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Synthesis, characterization, and metal uptake capacity of a new polyaniline and poly(acrylic acid) grafted sodium alginate/gelatin adsorbent

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ABSTRACT

The present work reports the development of new (sodium alginate-gelatin (SAG))-*g*-poly (acrylic acid)/polyaniline (SAPAPN) from sodium alginate/gelatin blend by cross-linking with glutaraldehyde, followed by grafting with poly(acrylic acid) and polyaniline by free radical polymerization using ammonium persulfate. The structure, thermal stability, and morphology of SAPAPN adsorbent was characterized by Fourier transform infrared spectroscopy, thermo gravimetric analysis, and scanning electron microscopy, and results were consistent with the expected structures. The influence of various experimental conditions like pH, time, and initial feed concentrations on the uptake of metal ions like Cu^{2+}, Ni^{2+} by SAPAPN adsorbent was tested. It was seen that the adsorption equilibrium data could be fitted to the Langmuir isotherm. Desorption studies were performed in acid media and EDTA, to examine whether the SAPAPN adsorbent can be recycled for the metal ion removal. The results showed that with SAPAPN adsorbent, the maximum metal ion uptake achieved is $0.8386\,\mathrm{mMg}^{-1}$ for Cu^{2+} and $2.2026\ \mathrm{mMg}^{-1}$ for Ni^{2+}, respectively. Metal ion sorption studies showed that the adsorbent 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 adsorbent to extract divalent toxic metals from industrial aqueous streams.

Keywords: Polyaniline; Toxic metal ions; Sodium alginate; Adsorbents

1. Introduction

The industrial effluents containing toxic metal ions are found to be very harmful and their removal is quite essential [1,2]. Toxic heavy metals like Hg, Pb, Ag, Cu, Ni, As, etc. 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

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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]. In view of this, environmental regulation act is enforced to be implemented to achieve removal/reduction of contaminants. Since, the metal ions must be removed before discharge from large volumes of waste streams is important. Precipitation, redox reactions, ion exchange, filtration, reverse osmosis, electro-chemical removal, and evaporative recovery can all potentially be used to treat industrial effluents for metals. However, these methods have limitations for toxic metal contaminants present at trace levels. Treatment processes of industrial effluents and ground water using sorbents have attracted wide attention in recent years [6]. 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 polychelatogens, 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 [7].

With the widespread usage of carbohydrates, their utilization has increased many folds as compared to the past decades. Biopolymers such as sodium alginate (SA), chitosan extracted from microalgae [8], shrimp, crab, and some fungi [9,10] are known to bind metal ions strongly and could be used for toxic metal adsorption. Biopolymers are nontoxic, selective, efficient, and inexpensive, and thus, highly competitive with ion-exchange resins and activated carbon. 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 block wise and in non-regular order along the chain. Cation specific affinity of the alginate gel and its fundamental physio-chemical and rheological properties are determined by this arrangement [11]. Coordination sites of two homo polymeric guluronic chains are aligned to accommodate divalent cations easily according to the well-known "egg-box model" [12]. Some studies showed that mainly ion-exchange are responsible for this, whereas, other studies reported the sorption through complexation in addition to the ion-exchange [13–17]. Removal of Cd(II) ion from waste water by adsorption onto polyaniline coated on sawdust was investigated by Lokesh et al. [18]. Nanocomposite blends of SA filled with polyaniline-coated titanium dioxide were used for dehydration of 1,4-dioxane/water mixtures [19,20]. Alginate derivatives were widely used as polychelatogens [21,22]. Polyaniline/poly(vinyl alcohol)/clinoptilolite nanocomposite was used as adsorbent for removal of methylene blue [23]. Poly(methyl methacrylate-co-ethyl acrylate) and poly(methyl methacrylate-co-butyl methacrylate) copolymers were used for adsorption of Fe(III), Cu(II), and Co(II) ions from aqueous solution [24].

In this study, SA blends cross-linked with glutaraldehyde (GA), through the grafting of poly(acrylic acid) and polyaniline were prepared by free radical polymerization using ammonium persulfate (APS). For the first time we used SA grafted with poly (acrylic acid) and polyaniline for metal extraction. Cu^{2+} and Ni^{2+} adsorption and efficiency of synthesized adsorbent 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.

2. Materials and methods

2.1. Materials

Analytical reagent grade samples of SA, aniline, hydrochloric acid, (25% aqueous solution) GA, acetone, and sodium hydroxide were purchased from S.D. Fine Chemicals, Mumbai, India. Cupric nitrate tri hydrate and nickel ammonium sulfate hexahydrate purchased from Merck. APS, acrylic acid, and gelatin (G) were purchased from Aldrich. All chemicals were used without further purification and double distilled (DD) water was used throughout the experiment. Stock solutions Cu^{2+} and Ni^{2+} were prepared using DD water and all working standards prepared by using the stock solution with DD water.

2.2. Preparation of polyaniline grafted SA/G adsorbent (SAPAPN)

Sodium alginate-gelatin (SAG) adsorbents were prepared by solution casting technique and were cross-linked with GA. Briefly, 5% of aqueous polymer solution was prepared, (1:0.052, NaAlg:G) SA powder and G were dispersed individually in DD water (90 and 5 mL, respectively), mixed, and stirred for 2 h. The SAG blend solution was spread on a clean glass plate, allowed it air dried at room temperature for 24 h, and was peeled off from the plate.

The SAG blend was cross-linked in a mixture of 2.5 mL GA, 2.5 mL HCl, and 75:25 ratio of acetone water mixture for 12 h. The cross-linked blend was washed with DD water and then dried at 40˚C for 24 h. Aniline (0.5 mL) was dissolved in 50 mL HCl (1 M). To this 0.2 mL acrylic acid, 1.41 g of APS was added. The composition of the SAPAPN adsorbent was 1:0.052:0.21:0.30 of SA, G, poly acrylic acid, and poly aniline. The adsorbent was cut into strips, dipped in the above solution, and stirred for 1 h. The grafted SAPAPN adsorbent was taken out, washed with distilled water, and dried in oven. The % grafting (104) and % grafting efficiency (8.1) were calculated as per our earlier report [25]. The proposed structure of SAPAPN adsorbent is shown in Scheme 1.

2.3. Swelling studies of SAPAPN

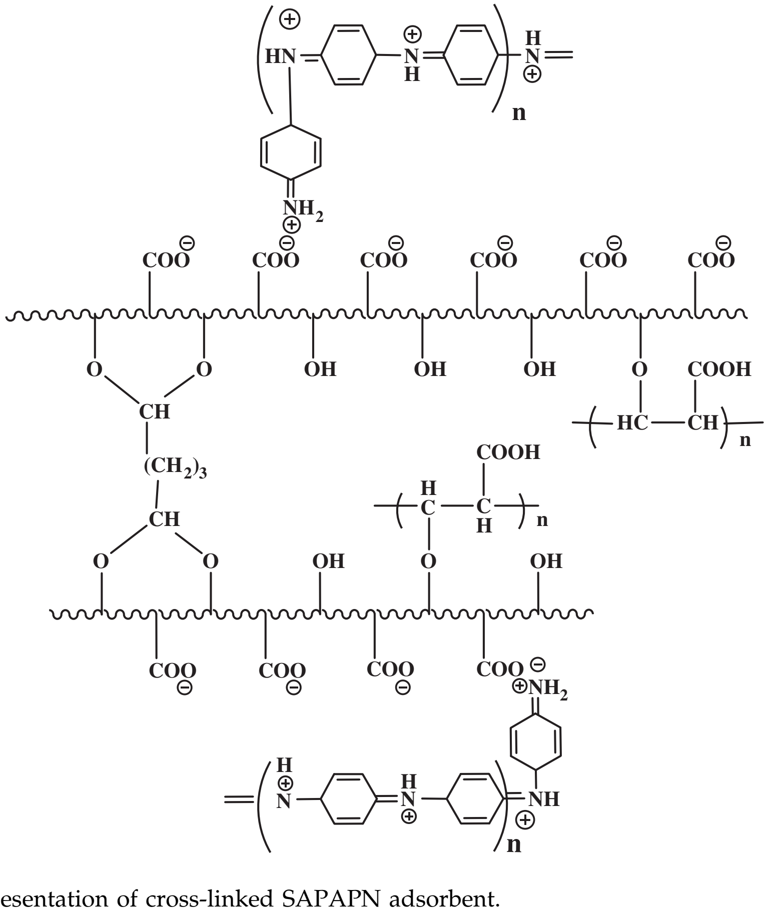
The swelling studies of SAPAPN adsorbents were performed in metal ion solutions by mass measurements at 30˚C. Fully dried adsorbents were immersed in metal ion solution and kept for equilibrium swelling (2 h). Adsorbents were taken out from metal ion solution carefully and surface adhered solution was removed with the help of tissue paper. The swollen adsorbents were weighed and determined the % of degree of swelling using Eq. (1),

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

where M_s and M_d are the mass of the swollen adsorbent and dry adsorbent, respectively.

Dynamic and equilibrium swelling of the known weight of SAPAPN adsorbent (2.5 cm dia) was carried out at 30˚C, maintained at desired constant temperature within an accuracy of ±0.5˚C in a thermostatically controlled oven until equilibrium was attained in the presence of an excess amount of water. Adsorbents were taken out of the liquid environment periodically and weight measurements were taken immediately after carefully wiping the excess surface liquid droplets adhered to the surface of the adsorbents.

During this period, total time spent by the adsorbent outside the solvent medium was kept minimum (30–40 s) to minimize the experimental error due to solvent evaporation. Weight measurements were done on a digital Mettler microbalance (Model BSA 2245-CW, Sartorius, Switzerland) sensitive to ±0.01 mg.



Scheme 1. Schematic representation of cross-linked SAPAPN adsorbent.

Weight gain, Q_t of the soaked SAPAPN adsorbents is expressed in mole percent units (i.e. number of moles of solvent sorbed by 100 g of the polymer), which is calculated as [26]:

$$Q_t = \left(\frac{W_t - W_i}{W_i}\right)\frac{100}{M_s} \tag{2}$$

where W_t and W_i are, respectively weight gains at time, t and initial weight; M_s is molecular weight of the sorbed liquid. Increase in mole % of solvent by the SAPAPN matrix is a consequence of filling up of the available free volume of the cross-linked matrix. Equilibrium is attained when no more increase in mole % takes place.

Since, permeation of a solvent through a polymeric adsorbent occurs due to diffusion of molecules, and hence, permeability coefficient, P can be calculated as:

$$P = DS \tag{3}$$

where D is diffusion coefficient and S is solubility or sorption coefficient. S is simply equilibrium sorption, which was calculated as:

$$S = \frac{M_\infty}{M_0} \tag{4}$$

where M_∞ is equilibrium mass of the adsorbent and M_0 is its initial mass. D was computed from sorption results using the equation [27,28]:

$$D = \pi\left(\frac{h\theta}{4Q_\infty}\right)^2 \tag{5}$$

where θ is slope of the linear portion of the sorption curve before attainment of 60% equilibrium and h is initial film thickness. Estimated values of D, S, and P are given in Table 1. The results of % sorption of SAPAPN adsorbents in water are presented in Table 1.

2.4. Metal ion sorption studies

The experiments were carried out by placing weighed circular pieces of adsorbents in 20 mL of 2 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^{-1}dry film) was determined using Eq. (2). Here, C_o and C_e are initial metal ion concentration and equilibrium metal ion concentration.

$$Q_e = (C_o - C_e)\frac{V}{M} \tag{6}$$

2.5. Characterization of SAPAPN adsorbent

Fourier transform infrared spectroscopy (FTIR, Perkin–Elmer, Germany) analysis was performed to identify the chemical structure of the SAPAPN adsorbents. The dry adsorbents (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. The grafting and thermal stability of the above adsorbents were given by thermo gravimetric analysis (TGA) studies (TA instruments, Model: STA, Q600, USA).

3. Results and discussion

3.1. FTIR studies

The characteristic pattern of FTIR spectra of SAG, SAPAPN, and metal loaded SAPAPN are given in Figs. 1(a) and 1(b). FTIR spectrum (Fig. 1(a)) of SA GA adsorbent shows a peak at 1,635 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. FTIR spectrum (Fig. 1(a)) of SAPAPN adsorbent shows clear evidence of GA cross-linked NaAlg is grafted with poly(acrylic acid) and polyaniline. A new peak appearing at 1,635 cm^{-1} due to imine bonds (–C=N) was formed as a result of cross-linking reaction between amino groups in SA and aldehydic groups in GA. Absorption peaks observed at 2,500 cm^{-1} are typical of C–H stretching

Table 1
Results of D, S, and P at different temperatures for SAG and SAPAPN adsorbents

Blend	Permeability coefficient $P \times 10^8$ (cm^2/s)			Sorption coefficient S			Diffusion coefficient $D \times 10^8$ (cm^2/s)		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
SAG	6.52	6.76	7.74	1.73	1.75	1.76	3.77	3.87	4.39
SAPAPN	6.21	7.94	8.10	1.48	1.49	1.50	4.20	5.32	5.41

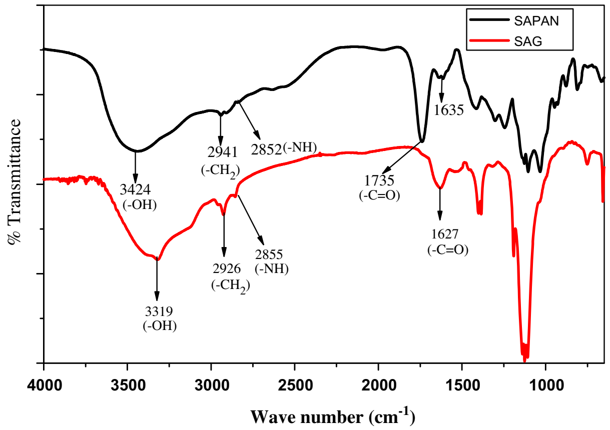


Fig. 1(a). FTIR spectra of SAG and PANI grafted SAGA (SAPAPN).

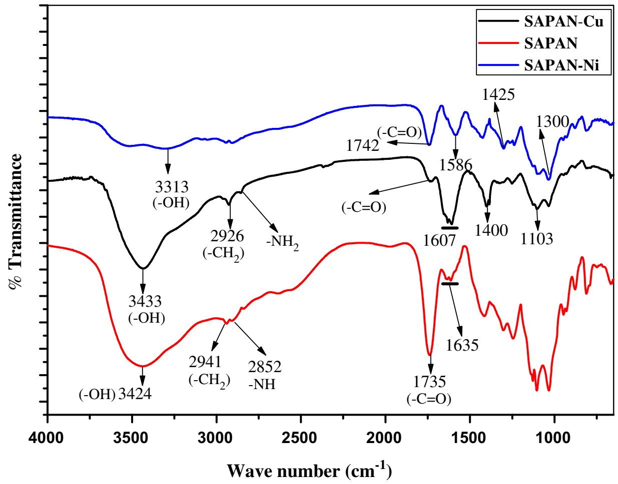


Fig. (1b). FTIR spectra of SAPAPN and loaded with Cu^{2+}, Ni^{2+}.

vibrations. The peaks appearing at 1,103, 1,030, and 1,265 cm^{-1} show prominent shifts due to C–O–C stretching vibrations of ether linkages. The increase in intensity and the shift of bands to a higher wave number in the region of 2,500 cm^{-1} are indicative of the increase in the number of $–CH_2$ groups in the cross-linked adsorbents. The other peaks which are appearing in SAPAPN adsorbents, i.e. 1,640 and 1,733 cm^{-1} correspond to polyaniline containing amine and C=O of poly(acrylic acid), respectively. FTIR spectra metal loaded SAPAPN (Fig. 1(b)) show shifts in the intensity in the absorption frequencies of hydroxyl (3,441–3,319 cm^{-1}), amine (2,940–2,926 cm^{-1}), and carboxyl (1,127–1,103 cm^{-1}) groups. This indicates that these groups in the SAPAPN adsorbents are responsible for adsorption.

3.2. Scanning electron microscopy (SEM) studies

SEM studies (Fig. 2) revealed that the morphology of the SA and SAPAPN adsorbents are having smooth and rough surface, respectively. This fact can be attributed to the smooth surface for SAG bends cross-linked with GA. In the case of SAPAPN, the surface evidence supports the homogeneity of the uniform grafting of poly(acrylic acid) and poly aniline on to SAG adsorbents.

3.3. TGA studies

The SAG and SAPAPN adsorbents were characterized by TGA (Fig. 3). The starting decomposition temperature of SAG is 210˚C which is higher than that of the SAPAPN (196˚C). The final decomposing temperature of SAG decreased compared to SAPAPN. The difference in decomposition temperature between

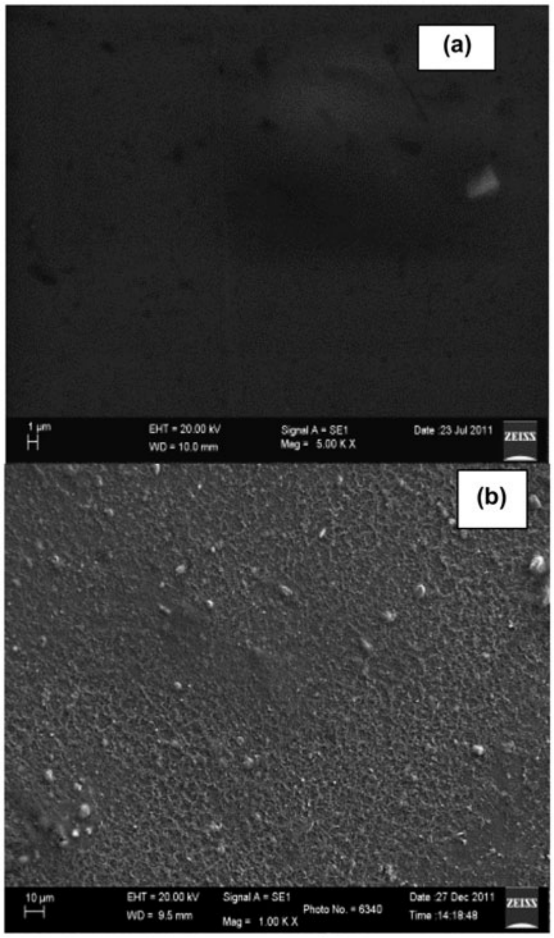


Fig. 2. SEM pictures of GA cross-linked SAG (a) and SAPAPN adsorbent (b).

the SAG and SAPAPN is found to be 8% and illustrates the grafting in the networks.

3.4. Swelling studies

The swelling behavior of SAPAPN was observed as pH dependent due to the ionization/deionization of the ionisable functional groups, such as –COO$^-$Na$^+$, –OH$^-$, and –NH$_2$ (Fig. 4). 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 SAPAPN. Table 2 gives the degree of swelling ratio of SAPAPN network.

It has been customary to understand the absorption of metal ions in terms of sorption, diffusion, and permeation of liquid molecules through the network barrier. To explore these concepts further, we have performed the sorption experiments on SAG and SAPAPN networks in aqueous media at 30, 40, and 50˚C, the results of the same are presented in Table 1. It is noticed that with an increase in temperature from 30 to 50˚C, the values of *S*, *P*, and *D* also increase systematically for the polymer matrices. The results of *S*, *P*, and *D* have increased, indicating that temperature as well as concentration of polyaninine in the matrix influenced the network transport properties because of the expansion of polymer chains in a systematic manner.

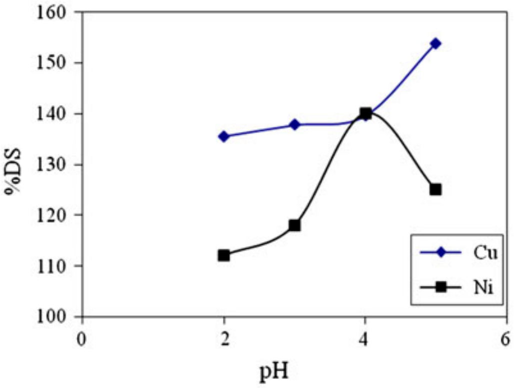


Fig. 4. Swelling of SAPAPN adsorbent in Cu^{2+} and Ni^{2+} solutions as a function of pH.

Table 2
Swelling data of SAPAPN adsorbent

pH	% DS	
	Cu^{2+}	Ni^{2+}
2	135.6	112
3	137.8	118
4	139.6	140
5	153.8	125

3.5. Effect of pH on metal ion adsorption studies

Of all the factors affecting the removal of heavy metals, pH is the most important. Within acidic solutions the high concentration of protons blocks the metal ions from binding to regions of electron density, reducing complexation which resulted in decrease in the separation. In the basic solutions, heavy metal ions are not hindered by protons for the complexation sites on the polymer resulting in increased complexation with the polymer. Although, high pH values are desirable for polymer metal complexation, the formation of metal hydroxides begins to form at high pH range. Metal hydroxides have small molecular weights and after formation,

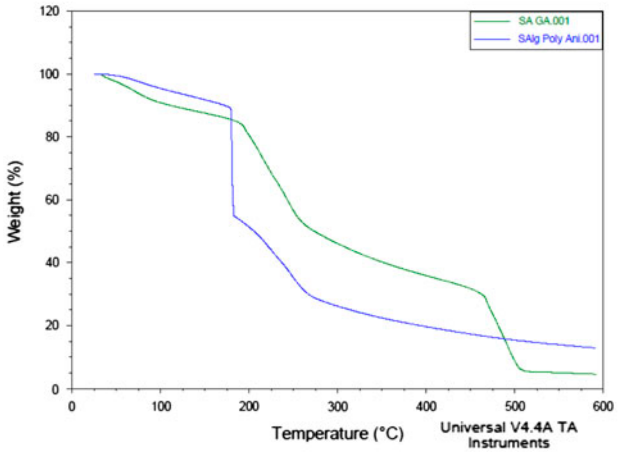


Fig. 3. TGA curves of SAPAPN adsorbent.

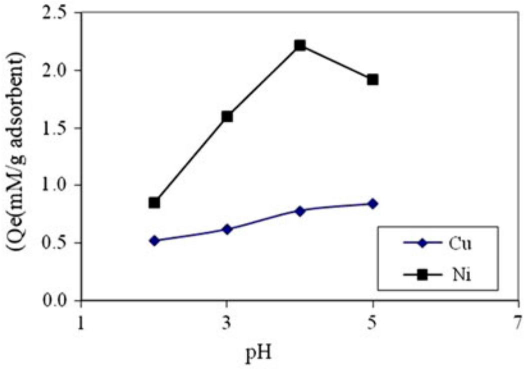


Fig. 5. Adsorption of Cu^{2+} and Ni^{2+} on SAPAPN adsorbent as a function of pH.

they pass freely through the polymer matrix, and thus, should be avoided.

The ionisable functional groups, such as –NH, $-NH_2$, –OH, or $-COO^-$ on the surface of alginate, 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 ionisable 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 SAPAPN matrix. As the pH value increases (pH 2–5), the removal capacity of Cu^{2+} and Ni^{2+} also increases (Fig. 5). In alkaline conditions, complete sorption was observed, but in this pH region the metal removal originates from precipitation $(M(OH)_2)$ 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 blends, the metal ion adsorption ability is due to the presence of the primary, secondary amino, and GA reaction (imine bond). Besides, hydroxyl and acetyl groups are also capable to adsorb metal ions. It may be predicted that uptake of metal ions not only based on adsorption, but also complexation, i.e. it may be possible both of them take place.

3.6. Effect of initial metal ion concentration on metal ion adsorption studies

Fig. 6 shows the relationship between initial metal ion concentration and the adsorbed amount. It is clear from Fig. 6 that 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 and 4, respectively. The experimental maximum adsorption capacities of the polymer matrix were found to be 0.830 mMg^{-1} for Cu^{2+} and 2.0 mM g^{-1} for Ni^{2+}, respectively.

These high adsorption efficiencies were attributed to hydrophilic nature of SAPPAN matrix due to the presence of hydroxyl (–OH), amine (–NH–), and carboxyl (C=O) groups, which have adequate affinity to the metal ions.

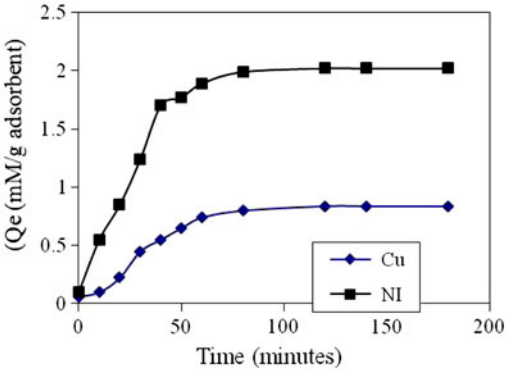


Fig. 7. Adsorption of Cu^{2+} and Ni^{2+} (b) on SAPAPN adsorbent as a function of contact time.

3.7. Effect of contact time on metal ion adsorption studies

Since, 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. Fig. 8 shows the kinetics of adsorption expressed as the adsorbed quantity of copper and nickel over one gram of solid support. It is evident from Fig. 8 that adsorption was rapid initially and became slower with time. At the initial stage, the process of adsorption was fast due to the availability

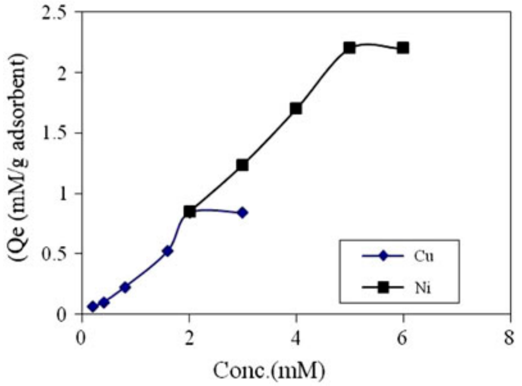


Fig. 6. Adsorption of Cu^{2+} and Ni^{2+} on SAPAPN adsorbent as a function of concentration.

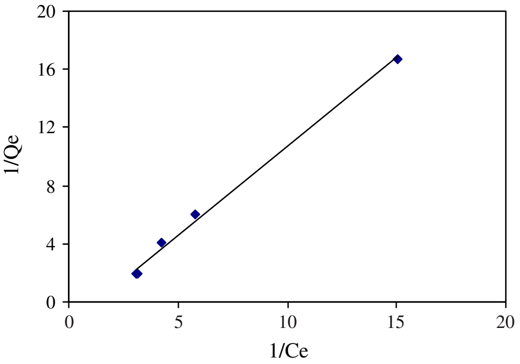


Fig. 8a. Langmuir isotherm for adsorption of Cu^{2+} on SAPAPN blends.

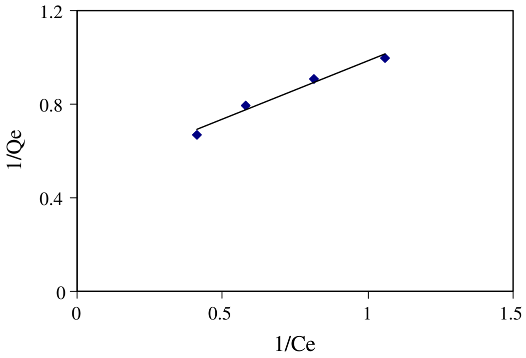


Fig. 8b. Langmuir isotherm for adsorption of Ni^{2+} on SAPAPN adsorbents.

Table 3
Langmuir parameters with regression analysis of copper and nickel sorption on SAPAPN

Metal ion	Langmuir constants		
	Q^o ($mM\,g^{-1}$)	b (L/mg)	r^2
Cu^{2+}	0.831	0.01	0.989
Ni^{2+}	2.02	0.01	0.983

of abundant free sites near the surface where there is less hindrance for the approaching metal ions. As indicated in Fig. 7, adsorption equilibrium for both metal ions was obtained within 120 min.

3.8. Desorption and reusability of SAPAPN

Desorption of Cu^{2+} and Ni^{2+} from cross-linked blends 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 cross-linked blend in to the solutions. As the concentration of the regenerent is increased to 0.1 M, desorption of ions increases to 80 and 94% for HCl and EDTA, respectively.

When acid was used as regenerate, 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 regenerent, 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 four 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.

3.9. Adsorption isotherm

The equilibrium data were better fitted to Langmuir adsorption isotherm model. The analysis of adsorption data are 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 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.

$$\frac{1}{Q_e} = \frac{1}{Q^o b C_e} + \frac{1}{Q^o} \qquad (7)$$

where Q_e is the amount of metal adsorbed per unit weight of the sorbent (mg/g) and Q^o and b are

Table 4
Comparison of the present work with literature

S.no.	Polymer	Metal [Cu^{2+}/Ni^{2+}]	Metal uptake ($mM\,g^{-1}$)	References
1	Protonated alginate beads	Cu^{2+}	0.308	[3]
		Ni^{2+}	0.172	
2	Modified magnetic chitosan & calcium alginate biopolymer	Ni^{2+}	1.24	[21]
	CA		0.888	
	CCA		1.0184	
	CCS			
3	Magnetic alginate microcapsules	Ni^{2+}	0.42	[22]
4	Cu-PVA-SA Cu(II)-imprinted porous film	Cu^{2+}	0.3172	[29]
5	Alginate beads	Cu^{2+}	0.384	[30]
6	SAPAPN	Cu^{2+}	0.8309	Present work

Langmuir constants indicating the adsorption capacity and energy of adsorption, respectively. The linear plot of $1/C_e$ vs. $1/Q_{e,}$ with high correlation coefficient (r^2) values, indicated the monolayer adsorption on SAPAPN. The values of Q^o and b were determined from linear plots and are presented in Table 3. The values of Q^o for Cu^{2+} and for Ni^{2+} are 0.830 and 2.0 mM g^{-1}, respectively (Fig. 8(a) and 8(b)). It was reported, in the literature that protonated alginate beads shows an adsorption capacity of 0.3080 mMg^{-1} 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, 1.0184 mM/g for Ni^{2+} (21), magnetic alginate microcapsules possess an adsorption capacity of 0.42 mM/g for Ni^{2+} (22) Cu-PVA-SA Cu(II)-imprinted porous film exhibit adsorption capacity of 0.3172 mM/g for Cu^{2+} (29) , alginate beads possess an adsorption capacity of 0.384 mM/g for Cu^{2+} (30), respectively (Table 4). The adsorption capacity values reported in the present study are considerably higher than the above values reported in the literature. From this observation it may be concluded that the process of modification of SA resulted in an enhancement of adsorption capacity.

4. Conclusions

SAPAPN adsorbents were successfully developed by grafting of poly(acrylic acid) and poly aniline on GA cross-linked SA/G blend. Cross-linking reaction was confirmed by FTIR; surface morphology of adsorbents was characterized by scanning electron microscopy and thermal stability was confirmed by TGA. Degree of swelling experiment was performed on the adsorbents at 30°C to test their diffusion characteristics in water. The adsorption of the metal ions on the adsorbents 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 maxium monolayer adsorption capacity of SAPAPN adsorbent was 0.8386 for Cu^{2+} mMg^{-1} and 2.2026 mM/g for Ni^{2+}, respectively. The present adsorbents, being multifunctional, were able to successfully separate Cu^{2+} and for Ni^{2+} metal ions from aqueous solutions. It may be proposed that these adsorbents are potential sorbents for the removal of Cu^{2+} and for Ni^{2+} metal ions from waste water.

Acknowledgments

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