

Development of Thiourea-Formaldehyde Crosslinked Chitosan Membrane Networks for Separation of Cu (II) and Ni (II) Ions

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Novel chitosan (CS) based membrane networks were developed by solution casting and followed by cross-linking with different crosslinkers such as glutaraldehyde, urea-formaldehyde, and thiourea-formaldehyde. The developed membrane networks were designated as CS-GA, CS-UF and CS-TF. Crosslinking reaction of CS membranes was confirmed by Fourier transform infrared spectroscopy. Membrane rigidity and compactness were studied by the differential scanning calorimetry. The surface morphology of CS membranes was characterized by scanning electron microscopy. The sorption behaviour with respect to contact time, initial pH and initial metal ion concentration were investigated. The maximum adsorption capacity of CS-GA, CS-UF and CS-TF sorbents was found to be 1.03, 1.2 and 1.18 mM/g for Cu²⁺ and 1.48, 1.55 and 2.18 mM/g for Ni²⁺ respectively. Swelling experiments have been performed on the membrane networks at 30 °C. Desorption studies were performed in acid media and EDTA and it was found that the membranes are reusable for the metal ion removal for three cycles. The developed membranes could be successfully used for the separation of Cu²⁺ and Ni²⁺ metal ions from aqueous solutions.

Key Words : Biodegradable, Chitosan, Membrane, Crosslinker, Toxic metal ions

Introduction

Increasing economic development has been accompanied by one of the most important world problems, environmental pollution. The industrial effluents with toxic metal ions are found to be very harmful and their removal is quite essential.^{1,2} Some of the most troublesome and hazardous group of water contaminants are those of heavy metals due to their accumulation in biological systems, their persistence and their toxicity even at relatively low concentrations.³ Sources of heavy metal water contamination are varied and can be seen in every step of production from mining, purification and processing to metal finishing and electroplating, as well as possibly after their end use.^{4,5} Heavy metals are common in industrial applications such as the manufacture of pesticides, batteries, alloys, textile dyes and tanneries.⁶

Waste water treatment processes, especially from industries and ground water using biosorbents, have fascinated wide attention in recent years.⁷⁻¹⁰ With the widespread production of carbohydrates, their utilization has been increased many times as compared to the past decades. Polysaccharides like chitosan, chitin, cellulose, xanthate, pectin, starch, amylase, dextrin and cyclodextrin are used for the membrane filtration of the toxic metal ions. Among them chitosan, a copolymer of glucosamine and *n*-acetyl glucosamine units linked by 1-4 glucoside bonds, is obtained by *n*-deacetylation of chitin,

which is one of the most abundant natural amino polysaccharide, and has been reported to have a variety of applications in pharmacy industry, metal ion uptake and biotechnology.¹² Chitosan has free amino and hydroxyl sites which enhance chelating and crosslinking ability.¹¹ Cross linked chitosan derivatives still retain the advantages of chitin and chitosan, which include biocompatibility, antibacterial activity, nontoxicity, adsorptive activity.⁸⁻¹⁴ Therefore, cross linked chitosan derivatives might be good candidates for application in various biomedical fields.¹⁵ Cross-linked chitosan has the ability to form heavy metal complexes more easily than the other materials supported. Because of this property chitosan is useful as a biosorbent for heavy metal separation which is attractive compared to conventional methods like chemical precipitation and ion exchange. Modified chitosan with incorporation of functional groups offers better stability.^{16,17} New grafting materials like heparin, succinic anhydride, carboxy methyl, histidine, glutaraldehyde and epichlorohydrin, are useful for modifying chitosan.¹⁸ In view of this, the present study made an attempt to develop novel CS membrane networks for separation of Cu²⁺ and Ni²⁺. Chitosan membrane networks were crosslinked with urea-formaldehyde and thiourea-formaldehyde. A comparative account of Cu²⁺ and Ni²⁺ adsorption and efficiency of membrane have been arrived at by considering different combinations of cross linkers viz., glutaraldehyde, urea and thiourea. To the best of our know-

ledge there have been no reports on thiourea- formaldehyde crosslinked chitosan membranes.

Materials

Chitosan (CS, low molecular weight with degree of deacetylation of 84%) was purchased from Aldrich, USA. Analytical reagent grade samples of urea, thiourea, sulphuric acid, hydrochloric acid, glutaraldehyde (25% aqueous solution) (GA), acetic acid, sodium hydroxide, copper nitrate $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$, nickel ammonium sulphate $[\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ were purchased from s.d. Fine Chemicals, Mumbai, India. These chemicals were used without further purification. Throughout the experiments double distilled water was used. Cu^{2+} and Ni^{2+} solutions were prepared by dissolving accurately weighed appropriate amounts of copper nitrate and nickel ammonium sulphate in double distilled water to obtain solutions in the concentration range of 0.5-5 mM.

Preparation of CS Membrane Networks. Biodegradable chitosan membranes were prepared by solution casting technique and were cross linked with different cross linkers (glutaraldehyde, urea-formaldehyde, and thiourea-formaldehyde). In a typical synthetic procedure chitosan powder (1 g) was dispersed in 25 mL of 2% acetic acid. The polymer solution was prepared by mechanical stirring for 24 h and then poured on a clean glass plate. It was allowed to dry at room temperature for 24 h and then peeled off from the plate carefully.

Preparation of GA Cross Linked CS Membrane. The CS membrane was dipped in a mixture of 1.25 mL GA, 1.5 mL 0.1 N HCl and 50:50 ratio of acetone water mixture for 2 h to achieve cross linked CS. The membrane was washed with DD water and then dried at 40 °C for 24 h.

Preparation of UF Cross Linked CS Membrane. The CS membrane was crosslinked in a mixture of 2.5 wt % urea, 2.2 wt % formaldehyde and 2.5 wt % sulphuric acid containing 50 wt % ethanol at room temperature for 2 h. The membrane was washed and rinsed repeatedly with DD water and then dried at room temperature for 24 h.

Preparation of TF Cross Linked CS Membrane. The CS membrane was immersed in a mixture of 2.5 wt % thiourea, 2.2 wt % formaldehyde and 2.5 wt % sulphuric acid containing 50 wt % ethanol at room temperature for 2 h. The membrane was washed and rinsed repeatedly with DD water and then dried at room temperature for 24 h.

Determination of Water Sorption and Swelling of the CS Membrane Networks. The swelling studies of the membranes were performed in water and at various pH levels and extent of swelling was determined from mass measurements at 37 °C. Fully dried membranes were immersed in water and after 2 days the membranes were taken out from water carefully. Surface adhered water was removed with tissue paper. The swollen membranes were weighed and determined the % of degree of swelling using the following equation.

$$\% \text{ DS} = \frac{M_s}{M_d} \times 100 \quad (1)$$

Metal Ion Sorption Studies. The experiments were carried out by placing weighed circular pieces of membranes in 20 mL of 5 mM metal ion solution. After 2 h they were removed from the solution. Initial and equilibrium concentrations were calculated from the measured absorbance values using UV spectrophotometer. The equilibrium adsorption amount, Q_e (mM/g-dry gel) was determined as follows.

$$Q_e = (C_o - C_e)V/M \quad (2)$$

Where, C_o is the initial concentration of the metal ion solution (mM L^{-1}), V is the volume of the solution used for the adsorption (L), M is the mass of the dry membrane (g) and C_e is the concentration of the ions remaining in solution.

Characterization of CS Membrane Networks. Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer, SPEC-TRUM-2 model), Germany) analysis was performed to identify the chemical structure of the chitosan membranes. The thermal stability of the above membranes was given by DSC studies (TA instruments, Model: STA, Q600, USA). The dry membranes (coated with a thin layer of palladium gold alloy) were studied for morphological variations by using a Carl Zeiss, EVO MA 15 scanning electron microscope.

Results and Discussion

FTIR Studies. The FTIR spectrum of the CS has shown a strong peak around 3400 cm^{-1} due to the stretching vibration of O-H, the extension vibration of N-H, and intermolecular hydrogen bonds of the polysaccharide (Fig. 1(a) curve a). Peaks observed at 2845 and 2919 cm^{-1} are due to C-H stretching vibrations. A new peak appearing at 1631 cm^{-1} is due to imine bonds ($-\text{C}=\text{N}$) which were formed as a result of crosslinking reaction between amino groups in chitosan and aldehydic groups in glutaraldehyde (Fig. 1(a) curve b). However, this could be due to the overlapping of peaks corresponding to $-\text{NH}$ stretching vibrations in $-\text{NH}-\text{C}=\text{O}-\text{CH}_3$ of the original chitosan with that of $>\text{C}=\text{N}$ stretching of the newly formed Schiff base complex between $-\text{NH}_2$ group of chitosan and $-\text{CHO}$ group of glutaraldehyde. Urea-formaldehyde (Fig. 1(a) curve c) also was found to be responsible for cross-linking the $-\text{NH}_2$ groups of chitosan in the presence of sulphuric acid. The increase in intensity and the shift of bands to a higher wavenumber in the region of $1200-1500 \text{ cm}^{-1}$ are indicative of the increase in the number of $-\text{CH}_2$ groups in the cross-linked membranes. The large increase in this band is due to a large increase in the number of C-O bonds, as well as the cross-linking. A strong peak around $1120-1130 \text{ cm}^{-1}$ is assigned to the formation of ionic bond between two chitosan chain molecules. The band appeared at 702 cm^{-1} is due to C-O-S bond of the cross-linked chains, indicating the reaction between HOSO_3^- and methylolurea. And also similar results were observed for the thiourea case.

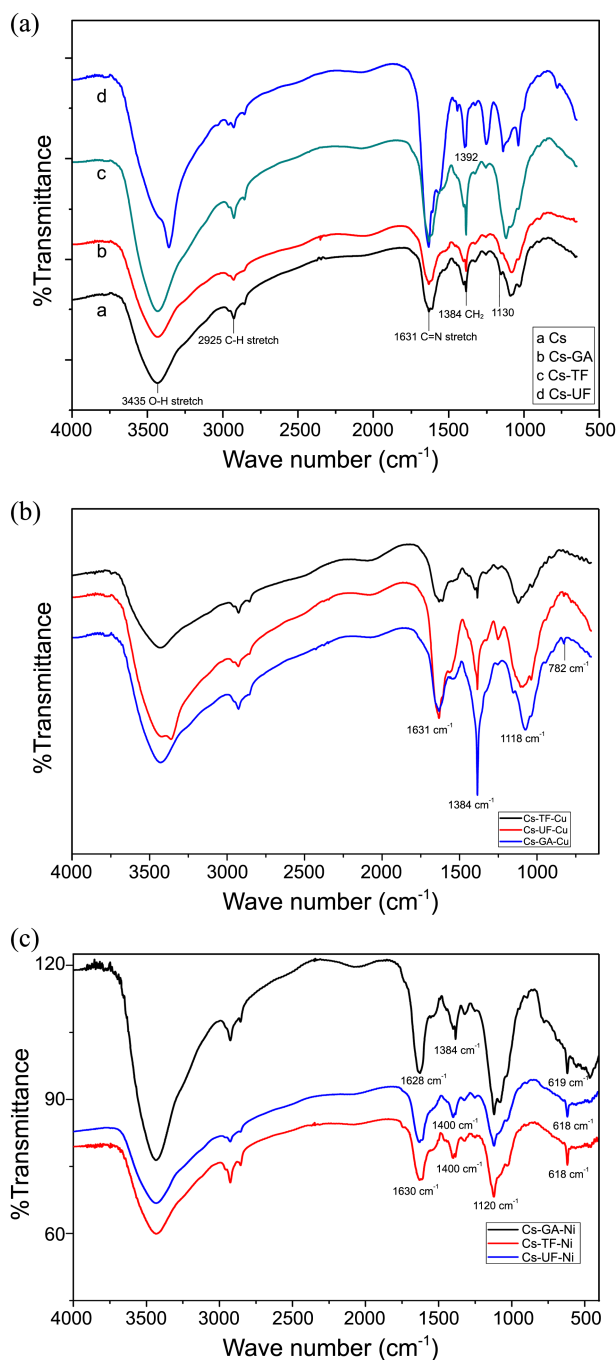
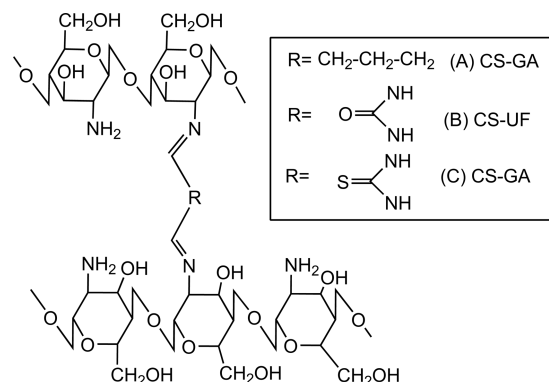


Figure 1. (a) FTIR spectra pure chitosan a) CS-GA b), CS-UF c), and d) CS-TF. (b) FTIR spectra Cu^{2+} loaded a) CS-GA b), CS-UF c), and d) CS-TF. (c) FTIR spectra Ni^{2+} loaded a) CS-GA b), CS-UF c), and d) CS-TF.

The schematic representation of crosslinking reaction is depicted in the Scheme 1.

Figure 1(b) and 1(c) shows the FTIR spectrum of cross-linked SAG membranes loaded with Cu^{2+} and Ni^{2+} ions. An interesting phenomenon is the sharp shift in the position and decrease in the intensity of the bands after metal binding. The FTIR analysis showed that the main chemical groups involved in the adsorption for membranes are -OH, -C=O, -C=S and -NH₂ groups. Shifts of the functional groups could



Scheme 1. Schematic representation of Chitosan based membrane networks.

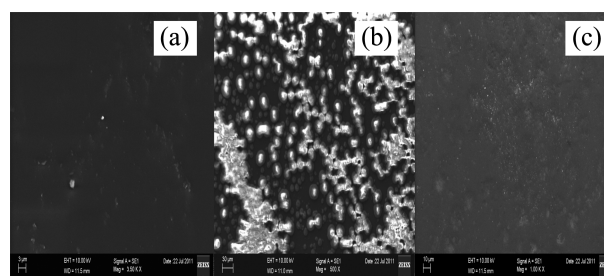


Figure 2. SEM pictures of chitosan membranes (a) CS-GA (b), CS-UF (c), CS-TF.

correspond to the complexation of these functional groups with metal ions.

SEM Studies. SEM studies (Fig. 2) revealed that the morphology of the CS membranes are having smooth and rough surface. This fact can be attributed to the smooth surface for GA grafted CS membranes and globular surface in the grafted UF, while TF showed sponge like accumulation and bears an irregular shape with rough surface. Hence, the surface evidence supports the homogeneity of the uniform grafting of GA, UF, and TF on to CS membranes.

DSC Studies. The DSC curves of the CS membrane and GA, UF and TF-grafted membranes are presented in Figure

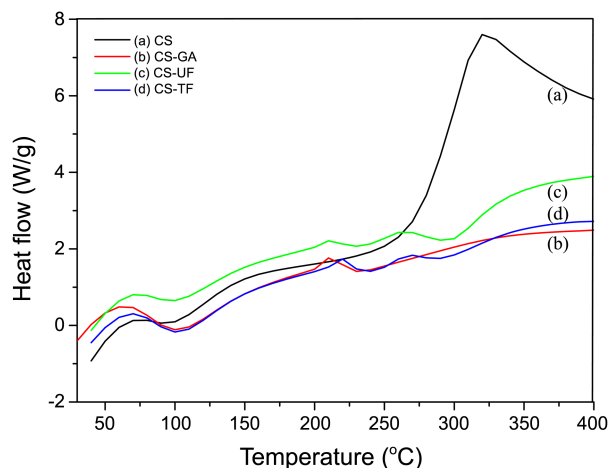


Figure 3. DSC thermograms pure chitosan (a) CS-GA (b), CS-UF (c), and (d) CS-TF.

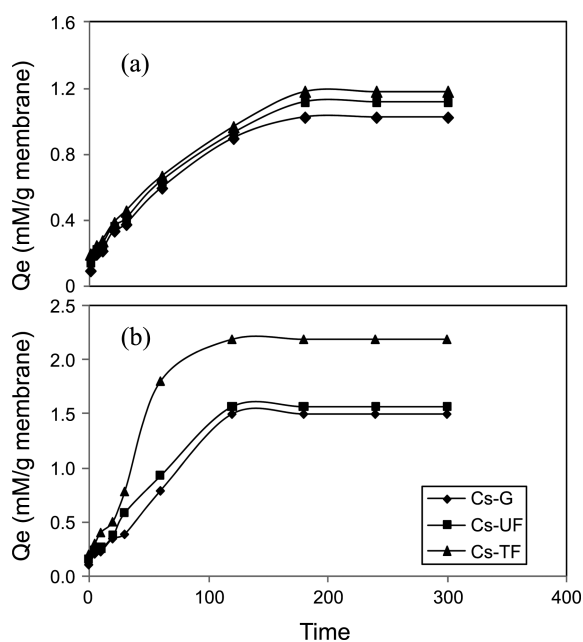


Figure 4. Effect of contact time for adsorption of Cu^{2+} (a) and Ni^{2+} (b) on CS membrane networks.

3. The grafted membranes (CS-GA, CS-UF and CS-TF) showed endothermic transitions at 230, 231 and 239 °C, respectively whereas the pure chitosan membrane exhibited an exothermic transition at 325 °C. This may be due to the interaction between the amino group of CS and aldehyde, hydroxyl groups of GA, UF and TF respectively which indicates grafting of the membranes. The endothermic transitions are increasing in the order as CS-GA < CS-UF < CS-TF and this increase indicates the increase of rigidity and compactness of the above membranes.

Swelling Studies. Degree of swelling ratio of CS membranes with different cross linking agents (CS-GA, CS-UF and CS-TF) was determined. The degree of swelling for CS-GA, CS-UF and CS-TF membranes were found to be 168.59, 196.58 and 256.53 respectively.

The swelling behaviour of CS membranes was observed as pH dependent. It could be due to the ionization/deionization of the ionisable functional groups, such as $-\text{NH}_2$ or $-\text{OH}$ (Fig. 5) present in the membranes. 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 charges repel each other, resulting in the swelling of the membrane.

Effect of pH on Metal Ion Adsorption Studies. The ionisable functional groups, such as $-\text{NH}_2$ or $-\text{OH}$, on the surface of chitosan, may gain or lose a proton, resulting in a surface charge that varies with pH (Figure 6). At low pH, surface sites are protonated and the surface becomes positively charged, while at high pH the ionisable groups lose their protons and the surface becomes negatively charged. The pH value in aqueous solution is a critical parameter affecting both the removal capacity and the removal mechanism of Cu^{2+} and Ni^{2+} ions by CS membrane with different cross linking agents (CS-GA, CS-UF and CS-TF).

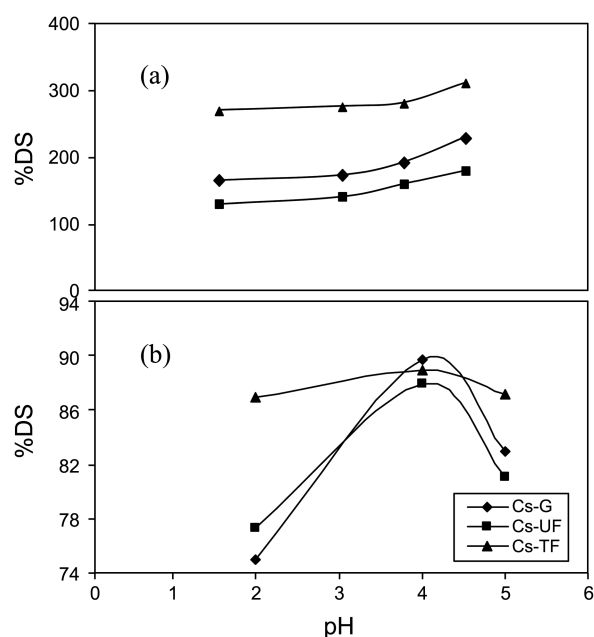


Figure 5. Effect of pH on the swelling of CS membrane networks in Cu^{2+} (a) and Ni^{2+} (b) solution.

As pH value increases (pH 2-5) its removal capacity of Cu^{2+} and Ni^{2+} by uptake also increases in all the membranes (CS-GA, CS-UF and CS-TF). In alkaline conditions, complete sorption was observed, but in this pH region the copper removal originates from precipitation ($\text{Cu}(\text{OH})_2$) rather than from sorption.¹³ The ability of a material to capture metals is controlled in part by the number of available functional groups used for binding metals. As UF crosslinked CS membranes contain accessible binding groups ($\text{C}=\text{O}$, $-\text{NH}$), the uptake capacity of Cu^{2+} increases compared to GA. In

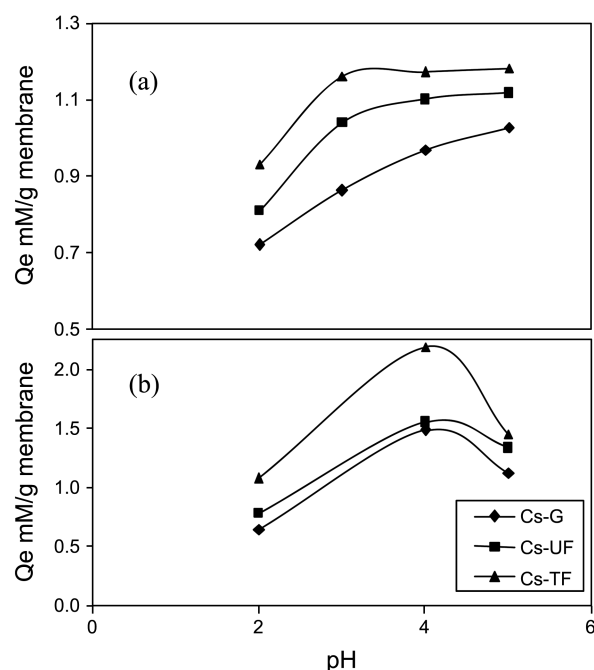


Figure 6. Effect of pH on adsorption of Cu^{2+} (a) and Ni^{2+} (b) for different cross linkers of CS membrane networks.

the case of GA cross linked membranes the metal ion absorption ability is due to presence of the primary amino and glutaraldehyde reaction (imine bond) and hydroxyl and acetyl groups are also capable to adsorb metal cations. The metal ion absorption capacity of TF crosslinked CS membranes is higher than compared to UF and GA crosslinked membranes.

Effect of Metal Ion Concentration on Metal Ion Adsorption Studies. The metal ions sorption by the membrane is a function of initial metal ion concentration. It has been measured at pH 5 for Cu^{2+} and pH 4 for Ni^{2+} and the results are shown in Figure 6. From the figure, it is clear that adsorption increased with increase in the concentration of metal ion in the feed mixture. This behavior can be explained in terms of increase in flux of the metal ion. 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.

Effect of Contact Time. Since, the adsorption process is a transfer of the metal ion from the liquid to the solid phase, the contacting time between the two phases has an effect on the mass transfer rate. Figure 4, shows the kinetics of adsorption expressed as the adsorbed quantity of copper and nickel over one gram of solid support. It is evident from the figure that adsorption was rapid initially and became slower with duration of time of contact. At the initial stages, the process of adsorption was fast due to the availability of abundant free sites near the surface where there is less hindrance for the approaching metal ions. Evidently CS-TF has higher sorption ability for the uptake of Cu^{2+} and Ni^{2+} than the other two cross linked membranes. All the materials reached saturation after 120 minutes of contact time.

The data were used to study the kinetics of adsorption of Ni^{2+} , Cu^{2+} on Cs-membranes. Kinetics of adsorption using different models was studied by many workers. The adsorption dynamics of the system were studied according to Lagergren equation.

In order to investigate the mechanism of sorption, the rate constants for the copper and nickel ions adsorption were determined by using Lagergren equation. The Lagergren first order kinetic equation is

$$dq_e = k_{ad}(q_e - q_t) \quad (3)$$

Linearised form of the above equation is

$$\log(q_e - q_t) = \log q_e - (k_{ad}/2.303) t \quad (4)$$

Where $K_{ad} (\text{min}^{-1})$ is the rate constant of adsorption, q_t and q_e are the amounts of metal ions adsorbed (mmg^{-1}) at time t and equilibrium respectively. Linear plots of $\log(q_e - q_t)$ against t gives a straight line that indicates the applicability of Lagergren equation (Fig. 8). The values of the rate constant (K_{ad}) and r^2 are presented in Table 2. From the K_{ad} values of the membranes, it can be concluded that the rate of adsorption of metal ions on Cs-TF membrane is faster than on the others. This gives us an understanding of Ni^{2+} ions 'rate constant is faster than Cu^{2+} on the developed membranes

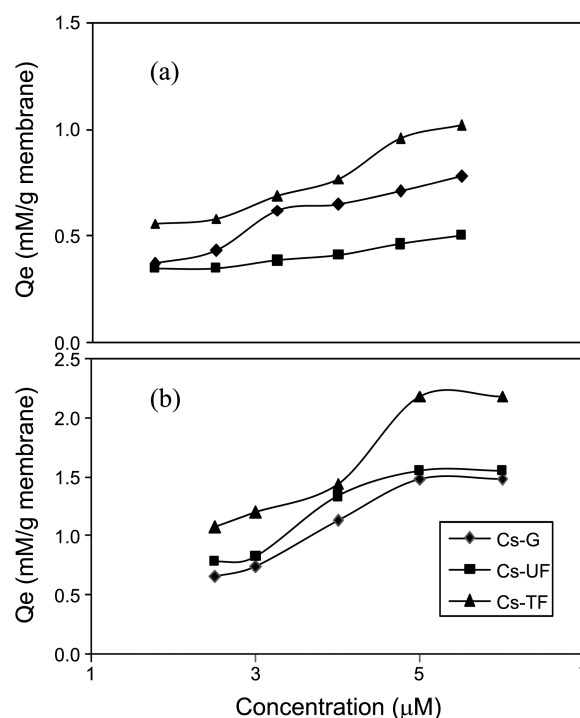


Figure 7. Effect of concentration on adsorption of Cu^{2+} (a) and Ni^{2+} (b) at pH 5 and pH 4 for CS membrane networks.

Desorption Studies of CS-GA/UF/TF. Desorption of Cu^{2+} and Ni^{2+} from crosslinked 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 is increased to 0.1 M the desorption of ions increases to 80% and 94% for HCl and EDTA respectively.

When acid is used as a regenerant, the amine functional groups of the sorbents get protonated and this induced the repulsive force between the adsorbed metal ions and NH_3^+ groups and hence Cu^{2+} and Ni^{2+} are released into the solution. However, when the complexing agent, EDTA is used as a regenerant, it showed a strong affinity for the adsorbed Cu^{2+} and Ni^{2+} . Thus the metal ions are released into solution in the form of a soluble Cu^{2+} and Ni^{2+} -EDTA Complex.

Reusability. The cycle of extraction-recovery-regeneration

Table 1. Lagergren first order rate constants for adsorption of Cu^{2+} and Ni^{2+} on CS membrane networks

Metal ion	Membrane	Langmuir constants		
		Q' (mm/g)	b (L/mg)	r^2
Cu(II)	Cs-GA	1.05	0.43	0.98
	Cs-UF	1.16	0.47	0.99
	Cs-TF	1.50	2.38	0.99
Ni(II)	Cs-GA	1.49	1.10	0.98
	Cs-UF	1.56	1.72	0.99
	Cs-TF	1.81	2.38	0.99

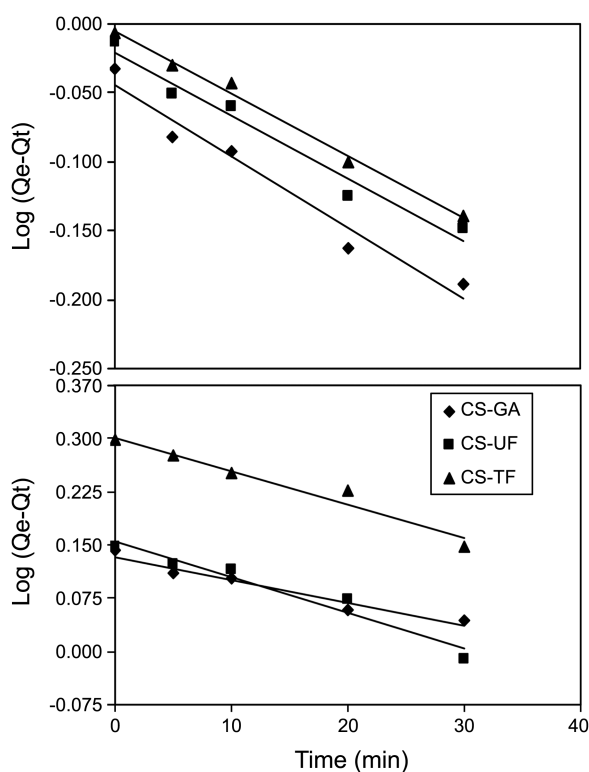


Figure 8. Lagergren plots for adsorption of Cu^{2+} (a) and Ni^{2+} (b) on CS membrane networks.

was repeated thrice. 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 atleast for three cycles.

Adsorption Isotherm. The equilibrium data were better fitted to Langmuir adsorption isotherm model. The analysis of adsorption data is important for developing an equation that accurately represents the results and that could be used for design purposes. The most widely used isotherm equation for modelling equilibrium is the Langmuir equation. In this study, we attempted to analyze adsorption at different concentrations (0.1–2.5 mM) by this model.

$$\frac{1}{Q_e} = \frac{1}{Q^0 b C_e} + \frac{1}{Q^0} \quad (5)$$

Where Q_e is the amount of metal adsorbed per unit weight of the sorbent (mg/g) and Q^0 and b are Langmuir constants indicating the maximum adsorption capacity and energy of adsorption, respectively. The linear plot of $1/C_e$ versus $1/Q_e$, with high correlation coefficient ($r^2 > 0.9$) values, indicate the applicability of Langmuir isotherm. The values of Q^0 and b were determined from the slope and intercept of linear plots and are presented in Table 1. The values of Q^0 for Cu^{2+} and for Ni^{2+} are 1.03, 1.12, 1.5 mM/g and 1.48, 1.55, 1.80 mM/g respectively. The experimental maximum adsorption capacities of the membrane were found to be 1.03, 1.12, 1.18 mM/g for Cu^{2+} and 1.48, 1.55, 2.18 mM/g for Ni^{2+} respectively (Fig. 7(a) & 7(b)). The values of Langmuir constants,

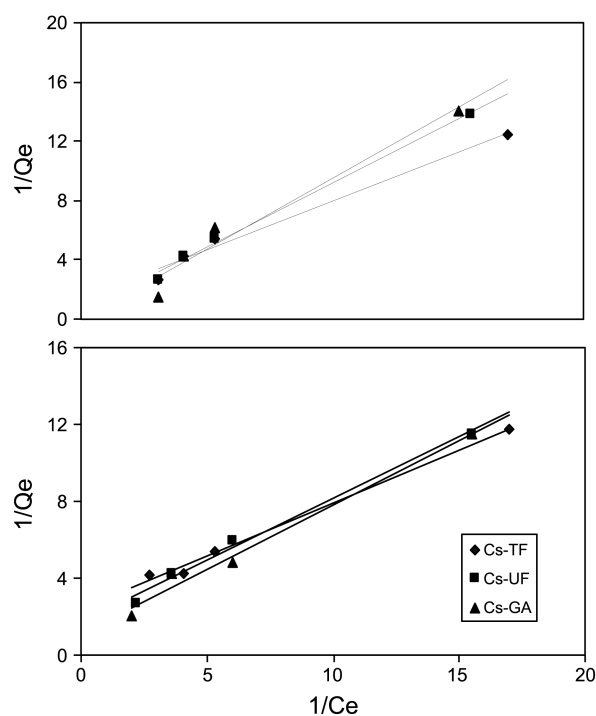


Figure 9. Langmuir isotherm for adsorption of Cu^{2+} (a) and Ni^{2+} (b) at pH 5 and pH 4 for CS membrane networks.

correlation coefficient, r^2 are given in Table 2. r^2 Values less than unity indicates favourable adsorption. Higher values of Q^0 and b for Cs-TF membrane compared to Cs-GA, Cs-UF confirm its stronger bonding affinity towards Cu^{2+} and Ni^{2+} ions. Values of Q^0 are significantly higher for Ni^{2+} compared with Cu^{2+} in all the three kinds of membranes. A large value of b also implied strong binding of Ni^{2+} to the membranes. The Langmuir model fitted better with the experimental data (Fig. 9) rather than the Freundlich model (not presented here). The adsorptive capacity of CS-GA, CS-UF and CS-TF membranes to remove Cu^{2+} and Ni^{2+} was compared with those of other adsorbents reported in the literature (Table 3).

Comparison with Literature. The present work is compared with the literature and is presented in Table 3. It was reported in the literature that epichlorohydrine cross linked xanthate shows an adsorption capacity of 0.17 mM/g Cu^{2+} ,²⁰ modified magnetic chitosan chelating resin possess an adsorption capacity of 0.41 mM/g,²¹ Cu imprinted poly(vinyl alcohol)-sodium alginate exhibit adsorption capacity of 0.32 mM/g²² and CS grafted poly(acrylamide) 0.66 mM/g²³ for

Table 2. Langmuir parameters with regression analysis of Cu^{2+} and Ni^{2+} sorption on CS membrane networks

Membrane	Concentration of Cu^{2+} solution (mM/L)		Concentration of Ni^{2+} solution (mM/L)	
	$K_{ad} (\text{min}^{-1})$	r^2	$K_{ad} (\text{min}^{-1})$	r^2
Cs-GA	1.01	0.96	1.36	0.98
Cs-UF	1.05	0.97	1.42	0.98
Cs-TF	1.10	0.98	2.04	0.99

Table 3. Comparison of the present work with literature

S.No.	Polymer	Metal [Cu ²⁺ /Ni ²⁺]	Metal uptake	Ref.
1	Epichlorohydrine cross linked xanthate CS	Cu ²⁺	0.17 mM/g	(20)
2.	Modified magnetic chitosan& calcium alginate CS coated calcium alginate CS coated silica	Ni ²⁺	1.24 mM/g 0.88 mM/g 1.018 mM/g	(19)
3	CS grafted poly(acrylic acid) CS grafted poly(acrylamide)	Cu ²⁺ Cu ²⁺	1.27 mM/g 0.66 mM/g	(23)
4	Modified magnetic chitosan Chelating resin	Cu ²⁺ Ni ²⁺	0.41 mM/g 0.160 mM/g	(21)
5	Cuimprinted polyvinyl alcohol-sodium alginate	Cu ²⁺	0.32 mM/g	(22)
6	CS-GA CS-UF CS-TF	Cu ²⁺ Cu ²⁺ Cu ²⁺	1.03 mM/g 1.12 mM/g 1.18 mM/g	Present study
7	CS-GA CS-UF CS-TF	Ni ²⁺ Ni ²⁺ Ni ²⁺	1.48 mM/g 1.55 mM/g 2.18 mM/g	

Cu²⁺ and modified magnetic chitosan-calcium alginate, CS coated calcium alginate, CS coated silica show an adsorption capacity of 1.24, 0.88, 1.018 mM/g,¹⁹ modified magnetic chitosan 0.160 mM/g for Ni²⁺²¹ respectively. The adsorption capacity values reported in the present study are considerably higher than the above values reported in the literature. The higher adsorption capacity is due to the presence of multi-functional groups, such as such as -OH, -C=O, -C=S and -NH₂, present in the membrane and it results the better chelation with the metal ions. From this observation it may be concluded that the process of modification of CS resulted in an enhancement of adsorption capacity.

Conclusions

Chitosan membrane networks were successfully developed with different cross linkers such as glutaraldehyde, urea-formaldehyde, and thio urea-formaldehyde. Chemical cross-linking reaction was confirmed by FTIR studies, rigidity and compactness of the membranes were confirmed by DSC and surface morphology of membranes was characterized by SEM. Degrees of swelling experiments have been performed on the membrane networks at 30 °C to test their diffusion characteristics in water. The adsorption equilibrium data correlate well with the Langmuir model. The adsorption of Ni²⁺ on the developed membranes is relatively more than that of Cu²⁺. This may be due to more chelation or complexation of Ni²⁺ with the groups present on the membranes. The maximum adsorption capacity of these sorbents was found to be 1.05, 1.16 and 1.50 mM/g for Cu²⁺ and 1.49, 1.56 and 1.81 mM/g for Ni²⁺ respectively. The present membranes, being multifunctional, were able to successfully separate Cu²⁺ and Ni²⁺ metal ions from aqueous solutions when tested for feed mixtures. The membranes can be reused over 3 cycles of sorption-desorption.

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