

UNIVERSIDAD DE CANTABRIA

ESCUELA TÉCNICA SUPERIOR DE INGENIEROS INDUSTRIALES Y DE
TELECOMUNICACIONES

DEPARTAMENTO DE INGENIERÍA QUÍMICA Y QUÍMICA INORGÁNICA



**VALORIZACIÓN DE EFLUENTES DE DECAPADO
ÁCIDO METÁLICO. RECUPERACIÓN DE ZINC**

**TESIS DOCTORAL PRESENTADA POR HENAR SAMANIEGO PEÑA
PARA OPTAR AL TÍTULO DE
DOCTORA POR LA UNIVERSIDAD DE CANTABRIA**

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ANEXOS


ANEXO**A1. FICHAS DE SEGURIDAD DEL TBP**

FOSFATO DE TRIBUTILO

ICSC: 0584

 MINISTERIO DE TRABAJO Y ASUNTOS SOCIALES		 INSTITUTO NACIONAL DE SEGURIDAD E HIGIENE EN EL TRABAJO	
<p>FOSFATO DE TRIBUTILO</p> <p>Fosfato de tri-n-butilo</p> <p>Acido fosfórico, éster tributílico</p> <p>$C_{12}H_{27}O_4P$</p> <p>Masa molecular: 266.3</p> <p>N°CAS126-73-8</p> <p>N°RTECSTC7700000</p> <p>N°ICSC0584</p> <p>N° CE 015-014-00-2</p>			
TIPOS DE PELIGRO/ EXPOSICION	PELIGROS/ SINTOMAS AGUDOS	PREVENCION	PRIMEROS AUXILIOS/ LUCHA CONTRA INCENDIOS
INCENDIO	Combustible.	Evitar llama abierta.	Polvos, AFFF, espuma, dióxido de carbono.
EXPLOSION			
EXPOSICION			
• INHALACION	Dolor de cabeza, vértigo, náusea, dolor de garganta, convulsiones,	Ventilación, extracción localizada o protección respiratoria.	Aire limpio, reposo, posición de semiincorporado y someter a atención médica.

	dificultad respiratoria.		
• PIEL	¡PUEDE ABSORBERSE! Enrojecimiento, aspereza, sensación de quemazón.	Guantes protectores, traje de protección.	Quitar las ropas contaminadas, aclarar y lavar la piel con agua y jabón.
• OJOS	Enrojecimiento, dolor.	Gafas ajustadas de seguridad o pantalla facial.	Enjuagar con agua abundante durante varios minutos (quitar las lentes de contacto si puede hacerse con facilidad), después consultar a un médico.
• INGESTION	Aumento de la secreción salivar, debilidad, calambres abdominales, dificultad respiratoria, náusea, vómitos, diarrea, pérdida de conocimiento.	No comer, beber ni fumar durante el trabajo.	Enjuagar la boca y someter a atención médica.

DERRAMAS Y FUGAS	ALMACENAMIENTO	ENVASADO Y ETIQUETADO
Recoger el líquido procedente de una fuga en recipientes herméticos, absorber el líquido residual en arena o absorbente inerte y trasladarlo a un lugar seguro.		símbolo Xn R: 22 S: (2-)25 CE: 

FOSFATO DE TRIBUTILO**ICSC: 0584**

D A T O S I M P O R T A N T E S	<p>ESTADO FISICO; ASPECTO Líquido viscoso, incoloro, inodoro.</p> <p>PELIGROS FISICOS</p> <p>PELIGROS QUIMICOS La sustancia se descompone al calentarla intensamente y al arder, produciendo vapores tóxicos y gases (óxido fosforoso, óxido de carbono y fosfina). Ataca algunas formas de plásticos, caucho y recubrimientos.</p> <p>LIMITES DE EXPOSICION TLV (como TWA): 0.2 ppm; 2.2 mg/m³ 2.5 mg/m³(ACGIH 1990-1991).</p>	<p>VIAS DE EXPOSICION La sustancia se puede absorber por inhalación del vapor, a través de la piel y por ingestión.</p> <p>RIESGO DE INHALACION Por evaporación de esta sustancia a 20°C no se alcanza, o se alcanza sólo muy lentamente, una concentración nociva en el aire.</p> <p>EFFECTOS DE EXPOSICION DE CORTA DURACION La sustancia irrita los ojos, la piel y el tracto respiratorio. La inhalación del vapor puede originar edema pulmonar (véanse Notas). La sustancia puede tener efectos sobre el sistema nervioso por su poder de inhibición de la colinesterasa. Los efectos pueden aparecer de forma no inmediata.</p> <p>EFFECTOS DE EXPOSICION PROLONGADA O REPETIDA El contacto prolongado o repetido con la piel puede producir dermatitis. Se puede producir una acción inhibitoria importante de la colinesterasa sanguínea por acumulación de efectos: (véanse Síntomas Agudos).</p>
PROPIEDADES FISICAS	<p>Punto de ebullición (se descompone): 289°C</p> <p>Punto de fusión: <-80°C</p> <p>Densidad relativa (agua = 1): 0.98</p> <p>Solubilidad en agua: escasa</p> <p>Presión de vapor, kPa a 177°C: 17</p>	<p>Densidad relativa de vapor (aire = 1): 9.2</p> <p>Punto de inflamación: 146°C</p> <p>Temperatura de autoignición: 410°C</p> <p>Coefficiente de reparto octanol/agua como log Pow: 4.0</p>

DATOS AMBIENTALES	
NOTAS	
<p>Los síntomas del edema pulmonar no se ponen de manifiesto a menudo hasta pasadas algunas horas y se agravan por el esfuerzo físico. Reposo y vigilancia médica son por ello imprescindibles.</p> <p style="text-align: right;">Código NFPA: H 2; F 1; R 0;</p>	
INFORMACION ADICIONAL	
FISQ: 1-112 FOSFATO DE TRIBUTILO	
ICSC: 0584	FOSFATO DE TRIBUTILO
© CCE, IPCS, 1994	

A2. PROGRAMAS DE gPROMS

Definición de variables

Variable Types

Name	Lower bound	Default value	Upper bound	Units
coeficientesTM	-1.0E30	1.0E-4	1.0E15	m/h
concentration_a	-1.0E10	1.499	1.0E15	mol/m3
concentration_o	-1.0E10	0.1	1.1E11	mol/m3
flow	0.0	0.01	100.0	m3/h
volume	0.0	0.0010	0.2	m3

Definición de corrientes

STREAM TYPE: mainstream_a

IS concentration_a, flow

STREAM TYPE: mainstream_o

IS concentration_o, flow

Modelo de conexión módulos - tanques

MODEL: ext_rext

```
-----#  
#           SUBprograma           #  
#           MODULO DE EXTRACCION-REEXTRACCION           #  
#-----#
```

VARIABLE

K AS Concentration_a

UNIT

MOD_EXT AS Extraction
TAN_EXT AS Tanka
TAN_ORG AS Tanko
MOD_REXT AS Rextraction
TAN_STP AS Tank

EQUATION

MOD_EXT.Aqueous_out IS TAN_EXT.In;
MOD_EXT.Organic_out IS MOD_REXT.Organic_in ;
MOD_REXT.Organic_out IS TAN_ORG.In;
MOD_REXT.Aqueous_out IS TAN_STP.In;
TAN_EXT.Out IS MOD_EXT.Aqueous_in;
TAN_STP.Out IS MOD_REXT.Aqueous_in;
TAN_ORG.Out IS MOD_EXT.Organic_in;

#Igualamos las Km de los modulos de extraccion y reextraccion.
MOD_EXT.Mass_trans_coeff= MOD_REXT.Mass_trans_coeff;

Comprobación del BM total del sistema

(1192.801-TAN_EXT.CONC)*TAN_EXT.VOL-TAN_ORG.CONC*TAN_ORG.VOL-TAN_STP.CONC*
TAN_STP.VOL=K;

Modelo del módulo de extracción

```

MODEL: extraction
-----
#
#                               SUBprograma
#                               MODULO DE EXTRACCION
#
#
-----

PARAMETER

      Length,Vol_a,Vol_o,Ain,Aout AS          REAL

      DISTRIBUTION_DOMAIN

            Axial_a AS (0:Length)
            Axial_o AS (0:Length)

      VARIABLE

      Conc_a AS DISTRIBUTION(Axial_a)          OF concentration_a
      Conc_o,Conc_oi AS DISTRIBUTION(Axial_o) OF concentration_o
      Inconc_o,Outconc_o AS                    concentration_o
      Inconc_a,Outconc_a AS                    concentration_a
      Flow_a,Flow_o AS                        flow
      Mass_trans_coeff AS                      coeficientesTM
      Equil_const AS                          coeficientesTM

      STREAM

            Aqueous_in: Inconc_a,Flow_a AS mainstream_a
            Aqueous_out: Outconc_a,Flow_a AS mainstream_a
            Organic_in: Inconc_o,Flow_o AS mainstream_o
            Organic_out: Outconc_o,Flow_o AS mainstream_o

      BOUNDARY

#      Inlet conditions at z=0 and outlet conditions at z=L

            Conc_a(0)=Inconc_a;
            Conc_a(Length)=Outconc_a;

            # conectados en paralelo
            Conc_o(0)=Inconc_o;
            Conc_o(Length)=Outconc_o;

#      Conditions at fibre wall (r=R)

            FOR z :=0 to Length DO

                    Equil_const*Conc_a(z)=Conc_oi(z);

      END

```

```

EQUATION

FOR z :=0|+ to Length DO

#Al Zn en la fase acuosa
-PARTIAL(Conc_a(z),Axial_a)=Mass_trans_coeff*(Conc_oi(z)-Conc_o(z))*Ain/(Flow_a*Length);

# Al complejo en la fase orgánica

# PARTIAL(Conc_o(z),Axial_o)=Mass_trans_coeff*(Conc_oi(z)-Conc_o(z))*(Aout/(Flow_o*Length));
PARTIAL(Conc_o(z),Axial_o)=Mass_trans_coeff*(Conc_oi(z)-Conc_o(z))*Aout/(Flow_o*Length);

END
```

Modelo del módulo de reextracción

MODEL: reextraction

```

-----#
#                                     #
#                               SUBprograma                               #
#                               MODULO DE REEXTRACCION                     #
#                                     #
-----#

PARAMETER

      Length,Vol_a,Vol_o,Ain,Aout AS      REAL

DISTRIBUTION_DOMAIN

      Axial_a AS (0:Length)
      Axial_o AS (0:Length)

VARIABLE

      Conc_a AS DISTRIBUTION(Axial_a) OF concentration_a
      Conc_o,Conc_oi AS DISTRIBUTION(Axial_o) OF concentration_o
      Inconc_o,Outconc_o AS concentration_o
      Inconc_a,Outconc_a AS concentration_a
      Flow_a,Flow_o AS flow
      Mass_trans_coef AS coeficientesTM
      Equil_const AS coeficientesTM

STREAM

      Aqueous_in: Inconc_a,Flow_a AS mainstream_a
      Aqueous_out: Outconc_a,Flow_a AS mainstream_a
      Organic_in: Inconc_o,Flow_o AS mainstream_o
      Organic_out: Outconc_o,Flow_o AS mainstream_o

BOUNDARY

# Inlet conditions at z=0 and outlet conditions at z=L

      Conc_a(0)=Inconc_a;
      Conc_a(Length)=Outconc_a;

#conectados en paralelo
      Conc_o(0)=Inconc_o;
      Conc_o(Length)=Outconc_o;

#Conditions at fibre wall (r=R)

FOR z :=0 to Length DO

      Equil_const*Conc_oi(z)=Conc_a(z);

END

```

```

EQUATION

  FOR z :=0|+ to Length DO

-PARTIAL(Conc_a(z),Axial_a)=Mass_trans_coeff*(Conc_oi(z)-Conc_o(z))*Ain/(Flow_a*Length);

PARTIAL(Conc_o(z),Axial_o)=Mass_trans_coeff*(Conc_oi(z)-Conc_o(z))*Aout/(Flow_o*Length);

  END

```

Modelo del tanque de la fase acuosa de alimentación

MODEL: Tanka

```

#-----#
#          SUBprograma          #
#          TANQUE DE ALIMENTACION #
#-----#

```

VARIABLE

Conc_in,Conc	AS	concentration_a
Vol	AS	volume
Flow_in,Flow_out	AS	flow

STREAM

In: Conc_in,Flow_in	AS	mainstream_a
Out: Conc,Flow_out	AS	mainstream_a

EQUATION

```
Vol*Sconc=Flow_in*Conc_in-Flow_out*Conc;
```

Modelo del tanque de la fase de reextracción**MODEL: Tank**

```

#-----#
#               SUBprograma               #
#               TANQUE DE REEXTRACCION     #
#-----#

VARIABLE

Conc_in,Conc      AS      concentration_a
Vol               AS      volume
Flow_in,Flow_out AS      flow

STREAM

In: Conc_in,Flow_in AS mainstream_a
Out: Conc,Flow_out  AS mainstream_a

EQUATION

Vol*$conc=Flow_in*Conc_in-Flow_out*Conc;

```

Modelo del tanque de la fase orgánica**MODEL: Tanko**

```

#-----#
#               SUBprograma               #
#               TANQUE DE ORGANICA        #
#-----#

VARIABLE

Conc,Conc_in      AS      concentration_o
Vol               AS      volume
Flow_in,Flow_out AS      flow

STREAM

In: Conc_in,Flow_in AS mainstream_o
Out: Conc,Flow_out  AS mainstream_o

EQUATION

Vol*$Conc=Flow_in*Conc_in-Flow_out*Conc;

```

"Process" : Valores de parámetros e inicialización de variables

```
PROCESS: simul
```

```
-----#
#           MENU DE ENTRADA DE DATOS           #
#           SIMULACION DE LA PLANTA PILOTO     #
#-----#

UNIT  PLT  AS  ext_rext

SET

    WITHIN  PLT  DO

        WITHIN  MOD_EXT  DO

            Length          :=0.19;
            Vol_a           :=7.7e-5;
            Vol_o           :=2.05e-4;
            Ain             :=1.4;
            Acut            :=-1.4;
            Axial_a         :=[BFDM,1,20];
            Axial_o         :=[BFDM,1,20];

        END

        WITHIN  MOD_REXT  DO

            Length          :=-0.19;
            Vol_a           :=7.7e-5;
            Vol_o           :=2.05e-4;
            {Ain            :=1.45;
             Acut           :=-1.82;}
            Ain             :=-1.4;
            Acut            :=1.4;
            Axial_a         :=[BFDM,1,20];
            Axial_o         :=[BFDM,1,20];
            #Axial_a        :=[FFDM,1,20];
            #Axial_o        :=[FFDM,1,20];

        END

    END

ASSIGN

    WITHIN  PLT  DO

        MOD_REXT.Mass_trans_coeff :=6.17e-4;
        MOD_EXT.Equil_const      :=3.4;
        MOD_REXT.Equil_const      :=1.5;
        TAN_EXT.Flow_in          :=0.0384;
        TAN_ORG.Flow_in          :=0.0382;
        TAN_STP.Flow_in          :=0.0166;
        TAN_ORG.Vol              :=1e-3;
        TAN_EXT.Vol              :=1e-3;
        TAN_STP.Vol              :=1e-3;

    END

INITIAL

    WITHIN  PLT  DO

        WITHIN  TAN_EXT  DO

            Conc=1192.801;
            Conc=136.04;

#
```

```

                                END
                                WITHIN TAN_STP DO
                                    Conc=0.0;
                                END
                                WITHIN TAN_ORG DO
                                    Conc=0.0;
                                END
                                END
                                solutionparameters
                                gPLOT :=ON;
                                ReportingInterval :=0.2;
#                                outputlevel :-2;
                                gExcelOutput:=OFF
#                                gexceloutput:="Resultados_Gproms";

                                SCHEDULE
#                                CONTINUE UNTIL PLT.TAN_EXT.Conc<30
                                    CONTINUE FOR 5

```

"Estimation" : Fichero para estimación de parámetros

ESTIMATION: simul

```
#FICHERO DE ESTIMACIÓN DE PARÁMETROS
```

```
ESTIMATE
PLT.MOD_REXT.Mass_trans_coeff
1E-3 1E-5 1E-1
```

```
MEASURE
PLT.TAN_EXT.CONC
CONSTANT_VARIANCE(1:1:1)
```

```
MEASURE
PLT.TAN_STP.CONC
CONSTANT_VARIANCE(1:1:1)
```

```
RUNS
```

```
EXP1
EXP2
EXP3
EXP4
EXP5
```


"Experiment" : Ficheros con los datos experimentales

EXPERIMENT (PARAMETER ESTIMATION) : EXP1

INITIAL-CONDITION

PLT.TAN_EXT.CONC 1192.81

PLT.TAN_STP.CONC 0.0

PLT.TAN_ORG.CONC 0.0

MEASURE

PLT.TAN_EXT.CONC

0.0 1192.81

0.2 854.49

0.4 600.26

0.6 475.247

0.8 312.56

1.0 228.14

1.4 164.29

2.0 125.91

2.4 112.45

3.0 100.79

4.0 100.45

5.0 100.23

MEASURE

PLT.TAN_STP.CONC

0.0 0.0

0.2 22.0

0.4 60.8

0.6 180.98

0.8 245.0

1.0 298.0

1.4 417.89

2.0 512.0

2.4 578.0

3.0 627.0

4.0 634.0

5.0 645.0

INTERVALS

1

1.0

PIECEWISE-CONSTANT

PLT.TAN_EXT.VOL

9.225E-4

PIECEWISE-CONSTANT

PLT.TAN_ORG.VOL

5.9E-4

PIECEWISE-CONSTANT

PLT.TAN_STP.VOL

9.225E-4

PIECEWISE-CONSTANT

PLT.TAN_EXT.Flow_in

0.03792

PIECEWISE-CONSTANT

PLT.TAN_ORG.Flow_in

0.03168

PIECEWISE-CONSTANT

PLT.TAN_STP.Flow_in

0.03552

EXPERIMENT (PARAMETER ESTIMATION): EXP2

INITIAL-CONDITION
PLT.TAN_EXT.CONC 565.82
PLT.TAN_STP.CONC 0.0
PLT.TAN_ORG.CONC 0.0

MEASURE
PLT.TAN_EXT.CONC
0.0 596.0
0.25 465.65
0.5 391.1
0.67 344.08
1.0 198.78
1.4 100.78
2.0 84.98
2.4 80.23
3.0 71.0
4.0 73.87
5.0 68.56

MEASURE
PLT.TAN_STP.CONC
0.0 0.0
0.25 28.44
0.5 87.55
0.67 130.75
1.0 168.78
1.4 201.34
2.0 245.96
2.4 257.89
3.0 281.26
4.0 298.59
5.0 302.25

INTERVALS
1
1.0

PIECEWISE-CONSTANT
PLT.TAN_EXT.VOL
9.225E-4

PIECEWISE-CONSTANT
PLT.TAN_ORG.VOL
5.9E-4

PIECEWISE-CONSTANT
PLT.TAN_STP.VOL
9.225E-4

PIECEWISE-CONSTANT
PLT.TAN_EXT.Flow_in
0.03396

PIECEWISE-CONSTANT
PLT.TAN_ORG.Flow_in
0.03156

PIECEWISE-CONSTANT
PLT.TAN_STP.Flow_in
0.02988

EXPERIMENT (PARAMETER ESTIMATION) : EXP3

INITIAL-CONDITION

PLT.TAN_EXT.CONC 263.64
PLT.TAN_STP.CONC 0.0
PLT.TAN_ORG.CONC 66.98

MEASURE

PLT.TAN_EXT.CONC
0.0 263.64
0.08333 238.94
0.1667 194.59
0.25 172.04
0.5 131.51
0.75 119.28
1.0 107.05
1.5 72.42
2.0 65.08
2.5 57.74
3.0 53.09
4.0 43.31
5.0 39.39

MEASURE

PLT.TAN_STP.CONC
0.0 0.0
0.08333 4.14
0.1667 11.25
0.25 21.1
0.5 50.46
0.75 74.63
1.0 98.12
1.5 128.7
2.0 156.9
2.5 159.65
3.0 171.58
4.0 177.39
5.0 188.4

INTERVALS

1
1.0

PIECEWISE-CONSTANT

PLT.TAN_EXT.VOL
9.225E-4

PIECEWISE-CONSTANT

PLT.TAN_ORG.VOL
5.9E-4

PIECEWISE-CONSTANT

PLT.TAN_STP.VOL
9.225E-4

PIECEWISE-CONSTANT

PLT.TAN_EXT.Flow_in
0.0324

PIECEWISE-CONSTANT

PLT.TAN_ORG.Flow_in
0.02628

PIECEWISE-CONSTANT

EXPERIMENT (PARAMETER ESTIMATION): EXP4

INITIAL-CONDITION
PLT.TAN_EXT.CONC 138.24
PLT.TAN_STP.CONC 0.0
PLT.TAN_ORG.CONC 0.0

MEASURE
PLT.TAN_EXT.CONC
0.0 138.24
0.08333 131.64
0.25 119.89
0.5 107.17
0.75 98.85
1.0 91.51
1.5 80.99
2.0 70.47
2.5 58.11
3.5 51.14

MEASURE
PLT.TAN_STP.CONC
0.0 0.0
0.08333 1.34
0.25 6.12
0.5 11.01
0.75 16.7
1.0 22.38
1.5 35.23
2.0 47.96
2.5 58.23
3.5 71.45

INTERVALS
1
1.0

PIECEWISE-CONSTANT
PLT.TAN_EXT.VOL
9.225E-4

PIECEWISE-CONSTANT
PLT.TAN_ORG.VOL
5.9E-4

PIECEWISE-CONSTANT
PLT.TAN_STP.VOL
9.225E-4

PIECEWISE-CONSTANT
PLT.TAN_EXT.Flow_in
0.0342

PIECEWISE-CONSTANT
PLT.TAN_ORG.Flow_in
0.0288

PIECEWISE-CONSTANT
PLT.TAN_STP.Flow_in
0.03312

EXPERIMENT (PARAMETER ESTIMATION): EXP5

INITIAL-CONDITION

PLT.TAN_EXT.CONC 136.04
PLT.TAN_STP.CONC 0.0
PLT.TAN_ORG.CONC 0.0

MEASURE

PLT.TAN_EXT.CONC
0.0 136.04
0.0833 114.26
0.16667 92.49
0.25 80.0
0.5 51.63
0.75 36.46
1.0 27.65
1.5 18.78
2.0 14.07
2.5 11.87
3.0 11.93
4.0 10.17
5.0 11.12

MEASURE

PLT.TAN_STP.CONC
0.0 0.0
0.0833 1.29
0.16667 4.33
0.25 9.16
0.5 27.89
0.75 46.92
1.0 62.09
1.5 79.52
2.0 91.91
2.5 94.81
3.0 101.05
4.0 103.01
5.0 102.76

INTERVALS

1
1.0

PIECEWISE-CONSTANT

PLT.TAN_EXT.VOL
9.225E-4

PIECEWISE-CONSTANT

PLT.TAN_ORG.VOL
5.9E-4

PIECEWISE-CONSTANT

PLT.TAN_STP.VOL
9.225E-4

PIECEWISE-CONSTANT

PLT.TAN_EXT.Flow_in
0.0324

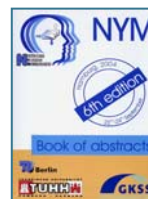
PIECEWISE-CONSTANT

PLT.TAN_ORG.Flow_in
0.0324

A3. ARTÍCULOS Y CONGRESOS

Congresos

a) 6th Network Young Membrains (NYM6), 22 – 24 Septiembre, 2004, Hamburgo (Alemania)



MEMBRANE-BASED SOLVENT EXTRACTION FOR THE RECOVERY OF ZINC FROM PICKLING EFFLUENTS

Keywords: membrane solvent extraction, zinc, TBP

PhD 10/2003 -

Introduction

Zinc hot dip galvanising is used to apply a corrosion resistant coating of zinc to protect steel goods from corrosion. This process produces a spent pickling hydrochloric acid effluent that is high in Fe^{2+} and Zn^{2+} and may contain other heavy metals (Pb, Ni, Cu, Mn, etc.) as impurities[1]. Therefore, the resulting effluent presents a strong hazardous character and needs to be cleaned before discharge. The development of a clean process allowing the recovery of zinc under conditions that permits the manufacture of electrolytic grade metal would reduce the effluent toxicity, recovering at the same time the component of higher added value. In previous papers, it was found that Zn^{2+} can be recovered from spent pickling solutions by means of membrane-based solvent extraction, using tributyl phosphate and service water as extractant and back-extraction agent respectively [2],[3].

Objectives

The aim of this work is to study the recovery of Zinc from spent pickling solutions by means of non-dispersive solvent extraction. Batch experiments were performed in order to analyse the influence of the initial metal concentration on the separation kinetics. A kinetic model has been proposed.

Materials & Methods

A frontal view of the non-dispersive experimental system is shown in Figure 1. Two hollow fiber modules are being used, flowing the organic phase from the EX module to the BEX one. In the first module, the solute was transferred from the aqueous feed to the organic phase, and in the second module the solute is transported to the BEX phase. The three phases (feed, organic and stripping) are pumped in a recycling model, and they flow concurrently. The extraction and back extraction agents are TBP and service water respectively.

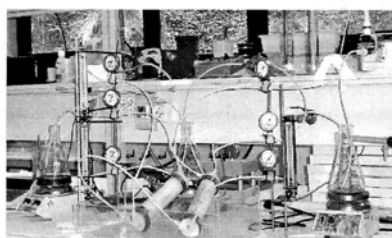


Figure1. Experimental set up

Results

A series of experiments, varying the initial concentration of zinc in the feed solution (80, 40, and 20 g/l approximately), has been carried out in order to analyse the influence of the initial metal concentration on the separation kinetics. Kinetic results of zinc separation were satisfactory enough and therefore it has been developed a kinetic model consisting of a system of partial differential and algebraic equations describing the mass balances of Zinc in the fluid phases of the hollow-fibre contactors and homogenisation tanks. The main

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hypothesis is that membrane mass transport controls the extraction kinetics. The equilibrium constants for the EX and BEX reactions, necessary for the resolution of the mathematical model, were calculated by means of a series of experiments carried out in a rotatory equipment (dispersive extraction), varying the initial feed concentration and the relations of volume between feed/organic and organic/stripping phases. ($[Zn]_{initial} \approx 80, 40, 20 \text{ g/l}$; $V_a/V_o = 1/1, 1/4, 1/8$; $V_o/V_s = 1/1, 1/4, 1/8$). It was found out two distribution coefficients for the extraction and back extraction equilibrium: 1 and 1.5 respectively.

The resolution of the mathematical model was performed by the gPROMS simulation package allowing the calculation of the optimum value of the mass transfer coefficient, $k_m = 1.7E-7 \text{ m/s}$. The comparison of experimental and simulated data confirms the validity of the kinetic analysis in this range of initial concentration. As an example, the comparison of estimated and experimental data for three experiments of $[Zn]_{initial} \approx 20 \text{ g/l}$, is shown in Figure 2. The experiments carried out with other initial concentrations of Zinc have a similar behaviour.

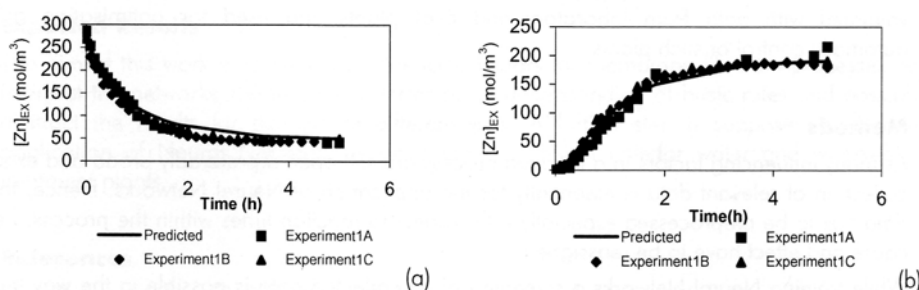


Figure 2: Comparison of estimated and experimental data in the EX (a) and BEX (b) tanks for experiments of $[Zn]_{initial} \approx 20 \text{ g/l}$

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b) 7th World Congress of Chemical Engineering (WCEE7), 10 – 14 Julio, 2005 Glasgow (Escocia)



P39-011 — Clean technologies in the treatment of waste effluents. Recovery of metallic pollutants.

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Engineering for Life - Sustainable and Clean Technologies

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Recovery of the valuable components that are contained in waste effluents is one of the best options both from the economic as well as from the environmental point of view. The difficulty in the development of recovery processes is associated i) to the low concentration of the components, and ii) to the physico-chemical complexity usually encountered in waste effluents, where the required component is present with different amounts of non-desirable compounds. Both aspects have been researched in the application of selective membranes to the treatment and recovery of metallic components in polluted waters obtaining promising results. In this work the experimental analysis and mathematical modelling of a selective membrane process that allows separation and concentration of metallic compounds from polluted waters is reported. Two different applications have been considered i) separation and concentration of chromate compounds contained in ground water reservoirs in low concentration, and ii) separation and recovery of zinc contained in spent pickling solutions. Zn⁺² was recovered from spent pickling solutions by means of membrane-based solvent extraction, using tributyl phosphate and service water as extractant and back-extraction agent respectively. Since the viability of this process was proved, a series of experiments, varying the initial concentration of zinc in the feed solution, has been carried out in order to analyse the influence of the initial metal concentration on the separation kinetics. Kinetic results of zinc separation were satisfactory enough and therefore it has been developed a kinetic model consisting of a system of partial differential and algebraic equations describing the mass balances of Zn⁺² in the fluid phases of the hollow-fibre contactors and homogenisation tanks. The technology used in the recovery of Cr⁺⁶ is called “emulsion pertraction”. This technology combines the advantages of the non dispersive solvent extraction with those of the emulsion membrane technologies. Alamine 336 and NaOH were selected as anionic extractant and aqueous strip solution respectively. Once the viability of the recovery of Cr⁺⁶ was checked, several experiments were carried out to analyse the influence of NaOH concentration in the extraction and back extraction steps. Therefore, a mathematical model has been developed in order to describe the process.

c) International Congress on Membrane and Membrane Processes 2005 (ICOM 2005), 21-26 A gosto, 2005, Seul (Korea)



MEMBRANE PROCESSES FOR THE EFFICIENT RECOVERY OF ANIONIC POLLUTANTS

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Introduction

The presence of pollutant anions in effluents and groundwaters, is an environmental problem that is necessary to solve due to the high toxicity of most of these compounds. The removal of these pollutants permits the discharge of the waste waters according to the law. On the other hand, the recovery of these compounds for selling or re-using in some industrial applications is an interesting alternative in order to compensate the costs associated to the cleaning processes. For these reasons, it is necessary to develop "zero discharge" technologies which also permit the recovery of the valuable compounds [1].

In this work, the membrane based solvent extraction technologies have been proposed to reach both of these objectives. The separations of two different anionic pollutants have been studied. In the first system the hexavalent chromium anions are dissolved in groundwater reservoirs, contaminated as a result of the filtration from surface deposition of industrial wastes. The second system is formed by the zinc chlorocomplexes contained in spent pickling solutions produced in the hot dip galvanizing processes. The membrane technologies used to reach the above defined objectives are respectively the emulsion pertraction (EPP) and the non dispersive solvent extraction (NDSX), using hollow fiber modules.

Experimental Section

The two membrane based technologies proposed use hollow fiber modules as membrane contactors. The extraction of the anions is carried out using a selective extractant as carrier. In the NDSX two hollow fiber modules are used. In the extraction (EX) module, the solute is transferred from the aqueous feed solution to the organic carrier phase, and in the back - extraction (BEX) module the solute is transported from the organic phase to the stripping phase [2, 3]. In the EPP process only one membrane module is used to carry out simultaneously the EX and BEX steps. The aqueous feed solution, with the solute to be extracted, flows through to the inner side of the hollow fibers. The aqueous strip solution is dispersed in the organic phase containing the carrier, and the emulsion formed is pumped through the outside of the hollow fibers. The solute is transferred from the aqueous feed solution to the organic phase which is embedded in the pores of the hollow fibers, and next it is transported to the inner side of the droplets where the strip phase is situated. The solute is recovered from the internal aqueous phase after emulsion breakage [4].

Table 1 shows the characteristics of the feed solutions used to carry out the experiments. For the EX and BEX of zinc chlorocomplexes pure TBP (tributyl phosphate) and service water were used as solvating extractant and stripping phase respectively. For chromium anions, Alamine 336 (10%v/v) and NaOH (3 -6 M) are the anionic extractant and the stripping phase respectively.

Table 1: Feed Solutions Characteristics

	Spent Pickling Solution (Real effluent)	Groundwater Solution (Synthetic solutions)
FEED COMPONENTS	[Zn] = 82 g/L [Fe ³⁺] = 96 g/L [Cl] = 227 g/L Mn, Pb, Al, Cr, Ni, Cd, Cu, Co (Impurities)	[Cr] = 0.5 g/L [SO ₄ ²⁻] = 1 g/L [Cl] = 0.3 g/L
pH	~ 0	Adjusted to 1.5 using H ₂ SO ₄

Results and Discussion

For the recovery of zinc from spent pickling solutions the influence of the initial metal concentration was experimentally studied. Starting with an initial concentration of zinc of 1200 mol/m^3 , two other feeds were prepared by dilution of the real effluent to give an initial zinc concentration of 600 and 300 mol/m^3 . Zinc separation experiments were performed in recycling mode. Figures 1 – 2 represent the evolution with time of the dimensionless concentration of zinc in the EX and BEX tanks.

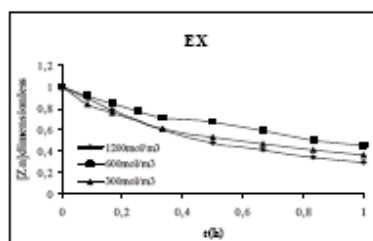


Figure 1: EX of zinc

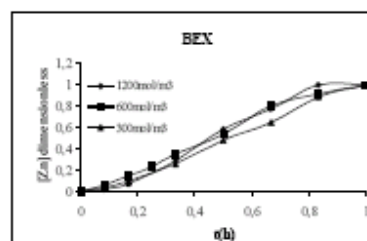


Figure 2: BEX of zinc

It can be observed that there is no influence of the initial metal concentration on the separation kinetics of zinc in the EX and BEX steps. Moreover the EX and BEX percentages for zinc are around 75 % for 1 hour of experimental running.

For the recovery of chromium from groundwaters a group of experiments were performed varying the NaOH concentration in the stripping phase. In these experiments the feed solution flows in continuous mode and the emulsion is pumped in a recycling mode. Figure 3 shows the concentration of chromium in the feed solution at the module outlet. It is observed that pseudo steady state of the system is reached rapidly and the chromium concentration goes from 500 mg/L at the module inlet to 0.8 mg/L at the module outlet. Figure 4 shows the evolution with time of the chromium concentration in the stripping phase contained in the emulsion tank, where it is observed that the chromium in the stripping solution is concentrated to a value of 15 g/L . It can be noted that the influence of the NaOH concentration in the range $3 - 6 \text{ mol/L}$, on the chromium EX and BEX steps is negligible.

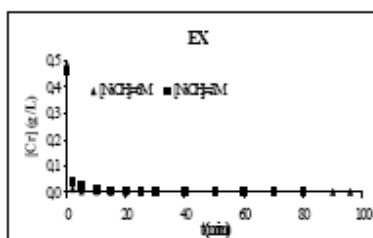


Figure 3: EX of chromium

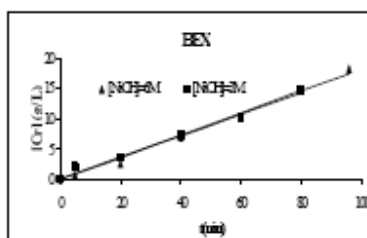


Figure 4: BEX of chromium

Conclusions

This work reports the viability of using membrane – based solvent extraction technologies for the recovery of i) chromium from contaminated groundwaters and ii) zinc from spent pickling baths. Current work under development is related to the modeling and design of the two processes.

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a) *Membrane processes for the efficient recovery of anionic pollutants.* Ortiz, I., Bringas, E., Samaniego, H., San Román, M.F., Urtiaga, A. *Desalination*. **2003**, 193, 17.



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Membrane processes for the efficient recovery of anionic pollutants

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Abstract

The development of new “zero discharge” technologies which also permit the recovery of pollutant anions from industrial waste waters is a way of minimizing the cost of the processes and the impact on the environment. The kinetic behaviour of the removal and recovery of two different anionic pollutants is reported using membrane-based solvent extraction technologies: (1) recovery of hexavalent chromium anions contained in groundwaters by means of emulsion pertaction (EPT) and (2) recovery of zinc chlorocomplexes from spent pickling solutions by means of non dispersive solvent extraction (NDSX). Kinetic experiments were performed in order to study the influence of different variables on the separation kinetics, i.e., the NaOH concentration in the stripping phase in the case of chromium and the initial metal concentration in the aqueous feed solution in the case of zinc recovery.

Keywords: Anionic pollutants; Emulsion pertaction; Non-dispersive solvent extraction

1. Introduction

The presence of pollutant anions in industrial effluents and/or in groundwaters is an environmental problem that is necessary to solve due to the high toxicity of most of these compounds. On

the other hand, the recovery of the valuable compounds for re-use in some industrial applications is an interesting alternative in order to minimize the environmental impact and to compensate for the costs associated to the cleaning processes. Therefore, the development of “near-zero discharge” technologies, which also permit the

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recovery of valuable compounds, is a sustainable alternative [1].

The difficulty in the development of recovery processes is associated to (1) low concentration of the components and (2) physicochemical complexity usually encountered in waste effluents where the required component is present in a heterogeneous mixture with different amounts of non-desirable compounds. Among the alternatives for the treatment of aqueous streams containing ionic pollutants, one of the most promising techniques is membrane-based solvent extraction. Several works have reported experimental applications at laboratory scale, i.e., separation of Ni–Cd mixtures by non-dispersive solvent extraction (NDSX) [2]; recovery of copper by means of emulsion extraction (EPT) [3,4]; iron (III) transport using supported liquid membranes (SLM) [5].

In this work two different applications have been considered: (1) separation and concentration of hexavalent chromium anions contained in ground water reservoirs in low concentration and (2) separation and recovery of zinc chlorocomplexes contained in spent pickling solutions.

The widespread use of chromium in industrial applications such as leather tanning, metallurgy and electroplating processes has caused chromium contamination of surface and ground waters. Due to the high toxicity of hexavalent chromium, clean technologies are needed for the treatment of the polluted ground waters, allowing at the same time the recovery of the metallic species [1,6].

Hot dip galvanizing is used to apply a corrosion-resistant coating of zinc to protect steel goods from corrosion. This process produces a spent pickling hydrochloric acid effluent with a high concentration of Fe^{2+} and Zn^{2+} ; the effluent also contains traces of other heavy metals (Pb, Ni, Cu, Mn, etc.). Therefore, the resulting waste is very hazardous and needs to be treated before disposal. The development of a clean process allowing the recovery of zinc under conditions that permit the recovery of electrolytic-grade

metal would reduce the effluent toxicity, recovering at the same time a component of high added value [7,8].

2. Experimental

The two membrane-based technologies proposed use hollow-fiber (HF) modules as membrane contactors and the extraction of the anionic pollutants is carried out using a selective extractant as carrier. The technology used in this work for the recovery of chromium is called EPT. It is an advanced membrane-based technology where the extraction (EX) and back extraction (BEX) steps take place simultaneously in the same HF module. The aqueous feed solution flows through the inner side of the microporous HF membranes, and the emulsion (formed by the organic extractant phase that contains inner droplets of the aqueous stripping phase) flows countercurrently through the shell side of the HF modules. The solute is transferred from the aqueous feed solution to the stripping phase contained in the emulsion droplets. The solute is recovered from the internal aqueous phase after emulsion breakage [9–11].

The removal and recovery of zinc chlorocomplexes from spent pickling solutions was performed following a similar background using a different manner of contact of the liquid phases i.e., NDSX. In this technology two HF modules are used. In the EX module, the solute is transferred from the aqueous feed solution to the organic phase, and in the BEX module the solute is transported from the organic phase to the stripping solution. The organic phase circulates from the EX module to the BEX module in a closed circuit. Figs. 1 and 2 show, respectively, the EPT and NDSX systems comprising the HF modules, the stirred tanks for the fluid phases, and accessories [12,13].

Zinc experiments were carried out using a real effluent as aqueous feed solution. In the study of chromium removal, the presence of high concen-

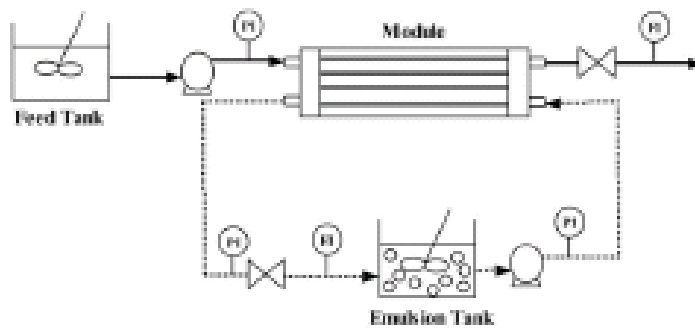


Fig. 1. Experimental set-up (EPT).

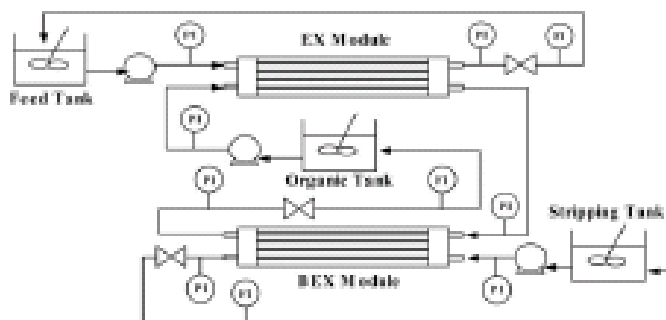


Fig. 2. Experimental set-up (NLGX).

trations of calcium in the groundwaters [14], required the elimination of the cation previous to the anionic separation in order to avoid precipitation of calcium hydroxide and fouling of the microporous HF membranes. For this reason, the experiments were carried out with synthetic solutions that simulated the composition of polluted waters, specially in anionic composition. Table 1 shows the composition of the feed solutions used in the experimental study.

In the chromium experiments the aqueous feed solution flowed in a single-pass mode whereas the emulsion was recycled in order to achieve a high chromium concentration in the stripping solution. For the performance of the zinc removal process, the fluid phases flowed co-currently in a recycling mode.

Table 1
Feed solutions characteristics

Zinc solution (real effluent)	Chromium solution (synthetic solutions)
[Zn] = 1254 mol/m ³	[Cr ^{VI}] = 9.6 mol/m ³
[Fe ²⁺] = 1719 mol/m ³	[SO ₄ ²⁻] = 10.4 mol/m ³
[Cl ⁻] = 6403 mol/m ³	[Cl ⁻] = 8.5 mol/m ³
Mn, Pb, Al, Cr, Ni, Cd, Cu, Co (impurities)	

pH < 0, adjusted to 1.5 using H₂SO₄.

The organic phase used for Cr^{VI} extraction was prepared using 10% v/v of tri-octyl/decyl amine (Alamine[®] 336, Cognis) as anionic extractant, Isopar L Fluid (Exxonmobile Chemical), that is

an isoparaffinic hydrocarbon, as solvent, 3% w/v of Pluronic PE 3100 (block copolymer of ethylene oxide and propylene oxide, BASF) as surfactant and 1% v/v of 1-Dodecanol (Merck) as modifier. The BEX step was performed using NaOH (Panreac) in a concentration range of 3000–6000 mol/m³. For Zn²⁺ extraction, pure tributyl phosphate (TBP) (Merck) and service water were the solvating extractant and the stripping phase, respectively.

The chromium and zinc concentrations were analyzed using an atomic absorption spectrophotometer (Perkin Elmer 3110).

3. Results and discussion

3.1. Zinc results

For the recovery of zinc from spent pickling solutions, different kinetic experiments were performed in order to analyze the influence of the initial metal concentration on the rate of zinc separation. Starting with an initial concentration of zinc of 1200 mol/m³, two different batches of feed solution were prepared by dilution of the real effluent to give an initial zinc concentration of 600 and 300 mol/m³. Fig. 3 shows the comparison of the kinetic extraction and back extraction results. The dimensionless concentration of zinc is given in order to make possible the comparison between the results obtained at different initial zinc concentrations. It can be observed that there is no significant influence of the initial metal concentration on the separation kinetics of zinc in the extraction and back extraction steps.

Previous works reported the evolution of the separation selectivity, $\alpha_{Zn/Fe}$, with the initial concentration of zinc in the feed solution, indicating that diluted solutions ($[Zn]_0 < 600$ mol/m³) lead to higher values of the separation selectivity, $\alpha_{Zn/Fe} = 125$ mol Zn/mol Fe, whereas with more concentrated feed solutions ($[Zn]_0 > 600$ mol/m³) the selectivity decreases to an almost asymptotic value around 30 mol Zn/mol Fe [8]. Therefore, a

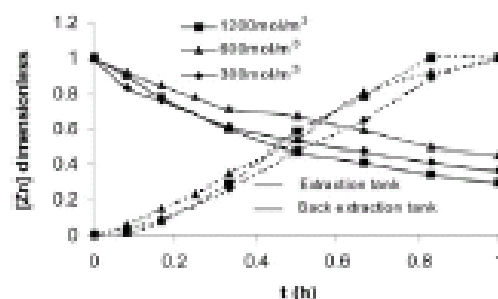


Fig. 3. Evolution with time of the dimensionless concentration of zinc in the EX and BEX tanks. Influence of the initial concentration of Zn²⁺ in the feed solution.

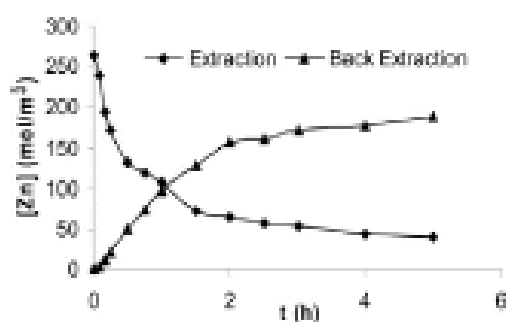


Fig. 4. Evolution with time of the concentration of zinc in the EX and BEX tanks.

set of experiments using diluted feed solutions were developed for 5 h of experimental running in order to study the behaviour of the extraction and back extraction processes for longer running times. Fig. 4 shows the kinetic results in the extraction and back extraction steps.

The concentration of Zn in the extraction tank decreased from the initial 264 mol/m³ to 39 mol/m³, achieving a stripping solution of 139 mol/m³. Extraction and back extraction percentages were around 85%.

3.2. Chromium results

For the recovery of chromium from ground waters, a group of experiments was performed

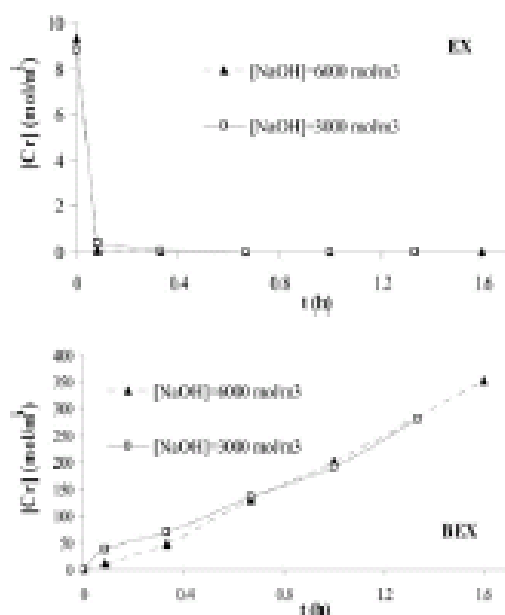


Fig. 5. Evolution with time of the chromium concentration in the EX and BEX steps.

varying the NaOH concentration in the stripping phase. Fig. 5 shows a comparison of the kinetic results in the extraction and back extraction steps. The first graph represents the evolution with time of the chromium concentration in the aqueous feed solution at the module outlet. In the second graph, the evolution with time of the chromium concentration in the stripping solution is represented.

In relation to the extraction results, it can be observed that the pseudo-steady state of the system is reached rapidly, and the chromium concentration goes down from 9.6 mol/m^3 at the module inlet to 0.015 mol/m^3 at the module outlet in one pass through the HF contactor (being the residence time in the module $t = 0.014 \text{ h}$) that is close to the wastewater maximum chromium level for final disposal into the environment according to environmental regulations (0.00961 mol/m^3) [15]. On the other hand, the back extraction results

show that chromium in the stripping solution is concentrated to a value of 281 mol/m^3 after 1.3 h of operation; thus a concentrating factor of 18,700 is obtained. It can be noted that the influence of the concentration of the solution hydroxide stripping agent, in the range 3000–6000 mol/m^3 , on the chromium EX and BEX results is negligible.

4. Conclusions

This work reports the experimental study of the behaviour of clean technologies based on the use of selective membranes applied to the recovery of anionic compounds from polluted waters. Two cases of study were considered: (1) the recovery of chromate anions from polluted ground waters by means of an EPT that used Alamine 336 as selective extractant and NaOH as stripping solution, and (2) the recovery of zinc chlorocomplexes from a spent pickling acidic effluent by means of NSEX, employing TBP as the selective extractant and service water as the back-extraction phase. For both systems the kinetic behaviour of the separation concentration was analyzed.

In future studies the kinetic modelling of both processes, that is, the necessary tool for design and optimisation, will be reported.

Acknowledgments

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Modelling of the Extraction and Back-Extraction Equilibria of Zinc from Spent Pickling Solutions

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Abstract: This work reports the study of the chemical equilibria of the extraction and back-extraction of zinc from spent pickling solutions. Tributyl phosphate was used as a selective extractant and service water as a back extraction agent. Feed solutions had an average composition of 6.4 M Cl^- , 1.2 M Zn^{+2} , 1.7 M Fe^{+2} and traces of other heavy metals i.e., Pb, Ni, Cu, Mn. Under the experimental conditions the ion ZnCl_4^{2-} was the predominant zinc species in feed. A careful experimental design was performed obtaining the equilibria mathematical models and parameters, $K_{\text{EX}} = 0.137 \text{ (mol/L)}^{-4}$, and $K_{\text{BEX}} = 1.46 [-]$.

Keywords: Extraction equilibrium, back-extraction, zinc chloride, tributyl phosphate, water

INTRODUCTION

Steel goods are most often coated with zinc to protect their surfaces against atmospheric corrosion. Zinc films are deposited by immersing steel details in molten zinc around 450°C. In order to obtain a high quality zinc film, pre-treatment of the steel surface is required, including several processes, i.e.,

1. degreasing with a hot alkaline solution;
2. rinsing with water;

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3. pickling with HCl 20%;
4. rinsing, and
5. fluxing with zinc and ammonium chlorides.

In the pickling step, hydrochloric acid is consumed during the process, but the concentration of chloride ions does not change. As a result, the spent pickling solution contains zinc and iron, present mainly in the form of iron(II), which form appropriate chlorocomplexes. Typical metallic concentrations lie in the range 20–120 g/L for zinc and 100–130 g/L for iron, whereas the hydrochloric acid concentration lies in the range 1–6 mol/L (1). Besides, the solution may contain other heavy metals such as Pb, Ni, Cu, Mn, etc. at low concentration. Thus, this effluent has a strong hazardous character and needs to be treated before disposal (2).

The spent pickling solution is conventionally processed by the Ruthner process in which the hydrochloric acid is evaporated and granules of iron oxide are formed in a fluidized bed at temperatures above 600°C; however, the presence of zinc in amounts higher than 0.5 g/L disturbs the process (2–6).

The development of a clean process allowing the recovery of zinc under conditions that permit the recovery of electrolytic grade metal would reduce the effluent toxicity, recovering at the same time the component of higher added value.

Solvent extraction and membrane based solvent extraction have received considerable attention and have been proved to be very efficient in the removal of solutes from aqueous solutions (7–12).

With regard to the separation of zinc (II) from solutions containing hydrochloric acid, Cierpiszewski et al. (2002) (5) studied the behavior of different extractants in the separation between zinc and iron concluding that solvating extractants led to better extraction results than other analysed compounds. In fact, tributyl phosphate (TBP) is the most suitable reagent and enables both the extraction (EX) of zinc (II) from HCl solutions and subsequent back extraction (BEX) with water (3, 5, 13). In a previous work it was reported the viability of applying the non dispersive solvent extraction (NDSX) technique to the recovery of zinc(II) from spent pickling solutions using TBP and service water as extraction and back extraction agents respectively (2). In the latter work it was reported that the transport of trace metals such as Mn, Pb, Al, Cr, etc., to the stripping solution was negligible. The homogeneous formation of zinc chloride complexes in hydrochloric acid solutions and the extraction of the formed complexes into organic phases has also been reported (14–16). However, a suitable equilibrium model of the extraction and back-extraction reactions together with their representative equilibrium parameters, has not been reported due to the complex behavior of the system.

The aim of this work is to study the chemical equilibrium of the extraction of zinc(II) from high acidic medium using TBP as extractant, as well as the back-extraction reaction using service water, in order to obtain the

mathematical model and parameters needed to design and optimisation of separation processes.

EXPERIMENTAL

Reagents and Analysis

Physicochemical characteristics of the industrial spent pickling solution used in the experimental study are shown in Table 1. Extraction and back-extraction agents were pure grade TBP (tributyl phosphate, MERCK) and service water, respectively.

Experiments conducted at different initial zinc concentrations were carried out by diluting the initial effluent. After dilution of the samples, the concentration of Cl^- ions was adjusted to 2.5M by addition of HCl, in order to avoid the influence of this variable in the studied system.

The metallic content of the feed solution was analysed using a Perkin Elmer Plasma Emission Spectrometer ICP 400; the iron(II) concentration was determined in a Spectrophotometer Spectroquant Nova 400; the concentration of chloride ions was analysed using an Ion Chromatograph Dionex-120 and finally the zinc content of the samples was determined using Atomic Absorption Spectrophotometry, Perkin Elmer 3110.

Experimental Methodology

Equilibrium experiments were carried out in separatory funnels, using a rotatory SBS stirrer (5–150 rpm), at room temperature ($18 \pm 2^\circ\text{C}$). Extraction

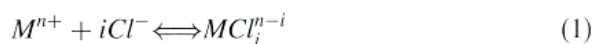
Table 1. Physico-chemical analysis of the feed solutions

Property color (pH)	Value (green \approx 0)	
	mg/L	mol/L
Zn	81,760	1.250
Fe	96,000	1.720
Fe + 2	96,000	1.720
Mn	174	3.17E-3
Pb	104.64	5E-4
Al	38.21	1.4E-3
Cr	18.99	0.365
Ni	18.73	3.2E-4
Cd	26.63	5.9E-5
Cu	5.18	8.1E-5
Co	0.14	2.4E-6
Cl-	225,920	6.400

experiments were carried out starting with four different initial concentrations of zinc(II) (1.2, 0.6, 0.3, and 0.15 mol/L) and using different volume ratios of the feed and organic phases: $V_a/V_o = 1/1, 1/2, 1/4$. Table 2 shows the experimental planning. In the extraction analysis 6 batches were prepared with similar conditions (E1-E6) in order to provide enough organic phase to replicate back-extraction experiments. The extractant (undiluted TBP) and the feed solution were mechanically shaken for 1 hour, time enough to reach equilibrium (experimentally determined). After equilibration, the solution was allowed to settle down for phase separation (few minutes). The content of zinc(II) in the aqueous solutions was analysed after complete separation of the phases. The study of zinc(II) stripping was performed in a similar way. Volumes of the loaded extractant (5–20 mL), were equilibrated for 1 hour at the selected organic/stripping ratios $V_o/V_s = 1/1, 1/2, 1/4$, using service water as stripping agent. Table 3 shows the experimental design. After separation of the liquid phases, the concentration of zinc(II) was measured. The contents of zinc(II) in the organic phase were calculated from the mass balance of the respective aqueous solutions.

RESULTS AND DISCUSSION

In the system under study that has a very high chloride concentration, metal ions formed chlorocomplex species according to the following reaction (3, 17).



where the stoichiometric coefficient “ i ” can take different values, $i = 1, 2, 3$, and 4 and

$$\beta_i = \frac{[MCl_i^{n-i}]}{[M^{n+}] \cdot [Cl^-]^i} \quad (2)$$

is the equilibrium parameter of the homogeneous reaction responsible of the formation of the complex species.

Table 2. Experimental planning in the study of the extraction of zinc(II) with pure TBP

[Zn] _o	V _a /V _o		
	1/1	1/2	1/4
1.2 M experiments	E1-E6	E25-E30	E49-E54
0.6 M experiments	E7-E12	E31-E36	E55-E60
0.3 M experiments	E13-E18	E37-E42	E61-E66
0.15 M experiments	E19-E24	E43-E48	E67-E73

Table 3. Experimental planning of the study of the back-extraction of zinc(II) from loaded TBP (from experiments E1-E24) with service water

[Zn] _o	V _a /V _o		
	1/1	1/2	1/4
ORG ^{E1-E6} experiments	B1-B2	B3-B4	B5-B6
ORG ^{E7-E12} experiments	B7-B8	B9-B10	B11-B12
ORG ^{E13-E18} experiments	B13-B14	B15-B16	B17-B18
ORG ^{E19-E24} experiments	B19-B20	B21-B22	B23-B24

Different values of β_i have been reported for the same system by various authors mainly due to its sensitivity to the presence of other ions that can be quantified by the value of the ionic strength and/or the water activity. (3, 5, 6, 13, 15–17) Regel et al. (2001) (3) reported that in a system containing 1 M Fe⁺², 0.1 M Zn⁺², 5 M Cl⁻ and 0.6 or 3.6 M HCl, with an ionic strength around 5, over 90% of the zinc was in the form of ZnCl₄²⁻ and only a few percent existed as ZnCl₃⁻. Similar results were reported by Cierpiszewski et al. (2002) (5), Mishonov et al. (2004) (6), Niemzcewski et al. (2004) (13) and Miesiac et al. (2004), (18) for 5 M Cl⁻, (0.5–2.5)M HCl, and very different zinc concentrations (0.0076–1)M. Table 4 summarizes the distribution of zinc(II) chlorocomplexes in aqueous solutions reported in the literature.

An increase in the ionic strength leads to an increase in the formation of complex species with high stoichiometric coefficients of Cl⁻ (13). In this work, aqueous feed solutions (undiluted and diluted solutions from real spent pickling solutions) contained high concentrations of Cl⁻ 1.6–6.4 M, of Zn⁺² 0.15–1.2 M, and of Fe⁺² 0.2–1.7 M, as well as traces of other heavy metals i.e., Pb, Ni, Cu, Mn, etc. Therefore, according to the literature, the ion ZnCl₄²⁻ can be expected to be the main anionic species of zinc(II) in the aqueous phase.

The extraction of zinc(II) complex species from hydrochloric acid using tributyl phosphate was studied by Morris et al. (1962) (16) and Forrest et al. (1968) (15). For aqueous feed solutions of high acidity, the zinc(II) complex species are extracted according to the following equation



This reaction is shifted to the right by an increase of the aqueous phase acidity and of the chloride concentration. Under milder conditions, lower HCl concentrations, other reactions become important,

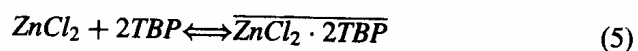
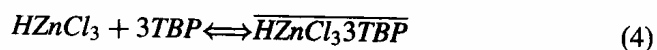


Table 4. Distribution of zinc(II) chlorocomplexes in acidic solutions

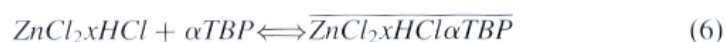
Author	Feed (M)						
	Zn ⁺²	Fe	Cl ⁻ /HCl	ZnCl ₄ ²⁻	ZnCl ₃ ⁻	ZnCl ₂	ZnCl ⁺
Regel et al. 2001	0.1	1 M Fe ⁺²	5 M Cl ⁻ 0.6–3.6 M HCl	90%	Few percent	—	—
Mishonov et al. 2004	0.9	—	5.2 M Cl ⁻ 0.5–2.3 M HCl	78%	11%	6%	5%
Cierpiszewski et al. 2002	7.6E-3	0.627 Fe ⁺³	5 M Cl ⁻	92%	7%	—	—
Niemczewska et al. 2004	0.3	—	5 M Cl ⁻	92%	8%	0%	—
Miesiac et al. 2004	0.076	—	5 M Cl ⁻ /2.5 M HCl	94%	6%	—	—
	0.076	—	3.40 M Cl ⁻ /2.5 M HCl	54%	34%	10%	2%
	0.305	—	5 M Cl ⁻ /2.5 M HCl	92%	8%	—	—
	0.305	—	3.8 M Cl ⁻ /2.5 M HCl	49%	36%	0.12%	3%

Reaction 4 becomes important for concentrations of hydrochloric acid in the range 0.8–2.7 M, and is shifted to the right with increasing concentration of protons. Reaction 5 is dominant for concentrations of HCl and Cl^- below 0.8 and 1 M respectively (16).

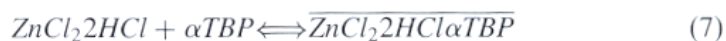
It is important to notice that those works (15, 16) determined the compositions of the extracted zinc(II) complex species using model dilute solutions. Thus, Eqs. (3)–(5) provide only general trends and boundaries of concentrations because it is very difficult to transfer the data, including the regions of complex existence, from dilute model solutions to the actual spent pickling solutions (5).

Equilibrium Study of the Extraction of Zinc(II)

According to the literature, extraction of zinc(II) with TBP can be described by a general reaction of the form (15, 16),



Considering ZnCl_4^{2-} as the predominant zinc species in the studied conditions, the equilibrium reaction transforms into,



and the equilibrium parameter can be expressed as,

$$\begin{aligned} K_{EX} &= \frac{\overline{\text{ZnCl}_2 \cdot 2\text{HCl} \cdot \alpha\text{TBP}}}{\text{ZnCl}_2 \cdot 2\text{HCl} \cdot \text{TBP}^\alpha} = \frac{\overline{\text{ZnCl}_2 \cdot 2\text{HCl} \cdot \text{TBP}}}{\text{ZnCl}_2 \cdot 2\text{HCl} \cdot (\text{TBP}_O - \alpha \cdot \overline{\text{ZnCl}_2 \cdot 2\text{HCl} \cdot \text{TBP}})^\alpha} \\ &= \frac{n}{\text{ZnCl}_2 \cdot 2\text{HCl}} \end{aligned} \quad (8)$$

where

$$n = \frac{\overline{\text{ZnCl}_2 \cdot x\text{HCl} \cdot \text{TBP}}}{(\text{TBP}_O - \alpha \cdot \overline{\text{ZnCl}_2 \cdot x\text{HCl} \cdot \text{TBP}})^\alpha} \quad (9)$$

Figure 1 shows the experimental data of the equilibrium isotherm obtained under the conditions specified in Table 1. Experimental points are the average value of 6 replicate experiments.

The equilibrium isotherm shows that the distribution coefficient varies in the range of the studied conditions. However in order to have an equilibrium expression that can explain the experimental behaviour in the whole range of concentrations, data of Fig. 1 were fitted to the linearized expression of Eq. (8). Plots of “ n ” in ordinates versus $\text{ZnCl}_2 \cdot 2\text{HCl}$ in abscissas were done for different values of α , obtaining the best fitting for $\alpha = 4$ (Fig. 2). The value of the regression coefficient, $r^2 = 0.98$, is high enough to consider

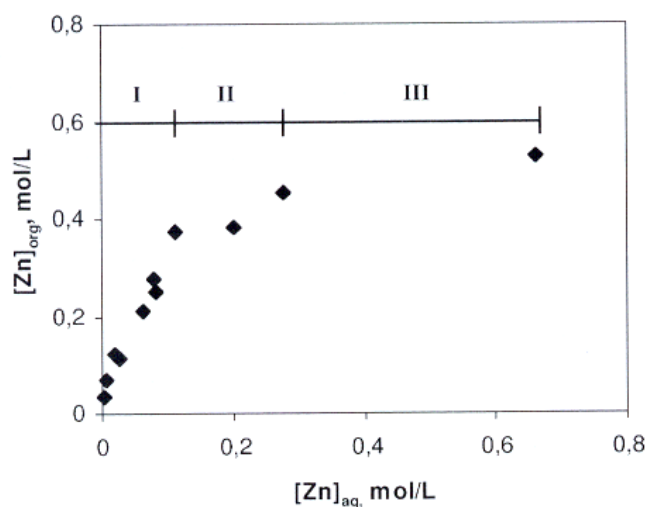
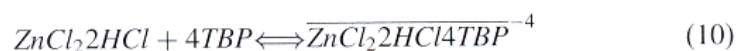


Figure 1. Equilibrium isotherm of zinc(II) extraction. Experiments E1-E76.

that the equilibrium reaction can be described by the stoichiometric equation,



being the value of the equilibrium parameter

$$K_{\text{EX}} = 0.137(\text{mol/L})^{-4} \quad (11)$$

No previous references have reported a value of the equilibrium parameter of the extraction of zinc(II) with TBP. However, several authors have reported values of the distribution coefficient (D). According to Fig. 1 the equilibrium

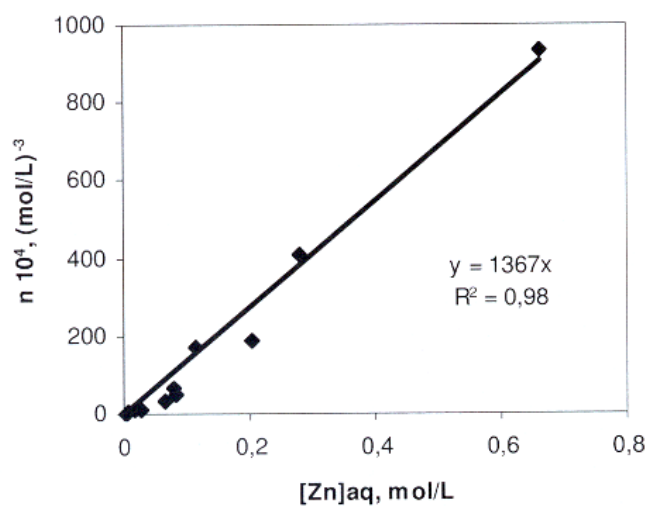


Figure 2. Linear fitting of $n \cdot 10^4$ values to zinc(II) concentration in the aqueous phase.

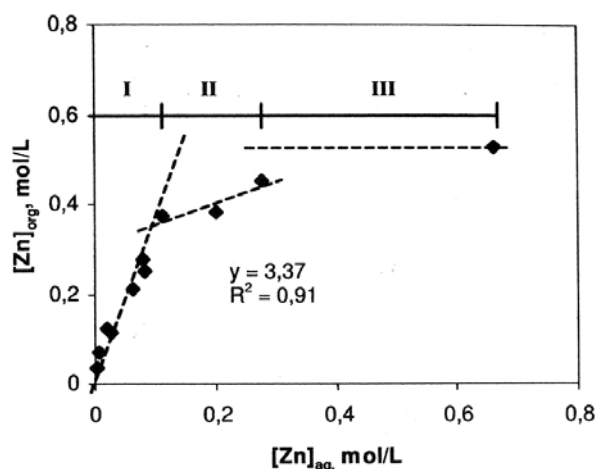


Figure 3. Linear regression of equilibrium data of region I.

isotherm can be divided in three regions with apparent constant distribution coefficients. Therefore, in order to compare the values of the extraction distribution coefficient (D_{EX}) reported in the literature with the results of this work, the value of D_{EX} was calculated in region I (Fig. 3) obtaining,

$$D_{EX} = \frac{[Zn]_{org}}{[Zn]_{aq}} = 3.37; r^2 = 0.91 \quad (12)$$

that is very close to the value of 3.33 reported by Niemczewska, et al. (2004), (13), who worked with a feed solution containing 0.31 M Zn^{+2} , 0.55 M H^+ , and 5 M Cl^- .

Thus, it is concluded that working with solutions of high acidity and low concentration of zinc ($[Zn]_{aq} \leq 0.15$ mol/L), the extraction equilibrium with TBP can be described by a distribution coefficient, whereas at higher concentrations, it is better described by a chemical equilibrium expression.

Equilibrium Study of the Back-Extraction of Zinc(II)

Figure 4 gives a representation of the experimental data of the back-extraction isotherm; replicate runs were performed for each point. As shown, zinc(II) can be effectively stripped from the organic phase using water as back-extraction agent (3, 5). Equilibrium data were fitted to a linear isotherm of the form,

$$[Zn]_{aq} = 1.46 \cdot [Zn]_{org}; r^2 = 0.98 \quad (13)$$

being $K_{BEX} = 1.46 [-]$.

Cierpiszewski et al. (2002), for (5) studied the stripping isotherm of zinc(II) from loaded TBP with water. The organic phase was loaded with a solution that contained 0.9M Zn^{+2} and 1M Fe^{+2} dissolved as chloride salts

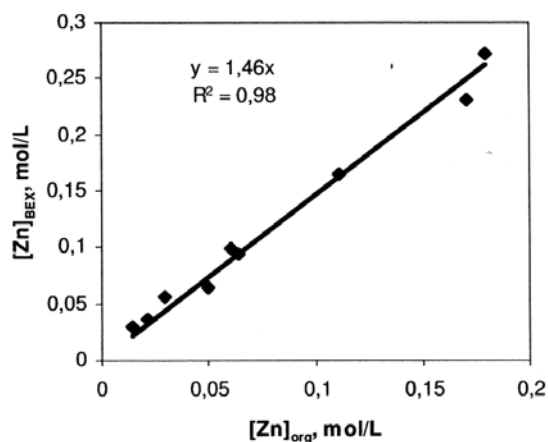


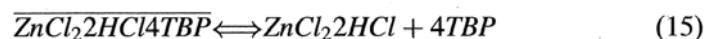
Figure 4. Zinc(II) stripping from loaded undiluted tributyl phosphate with water.

in 3.16M HCl. An approximately linear isotherm with a slope close to 1 was obtained. Regel et al. (2001) (3) determined the stripping isotherm using the loaded organic phase obtained in extraction experiments where the aqueous phase contained 3.6M HCl and the concentration of zinc(II) in the organic phase was below 0.24M. The obtained isotherm was approximately linear and the following equation was reported:

$$[Zn]_{aq} = 1.13 \cdot [Zn]_{org} - 0.32; r^2 = 0.99 \quad (14)$$

Thus, the results obtained in this study are in good agreement with those reported by other authors.

Additionally, the equilibrium data of the back extraction study have been compared to the extraction data. The system under study is the reversible reaction of zinc chloride chlorocomplexes with TBP, thus, according to the extraction reaction Eq. (10), the back-extraction equation can be described by



characterized by the equilibrium parameter

$$\begin{aligned} K'_{BEX} &= \frac{ZnCl_2 \cdot 2HCl \cdot TBP^4}{\overline{ZnCl_2 \cdot 2HCl \cdot 4TBP}} \\ &= \frac{ZnCl_2 \cdot 2HCl \cdot (TBP_o - 4 \cdot \overline{ZnCl_2 \cdot 2HCl \cdot 4TBP})^4}{\overline{ZnCl_2 \cdot 2HCl \cdot 4TBP}} = \frac{ZnCl_2 \cdot 2HCl}{n} \end{aligned} \quad (16)$$

Figure 5 gives a representation of the equilibrium concentration of zinc in the back-extraction phase in abscissas versus the parameter “n” in ordinates.

Although the data reported in Fig. 5 could be fitted to a straight line, the value of the slope $m = 0.0108$ leads to a value of the back-extraction

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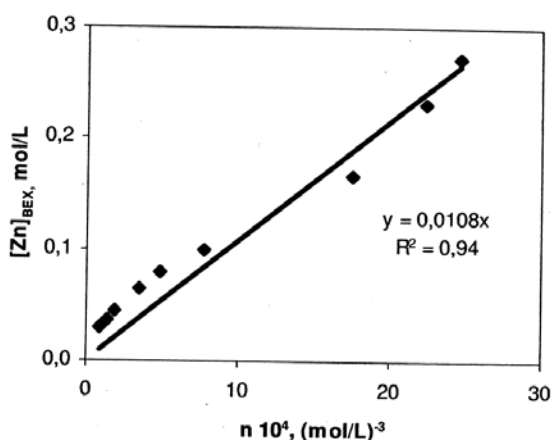


Figure 5. Linear fitting of zinc(II) concentration in the back extraction phase to $n \cdot 10^4$ values.

equilibrium parameter $K'_{\text{BEX}} = 108 (\text{mol/L})^4$ that is considerable higher than the corresponding value obtained from the reverse of the extraction parameter, i.e.,

$$K'_{\text{BEX}} = \frac{1}{K_{\text{EX}}} = 7.3 (\text{mol/L})^4 \quad (17)$$

The difference could be attributed to the influence of the acidity of the aqueous solutions used in the studied equilibria. Therefore it is concluded that under the experimental conditions the back-extraction equilibrium is best described by a linear isotherm $[\text{Zn}]_{\text{aq}} = 1.46 \cdot [\text{Zn}]_{\text{org}}$.

CONCLUSIONS

Taking into account the formation of different chlorocomplex species in the feed solution (high concentration of HCl), ZnCl_4^{2-} was considered as the predominant species in the experimental range of concentrations. Experimental data were satisfactorily fitted to a mathematical model with a stoichiometric coefficient of the extractant $\alpha = 4$, being the equilibrium parameter $K_{\text{EX}} = 0.137 (\text{mol/L})^{-4}$. The back extraction equilibrium has been described by a linear expression of the type $[\text{Zn}]_{\text{aq}} = 1.46 \cdot [\text{Zn}]_{\text{org}}$, that is in agreement with related studies reported in literature.

ACKNOWLEDGEMENTS

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Valorisation of Zinc contained in Spent Pickling Effluents. Kinetics of Metal Separation by means of Non-dispersive Solvent Extraction

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Key Words: Process kinetics, Zinc Removal, Spent pickling effluents, Tributyl phosphate.

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Abstract

This work has been focused on the study of the kinetics of zinc removal from spent pickling effluents by means of membrane assisted solvent extraction (NDSX), as the main step in the valorisation process of the metal. Tributyl phosphate (TBP) and service water were used as extraction (EX) and back-extraction (BEX) agents respectively.

Working with hollow fiber membrane contactors, kinetic experiments were performed in order to analyze the influence of operation variables on the rate of zinc separation. A mathematical model that considers diffusion through the organic membrane as the main kinetic resistance was developed and the membrane mass transport coefficient was estimated by means of the parameter estimation tool gEST (from gPROMS) obtaining a value of $K_m=3.89\times 10^{-4}$ m/h. Simulated results agreed satisfactorily well with experimental data, thus confirming the validity of the kinetic model and parameters.

1. Introduction

Acidic effluents coming from hot-dip galvanizing processes with molten zinc contain high quantities of both iron and zinc. Typical metallic concentrations lie in the range 20-120 g/L for zinc and 100-130g/L for iron, whereas the hydrochloric acid concentration lies in the range 1-6 mol/L (36.5-219 g/L).¹ Besides, the solution may contain other heavy metals such as Pb, Ni, Cu, Mn, and so forth at low concentration. Thus, this effluent has a strong hazardous character and needs to be treated before disposal.²

The spent pickling effluents are often neutralized with lime and then released to the environment, but the discharge of such wastes is highly undesirable because of their high acidity and eco-toxicity. Another method that has been considered appropriated for the treatment of spent pickling effluents is the Ruthner process where hydrochloric acid is evaporated and iron oxide granules are formed in a fluidized bed at temperatures

around 700°C. However, the presence of zinc in amounts higher than 0.5 g/L disturbs the process.²⁻⁷

The development of a clean process allowing the separation of zinc from the acid effluent under conditions that permit the recovery of electrolytic grade metal would reduce the effluent toxicity, with valorisation, at the same time, of the component of higher added value.

Membrane based solvent extraction (NDSX) has received considerable attention and has been proved to be very efficient in the recovery and/or removal of different solutes such as metallic elements⁸⁻¹³, organic compounds¹⁴⁻¹⁶, acids¹⁷⁻¹⁹, and so forth.

This technology presents several advantages in comparison to conventional processes that have been widely reported in literature.²⁰⁻²³ The benefits include low maintenance, non dispersion of the fluid phases and the high interfacial area provided when a hollow fiber configuration is applied.

With regard to the separation of zinc species from solutions containing hydrochloric acid, Cierpiszewski et al. (2002)⁵ studied the behavior of different extractants in the separation between zinc and iron concluding that solvating extractants led to better extraction results than other analyzed compounds. Tributyl phosphate (TBP) was selected as the most suitable reagent enabling both the extraction (EX) of zinc chloride from HCl solutions and subsequent back extraction (BEX) with water.^{3, 5, 24}

Previous works have dealt with the study of the viability of a solvent extraction process using hollow fiber (HF) modules for the recovery of zinc chloride from spent pickling effluents using TBP and service water as extraction and back extraction agents respectively.^{2,4,25} Additionally, the analysis of the interfacial extraction and back-extraction equilibria occurring in the system has also been reported by the authors.²⁶

In this paper, the kinetic analysis of the membrane assisted process of zinc recovery from spent pickling effluents is reported, obtaining the mathematical model and parameters needed for design and optimisation of the metal separation step in a valorisation process.

2. Experimental Section

Spent pickling effluents collected from surface treatment processes were used in the experimental analysis. Physicochemical characteristics are shown in Table 1.

Extraction and back-extraction agents were pure grade TBP (tributyl phosphate, MERCK) and service water, respectively.

Table 1. Physico-chemical analysis of the feed effluents.

Property	Value	
Colour	Green	
pH	≈0	
Composition	mg/L	mol/L
Zn	81,760	1.250
Fe	96,000	1.720
Fe ⁺²	96,000	1.720
Mn	174	3.17E-3
Pb	104.64	5E-4
Al	38.21	1.4E-3
Cr	18.99	0.365
Ni	18.73	3.2E-4
Cd	26.63	5.9E-5
Cu	5.18	8.1E-5
Co	0.14	2.4E-6
Cl-	225,920	6.40

Experiments conducted at different initial zinc concentrations were carried out by diluting the initial effluent. After dilution of the samples, the concentration of Cl⁻ ions was adjusted to 2.5M by addition of HCl, in order to avoid the influence of this variable in the studied system.

Separation experiments were done at laboratory scale using microporous polypropylene hollow fiber modules (Liqui-Cel Extra-Flow, Hoechst Celanese) as contactors that provide an effective membrane area of 1.4 m^2 . Other characteristics of the modules are given in Table 2.

Table 2. Hollow-Fiber Membrane Module Characteristics.

Module reference	Liqui-cel extra-flow 2.5' x 8'
Cartridge dimensions (D x L), cm	6.65 x 28.25
No. of fibers	10200
Effective surface Area, m^2	1.4
Effective length, m	0.15
Cartridge material	epoxy
Fiber type	Celgard X10
Fiber material	polypropylene
Inner diameter, μm	240
Thickness, μm	0.05
Porosity, %	30
Tortuosity factor	2.6

Figure 1 presents a flow diagram of the experimental setup.

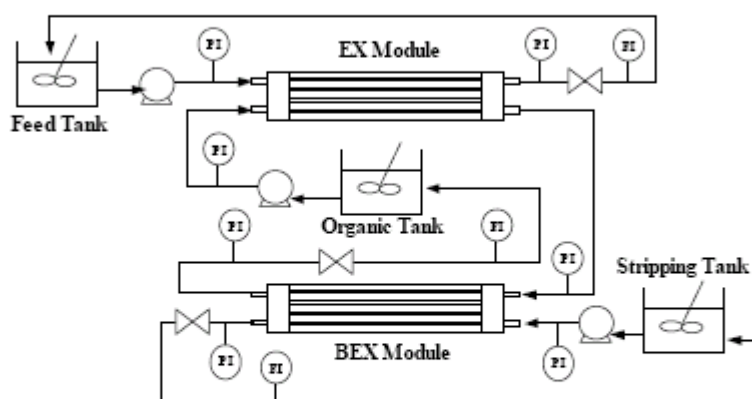


Figure 1. Experimental setup

In the extraction module (EX Module), the feed aqueous phase contacted the organic phase and the reaction between TBP and zinc chloride took place. In the back-extraction

module (BEX Module), the loaded organic phase reacted with the back extraction agent transferring zinc chloride to the stripping phase. Both extraction and back-extraction operations were carried out working in a recirculating mode with the fluid phases flowing cocurrently in each module. The aqueous phase solutions circulated through the inside of the hollow fibers at a flow rate of $3.6 \times 10^{-2} \text{ m}^3/\text{h}$, while the organic phase ran through the shell of the module at a flowrate of $3.3 \times 10^{-2} \text{ m}^3/\text{h}$. The differential pressure between the aqueous phase and the organic phase was maintained at 0.2 bar in all experiments. The positive pressure difference prevents penetration of the organic phase into the aqueous phase and permits to stabilize the interface between phases at the pores of the hydrophobic membrane.^{8,22,24,27}

Pumping of the aqueous phases was achieved by using peristaltic pumps 313 (Watson Marlow) capable of flows up to $0.06 \text{ m}^3/\text{h}$, while pumping of the organic phase was achieved by means of a gear pump A7144-07 (Micropump) capable of flows up to $0.012 \text{ m}^3/\text{h}$. Three flow meters were used to monitor the flow rates of the feed, stripping, and organic phases. They were situated at the outlet of the HF modules. The flow meters were equipped with back-pressure control valves to maintain the appropriate differential pressure of the aqueous-organic interface in both modules.

Three stirred tanks were also employed for homogeneisation of the liquid phases: feed aqueous phase, organic phase and back-extraction phase. Samples were taken out at different times from the aqueous reservoirs and, the zinc concentration was analyzed, after sample preparation, in a Perkin Elmer 3110 Atomic Absorption Spectrophotometer. The concentration of zinc in the organic phase was determined from mass balances. The metallic content of the feed solution was analyzed using a Perkin Elmer Plasma Emission Spectrometer ICP 400; the Iron(II) concentration was

determined in a Spectrophotometer Spectroquant Nova 400 and finally the total concentration of chloride ions was analyzed using an Ion Chromatograph Dionex-120.

3. Theoretical Background

Mass separation devices used in nondispersive solvent extraction normally contain a bundle of a large number of parallel hollow fibers through which the fluid flows, and it is reasonable to assume that the conditions in each fiber are identical and independent of the other fibers. Thus, it is sufficient to analyze the problem for a single fiber in order to predict the overall performance of the mass separation device.²⁸

In the proposed model, the mass transfer of zinc chloride species from the feed to the organic phase takes place in the following steps: (i) diffusion through the feed-phase stagnant layer to the interface with the membrane, (ii) instantaneous interfacial reaction of zinc chloride with the extractant TBP to form the organometallic complex species, (iii) diffusion of the latter species through the membrane, (iv) diffusion of the complex species through the boundary layer of the organic phase. The order of the steps is reversed during the back-extraction process. Additionally, several assumptions were made in the formulation of the mass balance equations:²⁸ (i) zinc in the reservoirs changes slowly compared to the concentration changes occurring in the module, thus steady state is assumed in the HF modules and, (ii) plug flow of the fluid phases inside the HF module is considered.

The kinetic resistances, corresponding to diffusion through the fluid phases boundary layers were considered negligible in the case under study. The latter assumption is supported by the high concentration of the metal in the feed phase and by the higher turbulence of the organic phase. Thus, the mass transfer rate is assumed to be dominated by the resistance of the membrane, as a result of the low diffusivity of the

organometallic complex species and to the thickness of the hollow fiber. With these assumptions mass transport balances to the separated zinc species were developed.²⁷

EX module mass balance,

Aqueous solution

$$\frac{dC_a}{dz} = -\frac{A}{L \cdot F_a} \cdot K_m^{EX} \cdot (C_{o,i}^{EX} - C_o^{EX}), \quad z=0 \quad C_a = C_a^T \quad (1)$$

Organic Solution

$$\frac{dC_o^{EX}}{dz} = \frac{A}{L \cdot F_o} \cdot K_m^{EX} \cdot (C_{o,i}^{EX} - C_o^{EX}), \quad z=0 \quad C_o^{EX} = C_o^T \quad (2)$$

BEX module mass balance,

Stripping Solution

$$\frac{dC_s}{dz} = -\frac{A}{L \cdot F_s} \cdot K_m^{BEX} \cdot (C_{o,i}^{BEX} - C_o^{BEX}), \quad z=0 \quad C_s = C_s^T \quad (3)$$

Organic Solution

$$\frac{dC_o^{BEX}}{dz} = \frac{A}{L \cdot F_o} \cdot K_m^{BEX} \cdot (C_{o,i}^{BEX} - C_o^{BEX}), \quad z=0 \quad C_o^{BEX} = C_o^{EX,z=L} \quad (4)$$

Mass Balance in the stirred tanks,

Feed Solution

$$V_a^T \cdot \frac{dC_a^T}{dt} = F_a \cdot (C_a^{z=L} - C_a^T), \quad t=0 \quad C_a^T = C_a^T(0) \quad (5)$$

Stripping Solution

$$V_s^T \cdot \frac{dC_s^T}{dt} = F_s \cdot (C_s^{z=L} - C_s^T), \quad t=0 \quad C_s^T = C_s^T(0) \quad (6)$$

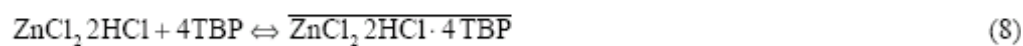
Organic Solution

$$V_o^T \cdot \frac{dC_o^T}{dt} = F_o \cdot (C_o^{BEX,z=L} - C_o^T), \quad t=0 \quad C_o^T = C_o^T(0) \quad (7)$$

It is considered that the solute concentrations in the reservoir and at the module inlet for both phases are identical.

The extraction and back-extraction steps take place consecutively, being connected by the organic phase. The complex species concentration at the fluid-membrane interfaces, $C_{o,i}^{EX}$ and $C_{o,i}^{BEX}$ are considered to be the equilibrium concentrations of the organic species with the solute concentration in the aqueous solution in both modules at each axial position value. Therefore, these concentrations can be obtained from the mathematical models of the chemical reaction equilibria.

In aqueous effluents with high concentration of hydrochloric acid, different chlorocomplex species have been reported in the literature; under the experimental conditions the ionic strength reaches high values ($I \gg 5$ m), so that more than 90% of the zinc is in the form of $ZnCl_4^{2-}$ and only a few percent exists as $ZnCl_3^-$. In a previous work, the authors reported²⁹ the modeling and parameters of the extraction equilibrium reaction of zinc chloride from spent pickling solutions using tributyl phosphate, and of the back-extraction equilibrium using service water. Under the experimental conditions, that is high concentrations of hydrochloric acid, the extraction reaction proceeds according to the following stoichiometric equation,



being the equilibrium parameter

$$K_{EX} = \frac{\overline{ZnCl_2 \cdot 2HCl \cdot 4TBP}}{ZnCl_2 \cdot 2HCl \cdot (TBP)^4} = \frac{\overline{ZnCl_2 \cdot 2HCl \cdot 4TBP}}{ZnCl_2 \cdot 2HCl \cdot (TBP_o - 4 \cdot \overline{ZnCl_2 \cdot 2HCl \cdot TBP})^4} \quad (9)$$

with a value of,

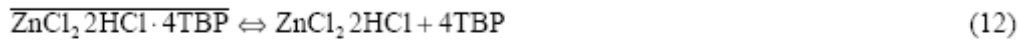
$$K_{EX} = 0.137 \text{ (mol/L)}^{-4} \text{ at 293K.} \quad (10)$$

Alternatively, Niemczewska et al. 2004 reported a linear expression in order to describe the extraction equilibrium behaviour of the type,

$$C_o^{EX*} = 3.37 \cdot C_i^* \quad (11)$$

Results predicted using eq. 11 do not differ significantly from those described by eq (9), when the metallic species concentration in the aqueous phase is high enough (concentration of zinc more than 0.3 mol/L).

The back extraction reaction is described by the stoichiometric equation,



and equilibrium data were described successfully by means of a simplified linear equation,

$$C_i^* = 1.46 \cdot C_o^{BEX*} \quad (13)$$

For simplicity reasons under the experimental range of variables, the linear expressions of the extraction and back extraction equilibria have been used in the mathematical modeling.

The values of the membrane mass-transport coefficient depend basically on the type of membrane used in the module and on the physico-chemical characteristics of the system. Considering that in the case under study the organic phase leaving the extraction module enters the back-extraction one, the physico-chemical characteristics of the system diffusing through the liquid contained in the pores of the hollow fibers are very similar in both HF modules, so that it is considered that $K_m^{EX} = K_m^{BEX}$,²⁷

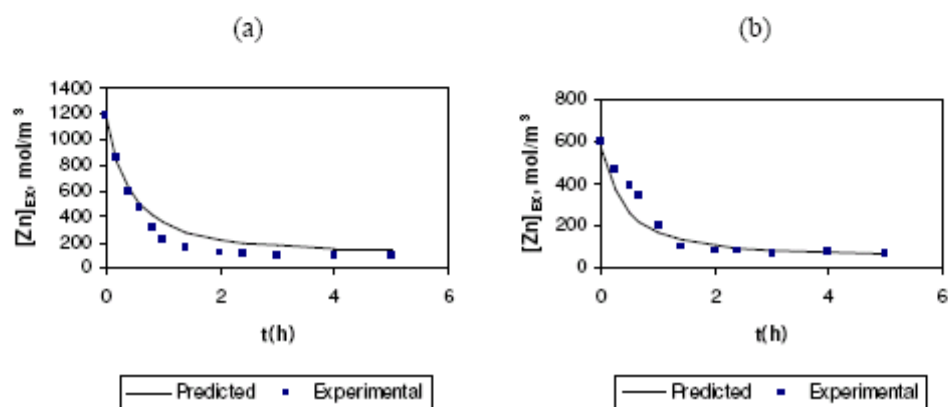
The dynamic response of the system is determined by simultaneously solving the set of differential equations 1 to 7. The use of the mathematical model would require the knowledge of the design parameter, that is the membrane mass transport coefficient K_m .

Results and Discussion

Different kinetic experiments were performed in order to analyze the influence of the initial concentration of the metals on the rate of zinc chloride separation. Experiments were duplicated so that the results presented here are average values of the metal concentration, zinc, obtained in both experiments.

Starting with the effluent that had an initial concentration of zinc(II) of 1200 mol/m^3 (experiment I), three different feed batches were prepared by dilution of the effluent to obtain initial zinc concentrations of 600, 300 and 150 mol/m^3 (experiments II, III and IV). When dilution was important (150 mol/m^3 of Zn), the concentration of Cl^- ions was adjusted to 2.5M by addition of HCl, in order to avoid the influence of this variable in the studied system. Figures 2 and 3 show the kinetic results of extraction and back extraction.

In Figure 2 it is observed that the concentration of zinc chloride in the aqueous feed phase decreases below 10-15% of the initial value within 2 hours, indicating that the extraction of zinc chloride is achieved with a satisfactory rate.



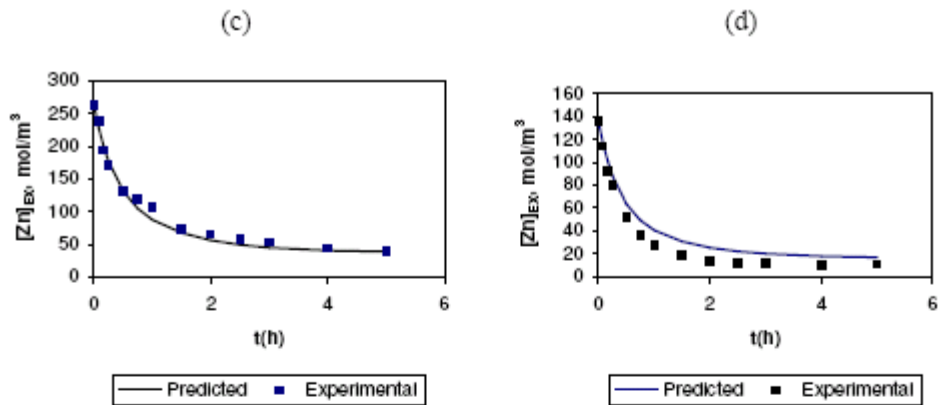


Figure 2. Experimental concentration of zinc in the extraction phase. Solid lines represent simulated curves. Experiment I (a), experiment II (b), experiment III (b) and experiment IV (d).

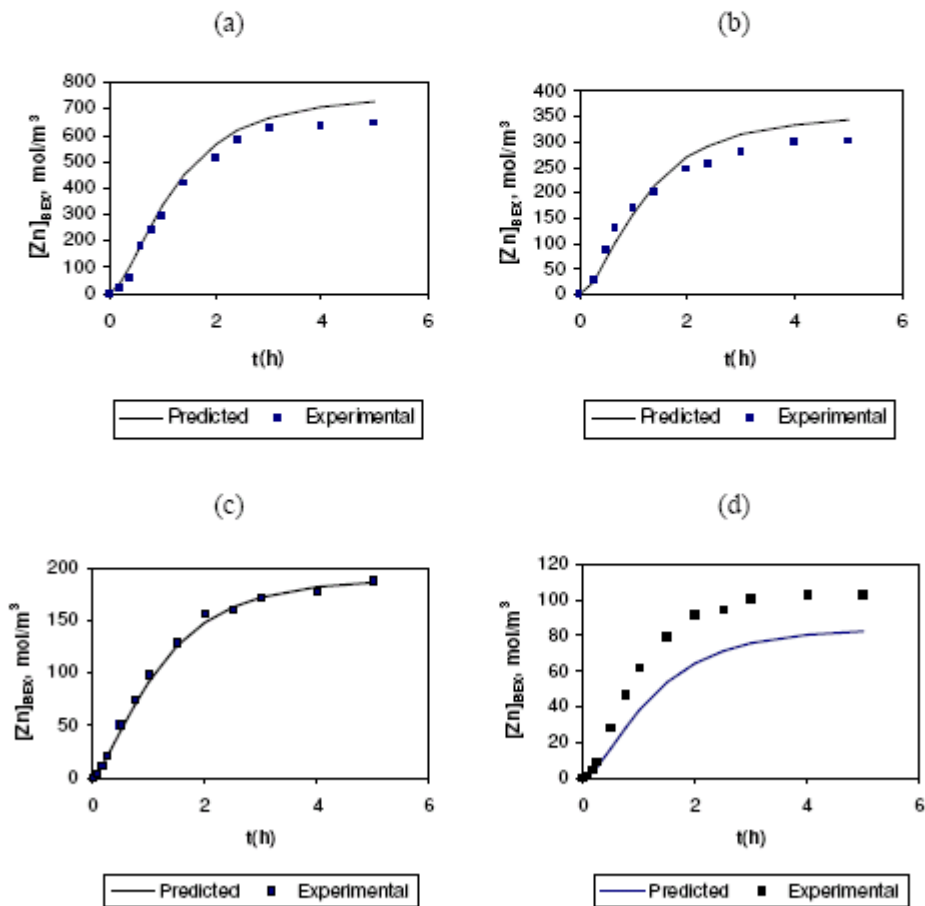


Figure 3. Experimental concentration of zinc in the back-extraction phase. Solid lines represent simulated curves. Experiment I (a), experiment II (b), experiment III (b) and experiment IV (d).

In Figure 3 it is observed that the concentration of zinc chloride in the stripping phase achieved maximum values around 700 mol/m^3 . The presence of other metals in the back-extraction solution was measured observing even lower values than the concentrations of the effluent shown in table 1 indicating a negligible extraction of those metals. Considering the average metallic concentrations of electrolytic solutions, $[\text{Zn}] \cong 480 \text{ mol/m}^3$ and $[\text{HCl}] \cong 120\text{-}200 \text{ mol/m}^3$ ²⁹, re-use of the obtained back-extraction solution would be a possible alternative.

In the mathematical model reported in previous section, the membrane mass transport coefficient K_m was the unknown parameter. The parameter estimation tool gEST of the gPROMS software was used. The system of differential and algebraic equations that form the mathematical model and the experimental values of the extraction and back-extraction phases were loaded in a file. The least-squares technique was used to find the numerical value of the parameter that minimizes the difference between experimental and simulated values, obtaining finally a value of $K_m = 3.89 \times 10^{-4} \text{ m/h}$. The comparison between simulated and experimental values of the concentration of zinc chloride in the extraction and back-extraction phases is shown in the parity graph of Figure 4. Eighty one percent of simulated feed concentration values fall in the range $C_{\text{EX,exp}} \pm 20\% C_{\text{EX,exp}}$, while 84% of simulated stripping concentration values fall in the range $C_{\text{BEX,exp}} \pm 20\% C_{\text{BEX,exp}}$. Considering the wide range of variation of the experimental conditions, varying the initial concentration of zinc chloride in the feed solution in the range between 150 and 1200 mol/m^3 , it is thought that the mathematical model together with the value of the estimated parameter permit a satisfactory description of the membrane assisted separation process applied to the recovery of zinc from spent pickling effluents and using TBP as extractant and service water as back-extraction agent.

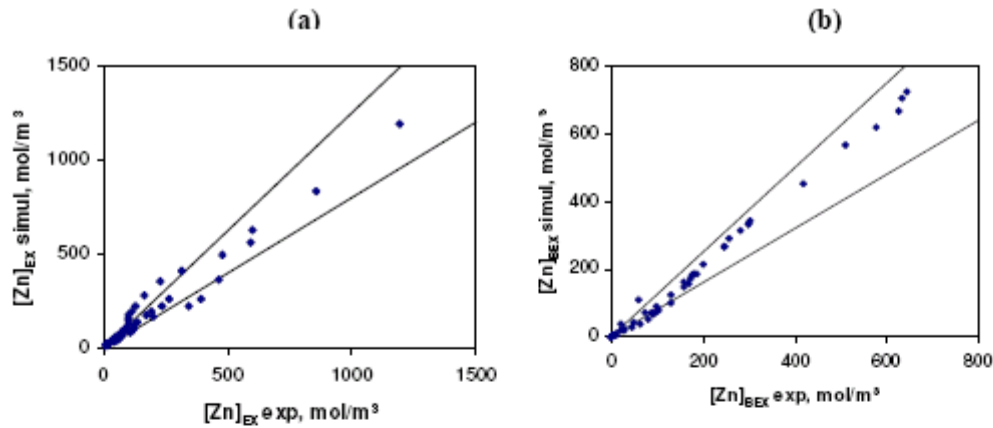


Figure 4. Parity Graph. Comparison of experimental and simulated results: (a) feed phase and (b) stripping phase.

Conclusions

In this paper, the kinetics of the non-dispersive extraction and back-extraction of zinc chloride from spent pickling effluents using TBP as selective extractant and service water as back-extraction agent are reported. Batch experiments were performed in order to analyze the influence of the initial metal concentration on the rate of zinc chloride separation. It was observed that there is no significant influence of the initial metal concentration on the separation kinetics of zinc chloride in the extraction and back-extraction steps.

The kinetic model consisted of a system of partial differential and algebraic equations corresponding to the mass balances of zinc chloride in the fluid phases that flow through the hollow-fiber contactors and in the homogenisation tanks. The proposed mathematical model considers that the mass transport is dominated by the resistance of the membrane. The membrane mass transport coefficient was estimated by means of the parameter estimation tool gEST of gPROMS obtaining a value of $K_m=3.89 \times 10^{-4} m/h$.

The comparison between experimental and simulated data in a parity graph confirmed the validity of the kinetic analysis.

The reported technology allows zinc separation from an industrial waste with strong hazardous character and recovery of the metal in a solution with physicochemical properties adequate for its recycling in electrolytic process.

Acknowledgment

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List of Symbols

A = effective surface area, m^2

C = zinc(II) concentration, $mol\ m^{-3}$

F = flowrate, $m^3\ h^{-1}$

K_{EX} = chemical equilibrium constant (extraction)

K_m = membrane mass transfer coefficient, $m\ h^{-1}$

L = fiber length, m

V = volume, m^3

z = axial distance, m

Subscripts

a = effluent phase

o = organic phase

o,i = organic interface

s = stripping phase

Superscripts

* = equilibrium

T = tank

EX = extraction

BEX = back extraction

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