Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1151380

57 (2016) 25729–25738
November

Taylor & Francis
Taylor & Francis Group

Development of novel blend membranes based on carbohydrate polymers for the removal of toxic metal ions through sorption

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Received 7 September 2015; Accepted 2 February 2016

ABSTRACT

The present study describes the development of novel sodium alginate–gelatin (SAG) blend membranes for the removal of copper(II) and nickel(II) ions from aqueous solutions through sorption. The SAG blend membranes were chemically crosslinked by various crosslinkers, such as glutaraldehyde (GA), urea-formaldehyde (UF) and thiourea-formaldehyde (TF) in order to enhance the strength of the membranes and reduce their swelling behaviour in presence of water. The resulting membranes were extensively characterized by FTIR, SEM and DSC to study various structural aspects of the membranes. Equilibrium swelling experiments were performed on SAG membranes in metal ion solutions at 30°C. The effect of contact time, initial pH and initial metal ion concentration on the sorption behaviour of the membranes was investigated. The adsorption capacities of copper(II) and nickel(II) on the SAG (SAG-GA/UF/TF) membranes as obtained from Langmuir adsorption isotherm were found to be 0.4284, 0.5307, 0.6847 mM/g and 1.7567, 3.3329, 4.1 mM/g, respectively.

Keywords: Sodium alginate; Gelatin; Crosslinking; Sorption; Copper; Nickel

1. Introduction

The industrial effluents containing toxic metal ions are found to be very harmful to the environment and their removal is quite essential [1,2]. Toxic heavy metals are considered to be one of the most troublesome and hazardous group of water contaminants due to their accumulation in the biological systems and its toxicity [3–7]. Mining and metal industries such as copper cleaning, plating and metal processing produce effluent water having about 120–400 mg/L of Cu(II) ions. These concentrations are too high and must be reduced to below the regulated value i.e. 1.0–1.5 mg/L. The production of several types of alloys and electroplating industries releases Ni(II). Nickel is toxic because it inhibits oxidative enzyme activity. It is highly carcinogenic and a high level of nickel induces the reduction of nitrogen and impaired growth. Therefore, removal of these metal ions is essential before being discharged into aquatic streams. Conventional methods, such as precipitation, oxidation, reduction,

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ion exchange, filtration, reverse osmosis, electro-chemical removal and evaporative recovery can potentially remove the metal ions from industrial effluents [8–10]. However, these methods are either inefficient or too expensive in removing metal ions at tracer level.

Biopolymers are non-toxic, selective, efficient and inexpensive and thus highly competitive with ion-exchange resins and activated carbon. The usage of carbohydrates in the adsorption of heavy metal ions from aqueous solutions is greatly increased in recent years. Many biopolymers such as sodium alginate, chitosan and some fungi are known to bind metal ions strongly and could be used for toxic metal adsorption [11,12]. Alginates are natural polyelectrolytes that comprise a family of polysaccharides which contain 1,4-linked β-D-mannuronic and α-L-guluronic acid residues arranged in a block wise, non-regular order along the chain. Cation specific affinity of the alginate gel and its fundamental physiochemical and rheological properties are determined by this arrangement. Coordination sites of two homopolymeric guluronic chains are aligned to accommodate divalent cations easily according to the well-known "egg-box model". Some studies showed that "egg-box model" is mainly responsible for ion exchange, whereas other studies reported the sorption through complexation in addition to the ion exchange [13–16].

In the present work we have synthesized novel sodium alginate-gelatin (SAG) blend membranes crosslinked with urea-formaldehyde (UF), thiourea-formaldehyde (TF) and compared with glutaraldehyde (GA) cross-linked SAG membranes for the removal of Cu(II) and Ni(II) ions. Further, the synthesized membranes were extensively characterized by Fourier transform infrared (FTIR) spectroscopy, Scanning electron microscopy (SEM) and Differential scanning calorimetry (DSC). Batch studies such as effect of time, effect of initial metal ion and solution pH were conducted in order to investigate adsorption efficiency of SAG membrane sorbents. The kinetic data were checked for the pseudo-first-order reaction, pseudo-second-order reaction and the rate constants were evaluated. The equilibrium data were modelled by Langmuir and Freundlich isotherms equations. A comparative account of metal adsorption and efficiency of membranes was determined by considering different combinations of crosslinkers GA, UF and TF.

2. Experimental

2.1. Materials

Analytical reagent grade of sodium alginate (SA), urea, thiourea, sulphuric acid, hydrochloric acid, GA (25% aqueous solution), acetic acid and sodium hydroxide were purchased from S.D. Fine Chemicals, Mumbai, India. Gelatin was purchased from Aldrich Chemicals Co., Ltd, USA. All the chemicals were used without further purification and double distilled (DD) water was used throughout the experiments.

2.2. Preparation of SAG membranes

The SAG blend solution was prepared by dissolving 4.75 g of SA powder in 85.25 mL of water and 0.25 g of gelatin in 9.75 mL of water, individually stirred for 12 h. These two clear solutions were then mixed and stirred continuously to get a homogeneous solution. The obtained polymer blend solution was casted on a clean glass plate and allowed to dry in the presence of air at room temperature for 24 h. Then the membranes were peeled off from the glass plate and further dried in vacuum to remove water moieties.

2.3. Preparation of cross-linked SAG membrane

The SAG blend membranes were crosslinked with various cross-linking agents such as GA, UF and TF, and the membranes were designated as SAG-GA, SAG-UF and SAG-TF. The SAG membrane was cross-linked in a mixture of 2.5 mL GA (cross-linking agent), 2.5 mL HCl (catalyst) and 3:1 ratio of acetone–water mixture as organic–water bath. The reagents used to prepare the SAG-UF membranes were 2.5 wt.% urea, 2.2 wt.% formaldehyde, 2.5 wt.% sulphuric acid and 50:50 ratio of ethanol–water mixture. The same composition of reagent mixture was maintained except the cross-linking agent (2.5 wt.% thiourea was used in the place of urea) for the preparation of SAG-TF membranes. The membranes were kept in a cross-linking bath for 6 h at room temperature. After crosslinking, the membranes were taken out and rinsed repeatedly with DD water and then dried at 40˚C for 24 h.

2.4. Swelling behaviour of SAG membranes

The swelling studies of SAG membranes were performed in a metal ion solution by mass measurements at 30˚C. Fully dried membranes were immersed in metal ion solution and kept for 2 h. After taking out the membranes from the metal ion solution, the surface-adhered solution was wiped out with the help of a tissue paper. The swollen membranes were weighed and determined the percentage of degree of swelling using the following equation:

$$\%\mathrm{DS} = \frac{M_s}{M_d} \times 100 \tag{1}$$

where M_s = mass of swollen membrane and M_d = mass of dry membrane.

2.5. Preparation of Cu(II) and Ni(II) solutions

Cu(II) and Ni(II) solutions were prepared by adding appropriate amounts of copper nitrate [Cu $(NO_3)_2{\cdot}3H_2O$] and nickel ammonium sulphate [$NiSO_4$ $(NH_4)_2SO_4{\cdot}6H_2O$] to aqueous solution to obtain solutions in the concentration range of 0.5–5 mM.

2.6. Equilibrium studies and desorption

Batch experimental studies were carried out with known weight of circular pieces of membrane in 20 mL of metal ion solution of desired concentration at an optimum pH in 50 mL Erlenmeyer flasks. The flasks were agitated on a mechanical shaker at 200 rpm for a known period of time at room temperature. After attaining equilibrium, the membrane was separated by filtration using filter paper and the aqueous-phase concentration of metal ion was determined with UV–vis spectrophotometer. The equilibrium adsorption amount, Q_e (mM/g-dry gel) was determined as follows:

$$q_e = \left(\frac{C_i - C_e}{m}\right) \cdot v \tag{2}$$

where q_e = amount sorbed per unit mass of the membrane (mM/g), C_i and C_e = initial and equilibrium concentrations of metal ion (mM), respectively, m = mass of the dry membrane (g), v = volume of solution used for the adsorption (L).

The effect of pH of the medium on metal ion removal was studied by performing equilibrium sorption experiments at different pH values. A pH meter with combined glass electrode was used for pH measurements. Adjustment of pH was made with 0.1 M HCl and 0.1 M NaOH solutions. The effect of pH was studied by keeping the metal ion concentration, the weight of membrane, contact time and the temperature constant.

Desorption of metal ions from loaded SAG membrane sorbents was carried out by solvent extraction method using 0.01 M HCl and 0.01 M EDTA solvents. To check the efficiency of concentration of the desorbing solvent, the concentration of both the solvents was increased to 0.1 M. The EDTA or HCl solution was added to the metal ion-loaded sorbents. After 2 h, the metal ion concentration was analysed using spectrophotometer.

In order to investigate the mechanism of sorption, the rate constants for the metal ion adsorption were determined using popular pseudo-first-order and pseudo-second-order equations. The linearized form of the pseudo-first-order rate expression is given by:

$$\log(Q_e - Q_t) = \log Q_e - \left(\frac{k_1}{2.303}\right)t \tag{3}$$

where Q_e and Q_t = the amounts of metal ion adsorbed per unit mass of adsorbent at equilibrium and at time t (min) respectively, k_1 = rate constant (min^{-1}).

The straight line plots of $\log(Q_e - Q_t)$ against t in the linearized form of above equation were used to determine the rate constant, k_1 and correlation coefficients, R^2 for different concentrations.

The linearized form of pseudo-second-order equation [17] may be expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2\, Q_e^2} + \frac{1}{Q_e}t \tag{4}$$

where k_2 (g/mg/min) = rate constant of the second-order kinetic equation, Q_t (mg/g) = amount adsorbed at time t (min), Q_e = amount adsorbed at equilibrium (mg/g).

Freundlich and Langmuir isotherms were used to fit the experimental data. Equilibrium adsorption data are generally described by Langmuir model [18] which is given by:

$$Q_e = \frac{Q^0\, b\, C_e}{1 + b\, C_e} \tag{5}$$

where Q^0 = maximum amount of the metal ion adsorbed per unit weight of sorbent to form a complete monolayer on the surfaces at equilibrium concentration, b = Langmuir constant related to affinity of the binding site.

The values of the parameters and correlation coefficient (R^2) of Cu(II) and Ni(II) ions are given in Table 1.

2.7. Characterization analysis

The SAG membranes used for the present study were extensively characterized using various characterization techniques such as FTIR spectroscopy, SEM and DSC. Fourier transforms infrared spectroscopy

Table 1
Langmuir parameters with regression analysis of Cu(II) and Ni(II) sorption on SAG membranes

		Langmuir constants		
Metal ion	Membrane	Q^0 (mM/g) ± SD	b (L/mg)	R^2
Cu(II)	SAG-GA	0.42 ± 0.0062	2.05	0.94
	SAG-UF	0.54 ± 0.0059	3.86	0.96
	SAG-TF	0.68 ± 0.0029	4.16	0.99
Ni(II)	SAG-GA	1.75 ± 0.0100	1.10	0.98
	SAG-UF	3.23 ± 0.0136	1.72	0.98
	SAG-TF	4.13 ± 0.0100	2.38	0.99

(FTIR) was used to confirm the presence of functional groups of SAG membranes before and after crosslinking (Perkin Elmer-410, USA). SEM images were taken with a Carl Zeiss, EVO MA15 Instrument at 20 kV. 10 to 12 mg of sample is used for thermal analysis and DSC curves were recorded on the instrument (Model: STA, Q600 USA). The samples were heated from 30 to 300˚C at a heating rate of 10˚C/min in nitrogen atmosphere (flow rate 100 mL/min).

3. Results and discussions

The present work describes the development of sodium alginate (SA) and gelatine (Gln) blend membranes, which were cross-linked by GA, UF and TF. In general, SA crosslinks with GA, but in the case of UF and TF, cross-linked products were not much stable in the aqueous medium. Hence, SA blended with 5% gelatin was used to get stable and multi-functional membranes. This is due to the incorporation of amino groups which led to cross-linking with UF and TF. The interaction between the chemical groups of SAG and cross-linking agents is presented in Scheme 1.

3.1. Characterization

3.1.1. FTIR spectroscopy studies

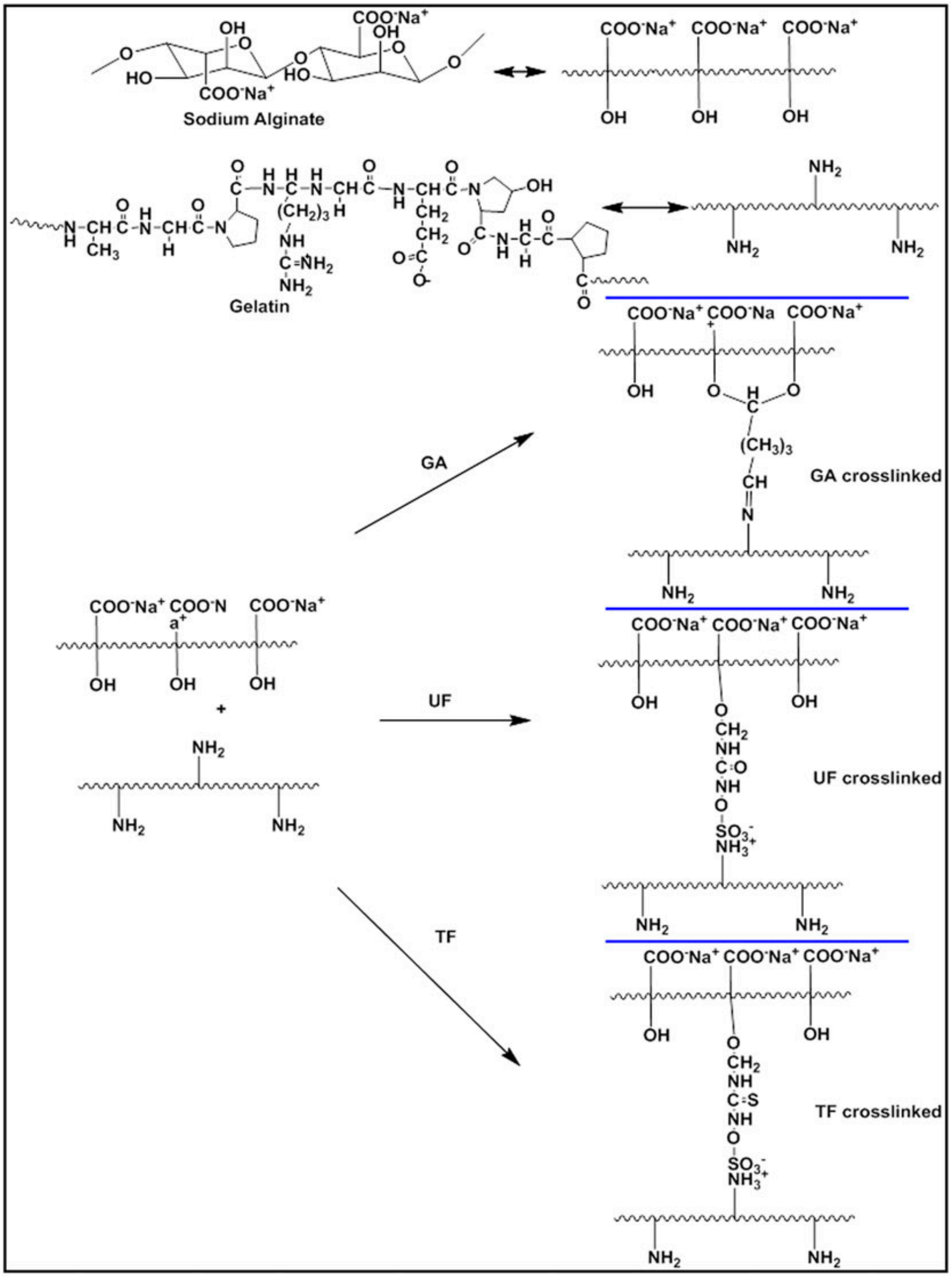
The characteristic pattern of FT-IR spectra of SA GA, SA UF, SA TF and their metal (Cu(II)- and Ni(II))-loaded membranes are given in Fig. 1.The IR spectrum of SAG (Fig. 1(a)) has a strong peak around 3,449 cm^{-1} due to the stretching vibration of –OH or NH_2 group, peaks at 1,612 and 1,390 cm^{-1} corresponds to COO^- asymmetric and symmetric stretching. In addition, the bands around 1,310 cm^{-1} (C–O stretching), 1,160 cm^{-1} (C–C stretching), 1,090 cm^{-1} (C–O stretching) and 990 cm^{-1} (C–O stretching) are attributed to its saccharide structure (Ho and McKay 2000). Peaks observed at 2,900 cm^{-1} are typical –CH stretching vibration. FTIR spectrum of SA GA membrane shows a peak around 1,750 cm^{-1} due to >C=O and a peak at 1,631 cm^{-1} due to imine linkage (–C=N) formed as a result of cross-linking reaction between amino groups in SAG and aldehydic groups in GA (Fig. 1(b)). The peak found at same wave number in SAG-UF membrane (Fig. 1(g)) is responsible for cross-linking the $–NH_2$ groups of SAG in the presence of sulphuric acid. A possible reaction between $HOSO_3^-$ and methylolurea is indicated by a band due to C–O–S bond of the cross-linked chains at 702 cm^{-1}. Similar results were observed in thiourea case (1,189 cm^{-1} corresponds to C=S) (Fig. 1(j)). Fig. 1(c)–(f), (h), (i) shows the FTIR spectra of cross-linked SAG membranes loaded with Ni(II) and Cu(II) ions. An interesting phenomenon is the sharp shift in the position and decrease in the intensity of the bands after metal binding. As indicated by Vijaya et al., the presence of functional groups like $–NH_2$, –OH, –CO, $–COO^-$ increases the interaction with metal ion thereby enhancing the adsorption. The FT-IR spectra of metal-loaded membranes (Fig. 1(c)–(f), (h), (i)) indicate the considerable change in the position and intensity of the peaks. From this it may be concluded that $–COO^-$, –OH, –CO, $–NH_2$ groups act as binding sites for metal ion adsorption. It was confirmed by the study of Chiou and Li that the amino groups of chitosan were the effective binding sites for metal ions, forming stable complexes by coordination [19].The nitrogen electrons present in the amino groups can establish dative bonds with transitional metal ions. Wavenumbers of significant functional groups of SAG-GA, SAG-UF and SAG-TF membranes from FTIR analysis are presented in Table S1.

3.1.2. SEM studies

SEM studies (Fig. S1) revealed that the morphology of the SAG membranes are having smooth and rough surface. This fact can be attributed to the smooth surface of GA cross-linked SAG membranes and globular surface of the cross-linked UF, while TF showed sponge like accumulation and bears an irregular shape with rough surface.

3.1.3. Differential scanning calorimetric studies

From the Differential scanning calorimetric (DSC) thermograms (Fig. S2), the melting transitions of pure SA, gelatin and SAG, are 212, 208 and 215, respectively. The DSC thermograms of the cross-linked SAG membranes are displayed in Fig. S3. The cross-linked blend membranes of SAG-GA,



Scheme 1. Schematics of cross-linking chemistry of SAG membranes.

SAG-UF and SAG-TF have the melting transitions at 200.56, 201.24 and 202.44℃, respectively. The melting transition temperatures increase as SAG-GA < SAG-UF < SAG-TF and this increase indicates the increase of thermal stability of the above membranes. Therefore, it can be concluded that these membrane sorbents can be used even at higher temperatures in water treatment.

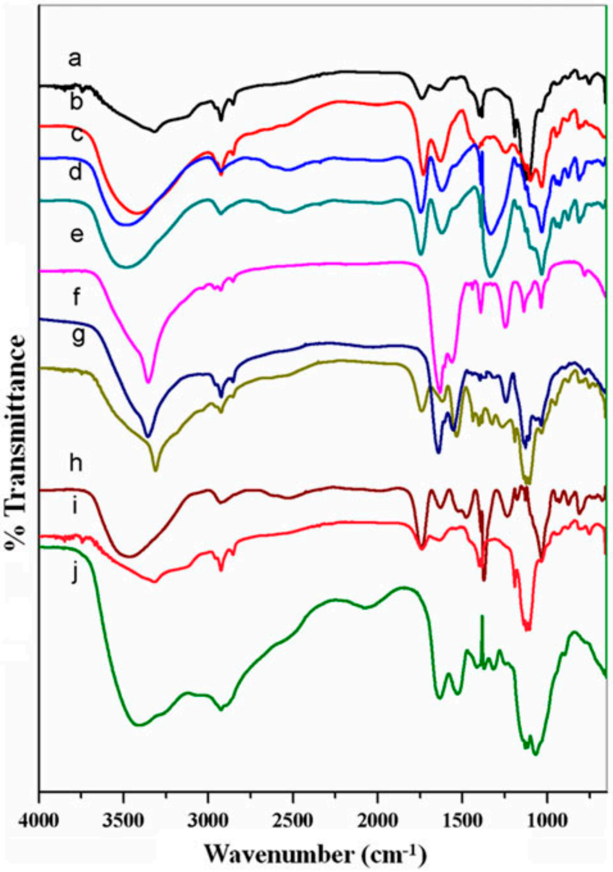


Fig. 1. FTIR spectra of uncross-linked SAG (a), GA cross-linked SAG (b), Ni-loaded SAG-GA (c), Cu-loaded SAG-GA (d), Ni-loaded SAG-UF (e), Cu-loaded SAG-UF (f), UF cross-linked SAG (g), Ni-loaded SAG-TF (h), Cu-loaded SAG-TF (i), and TF cross-linked SAG (j) membranes.

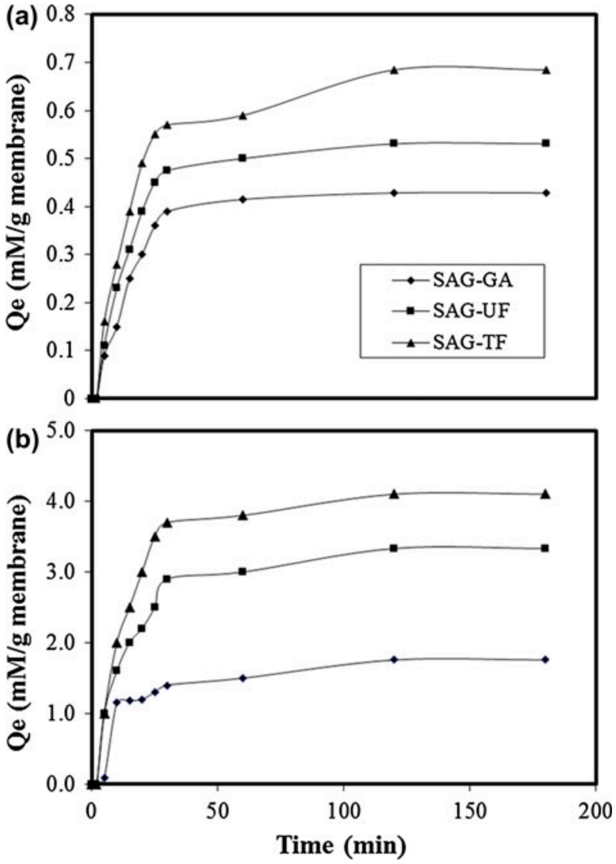


Fig. 2. Effect of time on adsorption of copper(II) (a) and nickel(II) (b) ion solutions.

3.2. Effect of agitation time and adsorption kinetics

Fig. 2 shows the kinetics of adsorption expressed as the adsorbed quantity of Cu(II) and Ni(II) ions over one gram of membrane. At the initial stage, the process of adsorption was rapid due to the availability of abundant free sites near the surface where there is less hindrance for binding of the metal ions and became slower with the lapse of time. SAG-TF has higher sorption ability for the metal ions than the other two cross-linked membranes. With respect to contact time, all the materials reached saturation after 180 min. The data were used to study the kinetics of adsorption of Cu(II) and Ni(II) ion on SAG membranes. Many kinetic models were developed and studied by several researchers to find out kinetic adsorption constants [20].

The straight line plots of t/q_t against t were used to obtain rate parameters. The values of the rate constants (k_1 and k_2) and R^2 are presented in Table 2. Higher R^2 values indicate that adsorption follows pseudo-second-order kinetic model. In many cases, the pseudo-first-order equation is generally applicable over the initial stage of the adsorption processes [21]. The second-order kinetic model assumes that the rate limiting step may be chemical adsorption [19]. In many cases, the adsorption data could be well correlated by second-order rate equation over the entire period of contact time [22].

3.3. Effect of pH on metal ion adsorption and degree of swelling

pH is the most important factor among all the factors that affects the removal of heavy metals. The effect of pH on the adsorption of Cu(II) and Ni(II) ions was studied at different pH values using SAG membrane sorbent at constant metal ion concentration (0.05 mM/L) and amount of membrane (1 g). The results (Fig. 3) indicate that the maximum uptake of Cu(II) ions takes place at pH 5.0 while the maximum uptake of Ni(II) ions occurs at an initial pH of 4.0. As pH value increases (pH 2–5) the adsorption capacity of Cu(II) and Ni(II) also increases in all membranes

Table 2
First-order (k_1) and second-order (k_2) rate constants for adsorption of Cu(II) and Ni(II) ions on cross-linked SAG membrane sorbents

	Cu(II)				Ni(II)			
Membrane sorbent	k_1	R^2	k_2	R^2	k_1	R^2	k_2	R^2
SAG-GA	0.007	0.976	0.114	0.992	0.010	0.971	0.024	0.997
SAG-UF	0.008	0.981	0.103	0.994	0.011	0.963	0.018	0.991
SAG-TF	0.011	0.990	0.058	0.995	0.015	0.991	0.019	0.996

Note: Concentration of metal ion solution = 0.5 mM/L.

(SAG-GA, SAG-UF and SAG-TF). Surface sites are protonated at low pH and the surface becomes positively charged. On the other hand, at high pH, the ionizable groups (–NH_2 or –COOH) lose their protons and the surface becomes negatively charged. Under alkaline conditions, complete sorption was observed, but in this pH region the copper removal originates from precipitation ($Cu(OH)_2$) rather than due to sorption. The uptake capacity of metal ions on SAG-TF and SAG-UF membranes is more compared to SAG-GA membranes due to binding groups like carboxylic, hydroxyl, amino and sulphonyl groups. In the case of GA cross-linked membranes, the key functional groups responsible for metal ion adsorption are hydroxyl and carboxylic groups.

The difference in the maximum uptake of the synthesized membranes towards Cu(II) and Ni(II) ions at different pH is due to different complexation ability of the metal ions. In general, the maximum adsorption capacity at optimal pH depends on the nature of biosorbent and the metal ion. Further, pH influences (Fig. S4) surface properties of the adsorbent by way of functional group dissociations and also surface charges. At pH value above 4.0, the carboxylic group present in alginic acid changes into carboxylate ion due to dissociation, which attracts positively charged metal ions. As nickel is strongly attracted by electric and magnetic field than copper, nickel ions exhibit maximum adsorption at pH 4.0 due to electrostatic attraction.

To understand the sorption capability of the SAG cross-linked membranes, swelling studies were carried out in the presence of 0.5 mM/L metal ion solution with varying pH from 3 to 5. Being hydrophilic polymers, sodium alginate and gelatin undergo excessive swelling during their interaction with aqueous solutions. From the results (Figure not shown), it was observed that the degree of swelling increases with increasing pH values (3–5). This was due to the ionization/deionization of the ionizable functional groups, such as –COO^- Na^+, –OH, and NH_2. At lower pH values, these groups do not ionize and keep the network at its collapse state. At higher pH values, these groups ionize and their charge repels each other, resulting in the swelling of the membrane. The sorption results were supportive to the adsorption capacities obtained above as the trend followed the same order. The per cent degree of swelling of SAG

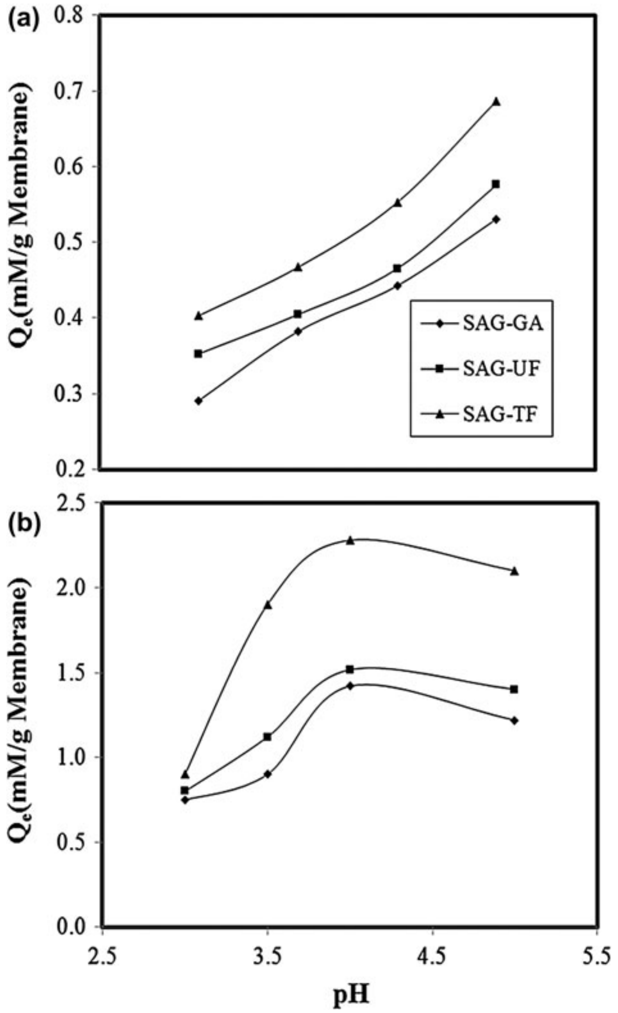


Fig. 3. Effect of pH on adsorption of Cu(II) (a) and Ni(II) (b) solutions.

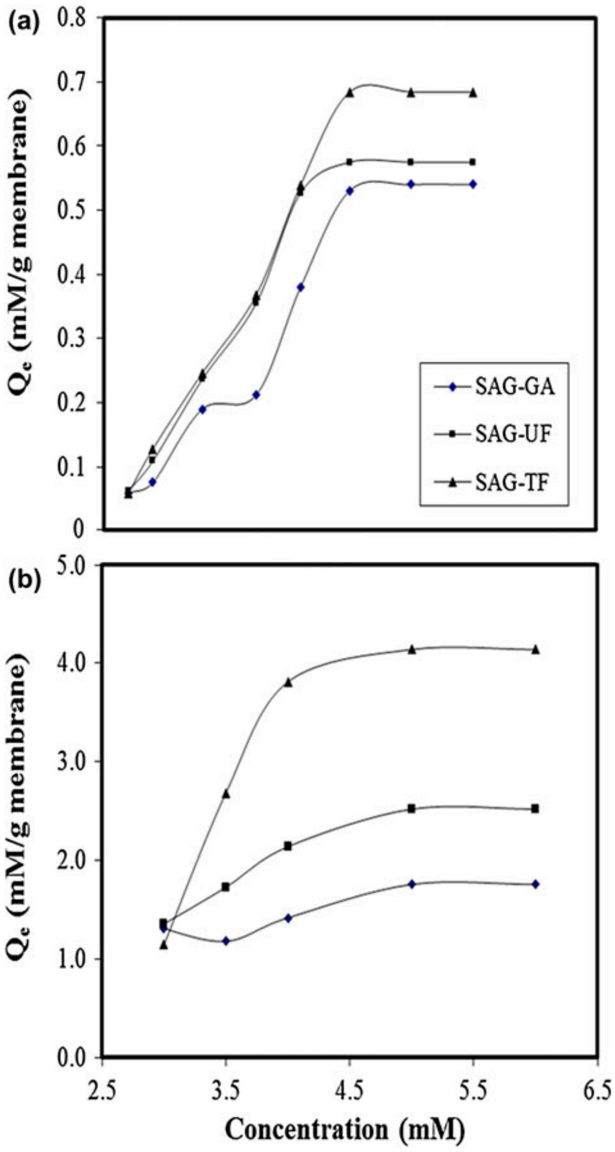


Fig. 4. Effect of concentration on adsorption of copper(II) (a) and nickel(II) (b) ions.

membranes at optimum pH values (5 for copper and 4 for nickel) is presented in Table S2.

3.4. *Effect of metal ion concentration and adsorption models*

Adsorption of Cu(II) and Ni(II) at different initial metal ion concentrations (3.0–6.0 mM/L) was performed on the synthesized membranes while keeping the time and pH optimum. Fig. 4 shows the relationship between initial metal ion concentration and the adsorbed amount. The adsorption capacity of the SAG-GA, SAG-UF and SAG-TF membranes increases by increasing the initial metal ion concentration and then reached a plateau value at higher concentration due to the saturation of the chelating sites of the membrane. The uptake of metal ion increases with increase in the initial concentration of metal ion because it overcomes mass transfer resistance of ions between the adsorbent and bulk fluid phases. The adsorption is measured at pH 5.The maximum adsorption capacities of the membranes SAG-GA, SAG-UF and SAG-TF were found to be 0.4284, 0.5307, 0.6847 mM/g for Cu (II) and 1.7567, 3.3329, 4.1 mM/g for Ni(II), respectively. These high adsorption efficiencies were attributed to the hydrophilic nature of SAG membrane matrix due to the presence of hydroxyl (–OH), amine (–NH–) and carboxyl (–COO$^-$) groups, which had an adequate affinity to the metal ions.

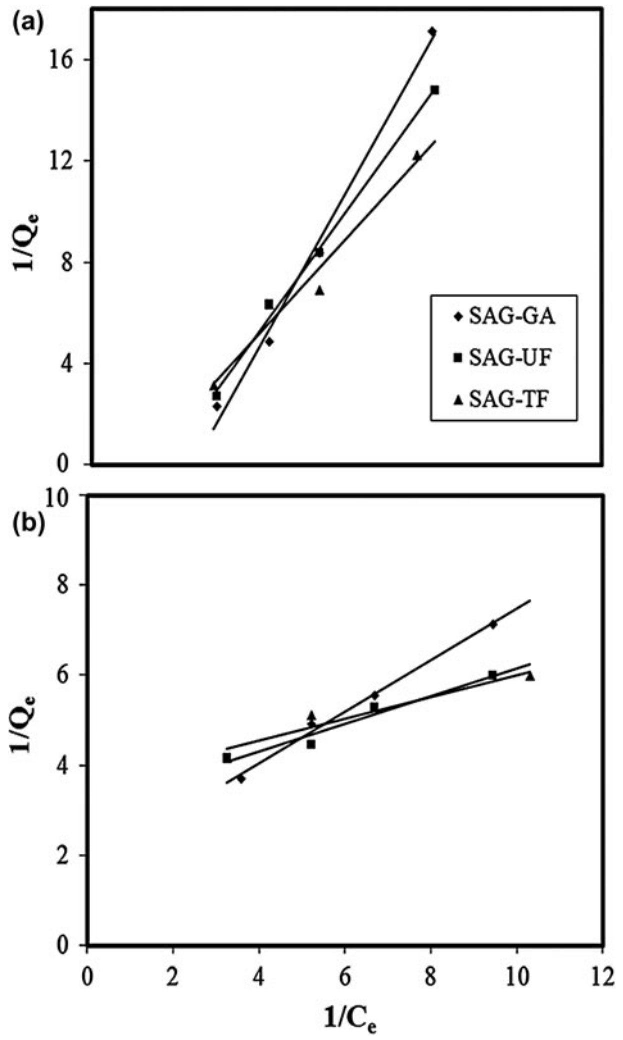


Fig. 5. Langmuir isotherm for adsorption of Cu^{2+} (a) and Ni^{2+} (b) at pH 5 and pH 4 for SAG membranes.

Moreover, an increase in the concentration of metal ions increases the number of collisions between metal ions and adsorbent, which results in the enhancement of adsorption process. The values of Q^0 and b were determined from the slope and intercept of linear plots. The values of Q^0 for Cu(II) and Ni(II) ions were 0.42, 0.54, 0.68 mM/g and 1.75, 3.23, 4.13 mM/g for membranes SAG-GA, SAG-UF and SAG-TF, respectively. From Fig. 5, it is noted that the Langmuir isotherm model exhibits better fit to the sorption data of Cu(II) and Ni(II) ions over the Freundlich isotherm model (not presented here). The values of Q^0 and b for SAG-TF membrane were higher than those of SAG-GA, SAG-UF which confirmed its stronger bonding affinity towards Cu(II) and Ni(II) ions. A large value of b also implied strong binding of Ni(II) ions to the membranes. A large value of b also implied strong binding of Ni(II) ions to the membranes. Comparing the monolayer adsorption capacity of cross-linked SAG membrane sorbents for Cu(II) and Ni(II) ions obtained in the present study with those included in Table S2 indicates that the SAG membranes show higher adsorption capacity compared with many of the adsorbents reported in literature [23–27]. These high adsorption efficiencies were attributed to the hydrophilic nature of SAG membrane matrix due to the presence of hydroxyl (–OH), amine (–NH) and carboxyl ($–COO^-$) groups, which had an adequate affinity to the metal ions.

3.5. Desorption studies and reusability of SAG membrane

Desorption of Cu(II) and Ni(II) from cross-linked SAG membranes was studied with HCl and EDTA as regenerants. When 0.01 M HCl or EDTA were used, desorption was only 60 and 72%, respectively of adsorbed ions on membranes in to the solutions. As the concentration of the regenerant increases (0.1 M), desorption increases to 80 and 94% for HCl and EDTA, respectively. When acid was used as a regenerant, the amine functional groups on the sorbents were protonated which induced the repulsive force between the adsorbed metal ions and NH_3^+ groups and hence Cu(II) and Ni(II) were released into the solution. The metal ions were released into solution in the form of soluble Cu(II) or Ni(II)-EDTA complex when EDTA was used as a regenerant. Hence, it has strong affinity for the adsorbed Cu(II) and Ni(II).

The cycle of extraction-recovery-regeneration was repeated three times. The uptake performance of regenerated sorbent was found to be close to the freshly prepared sorbents which indicate that the sorbents can be regenerated and reused, respectively for at least three times.

3.6. Comparision with literature

The adsorption capacity of the synthesized membranes for Cu(II) and Ni(II) is compared with the literature and is given in Table S3. It was reported in the literature that alginate beads and calcium alginate exhibit an adsorption capacity of 0.384 and 1.24 mM/g for Cu(II) [23], while modified chitosan and calcium alginate sorbents showed an adsorption capacity of 0.888 and 1.0184 mM/g for Ni(II) [24]. Magnetic alginate microcapsules exhibit an adsorption of 0.42 mM/g for Ni(II) [25]. Modified magnetic chitosan showed an adsorption capacity of 0.413 mM/g for Cu(II) and 0.160 mM/g for Ni(II) [26]. Cu-PVA-SA showed an uptake capacity of 0.3172 mM/g for Cu(II) [27]. Comparison indicates that SAG membranes show higher adsorption capacity compared with many of the adsorbents reported in literature. These high adsorption efficiencies were attributed to the hydrophilic nature of SAG membrane matrix due to the presence of hydroxyl (–OH), amine (–NH) and carboxyl ($–COO^-$) groups, which had an adequate affinity to the metal ions.

4. Conclusions

In this study, cross-linked SAG membranes were successfully developed with different cross-linkers such as GA, UF and TF as membrane sorbents for the removal of Cu(II) and Ni(II) ions from aqueous solutions. Cross-linking reaction was confirmed by FTIR spectroscopy and thermal stability was examined by DTA analysis. Degree of swelling experiments were performed on the membrane networks at 30°C to test their diffusion characteristics in water. Removal of Cu (II) and Ni(II) on biopolymer sorbents was maximum at pH 5.0 and 4.0, respectively. The equilibrium adsorption data were better fitted to Langmuir adsorption isotherm. The maximum monolayer adsorption capacity of SAG-GA, SAG-UF and SAG-TF was 0.42, 0.54, 0.68 mM/g for copper and 1.75, 3.23, 4.13 mM/g for nickel ions, respectively. The present membranes, being multifunctional, were able to successfully separate Cu(II) and Ni(II) metal ions from aqueous solutions when tested for feed mixtures. It may be proposed that these membranes promise to be potential sorbents for the removal of Cu(II) and Ni(II) metal ions from waste water.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.[10.1080/19443994.2016.1151380].

Acknowledgements

Authors gratefully thank the Board of Research in Nuclear Sciences (BRNS), India for financial support for this work (Grant No.: 2010/37C/53BRNS/2538, Dated 23 February 2011).

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