

Adsorptive Removal of Copper and Nickel Ions from Aqueous using Chitosan-g-Poly(Acrylic Acid)/Polyaniline Membrane

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ABSTRACT

The present work reports the development of new chitosan-based membrane by grafting with poly(acrylic acid) and polyaniline by free radical polymerization using ammonium persulfate. Grafting reaction of chitosan-g-poly(acrylic acid)-co-polyaniline (CPANI) was confirmed by Fourier-transform infrared spectroscopy, surface morphology of membranes was characterized by scanning electron microscopy. The influence of various experimental conditions such as pH, time, and initial feed concentrations on the uptake of Cu^{2+} and Ni^{2+} by CPANI membrane was tested. The optimum pH was found to be 5.0. It was seen that the adsorption equilibrium data could be fitted to the Langmuir isotherm. Desorption studies were performed in acid media and ethylenediaminetetraacetic acid, to examine whether the CPANI membrane can be recycled for the metal ion removal. The results showed that with CPANI membrane, the maximum metal ion uptake achieved is 1.01 mM g^{-1} for Cu^{2+} and 2.41 mM g^{-1} for Ni^{2+} , respectively. Metal ion sorption studies showed that the membrane can be used for the removal of hazardous metal ions from aqueous solutions. The copper and nickel uptake achieved suggests the potential use of the membrane to extract divalent toxic metals from industrial aqueous streams.

Key words: Chitosan, Copper, Membrane, Nickel, Poly(Acrylic acid), Polyaniline.

1. INTRODUCTION

It is found that the industrial effluents containing toxic metal ions are very harmful and their removal is quite essential [1,2]. Toxic heavy metals such as Hg, Pb, Ag, Cu, Ni, and As are considered to be one of the most troublesome and hazardous groups of water contaminants due to their accumulation in biological systems and its toxicity even in low concentrations levels [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, and even in the end use [4,5]. Precipitation, redox reactions, ion exchange, filtration, reverse osmosis, electrochemical removal, and evaporative recovery methods have limitations for toxic metal contaminants present at trace levels [6-10]. Treatment processes of industrial effluents and groundwater using sorbents have attracted wide attention in recent years [11,12]. The use of novel polymeric materials for removing and separating toxic heavy metal ions through complexation and ion-exchange mechanism has been increased. Metal ion chelating polymers called polychelators, contain one or more electron donor atoms such as N, S, O, and P that can form coordinate bonds with most of the toxic heavy metals [13,14].

Biopolymers are non-toxic, selective, efficient, and inexpensive and thus highly competitive with ion-exchange resins and activated carbon [15-18]. Biopolymers such as chitosan, sodium alginate extracted from microalgae [19], shrimp, crab, and some fungi [20,21] are known to bind metal ions strongly and could be used for toxic metal adsorption. Among them, chitosan, a copolymer of glucosamine and N-acetyl glucosamine units linked by 1-4- α -D glucoside bonds, is obtained by N-deacetylation of chitin, which is one of the most abundant natural aminopolysaccharides, and has been reported to have a variety of applications in pharmacy industry, metal ion uptake, and biotechnology [22]. Chitosan has free amino and hydroxyl sites which

enhance chelating and crosslinking ability [23]. Modified chitosan has the ability to form heavy metal complexes more easily than the other materials supported. Due to this property, chitosan is useful as a biosorbent for heavy metal separation which is attractive compared to conventional methods such as chemical precipitation and ion exchange. Modified chitosan with incorporation of functional groups offers better stability [24,25]. New grafting materials such as heparin, succinic anhydride, carboxymethyl, histidine, glutaraldehyde, and epichlorohydrin are useful for modifying chitosan [26]. In the present study, PANI has been grafted on to chitosan. Polyaniline/poly(vinyl alcohol)/clinoptilolite nanocomposite was used as membrane for removal of methylene blue [27]. Poly(methyl methacrylate-co-ethyl acrylate) and poly(methyl methacrylate-co-butyl methacrylate) copolymers were used for adsorption of Fe^{3+} , Cu^{2+} , and Co^{2+} ions from aqueous solution [28].

In this study, membranes through the grafting of poly(acrylic acid) and polyaniline were prepared by free radical polymerization using ammonium persulfate (APS). We used chitosan grafted with poly(acrylic acid) and polyaniline for metal extraction. Cu^{2+} and Ni^{2+} adsorption and efficiency of synthesized membrane are determined. The influence of treatment time, pH, and the initial feed concentration on the amount of the metal ions removed was investigated. Desorption and reusability were also examined.

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2. MATERIALS AND METHODS

Chitosan (CS, low-molecular-weight with degree of deacetylation of 84%) was purchased from Aldrich, USA. Analytical reagent grade samples of hydrochloric acid (HCl), acetic acid, sodium hydroxide, APS, acrylic acid and copper nitrate $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$, and nickel ammonium sulfate $[\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ 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 sulfate in double-distilled water to obtain solutions in the concentration range of 0.5–5 mM.

2.1. Preparation of Chitosan-g-Poly(Acrylic Acid)-co-Polyaniline (CPANI) Membranes

CPANI membranes were prepared by solution casting technique and followed by grafting. In a typical synthesis 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.

The CS membrane was immersed in a mixture of 0.5 mL aniline dissolved in 50 mL HCl (1M). To this 0.2 mL acrylic acid, 1.414 g of APS is added at room temperature and stirred for 1 h. The CPANI membrane was washed and rinsed repeatedly with double distilled and then dried at room temperature for 24 h.

2.2. Determination of Water Sorption and Swelling of the CPANI Membranes

The swelling studies of the CPANI membranes were performed in water and at various pH levels and extent of swelling as 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 (DS) using equation.

$$\% \text{DS} = \frac{M_s}{M_d} \times 100$$

2.3. Preparation of Cu^{2+} and Ni^{2+} Solutions for CPANI Membranes

Cu^{2+} and Ni^{2+} solutions were prepared by adding appropriate amounts of copper nitrate $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$ and nickel ammonium sulfate $[\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ to aqueous solution to obtain solutions in the concentration of 0.5–5 mM.

3. RESULTS AND DISCUSSION

3.1. Fourier Transforms Infrared Spectroscopy (FTIR) Studies

FTIR spectra C-g-PANI (Figure 1) showed characteristic peaks of PANI as well as chitosan. The infrared band at 3200 cm^{-1} corresponds to N-H stretching with hydrogen bonded 20 amino groups and free O-H stretching vibration, 3024 cm^{-1} corresponds aromatic C-H stretching, 2930 and 2864 cm^{-1} (due to aliphatic C-H stretching), 1632 cm^{-1} (due to C=O stretching of carbonyl group), 1526 cm^{-1} (due to C=C stretching of quinoid rings), 1462 cm^{-1} (due to C=C stretching vibration of benzenoid rings), and at 1284 cm^{-1} (C-N stretching). The absorption band at 1110 cm^{-1} was assigned to N=Q=N bending vibration shift toward the lower wave number corresponds to the PANI. The shift of 1130 cm^{-1} band to lower wavenumber could be attributed to the hydrogen bonding between chitosan and imine group of the grafted chain of PANI the

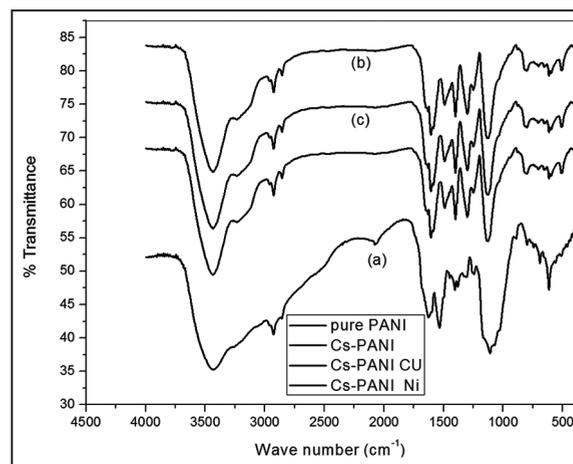


Figure 1: Fourier transforms infrared spectra of pure PANI, chitosan-g-poly(acrylic acid)-co-polyaniline (CPANI), CPANI- Cu^{+2} , CPANI- Ni^{+2}

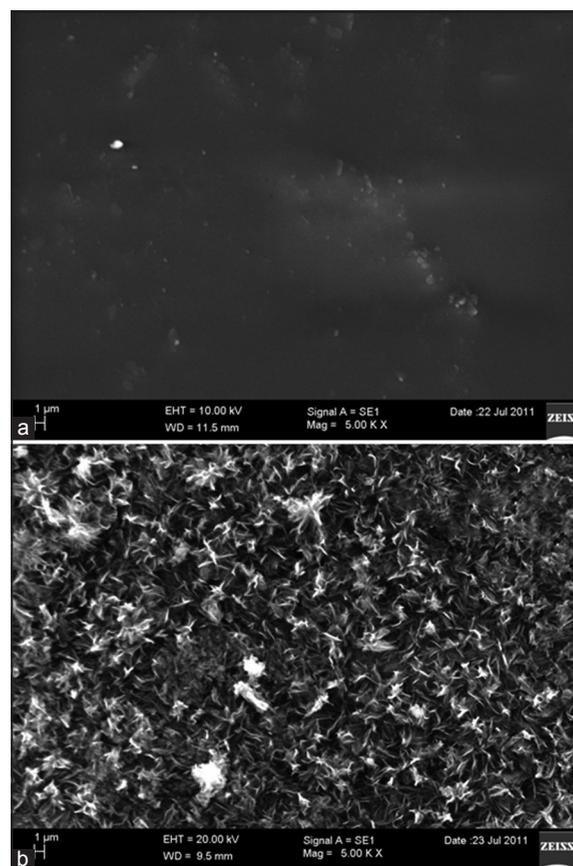


Figure 2: Scanning electron microscope pictures of CS (a), chitosan-g-poly(acrylic acid)-co-polyaniline membrane (b)

absorption band at 1030 cm^{-1} (due to O-H bonding), at 1076 cm^{-1} (C-O stretching), and at 830 cm^{-1} was assigned to aromatic C-H bending vibration band due to the 1, 4-disubstituted benzene ring, chitosan showed characteristic peaks of mucopolysaccharide [29]. Hence, FTIR studies clearly suggested the graft copolymerization of polyaniline on to chitosan. FTIR spectra of metal loaded CPANI indicate considerable change in the position and intensity of the peaks. Hence, we can conclude that functional groups such as $-\text{NH}_2$, $-\text{OH}$, $\text{C}=\text{O}$, and $-\text{CN}$ act as binding sites indicating that these groups are responsible for adsorption of metal ions.

3.2. Scanning Electron Microscope (SEM) Studies

SEM studies (Figure 2) revealed that the morphology of the CS and CPANI membranes is having smooth and rough surface, respectively. This fact can be attributed to the smooth surface for CS. In the case of CPANI, the surface evidence supports the homogeneity of the uniform grafting of poly(acrylic acid) and polyaniline on to CS membranes.

3.3. Swelling Studies

The swelling behavior of CPANI was observed as pH dependent due to the ionization/deionization of the ionizable functional groups such as $-\text{COO}^-\text{Na}^+$, $-\text{OH}^-$, and $-\text{NH}_2$ (Figure 3). 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 CPANI. Table 1 summarizes the DS ratio of CPANI network.

3.4. Effect of pH on Metal ion Adsorption Studies

The ionizable functional groups, such as $-\text{NH}$, $-\text{NH}_2$, $-\text{OH}$, or $-\text{COO}^-$ on the surface of CS membrane, may gain or lose a proton, resulting in a surface charge that varies with pH. At low pH, surface sites are protonated and the surface becomes positively charged. On the other hand, at high pH, the ionizable groups lose their protons and the surface becomes negatively charged. The pH value in aqueous solution is a very critical parameter affecting both the removal capacity and the removal mechanism of Cu^{2+} and Ni^{2+} ions by CPANI matrix. As

pH value increases (pH 2–5) the removal capacity of Cu^{2+} and Ni^{2+} also increases (Figure 4). In alkaline conditions, complete sorption was observed, but in this pH region, the metal removal originates from precipitation ($\text{M}[\text{OH}]_2$) rather than due to sorption. The ability of a material to capture metals is controlled in part by the number of available functional groups used for binding metal ions. In the case of cross-linked membranes, the metal ion adsorption ability is due to the presence of the primary, secondary amino. Besides, hydroxyl and acetyl groups are also capable to adsorb metal ions.

3.5. Effect of Initial Metal ion Concentration on Metal ion Adsorption Studies

Figure 5 shows the relationship between initial metal ion concentration and the adsorbed amount. It is clear from Figure 5 the adsorption amount of metal ions increased with increase in the concentration and reached a plateau value at higher concentration due to the saturation of the chelating sites of the polymer matrix. The adsorption is measured for Cu^{2+} and for Ni^{2+} at pH 5. The experimental maximum adsorption capacities of the polymer matrix were found to be 1.01 mM g^{-1} for Cu^{2+} and 2.41 mM g^{-1} for Ni^{2+} , respectively (Figure 7a and b). These high adsorption efficiencies were attributed to hydrophilic nature of CPANI matrix due to the presence of hydroxyl ($-\text{OH}$), amine ($-\text{NH}$), and carboxyl ($\text{C}=\text{O}$) groups, which have adequate affinity to the metal ions.

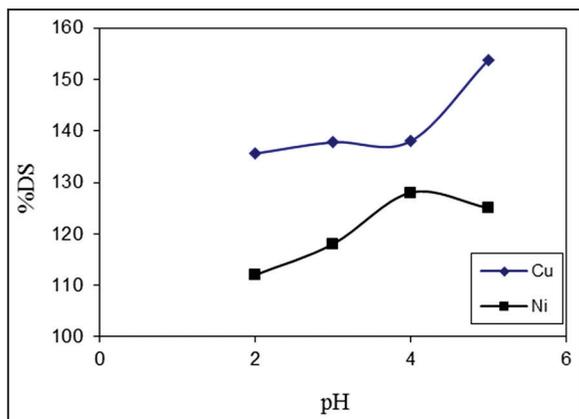


Figure 3: Swelling of chitosan-g-poly(acrylic acid)-copolyaniline membrane in Cu^{2+} and Ni^{2+} solutions as a function of pH.

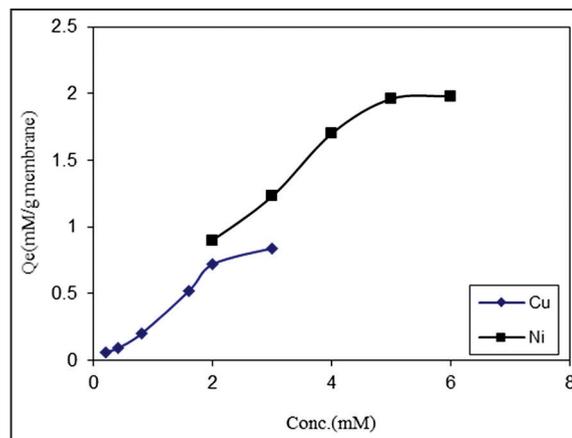


Figure 5: Adsorption of Cu^{2+} and Ni^{2+} on chitosan-g-poly(acrylic acid)-copolyaniline membrane as a function of concentration.

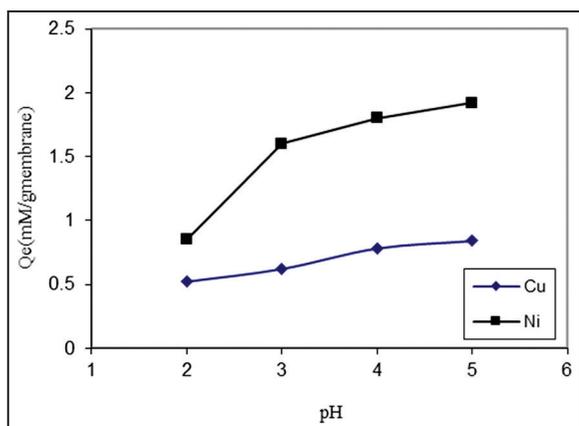


Figure 4: Adsorption of Cu^{2+} and Ni^{2+} on chitosan-g-poly(acrylic acid)-copolyaniline membrane as a function of pH.

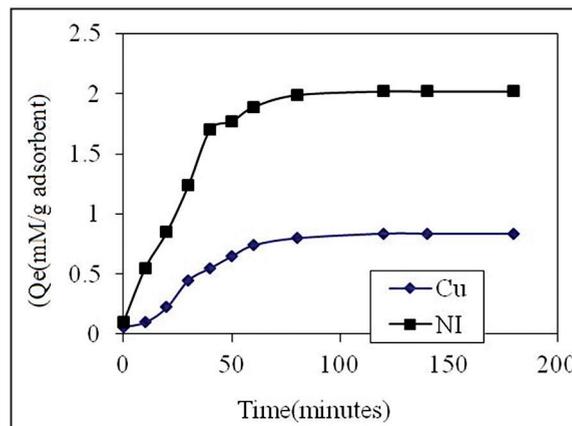


Figure 6: Adsorption of Cu^{2+} and Ni^{2+} on chitosan-g-poly(acrylic acid)-copolyaniline membrane as a function of contact time.

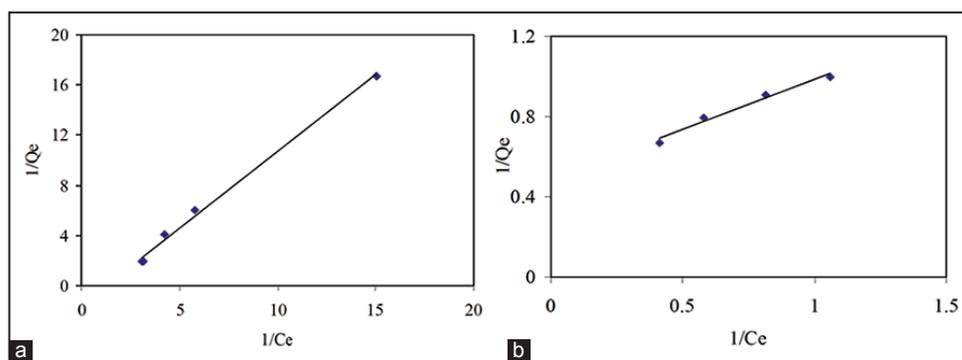


Figure 7: (a) Langmuir isotherm for adsorption of Cu^{2+} on chitosan-g-poly(acrylic acid)-co-polyaniline (CPANI) membranes. (b) Langmuir isotherm for adsorption of Ni^{2+} on CPANI membranes.

3.6. Effect of Contact Time on Metal Ion Adsorption Studies

The adsorption is a transfer process of the pollutant from the liquid to the solid phase, the contacting time between the two phases has an effect on the mass transfer rate. Figure 6 shows the kinetics of adsorption expressed as the adsorbed quantity of copper and nickel over 1 g of solid support. It is evident from Figure 6 that adsorption was rapid initially and became slower with time. At the initial stage, 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. As indicated in Figure 6, adsorption equilibrium for both metal ions was obtained within 130 min.

3.7. Desorption and Reusability of CPANI

Desorption of Cu^{2+} and Ni^{2+} from cross-linked membranes was studied with HCl and ethylenediaminetetraacetic acid (EDTA) as regenerants. When 0.01 M HCl or EDTA were used, desorption was only 62% and 72%, respectively, of adsorbed ions on cross-linked membrane into the solutions. As the concentration of the regenerant is increased to 0.1 M, desorption of ions increases to 80% and 94% for HCl and EDTA, respectively.

When acid was used as 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^{2+} and for Ni^{2+} were released into the solution. When the complexing agent, EDTA was used as regenerant, it had strong affinity for the adsorbed Cu^{2+} and for Ni^{2+} . The metal ions were released into solution in the form of a soluble Cu^{2+} and for Ni^{2+} -EDTA complex.

The cycle of extraction-recovery-regeneration was repeated 4 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, at least for four cycles.

3.8. Adsorption Isotherm

The equilibrium data were better fitted to Langmuir adsorption isotherm model. The most widely used isotherm equation for modeling equilibrium is the Langmuir equation. In this study, we attempted to analyze adsorption at different concentrations (0.1–2.5 Mm) by this model.

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

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 adsorption capacity and energy of adsorption, respectively. The linear plot of $1/Q_e$ versus $1/C_e$, with high correlation coefficient (r^2) values, indicated

Table 1: Swelling data of CPANI membrane.

pH	%DS	
	Cu^{2+}	Ni^{2+}
2	138.7	113
3	139.6	118
4	140.0	138
5	154.2	129

CPANI: Chitosan-g-poly (acrylic acid)-co-polyaniline

Table 2: Langmuir parameters with regression analysis of copper and nickel sorption on CPANI.

Metal ion	Langmuir constants		
	Q^0 (mM g^{-1})	b (L/mg)	r^2
Cu^{2+}	1.01	0.02	0.980
Ni^{2+}	2.41	0.02	0.989

CPANI: Chitosan-g-poly (acrylic acid)-co-polyaniline

the monolayer adsorption on CPANI. The values of Q^0 and b were determined from linear plots and are presented in Table 2. The values of Q^0 for Cu^{2+} and for Ni^{2+} are 1.01 mM g^{-1} and 2.41 mM g^{-1} , respectively. It was reported in the literature that protonated alginate beads shows an adsorption capacity of 0.3080 mM/g for Cu^{2+} and 0.172 mM/g for Ni^{2+} , modified magnetic chitosan and calcium alginate biopolymer exhibit adsorption capacity of 1.24, 0.88, and 1.0184 mM/g for Ni^{2+} [30], magnetic alginate microcapsules possess an adsorption capacity of 0.42 mM/g for Ni^{2+} [31] Cu-PVA-SA Cu^{2+} -imprinted porous film exhibit adsorption capacity of 0.3172 mM/g for Cu^{2+} [32], alginate beads possess an adsorption capacity of 0.384 mM/g for Cu^{2+} [33], respectively (Table 3). The adsorption capacity values reported in the present study are considerably higher than the values reported in the literature. From this observation, it may be concluded that the process of modification of chitosan resulted in an enhancement of adsorption capacity.

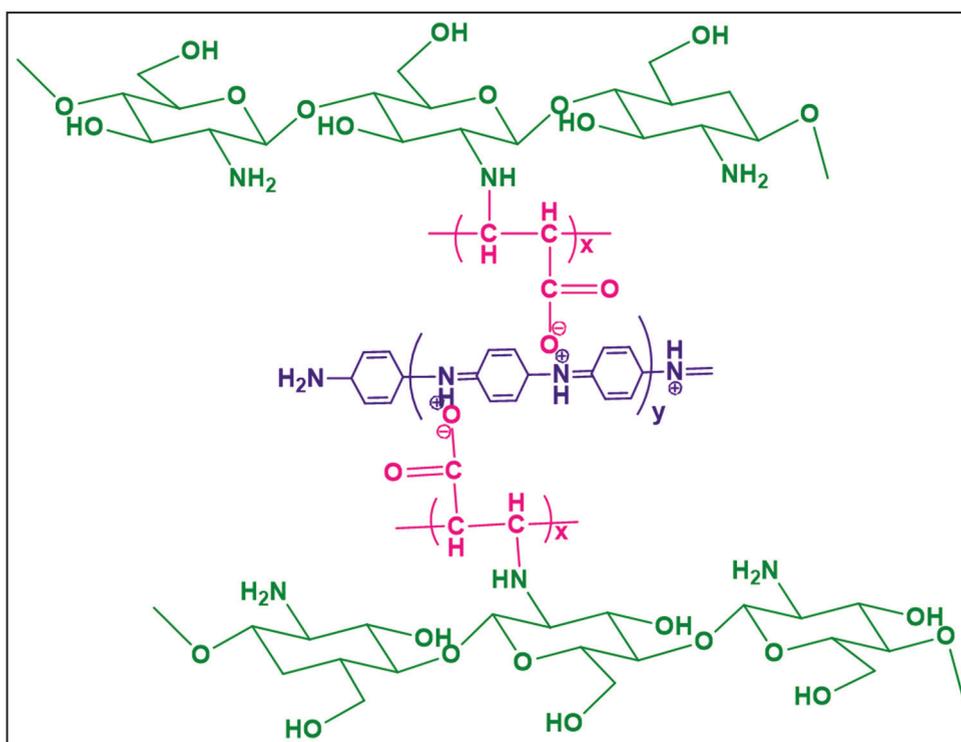
4. CONCLUSIONS

CPANI membranes were successfully developed by grafting of poly(acrylic acid) and polyaniline on chitosan membrane. Crosslinking reaction was confirmed by FTIR spectroscopy, surface morphology of membranes was characterized by scanning electron microscopy. DS experiments were performed on the membranes. The adsorption of the metal ions on the membranes depended on the concentration of metal ions, time, and pH of the metal solution. The adsorption equilibrium data were fitted to the Langmuir isotherm. The maximum monolayer

Table 3: Comparison of the present work with literature.

Polymer	Metal [Cu ²⁺ /Ni ²⁺]	Metal uptake (mM g ⁻¹)	References
Protonated alginate beads	Cu ²⁺ +Ni ²⁺	0.308 0.172	[3]
Modified magnetic chitosan and calcium alginate biopolymer	Ni ²⁺	1.24 0.888 1.0184	[30]
CA			
CCA			
CCS			
Magnetic alginate microcapsules	Ni ²⁺	0.42	[31]
Cu-PVA-SA Cu (II)-imprinted porous film	Cu ²⁺	0.3172	[32]
Alginate beads	Cu ²⁺	0.384	[33]
CPANI	Cu ²⁺ +Ni ²⁺	1.01 2.41	Present work

CPANI: Chitosan-g-poly (acrylic acid)-co-polyaniline

**Scheme 1:** Schematic representation of cross-linked chitosan-g-poly(acrylic acid)-co-polyaniline membrane.

adsorption capacity of CPANI membrane was 1.01 mM/g for Cu²⁺ and 2.41 mM/g for Ni²⁺, respectively. The synthesized membranes were able to successfully separate Cu²⁺ and Ni²⁺ metal ions from aqueous solutions as they are multifunctional. Hence, we propose that the membranes are potential sorbents for the removal of Cu²⁺ and for Ni²⁺ metal ions from wastewater.

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