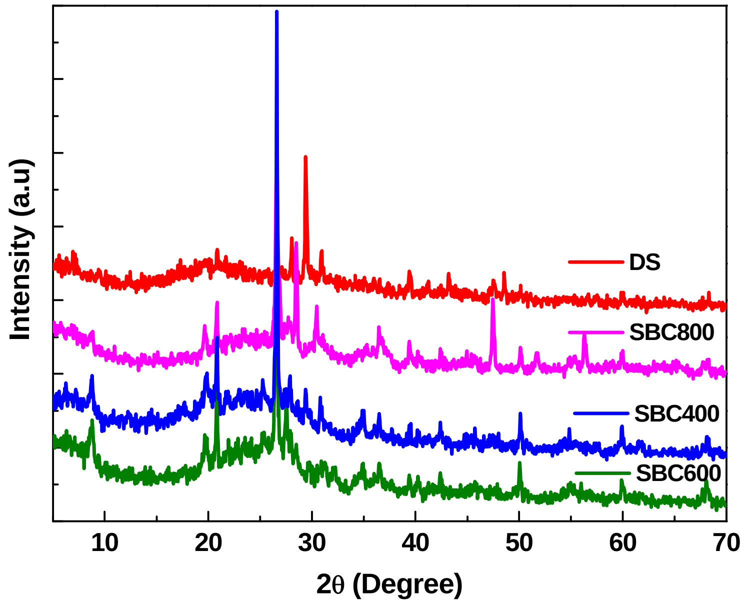


Figure 3. XRD patterns of DS and the CMs. Band labeling: Q, Quartz: C, Calcite

: D, Dolomite.

For the dried sludge, XRD spectra show a great peak of quartz (Q). This peak reduces with temperature. The presence of calcite (C) is greater in SBC600 and SBC800 than in DS and the presence of dolomite is very low in all cases.

Results of thermal analysis of DS and CMs are shown in Fig. 4. The initial weight loss of dried sludge, 14.1 % in the interval 20-300 °C, shown on the TGA curve, was mainly due to the desorption of physically adsorbed water [48].

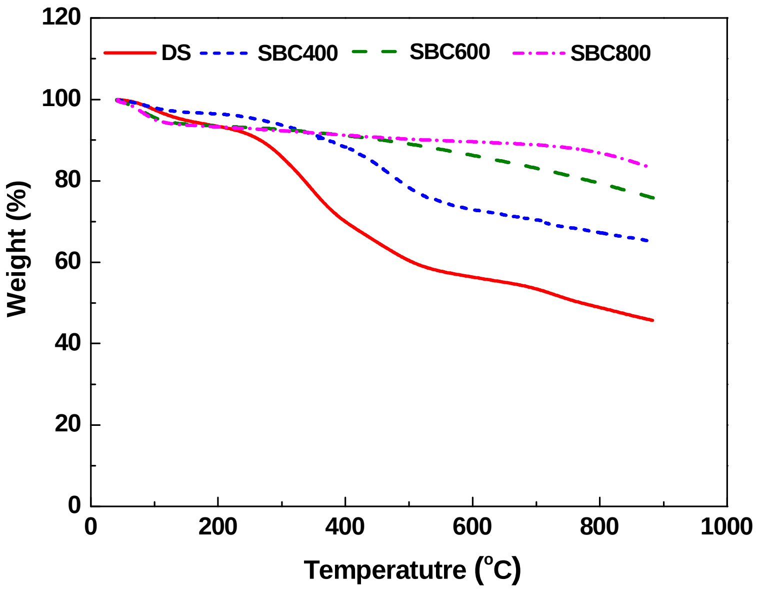


Figure 4. Thermal analysis curves of DS and the CMs.

The TGA curve for the DS also shows an overall weight loss of 54.3 % once reached 900 °C. The dried materials thermal curve was shown the highest weight loss rate at temperature between 350 and 400 ^{o}C. In the case of SBC400, SBC600 and SBC800 materials, the initial weight loss was of 6.3 %, 7.4 % and 8.0 % weight loss respectively, in the interval 20-300 °C. For SBC400, SBC600 and SBC800, total weight losses of 35.0 %, 24.2 % and 17.0 % were observed at 900 °C, respectively. It can be thus noticed that the weight loss of DS is higher than any of the prepared CMs.

ESEM images of the DS and the CMs can be seen in Fig. 5. The micro structure of dried sludge shows homogeneous porous and loosely arranged in space.

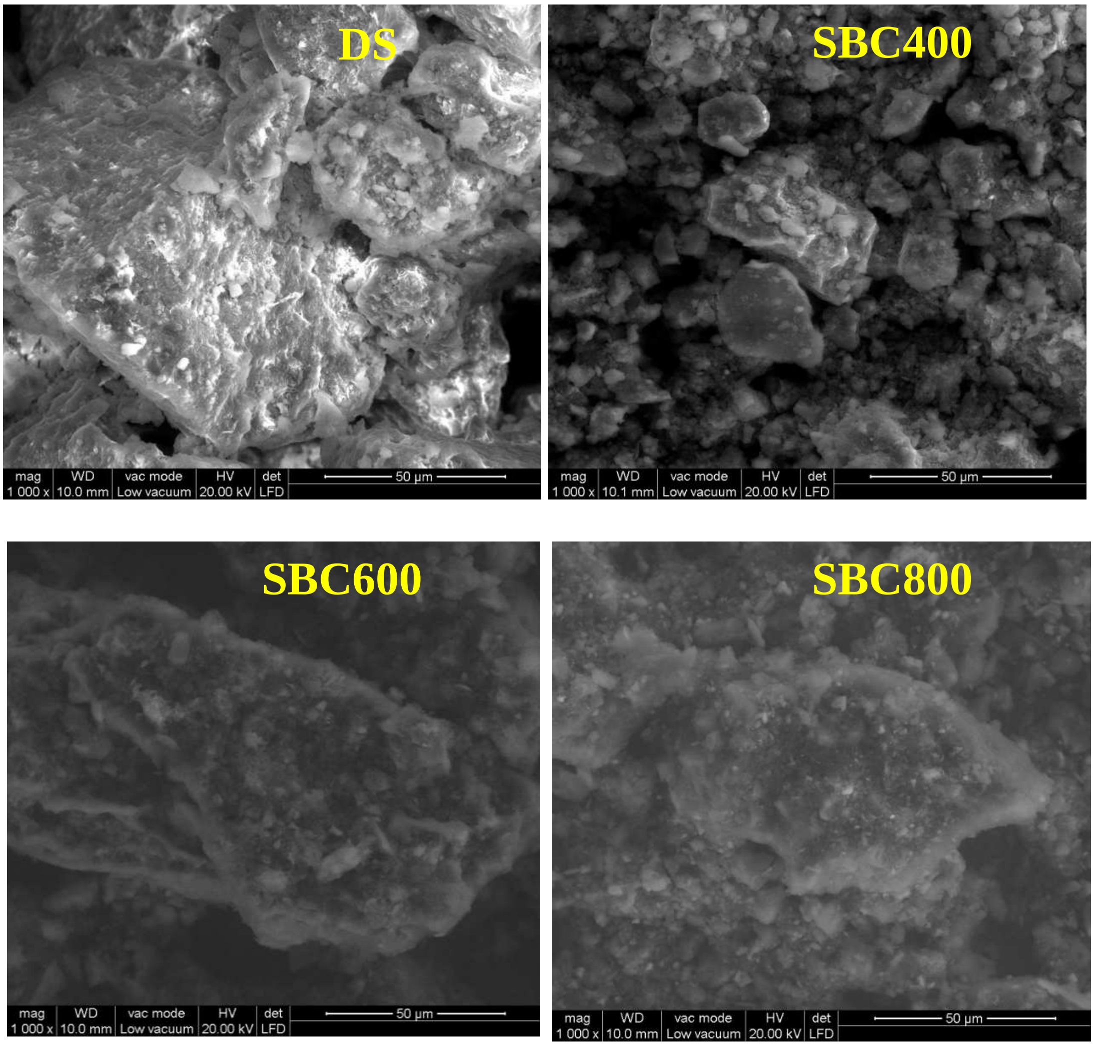


Figure 5. ESEM images of DS and the CMs.

The surface of prepared carbonaceous materials was loose and shows pores of different size, which can hinder the dye-molecule transfer and prevent the catalytic reduction on the material surface.

Energy dispersive spectra analysis permits to measure the weight percentage of carbon and metals, Mg, Al, Fe, Na, K, P, Co, Zn and Ti in the CMs. The results obtained from the chemical analysis data are presented in the Table 1.

Table 1. Ash content and the main elemental compositions of DS and the CMs (Mean value ± SD, *n=3* and **n=2*).

Samples	Ashes*	C	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Cu	Zn
DS	35.34±0.91	35±1.55	40.24±1.97	0.26±0.03	0.6±0.14	3.56±3.45	2.32±0.1	3.62±0.18	2.29±0.07	---	0.28±0.13	6.93±0.83	4.59±0.59	---	---
SBC400	34.53±0.09	53.03±2.26	25.16±0.77	0.31±0.32	0.38±0.13	3.05±0.57	7.76±1.72	0.59±0.29	1.85±0.15	1.86±0.03	0.6±0.05	0.74±0.22	1.53±0.14	0.76±0.23	2.38±0.23
SBC600	36.34±0.12	49.81±2.75	23.05±0.24	0.57±0.12	0.41±0.03	5.72±3.9	7.78±0.87	0.46±0.14	1.77±0.23	2.15±0.38	0.81±0.32	0.51±0.23	1.39±0.24	0.8±0.41	4.77±1.38
SBC800	40.43±0.08	41.85±4.14	25.33±1.48	0.66±0.05	0.92±0.24	7.8±4.27	6.19±1.68	---	2.11±0.22	1.3±0.34	0.37±0.08	0.9±0.71	5.97±1.15	---	6.6±0.84

The percentage of carbon in CMs was in the range of 41-53, higher than that in dried sludge (35 %). All the results reported were obtained from triplicate analysis.

Nitrogen adsorption /desorption isotherms are used to determine the surface area, total pore volume and pore diameter, which provide systematic information on the adsorption mechanism and porous structure. Fig. 6 shows the nitrogen adsorption/desorption isotherms of DS and CMs.

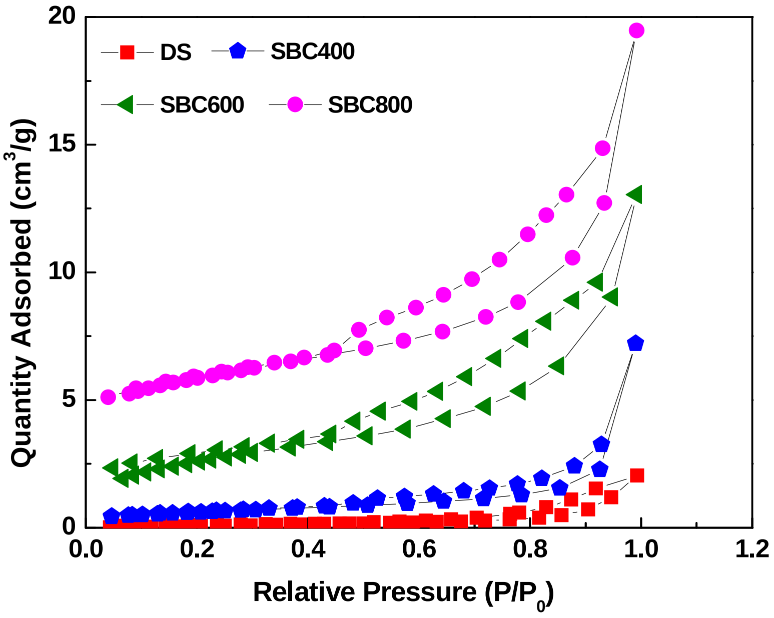


Figure 6. Nitrogen adsorption/desorptions isotherms of the DS and the CMs.

The lower curve of each isotherm measurement was obtained by adsorption, and the upper curve was obtained by desorption. The isotherm results of catalysts are close to each other that indicated the surface textures are almost similar and an isotherm also follows Type - IV adsorption model. The pore diameters of the CMs obtained were in the range of 3.4 to 5.4 Å and the mean pore diameter of dried sludge was 101 Å. The pore size distribution curve for the DS and CMs are shown in Fig. 7.

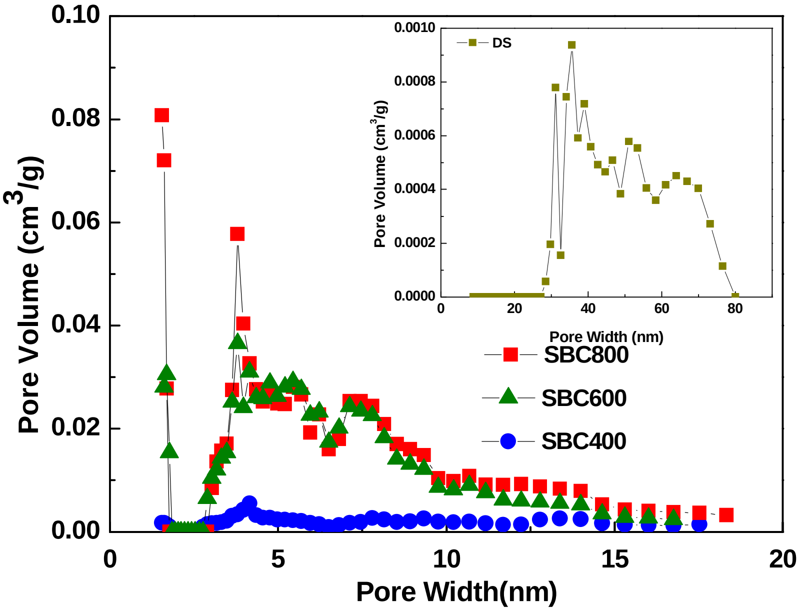


Figure 7. Pore size distribution curves of DS and the CMs.

The average pore diameter of the materials obtained is in the sequence of DS>SBC400>SBC600 >SBC800. Table 2 shows the surface area, total pore volume and average pore diameter of the DS, CMs and CAC.

Table 2. Specific area, total pore volume and average pore diameter of the DS, CMs, and CAC.

Sample code	Temperature (^oC)	BET surface area (m^2/g)	Total pore volume V_t (cm^3/g)	Average pore diameter D_p (Å)
DS	105	6.0	0.02	101.3
SBC400	400	13.0	0.03	5.4
SBC600	600	111.3	0.20	4.0
SBC800	800	202.0	0.24	3.4
CAC	--	1100.0	0.73	13.4

-- *without any treatment*

The specific surface area is often the primary role in an understanding the structure, which is the key characteristics, capable of affecting the quality and value of the materials. A very low surface area (6.0 m^2/g) and pore volume (0.02 cm^3/g) was observed for the CMs prepared at 400 ºC. This may be due to the insufficient heat transferred at its low carbonization temperature, and also due to the absence of volatile substance release, which is required for the development of pores. Low temperatures for carbonization are not adequate to dehydroxylate the inorganic acids and to fully carbonize the organic matter [49]. Also some evidence has suggested [50] that the temperature at 550 °C is enough to attain the required decomposition of the sewage sludge. But below this temperature, sintering and hence a drop in the BET surface area occurs.

The specific surface area of 111.3 and 202.0 m^2/g was obtained for the prepared carbonaceous materials SBC600 and SBC800, respectively. As the temperature is increased up to 600 or 800 °C, many substances decompose. Therefore, the surface area and pore volume of carbonaceous material greatly increase. It is well determined that, with increasing the carbonization temperature, the percentage of inorganic particles, especially Zn metal ions, that leached from the chars are reduced [51]. The higher temperature carbonization induces the conversion of inorganic fraction into mineral compounds. It produces the encapsulation of metals within the carbon phase. Therefore, both the organic and inorganic structures are more reactive to acids. The surface porosity results summarized that the chemical activation and low temperature carbonization created more micro pores than higher temperature activation. However, it has been demonstrated that it is possible to prepare an efficient carbonaceous material through minimal temperature carbonization.

3.2. Adsorption isotherms of carbonaceous materials

Adsorption isotherm is an important method to determine the relation between the dye molecule (adsorbate) and the carbonaceous materials (adsorbents). The correlation of equilibrium data is essential for fundamental understanding the adsorption mechanism. In this study, Langmuir and Freundlich isotherm models were developed. The detailed parameters of these two different forms of isotherm models are presented in Table 3. The Langmuir isotherm model fitted well to AOII with a maximum adsorption capacity of 4.5, 96 and 98 mg_{AOII}/g_{CM} for SBC400, SBC600 and SBC800 materials respectively.

Table 3. Different isotherm model parameters and correlation coefficient for CMs on AOII dye.

Sample code	Langmuir isotherm			Freundlich isotherm		
	K_L (L/mg)	*Qm* (mg/g)	R^2	K_F(mg/g (L/mg)$^{1/n}$)	*1/n*	R^2
SBC400	0.21	4.55	0.96	0.33	--	0.89
SBC600	0.22	96.15	0.99	0.41	1.13	0.79
SBC800	0.37	98.03	0.99	0.39	1.16	0.79

-- the experimental value has no physical sense

Whereas for SBC600 and SBC800, it was observed that the maximum adsorption capacity was found to be similar trend, the SBC400 adsorption capacity was very poor. Figure 8 shows the Langmuir isotherms for AOII onto carbonaceous materials.

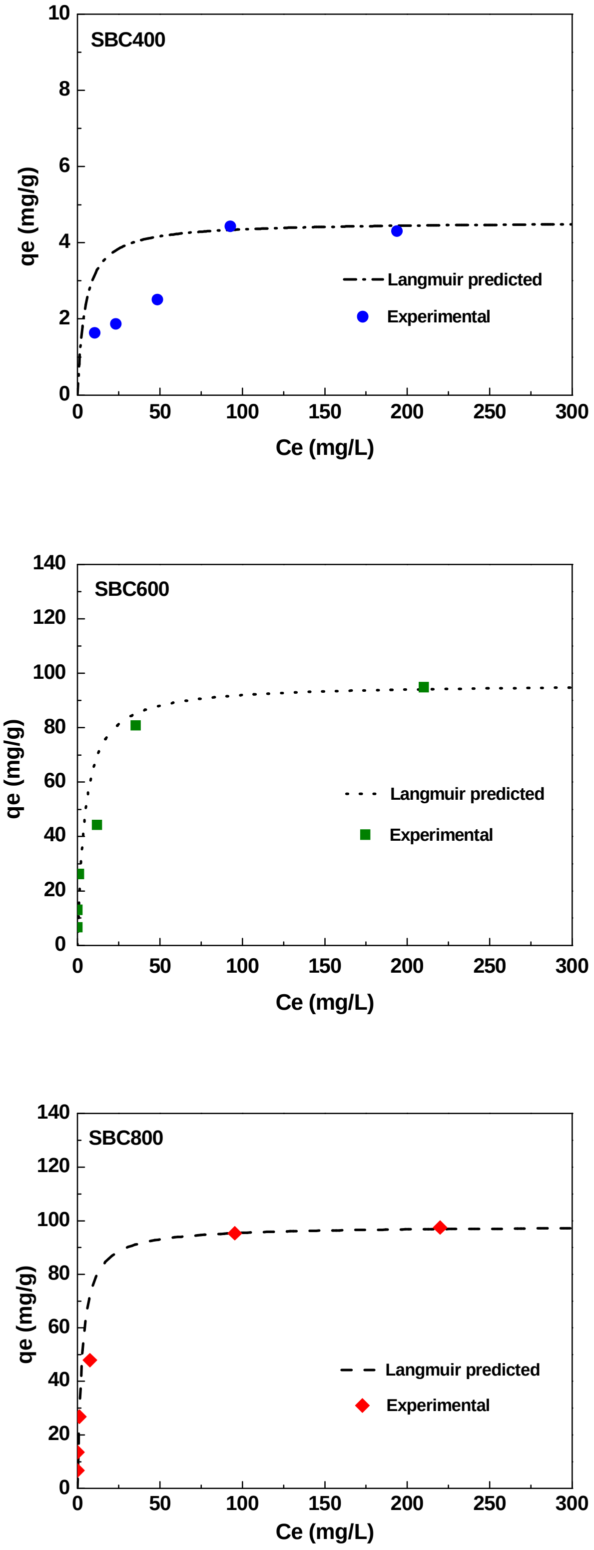


Figure 8. Langmuir isotherms for AOII onto CMs.

The adsorption isotherm of our materials was considered, the SBC600 and SBC800 materials shows similar performance. In case of Freundlich isotherm constants from Table 3, it was observed that isotherm constant K_F was found to be similar for SBC600 and SBC800, 0.41 and 0.39, respectively.

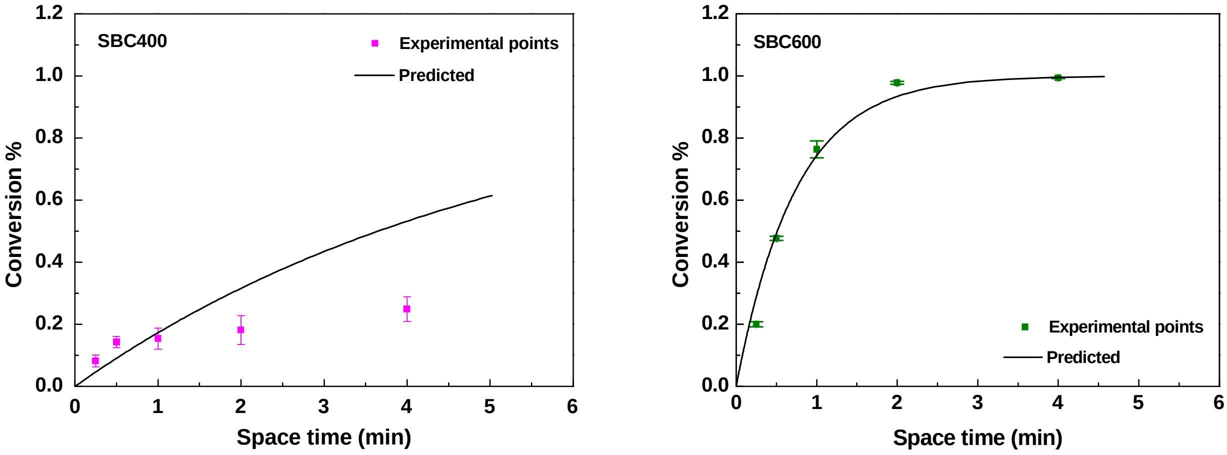
Table 4. First order kinetic model for anaerobic AOII in UPBR bio reactor (Mean value ± SD, *n=5*).

Samples	*Kinetic constants (min-^{1})
SBC400	0.198±0.12
SBC600	1.364±0.36
SBC800	1.801±0.36
CAC	2.844±0.93

* $r_{AOII} = -k.C_{AOII}$ *(First order equation)*

3.3. Catalytic performance of carbonaceous materials

Effective biodecolorization of AOII was carried out in a continuous anaerobic upflow packed bed reactor. The biodecolorization of Acid Orange II dye (Feed concentration: 100 mg/L) onto CMs was checked in an anaerobic continuous up-flow packed bed bioreactor (UPBR) system working at 35 ± 1 °C. The catalytic performance of CMs was checked at different space-times of 4, 2, 1, 0.5 and 0.25 min. At the test start, biodecolorization is high due to the adsorption of dye onto the CMs, until a pseudo steady state is attained. Usually, the surface area is an important factor for the adsorption of organic compounds, since larger surface area results in higher adsorption. The comparison was based on the different carbonization temperatures of the prepared sludge materials with commercial AC. In an UPBR bio reactor, better conversion is achieved even though at short space time (τ) when compared to commercial AC. The results show that the catalytic performances of the CMs are good for dye biodecolorization. AOII conversion about 100% at 4.0 min, 99.9% at 2.0 min, 98.3% at 1 min 74% at 0.5 and 44% 0.25 min were achieved in commercial AC. The achieved biodecolorization of our preparation materials concerned, viz., SBC600 and SBC800, were very similar, but the catalytic performance of SBC400 was observed to be very low. It must be noted that 99% biodecolorization of AOII was obtained with both SBC600 and SBC800 at a space time of 4.0 min operation. The degradation efficiency was 86% in 1 min and 64% in 0.5 min for SBC800. For SBC600, the biodecolorization efficiency is moderately less, being 76% in 1 min and 48% in 0.5 min. The dye removal efficiency of SBC800 and SBC600 is 30% and 20% respectively in 0.25 min. This compares well with the removal efficiency for SBC400, 25 % in 4.0 min and 15 % in 1 min. Only 14 % dye removal is for SBC400 in 0.5 min that cannot consider as a good removal. Table 4 shows the kinetic constants of first-order kinetic data model for AOII in UPBR bio reactor. The experimental data fitted well to the first-order kinetic model. The predicted result of AOII decolorization in bio reactor was favorable for short space time operation. The results show that the SBC400 material is unsuitable for packed bed reactor operation. The representations for first order kinetic modeling are shown in Fig. 9.



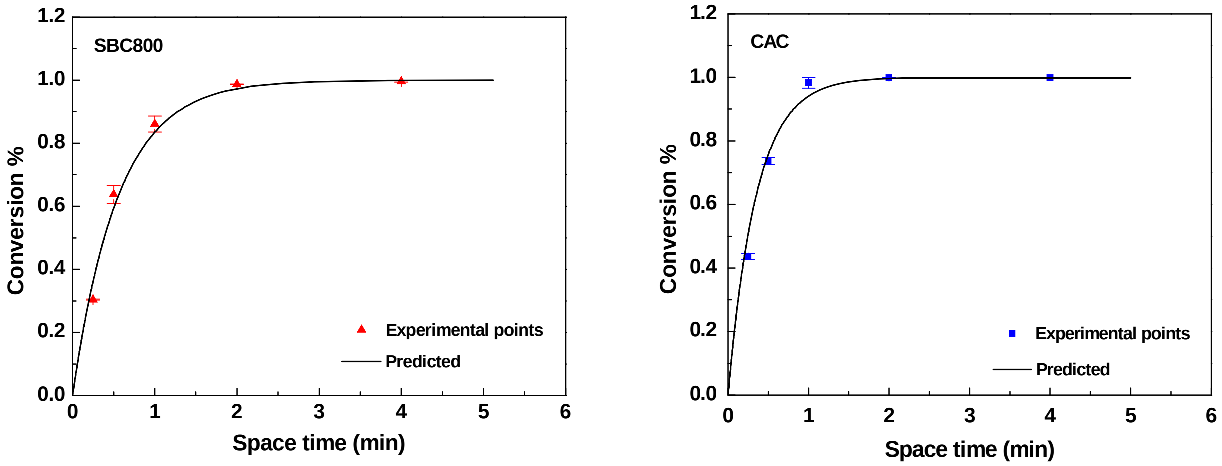


Figure 9. First order kinetic modeling of AOII anaerobic decolorization in UPBR results for fitting of CMs and commercial activated carbons.

The mechanism of the decolorization of azo dye the biomaterial involves a complex process in which biology, chemistry and physics act in a synergistic way for the removal of AOII dye. This mechanism has been already reported [52-53] and, shortly, implies the transport of electrons, produced in an oxidation, through the CMs and the reduction of the double bond catalyzed by the biomass, with the possible collaboration of metals, in anaerobic conditions. This combined action permits the electron to localize on the bio material surface, which is turned into breaking of coloured azo bond (-N=N-) and the formation of colorless aromatic amines of sulfanilic and the1-amino-2-naphthol. Figure 10 shows the decolorized AOII dye and the amount of produced sulfanilic acid (SA) under anaerobic condition. The produced SA molecule is directly proportional to decolorize AOII dye molecule.

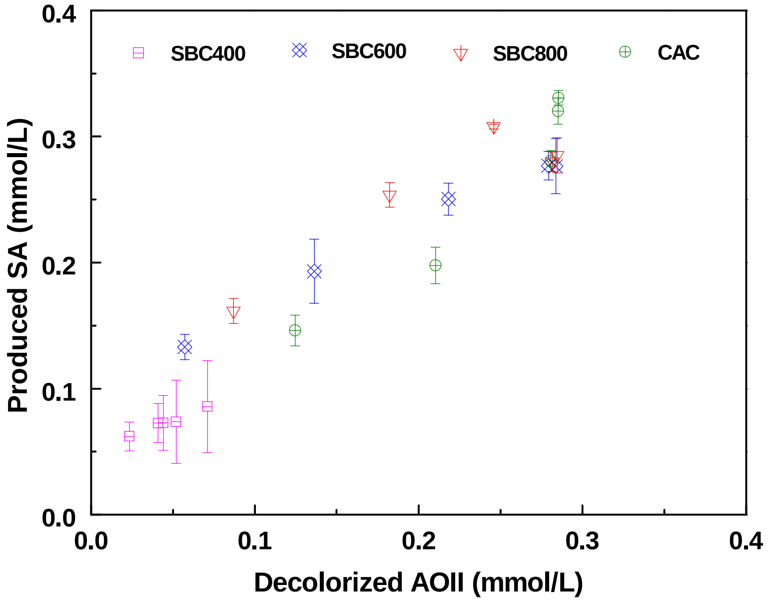


Figure 10. Decolorized AOII dye and the amount of produced sulfanilic acid.

The experimental results indicate that the efficiency of solid material CMs in the anaerobic reduction of azo dye molecule is dependent on its carbonization temperature and chemical treatment, being the conversion obtained comparable to that obtained with commercial activated carbons.

4. Conclusions

In the current work, a continuous up-flow packed bed reactor was used to check the performance of new materials obtained from the exhausted sludge materials for the anaerobic decolorization of AOII in continuous UPBR system at various space time operations.

It has been observed that the addition of zinc metal can increase the catalytic activity and the surface textures, which greatly influence the catalytic reduction of AOII dye molecules.

A better surface texture is developed on the material surface after the acid washing and so, BET surface area, total pore volume and pore diameter, improve after the heat treatment. Adsorption equilibrium data were fitted to Langmuir and Freundlich isotherms, although the equilibrium data were best represented by the Langmuir isotherm model. High conversion rate of AOII dye, with maximum values of 99 %, was achieved in short space times. The catalytic performance of CMs was found similar to that obtained with commercial activated carbon. Overall results show that these CMs are suitable for packed bed reactor operation for azo dye AOII. In the continuous treatment of AOII dye in the UPBR reactor for periods of 50 days no loose of catalytic performance has been observed.

It is possible; therefore, to develop an efficient sludge based carbonaceous material for the treatment of textile effluents, which offers significant advantages over currently available expensive commercial activated carbons.

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CHAPTER 3

A potential application of sludge based catalysts for the anaerobic bio decolorization of tartrazine dye

Two highly efficient (K_2CO_3/sludge carbon and $ZnCl_2$/sludge carbon) solids were prepared by chemical addition followed carbonization at 800 ^{o}C, and were tested for anaerobic reduction of tartrazine dye in a continuous packed bed reactor (UPBR), and their performance was compared to that of commercial activated carbon (CAC). The chemical and structural information of the solids were subjected to various characterizations in order to understand the mechanism for anaerobic decolorization, and efficiency for SBCZN800 and SBCPC800 materials was 87 % and 74 % respectively at a short space time (τ) of 2.0 min. A first-order kinetic model fitted the experimental points and kinetic constants of 0.40, 0.92 and 1.46 min-^{1} were obtained for SBCZN800, SBCPC800 and CAC respectively. The Langmuir and Freundlich model was successfully described the batch adsorption data. Based on these observations cost effective sludge based catalyst can produce from harmful sewage sludge for the treatment of industrial effluents.

Keywords: Sewage sludge; Carbonization; Biodecolorization, Tartrazine, Wastewaters

1. Introduction

Many industrial wastewater effluents, highly coloured, come from textile, paper processing, leather making unit and cosmetic industries, containing bio recalcitrants complex structure and toxic compounds. In Europe, 108 million tons of wastewaters are produced on a yearly basis, and about 36 million tons of chemicals, and other auxiliary substances must be removed from the textile wastewaters [1]. The majority of the textile industries are used about 60–70 % of synthetic azo dye throughout the textile processing steps [2]. In a study by Essawy group [3] has estimated that approximately 20 % of dyes are discharged into industrial wastewaters, and the exact data on the amount of dyes discharged into the environment are not available.

Tartrazine dye is a part of azo dye family, containing azo chromophores (-N=N-) and widely used for several industrial applications. To date, many authors have realized that removing tartrazine from the water, and wastewater is a hard task because it is a stable molecule, not easy to hydrolyze and also difficult to remove by an activated sludge process [4-5]. At present only some authors have demonstrated the removal of tartrazine from the water and wastewaters, including, electrochemical bleaching [6-7], anaerobic baffled reactor [8], and specific solid electrode [9]. Until now, most of the researchers focused on their study related to conventional physico-chemical techniques, which includes coagulation, ozonation, flocculation, membrane, nano- filtration and advanced oxidation processes for the removal of bio recalcitrants from the water and wastewaters [10-11]. However, these oxidative reaction practices greatly suffered from poor efficiency in practical applications. In this circumstance, biological treatment is one of the best tools, cost effective and attractive methods for removing the bio recalcitrants, which leads to complete detoxification, and avoiding the problems of sludge disposal, and it can effectively maximize the catalytic reaction. Currently available treatment methods are not enough to completely removing tartrazine dye from the water and wastewaters.

Activated carbon is porous and amorphous material that remove a variety of organic pollutants from liquid and gases phases by adsorption. On the features and specific use of activated carbon are mainly its surface functionality, adsorptive, electrochemical, thermal stability and low environment impact. Many researchers have sought that activated carbon is the best-suited material for cleaning of wastewaters, but in the economic point of view, it is unsuitable for many developing countries.

On the other hand, sewage sludge disposal practice is one of the big problems for wastewater treatment plants (WWTPs) in the around world. Available disposal practices such as agriculture use, incineration, landfill, fertilizer and other applications are still facing several environmental problems [12]. These huge amounts of sludge solid residues are available at low cost. If these sludge solid materials are converted into useful catalyst supporting materials they can be utilized for the treatment of bio recalcitrant compounds from the waste and waste waters. This sewage sludge basically contains complex mixture of organic, inorganic, volatile, bacterium and other substance that must be removed from the WWTPs. Unfortunately still there is no healthier solution for the proper sludge disposal methods. Since dewatering and drying of sewage biomass is a costly practice, if those are converted into useful products we can be solving a huge amount of sludge problems.

Lebigue's group has reported the solutions of healthier disposal, and produced inexpensive activated carbons from the sludge materials [13]. Some researchers have reported the goodness of sludge assited catalysts for the removal of pollutants from water and wastewaters [14-20]. The production of solid adsorbents from the sewage sludge has been utilized for the mineralization of organic pollutants such as, Methylene blue and Reactive red [21], 4-chlorophenol [22] and Tartrazine [23].

Fabregat's group recently reported the low-cost carbonaceous materials from sludge materials and their uses for anaerobic reduction of azo dye wastewaters in the continuous packed bed reactor system [24]. Generally, anaerobic treatment methods are effective in the removal of azo-dyes, are environmentally safe and cost effective. The anaerobic reaction is a non-specific, micro consortia mediated extra-cellular process. This process is an enzymatic reaction between molecules of dyes and cellular-reducing enzymes [25]. The biological colour removal method from effluents containing dyes has been reported [26].

The preparation of solids from harmful sludge materials for the anaerobic reduction of tartrazine dye in a continuous UPBR reactor was investigated in this work. The surface chemistry of solids was identified using various characterizations in order to obtain the fundamental information for the anaerobic reduction of tartrazine dye in the packed bed reactor system. The mechanism of solid sludge catalysts for biological reduction of tartrazine dye is explained. The adsorption capacity of solid was performed in a batch adsorption equilibrium experiment. To our best knowledge, there is no more study conducted for the anaerobic reduction of tartrazine dye using sludge catalyst in the packed bed reactor system.

2. Materials and methods

2.1. Preparation of sludge based catalysts

Diagram 1 shows the route for the sludge-based catalysts preparation from the sewage biomass. The anaerobic sludge biomass was dried in a furnace at 105 °C for 24 h. The dried product material was soaked in distilled water for 2 h followed by drying at 105 °C for 48h. The resulting dried-sludge materials were grinded and sieved approximately to mesh size ranges of 0.5 to 0.7 mm.

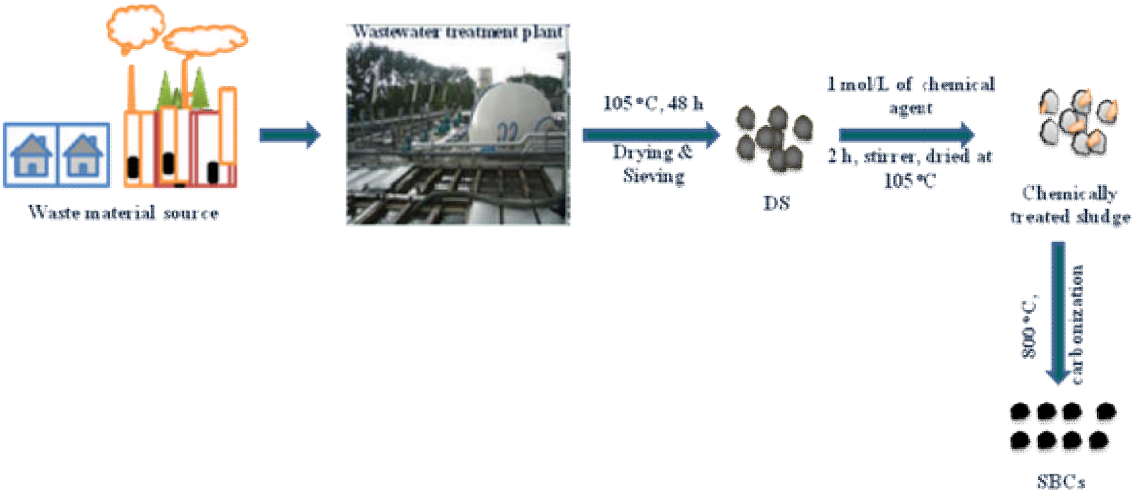


Diagram 1. Preparation of sludge based catalysts from the sewage sludge.

10 g of dried sludge (DS) was added to 25 mL of 1 mol/L K_2CO_3 (Sigma-Aldrich) solution and maintained under stirring for 2 h at room temperature (24 ^{o}C). The impregnated solid material was dried at 105 °C for 24 h, and was placed in a quartz reactor (AFORA, Ref no: V59922) and heated at 800 °C with a fixed dwell time for 2 h. After the carbonization process, product material was washed several times with distilled water and dried at 105 °C for 24 h. The preparation procedure for SBCZN800 solid has been reported [26]. The commercial activated carbon was directly used throughout the experiments.

2.2. Continuous biological UPBR operation

An anaerobic mixed culture was pumped continuously through the solid in the UPBR reactor for a week. The reactor outlet is serially connected to other reactors so that maintained the same culture for all. In the reactor (15 mm in diameter with an working volume of about 8 mL) was filled with a mixture of 10 g of carborundum granules (Carlo Erba Reagents) and 1 g of solid sludge catalyst were used as the biological supporting materials. The mixed anaerobic culture within the reactor was maintained at a temperature of 35 ^{o}C using a thernostatised bath. The feed solution contains tartrazine dye (85 %, Manuel Vilaseca, S.A), sodium acetate (Sigma-aldrich) and synthetic basal media with a composition reported elsewhere [24], the feed solution bottle was kept at inert conditions through bubbling helium gas into the bottom. The concentration of azo dye tartrazine was measured by HPLC instrument. The Agilent (USA) system equipped with a gradient pump, a reversed-phase column C18 Hypersil ODS and a DAD (Diode Detector Array) detector at the specific wavelength of compound to be analyzed (245nm for tartrazine). The mobile phase consists on a sulfuric acid buffer (pH 1.41) with milli-Q water and methanol.

2.3. Batch adsorption experiments

Batch adsorption test was conducted with a set of eight 250 mL of Erlenmeyer flasks. 100 mL of azo dye tartrazine solutions with initial concentrations starting from 25 to 200 mg/L was taken in each flask. 100 mg of solids was added to each flask at room temperature (20 ^{o}C) and the pH of the solutions was without any control. The adsorption experiment was observed for 15 days to reach the equilibrium and each day 30s was shaken to maintain a uniform contact between solid catalyst and dye solution. The initial and final concentration of tartrazine dye was measured by HPLC.

2.4. Surface textures of sludge based catalysts

The ash content of the solids was determined by standard ASTM procedure (2002). The FTIR spectra were recorded in ATR mode using a the Perkin Elmer instrument in the wavenumber range between 4000 to 400 cm^{-1}. BET surface area of the samples was measured by using a QuadrasorbTM SI (Quantachrome Instruments). Surface images of samples were obtained with electronic scanning microscopy (ESEM) (FEI Quanta 600) using an accelerating voltage of 15 to 20 kV, the elemental composition was obtained by Energy-dispersive X-ray spectroscopy (EDX) (Inca system, Oxford instruments). Thermo gravimetric analysis of samples using a TGA thermal analyzer (Perkin-Elmer TGA7) was carried out to investigate the weight loss. XRD spectra were obtained using a D/max-ra X–ray diffractometer (Bruker-AXS D8- Discover diffractometer) with CUk radiation at 40 kV and 40 mA over the 2Θ range of 5 - 70^{o}. The data were collected with an angular step of 0.05^{o} at 3s per step and sample rotation. Microsoft excel work sheet is used for the linear and nonlinear regression data process.

3. Results and discussion

3.1 Chemical and structural information of sludge catalysts

The porosity of new solid sludge catalyst was greatly improved after the chemical addition and high temperature treatment process. The materials originated from sewage sludge contain variety of impurities like ashes, bacterium, exhausted solids, chemical compounds and metal fractions. The textures of new materials were mostly mesoporous, and BET surface area of SBCZN800 material was quite higher in comparison to SBCPC800. BET surface area measured for SBCPC800 and SBCZN800 materials were 106.0 m^2/g and 202.0 m^2/g respectively. The decolorization results show that the removal of tartrazine dye in the packed bed reactor system was influenced for the surface porosity feature.

The adsorption/desorption isotherms of the dried sludge and SBCs are shown in figure 1. The surface area was obtained from the N_2 adsorption isotherms, includes the BET surface area, total pore volume and pore diameter. Isotherm results for both materials were close to each other, which indicated that the surface textures properties are quite similar. The isotherm patterns followed Type IV adsorption isotherm model. Both materials showed the hysteresis loop phenomena.

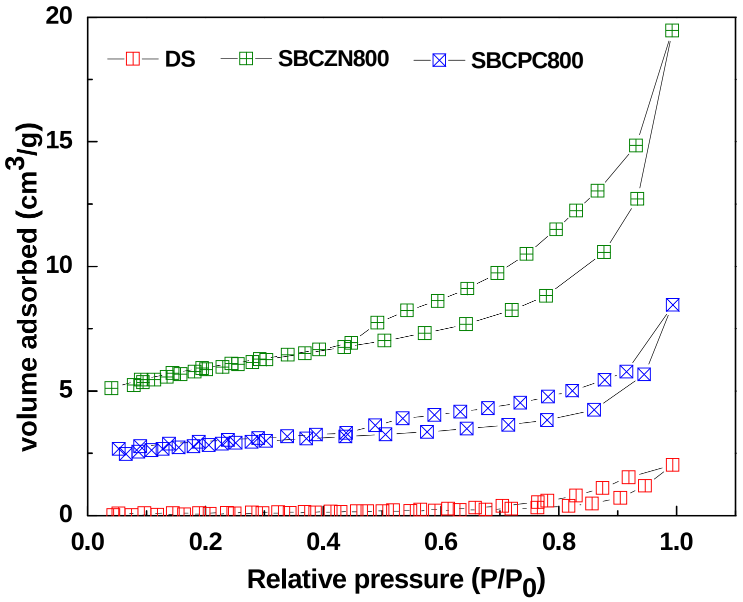


Figure 1. Nitrogen adsorption/desorptions isotherms of the dried sludge and sludge based catalyst.

The microstructure images of dried and SBCs are shown in figure 2. The image of dried sludge material has no detectable pores, and few inorganic particles were also present. After the treatment, the pore structure was clearly visible. Observation of surface porosity was agreed with N_2 adsorption and desorption isotherms. The surface of materials showed chemical particles as potassium carbonate or zinc chloride particles uniformly dispersed. SEM images are quite different for SBCZN800 and SBCPC800, mostly in the pores arrangement. The surface image of SBCPC800 solid has grained cluster and several grooves are visible.

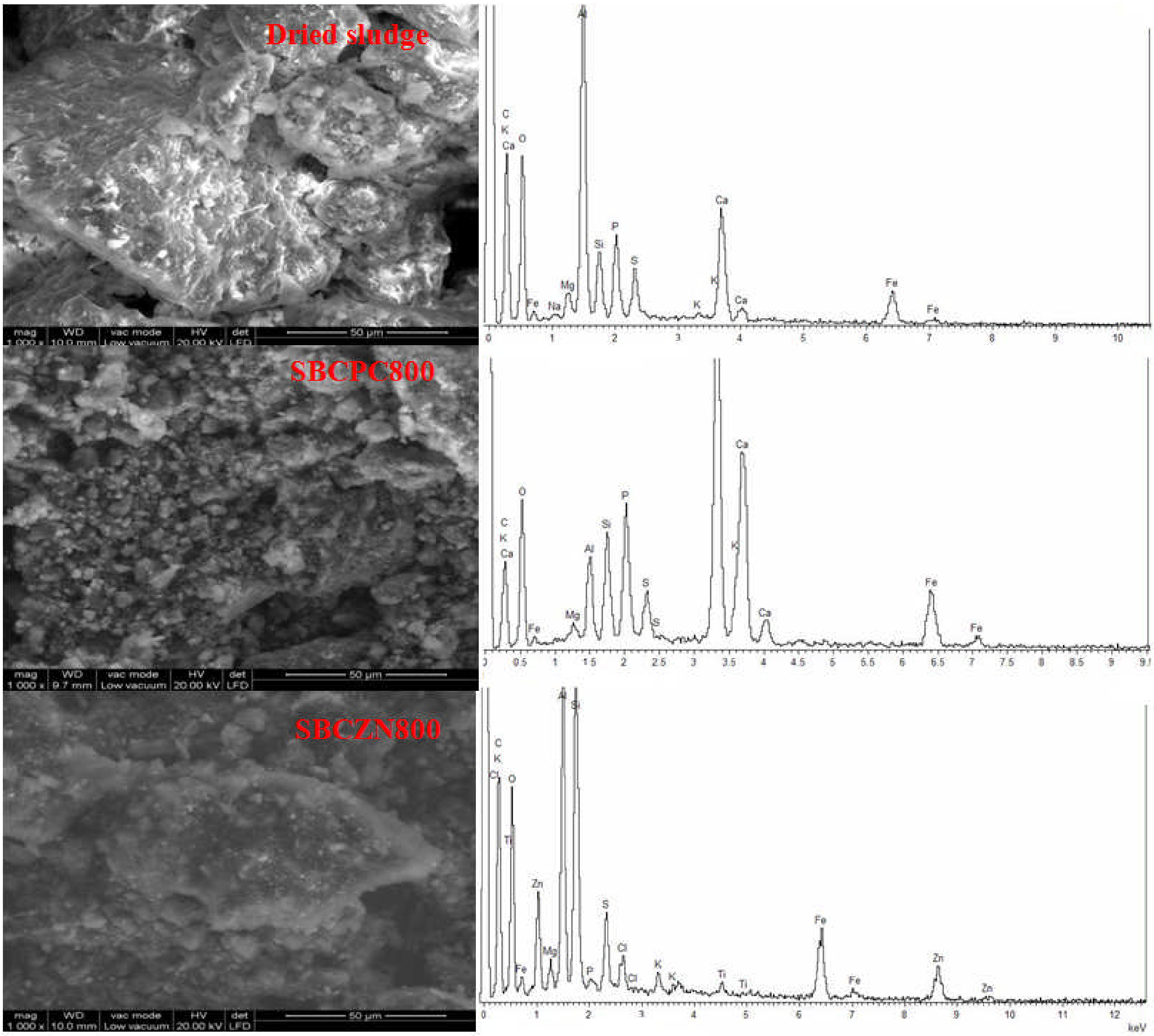


Figure 2. SEM images of the dried sludge and sludge based catalyst.

Figure 3 shows the TG / DTG curves of the dried sludge and SBCs. The weight loss of samples was determined up to 900 °C temperature. In this temperature range, almost all the compounds were decomposed. Since sewage sludge has several impurities such as organic, organic, exhausted solids, volatile matters and metal fractions, after the carbonization at 800 °C, most of the substances were reduced or decomposed. The chemical fractions were joined with the carbon matrix to form a cross-linked structure. Initially, the carbonization was performed at 800 °C most of the hydrates might decompose. Alongside, the evidences agreed with the surface characteristics information and the results show that there is no much hydrate content in the catalysts.

Heat treatment, the carbonaceous content was shrunk and the charred substances occupied the surface of solids. The highest weight loss was observed at 350 to 400 °C temperature range for dried sludge. Lower weight loss was observed for new materials due to the chemical particles incorporated in the interior wall and the solid become hard. It is necessary to have hard solids when the solids were applied in a packed bed reactor, otherwise it can be powdered during the long-term operation.

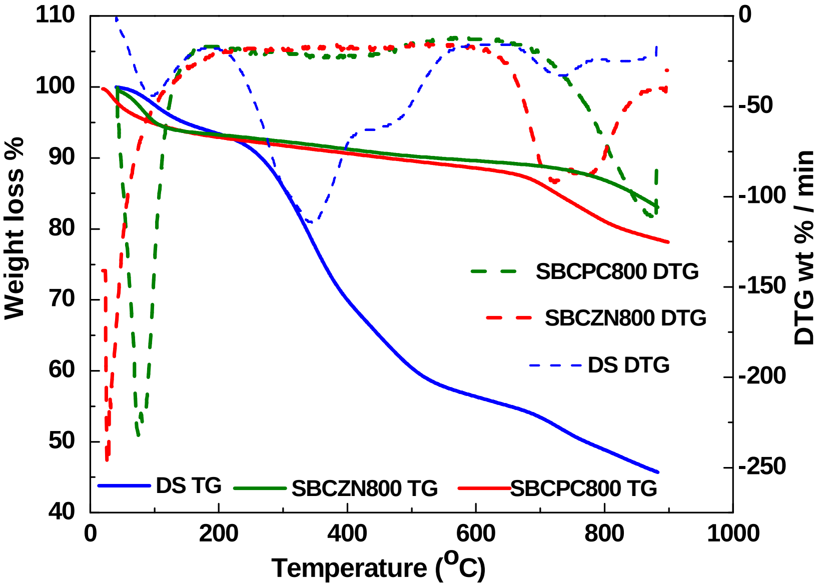


Figure 3. TG-DTG curves of the dried sludge and sludge based catalyst.

The XRD (X-ray diffraction) technique is used to determine the crystalline content of the materials. The results of XRD spectra are shown in figure 4. High amount of quartz (alpha-SiO_2), considerable amount of calcite ($CaCO_3$) and lower amount of dolomite ($CaMg(CO_3)_2$) was detected in the new solids. The presence of inorganic contents increases the mechanical strength of the solids. Higher amount of quartz, calcite, and less dolomite were detected in the DS material. After the thermal treatment, calcite content level was significantly reduced. The presence of the hydrates in the catalyst was very low, which agreed well with the EDX measurement.

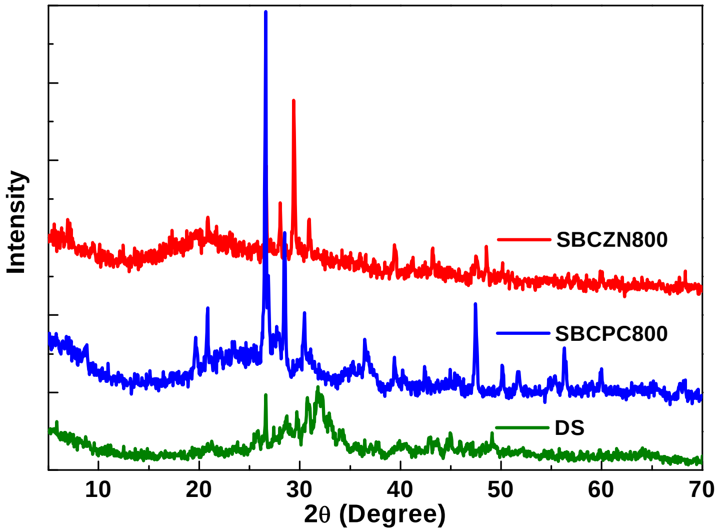


Figure 4. XRD patterns of the dried sludge and sludge based catalyst.

The chemical functional groups of the solids analyzed by FTIR and spectra are shown in figure 5. The sold material had a broad peak at 3400 cm^{-1} related to vibrations of OH groups, after the heat treatment obtained peak was reduced. The bands at 800 cm^{-1} and 1200 cm^{-1} in the solids were attributed to Si- O-Si and Si-O-Al bond. The IR peak at 800 cm^{-1} corresponds to the quartz. The band at 2300 cm^{-1} is mostly due to the alkyne stretching bond. The sharp peaks at 1400 cm^{-1} and 1700 cm^{-1} belong to oxygen and carboxylic groups respectively. The major chemical groups are present in the catalysts, including -OH, C=C, NH, Si-O-C or Si-O-Al. The band at 1612 cm^{-1} is related to vibration of quinine and C=O molecule. The chemical groups are mostly due to aromatic and aliphatic compounds. The functional groups played an important role for the reduction of tartrazine molecules.

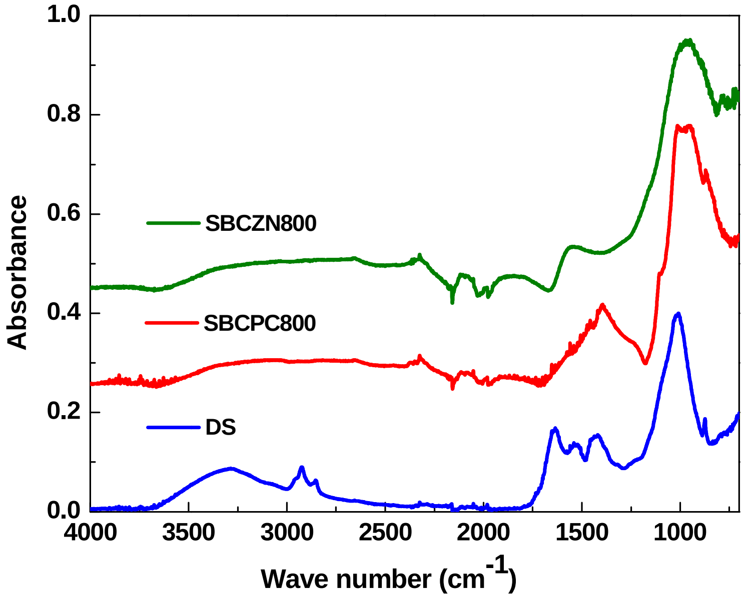


Figure 5. FTIR spectra of the dried sludge and sludge based catalyst

Ash content is an important factor, which is considered as an indicator for the quality of solid materials, but sometime it can reduce the efficiency of catalyst. Generally, ash consists on minerals such as silica, aluminum, iron, magnesium, and calcium. The presence of metal fractions in the SBCZN800 material was higher than that of SBCPC800 material. SEM/EDX analysis is used to detect the metallic content of the samples and are shown figure 2. The ash content for DS was 36 % and new solids were 40 % and 75 % for SBCNZ800, and SBCPC800 respectively. Carbon content is an important factor while considering the adsorption process and was 35, 19 and 42 % for DS, SBCPC800 and SBCZN800 respectively. A measurable amount of oxygen was also detected.

3.2. *Adsorption isotherms results*

Adsorption isotherm study explains how dye molecules interact with sludge-based catalyst, and it is necessary to optimize the adsorption capacity of catalysts in order to understand the adsorption features. The amount of adsorbed tartrazine dye at equilibrium q_e (mg_{AOII}/g_{CM}) was calculated using equation 1.

$$q_e = \frac{(C_o - C_e)\,V}{W} \qquad (1)$$

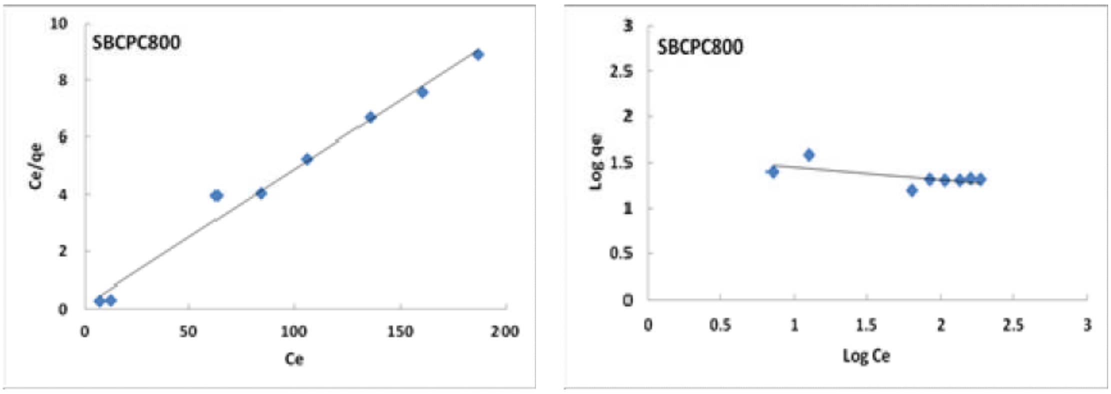
where, *Co* and *Ce* (mg/L) are the initial and the equilibrium concentration of tartrazine dye, respectively. *qe* is the amount of dye adsorbed per unit mass of catalyst (mg/g), *V* is the volume of the solution (L) and *W* is the mass of catalyst used (g).

The equilibrium data analysis was done using two different isotherm models: Langmuir and Freundlich models. The linearized Langmuir isotherm model describes the monolayer adsorption property of the catalysts, and the correlation coefficient (R^2) values was 0.98 and 0.98 for SBCZN800 and SBCPC800 solids, respectively. Results of the Freundlich isotherm correlation coefficient was 0.41 for SBCPC800 material. In case of SBCZN800 the value is very low and was not fitted with the Freundlich isotherm. The results of adsorption isotherm can explain the interactive features between the dye solution and sludge catalysts. The linearized Langmuir (2) and Freundlich (3) models equation are shown below.

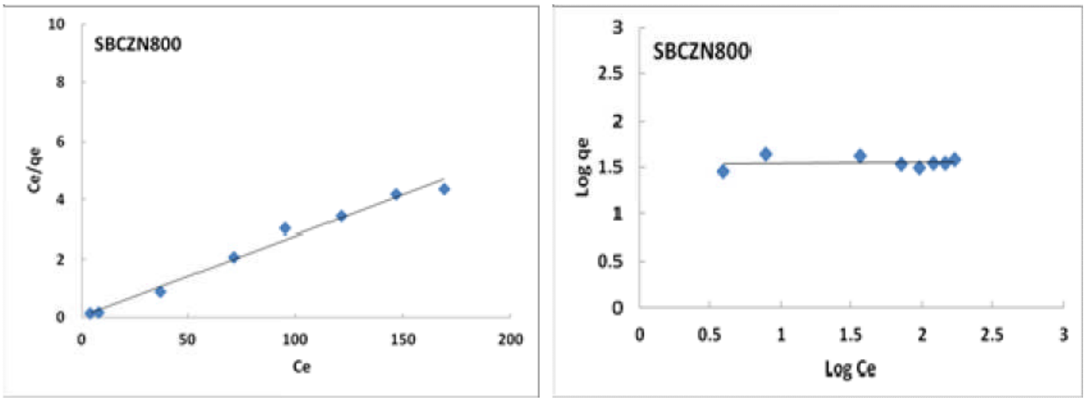
$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{1}{Q_m} C_e \qquad (2)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (3)$$

Figure 6 shows the Linearized plots of the Langmuir and Freundlich models for the adsorption of sludge based catalysts.



(a) (b)



(a) (b)

Figure 6. Linearized plots of the Langmuir (a) and Freundlich (b) models for the adsorption of sludge based carbons.

Isotherm constants were obtained from the linearized models; the obtained values are used to calculate the maximum adsorption capacity by using non linearized Langmuir (4) and Freundlich (5) isotherm equation.

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{4}$$

$$q_e = K_F C_e^{\frac{1}{n}} \tag{5}$$

From the data, Q_m (mg$_{AOII}$/g$_{CM}$) and K_L (L/mg) are the Langmuir constants related to adsorption capacity and rate of adsorption, respectively. K_F and n are the Freundlich constants. K_F (mg/g (L/mg) is the adsorption capacity of the adsorbent which is defined as the absorption coefficient.

Adsorption isotherm data of tartrazine onto the solid fitted better to the Langmuir isotherm, and the maximum monolayer adsorption capacity was 21.0 to 36.5 mg/g for SBCPC800 and SBCZN800, respectively. The adsorption capacity of SBCPC800 solid was low. The observation of batch adsorption isotherms revealed that surface area greatly influenced the adsorption process.

3.3. Biological removal of tartrazine dye

The biological removal of tartrazine dye using the sludge-based catalyst and commercial activated carbons are shown in figure 7. The anaerobic reduction was performed with 100 mg/L of azo dye tartrazine solution at different space time operation (4, 2, 1, 0.5 and 0.25 min). The space time (τ) is calculated using equation 6.

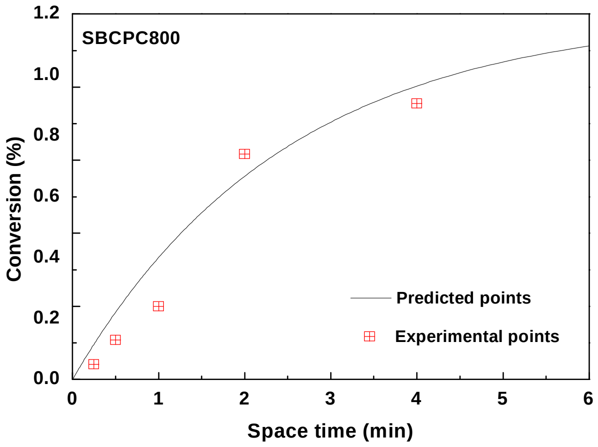
$$\tau = \frac{m_c}{F \cdot \rho} \qquad (6)$$

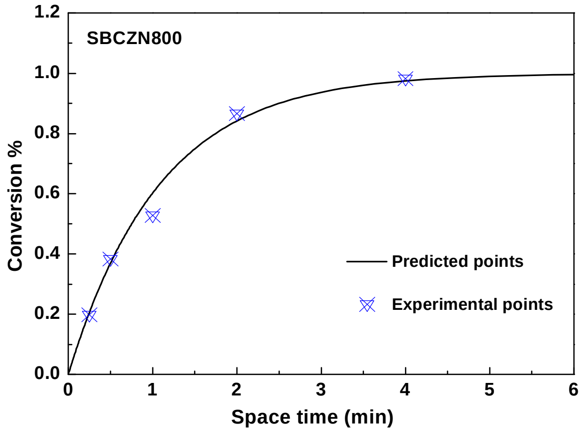
Whre m_c (g) is the amount of sludge based catalysts, F_V (mL/min) is the volumetric flow rate and ρ (g/mL) is the density of the solution.

The experimental results were used to validate the first-order kinetic model by plotting the conversion as a function of the space time (τ). The experimental points were well fitted to first-order kinetic model and the kinetic constants were 0.40, 0.92 and 1.46 min^{-1} for SBCZN800, SBCPC800 and CAC respectively. The SBCZN800 and CAC materials are the most suitable materials and were well fitted to first-order kinetic model in the packed bed reactor system. Whereas, it was imposible to fit to first-order kinetic model the SBCPC800 material.

The addition of chemical agents greatly stimulated the azo dye reduction. The presence of low metal contents could avoid the anti-microbial effects. It has been reported that high metal contents can diminish the microbial population [28]. The experimental result shows that the new solids act as an effective biological supporting catalyst. The performance of catalyst using potassium carbonate shows lower conversion rates and the presence of zinc chloride catalyst obtained a conversion of 53 % at a space time in 1.0 min. The SBCZN800 material shows greater degree of catalytic performance than the SBCPC800. In our previous study we have reported the goodness of SBCZN800 solid for the removal of acid orange II [26]. Only 25 % of dye removal was achieved for SBCPC800 catalyst. The dye removal was 98 % at a space time 4.0 min and 87 % for SBCZN800 material at a space time of 2.0 min operation. 91 % of dye conversion in 4.0 min and 74 % in 2.0 min was achieved for SBCPC800. Removals of 99.95 % at 4.0 min, 92.20 % at 2.0 min, 73.24 % at 1 min, 58.14 % at 0.5 and 30.10 % at 0.25 min were respectively measured for CAC.

In batch experiment, the performance of sludge-based catalyst showed less adsorption capacity. High tartrazine dye removal was measured using catalysts originated from waste sludge biomass, even in minutes of operation. The catalytic activity of SBCZN800 catalyst is only comparable to that of CAC. The experimental results revealed that performance of solids in the anaerobic reduction of tartrazine dye can depend on the several factors including, chemical agents, carbonization, microbial population, chemical groups and surface chemistry.





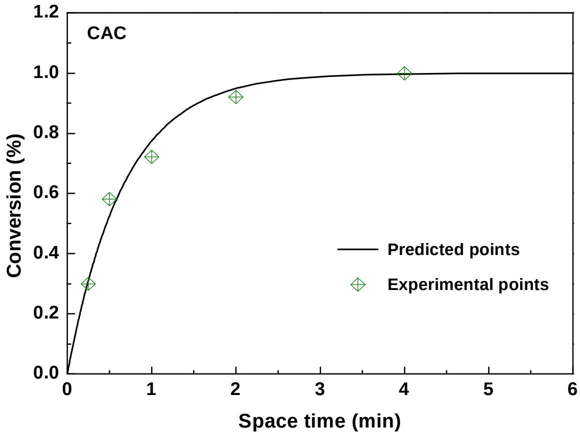


Figure 7. Catalytic performances of the carbonaceous materials and commercial activated carbon.

Figure 8 shows the proposed mechanism for anaerobic reduction of tartrazine dye in the UPBR reactor system. The combined solid sludge catalysts and microbial population acted in the ananerobic reduction process of azo dye. Chemical particles such as potassium or zinc also enhanced the anaerobic reduction. The chemical groups such as quinine and C=O molecule were detected in the FTIR spectra. It is believed that the quinine molecule in the surface of sludge carbon material act as an immobilized redox mediator. The presence of microbial population on the solid sludge carbon surface could act as an electron transmissor. Based on the all evidence, a possible anaerobic mechanism of sludge catalysts can be proposed. It is suggested that sludge carbon accepts the electron from the microbial activity and transfers the electrons to tartrazine dye molecule, further accelerating the biological reduction process to cleavage of -N=N- (azo bond) forms colorless amines. Several metal fractions, chemical groups and crystalline content are identified in the solid material, which also enhanced the anaerobic reduction process

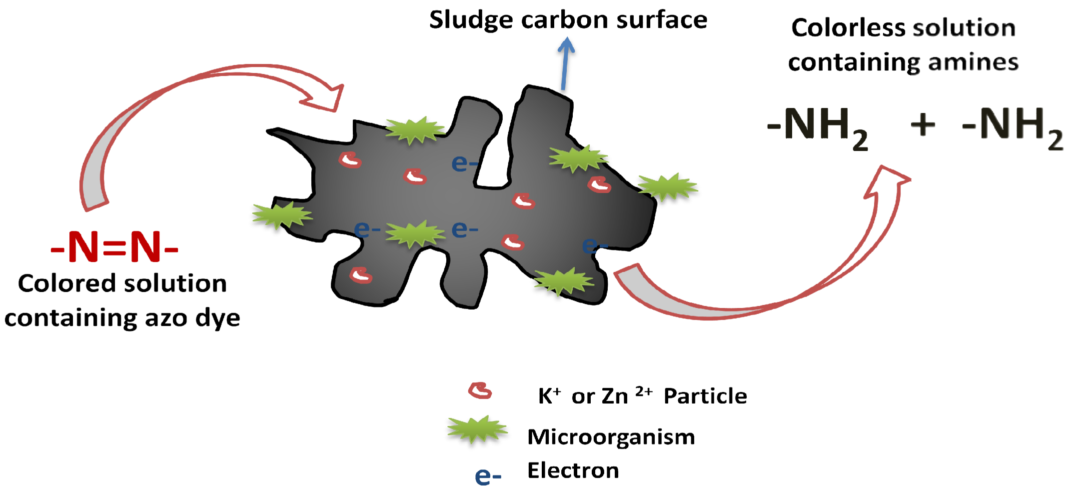


Figure 8. Proposed mechanism for tartrazine dye in the UPBR reactor system.

The catalysts stability was checked during a 30 days continuous experiment in the UPBR reactor system. Figure 9 shows the reduction of tartrazine temporal evolution during the 30-days continuous operations at a space time in 2 min. The samples were collected at regular intervals of each day. During the 30-days continuous operation, nearly 10 samples were taken and analyzed the dye removal rates. The observations show that the removal rates of tartrazine were almost similar for all the solids. Dye removal levels of 85, 73 and 92 % were achieved for SBCZN800, SBCPC800 and CAC respectively. The results show that the new solids have high catalytic stability and could be working for a long term operation in a packed bed reactor.

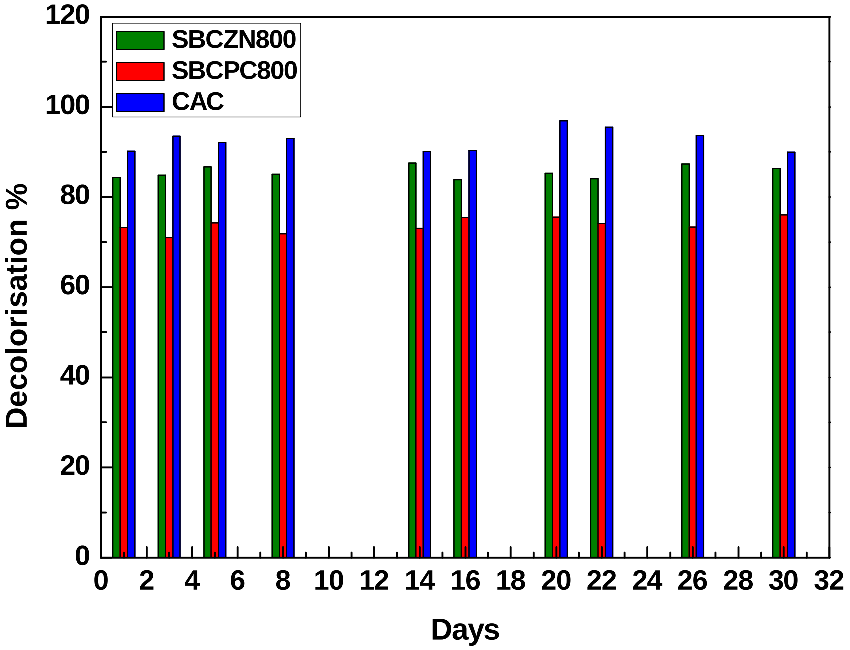


Figure 9. Decolorisation of tartrazine during 30 days continuous operations at space time of 2 min

The behaviour of the solid catalysts when they were introduced in the batch and the continuous experiment was totally different. High tartrzine removal level was achieved for continuous packed bed reactor operation. All the evidences suggested that the newly obtained solids have special synergistic activity when they were applied as biological catalysts. Very limited adsorption capacity was observed in the batch experiment. The adsorption isotherm results show that new solids have less adsorptive properties and act only as inert materials in the batch experiment. This work offers new paradigmatic opportunities for environmentally acceptable reuse of harmful sludge and microbial population for the removal of hazardous pollutants from water and wastewaters.

4. Conclusions

The performance of new solids for anaerobic decolorization of tartrazine dye was successfully investigated in continuous UPBR system. Almost complete biodecolorization of tartrazine dye was achieved at a very short space time. The results revealed that the surface textures and catalytic performances of solids were highly modified by the chemical addition followed of carbonization. Experimental points are well fitted to a first-order kinetic model that describes the behaviours of packed bed reactor operation. Based on these findings of new solids from the harmful sludge materials we can conclude that these materials can be used as cost effective material for the removal of industrial effluents.

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CHAPTER 4

New sludge-based carbonaceous materials impregnated with different metals for anaerobic azo-dye reduction

The addition of Ni^{2+}, Zn^{2+}, Fe^{2+} and Co^{2+} to the carbonaceous materials obtained from waste exhausted solid sludge and their use in the heterogeneous anaerobic reduction of aqueous solutions of the azo dye Acid Orange II (AOII) in a continuous up flow packed bed biological reactor (UPBR) were investigated. The surface chemistry of new sludge based catalysts (SBCs) was characterized by various tools in order to reveal the physico-chemical properties of the materials. The catalysts were also tested for isotherm batch adsorption with AOII dye showing good fitting to the Langmuir isotherm. The impregnation process of the dried sludge was carried out through 1 mol/L solution of salts of the different metals, followed by carbonization at 600 ^{o}C. In the UPBR, high values of AOII dye reduction were achieved at very short space times (τ). AOII conversion was 78 % for SBCZn600, 57 % for SBCFe600, and 55 % for SBCNi600 at a space time of 1.0 min, comparable with that obtained with commercial activated carbons (CAC). 97 % of AOII conversion was achieved for SBCFe600 catalyst at 4.0 min of space time, during 100-days continuous operation without loss of catalytic activity. The results show that the catalytic abilities of impregnated catalyst in the heterogeneous anaerobic reduction of dye molecules is depended on the distribution of metal particle on the surface and, can substitute commercial activated carbons for their use in the elimination of contaminated dye solutions from textile industries.

Keywords: Anaerobic reactor; Biodecolorization; Biofilm; Carbonaceous materials; Impregnation process.

1. Introduction

In recent years, the use of activated carbons for removal of pollutants in wastewater, through both physico-chemical and biological processes, has been reported. Such types of pollutants come from textile, paper and cosmetic industries; most of them are dye pollutants that are coloured, highly toxic in nature, and they are discharged in an open-water reservoir to potentially hazardously affect health and limit photosynthesis in the aquatic living organism. Textile industry is one of the most economic growth engines, particularly in the developing countries and azo dyes are the major constituents of textile wastewater. These substances have a complex structure that contains one or more azo bonds (-N=N-), are synthetic in origin, are hard to degrade in biological aerobic conditions and are also resistant into natural environments [1-2].

In general, the following techniques are used for treatment in the wastewater treatment plants (WWTPs): (i) Adsorption, (ii) Advanced Oxidation Processes (AOPs) (iii) Ozonation (iv) Photo catalysis and (v) Membrane filtration [3], etc. However, these conventional techniques are inefficient in many cases and very limited to destroy the complex compounds, also from an economic point of view. In the current scenario, the use of biomass (fungi, algal and bacteria) in the biologic anaerobic treatment of textile effluents has proven to be a better alternative option to the conventional methods. Recently, authors have been demonstrated the goodness of this approach in continuous mode, using a UPBR bio reactor system with carbonaceous materials (CMs) acting as both adsorbent and catalyst, for the destruction of azo-dye molecules under anaerobic conditions [4]. The effective degradation of azo dyes in wastewater effluents has also been successfully carried out by Coughlin et al. [5] and Khehra et al. [6], and they also reported that selected microorganisms such as bacteria, fungal and algal species have been able to absorb or degrade azo-dyes. Most of the biological reactions are non-specific extra-cellular processes, and the reaction is the interaction between the cellular enzymes and the dye molecules [7].

The biological treatment is one of the best options for the destruction of azo-dyes, considered as environmentally safe and cost effective methods [8]. To date, many studies have been conducted on the use of biological methods for the treatment of water and wastewaters contaminated by dye effluents [9]. The study has been reported on the kinetic parameters of some important catabolic reactions in digesting sludge [10].

Most of the purification methods are carried out through the adsorption onto activated carbons, and those carbons have complex structures and are relatively expensive for their use in catalytic oxidation reactions or other emerging wastewater treatment applications. The sludge based catalysts have been recently presented as good candidate materials in the wastewater treatment because on their surface chemistry and catalytic abilities [11]. Lately, the production of sewage sludge has been estimated around 9 million tonnes during the year of 2005 [12]. The sludge materials have increased tremendously due to the rapid urbanization and industrialization, and these huge amounts of waste materials are available free of cost. If these solid waste materials are converted into adsorbents or carbonaceous materials, they can solve the waste material disposal problems [13]. In general, sludge based adsorbents are a good candidate for removing the organic compounds or inorganic compounds in the aqueous solutions [14-22].

Interestingly, the sludge carbons are capable to attract various active chemical species, which leads to increase the catalytic activity [23-24], there are different protocols to modify their surface textures and access to a variety of pollutants, especially dye molecules. For example, NaOH, KOH, H_2SO_4, $ZnCl_2$, and H_3PO_4 are chemical reagents commonly used to produce the sludge based adsorbents or supporting catalysts [25-30].

Some studies have reported that the heavy metals, such as Zn, Fe, Ni, Co, Mg and Cu, enhance some enzymatic reactions, methane biogenesis and the chemical metabolism [31-34]. The researchers are still focused on the advanced techniques, cost effective, and environmentally friendly practices in the wastewater treatment applications.

The goal of the present work is to investigate the effect of the addition of either Ni^{2+}, Zn^{2+}, Fe^{2+} and Co^{2+} to the carbonaceous materials, and to test them in the bio reactor system for the biodecolorization of aqueous solutions of AOII. The obtained catalysts were characterized by various parameters such as, carbonaceous yields, ash content, BET surface area, total pore volume, TGA, SEM, XRD, FTIR and EDS micro elemental analysis in order to reveal the physico-chemical properties of the catalysts. The catalysts were also tested in an isotherm batch adsorption experiment with AOII dye. To the best of our knowledge, there is no research work reported on the metals impregnation on the carbonaceous materials and their use in biodecolorization of azo dyes.

2. Materials and methods

2.1. Dye and chemicals

The Acid Orange II (dye content, 87 %) and sulfanilic acid (min. 99%), sodium acetate (99 %), and acetic acid (99.8%), hydrochloric acid (min. 37%), were obtained from Sigma Aldrich. The carborundum granules (Carlo Erba Reagents) were used as inert diluents for the catalyst.

The zinc chloride ($ZnCl_2$), nickel chloride ($NiCl_2 \cdot 6H_2O$), ferrous sulphate ($FeSO_4 \cdot 7H_2O$) and cobalt sulfate ($CoSO_4 \cdot 7H_2O$) were used for impregnation process, and all chemicals were obtained from Sigma Aldrich.

2.2. Basal media composition

The basal media contained the following chemical compounds: $MnSO_4 \cdot H_2O$ (0.155 mg/L), $CuSO_4 \cdot 5H_2O$ (0.285 mg/L), $ZnSO_4 \cdot 7H_2O$ (0.46 mg/L), $CoCl_2 \cdot 6H_2O$ (0.26 mg/L), $(NH_4)_6 \cdot MO_7O_{24}$ (0.285 mg/L), $MgSO_4 \cdot 7H_2O$ (15.2 mg/L), $CaCl_2$ (13.48 mg/L), $FeCl_3 \cdot 6H_2O$ (29.06 mg/L), NH_4Cl (190.9 mg/L), KH_2PO_4 (8.5 mg/L), $Na_2HPO_4 \cdot 2H_2O$ (33.4 mg/L), and K_2HPO_4 (21.75 mg/L) were obtained from Fluka and Sigma Aldrich. The stock solution of basal media was prepared in 1000 mL of distilled water. One mL of basal media solution was added per litter of feed AOII dye solution and mixed well. The feed solution was placed in the refrigerator at below 5 ^{o}C in an inert condition for further study.

2.3. Preparation of SBCs

The new materials, Ni/sludge, Fe/sludge, Zn/sludge and Co/sludge, were prepared through an impregnation process, where 10 g of dried solid sludge (0.5 to 0.7 mm in diameter size) were soaked into 25 mL of 1 mol/L of metal salts solution for 2 h under stirring at 300 rpm at room temperature. The metal impregnated solid was separated from the solution, and the solid sample was dehydrated in an oven at 105 °C for 15 h. The solid sample was then carbonized at 600 ^{o}C for 2 h in a quartz reactor (AFORA, Ref no: V59922). The carbonized material was washed three times with 5 mol/L hydrochloric acid solution and then thoroughly washed with deionized water until the pH of 6.0 to 7.0 and, finally, the product was dried in an oven at 105 ^{o}C for 15h. The carbonaceous product yield was calculated as weight of produced carbonaceous materials divided by the weight of dried sludge material. The produced materials was stored in plastic bottles for further studies, and designated as SBCZn600, SBCNi600, SBCFe600 and SBCCo600.

2.4. Characterization of SBCs

The microstructure of catalysts was observed by electronic scanning microscopy (FEI Quanta 600, USA). Main elemental compositions of the catalysts were analyzed by EDS (Inca system, Oxford instruments) instrument. The specific surface area and total pore volume were obtained from N_2 adsorption-desorption isotherms at 77 K (Quadrasorb^{TM} SI Quanta chrome Instruments). The surface area was determined by the BET (Brunauer-Emmett-Teller) method. The inorganic content of the catalysts was determined by XRD (Bruker-AXS D8-Discover diffractometer). The functional groups of catalysts were analyzed by Fourier transform infrared spectrometer (FTIR) in the range of 400 - 4000 cm^{-1}. Thermo gravimetric analysis by the TGA thermal analyzer (Perkin-Elmer TGA7) was carried out to investigate the weight loss of catalysts. The amount of ashes was determined according to standard procedure [35].

2.5. Batch adsorption equilibrium tests

Different AOII solutions with concentrations ranging from 12.5 to 400 mg/L were set in a set of six 250 mL in Erlenmeyer flasks each containing 0.100 g of catalyst and 50 mL of AOII solutions and kept for 15 days at ambient temperature (20 ^{o}C). The pH of the solutions was maintained without any control and the flaks were shaken each day for 30 s to maintain a uniform contact between the catalysts and AOII dye solution.

The equilibrium (mg/L) adsorption capacity was calculated using the equation (1):

$$q_e = \frac{(C_o - C_e)\,V}{W} \qquad (1)$$

where, C_0 and C_e (mg/L) are the initial and the equilibrium concentrations of AOII, respectively; q_e is the amount of azo dye adsorbed per unit mass of adsorbent (mg/g); V (L) is the volume of AOII solution; and W (g) the weight of catalyst used.

2.6. UPBR bio reactor operation

The catalysts are used for the heterogeneous anaerobic reduction of AOII dye in the continuous UPBR system [4]. Operating conditions of continuous UPBR reactor during the experiments are presented in Table.1.

Table 1. Operating conditions of continuous UPBR reactor during the experiments.

Variables	Values
Mass of catalyst, g	1.0
Inert support material (Carborundum), g	10.0
Reactor working volume , mL	8.0
Reaction temperature, ^{o}C	35.0
pH inlet	6.8 - 7.4
Flow rate, mL min^{-1}	15 to 240
Redox Potential (Ag^{+}/AgCl electrode), mV	- 400 to - 500
AOII Concentration, mg/L	100
Sodium acetate concentration, mg/L	200

Before starting the operation, the mixed culture, filtered anaerobic sludge was continuously pumped through the reactor for one week in order to immobilize the microorganisms on the catalyst surface, thus forming a biofilm.

Feedstock contains AOII dye, sodium acetate and basal media and their solution was kept in inert conditions through bubbling helium gas at the bottom of the feed reservoir kept at 5 ºC. The inlet and outlet of AOII dye concentration was measured by High Pressure Liquid Chromatography (HPLC) using an Agilent 1100 series system equipped with a gradient pump, which impulse a methanol–water (M:W) ratio of 70:30 of detecting for AOII, M:W of 0:100 for sulfanilic acid and M:W of 70:30 for acetate with flow rate of 1 mL min^{-1} through a C18 Hypersil ODS column. A Diode array detector was used to identify the compounds. The outlet concentration of the UPBR reactor system was analyzed by specific wavelengths of each compound, at 487 nm for Acid Orange II, 252 nm for sulfanilic acid and 210 nm for acetate.

3. Results and discussion

3.1. Characterization of SBCs

Table 2 presents the carbonaceous yields, carbon, oxygen, silicon and ashes content of the dried sludge (DS) and impregnated catalysts. The carbonaceous product yield of the impregnated catalysts was 63.5 to 70.6 wt % and the ashes content level was 36.33 to 62.44 wt %, more than that of 35.0 wt % in the dried sludge (DS). Due to the heat treatment most of the volatile substances removed from the sludge materials. The sludge materials is decomposed into carbon dioxide and water in the carbonization finally it became a rough shape and metal particles are uniformly distributes on the surface, some metal particles also entrap into the pore cavity.

Table 2. The carbonaceous yield, ashes content and main chemical composition of dried sludge and SBCs

Weight (%)	DS	SBCZn600	SBCFe600	SBCNi600	SBCCo600
Carbonaceous yields	--	70.6	63.5	66.5	65.2
*Ash content	35.0	36.33	62.44	46.76	52.52
**Elemental analysis					
C	35.0	49.81	39.16	45.5	44.68
Si	2.32	7.78	6.29	5.82	5.64
O	40.24	23.05	29.29	21.7	24.2

**Dduplicates analysis, ** Triplicate analysis*

The carbon, oxygen and silicon amounts are significantly changed after the carbonization at 600 ^{o}C. The carbon content was increased up to 44.68 % and the amount of oxygen was slightly decreased. The product of catalysts has become hard and brittle because the amount of silicon content increased, that also may forms binary compounds with Zn, Fe, Ni and Co metal particle. The least amounts of metal elements such as, Na, Ca, K, P, Cl, Mg, and Al besides present on the catalyst; they are detected by EDS spectra.

3.2. Surface area and porosity

The measured values of BET surface area and total pore volume are presented in Table 3. The porosity measurement is an important factor while considering the adsorption of organic compounds on to carbonaceous catalysts. The addition of Ni, Zn, Fe and Co metal particle to carbonaceous materials became a better development of porosity. After the washing of hydrochloric acid solution the produced carbonaceous catalysts surface, area was greatly improved and may remove impurities like, organic, inorganic and ashes in the SBCs.

Table 3. The specific surface area and total pore volume of dried sludge and SBCs.

Sample Code	BET surface area (m^2/g)	Total Pore Volume Vt (Cm^3/g)
DS	6.0	0.02
SBCZn600	111	0.20
SBCFe600	107	0.15
SBCNi600	194	0.24
SBCCo600	161	0.20

For heterogeneous catalysts, surface area is a critical factor while considering in the catalytic reaction. The surface area and total pore volume of produced catalysts were measured 107 to 194 m^2/g and 0.15 to 0.24 cm^3/g, respectively. The SBCNi600 catalyst gave a highest BET surface area of 194 m^2/g and the total pore volume of 0.24 cm^3/g. Table 3 also presents the structural parameters determined by N_2 adsorptions/desorption. The lower curve of each isotherm measurement was obtained by adsorption, and the upper curve was obtained by desorption. The isotherms results of catalysts are close to each other indicating similar surface textures, and they are followed Type - IV adsorption isotherms model. The isotherm curves are shown in figure 1.

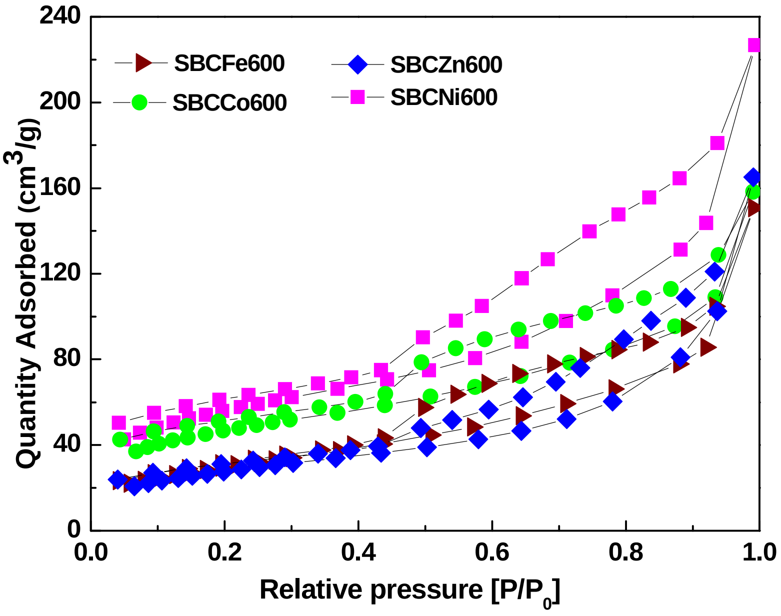


Figure 1. Nitrogen adsorption/desorptions isotherms of SBCs.

The surface porosity of the catalysts has a significant role in the term of adsorption of AOII dye on to catalysts. The pore volume of the catalyst was obtained in the following sequence Co > Fe > Zn > Ni. They are shown in figure 2.

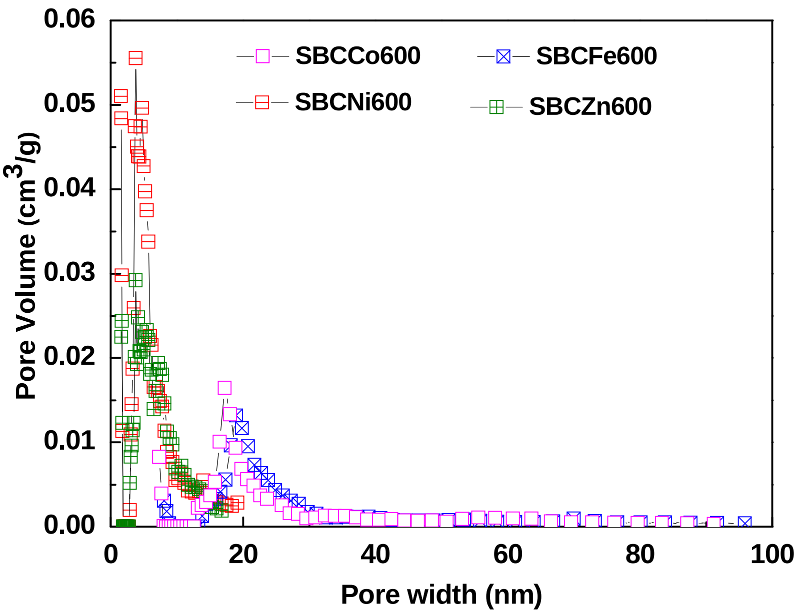


Figure 2. Pore size distribution curves of SBCs.

3.3. Thermo gravimetrical analysis

Figure 3 shows (A) DTG and (B) TGA curves of dried sludge and SBCs. The highest weight loss of materials was observed between 200 to 600 ◦C, which may be due to the decomposition of inorganic matters and oxy (hydroxide) compounds. The first peak was shown at nearly 100 ºC, that represented the physical desorption of water. Overall weight loss of SBCs was 20 to 37 %, less than that of dried sludge 54 % once temperature reached at 900 °C.

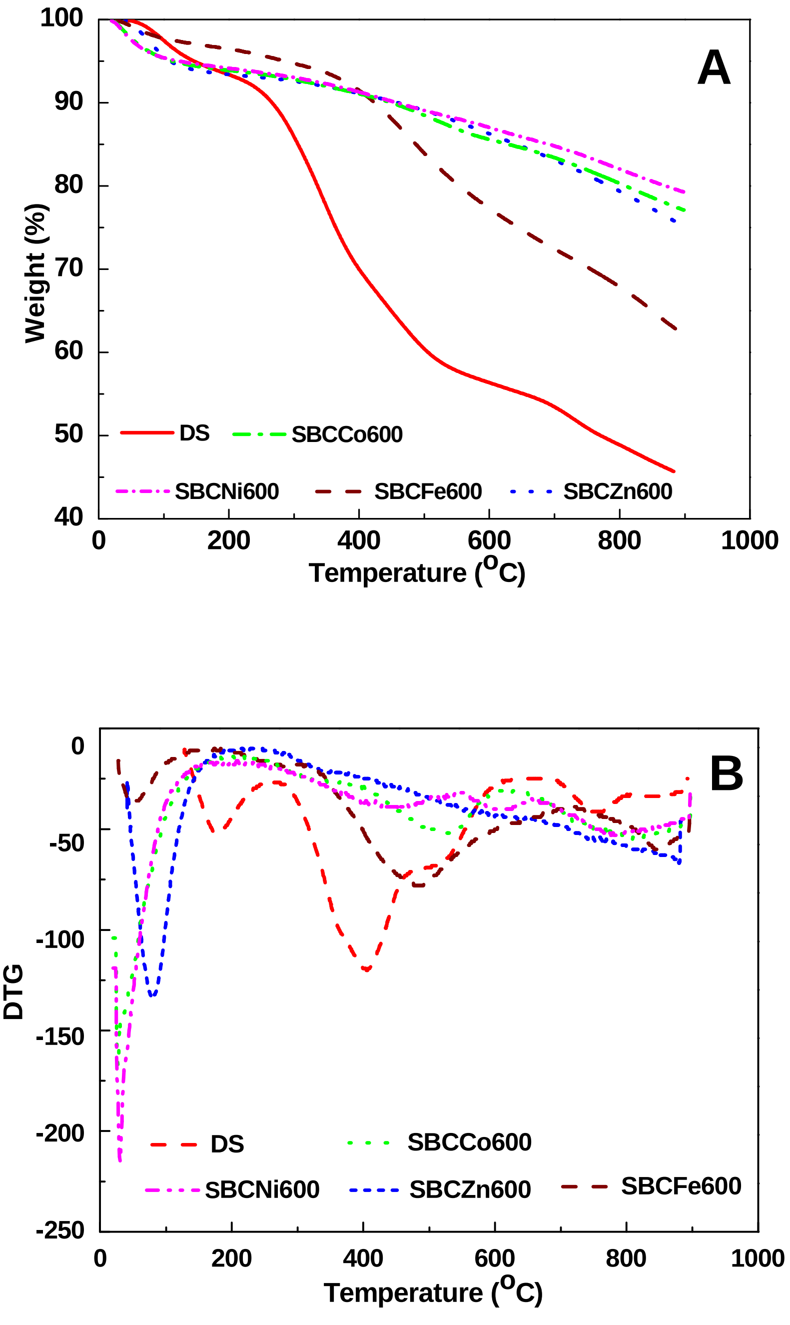


Figure 3. (A) TGA and (B) DTG curves of the dried sludge and SBCs.

3.4. Crystalline contents

The XRD technique is used to get information of inorganic compositions in the catalysts. XRD spectra of dried sludge (DS) material obtained four major sharp peaks at 2 theta 26.5, 28, 29.5

and 31, these peaks are related to quartz (SiO_2), polyhalite ($K_2Ca_2Mg\ (SO_4)_4 \cdot 2H_2O$), calcite ($CaCO_3$) and dolomite ($CaMg\ (CO_3)_2$, respectively. After the heat treatment at 600 °C, the calcite levels gradually decrease. The inorganic content may help to increases catalytic activity. Figure 4 shows the XRD spectra of dried sludge and SBCs.

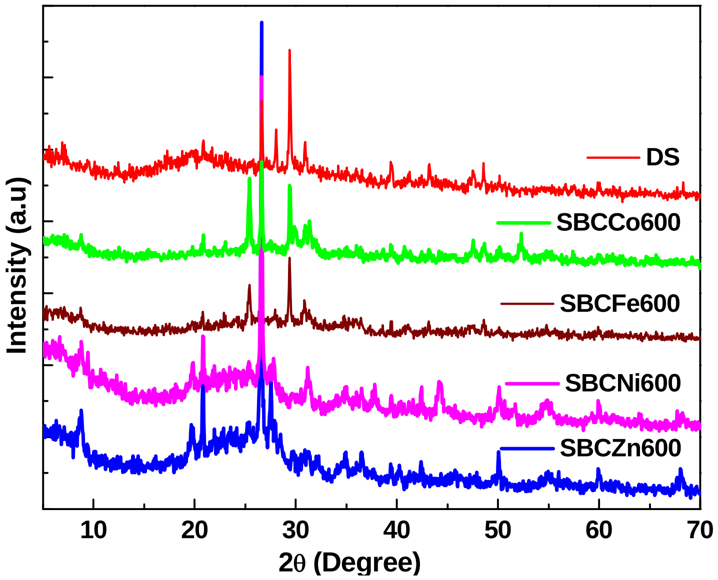


Figure 4. XRD patterns of dried sludge and SBCs.

3.5. Functional groups

FTIR spectra give the functional groups present on the surface of the catalyst. The strong peaks of dried sludge measured at 3286 cm^{-1}, 2924, 2853, 1635, 1539, 1419, 1020 and 873 cm^{-1}, after the heat treatment these peaks are eliminated or reduced (2923, 1539 and 1419 cm^{-1}). The deep bands between 800 and 1020 cm^{-1} are represented to Si-O-Si bond. The band measured in the wave numbers of 3200-3300 cm^{-1} is related to the vibration of -OH groups. The spectral results of various catalysts are very close to each other indicating they have identical structure and functional groups on the surface. After the heat treatment at 600 °C, the obtained peaks show slightly displacement. FTIR spectra are shown in Figure 5.

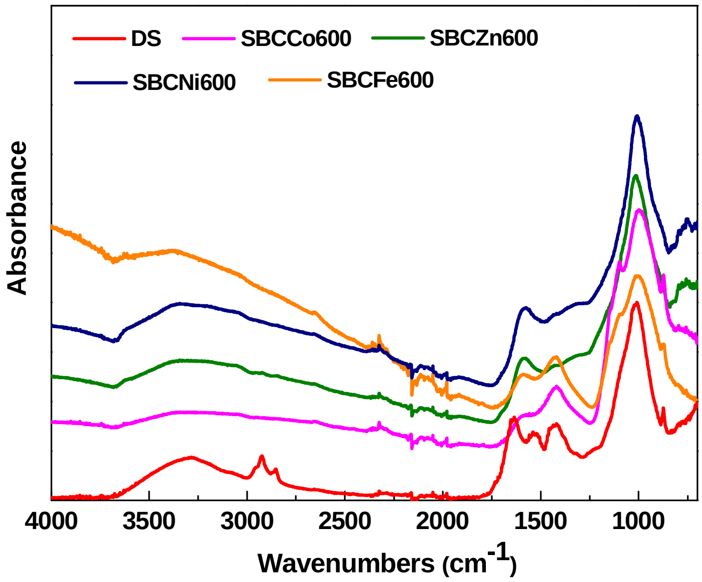
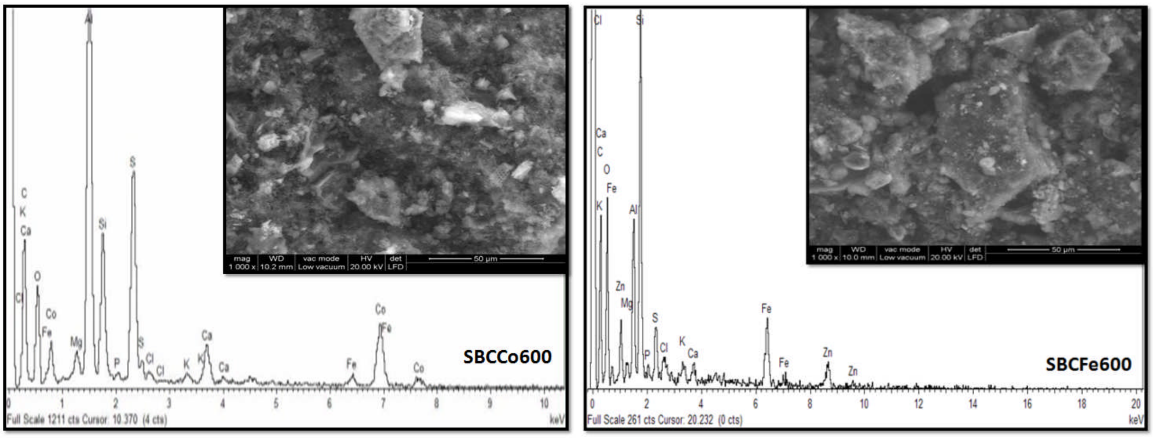


Figure 5. FTIR spectra of the dried sludge and SBCs.

3.6. Micro structure images

The microstructure analysis is used to obtain clear images on the internal surface of the catalyst. Figure 6 shows the micro structure images and EDS spectra of the SBCs.



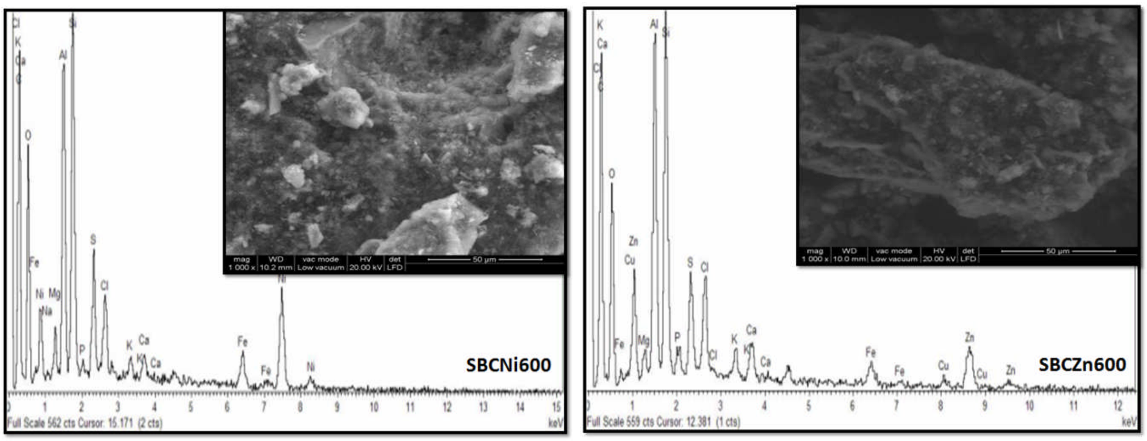


Figure 6. Microstructure images and EDS spectra of the SBCs.

The images of the catalysts are seen as rigid and hard surface that are irregular shape. The metal particles were uniformly distributed in the internal wall of the catalyst. The AOII dye molecule diffuses through the metal-carbon complex and absorbs onto it, after that the reaction products desorb from the surface of catalysts.

3.7. Adsorption isotherm results

Adsorption isotherm is described by two non-linearized isotherm models: the Langmuir (2) and Freundlich (3) isotherm models. The adsorption capacity of new materials is calculated from the linearized isotherm equation and the obtained values are used to calculate the maximum adsorption capacity by using non-linearized isotherm equation. Adsorption capacity of catalysts increases with the initial concentration of AOII dye solutions. The maximum adsorption capacity was reached at low concentrations of AOII dye.

The Langmuir isotherm equation is given as:

$$q_e = \frac{Q_m K_L C_e}{1+K_L C_e} \qquad (2)$$

The Freundlich isotherm equation is given as:

$$q_e = K_F C_e^{1/n} \qquad (3)$$

where, q_e (mg/g) is the amount of catalysts adsorbed per unit mass of adsorbent (mg/g). C_e (mg/L) the equilibrium concentration of AOII dye solution. Q_m (mg_{AOII}/g_{CM}) and K_L (L/mg) are Langmuir adsorption capacity and constants respectively.

Freundlich isotherm is to determine the heterogeneous surface on the surface of impregnated materials. K_F and n are Freundlich constants. K_F (mg/g (L/mg) $^{1/n}$) is the adsorption capacity of the adsorbent. Adsorption capacity of impregnated catalysts depends on the nature of catalyst, charges of metal, electron affinity and surface functional groups. The higher adsorption capacity was measured 172 mg/g for SBCNi600 catalyst. Table 4 presents the isotherm models fitting of AOII dye over different catalysts.

Table 4. Adsorption isotherm fitting data of AOII dye over SBCs.

Sample code	Langmuir isotherm			Freundlich isotherm		
	K_L (L/mg)	Q_m (mg/g)	R^2	K_F (mg/g (L/mg)$^{1/n}$)	1/n	R^2
SBCZn600	0.22	96	0.99	0.41	1.1	0.79
SBCFe600	0.03	156	0.96	0.54	1.0	0.96
SBCNi600	0.10	172	0.89	0.41	1.4	0.98
SBCCo600	0.10	154	0.98	0.6	1.1	0.90

The isotherm data was well fit to Langmuir isotherm model. Figure 7 shows the Langmuir isotherms and the predicted results of AOII dye over different catalysts.

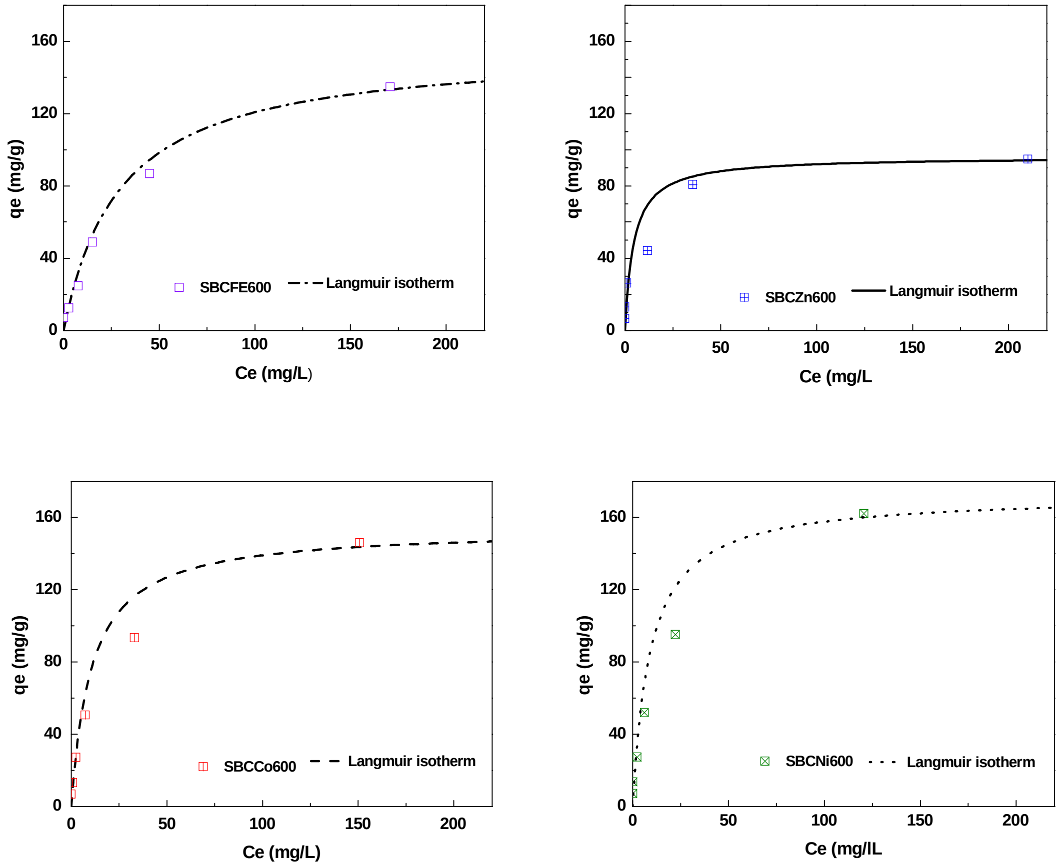


Figure 7. Langmuir isotherm of AOII dye over SBCs; Ambient room temperature: 20 °C; Catalysts amount: 0.100 g; Amount of AOII dye solution: 50 mg/L; Observation duration: 15 days.

3.8. Anaerobic reduction of AOII dye

The anaerobic reduction of AOII dye was carried out at different space times (4, 2, 1, 0.5 and 0.25 min) in the continuous UPBR system. In the reactor operation, steady state was reached within one-day continuous operation.

Figure 8 (A) show the continuous operation of 5 days in UPBR reactor for SBCNi600 catalyst. Nearly 98 % of dye conversion was achieved for SBCNi600 catalyst and the amount of produced sulfanilic acid (SA) level increases up to 57 mg/L in 4.0 min.

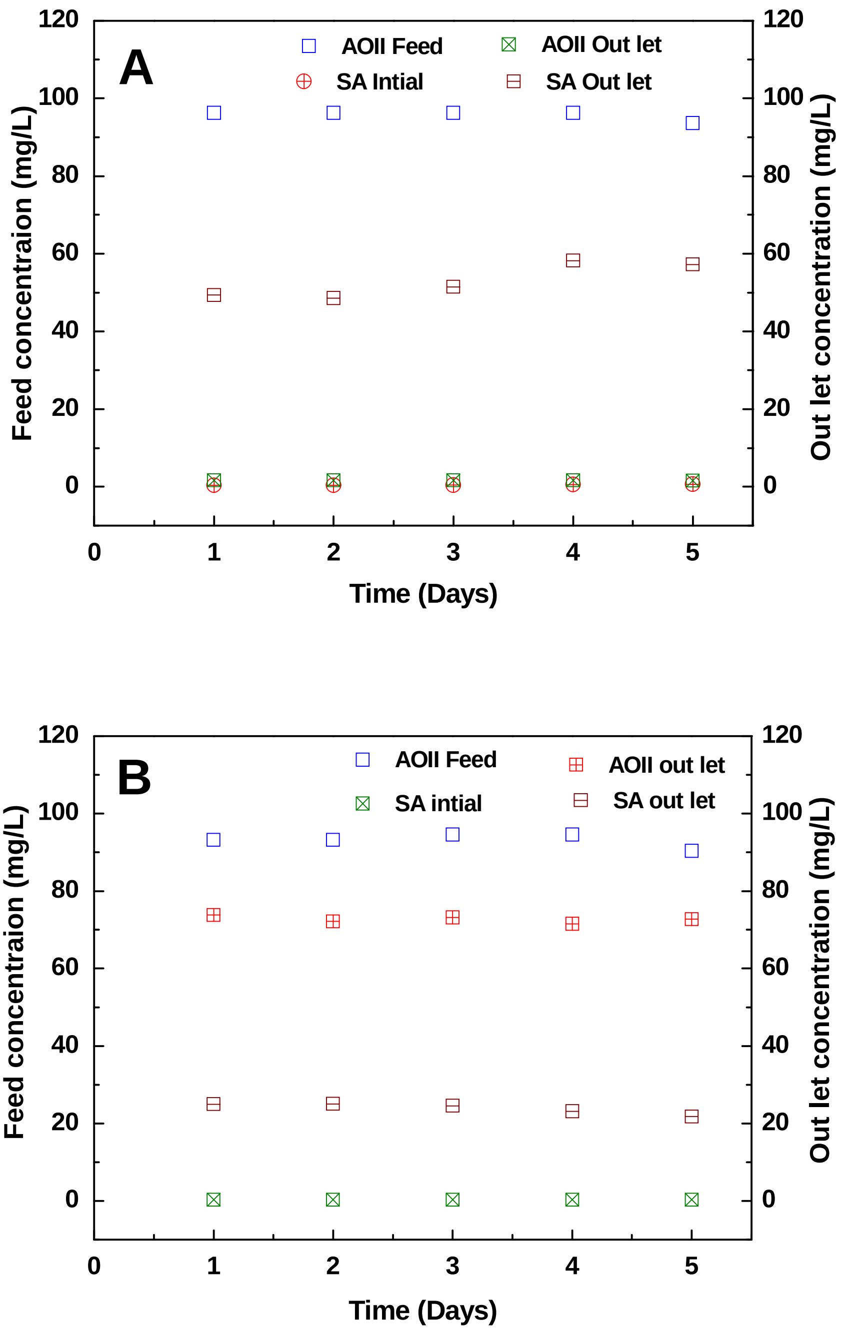


Figure 8. AOII and sulfanilic acid (SA) initial and out let concentration during 5 days steady state operation at various space time: (A) 4.0 min; (B) 0.25 min, in an anaerobic UPBR reactor system.

Only 20 % dye removal measured for SBCZn600 catalyst during the 5 days in 0.25 min continuous operation (Figure 8 B). The results show that the production of sulfanilic acid was very low.

Figure 9 shows removal of AOII dye and the amount of produced SA during the 100-days continuous UPBR reactor operation at a space time of 4.0 min for SBCFe600 catalyst. Removal of AOII dye was higher level without loss of catalyst stability and the growth of bio film on the catalyst is steady. For SBCFe600, 97 % of AOII dye conversion was measured, and the amount of SA levels increases up to 55 mg/L during the operation. It is important to say that the catalysts have a good life span in the reactor for long time operation without powdering the materials. In a continuous operation, dye conversion levels steady up to 40-days and after that, level was slightly decreased.

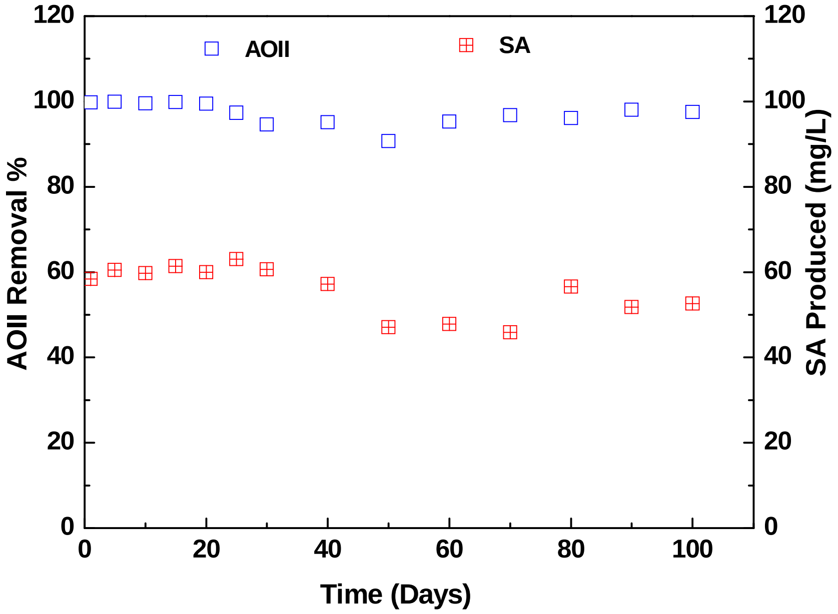


Figure 9. AOII removal and sulfanilic acid production during 100 days operation at space time of 4 min; AOII dye feed concentration: 100 mg/L; Catalyst: SBCFe600.

In UPBR system, the almost complete removal was achieved at very short space times (τ). AOII dye conversion 78 % was measured for SBCZn600, 57 % for SBCFe600; 55 % for SBCNi600 and 10 % for SBCCo600 respectively in 1.0 min operation. Our previous study has reported about 98 % dye removal was achieved for CAC in 1.0 min. The dye removal of SBCCo600 catalyst was 20 % in 1.0 min as compared to other impregnated catalysts. The dye removal of SBCFe600, SBCNi600 and SBCZn600 catalysts were 40 %, 37 % and 48 % respectively in 0.5 min. Only 10 % dye removal is for SBCCo600 in 0.5 min that cannot consider as good removal. The AOII removal of SBCFe600, SBCNi600, SBCZn600 and SBCCo600 was 27 %, 26 %, 19 %

and 6 % respectively in 0.25 min. In case of commercial AC about 44% AOII dye, removal was achieved in 0.25 min. Figure 10 shows the conversion of AOII dye over SBCs at various space time operation in UPBR bioreactor.

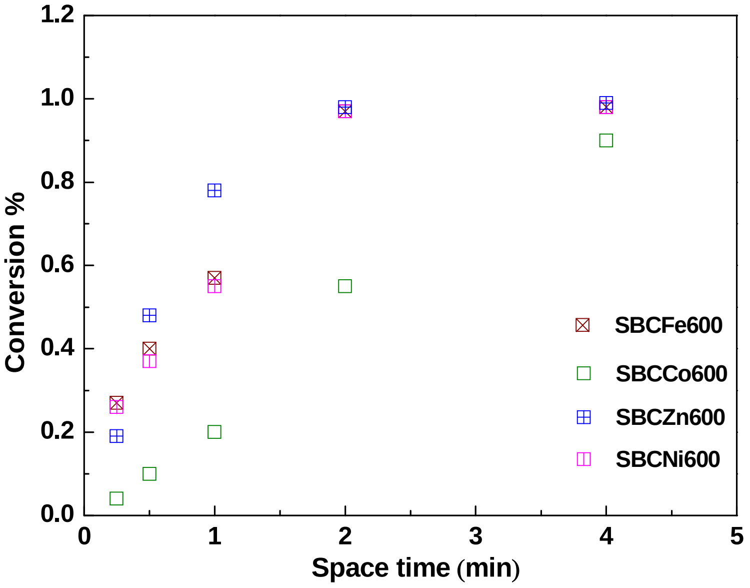


Figure 10. Conversion of AOII dye over SBCs at various space time operation in UPBR bioreactor.

The addition of metal particles to carbonaceous materials increases the catalyst mobility, electro negativity and electro affinities; those are influenced in the catalytic reduction process, which leads to higher level of AOII dye removal. The cobalt metal impregnated catalyst shows the lowest removal because the presence of Co inhibits the growth of biomass, hence the ability of the catalyst performs was very poor. Other selected metal particle such as Ni, Zn, and Fe stimulates the growth of biomass in the catalysts. The metal particles on the catalyst interact with the immobilized biomass forming a bio film. The presence of metal stimulates the growth of biomass in the bio reactor, which leads to highest AOII dye uptake. The catalysts abilities depend on the different metal, impregnated catalysts and the catalysts SBCZn600, SBCFe600 and SBCNi600 are the best materials due to the Zn, Fe and Ni metals are more adequate for the growth of biomass [36]. The SBCCo600 catalyst shows the lowest removal because the presence of Co inhibits the growth of biomass, hence the ability of the catalyst perform was very poor. In fact, the Co metal impregnated catalyst was toxic to the anaerobic culture. Figure 11 shows the schematic diagram of the sludge based catalyst and the mechanism of the reduction of azo dye under anaerobic conditions. This new solid supporting catalyst for the reduction of azo dyes in anaerobic conditions in which biology, chemistry and physics aspects combine to get synergistic effects in the solid materials surface for the biodecolorization of azo dyes and the product obtained mainly sulfanilic acid and the 1-amino-2-naphthol.

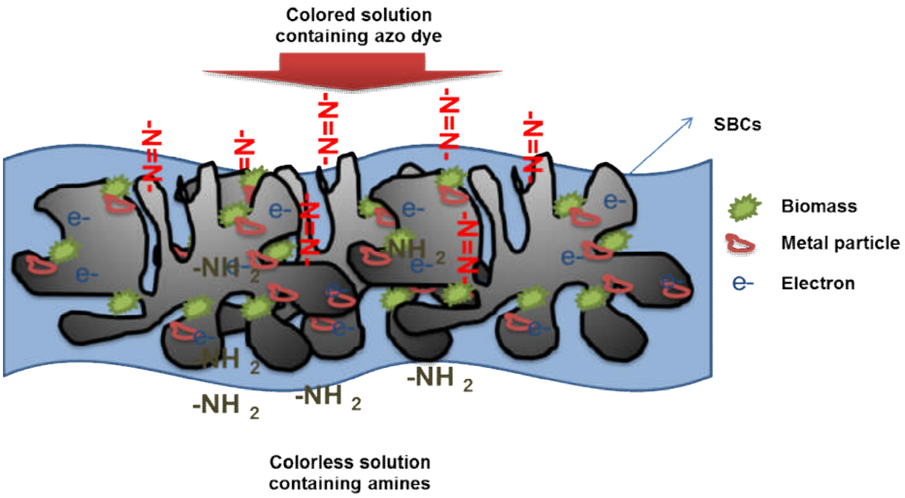


Figure 11. Schematic diagram of the sludge based catalyst and the mechanism of the reduction of azo dye under anaerobic conditions.

Figure 12 shows the decolorized AOII dye and the amount of produced SA under anaerobic conditions. The amount of produced SA molecules is directly proportional to decolorize AOII dye molecule. The amount of produced SA is an almost steady state throughout the anaerobic reaction but sometimes SA degrades in the presence of anaerobic biomass. In the reactor, during the 100-day continuous operation few amounts of SA molecule degrade by immobilized biomass.

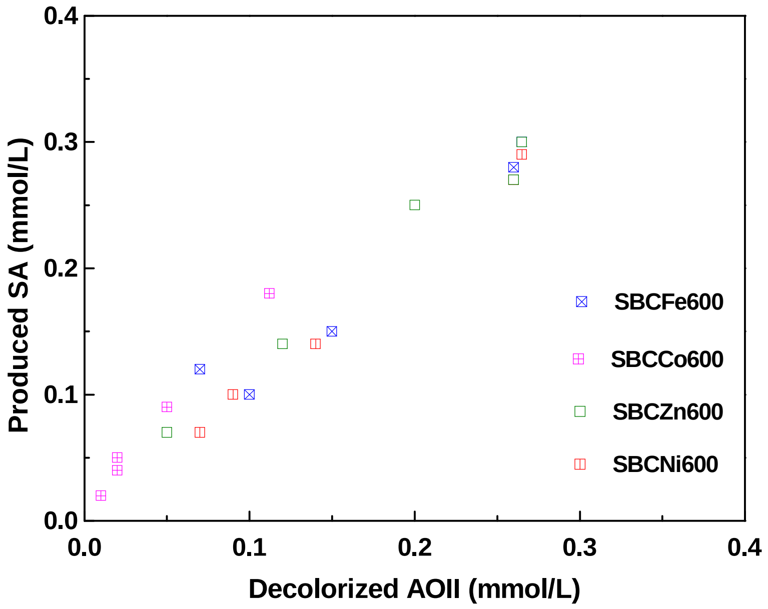


Figure 12. Decolorized AOII dye and the amount of produced of SA under anaerobic conditions.

Overall results noticed that anaerobic reduction of AOII dye influenced by the metal particle in the catalyst. The sludge based catalysts produced from the harmful sludge materials proved to be the most cost effective material and better choices for the treatment of contaminated dye solutions from textile industries.

4. Conclusions

The present work investigated the preparation of new sludge based carbonaceous materials impregnated with different metals for anaerobic reduction of AOII dye in a packed bed reactor. The SBCs exhibited several peculiarities, including cost effective, good surface texture, and environmentally acceptable conditions. The addition of metal particle to harmful exhausted solid sludge followed by heat treatment of the carbonaceous materials relatively high surface area (194 m^2/g) and enhances the AOII dye removal in batch adsorption and continuous bio reactor experiment. The immobilized anaerobic biomass on the catalyst in the anaerobic reactor greatly influences the heterogeneous catalytic reaction and without loss of catalyst stability. For SBCFe600, 97 % of AOII dye removal was measured, and the amount of SA levels increases up to 55 mg/L during the 100-day operation. Overall results indicate that the new materials possess excellent surface textures and removal rate of AOII dye is extremely high. The adsorption isotherm data of AOII are properly described by Langmuir isotherm model. The higher adsorption capacity was measured 172 mg/g for SBCNi600 catalyst. The SBCs performs closer capacity to commercial activated carbon, and they have remarkable physic-chemical properties, can introduce into various fields of catalytic reaction in the chemical reaction engineering. The addition of metal particle to carbonaceous materials further heat treatment is an excellent valorization option for converting harmful exhausted sludge into useful and inexpensive carbonaceous catalysts for treating textile effluents.

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CHAPTER 5

TiO_2-Sludge carbon enhanced catalytic oxidative reaction in environmental wastewaters applications

The enhanced oxidative potential of sludge carbon/TiO_2 nanocomposites (SNCs), applied as heterogeneous catalysts in advanced oxidation processes (AOPs), was studied. Fabrification of efficient SNCs using different methods and successful evaluation of their catalytic oxidative activity is reported for the first time. Surface modification processes of hydrothermal deposition, chemical treatment and sol-gel solution resulted in improved catalytic activity and good surface chemistry of the SNCs. The solids obtained after chemical treatment and hydrothermal deposition processes exhibit excellent crystallinity and photocatalytic activity. The highest photocatalytic rate was obtained for the material prepared using hydrothermal deposition technique, compared to other nanocomposites. Further, improved removal of bisphenol A (BPA) from aqueous phase by means of catalytic ozonation and catalytic wet air oxidation processes is achieved over the solid synthesized using chemical treatment method. The present results demonstrate that the addition of Ti nano particles on the surface of sludge carbon (SC) increases catalytic oxidative activity of SNCs. The latter produced from harmful sludge materials can be therefore used as cost-effective and efficient sludge derived catalysts for the removal of hazardous pollutants.

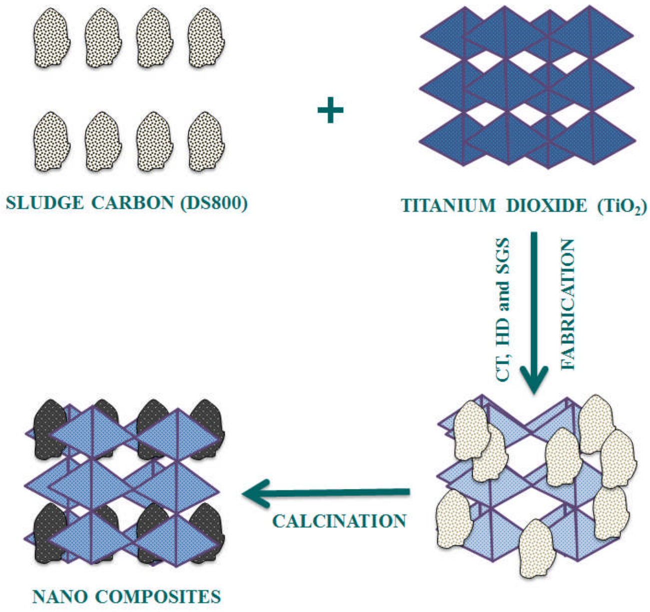
Keywords: sludge carbons, wastewater treatment, nano composites, fabrication process, catalytic oxidative reaction

1. Introduction

In recent years, titanium dioxide (TiO_2) nano materials have been successfully applied in many environmental treatment applications. TiO_2 nano materials have great practical importance due to their high stability, non toxicity, biocompatibility and useful properties for applications in photoreactions, semi conductors, solar cells and electro chemistry [1-2], but still suffer due to the low efficiency, high cost and short irradiation range. Generally, TiO_2 assisted nanomaterials are produced by different methods, including hydrothermal synthesis, chemical treatment, sol-gel solution and vapor phase deposition [3-6]. There have been many research reports of titanium TiO_2 nano materials (e.g., nanotubes, nanowires, nanorods, nanofibres and nanoclusters) that exhibit high surface area, good surface textures and excellent catalytic activity [7-10]. A landmark review reported on the carbon-titanium based photocatalysts that are fabricated with various supporting materials, including activated carbon, fullerene (60) and graphene [11]. Among them, activated carbons (AC) perform better in several environmental treatment applications such as photoreaction, ozonation and heterogeneous catalyzed reactions [12]. Due to the economic benefits, many researchers have been gearing up on the development of cost-effective and low toxicity catalysts from waste biomass [13]. Only few studies have reported TiO_2 deposited on the activated carbons for the removal of hazardous pollutants from water and wastewaters [14-17]. These activated carbon based nano materials have vouched for the cost-effective and good treatment methods to many environmental treatment applications.

On the other hand, the amount of sludge solid residues is increasing day by day due to the urbanization and industrialization, and such wastes are available at zero cost. These materials are rich in carbonaceous content, and consist of organic and inorganic compounds as well as small quantity of nutrients. Huge amounts of sludge waste materials cause disposal problems and are considered as one of the most costly and challengeable tasks in wastewater treatment plants (WWTPs) [18]. These sludge solid materials can be for instance converted into useful catalyst supporting materials that could be utilized for the treatment of hazardous compounds found in the environment.

In this study, sludge carbon/TiO_2 nano composites (SNCs) were fabricated using different preparation methods (**Scheme 1**), such as chemical treatment (CT), hydrothermal deposition (HD) and sol-gel solutions (SGS), and their catalytic activity was successfully evaluated in various advanced oxidation processes (AOPs) for water treatment, such as ozonation, photocatalytic oxidation and catalytic wet air oxidation.



Scheme 1. Schematic representation of sludge carbon/titanium oxide nano composites fabricated by different methods (chemical treatment (CT), hydrothermal deposition (HD), and sol-gel solutions (SGS)).

Bisphenol A (BPA) is an endocrine disrupting chemical (EDC) that has been extensively used in chemical industry, food industry and pharmaceutical applications. The EDCs once introduced into the aquatic environment exhibit high toxicity and estrogenic effects to living organisms [19,20]. In the present study, model BPA aqueous solution was treated by the above-mentioned AOPs utilizing the synthesized SNCs. The latter have shown high BET surface areas, and subsequently enhanced the catalytic oxidative removal of BPA. Additionally, the sludge carbon DS800 sample itself shows significant catalytic activity that was even further improved after a surface modification process. Based on these observations, one can produce a cheap and effective nano composite from the harmful sludge materials for the environmental treatment applications.

2. Experimental section

2.1 Fabrication of sludge carbon nano composites

Preparation of DS800 sludge carbons: The slurry anaerobic sludge was dried in a furnace at 105 ^oC for 24 h. This material was soaked in distilled water for 2 h and dried at 105 ^oC for 48 h. The resulting dried sludge (DS) material was grinded and sieved approximately to mesh size ranges from 0.5 to 0.7 mm. 10 g of dried sludge was placed in a quartz reactor (AFORA, Ref no: V59922) and carbonized at 800 ^oC for a fixed dwell time of 2 h. This material was washed several times with distilled water and then grinded to very fine powder using a mortar and pestle. The powder sludge carbon was denoted as DS800. The weight ratio of DS800 and TiO_2 was maintained at 1:1 for all the fabrication processes.

Chemical treatment: DS800 (1.0 g) and 1.0 g of TiO_2 P25 Degussa (Sigma-Aldrich) was added to 150 mL of 10 mol/L NaOH solution, then the solution was thoroughly mixed with ultrasonic homogenizer for 10 min. The solution was placed in a Teflon-lined autoclave, and hydrothermally treated at 130 ºC for 24 h. The solid was cooled and divided into two equal portions. The first portion was washed several times with Milli-Q water. The second portion was washed three times with 0.1 mol/L HCl solution and thoroughly washed with Milli-Q water. The final materials were separated by centrifugation and freeze-dried.

Hydrothermal deposition: 1.0 g of DS800 and 3.45 g of $TiOSO_4 \cdot H_2SO_4 \cdot H_2O$ (Sigma-Aldrich) were mixed in 100 mL of Milli-Q water. The solution was thoroughly mixed with ultrasonic homogenizer for 10 min and then the sample was placed in the Teflon-lined autoclave for 5 hours at 120 ºC. The obtained materials were throughly washed with Milli-Q water followed by centrifugation and the obtained material was dried at 80 ºC in air for 12 h.

Sol-gel solutions: 66.8 mL of isopropanol (Sigma-Aldrich) was added to a 250 mL RB flask and then 3.70 mL of $Ti[OCH(CH_3)_2]_4$ (Merck) solution was carefully added dropwise to the mixture at vigorous stirring conditions. Equal volume of water/nitric acid (65 %, Sigma-Aldrich) solution was added dropwise to the mixture and refluxed at 80 ºC under vigorous stirring for 60 min. After the formation of a white precipitate 1.0 g of DS800 was added. This suspension was stirred at room temperature for 180 min. The obtained material was seprated by means of centrifugation and dried at 80 ºC in air for 12 h. To obtain the sludge nano composites, all the fabricated materials were further calcinated at 300 ^oC in air for 60 min.

2.2. Characterization of nano composites

Micro structure images of nano composites were determined using scanning electron microscope (SEM) and transmission electron microscopy (TEM). Elemental compositions of the nano composites were analyzed by energy dispersive X-ray (EDX) spectrum (Inca system, Oxford instruments) instrument. FTIR spectra were recorded in ATR mode by using a Perkin Elmer spectrometer (model Frontier) in the frequency range between 4000 to 400 cm^{-1}. The surface area of materials was determined by measuring nitrogen adsorption and desorption isotherms at -196 ºC (Micromeritics, model Tristar II 3020). BET (Brunauer–Emmett–Teller) theory was applied in order to calculate the specific surface area of materials. XRD diffractograms were obtained using a D/max-ra X–ray diffract meter (Bruker-AXS D8- Discover diffractometer) with CUk radiation at 40 kV and 40 mA over the 2θ range of 5-70^{o}. Diffuse reflectance UV–Vis spectra were obtained using a Perkin-Elmer Lambda 35 spectrophotometer equipped with the RSA-PE-19M Praying Mantis accessory. BPA conversions were monitored using a HPLC instrument (Spectra System^{TM}), which operated in the isocratic analytical mode using 100 mm × 4.6 mm BSD Hypersil C12 2.4 µm column with the flow rate of 0.5 mL/min and methanol:ultrapure water of 70:30 (UV detection at λ = 210 nm).

2.3. Catalytic activity measurements:

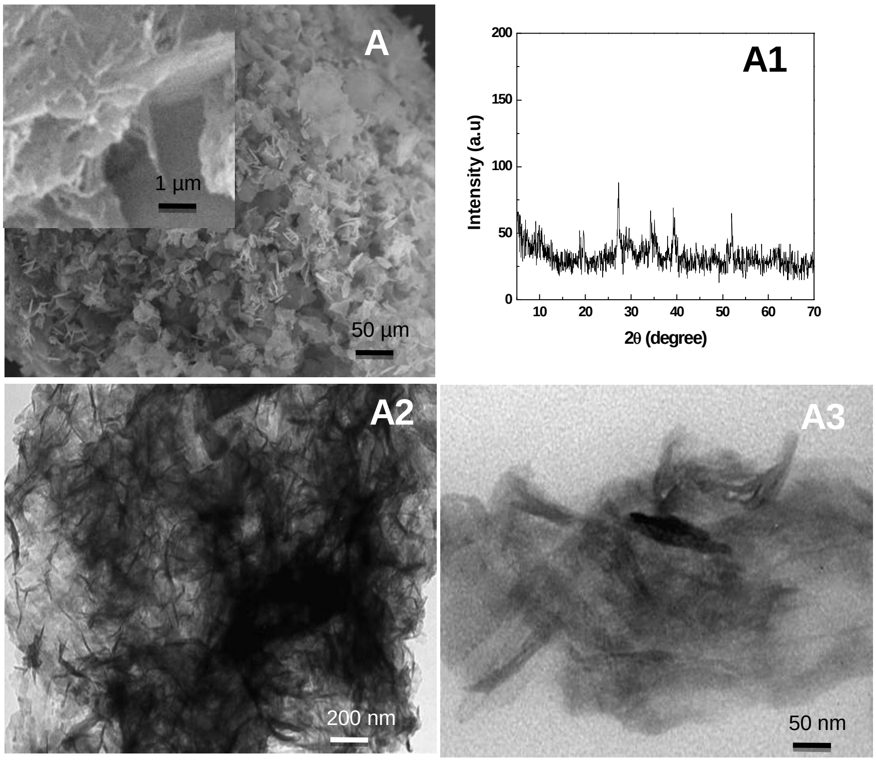
Ozonation reaction: Ozonation reaction was carried out in a batch reactor thermostated at 15 ºC. The ozone/oxygen mixture was used and flow was adjusted to 40 mL/min. 100 mg of SNCs material was homogeneously dispersed in 500 mL of BPA solution (c_0 =10 mg/L) by an ultrasonic homogenizer for 2 min. Before starting the experiment, the solution was stirred for 20 min in order to avoid the initial adsorption effect of the nano composites.

Photocatalytic reaction: For the photocatalytic reaction, 31.3 mg of SNCs was dispersed in 250 mL of BPA solution. The reactor unit was thermostated at T = 20 ºC (Julabo, model F25), magnetically sirred (300 rpm) and countinously sparged with purified air (45 L/h). Initially, the mixture of solution was stirred for 30 min (dark time) in order to avoid the adsorption activity effect of nano composites. The photocatalytic oxidation was carried out under the UV irradiation for 60 min.

Catalytic wet air oxidation: The catalytic wet air oxidation experiments were performed in a continuous-flow trickle-bed reactor with catalyst loading of 300 mg at 200 ^{o}C, total pressure of 25.5 bar and oxygen partial pressure equal to 10 bar. The aqueuos solution of BPA (c_{feed} = 10 mg/L) was fed ($\square_{\text{vol.}}$ = 0.5 mL/min) into the reactor unit by means of HPLC positive alternative dsplacement pump (Gilson, model 307). Liquid-phase samples were collected at the reactor outlet by an automated sampler at the regular time intervals, and the duration of the experiment was set to about 40 h.

3. Results and discussion

The fabricated SNCs were characterized using advanced techniques in order to examine their structural configurations and morphologies. The micro structure of nano composites was determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The micro structure images of SNCs are presented in **Figure 1**. The surface of SNCs was not uniform; further, they were highly impacted by the surface modifications process. **Figures 1** A and B show the SEM images of SNCs prepared via chemical treatment (CT) through the water and acid washing, denoted as (SNC-CT-W) and (SNC-CT-A), respectively; feather like nanostructures with small bundle shape were obtained. The observation shows that the surface of SNCs remains with little changes in the special arrangement after the acid washing process. The structure of SNC-CT-A sample (**Figure 1** B) confirms that the Ti nano particle aggregates have densely appeared around the sludge carbon (SC) surface. On the images 3D flower like structures are observed. TEM images of SNCs are shown in **Figure 1**. TEM images of SNC-CT-W (**Figure 1** A2, A3) and SNC-CT-A (**Figure 1** B2, B3) samples show the dark spots with spindle shape covered throughout the surface. The formation of SNCs using chemical treatment forms 3D flower like structures and a facial arrangement is clearly visible. The impurities of sludge carbon and amorphous carbon are also observed.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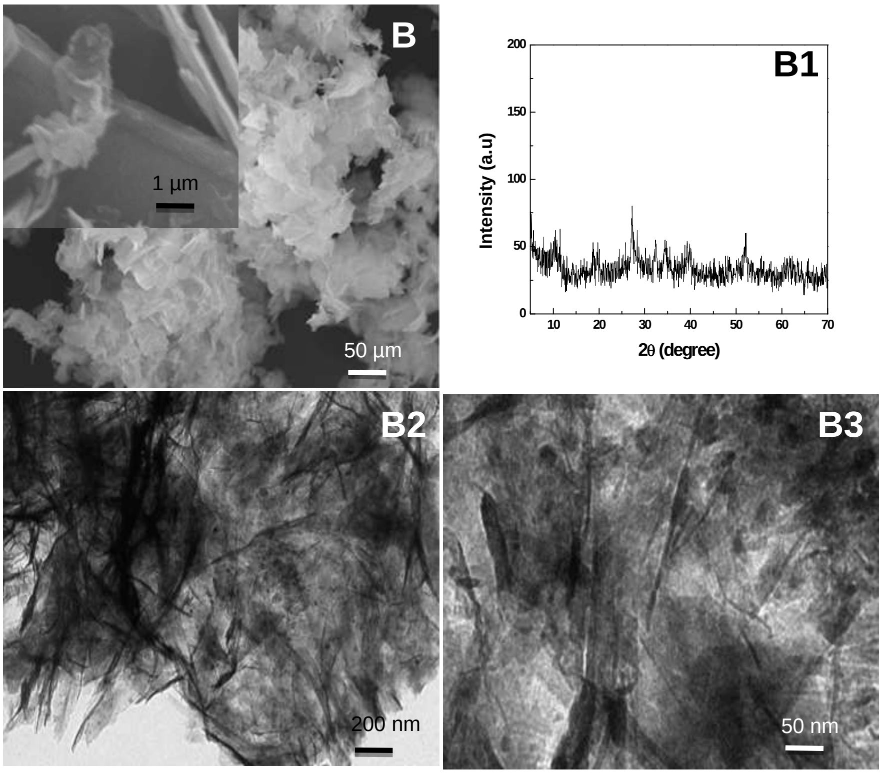
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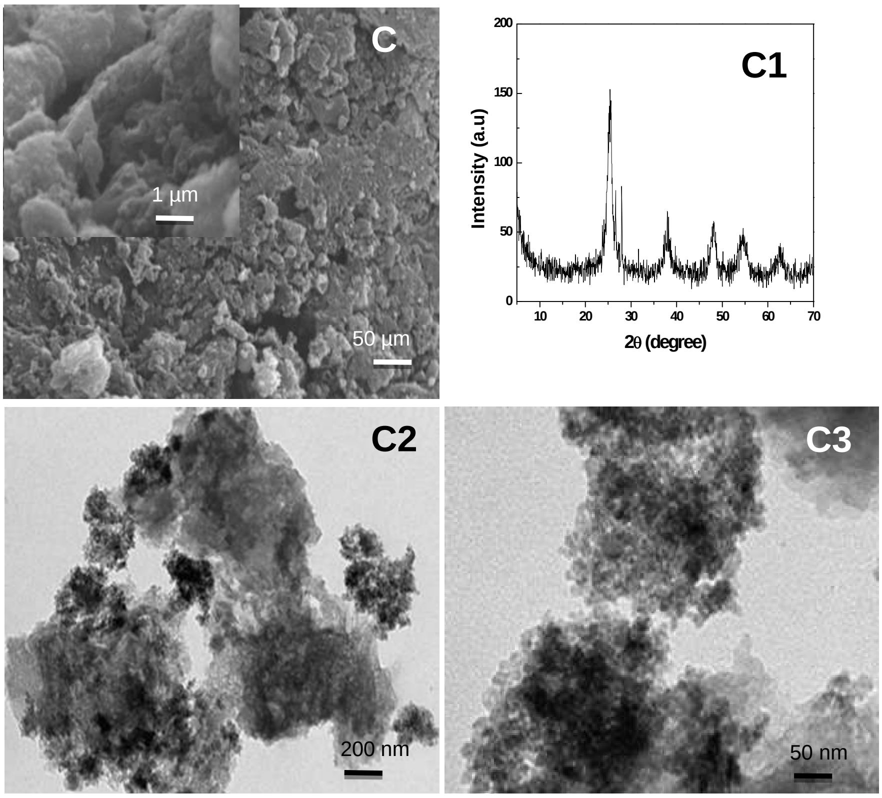
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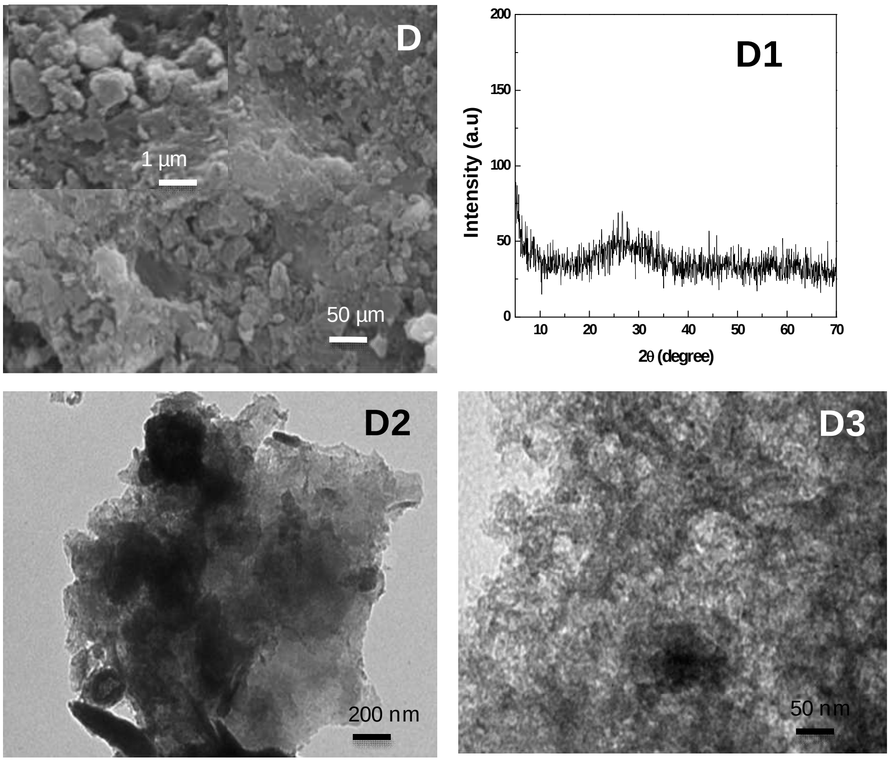
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Figure 1. Scanning electron microscope (SEM) images of sludge nano composites fabricated using different fabrication methods: chemical treatment after the washing with water (A), acid (B), hydrothermal deposition (C), and sol-gel solution (D). X–ray diffraction (XRD) patterns of sludge nano composites chemically treated after washing with water (A1), acid (B1), hydrothermal deposition (C1) and sol-gel solution (D1). TEM images of sludge nano composites fabricated using chemical treatment after washing with water (A2 & A3), acid (B2 & B3), hydrothermal deposition (C2 & C3) and sol-gel solution (D2 & D3).

Hydrothermally deposited materials (denoted as SNC-HD) exhibit small granular particle size that are thickly arranged in surface. Similar composites were also obtained using the sol-gel solution method. The growth of Ti nano particles was not homogeneous in the SNCs. It can be concluded that the fabrication methods as well as precursors considerably influence the properties of SNCs.

The SEM images of SNC-HD sample (**Figure 1** C) show hard grained clusters and consist of many ball-shaped nanoparticles over the surface. They are mostly nano particle sized and clearly observed on the TEM image (**Figure 1** C2 & C3). The SEM images of sol-gel developed SNCs, denoted as SNC-SG, are shown in **Figure 1** D. They show small ball-shaped size and densely arranged surface (**Figure 1** D2 & D3).

To obtain the sludge carbon DS800, sewage sludge was calcinated in the abscence of air at 800 ºC for 2 h. The derived DS800 solid has hard surface and shows pores of different size, which can hinder mass transfer and consequently decrease catalytic activity. The surface images of sludge carbon (DS800) are shown in **Figure 2**

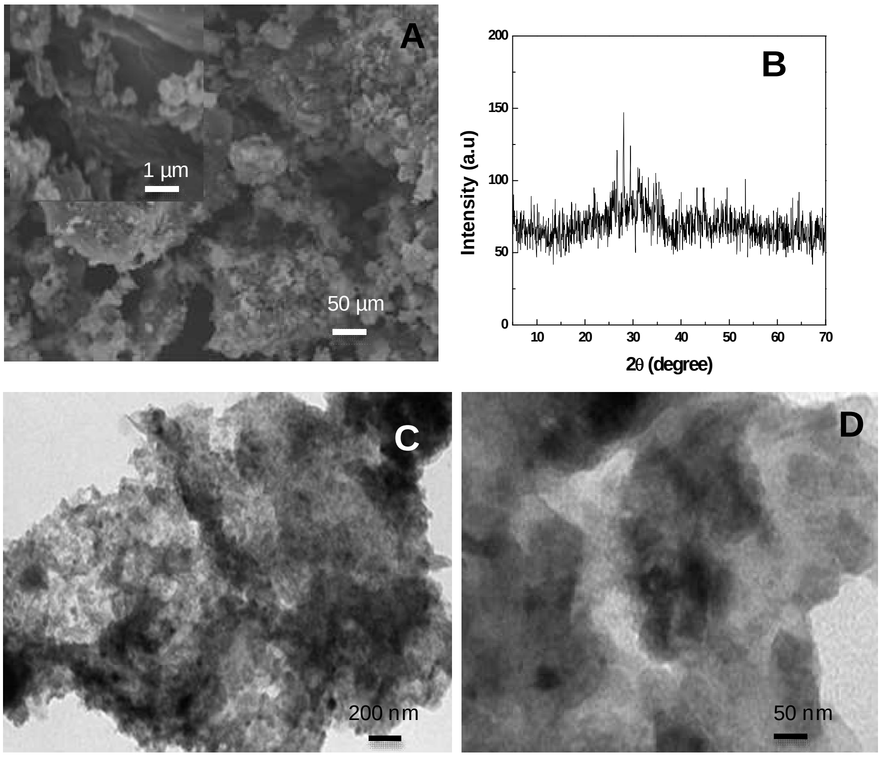


Figure 2. Scanning electron microscope (SEM) images (A), XRD pattern (B) and TEM images (C, D) of sludge carbon DS800 prepared from harmful sewage sludge materials.

Since the DS800 is originated from sewage sludge, it also contains impurities like organic, inorganic and volatile compounds. EDX spectral analysis detected the elemental fraction of the nano composites, which are mainly composed of metallic Ti and SC. The detection of metallic Ti fails in the SNC-SG material (**Figure 3**), while lower amount of Ti was observed in the SNC-HD solid.

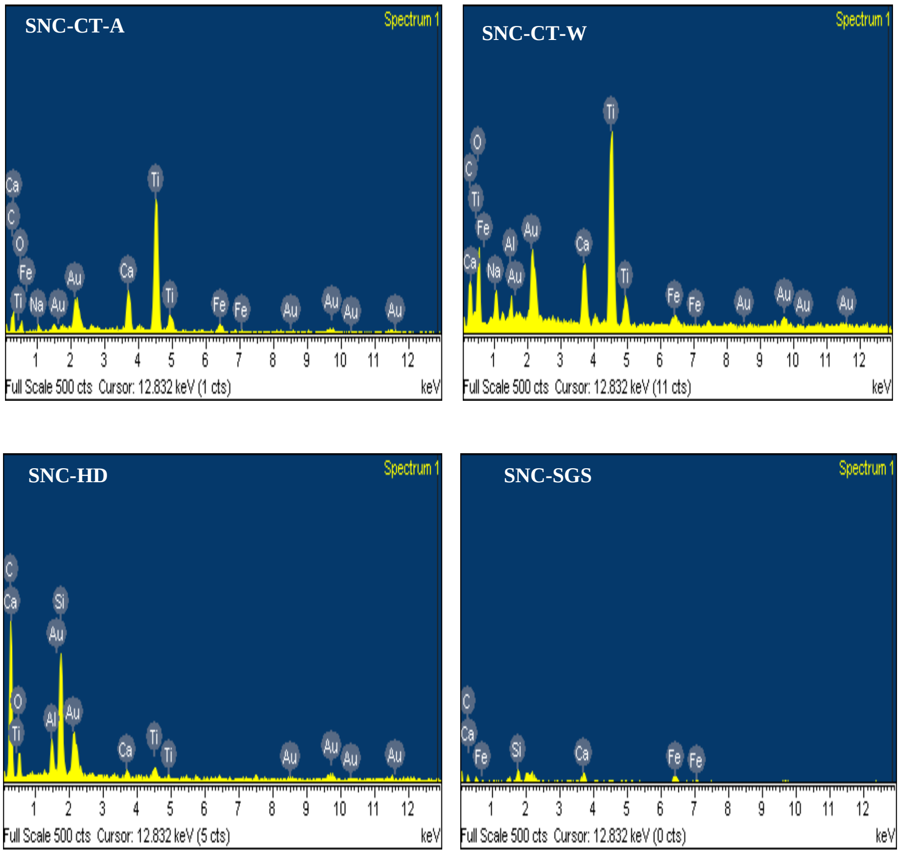


Figure 3. Energy dispersive X-ray (EDX) spectra of nano composites.

This is probably because of the growth mechanism of titanium particles utilizing the concerned methods. On the contrary, high amount of Ti particles was detected for chemically treated sludge nano composites.

The microcrystallinity of the SNCs was determined using XRD analysis, and the derived diffractograms are shown in **Figure 1**. The CT-W and CT-A materials (**Figure 1** A1 & B1) are composed mostly of rutile crystalline phase, and higher amount of anatase phase was observed for the hydrothermally deposited solid (**Figure 1** C1). In the case of sol-gel sample less anatase crystalline phase was found (**Figure 1** D1). The peaks at 25.4^{o} correspond to the plane of anatase phase in the SNC-HD solid. The peaks of rutile phase were detected at 27.5^{o} for CTs samples. The XRD examination of DS800 reveals the presence of amorphous carbon. Higher content of quartz (26.8^{o}), calcite (29.5^{o}) and a lower amount of albite (28^{o}) were detected in the DS800 sludge carbon (**Figure 2** A1).

Results of surface porosity of SNCs are presented in **Table S1**. The BET specific surface area and porosity were dramatically improved using different modification processes. BET specific surface area of SNC-HD material (309 m^2/g) was quite higher in comparison to other SNCs. Lower BET surface area was measured for the SNC-CT-W material (3.0 m^2/g), which is probably due to the sodium salts accumulated in the pore cavities.

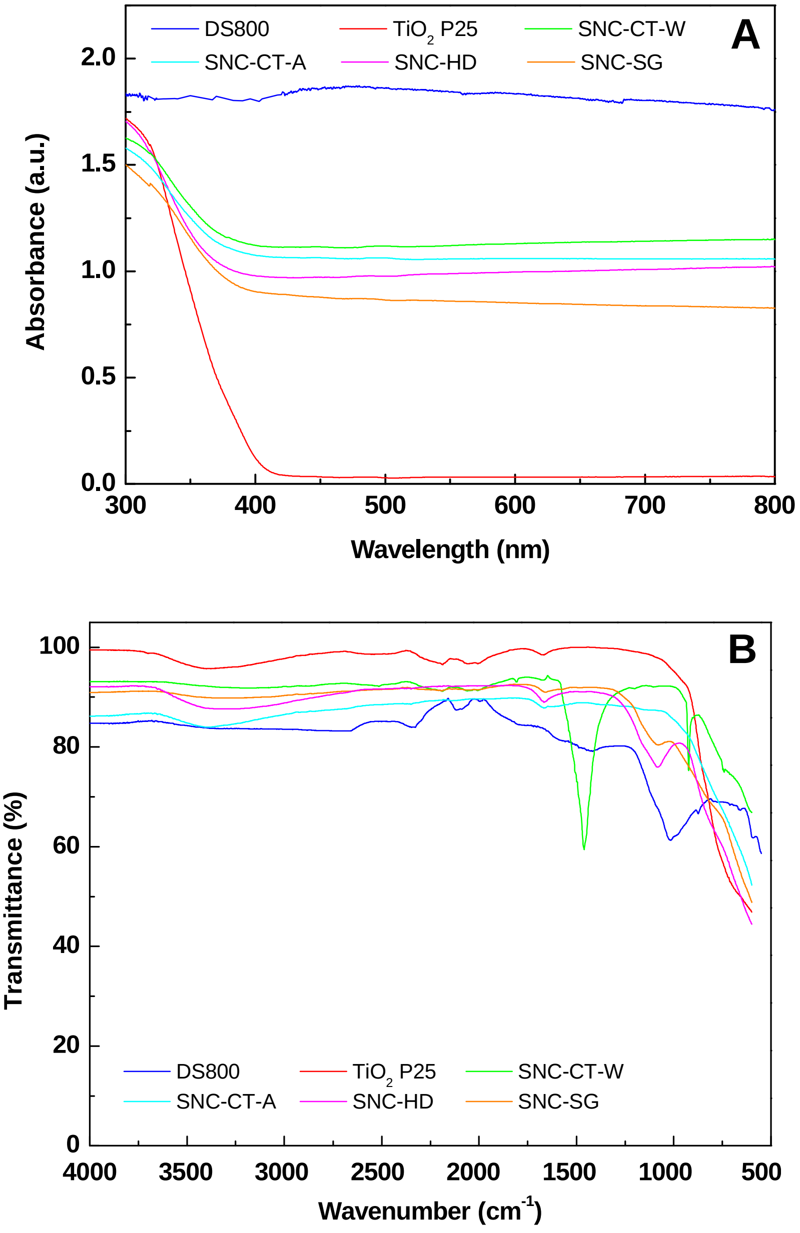
Table 1. Specific surface area (S_{BET}), total pore volume (V_{pore}) and average pore width (d_{pore}) of sludge nano composites and DS sludge carbon.

Sample	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	d_{pore} (nm)
DS800	74	0.09	5.0
SNC-CT-W	3.0	0.01	22.1
SNC-CT-A	173	0.36	8.5
SNC-HD	309	0.39	5.1
SNC-SGS	261	0.18	2.9

The surface porosity of the samples fabricated using hydrothermal and a sol-gel solution process is highly enhanced. The total pore volume of nano composites was in the range of 0.01-0.39 cm^3/g. The pore diameters of SNCs were in the range of 2.9-22.1 nm. Better porosity and the higher surface area could enhance the adsorption of BPA molecule.

The UV-Vis diffuse reflectance spectra of SNCs are shown in **Figure 4** A. These results were almost similar, but quite different from spectra of DS800 sludge carbon and commercial TiO_2 P25 sample. The SNCs exhibit an intense absorbance below 350-400 nm. The absorbance spectra of SNCs reasonably show a combination of features seen in the spectra of DS800 sludge carbon and TiO_2 P25 (commercial sample from Degussa) nano particles.

FTIR/ATR spectra illustrated in **Figure 4** B give information about functional groups present on the surface of solids. The main vibrations for sludge carbon DS800 are observed at 1000 cm^{-1}, which is related to Si-O vibration. Another major peak is observed at 1500 cm^{-1} for the SNCs material that could be attributed to stretching of aromatic compounds. The band at 1612 cm^{-1} appeared for SNCs, which is related to vibration of quinine and -C=O group. There are two peaks (in the range of 1000-1300 cm^{-1}) observed for SNCs associated to C-O stretching band of ethers. After the treatment process, oxygenated functional groups peaks are significatly reduced. The chemical groups present in the SNCs are mostly belonging to aromatic and aliphatic compounds.



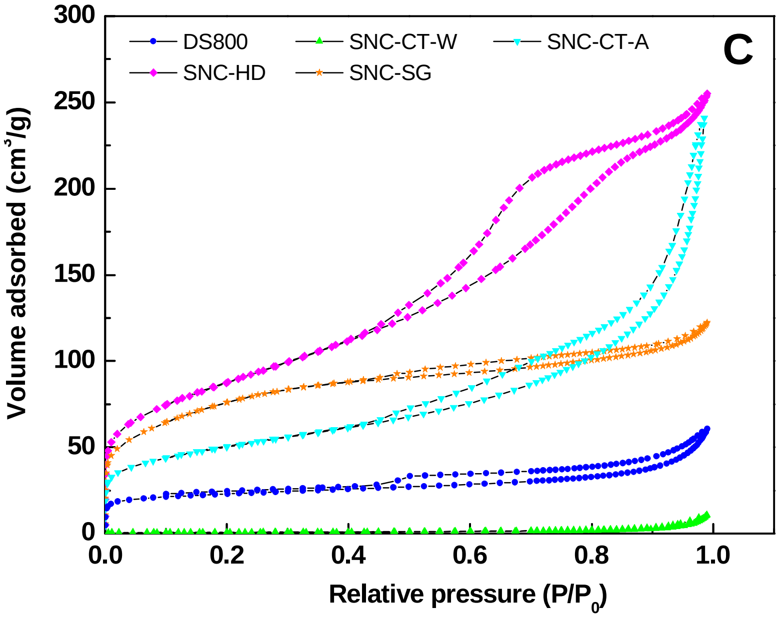
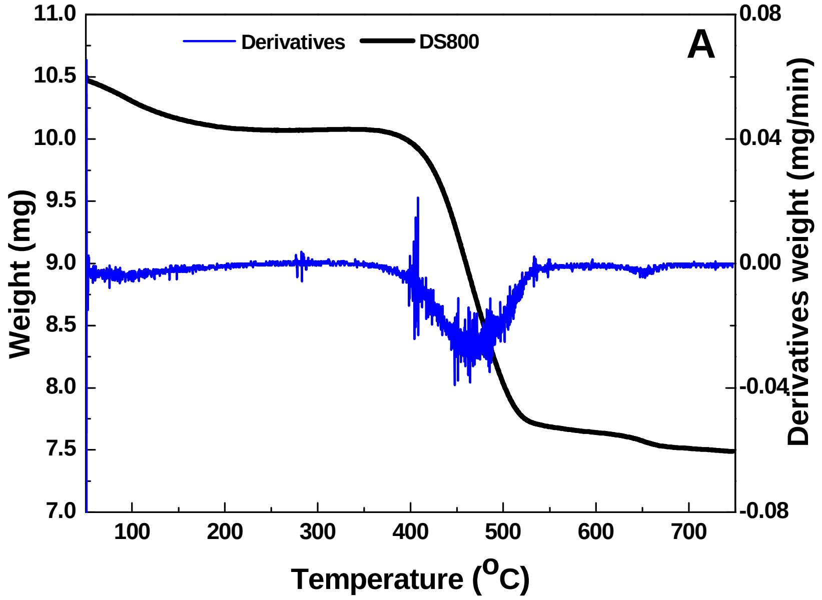


Figure 4. (A) UV-Vis diffuse reflectance spectra, (B) FTIR/ATR spectra, and (C) nitrogen adsorption/desorption isotherms of fabricated sludge nano composites, sludge carbon DS800 and TiO_2 P25 (Degussa).

The nitrogen adsorption/desorption isotherms of SNCs are shown in **Figure 4** C. It can be seen that the SNCs follow hysteresis cycles that are closely related to type IV adsorption isotherms. The SNC-HD isotherms are quite different from the other fabricated materials, since they exhibit a large hysteresis loop, associated to meso porosity.

The results of thermal reduction of SNCs are shown in **Figure 5**. This thermal study leads to an observation that novel SNCs had better thermal stability, which was further supported by the results obtained in the continuous-flow catalytic wet air oxidation process conducted at elevated temperature. The higher weight loss for DS800 sludge carbon was observed at 500 ºC. The major weight loss for the SNC-CT-A solid was observed at 450 ºC (**Figure 5** C). A weak weight loss was also observed at 550 and 500 ºC for SNC-HD (**Figure 5** D) and SNC-SG (**Figure 5** E) samples, respectively. The weight losses are mainly attributed to the removal of surface adsorbed compounds and their derivates in the SNCs.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Derivatives weight (mg/min)
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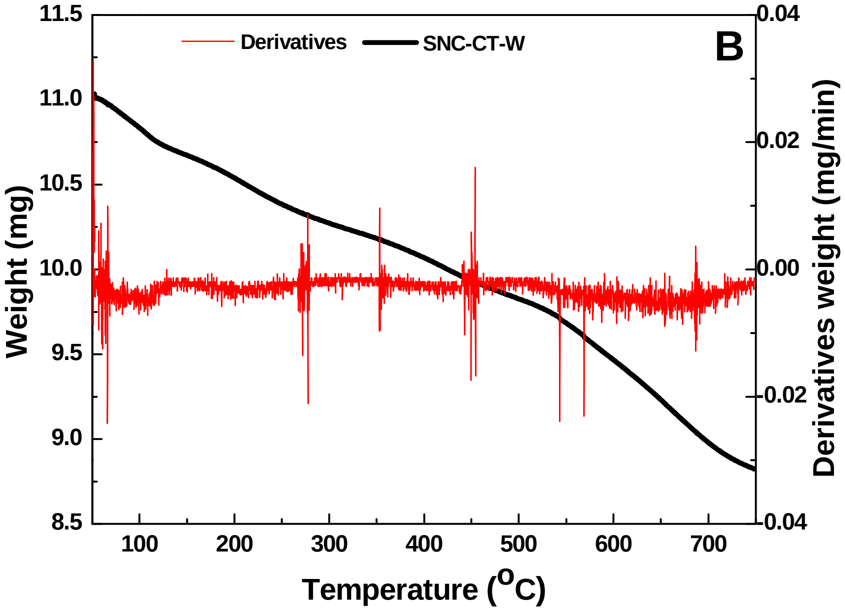
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9.5
9.0
8.5
Derivatives weight (mg/min)
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0.02
0.00
-0.02
-0.04
100
200
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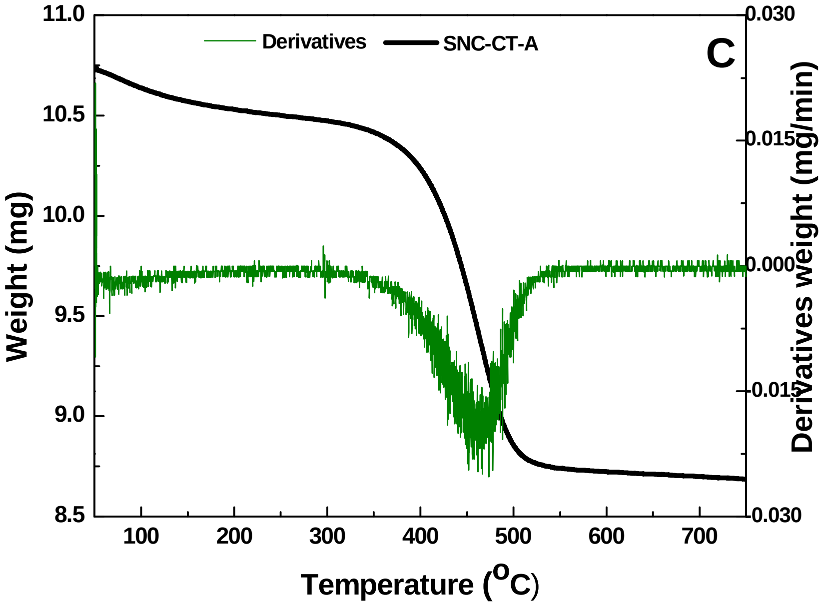
400
500
600
700
Temperature (^{O}C)


C
Derivatives
SNC-CT-A
Weight (mg)
Derivatives weight (mg/min)
Temperature (^{O}C)
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9.0
8.5
0.030
0.015
0.000
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100
200
300
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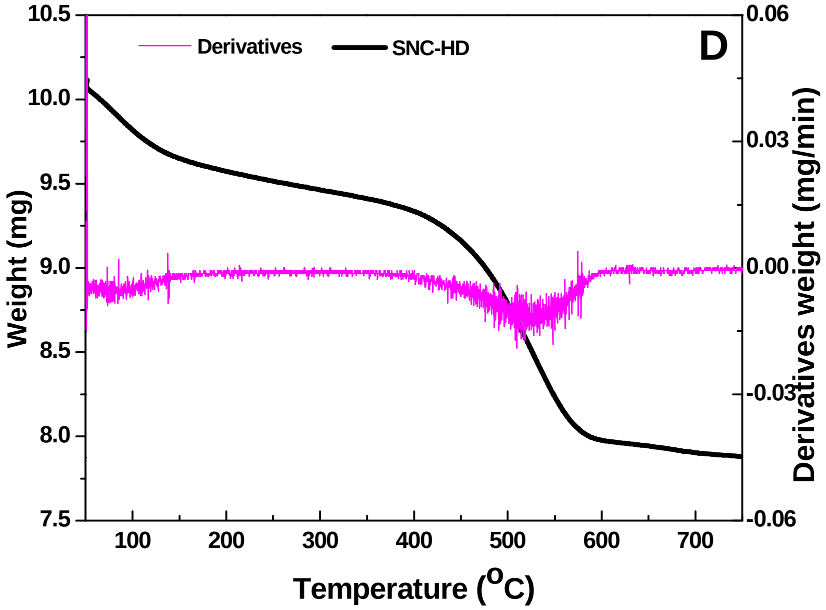
D
Derivatives
SNC-HD
Weight (mg)
Derivatives weight (mg/min)
Temperature (^{O}C)
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9.0
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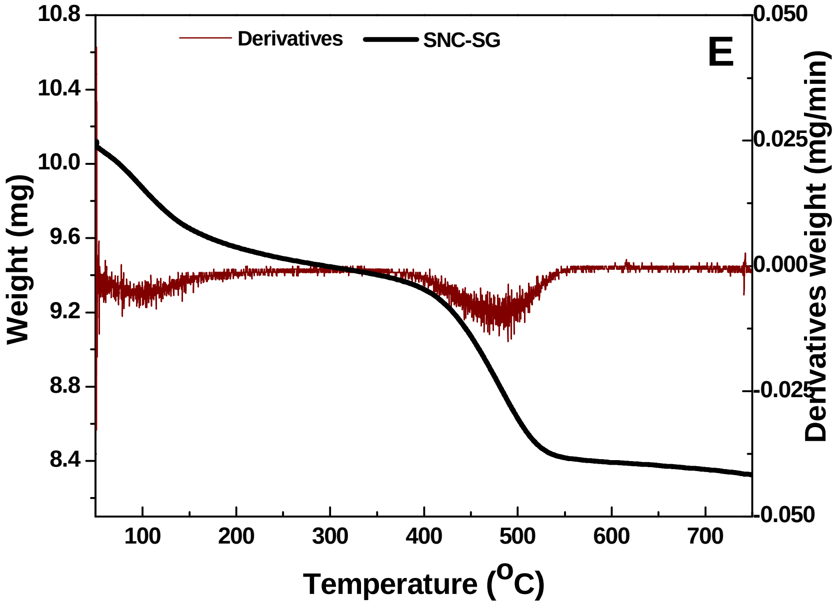
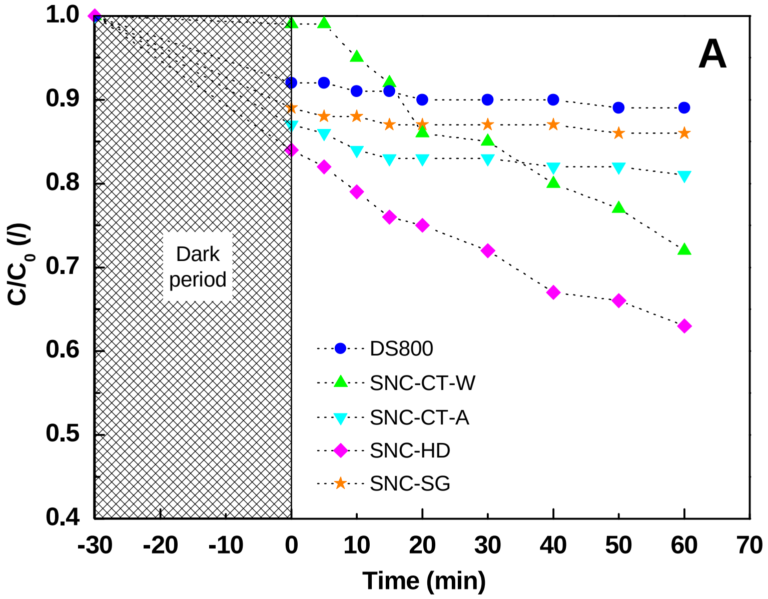


Figure 5. Thermal reduction of sludge nano composites and sludge carbon DS800.

Figure 6 A shows the photocatalytic activity of SNCs and sludge carbon for the removal of BPA from aqueous solution. Under the photoreaction in a period of 60 minutes, the SNC-HD particles were able to remove nearly 36 % of BPA from the solution. Photocatalytic activity of SNC-HD solid was obviously higher than of other nano composites.



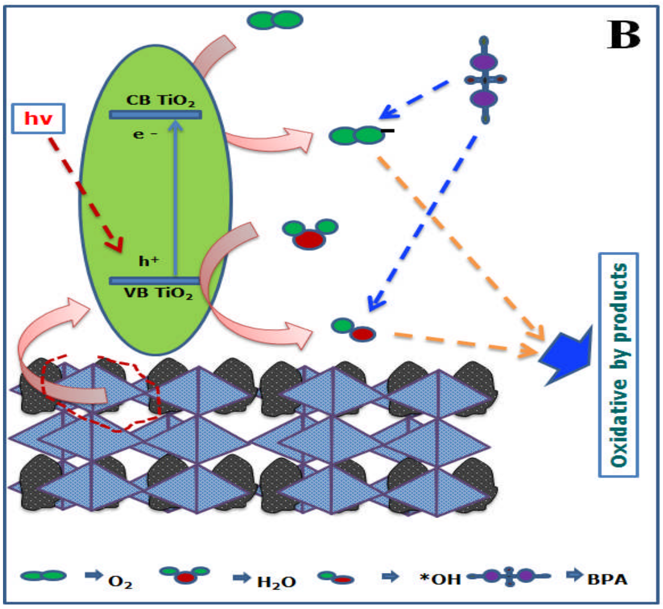


Figure 6. (A) Removal of BPA over sludge nano composites and sludge carbon DS800 during the period of 60 min under UV light; (B) schematic illustration of photocatalytic reaction mechanism using fabricated sludge nano composites.

BPA removal rate by using DS800 sludge carbon was very low compared to the other SNCs. DS800 material is obviously not a self-photocatalytic material under the UV irradiation range. The photoactivity of SNC-SG and SNC-CT-A materials was low, probably due to the lack of electron exchange over the sludge carbon matrix. Complete BPA removal in the presence of TiO_2 P25 sample was observed in the same period (**Figure 7**).

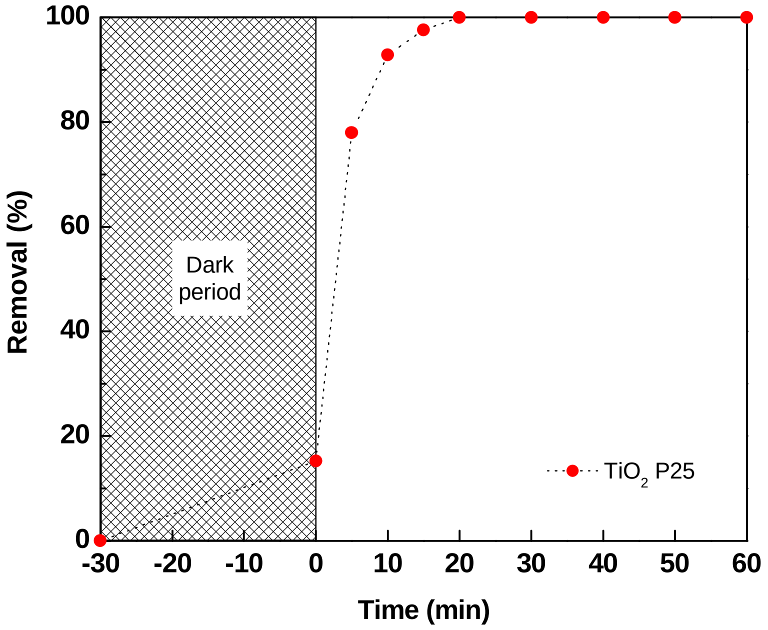
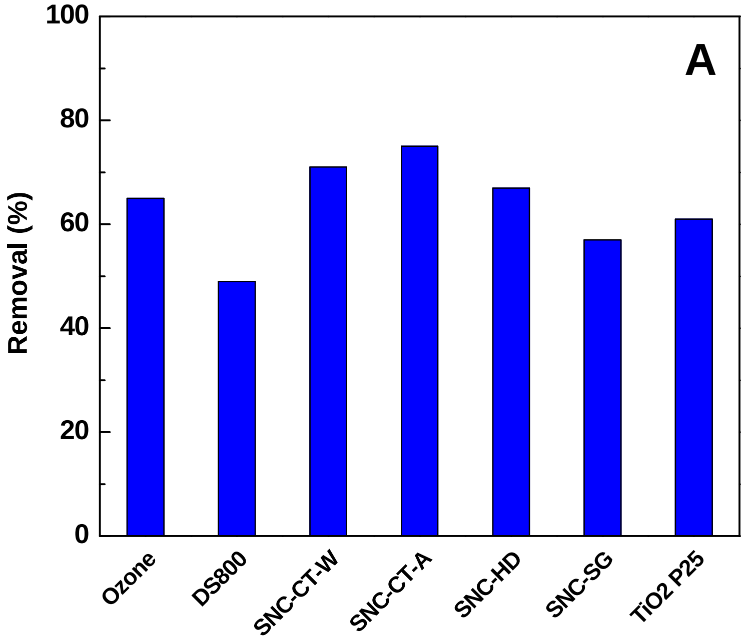
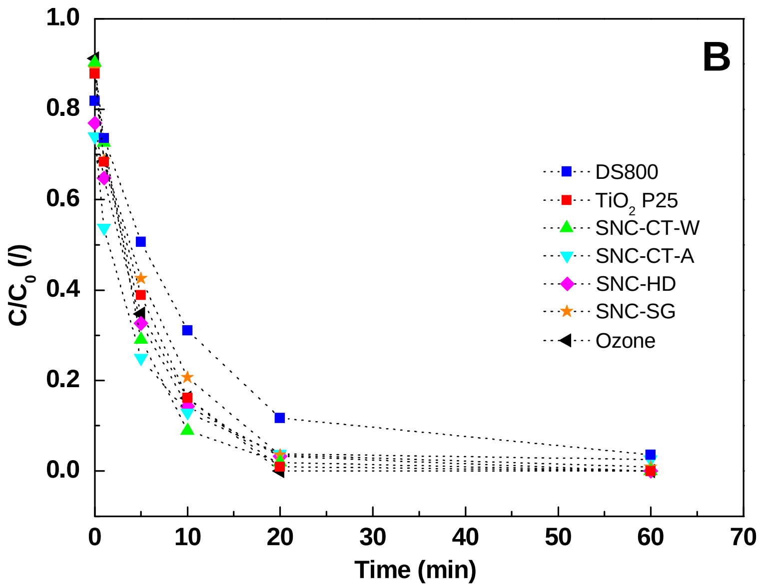


Figure 7. Photocatalytic removal of BPA in the presence of commercial P25 TiO_2 during the 60 min time period under UV light.

Only 27 % of BPA removal was measured over the SNC-CT-W solid. The results revealed that the SNC-HD material was the best candidate for the photocatalytic removal of emerging pollutant. The observation that the hydrothermal deposition conditions lead to the formation of more anatase phase, might favor the photocatalytic reaction. The surface textures of the nano composites play a major role in the photocatalytic oxidation of BPA in the reactor system. Enhancement of photocatalytic activity of SNCs under UV light can be due to the surface chemistry, surface area, presence of oxygen and functional groups, such as quinine and carbonyl (detected in the FTIR/ATR spectra). On the basis of above surface characteristic information, a possible photocatalytic mechanism of SNCs could be proposed. It is suggested that the complex SNCs materials provide the sludge carbon-oxygen-titania linkage that extends the photocatalytic activity. The specific characteristics of the SNCs enable that (i) the sludge carbon serves as an electron carrier, and (ii) the number of holes and positive charge build on TiO_2 surface. The electron carrier effects of SC contribute to avoid the recombination of photoelectrons and valence-band holes, which in turn enhances the formation of hydroxyl radicals and oxidation of liquid-dissolved BPA molecules. A mixture of SNCs and BPA solution was initially run in dark for 30 min, and no observable decrease of BPA concentration by adsorption was detected. This means that SNCs solids serve as photocatalysts to enhance BPA removal. **Figure 6** B shows the schematic illustration of photocatalytic reaction mechanism using SNCs.

Figure 8 A shows the removal of BPA in catalytic ozonation with SNCs and TiO_2 nano particles. SNC-HD and SNC-CT-W materials enabled complete removal of BPA during the 60 min ozonation reaction. Complete BPA removal was achieved as well in the presence of commercial TiO_2 P25 sample. In a short period of 5 min high BPA removal of 75, 71 and 67 % was achieved for SNC-CT-A, SNC-CT-W and SNC-HD samples, respectively. While using TiO_2 P25, SNC-SG and DS800 samples, these values were equal to 61, 57 and 49 %, respectively, in the same time period (**Figure 8** B).




B
1.0
0.8
0.6
0.4
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C/C0 (/)
0
10
20
30
40
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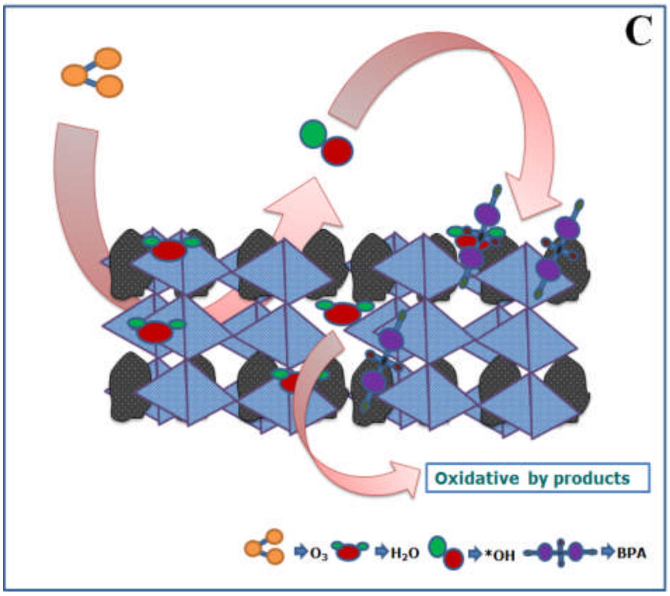
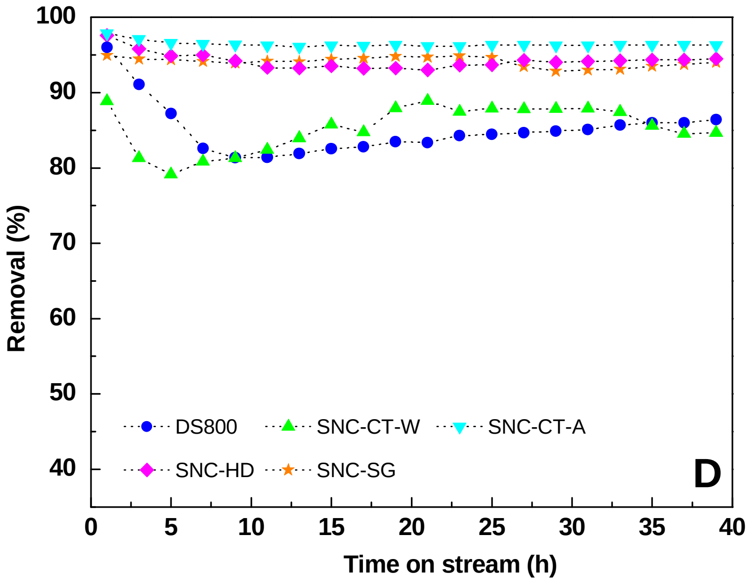
70
Time (min)
DS800
TiO2 P25
SNC-CT-W
SNC-CT-A
SNC-HD
SNC-SG
Ozone


C
Oxidative by products
O3
H2O
•OH
BPA



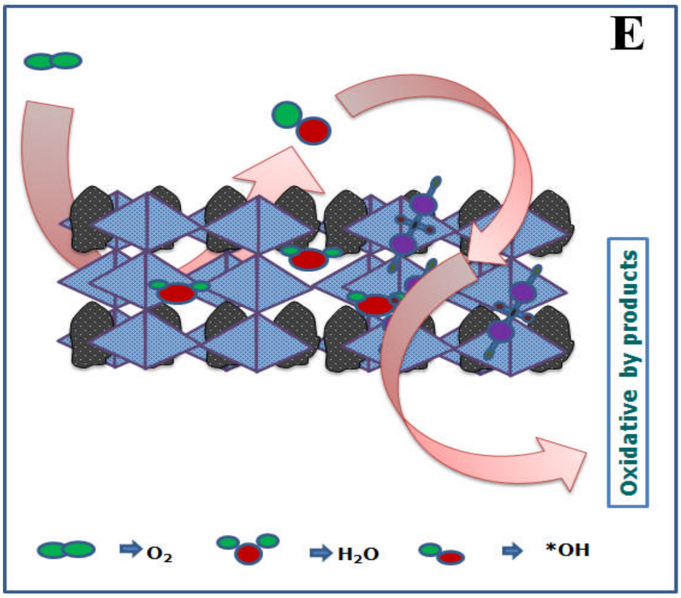


Figure 8. (A) Ozonation reaction after 5 min using fabricated sludge nano composites, sludge DS800 and P25 TiO_2; (B) temporal course of ozonation reaction during the 60 min; (C) the schematic representation of catalytic ozonation reaction mechanism; (D) removal of BPA in the presence of sludge nano composites and sludge carbon DS800 obtained in the continuous-flow catalytic wet air oxidation reaction carried out in the trickle-bed reactor; (E) the schematic illustration of catalytic oxidation reaction mechanism.

The SNCs as ozonation catalysts are shown to be more active in the removal of BPA from the liquid phase. SNCs with basic surface properties and with large pores enhanced this ozonation process. Suspensions of SNCs accelerate the decomposition of ozone, acting as initiators for the chain reaction and the transformation of the ozone molecules into secondary oxidants, which can react with adsorbed BPA molecules to form end products (**Figure 8** C). The surface textures of the SNCs play an important role in the ozonation of BPA solution. The adsorption of BPA solution could be strongly affected by the surface charge of nano composites.

Figure 8 D shows BPA conversions as a function of time on stream obtained in the presence of SNCs examined in the continuous-flow catalytic wet air oxidation (CWAO) process. Removal of BPA in the presence of SNC-CT-A solid was 96.4 %. For comparison, removal of BPA was 94.2 and 94.1 % for SNC-HD and SNC-SG samples, respectively. About 45 % BPA removal was measured using low surface area silicon carbide (SiC) as a reference inert material (**Figure 9**), which is in good agreement with the results reported [21].

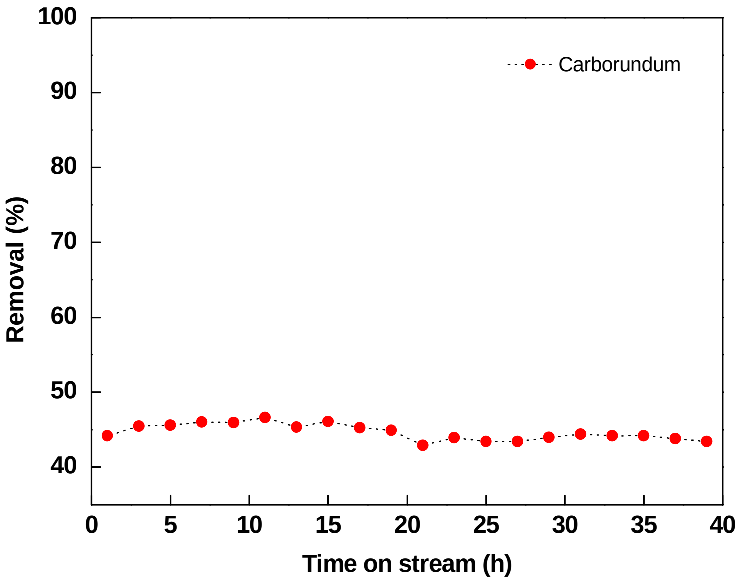


Figure 9. BPA conversion as a function of time on stream over carborundum (SiC) as a reference inert material obtained in the continuous-flow trickle-bed reactor.

This finding confirms that in the given range of experimental conditions BPA oxidation undergoes both catalyzed as well as non-catalyzed oxidation routes. Further, high BPA removal was attained using SNC-CT-A solid, compared to other materials. Based on this observation, the presence of oxygenated groups in the SNCs and continuous sparging with oxygen (O_2) accelerate the formation of hydroxyl radicals (HO*), which can activate the BPA aromatic ring in order to form end products. **Figure 8** E shows the schematic illustration of catalytic wet air oxidation. The results presented in this work give new paradigm for the re utilize of waste materials for the effective environmental wastewater applications.

4. Conclusions

In summary, surface modification processes of hydrothermal deposition, chemical treatment and sol-gel solution resulted in improved catalytic activity and good surface chemistry of the SNCs. Materials obtained after chemical treatment and hydrothermal deposition processes displayed crystallinity and photocatalytic activity. In this study, better removal of BPA was achieved over the SNC-CT-A material in the catalytic ozonation and catalytic wet air oxidation reaction. The highest photocatalytic efficiency was achieved in the presence of SNC-HD solid, compared to other materials. Based on these observations, one can conclude that the addition of Ti nano particles on the surface of sludge carbon (SC) increases the mobility of charges, electro negativity and electro affinities, which in turn enhances (photo) catalytic activity of these solids. Since the SNCs are produced from harmful sludge materials, they can be therefore used as cost-effective and efficient biomass derived catalysts for the removal of hazardous pollutants from water and wastewaters.

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CHAPTER 6

General conclusions and future recommendations

General conclusions

Many literature reviews have reported that the low-cost adsorbents can be utilized for the removal of aqueous solution of various pollutants. Most of the studies have mainly focused only in the adsorption activity of the solid materials and limited applications exist in batch and continuous systems. Until now, there is a lack of available information on the surface texture studies of sludge-derived catalysts and the ultimate uses for environmental applications, especially in continuous biological treatments. This research work has been successfully applied to the sludge-derived catalysts and the sludge based nanocomposites from sewage sludge materials, analyzing their surface textures, drawing the mechanism and finally using these new materials for environmental applications. The biggest strength of this research was to utilize zero cost waste solids for removal various pollutants from wastewaters by using biological and advanced oxidation processes in order to obtain biodegradable products at environmental acceptable conditions.

The major findings of this research work are compiled as below:

Chapter 1: Utilization of sludge based catalysts for environmental wastewater treatment applications: - A review.

The review gives a broad view about the sludge production, current status, sludge derived catalysts, and the catalytic performance of catalysts to the environmental treatment applications such as, biological and AOPs, besides the critical solution.

Chapter 2: Characterization and performance of carbonaceous materials obtained from exhausted sludge for the anaerobic biodecolorization of the azo dye Acid Orange II.

The catalytic efficiency of the new carbonaceous materials (CMs) was successfully evaluated in the biological treatment of the azo dye Acid Orange II in a continuous up-flow packed bed reactor system. The newly obtained carbonaceous materials show high level of biodecolorization even at very short space times. Experimental results were similar to that of obtained with commercial activated carbon (CAC).

Chapter 3: A potential application of sludge-based catalysts for the anaerobic bio decolorization of tartrazine dye.

Highly efficient (K_2CO_3/sludge carbon and $ZnCl_2$/sludge carbon) sludge-based catalysts were successfully prepared by chemical addition followed by carbonization (at 800 ^{o}C) and were tested for anaerobic decolorization of tartrazine dye. Experimental results were well fitted to a first-order kinetic reaction model that describes their behavior on packed bed reactor operation. Adsorption isotherm data was well fitted to classical isotherm models.

Chapter 4: New sludge-based carbonaceous materials impregnated with different metals for anaerobic azo-dye reduction.

Addition of different transition metal to carbonaceous materials was studied. Using these new metal impregnated catalysts in an UPBR reactor showed high removal of azo-dye acid orange II. The immobilized anaerobic biomass on the catalyst was greatly influenced in the heterogeneous catalytic reaction. The higher adsorption capacity obtained was 172 mg/g for SBCNi600 catalyst.

Chapter 5: TiO_2-sludge carbon enhanced catalytic oxidative reaction in environmental wastewaters applications.

The performance of titanium incorporated on the surface of the sludge carbons was successfully tested for the removal of Bisphenol-A. Interaction of sludge and titanium was very good in the surface modification process (chemical treatment, hydrothermal and sol-gel solution). Surface modification process gave desired crystalline, surface chemistry and catalytic activity. The nanocomposite showed excellent stability while it was applied to the catalytic wet air oxidation process (39h). The hydrothermal deposited nano-composites showed the higher photo catalytic efficiency. The chemical fabricated nanocomposite showed better removal of Bisphenol-A in the catalytic ozonation, and wet air oxidation reaction.

Future recommendations

Utilization of waste sludge materials to various attractive environmental applications has quite advantages and is cost effective. These waste sludge materials can develop low cost catalysts suitable for the removal of pollutants from water and wastewaters and, at the same time, reduce the huge amount of harmful sludge materials. The carbon-rich content sludge materials can produce a large diversity of catalytic materials using specific fabrication methods.

The following recommendations are proposed for future works.

The new findings presented in this study can help to improve the wastewater treatment processes in laboratory as well as in pilot scale applications. Since the obtained results are good and comparable to that obtained with commercial activated carbons, these study will provoke the scientific community to utilize the waste material for the novel applications for the purification of wastewaters.

About the author

Sunil Athalathil was born in Kerala, India, in 1983. He received his B.Sc. in Chemistry in 2013 from St. Thomas College, Palai, Kerala. In 2007 he obtained his M.Sc. degree in Applied Chemistry from National Institute of Technology (NIT), Tiruchirappalli, India, with the dissertation topic “Studies on the synthesis and characterization of new amino acid derived chiral ligands”. After receiving his masters he moved to CWRDM, Calicut, Kerala, where he worked as a junior research fellow (DST-BARC project) in the laboratories of Dr. Shahul Hameed (2007−2008). In a short period he worked as a junior research fellow (CCRI-BARC project) in CCRI, Alappuzha, Kerala, in the chemistry lab of Dr. U.S Sharma (2008-2009). Then he moved to KVASU, Wayanad, Kerala, where he worked as a senior research fellow (World bank-ICAR project) in the laboratories of Dr. Raghu Ravindran (2009-2010). In October 2010 he started the Ph.D. research under Prof. Dr. **Azael Fabregat** and Dr. Agustí Fortuny at the Department of Chemical Engineering of Rovira i Virgili University, Tarragona, Spain.

Email: sunilarchem@gmail.com

Publications

Athalathil S., Fortuny, A., Font, J., Stüber, F., Bengoa, C., and Fabregat, A. *Characterization and performance of carbonaceous materials obtained from exhausted sludges for the anaerobic biodecolorization of the azo dye Acid Orange* II, Journal of Hazardous Materials 267 (2014) 21–30.

Sunil Athalathil, Frank Stüber, Cristophe Bengoa, Josep Font, Agusti Fortuny, Azael Fabregat. "*New sludge-based carbonaceous materials impregnated with different metals for anaerobic azo-dye reduction*" (Published in Journal of Environmental Chemical engineering).

Athalathil S., Fortuny, A., Font, J., Stüber, F., Bengoa, C., and Fabregat, "*A potential application of sludge based catalysts for the anaerobic bio decolorization of tartrazine dye".* (Submitted to Journal of Environmental Technology).

Sunil Athalathil, Bostjan Erjavec, Renata Kaplan , Frank Stüber, Cristophe Bengoa, Josep Font, Agusti Fortuny, Albin Pintar and Azael Fabregat. *"*TiO_2-Sludge carbon enhanced catalytic oxidative reaction in environmental wastewaters applications*".* (Submitted to journal of advanced functional materials).

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