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Dye-Ligand Immobilized IPNs Membrane for Removal Heavy Metal Ions

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Summary: We have developed a novel approach to obtain high metal sorption capacity utilizing a membrane containing chitosan and an immobilized reactive dye (i.e. Reactive Yellow-2). The composite membrane was characterized by SEM, FT-IR, swelling test, and elemental analysis. The membrane has uniform small pores distribution and the pore dimensions are between 5 and 10 μm, and the HEMA:chitosan ratio was 50:1. The reactive dye immobilized composite membrane was used in the removal of heavy metal ions [i.e., Pb(II), Hg(II) and Cd(II)] from aqueous medium containing different amounts of these ions (5-600 mg l^{-1}) and at different pH values (2.0-7.0). The maximum adsorption capacities of heavy metal ions onto the composite membrane under non-competitive conditions were 64.3 mmol m^{-2} for Pb(II), 52.7 mmol m^{-2} for Hg(II), 39.6 mmol m^{-2} for Cd(II) and the affinity order was Pb(II) > Hg(II)>Cd(II).

Keywords: adsorption; heavy metal removal; hydrophilic polymers; membranes; Reactive Yellow-2

Introduction

Pollution of water sources (e.g. rivers, lakes and underground-water) by heavy metal ions is important due to their toxic effects on human physiology and other living systems event at very low concentrations.[1] Recently, chelating polymers have found widespread applications in the enrichment and removal of heavy metals from various wastewater sources.[2,3] Several criteria are important in the design of chelating polymers with substantial stability for the selective removal of heavy metal ions: specific and fast complexation of the metal ions as well as the reusability of the chelating ligand immobilized polymer matrices. The use of chelating ion exchange for wastewater remediation has been gaining attention in the recent past. Chelating ion exchange, in contrast to simple ion exchanges, takes advantages of removing only toxic metal ions whiles the harmless ions move on into the environment.[4,5] Some of the best

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chelating ion-exchange materials consist of different polymers and their derivatives because of the variety of functional groups, like –OH, –NH_2 and =NH, with which other chemical moieties, e.g., metal ions, can easily react or be bound. A large number of heavy metal chelating polymers after incorporation of various ligands (e.g., polyethyleneimine, amino acids, iminodiacetate, phosphoric acid, oxime have been prepared and their metal chelating properties investigated.[6-9]

Membrane separation has attracted increasing attention for its potential capability in the field of separation technology, and it has been shown to be an effective technique (minimize mass transfer limitations and diffusion times) in removal of heavy metal ions from aquatic media.[10,11] The porosity, thickness, metal-complexion ligand density, and pore size can dramatically affect the overall performance of the membranes separation. An ideal metal chelating membrane should have (a) porous structures, (b) available metal chelating groups, (c) chemical and physical stability under harsh conditions.

In the present study, we have focused our attention on the development of a microporous composite membrane from poly(hydroxyethylmethacrylate) and chitosan, pHEMA/chitosan, carrying a dye ligand (i.e., Reactive Yellow-2) for removal heavy metal ions from artificial wastewater. The preparation of composite membrane from these polymers is a simple method and the presence of hydroxyl and amino groups on the composite membrane could also offer easy attachment sites for a variety of ligands.[3] This metal chelating polymer membrane system was studied in adsorption/desorption of some selected heavy metal ions (i.e, Pb(II), Cd(II) and Hg(II)) from artificial wastewater.

Experimental

The monomer 2-HEMA and α–α-azobisisobutyronitrile were obtained from Fluka AG (Buchs, Switzerland). Chitosan and Reactive Yellow-2 (dye-ligand) was purchased from Sigma (St Louis, USA). All the chemicals used were reagent grade from Merck AG (Darmstadt, Germany).

The composite membrane synthesis was achieved by mixing a chitosan solution (1.0% chitosan in 4.0 mL of 1.0% acetic acid) with 2-HEMA monomer (2.0 mL) containing 20 mg AIBN. The solution was poured into a round glass mold, sealed and exposed to UV radiation under nitrogen atmosphere for 1.0 h at room temperature.

The dye-ligand was immobilized on the composite membrane under alkaline conditions. Reactive Yellow-2 (300 mg) was dissolved in distilled water (10 mL), and transferred to the medium (90 mL) containing NaOH (4.0 g) in which the membrane disks (15 g) were equilibrated. It was then heated at 80°C for 4 h. After the period, the membrane disks were washed with distilled water, 2.0 M NaCl and 10% methanol. The amount of bound Reactive Yellow-2 on the membrane was estimated by using an elemental analysis instrument (Leco, CHNS-932, USA), by considering the sulphur stoichiometry.

FTIR spectra of the composite membrane, and dye-ligand immobilized membranes were obtained by using a FTIR spectrophotometer (Mattson 1000 FTIR, England). The scanning electron micrographs (SEM) of the membrane were obtained after coating gold using a JEOL (JSM 5600) scanning electron microscope.

The adsorption of Pb(II), Hg(II) and Cd(II) and ions by the dye-ligand immobilized membranes from aqueous solutions was studied in a batch system. After the desired contact periods the membranes were removed from the adsorption medium, and the residual concentrations of the metal ions were measured by using an Atomic Absorption Spectrophotometer (AAS; Shimadzu Model AA-6800). For mercury determinations, MVU-1A was employed. The working current/wavelength values were as follows: 10 mA/283.3 nm for Pb(II), 6 mA/253.6 nm for Hg(II), 8 mA/228.8 nm for Cd(II). Competitive heavy metal adsorption from artificial wastewater solutions containing Pb(II), Hg(II) and Cd(II) ions were investigated as described above.

Results and Discussion

Reactive Yellow-2 is an aromatic polysulphonated triazidine dye, and it contains three acidic sulfonate groups and three basic secondary amino groups. The hydroxyl and amino groups of the composite membrane can react with the chloride of the triazine ring of the dye-ligand, thus giving rise to covalent bonds. The immobilized dye on the membrane was found to be 87 μmol g^{-1} from the sulphur stoichiometry. The major physical and morphological properties of composite membranes were as follows: the water content 76±2%, the thickness in the wet state 0.06 cm; the density in the dry state 1.26 g cm^{-3}, the surface area of the 1.0 mL wet membrane

38.5 cm^2.

The microstructure of the membrane surface was investigated by scanning electron microscopy The membrane displayed a smooth, and porous structure (Figure 1). The FT-IR spectra of dye-ligand-immobilized membrane had an absorption band different from that of plain at 1575 cm^{-1}. It is the characteristic of aromatic rings stretching vibration band (C....C) arising from immobilized dye-ligand molecules.

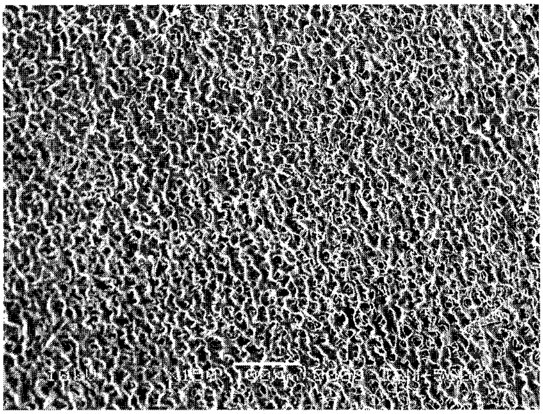

Fig. 1. The surface SEM micrograph of the composite membranes.

Metal ion adsorption onto metal chelating polymer is pH dependent.[8] Reed and Matsumoto[9] reported that hydrolysis of metal ions such as Cu(II), Cd(II) and Pb(II) becomes significant at approximately pH 7.5-8.5. The effect of pH on the adsorption capacity of the dye-ligand immobilised membrane is presented Figure 2. The adsorption of Pb(II), Cd(II) and Hg(II) ions by the adsorbent first increased with pH, and then almost reached a plateau value at about 5.5.

The heavy metal adsorption capacities of Reactive Yellow-2 immobilized membranes are presented in Figure 3 as a function of the initial concentration of Pb(II), Cd(II), and Hg(II) ions within the adsorption medium. As expected, the amount of metals adsorbed per unit area of the membranes increased with the increase in the initial concentration of metal ions. The maximum adsorption capacities of the dye-ligand immobilized membranes were 64.3 ± 0.5 mmol m^{-2} for Pb(II), 52.7 ± 0.4 mmol m^{-2} for Hg(II) and 39.6 ± 0.3 mmol m^{-2} for Cd(II). The dye-ligand immobilized membranes showed the following metal ion affinity order, Pb(II)>Hg(II)>Cd(II). The heavy metal ion adsorption on the plain membranes were relatively low; 18.73 ± 0.4 mg/g for Pb(II), 18.82 ± 0.4 mg/g for Hg(II) and 6.31 ± 0.2 mg/g for Cd(II).

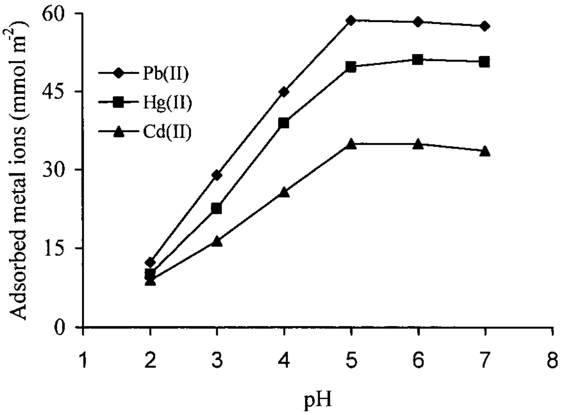

Fig. 2. Effect of pH on the adsorption capacity of the dye-ligand immobilized composite membranes for Cd(II), Pb(II) and Hg(II) ions. Adsorption conditions: initial concentration of metal ions: 200 mg L^{-1}; volume of the adsorption medium: 25 mL; temperature: 20 °C; contact time: 60 min.

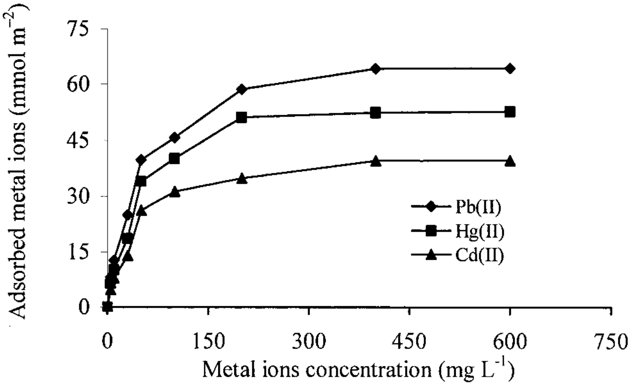

Fig. 3. Adsorption capacities of the-dye-ligand immobilized composite membranes for Pb(II), Cd(II), and Hg(II) ions. Adsorption conditions: volume of the adsorption medium: 25 mL; pH 5.5; temperature: 20°C; contact time: 60 min.

Conclusions

At least 20 metals are classified as toxic and half of these, including cadmium, arsenic, mercury, chromium, copper, lead, nickel, selenium, silver and zinc are emitted into the environment in quantities that pose risk to human health. Among them, perhaps the most toxic ones are lead, mercury and cadmium. The necessity to decrease the amount of heavy metals in wastewater streams, and subsequent possible reuse of these metal ions, has led to an increasing interest in selective adsorbents.[12-14] This study investigates the removal of heavy metal ions [i.e., Pb(II), Hg(II) and Cd(II)] on the novel Reactive Yellow-2 immobilized IPNs membranes, including pH, temperature and the effects of the initial metal ions concentrations. When compared with the adsorption capacity values obtained by various materials in the literature, Reactive Yellow-2 immobilized membranes showed great promise in the removal of heavy metal ions from aqueous media.[5-7] The immobilization of the dye-ligand membranes increased the adsorption capacity values 3.4 fold for Pb(II), 2.8 fold for Hg(II) and 6.3 fold for Cd(II). More than 95% of the adsorbed metals were desorbed with HNO_3 solution and the adsorption capacities of the membranes did not significantly changed during the five repeated adsorption-desorption cycles. The adsorption medium temperature had no significant effect on the sorbent adsorption capacity over the tested temperature range of 15-45 °C. The overall performance of the dye-ligand immobilized membranes indicated the feasibility of continuous use of these novel membranes in adsorption columns for removal of heavy metal ions from polluted environmental waters.

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