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Sorption of Cr(III) onto chelating b-DAEG–sporopollenin and CEP–sporopollenin resins

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Abstract

In the present study, the removal of Cr(III) from aqueous solution was studied using a new chelate-resins (b-DAEG–sporopollenin and CEP–sporopollenin). Mechanisms including ion exchange, complexation and adsorption to the surface are possible in the sorption process. Adsorption analysis results obtained at various concentrations of Cr(III) showed that the adsorption pattern on the resin followed a Langmuir isotherm. Langmuir constant Γ_{max} and k for Cr(III) were found as 1.23, 84.84 mmol/g for b-DAEG–sporopollenin, 133.33, 10.39 mmol/g for CEP–sporopollenin at 20 ± 1 °C, respectively. In addition, kinetic and thermodynamic parameters such as enthalpy (ΔH^0), free energy (ΔG^0) and entropy (ΔS^0) were calculated and these values show that adsorption of Cr(III) on b-DAEG–sporopollenin and CEP–sporopollenin was an exothermic process and the process of adsorption was favored at high temperatures. Maximum Cr(III) removal was observed near a pH of 6.

Keywords: Adsorption; Chelate resin; Sporopollenin; Chromium; Langmuir

1. Introduction

Due to the toxicological importance in the ecosystem, agriculture and human health, pollution by heavy metals has received wide spread attention in the recent years (Lin and Juang, 2002; Abollino et al., 2003). Industrial wastewaters frequently contain high levels of heavy metals and treatment is needed before disposal, in order to avoid water pollution. There are numerous sources of industrial effluents leading to heavy metal discharges apart from the mining and metal related industries (Inglezakis et al., 2002; Yavuz et al., 2003; Petrus and Warchol, 2003; Abollino et al., 2003; Kesenci et al., 2002).

The main industrial sources of chromium pollution are leather tanning, electroplating, metal processing, wood preservatives, paint and pigments, textile, dyeing, steel fabrication and canning industries (Acar and Malkoc, 2004; Garg et al., 2004; Selvaraj et al., 2003; Hu et al., 2003; Inglezakis et al., 2003; Kang et al., 2004; Kocaoba and Akcin, 2002; Petrus and Warchol, 2003; Rengaraj et al., 2003). Chromium is unique among regulated toxic elements in the environment in that different species of chromium, specifically Cr(III) and Cr(VI) are regulated in different ways based on their differing toxicities. Once chromium is introduced into the environment it exists in two stable oxidation states, Cr(III) and Cr(VI) and the trivalent form is relatively innocuous (Bishnoi et al., 2004; Selvaraj et al., 2003). The inter-conversion of Cr(III) is controlled by several factors, including the presence and concentrations of Cr(III) ion and oxidizing or reducing agents, the electrochemical potentials of the oxidation and reduction reactions, ambient temperature, light, sorbents, acid–base reactions, complexing agents, and precipitation reactions. When low levels of chromium are present in the environment,

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trivalent chromium apparently plays an essential role in plant and animal metabolism, while hexavalent chromium is directly toxic to bacteria, plants and animals (Acar and Malkoc, 2004; Rengaraj et al., 2003).

There are several methods to treat the metal contaminated effluent such as precipitation, ion exchange and adsorption, as well as others but the selection of the wastewater treatment methods is based on the concentration of waste and the cost of treatment (Yavuz et al., 2003). Ion exchange resins have been used in the chemical analysis for over 50 years and it is now well established that heavy metals are taken up from water predominantly by ion exchange. Carboxyl, sulphate groups have been identified as the main metal-sequestering sites and, as these groups are acids; its availability is pH dependent. At pH in the range 3.5–5.5 these groups generate a negatively charged surface, and electrostatic interactions between cationic species and this surface can be responsible for metal sorption (Jeon and Höll, 2004; Kang et al., 2004; Kara et al., 2003; Rengaraj et al., 2002). Their abilities to separate and preconcentrate analytes are widely applied in the atomic spectrometry techniques, minimizing the limitations related to the sensitivity and the selectivity (Pohl and Prusisz, 2004). Chelate exchange is one of the more popular methods for the removal of chromium from aqueous solutions (Demirbaş et al., 2005; Gode and Pehlivan, 2003; Pesavento and Biesuz, 1998). A conventional ion exchange technique that employs a strong acid cation-exchanger can efficiently remove the heavy metal ions; however, it may also remove innocuous cations such as sodium, calcium and magnesium. In such cases, selectivity can be enhanced by the use of weak acid cation-exchange resins, wherein carboxylate groups are linked to either a styrenic or ethylenic backbone. Improvement of resin selectivity for heavy metals involves the introduction of special functional groups onto the polymer matrix of the ion exchange resin (Kang et al., 2004).

Metal adsorption through precipitation and ion exchange/chelation is a common approach to reduce metal toxicity in the environment (Cortina et al., 1996; Soylak and Elçi, 1997; Yu et al., 2000; Seco et al., 1999; Brown et al., 2000). Polymeric adsorbents are one type of agent that can be used for the removal of metals from wastewaters. They are composed of synthetic polymer and ligand, wherein the metal ions are bound to the polymer ligand by a coordinate bond. A ligand contains anchoring sites like nitrogen, oxygen or sulfur obtained either by polymerization of monomer possessing the coordinating site or by a chemical reaction between a polymer and a low molecular weight compound having coordinating ability (Kesenci et al., 2002). In addition, several recent publications concerning the separation of Cr(III) in various aqueous solutions generally show that carboxylic resin also offers a higher apparent capacity and slow sorption kinetics (Kocaoba and Akcin, 2002; Rengaraj et al., 2002). Adsorption has been found to be an effective process for Cr(III) removal, but sometimes it is too expensive. New economical, easily available and highly effective adsorbents are still needed (Yu et al., 2003; Park and Jung, 2001; Kocaoba and Akcin, 2003).

Oxime functional group resins are solvent impregnated resins and differ from the conventional chelating ion-exchange resins, which contain chelating ligand covalently bonded to a polymeric matrix (Sahni and Reedijk, 1984).

The outer wall of spores and pollen contains a highly resistant bio-macromolecule, sporopollenin, which can survive in geological strata over millions of years with full retention of morphology (Brooks and Shaw, 1978). Sporopollenin is a natural polymer obtained from *Lycopodium clavatum* which is highly resistant to chemical attack, has a high capacity, is stable, has a constant chemical structure and occurs naturally as a component of spore walls, and exhibits very good stability even after prolonged exposure to mineral acids and alkalies. Sporopollenin is produced by oxidative polymerization of carotenoids and carotenoid esters, which lead to the proposed monomer structures of the macromolecular sporopollenin. At present sporopollenin is generally considered to be a biopolymer and the detailed chemical structure of sporopollenin is as yet unknown. Its empirical formula has been found to be $C_{90}H_{144}O_{27}$ (Brooks and Shaw, 1968; Shaw et al., 1971).

A number of chelating exchangers of sporopollenin, formed from carboxyl, epoxy, and glyoxime, have been investigated as ligand exchangers. This material may be usefully applied at high temperatures, since it is stable under high temperature and in the presence of concentrated acids. Ethylenediamine complexes possess a very stable structure and have minor dissociation tendencies, and they act as suitable functional groups for a ligand-exchange matrix. Therefore, it is suitable for use as an adsorbent (Vural et al., 1995; Ersoz et al., 1995; Pehlivan et al., 1994, 1995, 1996).

The objective of this work was to prepared the new chelate resins and to evaluate the adsorption capacity of Cr(III) from aqueous solutions by b-DAEG–sporopollenin and CEP–sporopollenin by varying Cr(III) concentration, pH and temperature.

2. Experimental

2.1. Materials

The resin used was *L. clavatum* with 20 μm particle-size mesh from BDH chemicals. All the chemicals used were of analytical grade and obtained from Merck. A stock solution of 1×10^{-3} mol/l of Cr(III) was prepared by dissolving 0.2380 g of $Cr(NO_3)_3$ in 1000 ml distilled water. This solution was diluted as required. A series of standard metal solution by appropriate dilution of the stock metal solution were prepared. Solutions of 0.01 M NaOH and HCl were used for pH adjustment. The concentration of dissolved metals in the samples (at least three concentrations of each) was determined from the linear calibration curve.