Use of di-(2-ethylhexyl) Phosphoric Acid (DEHPA) Impregnated XAD7 Copolymer Resin for the Removal of Chromium (III) from Water

CORNELIU MIRCEA DAVIDESCU[1], MIHAELA CIOPEC[1]*, ADINA NEGREA[1], ADRIANA POPA[2], LAVINIA LUPA[1], PETRU NEGREA[1], CORNELIA MUNTEAN[1], MARILENA MOTOC[3]

[1] University Politehnica Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 2 Piata Victoriei, 300006 Timisoara, Romania,

[2] Romanian Academy, Institute of Chemistry, 24 Mihai Viteazul Blv., 300223, Timisoara, Romania

[3] ”Victor Babes” University of Medicine and Pharmacy, 2 Piata Eftimie Murgu, 300041, Timisoara, Romania

Industrial processes generate waste that if disposed untreated would have a detrimental effect on the environment and human health. Metals such as chromium are often present in effluent streams. The paper presents a novel support for chromium sorption and its removal from wastewaters. The support is a solvent-impregnated resins (SIR) formed by impregnating Amberlite XAD7 with DEHPA as extractant and ethylic alcohol as solvent by dry impregnation method. Adsorption on the XAD7 support macro and interaction between the extractant and support was proven by physicochemical methods of analysis (FTIR spectroscopy, EDX). In order to establish the sorption performance of the impregnated XAD7, the influence of different physicochemical parameters (pH, contact time and initial concentration of chromium) upon the Cr(III) sorption onto XAD7 was investigated. The optimum pH for Cr(III) sorption was found as 3.0 for this material. To express the kinetics of chromium sorption onto XAD7 the results were analyzed using the pseudo-first order and pseudo-second order models. The sorption process is best described by the pseudo-second order kinetic model. Langmuir and Freundlich isotherm studies were conducted in order to determine the maximum adsorption capacity of XAD7 towards chromium. Langmuir adsorption isotherm gave a satisfactory fit of the equilibrium data. The maximum adsorption capacity is of ~5 mg Cr(III)/g SIR.

Keywords: Amberlite XAD7; DEHPA; Solvent impregnated resin (SIR); Chromium (III), Sorption Kinetics

Heavy metals, including chromium, are widely distributed in the environment as a result of numerous industrial processes that include galvanization, steel, paints, textiles, oxidative dyeing, cooling water towers, leather tanning, corrosion inhibitors, electroplating and batteries. Such processes add heavy metals, such as chromium, to industrial wastewater, thereby posing a great hazard to humans, animals and plants through their incorporation in the food chain and the bioaccumulation effect [1-3]. Chromium is found in two oxidation states, Cr(III) and Cr(VI), the latter being toxic [4].

Increasingly, industry is seeking replacements of traditional metal recovery and separation techniques such as precipitation, solvent extraction, ion exchange. This has led to the development of new technology such as membrane separation, electrodialysis and selective adsorption, especially effective for metal ions removal from dilute solutions. Selective adsorption is one such method being developed to obtain separation systems with high selectivity efficiency. Systems of this type combine characteristics of ion exchange with liquid-liquid extraction and have led to the development of solvent impregnated resins (SIR). The recovery of metal ions from dilute solutions using solvent impregnated resins (SIR) has been proposed as a technological alternative to solvent extraction techniques [5, 6].

Solvent impregnated resins are obtained by the simple immobilization of a common extracting agent into or onto an insoluble, non-functionalized polymer support [7, 8]. Solvent impregnated resins are modeled as liquid complexing agents dispersed homogeneously in a solid polymeric medium. To produce a material fitting this model, requirements need to be met by the supporting structure, extractant and process of impregnation. The extractant must be a liquid or be retained in a liquid state by the addition of a diluent; the extractant and diluent should have minimal solubility in the aqueous phase used; the polymeric support should be fully expanded during impregnation and remain so; the impregnation process should not destroy the properties of the extractant or the polymer; the supporting structure should be chemically inert so that the extractants do not react with it and the supporting structure should have good mechanical stability.

Meeting all of these requirements would produce the "ideal" SIR, the properties of which are characterized as (i) good extractant mobility in the resin phase and good metal mobility between the aqueous and resin phase; (ii) high binding capacities; (iii) high ion selectivity and (iv) good chemical and physical stability and low extractant loss. The support resins are ideally macroporous organic polymers with a high specific surface area and good mechanical stability, flow characteristics and have low solvent swelling during the impregnation process. One type of commercially available supporting structure fulfilling these requirements is the Amberlite XAD type resins [9].

There are four methods available for the immobilization of the desired extractant into the polymeric supporting structure: the dry method, the wet method, the modifier addition method and the dynamic column method [9-13]. All of the preparation methods have the same mechanism of impregnation [14-21]. When impregnating a resin, the extractant fills the pore space, starting with the smallest pores and moving up to pores of about 10 nm, after this surface adsorption is the dominant force.

The paper presents a novel support for chromium sorption and its removal from wastewaters. SIR were formed by impregnating Amberlite XAD7 with DEHPA as extractant and ethylic alcohol as solvent by the dry

"Gheorghe Asachi" Technical University of Iasi, Romania

USE OF D2EHPA-IMPREGNATED XAD7 RESIN FOR THE REMOVAL OF Cd(II) AND Zn(II) FROM AQUEOUS SOLUTIONS

Mihaela Ciopec[1]*, Corneliu Davidescu[1], Adina Negrea[1], Lavinia Lupa[1], Petru Negrea[1], Adriana Popa[2], Cornelia Muntean[1]

[1]*University „Politehnica" Timisoara Faculty of Industrial Chemistry and Environmental Engineering, 2 Piata Victoriei, 300006 Timisoara, Romania*
[2]*Romanian Academy, Institute of Chemistry, 24 Mihai Viteazul Blvd., 300223 Timisoara, Romania*

Abstract

The adsorption performance of a novel support for metal ions sorption and their removal from aqueous solutions was examined. The support is a new solvent-impregnated resin (SIR) which can be considered as an alternative adsorbent material capable of selective sorption. The adsorbent was prepared by impregnating di-(2-ethylhexyl)-phosphoric acid (D2EHPA) onto Amberlite XAD7 resin beads, by dry impregnation method. The interaction between XAD7 resin and D2EHPA was evaluated by FTIR spectroscopy. Batch sorption experiments were carried out for the removal of Zn(II) and Cd(II) from synthetic aqueous solutions using the impregnated resin. The influences of various experimental parameters like pH, initial concentration, contact time and the effect of temperature were evaluated. The optimum pH range was 4-8 for Cd(II) ions and 4-7 for Zn(II) ions. The equilibrium was reached after 30 min with an overall adsorption performance of ~85% for Cd2+ and ~96% for Zn2+. The equilibrium adsorption data were well described by the Langmuir model. The values of the dimensional separation factor, RL, indicated favorable adsorption. The maximum adsorption capacities of the XAD7-D2EHPA were ~5.0 mg Zn(II)/g and ~4.5 mg Cd(II)/g, respectively. The kinetics of the adsorption process was well explained and approximated by the pseudo-second-order kinetic model, and intra-particle diffusion was the rate-controlling step after rapid saturation of surface and big pores of XAD7-D2EHPA beads. The variation in the extent of adsorption with temperature was used to evaluate the thermodynamic parameters for the adsorption process. The values of ΔH^o and ΔG^o obtained demonstrated that the adsorption process was exothermic and spontaneous.

1. Introduction

Heavy metals have many industrial applications due to their technological importance. Heavy metal ions are often present in wastewater from industries such as mining, metallurgy, surface finishing, fire protection systems, battery manufacture, pesticides, pigment manufacture, dyes and textile operation, printing and photographic industries (Hlihor and Gavrilescu, 2009). Heavy metal pollution of industrial wastewaters represents a major problem for the environment, since heavy metal ions are nonbiodegradable, and tend to accumulate in the food chain, which causes varieties of serious health problems (Bulai et al., 2009; Gavrilescu, 2009; Robu et al., 2008). They have remarkably high toxicity; some of them even have been confirmed to be carcinogenic (Benamor et al., 2008; Draa et al., 2004; Demirbas et al., 2005; Gode and Pehlivan, 2003; Hosseini-Bandegharaei et al., 2010; 2011; Huynh and Tanaka, 2003; Navarro et al., 2008; 2009; Pehlivan and Altun, 2006; Xiong et al., 2009; Xiong and Yao, 2009a, b).

* Author to whom all correspondence should be addressed: e-mail: mihaela.ciopec@chim.upt.ro; Phone +40256404192

Equilibrium and Kinetic Studies of the Adsorption of Cr(III) Ions onto Amberlite XAD-8 Impregnated with Di-(2-ethylhexyl) Phosphoric Acid (DEHPA)

Mihaela Ciopec, Corneliu Mircea Davidescu, Adina Negrea, Cornelia Muntean, Adriana Popa, Petru Negrea and Lavinia Lupa

Equilibrium and Kinetic Studies of the Adsorption of Cr(III) Ions onto Amberlite XAD-8 Impregnated with Di-(2-ethylhexyl) Phosphoric Acid (DEHPA)

Mihaela Ciopec[1], Corneliu Mircea Davidescu[1], Adina Negrea[1], Cornelia Muntean[1*], Adriana Popa[2], Petru Negrea[1] and Lavinia Lupa[1] *(1) Faculty of Industrial Chemistry and Environmental Engineering, University "Politehnica" Timisoara, 2 Piata Victoriei, 300006 Timisoara, Romania. (2) Institute of Chemistry Timisoara of the Romanian Academy, 24 Mihai Viteazul Blv., 300223 Timisoara, Romania.*

ABSTRACT: The adsorption performance of Amberlite XAD-8 impregnated with di(2-ethylhexyl) phosphoric acid (DEHPA) in the process of Cr(III) ion removal from aqueous solutions was examined. The equilibrium adsorption data were well described by the Langmuir model. The values of the dimensional separation factor, R_L, indicated favourable adsorption. The maximum adsorption capacity of the DEHPA-impregnated XAD-8 material was 5.64 mg Cr(III) ion/g. The kinetics of the adsorption process were best described by the pseudo-second-order kinetic equation. The variation in the extent of adsorption with temperature was used to evaluate the thermodynamic parameters for the process. The values of ΔH^0 and ΔG^0 obtained showed that the adsorption process was endothermic and spontaneous. The adsorption activation energy also showed that the process was endothermic.

INTRODUCTION

Wastewater generated by industrialization may include various heavy metal ions which are poisonous to humans. When their quantities are greater than a specific limit, such heavy metal ions are not only dangerous to living organisms but also have a tendency to accumulate in Nature because they are not biodegraded. Of these heavy metal ions which occur in industrial wastewater, Cr(III) ions stand out since they are generated by industries such as galvanization, steel, paints, textiles, oxidative dyeing, cooling water towers, leather tanning, corrosion inhibitors, electroplating and batteries (Kul and Caliskan 2009). Chromium is found in two oxidation states, Cr(III) and Cr(VI), the latter being the more toxic (Goyal *et al.* 2003).

Heavy metal ions which are dangerous to health can be removed from wastewater by known physicochemical methods (Lin and Juang 2002). Widely used methods for removing inorganic and organic wastes which cause environmental pollution and harm human health involve chemical precipitation, membrane filtration, ion exchange, coagulation and adsorption (Bhattacharyya and Sen Gupta 2008; Orhan and Buyukgungor 1993). Of those listed, adsorption is widely used because of its high efficiency in the removal of heavy metal ions. Adsorption has been found to be an effective and economical method with a high potential for the removal, recovery and

*Author to whom all correspondence should be addressed. E-mail: cornelia.muntean@chim.upt.ro; cornelia.muntean@yahoo.com.

Adsorption studies of Cr(III) ions from aqueous solutions by DEHPA impregnated onto Amberlite XAD7 – Factorial design analysis

M. Ciopec[a], C.M. Davidescu[a], A. Negrea[a], I. Grozav[b], L. Lupa[a,*],
P. Negrea[a], A. Popa[c]

[a] Faculty of Industrial Chemistry and Environmental Engineering, University "Politehnica" Timisoara, 2 Piata Victorie, 300006 Timisoara, Romania
[b] Faculty of Mechanics, University "Politehnica" Timisoara, 2 Piata Victoriei, 300006 Timisoara, Romania
[c] Romanian Academy, Institute of Chemistry, 24 Mihai Viteazul Blv., 300223 Timisoara, Romania

ABSTRACT

The present paper investigates the adsorption of Cr(III) ions using the SIR, prepared by impregnation of Amberlite XAD7 with di-(2-ethylhexyl)-phosphoric acid (DEHPA), which has been chosen as an extractant for the purpose of this study. The Amberlite XAD7–DEHPA resin was impregnated with DEHPA and ethylic alcohol as solvent trough dynamic column impregnation method. The influence of different physicochemical parameters (pH, resin dosage, initial concentration of Cr(III) ions, contact time and temperature) upon the adsorption capacity of XAD7–DEHPA, in the Cr(III) ions removal process from aqueous solution, has been investigated. The pH for Cr(III) ions adsorption was found as 3.0 for this material. The results showed that the adsorption equilibrium was reached after 45 min. The adsorption process is best described by the pseudo-second order kinetic model. Langmuir adsorption isotherm gave a satisfactory fit of the equilibrium data. The maximum adsorption capacity is ∼3 mg Cr(III) ions/g SIR. The thermodynamic studies allowed us to determine the thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$. In this paper the factorial design of experiments was used to study the performance of the adsorption process.

© 2012 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

Keywords: Amberlite XAD7; DEHPA; Solvent impregnated resin (SIR); Cr(III); Sorption kinetics; Factorial design

1. Introduction

Industrial processes generate waste that if disposed untreated would have a detrimental effect on the environment and human health. Heavy metals like Cr, Cu, Pb, Mn, Hg and Cd are common pollutants in soil as well as in water. Due to their greater stability they cannot be degraded and removed from the environment (Mustafa et al., 2008).

Chromium is found in two oxidation states, Cr(III) and Cr(VI), the latter being the more toxic (Hosseini-Bandegharaei et al., 2010; Mustafa et al., 2008; Saha et al., 2004). It is extensively used in pigments and paints, leather tanning, fungicides, ceramic and glass industries. Cr(III) ion is an essential nutrient for human health also. However, the presence of strong oxidants can change it to harmful Cr(VI) (Mustafa et al.,

2008; Tadesse et al., 2006). A lot of work is present in literature on Cr(VI) ions removal but very limited research work is done on the removal of Cr(III) ions from aqueous solutions (Deepa et al., 2006; Lazaridis et al., 2005; Lazaridis and Charalamous, 2005; Mustafa et al., 2008; Taeyoon et al., 2003).

Conventional techniques of metal ions removal from environmental matrices include the following processes: precipitation, solvent extraction, electrochemical recovery, and membrane separation (Belkhouche and Didi, 2010; Chabani et al., 2007; Chun-hua et al., 2009; Kocaoba and Akcin, 2005; Mustafa et al., 2008; Saha et al., 2004). Most of these processes may be ineffective, extremely expensive, or generate secondary pollution. In recent years, adsorption process has been widely practiced for metal ions removal, because of its competitive and effective process for the above purpose. The

"Gheorghe Asachi" Technical University of Iasi, Romania

STATISTISTICAL OPTIMIZATION OF CHROMIUM IONS ADSORPTION ON DEHPA-IMPREGNATED AMBERLITE XAD7

Mihaela Ciopec[1*], Corneliu Mircea Davidescu[1], Adina Negrea[1], Ion Grozav[2], Lavinia Lupa[1], Cornelia Muntean[1], Petru Negrea[1], Adriana Popa[3]

[1] *"Politehnica" University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 2 Victoria Square, 300006 Timisoara, Romania*
[2] *"Politehnica" University of Timisoara, Faculty of Mechanics, 2 Victoria Square, 300006 Timisoara, Romania*
[3] *Romanian Academy, Institute of Chemistry Timisoara of Romanian Academy, 24 Mihai Viteazul Blvd., 300223 Timisoara, Romania*

Abstract

Statistical thinking and statistical methods play an important role in planning, conducting, analyzing and interpreting data from experiments. When several variables influence a certain characteristic of a product, the best strategy is then to design an experiment so that valid, reliable and sound conclusions can be drawn effectively, efficiently and economically.
The present paper investigates the efficiency of chromium ions removal onto Amberlite XAD7 using the solvent impregnated resin (SIRs) method. The Amberlite XAD7 resin was impregnated with di-(2-ethylhexyl)-phosphoric acid (DEHPA) and ethylic alcohol as solvent by dynamic column impregnation method. The results showed that the maximum efficiency of chromium ions removal was reached after 60 min. At this moment, the efficiency of chromium ions removal was of ~90%. In this paper the design of experiments was used to study the performance of a chemical process. The process transforms the inputs into an output that has two observable responses (absorbability and efficiency). By analyzing the results of the second-order model, the process has been optimized.

Key words: Amberlite XAD7, chromium, design, di-(2-ethylhexyl)-phosphoric acid, SIRs

Received: September, 2011; Revised final: February, 2012; Accepted: March, 2012

1. Introduction

Increasing the awareness on the importance of environmental protection and resources conservation, together with more stringent wastewater discharge legislation have generated a strong interest in developing efficient wastewater treatment process for the recovery of resources (UNDESA, 2003).

Most heavy metals are highly toxic to humans and other living organisms, and their presence in surface waters at above background concentrations is undesirable (Radojovic and Bashkin, 2006). Major anthropogenic sources of metals in water systems are industrial wastes from mining, manufacturing and electroplating plants (Baral and Engelken, 2002;

EIPPCB, 2006). Metals can react in the environment forming even more toxic metal-containing compounds (Hategan et al., 2011; Schaider et al., 2004). The use of chromium and cadmium in the electroplating industry, though was very effective and commonly practiced for a long period of time (Gupta et al., 2002; Nishihama et al., 2004), is being criticized because of the toxicity of chromium and cadmium in humans and in the natural environment (Baral and Engelken, 2002; EIPPCB, 2006; Gupta et al., 2002; Nishihama et al., 2004, Shahin, 1998).

Solvent-impregnated resins (SIR) have been postulated as an effective alternative for the separation and recovery of metals ions from dilute solutions (Cortina et al., 1997). The impregnation of

---
* Author to whom all correspondence should be addressed: e-mail: mihaela.ciopec@chim.upt.ro; Phone/Fax: 004 0256 404192

Kinetic and Thermodynamic Studies Regarding Cu(II) Ions Removal from Aqueous Solution by Poly(Styrene-Divinylbenzene)-Supported Aminophosphonic Acids

MIHAELA CIOPEC[1]*, LAVINIA LUPA[1], ADINA NEGREA[1], CORNELIU MIRCEA DAVIDESCU[1], ADRIANA POPA[2], PETRU NEGREA[1], MARILENA MOTOC[3], DANA DAVID[3], DANA KAYCSA[3]

[1] Politehnica" University, Faculty of Industrial Chemistry and Enviromental Engineering, Physical Chemistry Department, 6 V. Parvan Blv., 300223 Timisoara, Romania

[2] Romanian Academy, Institute of Chemistry Timisoara, 24 Mihai Viteazul Blv., 300223 Timisoara, Romania

[3] "Victor Babes" University of Medicine and Pharmacy, 2Piata Eftimie Murgu, 300041, Timisoara, Romania

In industrial processes, e. g., the leather industry, mineral extraction and electroplating, there is a considerable emission of residual water contaminated with heavy metals such as cadmium, lead, copper, nickel, zinc, and chromium. The use of chelating polymers for the preconcentration and separation of heavy metals is reasonably well understood and progress today is mainly in improving the specificity of the resin and the techniques of application. In this paper the aminophosphonic resins were used in the removal of Cu(II) ions from aqueous solutions. The kinetic models applied to the experimental data showed that the adsorption of Cu(II) ions onto studied materials is described by the pseudo-second-order kinetic model. Temperature dependence of sorption reveals the increase in sorption performance of the sorbent with temperature increasing. The equilibrium adsorption data were described by the Langmuir model.

Keywords: aminophosphonic acid, cooper, removal, isotherm, kinetic

Metals ions are often present in wastewaters from industries such as mining, metallurgy, and surface finishing at a concentration from a few to several hundred milligrams per liter. Elimination of heavy metals from industrial wastewaters is one of the compulsory conditions for their discharge into sewage systems or bodies of waters [1-3]. Metal recovery from solution is typically achieved by techniques including chemical precipitation, solvent extraction and adsorption. Some of these methods are expensive and have limitations. Currently, the usual treatment technology of metal-bearing wastewater is chemical precipitation; however, this method often creates secondary problems with sludge generation. Solvent extraction and resin ion exchange involve similar chemical principles, each offering advantages and drawbacks [4-6]. As examples of the general advantages, solvent extraction is effective for the recovery of metal ions at high concentration with high selectivity and is suitable for continuous operation, while resin ion exchange is effective for the removal of metal ions at low concentration and simplifies the equipment and operation [7-9]. As examples of the general drawbacks, solvent extraction is associated with the loss of organic compounds (extractant and diluents) into the aqueous phase, while resin ion exchange has a low selectivity for metal ions except in the cases using chelating resins, which show slow complexation with metal ions and are expensive. The development of solvent-impregnated resins as a link between solvent extraction and resin ion exchange has become an important direction in separation science and technology. Solvent-impregnated resins have been shown to be effective sorbents for the removal of metal ions at low concentration [10-13].

The purpose of this study is to explore the ability of removing Cu(II) ions from aqueous solutions by using two synthesized and two commercial aminophosphonic acid grafted on styrene-divinylbenzene copolymer. In order to determine the adsorption performance of the studied materials the equilibrium, kinetic and thermodynamic studies, were performed.

Materials and methods

The studied adsorbent materials were obtained by chemical method, using the "One-Pot" functionalizing reaction, using two materials (benzaldehyde and propionaldehyde), a synthesized co-polimer (S) and a commercial one (C), using different quantities of divinylbenzene grafted with amino groups b(1% and 15%) and two types of acids (phosphorous and aminophosphonic acid).

Stock solution of Cu(II) were prepared using Merck Standard Solutions of $Cu(NO_3)_2$, in HNO_3 0.5 mol/L.

All other chemicals used for experiments were of analytical reagent grade, and were used without further purification. Distilled water was used in all experiments.

The pH of the solutions was measured with a digital pH meter CRISON Multimeter MM41, using a glass electrode calibrated with buffer solutions.

Cu(II) ions concentrations were determined using a Varian SpectrAA 280 Fast Sequential Atomic Absorption Spectrometer with an air-acetylene flame at wavelengths λ = 324.8 nm.

For batch experiments a mechanical shaker bath MTA Kutesz, Hungary was used.

In order to establish the adsorption performance of the studied materials, in the process of Cu(II) ions removal from water, kinetic, thermodynamic and equilibrium studies were performed.

The adsorption performance is expressed as the adsorption capacity q_t (mg/g) of the adsorbent, corresponding to the amount of Cu(II) ions sorbed per g

"Gheorghe Asachi" Technical University of Iasi, Romania

KINETIC, EQUILIBRIUM AND THERMODYNAMIC STUDIES OF CESIUM REMOVAL FROM AQUEOUS SOLUTIONS USING AMBERJET UP1400 AND AMBERLITE IR120 RESINS

Adina Negrea, Mihaela Ciopec, Corneliu Mircea Davidescu, Cornelia Muntean*
Petru Negrea, Lavinia Lupa

Faculty of Industrial Chemistry and Environmental Engineering, University „Politehnica" Timişoara
6 V. Pârvan Blvd. 300223 Timişoara, Romania

Abstract

The performance of two cation exchanger resins, Amberjet UP1400 and Amberlite IR120 in the process of Cs(I) ions removal from aqueous solutions was examined. Batch experiments were carried out to determine the influence of several parameters (resin dosage, contact time, temperature and initial concentration of Cs(I) ions) on the removal process. The equilibrium was reached after 60 min for Amberlite IR120 and after 120 min for Amberjet UP1400, with an overall adsorption performance of ~97% for both materials. The kinetics of the adsorption process was well approximated by the pseudo-second-order kinetic model. The equilibrium adsorption data were well described by the Langmuir model for Amberjet UP1400 and by the Sips model for Amberlite IR120. The calculated maximum adsorption capacities towards Cs(I) were of 6.36 mg/g for Amberjet UP1400 and of 8.67 mg/g for Amberlite IR120. The values of thermodynamic parameters ΔH^o and ΔG^o obtained demonstrated that the adsorption process was endothermic and spontaneous. The values calculated for the activation energy were of 3.48 kJ/mol for Amberjet UP1400 and 4.85 kJ/mol for Amberlite IR120.

Key words: cation exchanger resin, cesium ion, isotherm, kinetic, thermodynamic

Received: January 2013; Revised final: May, 2013; Accepted: May, 2013

1. Introduction

Following the nuclear accident at Chernobyl in 1986, Fukushima in 2011, and other nuclear accidents and nuclear testing, radioactive cesium ^{137}Cs was dispersed in the environment contaminating environmental factors (air, water, soil) (Bergaoui et al., 2005; Giannakopoulou et al., 2007).

Radioactive cesium may also enter the environment from wastes from nuclear power plants (Abd El-Latif and Elkady, 2011; Chang et al., 2008; Hassan and Adu-Wusu, 2005; Mohapatra et al., 2009; Ramanjaneyulu et al., 2012; Sangvanich et al., 2010; Sinha et al., 1995; Wang et al., 2008), from various industries such as manufacturing of semiconductors, selective electrodes, thermionic converters, photoelectric cells and vacuum tubes (Messiha, 1984), from food preservation and medicine (applications of radionuclides in imaging and radiotherapy, sterilization of medical accessories) (Messiha, 1984; Mohapatra at al., 2009).

Cesium is toxic for human health affecting red blood cells and soft tissues by displacing potassium and causing increased mortality when ingested; the exposure to ^{137}Cs causes especially thyroid cancer (Miah et al., 2010; Ramanjaneyulu et al., 2012; Sangvanich et al., 2010).

Radiocesium has a long half-life (about 30 years), high solubility, it is differently dispersed in aquatic medium and in soil and it is easily

---

* Author to whom all correspondence should be addressed: E-mail: cornelia.muntean@chim.upt.ro; Phone +40 256 404164

Synthesis, Characterization, and Adsorption Behavior of Aminophosphinic Grafted on Poly(styrene-*co*-divinylbenzene) for Divalent Metal Ions in Aqueous Solutions

Mihaela Ciopec,[1] Corneliu M. Davidescu,[1] Adina Negrea,[1] Lavinia Lupa,[1] Adriana Popa,[2]
Cornelia Muntean,[1] Radu Ardelean,[1] Gheorghe Ilia[2]
[1] 'Politehnica' University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering,
Physical Chemistry Department, Bul. V. Parvan 6, 300223 Timisoara, Romania

[2] Organic Department, Institute of Chemistry Timisoara of Romanian Academy, Romanian Academy,
24 Mihai Viteazul Blv., RO-300223 – Timisoara, Romania

In the present work, two novel aminophosphinic acid ligands grafted on poly(styrene-1%divinylbenzene) (St-1%DVB) have been synthesized by reacting polymer precursors bearing primary amino groups with benzaldehyde (or propionaldehyde) and phenylphosphinic acid by the 'one-pot' Kabatachnik-Fields reaction. The resins functionalized with aminophosphinic pendant groups were characterized by means of Fourier transform infrared spectroscopy (FTIR), thermal analysis, energy dispersive X-ray microanalysis (EDX), and Scanning electron microscopy (SEM) imaging. Its adsorption capacity for divalent metal ions such as Cu(II) and Ni(II) were investigated. The adsorption procedure of Cu(II) and Ni(II) ions on polymer-grafted aminophosphinic acid ligands was carried out by batch experiments. The result also shows that the adsorption process was best described by a pseudo-second-order kinetic equation and by the Langmuir adsorption isotherm. The best maximum adsorption capacity was obtained for resin with aminobenzylphosphinic acid groups [1.46 mg Cu(II)/g and 1.36 mg Ni(II)/g]. POLYM. ENG. SCI., 53:1117–1124, 2013. © 2012 Society of Plastics Engineers

INTRODUCTION

In recent years, public awareness has increased on the long-term toxic effects of water containing dissolved metal ions. Many industries such as textile industry, oil refining, metal plating facilities, electroplating, pigments and dyes manufacturing, mining operations, fertilizers production, and batteries manufacturing produce heavy metals such as nickel, copper, lead, zinc, chromium, cadmium, cobalt, etc [1, 2]. The released heavy metals could cause serious environmental problems for humans, animals, and plants due to their extreme toxicity [3]. Moreover, these heavy metals can contaminate the soil, drinking water sources, groundwater, and crops [4]. Environmental contamination with heavy metals gained lately more reasons for concern due to their high persistency, damaging effects on the nervous system, and even concern, caused by their accumulation at certain levels. Copper is an essential element for human body; its discovery in human brain in 1921 was important in order to establish its functions in the body: oxygen and electrons transport, constituent of enzymes to redox reactions, and involvement in the mobilization of iron to hemoglobin synthesis [5]. Nickel is one of the most important metals among heavy metals. Nickel is used in many industrial applications and consumer products including magnets, stainless steel, plating, and special alloys (such as nickel steels, nickel cast irons, nickel brasses, and bronzes) [6]. Divalent nickel especially causes cancer of lungs, nose, and bones [7–12].

Polymers functionalized with phosphorus-based ligands display unique selectivity for metal ions. In the current research, we have introduced aminophosphinic acid ligands onto polystyrene through "one-pot" reactions.

Quite a few phosphorus based ion-exchangers as well as ligand-loaded resins are being used for metal ion extraction [13–15]. Trochimczuk[16] obtained resins functionalized with phenylphosphinic acid ligands via the Michael reaction. The most promising technique for removal of metal cations is their adsorption on organic sorbents containing chelating functional groups [17, 18].

The synthesis of phosphonate ester and phosphonate/phosphonic acid grafted on styrene-divinylbenzene copolymers (St-7% DVB) was previously reported [19] and we

Synthesis, characterization, and Ni(II) ion sorption properties of poly(styrene-*co*-divinylbenzene) functionalized with aminophosphonic acid groups

**Corneliu-Mircea Davidescu · Mihaela Ciopec ·
Adina Negrea · Adriana Popa · Lavinia Lupa ·
Ecaterina-Stela Dragan · Radu Ardelean ·
Gheorghe Ilia · Smaranda Iliescu**

Abstract   In this study, novel chelating resins containing aminophosphonic acid groups grafted on poly(styrene-*co*-divinylbenzene) (1 % or 15 % DVB) were obtained by "one-pot" reactions. The phosphorus contents were determined in order to calculate the degree of functionalization with pendant aminophosphonic acid groups. The fraction of repetitive units functionalized with aminophosphonic acid groups was determined by accepting the statistical structure of the repetitive unit of initial and final copolymer. These materials were characterized by FT-IR spectroscopy, EDX, and TGA. Adsorption properties of aminophosphonic acids grafted on poly(styrene-*co*-divinylbenzene) were examined for the removal of Ni(II) ions from aqueous solutions using the batch equilibrium procedure. By applying the kinetic models to the experimental data it was found that the adsorption of Ni(II) on the studied chelating resins is described by the pseudo-second-order kinetic model. For all the studied systems, Langmuir isotherm model provided an excellent fit of the equilibrium adsorption data.

Keywords   Aminophosphonic acids · Styrene–divinylbenzene microbeads · Removed · Ni(II)

C.-M. Davidescu · M. Ciopec · A. Negrea · L. Lupa · R. Ardelean
Faculty of Industrial Chemistry and Enviromental Engineering, Physical Chemistry Department,
"Politehnica" University of Timisoara, Bul. V. Parvan 6, 300223 Timisoara, Romania

A. Popa (✉) · G. Ilia · S. Iliescu
Institute of Chemistry Timisoara of Romanian Academy, Romanian Academy,
24 Mihai Viteazul Blv, 300223 Timisoara, Romania
e-mail: apopa@acad-icht.tm.edu.ro; apopa_ro@yahoo.com

E.-S. Dragan
"Petru Poni" Institute of Macromolecular Chemistry,
Aleea Grigore Ghica Voda 41 A, 700487 Iasi, Romania

Di-2-Ethylhexyl Phosphoric Acid Immobilization with Polysulfone Microcapsules for Cu(II) Extraction

M. Ciopec[*], C.M. Davidescu[*], A. Negrea[*], L. Lupa[*], P. Negrea[*], A. Popa[**]

[*] „POLITEHNICA" University of Timisoara, 2 Piata Victoriei, 300006 Timisoara, Romania,
e-mail: mihaela.ciopec@chim.upt.ro

[**] Romanian Academy, Institute of Chemistry, 24 Mihai Viteazul Blv., 300223 Timisoara, Romania

Abstract: This paper reports the results of the adsorption performance of Cu(II) removal from aqueous solutions by an impregnated resin, polysulfone microcapsules (PS) containing di-2-ethylhexyl phosphoric acid (D2EHPA). The adsorbent was obtained by solvent impregnated resin (SIR) method. The adsorption performance of the studied material was evaluated studying the effects of two physico-chemical parameters: contact time and Cu(II) initial concentration. The adsorption experiments were carried out following batch equilibrium techniques. The kinetic parameters of different models were calculated and discussed. The equilibrium adsorption data were modeled using Freundlich and Langmuir isotherm equations and the corresponding isotherm parameters were calculated and discussed in detail. The material showed good adsorption performance in the removal process of Cu(II) ions from aqueous solution.

Keywords: polysulfone microcapsules; removal; di-(2-ethylhexyl) phosphoric acid, copper

1. Introduction

Ion exchange now is a well-established technology, particularly in water purification and the concentration and removal of hazardous substances at very low concentrations in chemical process industries. For example, it has been applied for the recovery of copper from rayon spinning wastewater and the recovery of gold from cyanide solution in metallurgical industries [1].

Ion exchange resins have low selectivity in the extraction of metal ions and high saturation with ions different from those of interest, decreasing their yield. Highly selective chelating ion exchange resins have been developed, but these are only available for a limited number of metal ions and they are expensive in relation to the generation of polymers with selective ion groups. An interesting alternative to these processes is the use of solvent-impregnated resins (SIR) [2].

The concept of SIR is now well developed and has a strong place in extraction chromatography at analytical application scale and is of potential application at industrial scale [3, 4].

There are four methods available for the immobilization of the desired extractant into the polymeric supporting structure: the dry method, wet method, modified addition method and the dynamic column method [5-7].

The use of macro porous organic polymer supports, with a high surface area and good mechanical stability, is found more suitable for the removal of toxic elements from dilute solution, due to their faster kinetics, ease of regeneration and high adsorption capacity. The development and application of these systems in metal extraction processes has been intensively investigated for the purpose of applications on metal separation and recovery processes [8-17].

In this paper the adsorption performance of the D2EHPA impregnated polysulfone microcapsules (PS) has been investigated. In this purpose, the influence of two physicochemical parameters (contact time and initial concentration of Cu^{2+}) upon the Cu^{2+} adsorption onto PS was studied.

2. Experimental

The polysulfone microcapsules (PS) (Typical M_n=26,000, T_g=190ºC) by Sigma Aldrich was impregnated with di(2-ethylhexyl)phosphoric acid (D2EHPA) trough dry method. The DEHPA ~ 98.5% used as extractant, was supplied by BHD Chemicals Ltd Poole England and used as received. One gram of polysulfone microcapsules (PS) has been placed for 24 h in absolute ethanol (Chimopar Romania) containing 0.1 g/mL extractant (D2EHPA). The microcapsules have been separated through a porous filter using a vacuum pump, washed with water and dried at 50°C for 24 h [18].

In order to establish the adsorption performance of the D2EHPA impregnated polysulfone (PS), the influence of contact time and initial concentration of copper on the adsorption capacity was investigated.

The adsorption capacity q_t (mg/g) of the PS-D2EHPA towards Cu(II) ions was calculated with the following equation:

$$q = \frac{(C_0 - C_t)V}{m} \quad \text{[mg Cu(II)/g PS-D2EHPA]} \quad (1)$$

where C_0 and C_t are the concentrations of Cu(II) ions (mg/L) in the solution initially (t =0) and after a time t (min), respectively, V is the volume of the solution (L) and m is the mass of adsorbent employed (g).