Synthesis of Ion-Imprinting Chitosan/PVA Crosslinked Membrane for Selective Removal of Ag(I)

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ABSTRACT: A novel ion-imprinted membranes were synthesized for selective removal and preconcentration for Ag(I) ions from aqueous solutions. The membranes were obtained via crosslinking of chitosan (CS), PVA, and blend chitosan/PVA using glutaraldehyde (GA) as crosslinker. The FTIR spectra were used to confirm the membrane formation. Comparing with the nonimprinted membranes, Ag(I)-imprinted CS and CS/PVA has higher removal capacity and selectivity for Ag^+ ions. An enhancement in the Ag^+ removal capacity by $\sim$ 20% (from 77.8 to 94.4 mg g^{-1}) and $\sim$ 50% (from 83.9 to 125 mg g^{-1}) was found in the Ag(I)-imprinted CS and Ag(I)-imprinted CS/PVA membranes, respectively, when compared with the nonimprinted membranes. Removal equilibra was achieved in about 40 min for the non- and ion-imprinted CS/PVA. The pH and temperature significantly affected the removal capacity of ion-imprinted membrane. The relative selectivity coefficient values of Ag^+/Cu^{2+} and Ag^+/Ni^{2+} are 9 and 10.7 for ion-imprinted CS membrane and 11.1 and 15 for ion-imprinted CS/PVA membrane when compared with nonimprinted membranes. The imprinted membranes can be easily regenerated by $0.01M$ EDTA and therefore can be reused at least five times with only 15% loss of removal capacity. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2608–2615, 2009

Key words: Ion-imprinting membrane; chitosan/PVA; silver removal; selectivity; desorption

INTRODUCTION

The presence of soluble silver in wastewater is a problem shared by many industrial processes. The two major sources are the photographic and electroplating industries, but mining, silver recovery plants, and the medical technology industry are also contributors. Local regulations limit the amount of silver that may be present in wastewater and classifies silver as a hazardous substance.[1] Noteworthy to maintain that silver is a valuable metal, several recovery methods, primarily electrodeposition and metallic replacement, have had a history of use before implementation of wastewater regulations. Precipitation and ion-exchange are two additional methods currently used to remove silver from wastewater. All these methods have associated problems.[2,3] Electrodeposition is expensive and does not easily remove silver at low concentrations. Metallic replacement is cheaper, but it only removes $\sim$ 95% of the silver from solution, and the treated wastewater can still be above the legal limit. Furthermore, the product of both these techniques is a sludge that is expensive to refine. Precipitation works well to reduce silver concentration to low levels but requires the use of additional chemicals to perform the task, and the resulting precipitates are also impure sludges that require further treatment. The ion-exchange method is effective at any silver ion concentration but is expensive to install and maintain.

One of the new developments in recent years to accumulate precious metals or remove toxic metals from dilute solutions is the use of adsorbents of biological origin, including alginate, dead and living biomass, chitosan, lignin, carrageenan, and so on.[4–6] Chitosan (CS) is produced from N-deacetylation of chitin, a major component of crustacean shells and fungal biomass, and is readily available from seafood processing wastes. The presence of amine groups make chitosan unique among biopolymers, for example, its cationic behavior in acidic solutions and its affinity for heavy metal ions. Therefore, it has increasingly been studied for the adsorption of various metal ions from dilute solution or wastewater.

CS appears to be more useful when compared with chitin, because it has both amine and hydroxyl groups that can serve as chelating sites and can be chemically modified.[7] CS has been reported for the high potentials of adsorption metal ions,[8–10] noble ions,[11–13] dyes,[14,15] proteins,[16] humic acid,[17,18] etc.

CS membranes have been extensively prepared and used for different purposes.[6,19] The use of CS

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membranes as an adsorbent also provides the potential for regeneration after adsorption and reuse of the membranes in subsequent adsorption operations. However, these membranes have the disadvantage of poor chemical resistance and mechanical strength. This disadvantage significantly reduces the recycle life of the chitosan beads.

On the other hand, poly(vinyl alcohol) (PVA) is well known as a membrane-forming material with high hydrophilicity, good chemical resistance, and mechanical property.

Glutaraldehyde (GA) is a common crosslinker used in polypeptide and protein crosslinking because of the high activity of the aldehyde groups, which readily form Schiff's base with amino groups of proteins. GA is also used as a crosslinking agent for PVA[20] and CS.[21]

CS/PVA combination in the presence of GA has shown promising attributes for practical application, such as high mechanical strength, high swelling and shrinking ratio, high pH sensitivity, and biodegradability.[20] However, the adsorption capacity for heavy metal ions for crosslinked CS was lower when compared with free CS, because of functional groups ($-NH_2$) being crosslinked.

Molecularly imprinted polymers represent a new class of materials possessing high selectivity and affinity for the target molecule. Molecular imprinting involves arranging of functional groups around a template molecule, subsequent polymerization results in trapping template molecules in highly crosslinked polymer matrix.[22] Extraction of the imprint molecules from matrix leaves predetermined arrangement of ligands and a tailored-binding pocket. Three steps are involved in ion-imprinting process: (i) complexation of metal ion (template) to polymerizable ligand; (ii) polymerization of this complex; (iii) removal of metal ion after copolymerization. After removal of the target ion, the prepared polymer is put into a solution containing metal ions from which the imprinted ion should thus be preferentially extracted. An ion-imprinting CS adsorbent was reported to show good chemical and physical stability as well as high selectivity toward metal ions.[23–25]

Nishide et al.[26,27] have utilized for the first time ion template effect in the synthesis of chelating polymers way back in 1976. They crosslinked a linear chain polymer, poly(4-vinylpyridine) with a bifunctional reagent (dibromoalkane) in the presence of metal ions. Takagi and his colleagues[28,29] introduced the concept of surface imprinting polymers, wherein ion imprinted polymer (IIP) particles were prepared by emulsion polymerization involving a functional host monomer, an emulsion stabilizer, a crosslinking agent, and a metal cation template, which was selectively complexed by the metal binding groups at the aqueous–organic interface to form recognition sites.

Subsequently, the template cation was removed by acid stripping. An alternative approach was based on the copolymerization of isolated or nonisolated monomer/ion complexes with the crosslinking agents. Using this approach, IIP's were developed with different inorganic ions as imprint ions.[30–33]

In this study, an ion-imprinting membrane is synthesized and used for selective removal and preconcentration of Ag(I) ions from aqueous solutions. CS and PVA were selected as the metal complexing by template polymerization. GA was used as crosslinker for polymerization and formation of Ag-imprinting CS/PVA membrane. The synthesized membrane was applied for the selective removal of Ag(I) from aqueous media. The effect of various experimental conditions, for example, pH, removal time, temperature, and type of eluent on the extraction efficiency were investigated and optimized. The characterizations of the prepared membrane were also studied to elucidate its practical use as an ion-selective membrane.

EXPERIMENTAL

Materials

Chitosan (M_w 100,000–300,000) was supplied by Acros Organics. Poly(vinyl alcohol) (assay, 87% and M_w 100,000) was purchased from Fisher Scientific. Glutaraldehyde (GA, 50 wt % content in distilled water) was supplied by Fisher Scientific. All other reagents used were of analytical-reagent grade.

Apparatus

NANOpure diamond, Barnstead, USA with 18.2 MΩ cm was used for water supply. pH/conductivity meter model XL 20, Fisher Scientific was used for pH adjustment. The presence of functional groups of the synthesized membrane was observed by the use of Fourier transform infrared spectroscopy (Nicolet 8700, ThermoScientific) with an Attenuated Total Reflection (ATR) unit (ZnSe crystal, 45°). The membrane samples were completely rinsed with deionized water and then dried in vacuum oven before analysis. IR spectra of the membranes were recorded in transmittance mode over a wave number range of 4000 to 650 cm^{-1} at 25°C. Determination of heavy metals was performed with Prism, high Dispersion ICP, TELEDYNE instruments. The equipment used for carrying out the mechanical properties was Micro-Strain Analyzer, TA instruments RSA III. Maximum force applied was 500 gm with Force and Strain resolutions, 0.0001N and 1 nm, respectively. Cross-sectional area of the sample of known width and thickness was calculated. The film was then placed between the grips of the testing machine. The

grip length was 5 cm and the speed of testing was set at the rate of 2 mm/min.

Preparation of ion-imprinting membranes

A 3.14 g of $AgNO_3$ was dissolved in 1 L of dilute acetic acid solution (2% (w/w)) to give Ag(I) of 2 mg cm^{-3}. CS solution (4.0%, w/w) was prepared by dissolving 4.26 g of CS into 100 g of the dilute acetic acid and stirred for 2–3 h until complete dissolution. PVA solution (12.5% w/w) was prepared by dissolving 14.36 g of PVA in 100 g of dilute acetic acid stirred for 5 h. A mixture of 17.2 g of CS solution (4.0%, w/w) and 2.8 g of PVA solution (12.5%, w/w) was heated to 70°C and stirred for 6 h, followed by another 12 h stirring at room temperature forming a homogenous solution with 2/1 (w/w) CS/PVA. A 0.33 g of GA was added to the solution with stirring and just before gel formation, membrane was prepared by casting solution onto Petri-dish. An individual ion-imprinted CS and PVA membranes were also obtained. Allow the water in the casting membranes to evaporate at room temperature for 2–3 days. After that, membranes were immersed in 1M NaOH for 1 day, followed by repeatability washing with de-ionized water to eliminate any unreacted GA.

Finally, the Ag(I) imprinted in the membrane was removed by treating with EDTA and HNO_3 in a shaker bath 48 h. The silver released was determined by ICP. Regeneration was carried out by washing the membrane with 0.5M NaOH for 2 h in shaking bath, followed by washing several times with de-ionized water.

For a better judgment on the efficiency of the synthesized membrane, CS, PVA, and CS/PVA control membranes were also prepared by the same abovementioned method but without ion-imprinting Ag(I). The resulting control membranes were also subjected to the same treatment processes as in case of ion-imprinting membranes to compare their performance for the removal and selective recovery of silver from dilute aqueous solution. When not in use, the resulting membranes were kept in deionized water at 25°C for further experiments.

Ag(I) removal from aqueous solution

Removal of Ag(I) from aqueous solutions was investigated in a batch experiments. All the membranes were cutted into 1 cm$\times$ 1 cm pieces. In all the experiments, membrane concentration was kept constant at 50 mg/50 mL with an initial Ag (I) concentration of 250 mg/L in the flasks stirred magnetically at 600 rpm. Effects of the contact time, pH of the medium, and temperature of the medium on the removal were studied. The suspensions were brought to the desired pH by adding 0.1M NaOH and 0.1M HNO_3. The concentration of the metal ions in the aqueous phases after desired treatment periods were measured by using ICP. The experiments were performed in replicates of three and the samples were analyzed in replicates of three as well. Removal values (mg/g) were calculated as the difference in Ag(I) ion concentration of the pre- and postremoval solutions divided by the weight of dry membranes according to:

$$\text{removal capacity } Q = \frac{(C_o - C_e)V}{W}$$

where C_o is the initial Ag(I) concentration (ppm), C_e is the final or equilibrium Ag(I) concentration (ppm), V is the volume of the Ag(I) solution (mL), and W is the weight of membranes (g).

Selectivity experiments

To measure Ag(I) specifity of the synthesized ion-imprinted membranes, competitive removal of Cu(II), Ni(II) from their mixture was also investigated in a batch system. A solution (50 mL) containing 250 mg/L from each metal ions was treated when compared with Ag(I) in batch process by the same procedure as maintained before. After adsorption equilibrium, the concentration of the metal ions in remaining solution was measured by ICP as well.

Selectivity coefficients of Cu(II) and Ni(II) with respect to Ag(I) can be obtained from equilibrium binding data according to:

$$k = \frac{k_d(\text{Ag}^+)}{k_d(\text{X}m^+)}$$

where k is the selectivity coefficient and Xm^+ represents Cu(II) and Ni(II) ions. k_d represents the distribution coefficient and can be determined as follow:

$$k_d = \left[\frac{C_o - C_e}{C_e}\right]\frac{V}{W}$$

A comparison of the k values of the different prepared membranes with those metal ions allows an estimation of the effect of imprinting on selectivity. A relative selectivity coefficient k' can be defined as:

$$k' = \frac{k_{\text{imprinted}}}{k_{\text{control}}}$$

Desorption and repeated use

Desorption of Ag^+ ions were studied with 0.01M EDTA solution. The membranes were placed in this
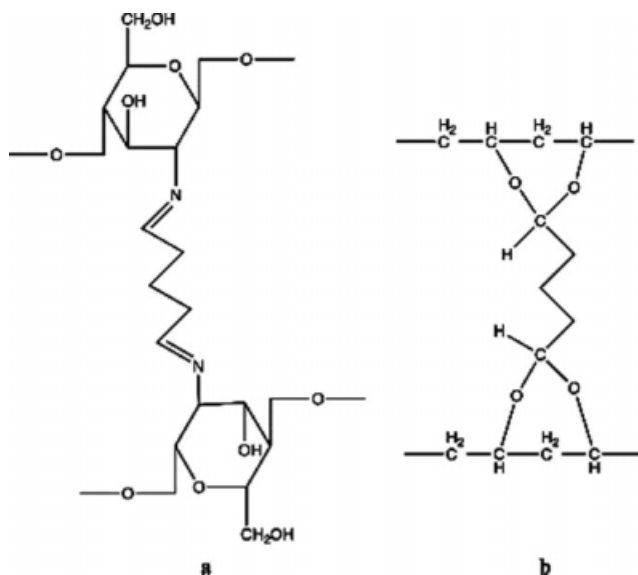
Figure 1 Schematic representation of (a) chitosan and (b) PVA crosslinked with glutaraldehyde.

desorption medium and stirred continuously (at a stirring rate of 600 rpm) for 2 h at 60°C. The final Ag^+ concentration in the aqueous phase was determined by ICP. The desorption ratio was calculated from the amount of Ag^+ ions adsorbed on the membrane and the final Ag^+ ions concentration in the desorption medium. To test the reusability of the membranes, Ag^+ ions sorption–desorption procedure was repeated five times using the same membrane. To regenerate after desorption, the membranes were washed with $0.5M$ NaOH for 2 h in shaking bath, followed by washing several times with deionized water.

RESULTS AND DISCUSSION

Membrane synthesis

GA is a well-known crosslinking agent in interfacial polymerization, where it reacts at the liquid interface with functional groups, such as amino and hydroxyl groups. In this study, GA was used for further crosslinking of the ionically crosslinked blend of the CS and PVA as well as individual crosslinking of both. After the membranes were prepared, the formation of crosslinking was confirmed by immersing in water to verify their insoluble nature. The resulting crosslinked membranes possessed low water content and thus high mechanical strength. Figure 1 shows a schematic representation of CS and PVA crosslinked by GA. As amino groups are much more reactive with aldehyde than hydroxyl groups, crosslinker GA should mainly react with amino groups of CS to form Schiff's base crosslinkage.[34] This is supported by much shorter gelation times (few seconds) for both individual and blend CS.

Membrane characterization

FTIR spectroscopy

FTIR spectra are a useful tool to identify the presence of certain functional groups in a molecule as each specific chemical bond often has a unique energy absorption band.

The spectrum of CS [Fig. 2(a)] shows the characteristic absorption bands at 1650 cm^{-1} (amide I), 1556 cm^{-1} (amide II), and 1402 cm^{-1} (—CH2 bending). The absorption bands at 1140 cm^{-1} (anti-symmetric stretching of the C—O—C bridge), 910 and 1063 cm^{-1} (skeletal vibrations involving the C—O stretching) are characteristics of its saccharide structure.[35] The broad peak at 3349 cm^{-1} is caused by amine N—H symmetrical vibration. Meanwhile, FTIR spectra of pure PVA [Fig. 2(b)] shows the predominant O—H stretching of alcohols appearing at 3333 cm^{-1}. The vibrational peak appearing at 835 cm^{-1} is assigned to C—H rocking mode of PVA and a CH&CH$_2$ asymmetric stretching vibration of PVA also appearing at 2927 cm^{-1}. The peaks pertaining to C=O in acetate (1730 cm^{-1}), C—O bend deformation (1252 cm^{-1}), and C—C stretching (1095 cm^{-1}) of PVA are also found. The broader peak at 3350 cm^{-1} of the CS/PVA as shown in Figure 2(c), indicating most of the crosslinkages were formed between the amino groups of CS but not hydroxyl groups of PVA. A peak can be found at $\sim$ 1643 cm^{-1} corresponding to the formation of imine bond (C=N), that is, Schiff's base structure by the reaction of amine groups of CS and aldehyde groups of GA.

Mechanical properties

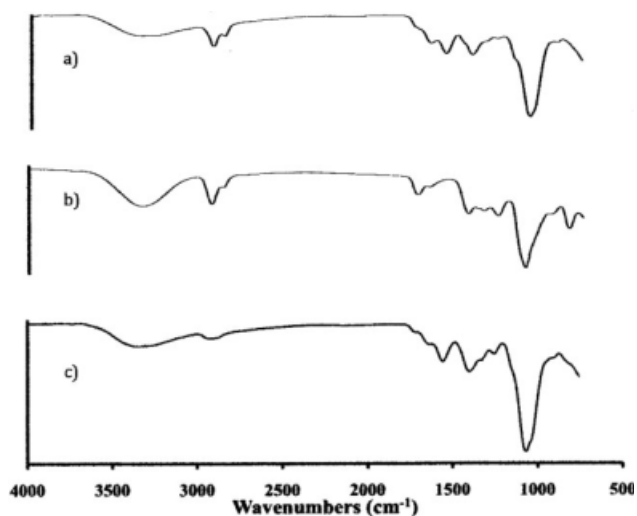The tensile stress at break of the synthesized CS/PVA membrane is shown in Figure 3. From the

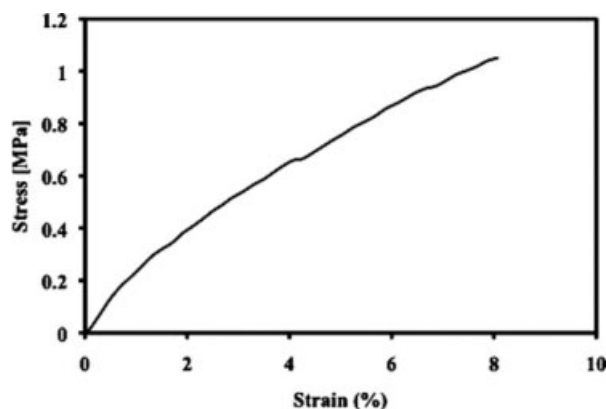**Figure 2** FTIR characteristic peaks of (a) CS, (b) PVA, and (c) CS/PVA.

Figure 3 Stress–strain curve of imprinted-CS/PVA membrane.

Figure 4 Maxiumum Ag(I) removal by different prepared membranes; pH, 6; time, 40 min.; T, 25°C.

result, it can be observed that the membrane exhibits a higher tensile stress of 1.05 MPa with point of break at strain %, 8.06. This enhancement may be attributed to the ionic-crosslinking of the membranes as proved by FTIR results. Polymer chains in the polyion complex having electrostatic interactions with another polymer chain experience a restriction in the mobility.[34] This restriction results in an increase in the rigidity or the tensile stress, thereby reducing the elongation at break.

Membrane adsorption characteristics

Eluent type

Ag(I)-imprinting were eluted from the different synthesized membranes with two types of eluting agents. From the data given in Table I, it is obvious that the use of 10^{-2} M EDTA as an eluent can accomplish the higher Ag(I) elution from the imprinted membranes.

Removal capacity of the imprinted membranes

When compared with free CS, the adsorption capacity of crosslinked CS adsorbent for heavy metal ions is lower because of functional groups ($-NH_2$) being crosslinked.[25] Therefore, ion imprinting for the crosslinked CS adsorbent prepared by using molecular imprinting method may overcome this problem. When the heavy metal ions selected are reversibly

bound on the CS in the preparation of an adsorbent and subsequently desorbed, the imprinting sites, or specific spaces of the imprinted metal ion are retained on adsorbent, so enhancing the selectivity for imprinted ions.

When Ag^+ was used as the imprinted metal ion in the membranes synthesis, the removal ability for Ag^+ increased considerably when compared with that of the nonimprinted one. Also, with the imprinted higher Ag^+ concentrations in synthesis increasing, the more effective functional groups ($-NH_2$) were protected and the more imprinting sites on the adsorbent surface were retained. From Figure 4, the removal capacity increased 20%, from 77.8 to 94.4 mg g^{-1} in case of nonimprinting and ion-imprinting CS, respectively, and increased about 50% from 83.9 to 125 mg g^{-1} in case of nonimprinting and ion-imprinting CS/PVA, respectively. Although a very high increase in Ag^+ removal was also observed in case of ion-imprinting PVA when compared with the nonimprinting, the removal capacity remains very low when compared with the other synthesized membranes. Thus, the removal capacity for Ag^+ of the ion-imprinted membranes obviously enhanced when compared with that of the nonimprinted. The results also reveal that, Ag^+-imprinting-CS/PVA membrane exhibits the highest removal capacity for Ag(I).

Kinetics of Ag(I) removal

To determine the rate of maximum capacity loading of Ag^+ on non- and ion-imprinting membranes, batch experiments were carried out. Figure 5 shows that an equilibration time of about 40 min was required for maximum loading capacity. However, the time ($t1/2$) of 50% sorption was less than 30 min. The results show also that the rate of Ag(I) removal by ion-imprinted CS/PVA membrane is fast when compared with the nonimprinted CS/PVA membrane.
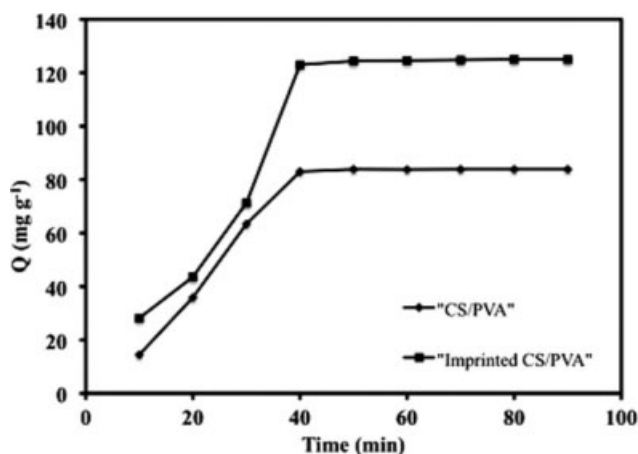
TABLE I
Elution (%) of Ag(I) from Ag(I)-Imprinted Membranes; time, 48 h; T, 25°C

Eluting	Concentration (M)	Elution (%)		
		CS	PVA	CS/PVA
EDTA	1.0×10^{-2}	95.6	99	93.4
HNO$_3$	1.0×10^{-2}	84.3	87	79.2

Figure 5 Removal rate of Ag(I) ions on non- and imprinted CS/PVA membranes; pH, 6; T, 25°C.

Effect of pH

Knowledge of pH is important because the pH of solution strongly affects the removal capacity of different adsorption materials. Figure 6 shows the effect of pH on the removal of Ag$^+$ by ion-imprinted CS/PVA membrane. From which it can be seen that the maximum removal of Ag$^+$ on CS/PVA membrane was found at pH 6.0. At pH values higher than 7, Ag$^+$ precipitation occurred simultaneously. pH 6 was chosen for the removal of Ag$^+$ ions to avoid the formation of Ag$^+$ hydroxide which will affect the removal by the membrane. Also, It can be observed from the figure that the removal increases with increasing pH of the solution. This could be explained by the fact that at low pH, the membrane exhibited a drastic decrease in metal ions affinity at low pH conditions due to formidable competition with hydronium ions. Thereafter, increasing the pH of the medium will increase the hydrolysis of the membrane in the aqueous solution. The hydrolysis of Ag$^+$ ions also occurs simultaneously in the aque-
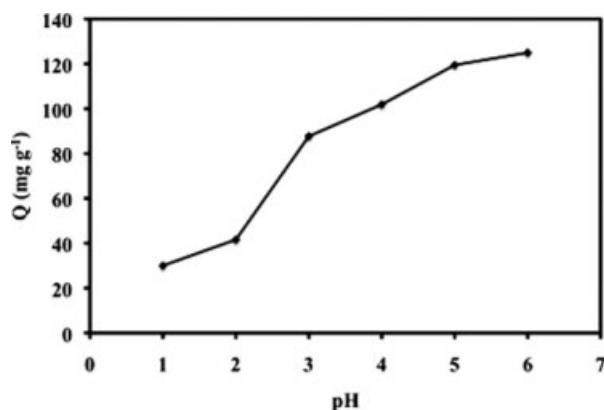

Figure 6 Effect of pH on Ag(I) removal by imprinted-CS/PVA membrane; adsorption time, 40 min.; T, 25°C.
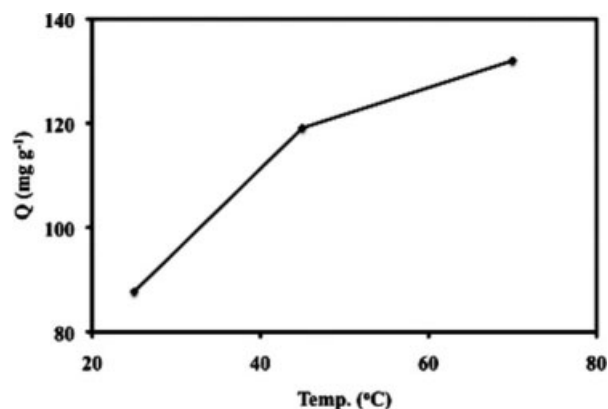

Figure 7 Effect of temperautre on the removal of Ag(I) by the imprinted-CS/PVA membrane; pH, 3; time, 40 min.

ous solution, and the degree of hydrolysis increases with the increase in the pH of the solution.

Therefore, it can be inferred that the solution pH not only affects the surface charge of the adsorbent (membrane) but also inferences the degree of ionization and speciation of the Ag$^+$ ion. It was proposed that the removal of metal ions at the solid-solution interface is not governed by the "free" metal concentration, but is instead governed by the much stronger adsorbed hydroxo, sulfato, carbonato, and other metal species.[36–38]

Effect of temperature

It has been observed that the removal of Ag$^+$ ion from aqueous solution by the ion-imprinted CS/PVA membrane is affected by the temperature, with the removal being increased remarkably as the temperature increased (Fig. 7). This increase may be due to the enhanced rate of intraparticle diffusion of Ag$^+$ ion and changes in the size of the pores of the membrane.[5]

Selectivity studies

Competitive removals of Ag$^+$/Cu^{2+} and Ag$^+$/Ni^{2+} from their mixtures were also studied in a batch system. Figure 8 shows the selectivity of all the synthesized non- and ion-imprinting CS and CS/PVA membranes towards Ag$^+$/Cu^{2+} and Ag$^+$/Ni^{2+} binary mixtures. It is obvious from the figure that the nonimprinting membranes are selective towards Cu^{2+} and Ni^{2+}. Meanwhile, ion-imprinting membranes are reversed to be highly selective towards Ag$^+$. Table II summarizes k and k' values of Cu^{2+} and Ni^{2+} with respect to Ag$^+$. A comparison of the k values for the nonimprinting membranes (0.4–0.45) with that of ion-imprinted membranes[4–6] reveals the high selectivity of the ion-imprinted membranes towards Ag$^+$ ions. The relative selectivity coefficient is an indicator to express metal removal affinity of
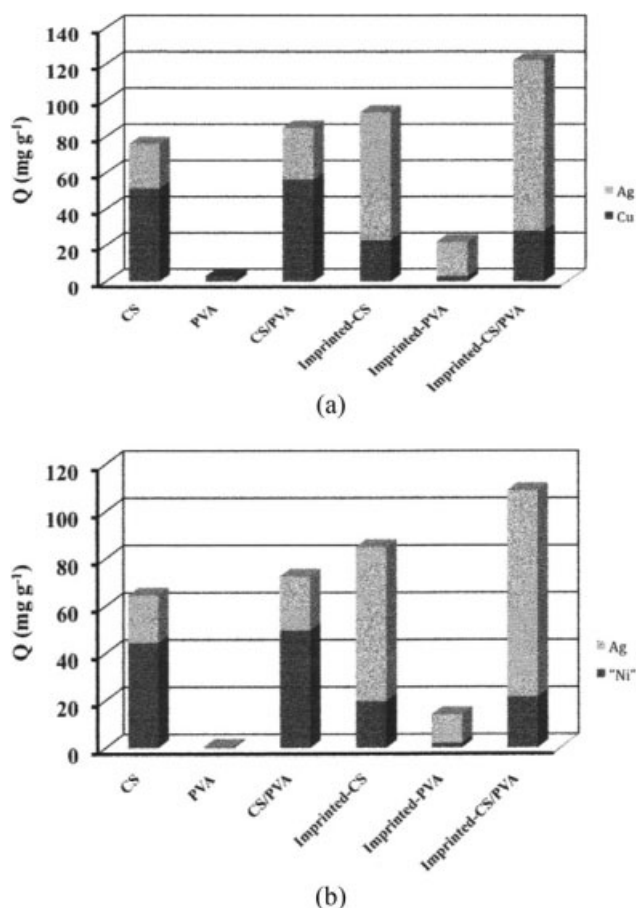
(a)

(b)

Figure 8 Competitive removel of Ag(I) in mixture with; (a) Cu(II) and (b) Ni(II) ions by different synthesized membrnes, adsorption time, 40 min.; T, 25°C and pH, 6.

recognition sites to the imprinted Ag^{+1} ions. These results show that relative selectivity coefficients of ion-imprinted CS membrane for Ag^+/Cu^{2+} and Ag^+/Ni^{2+} are 9, 10.7 times greater than nonimprinted membrane, respectively. Also, k' values for the ion-imprinted CS/PVA membranes for Ag^+/Cu^{2+} and Ag^+/Ni^{2+} are 11.1, 15 times greater than nonimprinted membrane, respectively.

These could be explained as follows, in case of nonimprinting membranes selectivity will be towards metals ions of higher velancies (2+ in case of Cu and Ni and 1+ for Ag) and lower ionic radii [Ni(II) = 69 pm, Cu(II) = 71 pm, and Ag(I) = 114

TABLE II
k, k' Values of Cu^{2+} and Ni^{2+} with Respect to Ag^+

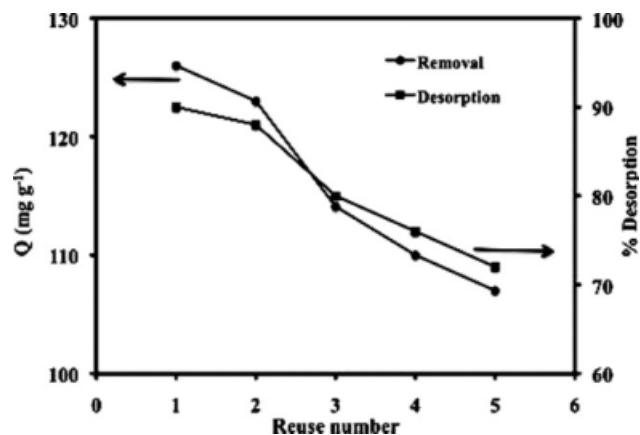| Metal ion	CS		CS/PVA	
	Nonimprinted	Imprinted	Nonimprinted	Imprinted
Cu^{2+}				
k	0.44	4	0.45	5
k'		9		11.1
Ni^{2+}				
k	0.4	4.3	0.41	6
k'		10.7		15

Figure 9 Removal–desorption cycle of Ag(I) ions by imprinted CS/PVA membrane.

pm]^{39}; resulting in an overall selectivity for Cu(II) and Ni(II). Meanwhile, the significant increase in the selectivity of the ion-imprinted membranes towards Ag^+ ions may be attributed to molecular geometry as the membranes prepared in the presence of Ag(I) as target ion.

Desorption and repeated use

The regeneration of the adsorbent is likely to be a key factor in improving process economics. Desorption of the Ag^+ ions from the ion-imprinted CS/PVA membrane was performed in a batch experimental set-up. The adsorption capacity of the recycled imprinted CS/PVA membrane can still be maintained at 85% of its original value at the fifth cycle (Fig. 9). It can be seen concluded that the ion-imprinted CS/PVA membrane can be used many times without decreasing their removal capacities significantly. The desorption percent of Ag^+ ions was also given in Figure 9. As seen in this figure the desorption percent of Ag^+ ions is slightly decrease with increasing reuse number, resulting in an accumulation of Ag(I) ions in the membrane. This accumulation might be the reason for the decrease in the adsorption capacity for the membrane towards Ag^+ ions upon recycling.

CONCLUSION

The ion-imprinting method is a useful technique for the preparation of adsorbents for the selective separation of ions, such as silver from aqueous solutions. Ion-imprinted adsorbent is a new type of carrier that can considerably enhance the removal capacity and the selectivity of ions.

Silver ion imprinted membranes were synthesized via individual and blend crosslinking of CS and PVA. Characterization of the synthesized membranes was identified by FTIR.

The competitive removal capacity of the imprinted membranes for Ag(I) is higher than nonimprinted membranes. The imprinted membranes are good enough for selective silver removal in a matrixes containing interferent ions such as Cu(II) and Ni(II). Moreover, ion-imprinted membrane has a good reusability and stability, which can be repeated to use 5 cycles with removal not less than 85% of the original removal.

Therefore, Ag(I)-imprinted CS/PVA membranes, which has high selectivity towards Ag ions, is expected to be useful materials for the interference-free extraction and preconcentration of Ag^+ ions.

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