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Effective removal of divalent metal ions: synthesis and characterization of pH-sensitive guar gum based hydrogels

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ABSTRACT

The present paper reports the modification of Guar gum network through grafting of acrylamide by free radical polymerization. The amide groups in the grafted network have been subsequently hydrolyzed by saponification. The hydrogels have been characterized by FTIR, Elemental Analysis, DSC, and TGA techniques. The nature and extent of swelling of these hydrogels is observed to be dependent on gel structure and pH. The pH dependence of uptake capacity of the hydrogels for metal ions Cu, Ni, Pb, and Zn^{2+} has been studied. The results reveal a very high metal uptake capacity of modified hydrogel attributed to the presence of carboxylic acid functionality. The metal adsorption is found to follow pseudo-first-order kinetics under pH 1.2 and pseudo-second-order kinetics under pH 7.0.

Keywords: Hydrogel; Guar gum; Polyacrylamide; Hydrolysis; Metal uptake; pH-responsive swelling

1. Introduction

Heavy metals are considered to be the most dangerous polluting agents in water. Their nonbiodegradability and tendency to bioaccumulate make them remain in natural environment for a long time. When the metal ions accumulate beyond their permissible levels, they tend to cause serious environmental and public health problems [1]. Hence, the development of the effective techniques for the removal of toxic metal ions from wastewater is very important for the remediation of water pollution. A number of technologies have been developed over the years to remove toxic metal ions from water. The most important of these are filtration, chemical precipitation, ion exchange, adsorption, electrodeposition, and membrane separation. These techniques have their inherent limitations such as incomplete removal of metal ions and limited tolerance to pH change [2–4].

Adsorption is versatile and effective method for removing toxic metal ions, particularly, when it is combined with appropriate regeneration step. Adsorption has been utilized for the removal of pollutant metal cations using activated carbon [5], polymers [6], zeolites [7], and clays [8]. The adsorption of pollutant metal cations by functionalized mesoporous silica are being investigated [9].

The use of hydrogel materials with specific functional groups for binding and removal of heavy metal ions from water is wide spread [10,11]. Easy handling and reusability make hydrogels promising materials for water purification. The adsorption of metal ions on

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the gel material depends on the macromolecular characteristics such as extent of crosslinking, the hydrophilic–hydrophobic balance, the structure of the attached ligand function, and the stability constant of the resulting polymer–metal complex [12–14]. A vast number of polymeric sorbents with different functional groups were made and their complexing abilities were investigated [15–17]. The main advantages of the hydrogel materials compared to other type of adsorbents are easy and cost-effective preparation methods, high efficiency of adsorption and in most cases, easy stripping of adsorbates with simple chemicals, reusability, and the possibility of semi-continuous operation.

Polyacrylamide is a water-soluble polymer with a hydrophobic main chain and a hydrophilic side group. Crosslinked polyacrylamide is a well-known hydrogel [18,19], whose swelling nature is not very sensitive to pH or to the presence of electrolytes. The advantage of amide functional group is that it can be used to introduce required number of ionic groups, imparting pH sensitivity to the gel. The ionic functionality introduced by chemical modification of amide groups helps in the removal of metal ions from aqueous solutions [20–22].

We have reported studies on polysaccharide-based hydrogels containing polyacrylamide [23,24]. Microwave-mediated synthesis of polyacrylamide grafted on Guar gum (GG) has also been reported [25]. The main focus of the present investigation is to modify the polyacrylamide-grafted GG by conversion of acrylamide (AAm) groups to carboxylic groups, and to compare the effectiveness of the two gels for the removal of metal ions from wastewater. Grafting of AAm on GG has been carried out using potassium persulfate (KPS) as initiator. Network formation has been achieved by the addition of two crosslinking agents, N,N´-methylene-bis-acrylamide (MBA) and gluteraldehyde (GA), the former for linking the grafted poly(acrylamide) chains and the latter for the GG chains. The amide groups in the network have been hydrolyzed subsequently by saponification. Further, the hydrogels have been evaluated for removal of heavy metal ions from wastewater.

2. Experimental

2.1. Materials and methods

AAm, MBA (s.d.fine, Mumbai, India), GG, KPS (Merck,Mumbai), and GA (25%w/v) (Lobo, Mumbai, India) were used as received. AAm was purified by recrystallisation from chloroform before use. All other reagents were of analytical grade. Double distilled water was used in the preparation of hydrogel and for swelling studies.

2.2. Synthesis of guar gum-polyacrylamide network polymer (GG-PAAm)

The hydrogel composed of AAm and GG was made by simultaneous free radical polymerization and crosslinking. Briefly, 0.04 g of GG was dispersed in 2.5 mL water in a closed container and stirred overnight. AAm (0.028 mol) and KPS (7.39 mmol) were dissolved in 1 mL water and added to the GG solution under stirring, and stirring was continued for 1 h. 1 mL of solution containing MBA (7.39 mmol) and GA (0.024 mol) was added to the above solution. The mixture was thermostated at 60˚C for 3 h. The hydrogel, GG-PAAm, obtained was purified by washing with boiling water in a soxhlet extractor. The purified hydrogel was dried at 40˚C under vacuum (60 mm Hg) overnight and used for further modification by alkaline hydrolysis.

2.3. Preparation of modified GG-g-polyacrylamide network polymer (mGG-PAAm)

To 0.1 g dry hydrogel, 1 N NaOH (30 mL) was added and the mixture was maintained at 60–80˚C for 3 h. It was then allowed to cool to room temperature and neutralized to pH 8.0 by addition of aqueous acetic acid (10%). The resulting mixture was added to methanol (200 mL). After an hour, the hydrogel was filtered off and dried at 50˚C under vacuum for 5 h. It was designated as modified mGG-PAAm.

2.4. Characterization of GG-PAAm and mGG-PAAm hydrogels

2.4.1. FTIR analysis

The FTIR spectra of dry GG, GG-PAAm, and mGG-PAAm samples were recorded as KBr pellets on a Fourier transform infrared spectrophotometer (Perkin-Elmer, USA) in the range 4,000–400 cm^{-1}.

2.4.2. Elemental analysis

Elemental analyses of GG, AAm, GG-PAAm, and mGG-PAAm samples were carried out on a Vario EL III CHN analyzer (Germany) and percentages of carbon, hydrogen, and nitrogen were determined.

2.5. Determination of neutralization equivalent (NE) of GG-PAAm and mGG-PAAm samples

The NE is the equivalent weight of the acid as determined by titration with standard base [22]. In order to ascertain the conversion of amide functionality to carboxylic acid, NEs of GG-PAAm and mGG-PAAm samples were determined in the following way: 0.2 g of the sample was dissolved in 150 mL water. 40 mL 0.1 N HCl was added and the resulting solution was left undisturbed for 6 h under this condition. The solution was then titrated with 0.1 N NaOH, and the volume of NaOH required to neutralize the excess HCl was determined. Similarly, the volume of 0.1 N NaOH required to neutralize 40 mL 0.1 N HCl was determined by titration. The difference between the volume of NaOH consumed by HCl and the polymer solutions gives the volume of alkali required for titrating the acid formed during the acidification of the polymer. The NE value of the polymers GG-PAAm and mGG-PAAm were calculated using the following expression,

$$\text{Neutralization equivalent (NE)} = \frac{\text{Weight of the sample taken (g)} \times 100}{\text{Volume of NaOH (ml)} \times \text{Normality of NaOH}} \quad (1)$$

2.6. Thermal analysis

TGA of GG, GG-PAAm, and mGG-PAAm hydrogels was carried out on SDT Q600 V20.9 (Japan) thermogravimetric analyzer. The samples were heated from 0 to 600˚C, under nitrogen atmosphere, at a rate of 10˚C/min.

DSC of the hydrogel samples was recorded on Q20 V24.4 Build 116 (USA) calorimeter by heating the samples under nitrogen atmosphere from 40 to 400˚C, at a rate of 10˚C/min.

2.7. Swelling behavior of the GG-PAAm and mGG-PAAm hydrogels

Known weights of dried GG-PAAm and mGG-PAAm samples were soaked in buffered aqueous media (pH 1.2, 4.0, 7.0, and 9.0) for 24 h at room temperature (30 ± 1˚C). The weight of hydrated (swelled) samples was measured after the hydrogels had equilibrated in test solutions. The equilibrium swelling ratio (q_w) was calculated based on the following equation [26]:

$$q_w = \frac{m_d}{m_s} \quad (2)$$

where m_d and m_s are the weights of the gel samples in the dry and the swollen states, respectively.

2.8. Metal ion adsorption studies

Adsorption of bivalent metal ions by the GG-PAAm and mGG-PAAm hydrogels has been studied by equilibrium method. 0.1 g of hydrogels were equilibrated in metal salt solutions (50 ppm) for 8 h and removed by filtration. The concentration of metal ions in the filtrate was analyzed using atomic adsorption spectrophotometer (GBC-932 AAS) (Australia). Using the data, the percent uptake (Pu), partition coefficient (Kd), retention capacity (Qr), and amount of metal ion absorbed per unit weight of hydrogel ($Q(t)$) at time t, (mg/g) were calculated according to the following expressions.

$$\text{Pu} = \frac{\text{Amount of metal ions in feed - Amount of metal ions rejected}}{\text{Amount of metal ions in the feed}} \times 100 \quad (3)$$

$$\text{Kd} = \frac{\text{Amount of metal ions absorbed by hydrogel}}{\text{Amount of metal ions rejected}} \times \frac{\text{Volume of solution}}{\text{Weight of dry hydrogel (g)}} \quad (4)$$

$$\text{Qr} = \frac{\text{Amount of metal ions in the hrdrogel (mEq)}}{\text{Weight of dry hydrogel (g)}} \quad (5)$$

$$\text{Q}(t) = \frac{\sum (\text{C}_\text{o} - \text{C}_\text{t}) V_\text{t}}{m} \quad (6)$$

where C_o and C_t are the metal concentrations (mg/L) present in the adsorbate solution initially and after a time t, respectively; V_t is the volume of solution (L) at time t, and m is the weight (g) of dry hydrogel initially taken.

3. Results and discussion

The synthesis of GG-PAAm network was achieved by polymerization of AAm in the presence of GG by free radical polymerization along with simultaneous crosslinking of the two components using two cross-linkers, namely, MBA and GA. The grafting of AAm is expected to occur at the active site of GG followed by crosslinking of the chains. In addition, a tight network structure is ensured by linking few repeating units of GG. This reaction leads to formation of the network, and the possible structure of the network is shown in Fig. 1. The hydrogels were purified and subjected to subsequent hydrolysis using NaOH. Alkaline hydrolysis resulted in the mGG-PAAm network with the amide groups partially converted to carboxylic acid groups [22,27].

3.1. FTIR characterization of GG-PAAm and mGG-PAAm networks

The FTIR spectra of GG, GG-PAAm, and mGG-PAAm samples have been compared in Fig. 2. The decrease in the broadness of the peak at 3,400 cm^{-1} attributed to O–H stretching in the sample GG-PAAm (Fig. 2(b)) when compared to GG (Fig. 2(a)), gives a clear indication of involvement of O–H groups of GG in grafting and network formation. The spectrum of GG-PAAm network (Fig. 2(b)) exhibits peaks at 2,923 and 1,630 cm^{-1} due to C–H stretching and C=O stretching of amide groups, respectively. In the spectra of mGG-PAAm (Fig. 2(c)), peaks appearing at 3,428 and 2,923 cm^{-1} correspond to O–H and C–H stretching of GG backbone, respectively. The peak at 2,854 cm^{-1} corresponds to C–H stretching of polyacrylamide chains and at 1,457 cm^{-1} corresponds to $–CH_2$ bending vibration, respectively. Moreover, the new peaks observed at 1,747, 1,657, and 1,600 cm^{-1} are attributed to C=O stretching of carboxylic acid groups formed on hydrolysis of polyacryamide, –C=O and N–H stretching of amide groups of MBA, respectively. These observations confirm the formation of crosslinked network, and amide to carboxylic acid conversion in mGG-PAAm sample.

Upon hydrolysis of the amide groups, the molecular weight of the polymer would remain nearly the same . Hence, greater the number of carboxyl groups (basicity), lower will be the NE value. The NE values

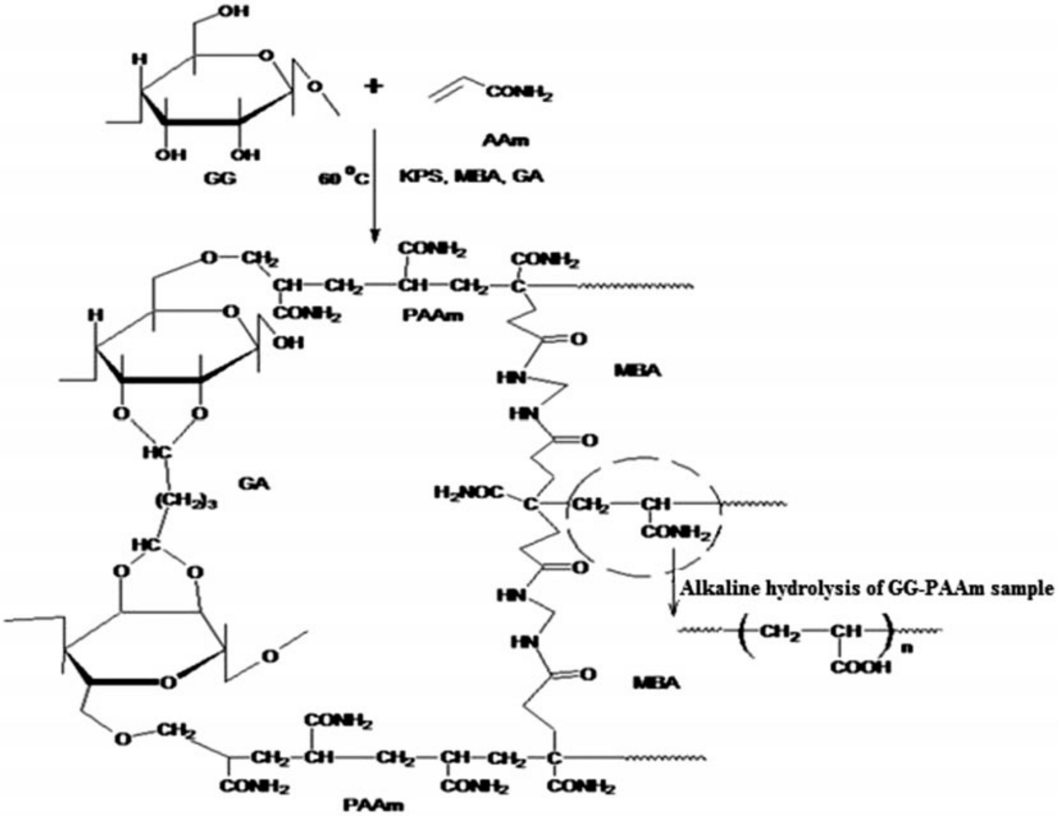

Fig. 1. Formation of mGG-PAAm network.

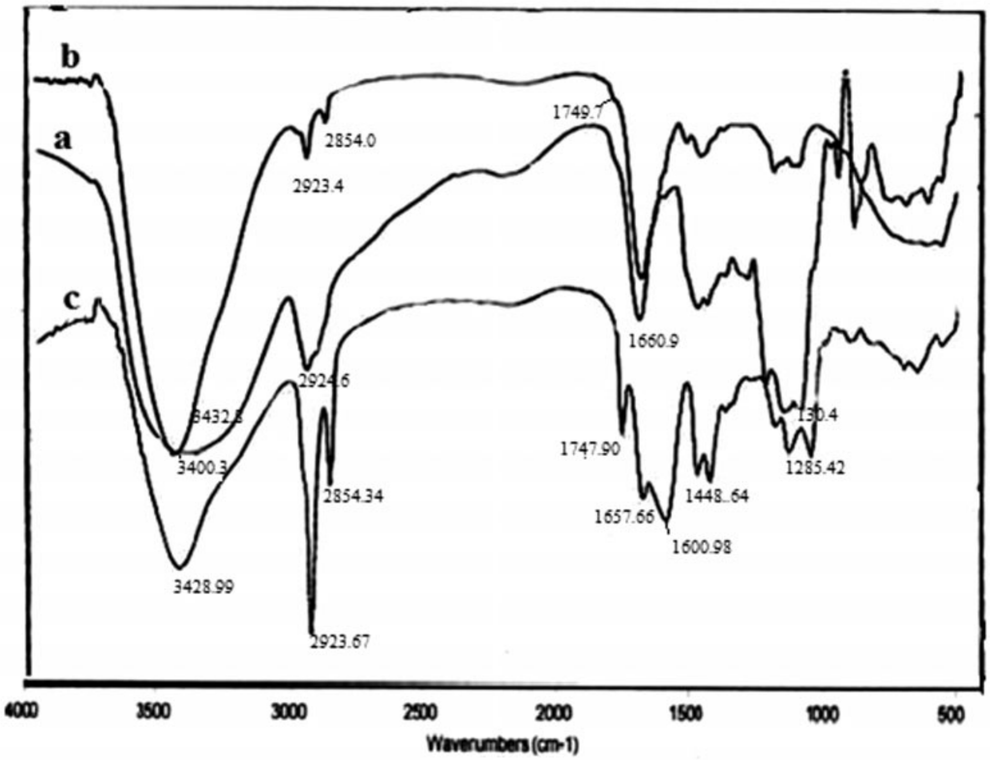

Fig. 2. FTIR spectra of (a) GG, (b) GG-PAAm, and (c) mGG-PAAm samples.

for GG-PAAm and mGG-PAAm were found to be 1,560 and 222, respectively, indicating a high degree of conversion of amide groups to acid groups. The conclusive proof for this result comes from the elemental analysis data shown in Table 1. The % N of mGG-PAAm sample is reduced by 70% compared to GG-PAAm sample (from 13 to 4%) without much variation in the % C and H, indicating large conversion of –CONH$_2$ to –COOH groups.

3.2. Thermal analysis

Derivatograms and thermograms of GG, GG-PAAm, and mGG-PAAm are presented in Fig. 3(a) and (b), respectively. In the GG sample, the initial mass loss of about 15% occurring in the range 50–120°C may be due to the loss of free and bound water molecules. A major weight loss of about 60% is observed between 250 and 400°C, the rate being highest at 300°C. This stage of degradation is attributed to the loss of hydroxyl group of GG as water molecules. Very little weight loss occurs in the final stage leaving behind 15% of residual mass at 700°C. The thermal stability of GG is affected on grafting and network formation, as indicated by the TGA of GG-PAAm sample. It exhibits a three-step degradation, the rates being highest at 210, 300, and 380°C, respectively. The additional step occurring in the range 320–500°C is attributed to the crosslinked chains of polyacrylamide in the grafted network. The pattern of weight loss in the mGG-PAAm sample is much similar to that of GG-PAAm up to 350°C, beyond which very little mass loss is observed owing to the lowering of amide content. A residual mass of 35% remains in the mGG-PAAm sample at 700°C. Similar results are reported in earlier studies [28].

Table 1
Elemental analysis data

Sample code	% N	% C	% H
GG	0.8	38.08	6.54
AAm	18.78	49.76	6.7
GG-PAAm	13.06	43.85	7.05
mGG-PAAm	4.06	42.31	7

DSC curves for GG, GG-PAAm, and mGG-PAAm samples are displayed in Fig. 4. The endothermic peak exhibited by GG between 70 and 100°C is due to desorption of water contained in the hydrogel sample, and the exotherm at 311°C marks the degradation of the sample. The incorporation of polyacrylamide chains in GG-PAAm explains the origin of the endotherm at 237.1°C [29] which disappears in

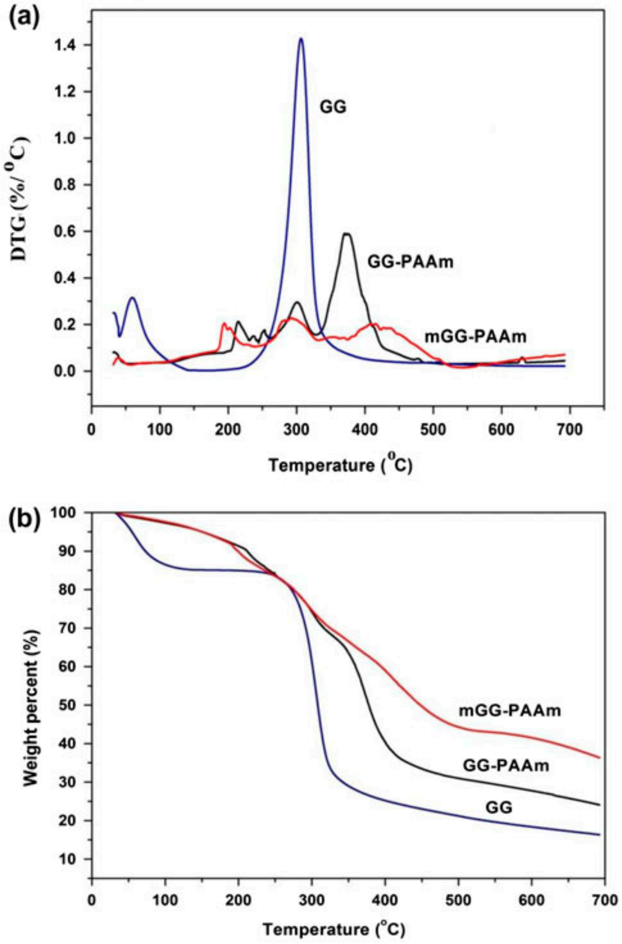

Fig. 3. (a) DTG and (b) TGA of GG, GG-PAAm and mGG-PAAm samples.

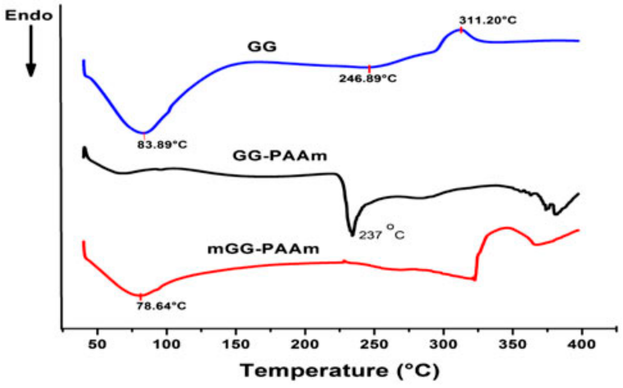

Fig. 4. DSC of GG, GG-PAAm, and mGG-PAAm samples.

mGG-PAAm sample, indicating the –$CONH_2$ to –COOH conversion in the sample. This observation further confirms the formation of –COOH in segments of grafted chains.

3.3. Swelling behavior of GG-PAAm and mGG-PAAm hydrogels

The effect of pH on the swelling ability of the GG-PAAm and mGG-PAAm hydrogels is shown in Fig. 5. At pH 1.2, the modified hydrogel exhibited lower swelling than the GG-PAAm, due to complete protonation of the carboxylic groups, the pKa of carboxylic acid being 4.2 [30]. At pH 4.0, the swelling is higher than at pH 1.2, and due to increased number of dissociated carboxylic groups, the modified hydrogel exhibits higher swelling than the parent. As the pH was increased to 7.0, dramatic change in the swelling of mGG-PAAm occurs, the equilibrium swelling ratio being as high as 123, but not much change is observed in swelling of GG-PAAm hydrogel. On further increase of pH to 9.0, contraction of modified hydrogel network occurs, reducing swelling, which could be due to high ionic strength of the swelling medium.

3.4. Noncompetitive metal ion adsorption studies

Hydrogels “partition” metal ions between the solution and the gel phase resulting in “sorption” of metal ions [31]. Depending on the structure of the support, sorption is a combination of ion exchange and a simple adsorption processes. Polymers, based on hydroglucose units, afford active glycolic functionalities for metal ion complexation [22,32]. The linkage is mainly of co-ordinate type. In addition to presence of a hydroglucose units, the presently studied hydrogel contains ionic functionality which is an added advantage for adsorption of metal ions. The adsorption capacities of GG-PAAm and mGG-PAAm for Cu, Ni, Pb, and Zn^{2+} ions were evaluated, to understand the influence of –NH_2 and –COOH groups on the metal ion adsorption behavior of the hydrogels.

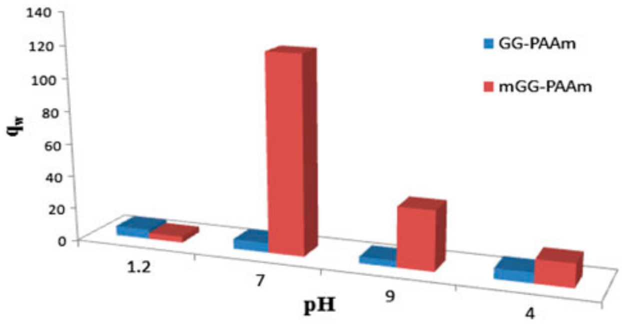

Fig. 5. Effect of pH on the equilibrium swelling ratio (q_w) of the GG-PAAm and mGG-PAAm hydrogels.

The adsorption study was performed in media of pH 1.2, 4.0, 7.0, and 9.0 as a function of time. Precipitation of metal ions occurred at pH 9.0 and hence, data could not be collected under this condition. The data obtained under the other three pH conditions indicated swelling-controlled adsorption process. Based on the adsorption data, various sorption parameters were calculated and the results are tabulated in Table 2.

The GG-PAAm hydrogel showed very low adsorption capacity under all the pH conditions studied here. The extent of adsorption was comparatively higher at pH 7.0. The electrostatic repulsion between the protonated amide groups in the hydrogel matrix and the positively charged metal ions, account for low values of adsorption parameters for this hydrogel. The sorption behavior of GG-PAAm was also influenced by the nature of metal ions, the order of adsorption being $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$.

The mGG-PAAm hydrogels showed much higher adsorption capacity under the pH conditions studied here. Because of the changing of ionization degree of this sample with pH [21,33], adsorption capacities increased with increase in pH as shown in Fig. 6 and Table 2. The adsorption appears to be in the order $Pb^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+}$.

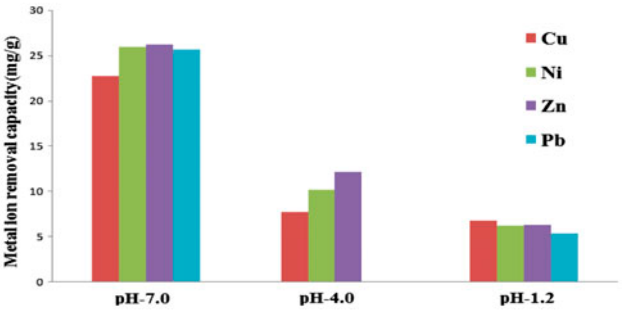

Fig. 6. The effect of the pH on the divalent metal ion removal capacity of mGG-PAAm hydrogel.

3.5. Kinetic studies

The kinetic aspects of adsorption was studied using pseudo-first-order and pseudo- second-order-kinetic models [21]. If adsorption is a first-order process, the adsorption data should fit into the pseudo-first-order equation given by,

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{7}$$

where Q_e and Q_t are the amount of metal ions adsorbed by the hydrogel (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the pseudo-first-order constant (min^{-1}). On the other hand, if it is a second-order kinetic phenomenon, the following linearized pseudo-second-order equation describes the adsorption process well.

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{8}$$

Table 2
Sorption parameters for GG-PAAm and mGG-PAAm samples under different pH conditions

		GG-PAAm			mGG-PAA		
		pH			pH		
Metal ions used	Sorption parameters	1.2	4.0	7.0	1.2	4.0	7.0
Cu^{2+}	Pu	0.45	6.0	9.2	10.3	19.9	81.3
	Kd (g/g)	2.3	32.7	52.3	56.2	171.4	2,982.5
	Qr (meq/g)	0.008	0.10	0.14	0.146	0.490	1.12
Ni^{2+}	Pu	1.15	1.7	1.03	4.9	7.5	79.6
	Kd (g/g)	6.2	9.0	5.2	30.2	56.0	2,398.8
	Qr (meq/g)	0.02	0.02	0.09	0.100	0.18	1.74
Zn^{2+}	Pu	3.2	3.6	4.9	12.0	19.0	76.6
	Kd (g/g)	4.0	45.0	87	75.8	146.3	2,183.5
	Qr (meq/g)	0.01	0.12	0.20	0.052	0.074	1.318
Pb^{2+}	Pu	3.7	[a]	11.7	4.5	[a]	82.7
	Kd (g/g)	9.2	[a]	94.2	27.2	[a]	3,033.9
	Qr (meq/g)	0.01	[a]	0.17	0.029	[a]	0.605

[a] Precipitation occurred.

Table 3
Kinetic parameters for the adsorption of divalent metal ions on mGG-PAAm hydrogel

Metal ion	Q_e-exp (mg/g)	Pseudo-first-order			Pseudo-second-order			$(k_2Q_e^2)$
		Q_e (mg/g)	k_1 (min^{-1})	R^2	Q_e (mg/g)	k_2 (g/mg min)	R^2	
pH-7.0								
Cu^{2+}	22.69	23.45	−0.014	0.990	25.64	2.128	0.995	1,398.9
Zn^{2+}	26.19	19.56	−0.003	0.979	27.77	3.177	0.985	2,450.0
Ni^{2+}	25.91	26.84	−0.005	0.990	26.30	5.708	0.992	3,948.1
Pb^{2+}	25.66	17.39	0.003	0.352	24.3	7.718	0.991	4,557.4
pH-1.2								
Cu^{2+}	6.77	6.46	−0.017	0.987	9.09	7.25	0.983	599.0
Zn^{2+}	6.18	4.20	−0.014	0.988	6.89	4.01	0.995	190.3
Ni^{2+}	6.32	7.54	−0.013	0.991	10.30	6.63	0.973	703.3
Pb^{2+}	5.39	4.87	−0.014	0.993	7.35	9.25	0.991	499.7

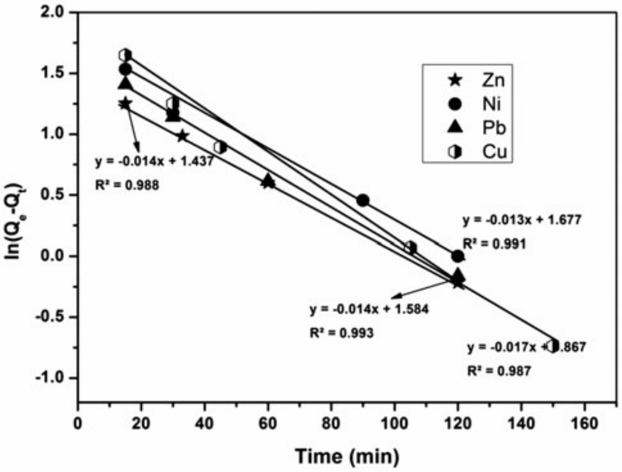

Fig. 7. Pseudo-first-order kinetic plot for the adsorption of divalent metal ions on mGG-PAAm hydrogel at pH-1.2.

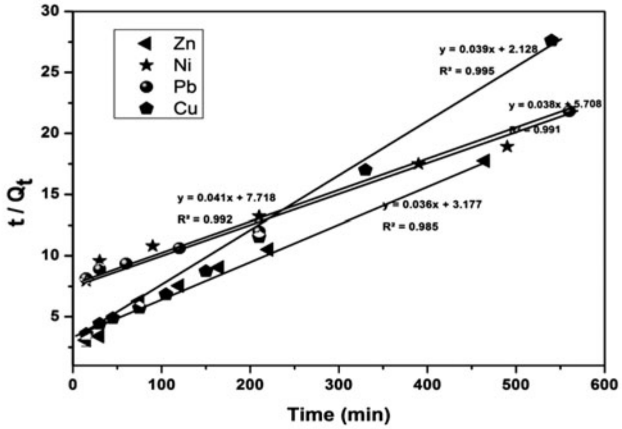

Fig. 8. Pseudo-second-order kinetic plot for the adsorption of divalent metal ions on mGG-PAAm hydrogel at pH-7.0.

where k_2 is the pseudo-second-order rate constant in (g/mg min). The kinetic data for mGG-PAAm plotted as per Eqs. (7) and (8) are shown in Figs. 7 and 8, respectively.

The values of constants calculated from the plots along with the regression coefficient for the liner plots are given in Table 3. The experimental values of equilibrium adsorption, Q_e, were also given for comparison.

At pH 7.0, the Q_e values calculated according to pseudo-second-order kinetic model matches well with the experimental values. Moreover, the second-order model shows better fit with higher R^2 values, suggesting that adsorption under pH 7.0 is a second order kinetic process. However, the experimental Q_e values match well with the theoretical Q_e values obtained from pseudo-first-order kinetic model for adsorption under pH 1.2 conditions. Thus, adsorption under acidic conditions is well described by the first-order kinetic model.

4. Conclusion

The free radical polymerization of AAm in the presence of GG and two crosslinking agents resulted in the firm network of PAAm-grafted GG structure. Alkaline hydrolysis of amide groups was carried out to incorporate carboxylic groups in the network. The hydrogels containing amide and carboxylic acid functionalities exhibited pH-dependent swelling due to the presence of weakly acidic and basic groups.

The possibility of using these IPN systems for metal ion removal from aqueous solutions was explored. The modification carried out on GG-PAAm sample is proved to enhance the adsorption capacity of the hydrogel considerably. The adsorption efficiency is observed to be maximum under neutral pH conditions. Further, the adsorption process is observed to follow pseudo-first-order kinetics under pH 1.2 and pseudo-second-order kinetics under neutral pH. Based on the results, it is proposed that the modified GG-PAAm hydrogel can be considered as a potential candidate for the development of cost effective, environmentally friendly, effluent treatment material for metal ion removal from aqueous effluents.

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