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Development of crosslinked chitosan membrane networks for uptake of copper and nickel metal ions

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ABSTRACT

Novel chitosan membranes crosslinked with glutaraldehyde, oxalic acid, and succinic acid were synthesized and analyzed as a sorbent for removing copper (Cu^{2+}) and nickel (Ni^{2+}) ions. In the present study, the sorption behavior with respect to initial metal ion concentration and contact time has been investigated. The obtained results clearly indicate that with an increase in the contact time the concentration of metal ions increases while uptake of metal ions decreases simultaneously. From the kinetic studies carried out using Langmuir isotherm model, the maximum adsorption of 0.46 and 0.99 mM/g has been observed in case of chitosan membrane crosslinked with glutaraldehyde for a contact time of 2 h for Cu^{2+} and Ni^{2+} ions respectively. However, in case of Freundlich isotherms, the Freundlich constant and relative adsorption capacity were found to be maximum in case of chitosan crosslinked with succinic acid and oxalic acid with a contact time of 6 h for Cu^{2+} and Ni^{2+} ions respectively.

Keywords: Chitosan; Membrane; Adsorption

1. Introduction

Escalating economic development is one of the major causes of environmental pollution. The traces of toxic metals in industrial effluents are a global environmental concern. Minerals mining, pigment manufacturing, painting, photographic industries, metal-working, and finishing processes are some of the foremost industrial processes liable for the excessive enrichment of metal ions concentration in wastewater. Since metals are non-biodegradable and may be bioaccumulated in living tissues, their removal is legally imposed [1,2]. Some of the heavy metals are considered as troublesome and hazardous contaminants due to their bioaccumulation, persistence, and toxic nature even at relatively lower concentrations [3]. Usually, heavy metals are used in the manufacturing processes of pesticides, batteries, alloys, textile dyes, and tanneries [4]. Nickel (Ni^{2+}) and copper (Cu^{2+}) ions are of greater concern as they get accumulated in the food chain and once adsorbed into body tissues cannot be easily excreted. The treatment of wastewater discharged from industries

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employing emerging adsorption technique has attained much significance in recent years [5].

The increased rate of production of carbohydrates has boosted its utilization. In present times, toxic metals ions are filtered by employing polysaccharides such as cellulose, chitosan, chitin, xanthate, amylase, pectin, starch, dextrin, and cyclodextrin [6]. Chitosan is a copolymer of glucosamine and n-acetyl glucosamine units linked by 1–4 glucoside bonds, obtained from n-deacetylation of chitin [7]. Chitosan and chitin have found various applications in the biomedical and environmental field, due to its widespread abundance, low toxicity, good chemical reactivity, versatile chemical, and physical properties.

For a high percentage of nitrogen (6.89%), chitin and chitosan have gained much commercial interest when compared with synthetically substituted cellulose (1.25%) [8]. The alkaline and reactive hydroxyl and amine group present in chitosan are responsible for the absorption of heavy metal ions. The proton of metal compounds is exchanged with the electrons of nitrogen. In acidic medium, the amine group is reduced that affects the binding of metal ions [9]. The weak mechanical strength and dissolubility in acidic solution are the main drawbacks of chitosan as an adsorbent [10]. The modified performance of chitosan is achieved by immobilizing chitosan on common substances with a support of commercial and appropriate materials such as Ethylenediaminetetraacetic acid, Nitrilo tri acetic acid, Amino polycarboxylic acids and Diethylenetriaminepentaacetic acid [11].

Crosslinking chitosan restricts its dissolution in acidic medium. The crosslinked beads instead of being dissolved get swell and the swelling depends upon the hydrophilicity of the matrix (hydrogels) and degree of crosslinking [12]. The swelling, therefore, increases the surface area along with the chitosan axis value. The proton and electron exchange, aforementioned, results in the protonation of the amine group, which adsorbs the positively charged metal ions through the mechanism of exchanging bonds [9]. Apart from this exchange, the H^+ atom of OH^- group of chitosan also undergoes ion exchange with the metal ion from the wastewater. This results in the metal ion-chitosan complex formation. Recently, for the adsorption of dyes and heavy metals from wastewater, chitosan composites with its lower concentrations, has been developed [13]. Variety of substances including sand, clay, polyvinyl chloride beads, and perlite are being utilized to form a composite with chitosan [14–15]. Starch-based nanocomposite was used for adsorption of mercury [16].

Several studies conducted by various investigators on chitosan-based adsorbents, related to metals removal have been studied. Mirabedini et al., [17] conducted a study on the use of modified chitosan-based derivatives and developed a magnetic chitosan hydrogel film, crosslinked with glyoxal for the removal of 80%–90% chromium. The Fourier-transform infrared spectroscopy analysis, X-ray powder diffraction and scanning electron microscopy (SEM) analysis has also been carried out in the study. Muzzarelli [18] carried out a study on the interaction of chitosan with metals and investigated the role of chitosan in uranium recovery from seawater or radioactively contaminated environment. Ngah et al., and Liu et al., [13,15] carried out a study on metal removal by using a prepared chitosan membrane.

Yong et al., and Kong et al., [19,20] carried out studies on heavy metals removal using the laboratory prepared sulfur-containing chitosan-based bio sorbents. Liao et al., [21] investigated the efficient separation of cobalt and nickel from manganese solution using a chitosan-based derivative. They also studied the competitive behavior and interaction mechanisms of chitosan membrane prepared in manganese solution. Albadarin et al., [22] fabricated an activated lignin-chitosan for adsorption of methylene blue. Esmaeili and Beni [23] designed a continuous biosorption process employing brown algae and chitosan. The researchers studied membrane behavior by varying adsorption dose with respect to pH and time and observed the ions removal efficiency of 97% and 96% at pH 6.8 and 6.9 respectively [23].

Crosslinked chitosan retains the advantages of chitin and chitosan which includes biocompatibility, antibacterial activity, nontoxicity, and adsorptive activity [6,7,24,25]. Therefore, crosslinked chitosan derivative may be a suitable candidate for application in various biochemical fields [26]. The ease information of heavy metal complexes offered by crosslinked chitosan turns it into useful bio sorbent for heavy metal separation over conventional methods of chemical precipitation and ion exchange process. Modified chitosan with the incorporation of functional groups offers better stability [27,28]. New grafting materials like heparin, succinic anhydride, carboxymethyl, histidine, glutaraldehyde, and epichlorohydrin are useful for modifying chitosan [29]. Sharma et al., [30] prepared a chitosan-crosslinked-poly nanohydrogel for adsorptive removal of chromium metal. Considering the earlier-mentioned facts in view a study was being planned with the objectives to develop a novel chitosan membrane networks crosslinked with glutaraldehyde, oxalic acid, and succinic acid for separation and removal of Cu^{2+} and Ni^{2+} ions from their respective solutions and the removal efficiency for the same has been measured and compared.

2. Material and methods

Chitosan (low molecular weight with a degree of deacetylation of 84%) was purchased from high media chemicals. During the experimental study, high-grade reagent water (Millipore-Merck make (Milli-Q@Direct)) was used and chitosan crosslinked with glutaraldehyde, oxalic acid, and succinic acid as crosslinkers. All the chemicals of AR grade of Himedia made with highest purity were used. The chitosan crosslinked preparation is mentioned below as:

2.1. Preparation of chitosan solution

Biodegradable chitosan membranes were prepared by solution casting technique. In a typical synthetic procedure, chitosan powder of 2 g weight was dissolved in 100 mL of 2% acetic acid solution.

2.2. Preparation of crosslinked chitosan membrane

Samples were prepared by adding glutaraldehyde, oxalic acid, and succinic acid in four distinct concentrations of 1, 2, 3, and 4mL to the 20 mL chitosan solution to obtain chitosan films of diversified properties. The molecular weight of chitosan membrane ranges from 180–300 kDa. The polymer solution was being stirred mechanically for 24 h and poured on a clean glass plate. The solution was left for 24 h at room temperature to dry and the synthesized membrane was then peeled off from the plate carefully.

2.3. Substrate analysis

Copper chloride and nickel sulphate have been used for metal ion sorption study. In order to prepare a calibration curve in terms of concentration vs. absorbance for copper chloride and nickel sulphate the standards ranging from 1 to 5 mM were prepared accordingly. The absorbance values for the same were measured using spectrophotometer (HACH DR 5000, New Delhi) at a wavelength of 600 nm. However, the SEM analysis of the prepared membranes of pure chitosan film and chitosan crosslinked with various crosslinkers were carried out by using Carl Zeiss, EVO MA 15 scanning electron microscope. For performing SEM studies, the sample preparation was carried out as per the standard method FEI [31].

2.4. Adsorption studies

The swelling studies of the membranes have been carried out in water and at various pH values of 1.0, 1.5, 2.0, 3.5, 4.5, 5.5, 6.0, 7.4, 8.5, and 9.0. The extent of swelling was being determined from mass measurements at 37°C [29]. Fully dried membranes were immersed in distilled water for two days and thereafter the membranes were carefully taken out. The swollen membranes were weighed and the percentage degree of swollen has been estimated using Eq. (1).

$$\% DS = \left(\frac{M_s}{M_d}\right) \times 100 \tag{1}$$

where M_S = mass of swelled membrane (g) and M_d = mass of dry membrane (g)

Initial and equilibrium concentrations were calculated from the measured absorbance values using UV-1650pc, UV-VIS spectrophotometer SHIMADZU (New Delhi) at 530 nm. The equilibrium adsorption concentration in terms of Qe (mM/g) was determined using Eq. (2) as:

$$Q_e = \frac{\left(C_o - C_e\right)V}{M} \tag{2}$$

where C_o is the initial concentration of the metal ion solution (mM/L), 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 the solution (mM/L).

3. Results and discussion

3.1. Effect of swelling

The percentage degree of swelling of chitosan membrane crosslinked with glutaraldehyde, oxalic acid, and succinic acid films at pH 7.4 for 6 h has been evaluated and presented through Fig. 1. The hydrophilic matrices of chitosan crosslinked with glutaraldehyde, succinic acid, and oxalic acid restrict the dissolution of chitosan, but swelling takes place [12]. It has also been reported that the degree of swelling for all crosslinked membranes increases up to 3 mL concentration until it reaches the equilibrium state [5]. In the case of glutaraldehyde and oxalic acid, it has been observed that the degree of swelling increased further. However, in the case of succinic acid, an early equilibrium state has been observed that resulted in a decrease of swelling degree. It has been reported that the crosslinking causes limited swelling due to the chain mobility restrictions [29]. However, in the present study, the maximum degree of swelling has been found to be 55% at 4 mL glutaraldehyde concentration. The results are analogous to the previous studies [32].

3.2. Effect of metal ion concentration on metal ion adsorption studies

The metal ion concentration is a function of the adsorption concentration by the membrane. It has been observed that with an increase in the concentration of the metal ions the adsorption capacity of the membrane also increases for both copper chloride and nickel sulphate.

3.3. Scanning electron microscopy studies

SEM revealed that the morphology of the chitosan membranes is having a smooth, homogeneous, and rough surface. While performing SEM studies sample preparation was being carried out as per standard method [33]. The pure chitosan membrane confirms a smooth surface while the chitosan membrane crosslinked with glutaraldehyde showing smooth and homogenous surface. However, chitosan membrane crosslinked with oxalic acid confirms homogenous and rough surface and the chitosan membrane crosslinked with succinic acid shows globular and rough surface as shown in Figs. 2(a)–(d).

3.4. Metal ion sorption studies

The remaining concentration of copper chloride ion in the solution after chitosan film crosslinked with glutaraldehyde, oxalic acid, and succinic acid dipped for a period 2, 4 , and 6 h have been assessed and summarized in Table 1. The oxalic acid and succinic acid are dicarboxylic acids; glutaraldehyde is an aldehyde. The carboxylic

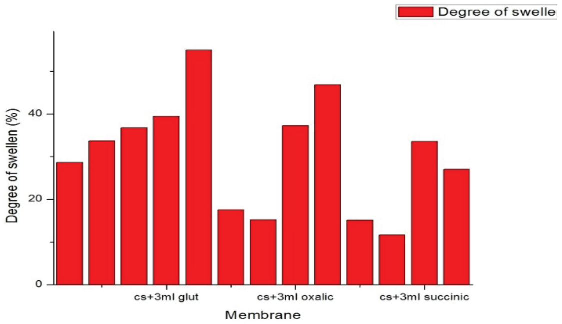


Fig. 1. Degree of swelling for various chitosan crosslinked membranes at pH 7.4 for 6 h.

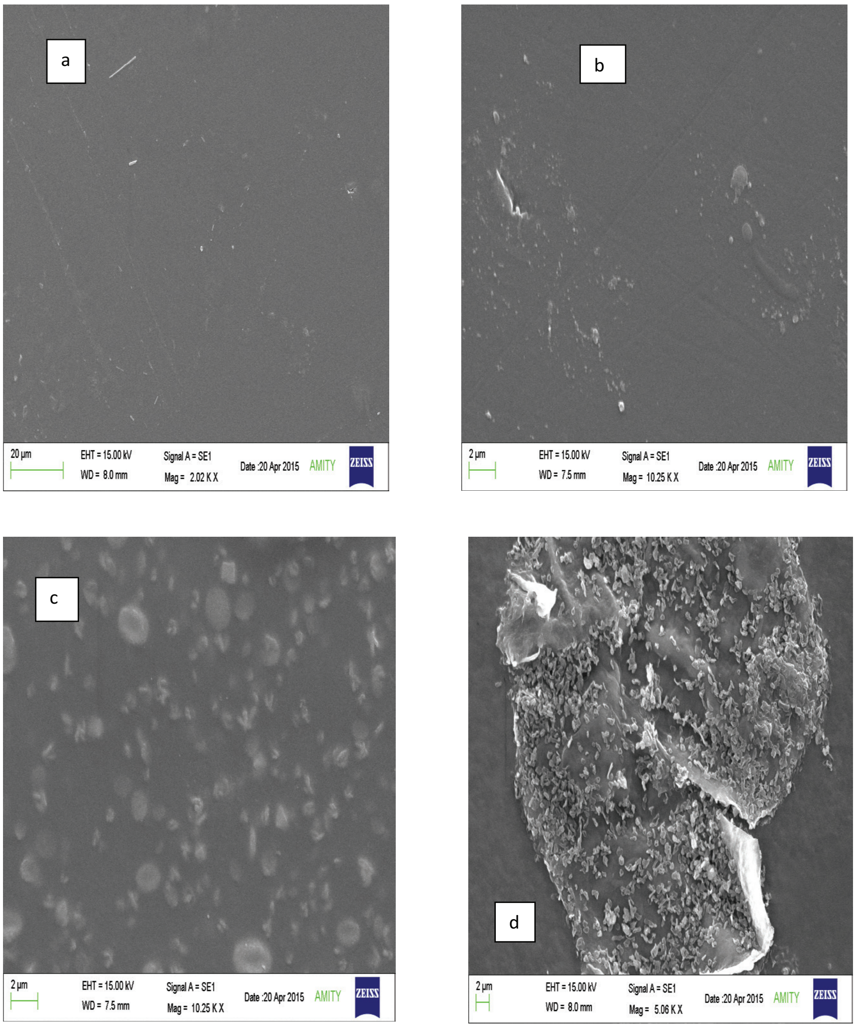


Fig. 2. SEM pictures of chitosan membranes (a) pure (b) linked with glutaraldehyde (c) linked with oxalic acid (d) linked with succinic acid.

group of oxalic acid and succinic acid combined with the amide group of chitosan provides more adsorption sites for heavy metal ions [12]. Imine or Schiff base adducts are produced when carbonyl group of glutaraldehyde reacts with a primary amino group of chitosan. The produced Schiff base adducts enclose carbon-nitrogen double bond. Afterward, a complex mechanism involving aldol condensation occur which results in the generation of different oligomer products. Further polymerization leads to the formation of the gel [29].

Concentration values were determined and thus can be fitted in earlier-mentioned Eq. (2). The concentration of Cu^{2+} or Ni^{2+} ions remaining and concentration of Cu^{2+} or Ni^{2+} ions uptake by chitosan has been illustrated in Figs. 3 and 4 respectively. The metal ion uptake of chitosan film crosslinked with glutaraldehyde, oxalic acid, and succinic acid has been evaluated by using Eq. (1) and the same have been tabulated in Table 1. It can be inferred that the concentration of ions in solution is increasing with increase in time while metal ion uptake for the same decreases with increase in time. Metal ion uptake was found to be maximum after a period of 2 h in both copper chloride and nickel sulphate solutions. The metal ion uptake depends on the initial concentration present in the solution, the nature of the prepared material and on the type of metal cations [34]. Maximum metal ion uptake and metal removal efficiency for a copper chloride solution has been found for chitosan membrane linked with glutaraldehyde for 2 h duration, which is 1.108 mM/g and 33.19% (Fig. 3(a)), respectively.

The hydroxyl and amine groups of chitosan act as a chelation site for Cu^{2+} ions. However, in case of nickel sulphate solution, maximum metal uptake, and metal removal efficiency were found for chitosan membrane linked with succinic acid for 2 h duration which is 1.552 mM/g and 58.08% (Fig. 4(c)), respectively. The crosslinked chitosan with glutaraldehyde was found effective for Cu^{2+} ions and chitosan crosslinked with succinic acid was found efficient in the adsorption of Ni^{2+} ions. The metal removal efficiency offered by glutaraldehyde is low as compared with succinic acid, due to the dominating covalent interactions, which does not allow the matrix to gain the desired mechanical strength [35]. On the other hand, succinic acid is advantageous over the glutaraldehyde, as it is nontoxic, bioavailable, and it shows appreciable mechanical strength [35].

Table 1
Concentration of ion remaining in solution dipped with and concentration of metal ion uptake by Chitosan film crosslinked with Glutaraldehyde, Oxalic acid, and Succinic acid

Synthetic solution	Film type	Concentration of ion remaining in solution (mM/L)			Concentration of metal ion uptake (mM/L)		
		2 h	4 h	6 h	2 h	4 h	6 h
$CuCl_2$	Chitosan+1 mL glutaraldehyde	2.4	3.59	3.68	1.04	0.564	0.528
	Chitosan+2 mL glutaraldehyde	2.47	3.62	3.89	1.012	0.552	0.444
	Chitosan+3 mL glutaraldehyde	3.05	4.36	4.52	0.78	0.256	0.192
	Chitosan+4 mL glutaraldehyde	2.23	3.73	3.94	1.108	0.508	0.424
$NiSO_4$	Chitosan+1 mL glutaraldehyde	1.31	2.61	2.77	1.476	0.956	0.892
	Chitosan+2 mL glutaraldehyde	1.36	1.56	1.84	1.456	1.376	1.264
	Chitosan+3 mL glutaraldehyde	2.03	2.56	2.71	1.188	0.976	0.516
	Chitosan+4 mL glutaraldehyde	1.34	1.72	2.17	1.464	1.312	1.132
$CuCl_2$	Chitosan+1 mL oxalic acid	3.98	4.16	4.43	0.408	0.336	0.228
	Chitosan+2 mL oxalic acid	4.47	4.49	4.67	0.212	0.204	0.132
	Chitosan+3 mL oxalic acid	3.52	3.87	4.24	0.592	0.452	0.304
	Chitosan+4 mL oxalic acid	2.98	3.17	3.39	0.808	0.732	0.644
$NiSO_4$	Chitosan+1 mL oxalic acid	1.87	2.13	2.47	1.252	1.148	1.012
	Chitosan+2 mL oxalic acid	2.09	2.32	2.9	1.164	1.072	0.84
	Chitosan+3 mL oxalic acid	1.57	2.52	2.85	1.372	0.992	0.86
	Chitosan+4 mL oxalic acid	1.02	1.94	2.42	1.592	1.224	1.032
$CuCl_2$	Chitosan+1 mL succinic acid	3.46	4.24	4.68	0.616	0.304	0.128
	Chitosan+2 mL succinic acid	3.81	3.95	4.42	0.476	0.42	0.232
	Chitosan+3 mL succinic acid	3.55	4.11	4.57	0.58	0.356	0.172
	Chitosan+4 mL succinic acid	3.16	3.24	3.75	0.736	0.704	0.5
$NiSO_4$	Chitosan+1 mL succinic acid	2.92	3.01	3.34	0.832	0.796	0.664
	Chitosan+2 mL succinic acid	1.12	1.32	1.58	1.552	1.472	1.368
	Chitosan+3 mL succinic acid	1.73	2.28	3.56	1.308	0.688	0.576
	Chitosan+4 mL succinic acid	2.75	3.34	3.82	0.9	0.664	0.472

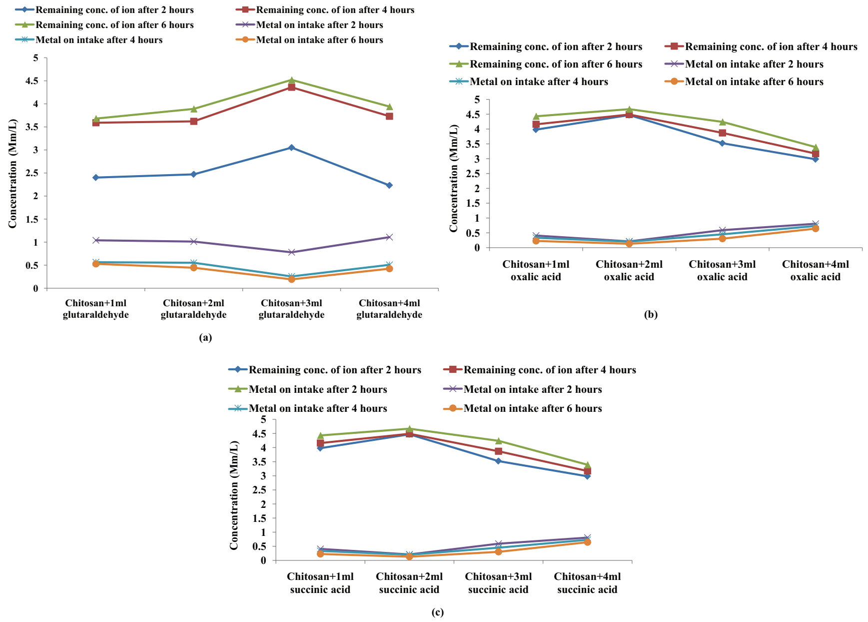


Fig. 3. (a)–(c) Concentration of Cu^{2+} remaining and concentration of Cu^{2+} uptake by chitosan film cross linked with (a) Glutaraldehyde (b) Oxalic acid (c) Succinic acid.

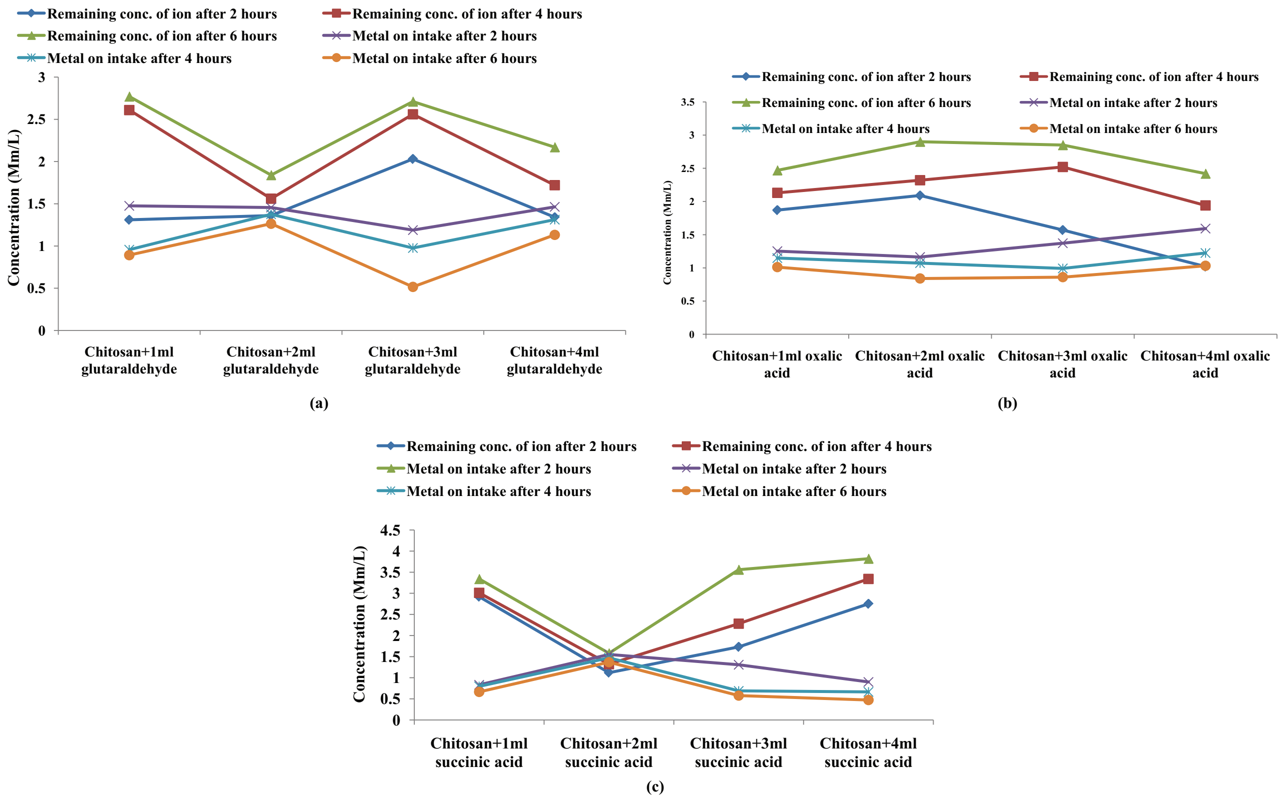


Fig. 4. Concentration of Ni^{2+} remaining and concentration of Ni^{2+} uptake by chitosan film cross linked with (a) glutaraldehyde. (b) oxalic acid (c) succinic acid.

3.5. Kinetic studies using adsorption isotherms

For determining the amount of metals adsorption onto the adsorbent, the two mainly accepted equations are Langmuir and Freundlich isotherms [36,37].

Langmuir isotherm can be expressed as Eq. (3): [38]

$$\frac{1}{Q_e} = \frac{1}{Q_{\max}} + \frac{1}{bQ_{\max}C_e} \tag{3}$$

where C_e is the equilibrium concentration of metal ion (mM/L), Q_e is the amount adsorbed (mM/g), $Q_{\max}$ is the maximum amount of adsorbed metal ion/unit mass of adsorbent corresponding to complete coverage of the adsorption sites and b is the Langmuir constant (L/mM) which is the adsorption equilibrium constant that relates to the energy of adsorption [33,35]. The graph is plotted between $1/C_e$ and $1/Q_e$.

Freundlich isotherm can be expressed by Eq. (4): [39]

$$\log Q_e = \log K_f + \frac{1}{n \log C_e} \tag{4}$$

where C_e is the equilibrium concentration of metal ion (mM/L), Q_e is the amount of metal ion/unit mass of the adsorbent (mM/g), K_f is the Freundlich constant (mM/L) defining the adsorption coefficient that specifies the relative adsorption capacity of the adsorbent bonding energy, n is the Freundlich equation exponential that represents quasi-Gaussian energetic heterogeneity of the adsorption surface [33]. From the plotted graph in between $\log Q_e$ vs. $\log C_e$, are the coefficient values can be calculated, where K_f is the intercept of the graph and n^{-1} is the slope of the graph. The coefficient of correlation (R^2) provides the best fit for adsorption of Cu^{2+} and Ni^{2+} ions and is obtained from Langmuir and Freundlich isotherms. The values obtained under different dosing has been evaluated using both the models and is summarized in Tables 2 and 3. The Langmuir and Freundlich isotherms have been presented through Figs. 5 and 6 respectively.

From the present study using Langmuir isotherm model, the $Q_{\max}$ is the highest value of 0.46 mM/g and 0.99 mM/g has been observed in case of Cu^{2+} and Ni^{2+} ions adsorption using chitosan membrane crosslinked with glutaraldehyde for a contact time of 2 h. However, the R^2 value for the same has been observed to be 0.96 and 0.74 respectively. The b value for the same has been found to be –0.72 and –2.1 L/mM respectively. The negative value of Langmuir constant (b) for Cu^{2+} and Ni^{2+} ions indicates separation factor (R_L) value more than 1 indicating the decrease in adsorption of Cu^{2+} and Ni^{2+} on chitosan membrane crosslinked with glutaraldehyde. It may be due to the increase in copper and nickel ionic radius, decrease in charge density due to which the adsorption capacity of crosslinked chitosan membrane decreases for copper and nickel ions.

From the data analysis using Freundlich isotherm model, it can be observed that the K^f value of 28.0 L/Mm is the highest in case of Cu^{2+} adsorption using chitosan membrane

Table 2
Langmuir isotherm constants for sample adsorption of Cu^{2+} and Ni^{2+} using chitosan crosslinked with glutaraldehyde, oxalic acid, and succinic acid for contact time 2, 4, and 6 h

Membrane	2 h					4 h					6 h				
	C_e	Q_e	Q_{max}	B	R^2	C_e	Q_e	Q_{max}	B	R^2	C_e	Q_e	Q_{max}	B	R^2
Copper															
Chitosan+ Glutaralde-hyde	2.54	1.04	0.46	–0.72	0.96	3.82	0.5	0.09	–0.32	0.95	4.01	0.42	0.05	–0.29	0.91
Chitosan+ oxalic acid	3.74	0.54	0.09	–0.36	0.81	3.92	0.46	0.09	–0.34	0.8	4.18	0.35	0.05	–0.3	0.74
Chitosan+ succinic acid	3.49	0.64	0.17	–0.36	0.95	3.88	0.48	0.11	–0.4	0.89	4.35	0.28	0.04	–0.28	0.81
Nickel															
Chitosan+ Glutaraldehyde	1.51	1.48	0.99	–2.1	0.74	2.11	1.23	0.66	–1.13	0.89	2.37	1.18	0.57	–0.92	0.82
Chitosan+ oxalic acid	1.64	1.43	0.93	–1.98	0.92	2.23	1.78	0.62	–0.97	0.84	2.66	0.99	0.45	–0.69	0.82
Chitosan+ succinic acid	2.13	1.22	0.72	–1.49	0.77	2.49	1.06	0.6	–1.18	0.82	3.07	0.81	0.41	–0.88	0.95

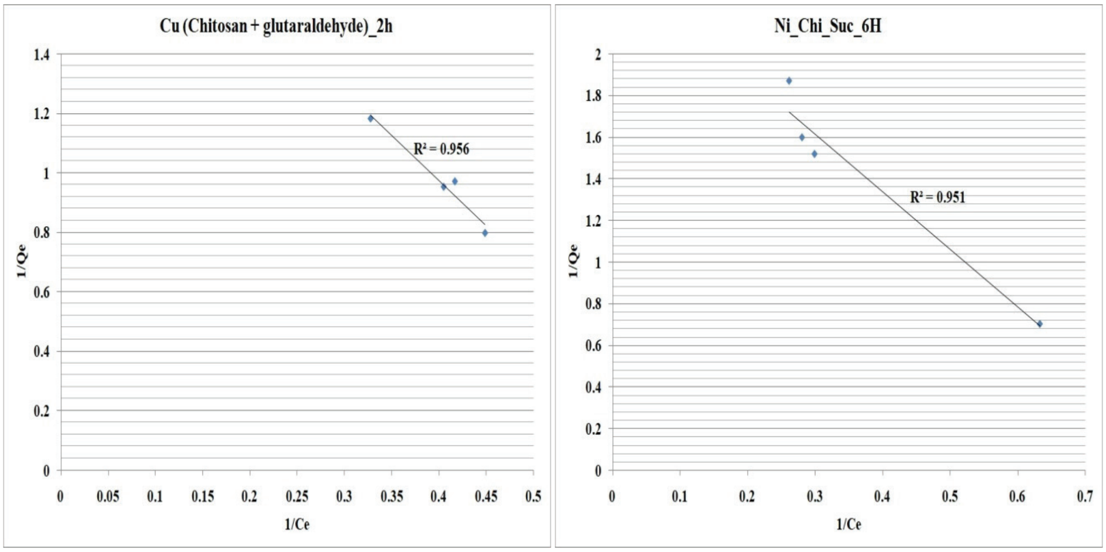
Table 3
Freundlich isotherm constants for sample adsorption of Cu^{2+} and Ni^{2+} using chitosan crosslinked with glutaraldehyde, oxalic acid, and succinic acid for a contact time duration of 2, 4, and 6 h

Membrane	2 h					4 h					6 h				
	C_e	Q_e	K_f	N	R^2	C_e	Q_e	K_f	n	R^2	C_e	Q_e	K_f	N	R^2
Copper															
Chitosan+ glutaralde-hyde	2.53	1.05	1.61	–0.87	0.91	3.82	0.5	6.82	–0.26	0.96	4.01	0.42	11.6	–0.21	0.94
Chitosan+ oxalic acid	3.74	0.54	5.22	0.29	0.96	3.92	0.46	6.35	–0.26	0.95	4.18	0.35	11.7	0.21	0.94
Chitosan+ succinic acid	3.49	0.64	3.59	–0.38	0.96	3.88	0.48	5.10	–0.29	0.97	4.35	0.28	28.0	–0.16	0.96
Nickel															
Chitosan+ glutaralde-hyde	1.51	1.48	1.27	–2.39	0.71	2.11	1.23	1.39	–1.25	0.92	2.37	1.18	1.47	–1.07	0.87
Chitosan+ oxalic acid	1.64	1.43	1.33	–1.73	0.97	2.23	1.78	1.47	–1.1	0.8	2.66	0.99	1.64	–0.84	0.8
Chitosan+ succinic acid	2.13	1.22	1.3	–1.55	0.90	2.49	1.06	1.35	–1.27	0.93	3.07	0.81	1.44	–0.94	0.99

crosslinked with succinic acid for a contact time of 6 h. However, the value of n and R^2 has been found to be –0.16 and 0.96 respectively. In the case of Ni^{2+} ions adsorption, the K_f value of 1.64 L/mM has been obtained using chitosan membrane crosslinked with oxalic acid. However, the value of n and R^2 has been found to be 0.84 and 0.80 respectively. The negative n value in case of Cu^{2+} adsorption carried out using chitosan membrane crosslinked with succinic acid for a contact time of 6 h indicates the poor sorption. The result can be analogous to the previous studies of Villaescusa et al., Ulucan-Altuntas et al., and Barquilha et al., [40–42].

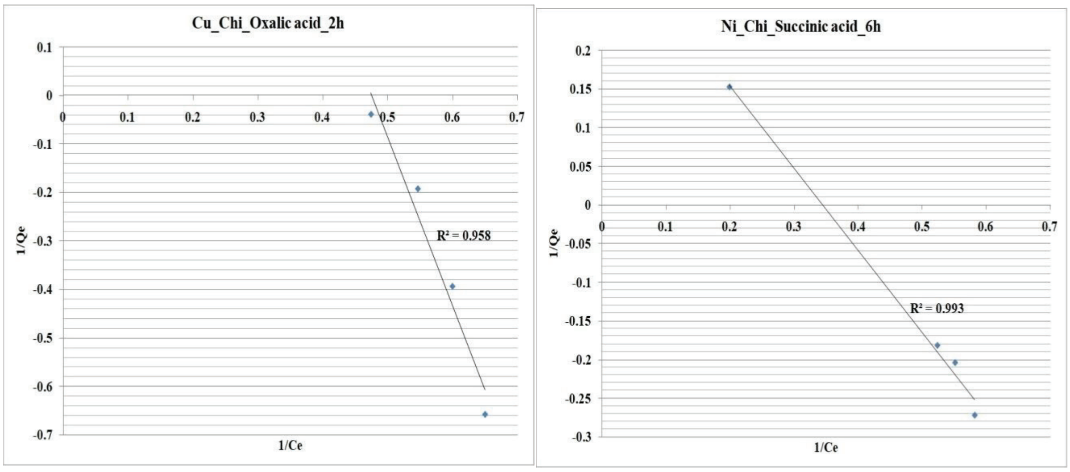
4. Conclusion

Chitosan membrane networks have been successfully developed with crosslinker glutaraldehyde, oxalic acid, and succinic acid. The adsorption of Ni^{2+} ions on the developed membranes is relatively more than that of Cu^{2+} ions. This may be due to the chelation or complexation of Ni^{2+} ions with the groups present in the membranes. Cu^{2+} ions uptake has been found to be maximum in case of glutaraldehyde whereas Ni^{2+} ions uptake and was maximum in case of succinic acid. The study further reveals the fact that the metal ion uptake



(a) (b)

Fig. 5. Langmuir isotherm model for adsorption of Cu^{2+} and Ni^{2+} using chitosan crosslinked with (a) glutaraldehyde for contact time 2 h (b) succinic acid for a contact time of 6 h.



(a) (b)

Fig. 6. Freundlich isotherm model for adsorption of Cu^{2+} and Ni^{2+} using chitosan crosslinked with (a) oxalic acid for contact time of 2 h (b) succinic acid for a contact time of 6 h.

decreases with an increase in time and the peak value of the adsorption has been observed in the initial 2 h phase both for Cu^{2+} and Ni^{2+} ions.

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