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

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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 ΔG°, ΔH° and ΔS°. In this paper the factorial design of experiments was used to study the performance of the adsorption process.

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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

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 (Belkhouche and Didi, 2010; Chabani et al., 2007; Hosseini-Bandegharaei et al., 2010; Mustafa et al., 2008; Saha et al., 2004). Impregnating appropriate solid supports, such as Amberlite XAD series, is one of the well-known and effective solid sorbent preparation methods for treatments purposes (Belkhouche and Didi, 2010; Hosseini-Bandegharaei et al., 2010; Mustafa et al., 2008; Narin et al., 2008). There are four methods available for the impregnation of the desired extractant into the polymeric supporting structure: the dry method, wet method, modifier addition method and dynamic column method (Mendoza et al., 2000; Muraviev et al., 1998; Saha et al., 2004). The dynamic column method has the advantages of short impregnation time and high efficiency, which can be obtained not only in laboratory test but on an industrial scale (Juang, 1999).

The aim of this present work is to study the adsorption performance of Amberlite XAD7 resin impregnated with DEHPA as organophosphorus extractant trough dynamic column impregnation method in the process of Cr(III) ions removal from aqueous solutions.

In many process development and manufacturing applications, the number of potential process or design (factors) is large. Screening design is used to reduce the number of factors or design parameters by identifying the key ones that affect product quality or process performance. This reduction allows one to focus process improvement efforts on the few really important factors, or the "vital few" (Montgomery, 2001; Stas et al., 2002). From these reasons, in this paper, the factorial design of experiments was used to study the adsorption performance of XAD7–DEHPA in the removal process of Cr(III) ions from aqueous solutions.

2. Materials and methods

2.1. Reagents

The di(2-ethylhexyl)phosphoric acid (DEHPA) ~98.5% used as extractant, was supplied by BHD Chemicals Ltd. Poole England and used as received.

Amberlite XAD7 resin (supplied by Rohm and Hass Co.), size 0.3–0.9 mm, was used as support. The mean particle diameter r_o was taken equal to 0.6 mm. The mean pore size is ~9 nm with a surface area of 450 m^2/g. As organic solvent was used ethanol from Chimopar Romania.

A stock solution of 1 g/L Cr(III) ions was prepared by diluting an appropriate amount of $Cr(NO_3)_3$ in 0.5 mol/L HNO_3 solution (Merck Standard Solution). Other solutions of Cr(III) ions were prepared from the stock solution by appropriate dilution.

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

2.2. Preparation of impregnated resins

The Amberlite XAD7 resin was impregnated with DEHPA and ethylic alcohol as solvent by dynamic column impregnation method (Juang, 1999). A certain amount of polymer fully swollen by the solvent was packed in a glass column of 4 cm diameter and 15 cm height. Then the extractant solution was fed into the column with a 0.1 L/h flow rate until the

extractant concentration in the outlet was equal to the feed one. The polymeric beads were separated through a porous filter using a vacuum pump, washed with water and dried at 50 °C for 24 h (Benamor et al., 2008). The resulting SIR were finally washed with distilled water.

2.3. Adsorption experiments

The influence of different physicochemical parameters (pH, resin dosage, contact time, initial concentration of Cr(III) ions and temperature) upon the adsorption capacity of XAD7–DEHPA, in the Cr(III) ions removal process from aqueous solution, has been investigated.

The initial pH of the sample solutions were adjusts in the range of 1–5 by using HNO_3 or NaOH solution. In each experiment 0.1 g of sorbent was suspended in 25 mL of 10 mg/L Cr(III) ion solution. The samples were stirred for 2 h. A pH-meter CRISON Multimeter MM41 was used to measure the pH of all solutions.

In order to determine the effect of S:L ratio on adsorption, experiments were conducted with 10 mg/L Cr(III) ion concentration and samples having different XAD7–DEHPA dosage ranging from 0.05 to 0.2/25 mL Cr(III) ion solution at different contact times (1, 2, 3, 4, 5, 15, 30, 45, 60, 90 and 120 min) and at the room temperature 25 ± 1 °C.

To investigate the effect of the temperature (298, 308 and 318 K) on Cr(III) adsorption, the experiments were conducted at constant concentration of Cr(III) ions (10 mg/L) and different stirring time (5, 15, 30, 45, 60, 90 and 120 min).

Adsorption isotherm were carried out with different initial concentrations varying from 5 to 50 mg/L Cr(III) ions while keeping the resin amount at constant value (0.1 g in 25 mL Cr(III) ion solution) at room temperature (25 ± 1 °C) at the stirring time of 45 min.

All the samples were stirred using a shaker bath MTA Kutesz, Hungary.

After stirring, the samples were separated trough filtration. The residual concentration of Cr(III) ions from filtrate was analyzed trough atomic adsorption spectrophotometer using an atomic adsorption spectrophotometer Varian SpectrAA 280 Fast Sequential Atomic Absorption Spectrometer with an air-acetylene flame at wavelength λ = 357.9 nm.

The amount of adsorbed Cr(III) ions per unit of XAD7–DEHPA was determined by using the following equation (Abdel Raouf and El-Kamash, 2006; Davidescu et al., 2011; Gode and Pehlivan, 2006; Uysal and Ar, 2007; Yu et al., 2009):

$$q = \frac{(C_0 - C_e)v}{m} \tag{1}$$

where q_e is the adsorption capacity (mg/g) and C_0 and C_e are the concentration of the Cr(III) ions in the solution (mg/L) before and after adsorption, respectively. v is the volume in aqueous solution (L) and m is the amount of the resin (g).

2.4. Kinetic models for the adsorption

In order to investigate the mechanism of adsorption, the pseudo-first-order and the pseudo-second-order adsorption models were used to test dynamical experimental data. The pseudo-first-order rate expression of Lagergren is generally described by the following equation (Abdel Raouf and El-Kamash, 2006; Davidescu et al., 2011; Deepa et al., 2006;