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Selective separation of mercury(II) using magnetic chitosan resin modified with Schiff's base derived from thiourea and glutaraldehyde

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Abstract

Magnetic chitosan resin was chemically modified by a Schiff's base cross-linker. The interaction of the resin obtained with Hg(II) was studied and uptake value of 2.8 mmol/g was reported. The kinetic and thermodynamic parameters of the adsorption process were estimated. These data indicated that the adsorption process is exothermic and follow the pseudo-second-order kinetics. The selectivity of Hg(II) from other different metal ions in solutions using the studied resin was also reported. Breakthrough curves for the recovery of Hg(II) were studied. The critical bed height was found to be 2.05 cm. The adsorbed Hg(II) was eluted from the resin effectively using 0.1 M potassium iodide.

Keywords: Mercury; Resins: Chitosan; Recovery; Elution; Schiff's base

1. Introduction

Mercury contamination of the environment is caused by both natural and manmade sources. Natural sources include volcanic action and erosion of mercury-containing sediments. Some of the ways in which humans contaminate the environment with mercury include, mining, transportation and processing of mercury ores, dumping of industrial wastes into rivers and lakes, combustion of fossil fuels, pulp and paper industry, the use of mercury compounds as seed dressings in agriculture, and exhaust from smelters [1]. A broad spectrum of mercury treatment technologies has been described in the literature. These include precipitation, coagulation/co-precipitation, chemical reduction, membrane separation, biological treatment, and solid phase extraction (SPE) [2]. One of the promising methods is the use of chelating resins. Chelating resins are easily regenerated from metal ions and they differ from activated carbon and ion exchange resins in their high selectivity in sorption processes [3]. Many articles that cover a vast number of different chelating resins were reported [4–8]. Recently, we reported on the use of different chelating resins with various functionalities for the selective separation of mercury [9–12]. We also reported on the use of magnetic resins in removal of some metals from aqueous solutions. These magnetic resins are easily collected from aqueous media using an external magnetic field and displayed higher uptake capacity compared to the magnetic particles-free resin [13,14]. These methods are also cheap and often highly scalable. Moreover, techniques employing magnetism are more amenable to automation [15]. Attention has recently been focused on chitosan and its derivative as bioadsorbents. Chitosan is a major component of crustacean shells and one of the most abundant biopolymers in nature [16]. It is characterized by its ability to uptake several metal ions through different mechanisms, depending on the type of metal ion and the pH of the solution. The dissolution of chitosan was decreased through cross-linking treatments. The cross-linking procedure may be performed by reaction of chitosan with different cross-linking agents such as glutaraldehyde [17,18], 1,1,3,3-tetramethoxypropane [19], oxidized β-cyclodextrin (β-cyclodextrin polyaldehyde) [20], ethyleneglycol diglycidyl ether [21] or glycerolpolyglycidylether [22]. Tri-polyphosphate has also been selected as a possible cross-linking agent, which can be used for the preparation of chitosan gel beads by the coagulation/neutralization effect [23]. The cross-linking step may cause a significant decrease in metal uptake efficiency especially in the case of chemical reactions involving amine groups [24]. However, this limiting effect of chemical cross-linking significantly depends on the procedure used [12,18,25,26]. So the efforts have been

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directed towards modification by cross-linkers with chelating functionalities to improve the adsorption capacity. In the present work chemically modified magnetic chitosan with Schiff's base cross-linker will be prepared. The adsorption behaviour of the resin obtained towards Hg(II) will also be studied. Both kinetic and thermodynamic parameters of the adsorption process will also be calculated.

2. Experimental

2.1. Chemicals

Chitosan, glutaraldehyde, thiourea, ferric chloride, ferrous sulphate were Aldrich products. All other chemicals were Prolabo products and were used as received. Mercuric chloride, cadmium nitrate, lead acetate, zinc chloride, copper acetate, calcium chloride and magnesium sulphate were used as a source for Hg(II), Cd(II), Pb(II), Zn(II), Cu(II), Ca(II) and Mg(II), respectively.

2.2. Preparation of magnetite

Magnetite was prepared using the modified Massart method [27]. A 250 mL (0.2 M) of $FeCl_3$ solution was mixed with 250 mL (1.2 M) of $FeSO_4$ solution. A 200 mL (1.5 M) of NH_4OH solution was added to the above solution of $FeCl_3$/$FeSO_4$ under vigorous stirring. A black precipitate was formed which was allowed to crystallize for another 30 min under magnetic stirring. The precipitate was filtered off and washed with deoxygenated water through magnetic decantation until the pH of the suspension became below 7.5.

2.3. Preparation of magnetic chitosan resin

One gram of chitosan was dissolved in 50 mL of 25% aqueous acetic acid solution. Three grams of thiourea (39.47 mmol) were dissolved in 100 mL distilled water. Twelve millilitres (25%) of glutaraldehyde solution (31.2 mmol) was added to thiourea solution in a round flask. The mixture was heated on a water bath for 2 h at 50 °C. Thereafter magnetite powder was added while stirring. The contents of the flask were then added to the chitosan solution and stirred until the solution become homogenous then heated up to 70 °C for 6 h. A large quantity of gel was formed, washed repeatedly with 0.5 NaOH solution then water and dried at 70 °C for 8 h. The dried gel was then grinded and sieved where the particle size fraction (−0.6/+0.5) mm was used in this study.

IR-spectra of the synthesized resin were performed using a Perkin-Elmer IR-spectrophotometer 550.

2.4. Preparation of solutions

A stock solution of Hg(II) (2×10^{-2} M) was prepared in distilled water. A stock solution of EDTA (5×10^{-3} M) was prepared and standardized against a solution of $MgSO_4 \cdot 7H_2O$ using Eriochrome Black-T (EBT). HCl and NaOH were used to change the acidity of the medium. Potassium iodide (0.1 M) was used as an eluent for stripping of Hg(II) from the resin.

2.5. Batch experiments

The effect of contact time on the uptake of Hg(II) by resin was studied by placing 0.1 g of dry resin that was swelled in a flask containing 50 mL of distilled water for 1 h. Fifty millilitres of metal ion solution (2×10^{-2} M) was added to the flask, where the concentration of the metal ion becomes (1×10^{-2} M) and pH 5. The contents of the flask were equilibrated for 3 h on a Vibromatic-384 shaker at 300 rpm and 28 ± 1 °C. Five millilitres of the solution was taken at different time intervals then filtered off, where the residual concentration of metal ion was determined via the titration against 5×10^{-3} M EDTA using PAR as indicator for Hg(II).

The selectivity studies of the investigated resin towards Hg(II) in the presence of binary mixtures of Cu(II), Pb(II), Cd(II), Zn(II), Ca(II) or Mg(II) was carried at pH = 1. The estimation of these metal ions in the binary mixture was carried complexiметrically as above using murexide for Cu(II) and EBT for Ca(II), Mg(II), Cd(II), Zn(II) and Pb(II). KI was also used as a masking agent for Hg(II) [28].

Adsorption of Hg(II) on the resin obtained under controlled pH was carried out following the above procedures. The desired pH was controlled using HCl and NaOH while the equilibrium time was fixed at 3 h and 30 °C.

Complete adsorption isotherms were obtained by soaking 0.1 g of dry resin in a series of flasks containing 50 mL of distilled water for 1 h. Fifty millilitres of metal ions with different concentrations were added to each flask and pH 5 was recorded. The flasks were conditioned at 300 rpm while keeping the temperature at 30, 40, 50 or 60 °C for 3 h. Later on, the residual concentration was determined where the metal ion uptake was estimated.

2.6. Column experiments

Column experiments were performed in a plastic column with a length of 10 cm and a diameter of 1.0 cm. A small amount of glass wool was placed at the bottom of the column to keep the contents. A known quantity of the resin under investigation was placed in the column to yield the desired bed height. Hg(II) solution having an initial concentration of 1×10^{-2} M was flowed downward through the column at a desired flow rate. Samples were collected from the outlet of the column at different time intervals and analyzed for metal ion concentration. The operation of the column was stopped when the outlet metal ion concentration matches its initial concentration. The outlet metal ion concentrations were plotted versus time at different flow rates and bed heights to give the breakthrough curves.

2.7. Elution

One gram of the studied resin was placed in a plastic column (10 cm length and 1.0 cm diameter). A solution of the studied Hg(II) with the desired initial concentration of (1×10^{-2} M) was allowed to flow gradually through the column under the force of gravity at flow rate of 1 mL/min. Five millilitres of the underflow solution was removed every 10 min where the resid-