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Characterization and adsorption behavior of newly synthesized sodium bis(2-ethylhexyl) sulfosuccinate–cerium (IV) phosphate (AOT–CeP) cation exchanger

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ABSTRACT

A new cationic exchange material, sodium bis(2-ethylhexyl) sulfosuccinate (AOT) with cerium (IV) phosphate (AOT–CeP) has been synthesized. The characterization of the ion exchanger was performed by using infra red spectroscopy (IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), thermo gravimetric analysis/differential thermo gravimetric analysis (TGA/DTA/DTG) and elemental analysis. The ion exchange properties like ion exchange capacity, elution and concentration behavior of AOT–CeP were determined by taking the material into a column and elution of H^+ was done by $NaNO_3$. The thermal stability of the ion exchanger was studied by determining ion exchange capacity after heating to different temperatures for one hour. The adsorption studies on AOT–CeP demonstrated that the material is selective for Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+} and Hg^{2+} ions. AOT–CeP was found to be effective for the separation of Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+} and Hg^{2+} ions in the presence of alkali metals/alkaline earth metals. This cationic exchanger was also effective for the removal of Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+} and Hg^{2+} ions in the presence of acid and other transition metal ions. Thus, AOT–CeP can be used for the removal of these ions from the waste water during its treatment.

Keywords: Fibrous ion exchanger; Ce (IV) phosphate; Sodium bis(2-ethylhexyl) sulfosuccinate; Adsorption studies; Environmental studies; Differential pulse polarography

1. Introduction

One of the significant adverse influences of industrial revolution is the fast and indiscriminate destruction of our flora and fauna. Different kinds of health problems are arising due to the heavy metals contamination in the food chain and drinking water. The heavy metals are non-biodegradable and may continue to increase on each successive level in food chain. The anthropogenic activities and industrial growths are responsible for the increased level of heavy metals. Some of the metals in the minute amounts are actually necessary for humans while others are carcinogenic or toxic. These metals/ions may affect central nervous system (e.g. Mn, Hg, Pb, etc.), the kidneys or liver (e.g. Hg, Pb, Cd, Cu, etc.) or skin, bones, or teeth (Ni, Cd, Cu, Cr, etc.) (Fowler and Mahaffey, 1978; Foulkes, 2000; Ercal et al., 2001). Many adsorption and bioadsoprtion techniques (Sari and Tuzen, 2008; Sari et al., 2008; Uluozlu et al., 2008) have been recently studied for the removal of heavy metal ions from waste water for recycling it at lower cost. Anayurt et al. (2009) and Sari and Tuzen (2009) studied the removal of Pb^{2+} and Cd^{2+} from aqueous solution using macrofungus biomass. The ion exchange method has been one of the most promising, simple and widely used chromatographic techniques employed for the purification of water. The ion exchangers remove the charged species including metal ions either by exchanging it from other mobile ions or by adsorbing it (Keary and Mortimer, 1996). The improvement in the properties of ion exchange materials have always been an objective

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of the workers by modifying the natural, inorganic and polymeric ion exchangers to obtain the material with desirable ion exchange characteristics, stability and reproducibility (Lee et al., 2000).

Surfactants are the amphiphilic substance having the hydrophilic charged or polar head group and hydrophobic tail made up of hydrocarbon chain (Schramm et al., 2003). The ability of the charged headgroup of surfactant molecules to bind with oppositely charged ions make the ion exchange material quite effective and selective in nature (Somya et al., 2008, 2009; Varshney et al., 2007a,b). The head groups of surfactant molecule bind metal ions reversibly through complexation, electron attraction and/or charge neutralization. The surfactant molecule increase the wettability of surface by reducing the interfacial tensions between solid and liquid phases and, thereby provide better chance of interaction between the mobile phase and the ion exchange material (Varshney et al., 2006). The synthesis and characterization of the hybrid ion exchange material based on surfactant and inorganic material CeP was under taken to develop an environmentally compatible ion exchanger. In AOT–CeP polymeric resins are not used during the synthesis, so, it does not cause any environmental hazard. The material is hybrid in nature and the constituent substances can be separated chemically and can be reused. Thus, in continuation of our earlier efforts (Iqbal and Rafiquee, 2010; Iqbal et al., 2011; Somya et al., 2008, 2009; Varshney et al., 2007a, 2008), we are reporting herewith the synthesis of the environment friendly, clean and efficient AOT–CeP ion exchange material having better thermal and mechanical stability. The present work also describes the studies on the characterization of AOT–CeP cation exchanger, its ion exchange capacity, elution behavior and selectivity toward the heavy metal ions.

2. Experimental

2.1. *Reagents and chemicals*

Ceric sulphate (CDH, India), cadmium (II) nitrate (CDH, India), magnesium (II) nitrate (CDH, India), strontium (II) nitrate (CDH, India) were used during the experimental work. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT, Merck-Schuchardt, Germany), calcium nitrate (Merck-Schuchardt, Germany), barium nitrate (Merck-Schuchardt, Germany), nickel (II) nitrate (Merck-Schuchardt, Germany), sodium nitrate (Merck-Schuchardt, Germany) were used as obtained from supplier. Phosphoric acid, copper (II) nitrate, lead (II) nitrate were obtained from (Qualigens, India) and mercuric (II) nitrate, zinc (II) nitrate were obtained from (Thomas Baker, UK). Doubly distilled demineralized water with specific conductance, $1–2 \times 10^{-6}\,\Omega^{-1}\,\text{cm}^{-1}$was used throughout the experimental work.

2.2. *Instruments used*

X-ray diffraction studies were performed on a Philips Analytical X-ray B.V. diffractometer type PW 170 B.V. (The Netherlands) and IR studies were carried out on Shimadzu 8201 PC spectrophotometer (Japan). The elemental analysis was performed by Heraeus Carlo Erba-1108 analyzer (Italy). Elico CL-362 Pulse Polarograph (India) was used to record differential pulse polarograms and Hitachi-S520 (Japan) was used to take SEM photograph. The TGA/DTA/DTG curves were obtained from Perkin Elmer Pyris Diamond (USA).

2.3. *Preparation of the reagent solutions*

The stock solutions of 0.1 M Sodium bis(2-ethylhexyl) sulfosuccinate (AOT), 6.0 M solution of phosphoric acid, 0.1 M sodium hydroxide, 1.0 M sodium nitrate, 0.01 M cadmium nitrate, 0.01 M lead nitrate, 0.01 M zinc nitrate, 0.01 M copper nitrate, 0.1 M sodium nitrate, 0.1 M magnesium nitrate, 0.1 M potassium nitrate, 0.1 M calcium nitrate were prepared in the doubly distilled water. Solution of cerium (IV) sulphate was prepared in 0.5 M H_2SO_4.

2.4. *Synthesis of the ion exchange material*

Various samples of AOT–CeP (sodium bis(2-ethylhexyl) sulfosuccinate–cerium (IV) phosphate) were prepared by adding one volume of 0.05 M cerium (IV) phosphate solution to two volumes of a (1:1) mixture of 6.0 M H_3PO_4 and sodium bis(2-ethylhexyl) sulfosuccinate solutions drop-wise with the constant stirring by using a magnetic stirrer at room temperature. The resulting slurry, was stirred for 3.5 h at room temperature, filtered and then washed with demineralized water till pH ~4 was achieved. The samples were then left to dry at room temperature. The dried material was having the sheet-like structure. It was then crushed into small pieces. The synthesized material was kept in 1.0 M HNO_3 for 24 h to charge it into the H^+ form. After keeping in HNO_3, AOT–CeP was filtered, washed with double distilled water several times to remove the residual H^+ ions completely. The material in H^+-form was left to dry at 45 °C for a day and then sieved to obtain particles of size 50–70 mesh. Then the ion exchange capacity of the various synthesized samples were determined by column process and it was found that the sample-3 possessed the highest ion exchange capacity and, therefore, it was selected for further studies.

2.5. *Characterization of AOT–CeP*

The ion exchange capacity of AOT–CeP and the optimum concentration and volume of $NaNO_3$ needed for complete elution of H^+ ions from AOT–CeP were determined by the earlier used method (Iqbal and Rafiquee, 2010; Iqbal et al., 2011). The thermal stability of AOT–CeP was determined by heating several 1.0 g sample of the material at temperatures 100 °C, 150 °C, 200 °C and 300 °C in a muffle furnace for one hour. After cooling to room temperature, their ion exchange capacities were determined.

2.6. *Adsorption studies*

The adsorption behavior of AOT–CeP was determined by taking its 200 mg sample in a conical flask containing 20 mL of metal nitrate solutions. The mixture was thermostated at room temperature (25 ± 0.5 °C) for 24 h. The flask was shaken intermittently to achieve equilibrium. The concentration of adsorbed Hg^{2+}, Ni^{2+}, Ba^{2+}, Mg^{2+}, Ca^{2+} and Sr^{2+} ions were determined by titration with standardized disodium salt of EDTA solution (Reiliy et al., 1959). The concentrations of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} ions were calculated by measuring the diffusion current (Mendham et al., 2000) and Fe^{2+} ion concentration was determine by Spectrophotometric method. Iron (II) gave an orange red complex with hydroxyl amine, sodium acetate and