

Full Length Research Paper

Application of grafted membranes for sorption of Cd^{2+} , Fe^{2+} and Zn^{2+} ions in aqueous solution

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Sorption of Cd^{2+} , Fe^{2+} and Zn^{2+} by blend membrane of sodium alginate (Na-Alg) and poly (acrylamide) grafted konkoli gum (KG-g-PAAM) in aqueous solution was studied. Membrane sorption capacities for Cd^{2+} , Fe^{2+} and Zn^{2+} were found to be 97.85, 80.65 and 64.46% respectively. The sorption behavior with respect to contact time, initial pH, temperature, ionic strength and initial metal ion concentration were investigated in order to determine the optimum sorption conditions. Results showed that metal ion uptake by the membrane decreased with increase in ionic strength and after a temperature of 40°C while increase in initial metal ion concentration led to increase in metal ion uptake. Maximum sorption was found to occur at pH of 6.0, 3.0 and 5.0 for Cd^{2+} , Fe^{2+} and Zn^{2+} respectively. The ability of the grafted membrane to remove some heavy metals from aqueous solution is encouraging and may be used in bioremediation of wastewaters.

Key words: Konkoli gum, blending, sodium alginate, membrane, sorption, metal ions

INTRODUCTION

The removal of heavy metals from aqueous streams represents a significant industrial waste problem (Kim and Yi, 2000). Although various inorganic salts and trace elements are required to maintain normal good health, they can be toxic above threshold levels. Toxicity generally results when an excessive concentration is presented to an organism over a prolonged period of time and when the metal is present in an unusual biochemical form. Toxicity may also result when the metal is presented to the organism by way of unusual route (Tolba, 1980). Heavy metals pollution may be traceable to industrial activities such as smelting of ores or refining of metals, both of which metals may be introduced into the air, water and soil.

In recent years, widespread concern over the cumulative toxicity and environmental impact of heavy metals such as Cd^{2+} , Fe^{2+} and Zn^{2+} has led to extensive research into developing alternative technologies for the removal of these potential damaging substances from effluents and industrial wastewaters. There are several options currently available for the removal of heavy metals from industrial wastewaters. The main methods

are precipitation, ion exchange and electrolytic methods. Others are membrane processes, osmosis and dialysis, which are occasionally utilized, in very specialized applications (Aldehold et al., 1996). It has also been reported (Barminas et al., 2005; Aldehold et al., 1996) that the precipitation method is not suitable where final clarification of wastewater is required, the ion exchange method is highly capital intensive, the electrolytic method requires high energy while the membrane method is faced with problems of limited flow coupled with instability in salt and acid conditions. These shortcomings therefore necessitate the search for either a new technology or improvements on the present ones.

'Konkoli' seed gum (KG) from *Mesopsis eminii* plant is widely used as thickeners in soup and other traditional baked food products in Nigerian, primarily because of its high viscosity, binding and swelling propensity (Barminas and Eromosele, 2002). In Nigeria this plant grows wild in the east, south and middle belt of the country. It shoots greenish flowers around April and May and bears fruits, which get matured around August and September as the fruits become publish black containing a very hard seed. The seeds are normally removed from the dried fruits and used in the preparation of soups and other traditional baked foods (Barminas et al., 2005; Barminas and Eromosele, 2002). Presently, only about 10% of KG

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is utilized and the rest left to rot away in the wild (Barminas and Eromosele, 2002). This situation calls for additional product outlets to be identified to create higher value products from KG.

In our last study (Barminas et al., 2005), we reported the successful grafting of acrylamide onto KG and blending of the KG-g-PAAM with sodium alginate to develop sodium alginate and KG-g-PAAM blend membrane. Preliminary investigation on the swelling properties of the grafted membrane in aqueous medium was also reported. In our continuous effort aimed at investigating the properties of this membrane, this article studied the application of this blend membrane for the removal of Cd^{2+} , Fe^{2+} and Zn^{2+} from aqueous solution under different experimental conditions.

MATERIALS AND METHODS

Materials

Sodium alginate, ceric ammonium nitrate, methanol, acrylamide, glutaraldehyde, hydrochloric acid, sulphuric acid, sodium hydroxide, sodium chloride and acetone were obtained from British Drug House (BDH). The konkoli gum (KG) which is the main raw material was obtained locally; all chemicals used in this work were of analar grades.

Preparation of konkoli gum (KG) and sodium alginate

Gum samples were obtained from Konkoli (*M. eminii*) seed by decoating the dried seeds and crushed into powder. This was then filtered through 100 μm sieve screen to obtain fine powder, which was packaged in a polyethylene bag and stored at room temperature (25°C). No examination and further purification of sodium alginate was carried out.

Synthesis of graft copolymer

Konkoli Gum-g-polyacrylamide (KG-g-PAAM) was synthesized by reacting konkoli gum with acrylamide at 60°C using ceric ammonium nitrate (CAN) as an initiator (Toti and Aminabhavi, 2002). In brief, a 2% aqueous konkoli gum solution was prepared and stirred well for 1 h with 0.105 mol of acrylamide at 60°C. The initiator solution containing 2.5×10^{-3} mol. of CAN was added to the mixture and stirred well by using magnetic stirrer (Griffin minimal model SMT-180-010K) for another 5 h. The mass obtained at the end of this period was precipitated in excess acetone. This was then filtered, washed with a 7:3 ratio of water/methanol mixture to remove the homopolymer formed. The solid mass was then dried in an electrically controlled oven (pickstone oven model HP.30) at 40°C and weighed using mettler balance AB 204.

Membrane preparation

A 4% mass of stock solution of sodium alginate (Na-Alg) was prepared in water (Toti et al., 2002). The stock solution with a volume of 100 ml was taken in a beaker and mixed with 0.00175 mol of glutaraldehyde (GA). This mixture was stirred for 2 h at 25°C and then poured uniformly on a plastic tray. The membrane was dried at room temperature (25°C) for 12 h. The cast membranes were crosslinked by immersing in a 1% HCl solution taken in an equimolar mixture of methanol and water for 24 h, then washed tho-

roughly in water and dried (Barminas et al., 2005).

To prepare the blend membranes, a 4% mass of the stock solutions of Na-Alg and KG-g-PAAM were mixed in the ratios of 80:20 at 60°C for 4 h and the solution cooled to room temperature. To this, 0.00175 mol of GA (0.1 ml of 25wt % in water) was added and the mixture stirred for another 2 h. This mixture was poured onto a plastic tray and then cross-linked (Toti et al., 2002).

Determination of metal ion in solutions

The metal ions chosen for this study were Cd^{2+} , Fe^{2+} and Zn^{2+} . A concentration of 200 ppm of each of the metal ion was prepared with distilled water. From the above concentration, 50 ml of solution of metal ion was taken into a conical flask; 0.2 g of dried membrane was added and then shaken vigorously for 2 h by using flask shaker (Stuart Scientific, SF1). The mixture was then filtered and the residual metal ion concentrations determined using Atomic Absorption Spectrophotometer (AAS) (Pyeunicam Model SP9) (Barminas et al., 2005).

Membrane sorption capacity

For this equilibrium studies, 0.2 mg of the membrane (Sorbent) was shaken with 50 ml of 200ppm of metal ion solution at room temperature (25°C) for 24 h (Chamarthy et al., 2001). The synthetic waste water sample was filtered and analyzed for residual metal ion concentration using AAS.

Effect of pH on sorption capacity

The sorption characteristic of the membranes at different pH values (1 – 6) was investigated at 25°C (Chamarthy et al., 2001). A 2.0 M hydrochloric acid and 2.0 M, sodium hydroxide were used to adjust the solutions to the required pH as the case may be. The residual metal ion concentrations were measured by using AAS (Chamarthy et al., 2001).

Effect of ionic strength on sorption capacity

Useful information regarding salts effect was obtained by measuring sorption capacity of the membrane in various concentrations of NaCl solutions. Different concentrations (0.00 – 0.34M) of NaCl were added to adjust the ionic strength of metal ion solutions and the equilibrium concentration of the residual metal ion determined.

Effect of temperature on sorption capacity

The effect of temperature on the absorption capacity of the membrane was investigated. A 0.2 g of the dried membrane was shaken with 50 ml of the metal ion solution at 25°C. The synthetic wastewater was filtered and analyzed for residual metal ion concentration. This process was repeated at different temperature ranging from 30 to 90°C.

Sorption kinetics

To determine the kinetics of sorption, eight different sets of samples consisting of 0.2 g of the dried membrane and 50 ml of metal ion solution were prepared. As the samples were undergoing agitation (with flash shaker), they were removed one after the other at a predetermined time interval ranging from 3 min – 24 h. The solutions were filtered and analysed for residual metal ion at 25°C.

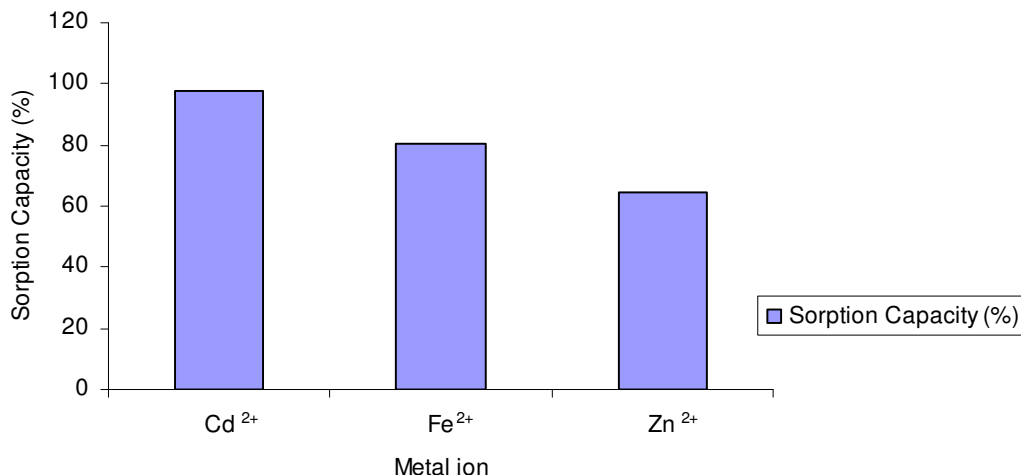


Figure 1. Sorption capacity for Cd²⁺, Fe²⁺ and Zn²⁺ by Na-Alg and KG-g-P AAM blend membrane: Temperature = 30°C, Time = 2h, initial metal ion concentration = 200 ppm.

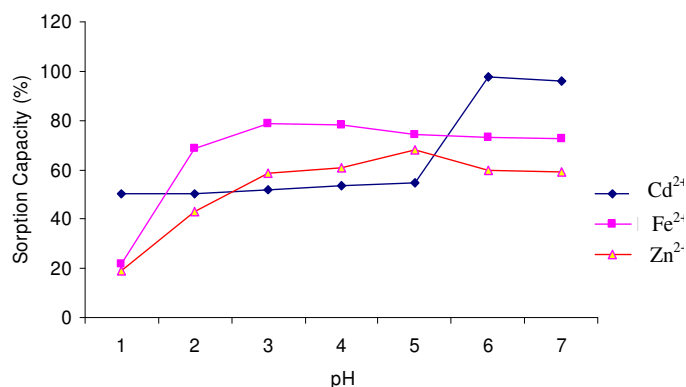


Figure 2. Effect of pH on sorption capacity.

Effect of initial metal ion concentration on sorption capacity

To investigate the effect of initial metal ion concentration on sorption capacity, different samples consisting of 50 ml each of different metal ion concentrations ranging from 5 – 100 ppm but each containing 0.2 g of the dried membrane were prepared and shaken until equilibrium was obtained at 25°C. The synthetic waste water was filtered and analysed for residual metal ion concentration.

RESULTS AND DISCUSSIONS

Membrane sorption capacity

Figure 1 indicates the equilibrium sorption for Cd²⁺, Fe²⁺ and Zn²⁺ by this grafted membrane. It is observed that this membrane has the ability to take up significant quantities of Cd²⁺, Fe²⁺ and Zn²⁺. The values 97.85, 80.65 and 64.46% for Cd²⁺, Fe²⁺ and Zn²⁺ respectively were obtained as sorption capacity from the present study and are comparable with those reported by similar workers (Lee and Lin, 2000; Chamarthi et al., 2001).

The differences observed in the sorption capacity for the different metal ions can be explained in terms of differences in hydration free energy, the ability of the metal ion to form covalent bond with ligands, the metal polymeric cations within the membrane structure and the nature of the surface sites available (Cooper et al., 2002). Hydrated size of the different ions could also affect the sorption.

Effect of pH

The pH of the sorption media reflects the nature of the physicochemical interaction of both the ions in solution and the nature of the sorption site (Mcox and Pichugin, 2002). The effect of the solution pH on the sorption of metal ions on Na-Alg/KG-g-PAAm membrane is represented in Figure 2. In the range of pH 1.0 – 6.0 more metal ions were absorbed at higher pH values and there was low absorption at low pH value of 1.0 for all the metal ions studied and 1.0-3.0 in the case of Cd²⁺. From this figure, Cd²⁺, Fe²⁺ and Zn²⁺ have optima pH values of 6.0, 3.0 and 5.0 respectively. These values therefore represent the respective pH under which this membrane may be used for the sorption of these metal ions from aqueous solution.

pH influences the equilibrium of metal ion uptake in aqueous solution by affecting the speciation of the metal ion(s) in solution, the concentration of the competing hydrogen ions as well as the chemistry of the active binding sites on the sorbent (Yen-peng and Sung, 2000). Increasing pH leads to precipitation as insoluble hydroxides or hydrated oxides thereby lowering metal ion availability for sorption. On the other hand, a decrease in pH results in an increase in the hydrogen ion concentration and hence possible competition with the metal ions for the available binding site (Toti et al., 2002).

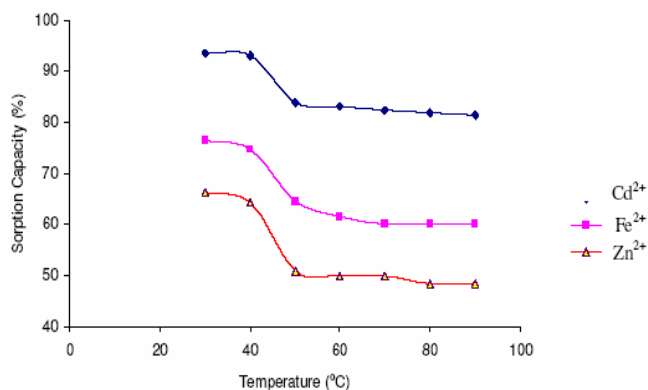


Figure 3. Effect of temperature on sorption capacity.

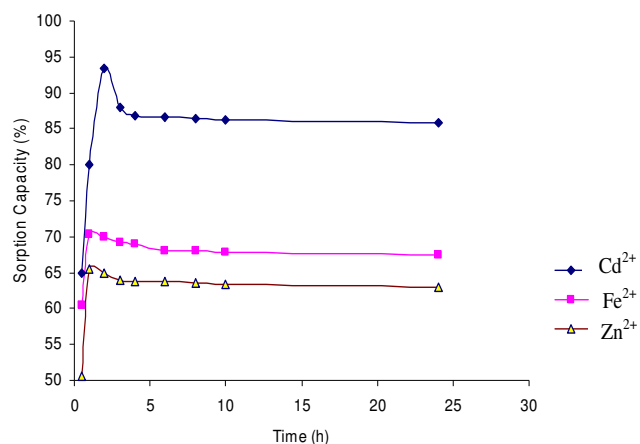


Figure 4. Effect of Time on sorption capacity at 30°C.

Effect of temperature

The effect of temperature on the sorption capacity for Cd²⁺, Fe²⁺ and Zn²⁺ by the grafted membrane is shown in Figure 3. The sorption of metal ions decreased with increase in temperature for all the metal ions studied. Temperature of 40°C seems to represent the optima temperature at which the grafted membrane could be used for the removal of these metal ions in aqueous solution. This trend of result may be explained by the following factors: (a) the sorption process may be physical adsorption. Physical adsorption are normally exothermic, thus the extent of adsorption generally increases with decreasing temperature (Ozer et al., 2002). (b) Inherent molecular structure of the polymer structure (KG) which influenced the properties of the membrane prepared from it (Huang et al., 2002). (c) Contraction of the membrane molecules with increase in temperature to give a more compacted form of membrane which causes the pores to be narrower and some sorption sites to be hidden or inaccessible to the metal ions (Mcox and Pichugin, 2002) and (d) dissolution of low molecular weight polymers and

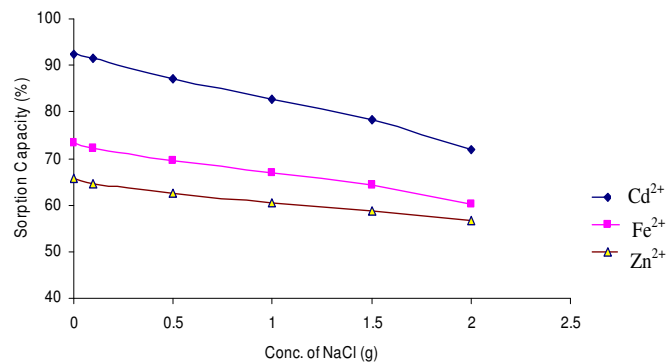


Figure 5. Effect of ionic strength on sorption capacity at 30°C.

and noncrosslinked polymers with increasing temperature (Horike et al., 2002).

Effect of Time

Figure 4 presents the kinetics of sorption for Cd²⁺, Fe²⁺ and Zn²⁺ by the membrane. Complete saturation was reached after 1h for both Fe²⁺ and Zn²⁺ while 2h was recorded for Cd²⁺. The relative rapid uptake for Fe²⁺ and Zn²⁺ by the prepared membrane could be explained by the porous structure of the membrane, which accelerated metal ion diffusion to the functional groups (Godjevargova et al., 2001). This result is a positive development especially in terms of economy. The observed trend after maximum absorption by the membrane may be due to inadequate drying of membrane after cross linking or partial dissolution of the membrane due to long period of incubation (Barminas et al., 2005).

Effect of ionic strength

Industrial wastewater or natural water often contains Na⁺, Mg²⁺ Ca²⁺ etc; hence the influence of ionic strength on the sorption capacity of this membrane Cd²⁺, Fe²⁺ and Zn²⁺ was investigated. Figure 5 indicates the effect of ionic strength on the membrane performance. The result shows that sorption capacity for the metal ions decreased with increase in ionic strength of the salt solutions for all the metal ions studied. The decrease in sorption capacity with increase in ionic strength is primarily attributed to the reduction of the difference in ionic osmotic pressure between the membrane and the external solution (Lee and Lin, 2000). The difference in ionic osmotic pressure between the membrane and the external solution decreases as the ionic strength of the external solution increases. Therefore, the sorption of metal ion decreases when the ionic strength in the external solution increases (Lee and Lin, 2000). From this experiment, the coexistence of metal ions in solution caused an interference with the performance of N-Alg and KG-g- PAAm blend membrane. A pretreatment of effluent to remove the interfering

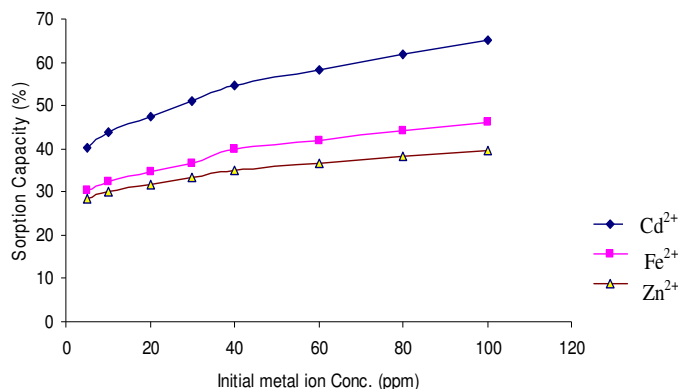


Figure 6. Effect of initial metal ion concentration on sorption capacity at 30°C.

ions seems necessary for effective application of the membrane.

Effect of initial metal ion concentration

The result of metal ions sorption by the membrane as a function of initial metal ion concentration is shown in Figure 6. The sorption of metal ion by the membrane increased with increase in the initial metal ion concentration for the three metal ions studied. This behavior can be explained in terms of increase in flux of the metal ions (Yen-Peng, 2000). The flux of a cation varies in direct proportion with the metal ion concentration and hence there should be an increase in flux with an increase in metal ion concentration.

Conclusion

Sorption of Cd²⁺, Fe²⁺ and Zn²⁺ by blend membrane of Na-Alg and KG-g-PAAm was studied. The maximum sorption capacities of the membrane were 97.85, 80.65 and 64.46% for Cd²⁺, Fe²⁺ and Zn²⁺ respectively. The sorption equilibrium studied also showed that metal ion uptake by the membrane decreased with increasing ionic strength and after a temperature of 40°C while increase in initial metal ion concentration recorded increase in metal ion uptake. This study on the sorption behavior of the blend membrane for Cd²⁺, Fe²⁺ and Zn²⁺ has demonstrated that the membrane is a potential material for the removal of these metal ions from wastewater.

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