

# Adsorption Capacity, Kinetics, and Mechanism of Copper(II) Uptake on Gelatin-Based Hydrogels

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**ABSTRACT:** Gelatin-based hydrogels were synthesized and characterized for use as  $\text{Cu}^{2+}$ -ion sorbents. Gelatin was crosslinked in the presence of two different monomers, that is, acrylamide (AAm) and/or 2-hydroxypropyl methacrylate, with *N,N*-methylenebisacrylamide, ammonium persulfate, and sodium bicarbonate. The as-prepared hydrogels were further characterized by scanning electron microscopy, Fourier transform spectroscopy, and the study of their swelling behavior as a function of temperature, time, and pH to evaluate their structure–property relationships. The hydrogels were observed to be good sorbents of

$\text{Cu}^{2+}$ , and a maximum uptake of 84.8% was observed within 2 h at 37°C and with 10 ppm of the  $\text{Cu}^{2+}$ -ion solution for the gelatin and polyacrylamide hydrogel, which also exhibited the maximum retention capacity at 14.9 mg/g after four feeds. All of the experimental data exhibited good matches with the Langmuir isotherm and followed pseudo-second-order kinetics. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 363–370, 2011

**Key words:** adsorption; hydrogels; structure–property relations; supports; swelling

## INTRODUCTION

$\text{Cu}^{2+}$  is present in the wastewater of several industries, including metal cleaning and plating baths, refineries, article and pulp, fertilizer, and wood preservatives.<sup>1</sup> Copper is an irreplaceable microelement present as a cofactor in some oxidases, oxygenases, and other enzymes. At a high concentration, it is dangerous to living beings.<sup>2</sup> It catalyzes the formation of highly reactive oxygen species, which leads to lipid peroxidation and the lack of the reduced form of glutathione and increases the methemoglobin content.<sup>3</sup> Free or bound  $\text{Cu}^{2+}$  also catalyzes the formation of hydroxyl radicals; this leads to the chemical modification of proteins, alteration in protein structure, and oxidative damage to the surrounding tissues.<sup>4</sup> Toxic materials and hazardous ions from industrial effluents adversely affect the environment and human health. The toxicity of wastewater can be reduced and nonsafe organic materials from industrial effluents can be affected by adsorption processes with solids sorbents.<sup>5,6</sup> In the recent past, a number of nonconventional strategies have been followed to remove  $\text{Cu}^{2+}$  ions from domestic water. These include the use of lignocellulosic materials,<sup>7–10</sup> biopolymers,<sup>11</sup> and synthetic polymer-based hydrogels.<sup>12–19</sup> The sorption of metal ions on gelatin and acrylamide (AAm)-based

hydrogels was studied by Chauhan et al.<sup>20</sup> Pourjavadi et al.<sup>21</sup> reported the synthesis, characterization, and swelling behavior of gelatin-g-poly(sodium acrylate)/kaolin composites as superabsorbent hydrogels.

Apart from environmental concerns and the necessity to remove  $\text{Cu}^{2+}$  as effluents from wastewater,  $\text{Cu}^{2+}$ -loaded polymers are of interest because of their use in bioseparation and purification technology. Biomolecules replace water molecules from complex-metal-ion-loaded polymers/hydrogels. In such cases, protein loading has been reported to increase in a significant manner.<sup>22,23</sup> Cu(II)-chelated poly[(*N*-vinylimidazole)-maleic acid] copolymeric hydrogels were prepared by Pekel et al.<sup>24</sup> for bovine serum albumin adsorption. Garipcan et al.<sup>25</sup> reported the synthesis of Cu(II)-incorporated poly[(hydroxyethylmethacrylate)-*co*-(methacrylamidoalanine)] membranes and their utilization as an affinity sorbent for lysozyme adsorption. The separation was based on differential binding abilities of the proteins or enzymes to interact with chelated metal attached to a solid carrier.<sup>26</sup> Kumar et al.<sup>27</sup> studied the purification of histidine-tagged green fluorescent protein from recombinant *Escherichia coli* through binding of the enzyme with  $\text{Cu}^{2+}$ -poly(*N*-isopropylacrylamide/vinylimidazole) copolymer.

In view of the previous studies, this study was designed to develop gelatin-based hydrogels for use in the removal of  $\text{Cu}^{2+}$  from aqueous systems and for bioseparation. In this article, we report the synthesis and characterization of the gelatin-based hydrogels for  $\text{Cu}^{2+}$  uptake. Gelatin is a biopolymer. The advantages of using a protein as one of the

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hydrogel components, apart from its being biocompatible and biodegradable, is the presence of many active groups on the main chain that play role in targeted applications, and it is also easy to manage. Because the other component is biocompatible as well, the resulting hydrogels are nontoxic and do not generate waste after use. Three different hydrogels were synthesized with AAm or/and 2-hydroxypropyl methacrylate (HPMA) as monomers to obtain a series of functional hydrogels. The former is a very good adsorbent of metal ions, whereas the latter, apart from being a surface-active component, also improves the mechanical strength of a hydrogel by imparting it with hydrophobicity. The resulting hydrogels were good candidates for  $\text{Cu}^{2+}$  uptake.

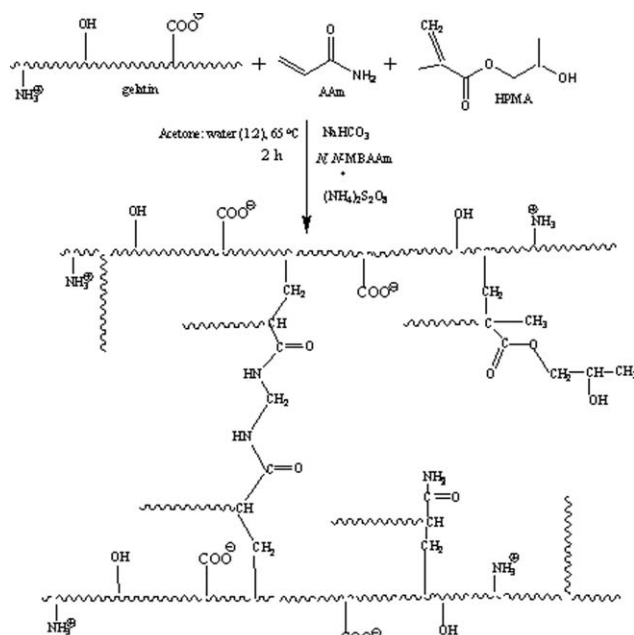
## EXPERIMENTAL

### Materials

Gelatin (Loba Cheme, Mumbai, India), AAm (SRL, Mumbai, India), HPMA (Merck, Hohenbrunn, Germany), ammonium persulfate (Merck, Hohenbrunn, Germany), copper sulfate, sodium hydrogen carbonate (Merck, Mumbai, India), and *N,N*-methylenebisacrylamide (S. D. Fine, Mumbai, India) were used as received.

### Preparation of the hydrogels

A series of gelatin-based hydrogels were synthesized as monoliths with AAm ( $\text{CH}_2=\text{CH}-\text{CONH}_2$ ) and/or HPMA [ $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOCH}_2-\text{CH}(\text{OH})-\text{CH}_3$ ] as monomers with water and acetone (2 : 1) as the solvent system. During preparation of the AAm/HPMA gelatin-based hydrogels ( $\text{HG}_{\text{AAm/HPMA}}$ 's), the ratio of gelatin to monomers, that is, AAm and HPMA, was kept at 1 : 1 w/w, and to it was added *N,N*-methylenebisacrylamide ( $\text{CH}_2=\text{CHCONHCH}_2\text{NHCCH}=\text{CH}_2$ ; 5 wt % total reaction mixture) as a crosslinker and ammonium persulfate (1 wt % total reaction mixture) as an initiator. Sodium bicarbonate (1 wt % of total reaction mixture) was added to increase the gel porosity. The reaction set was carried out at a temperature  $65^\circ\text{C}$  for 2 h. The prepared monolith was washed with water, dried in air, and weighed.



**Scheme 1** Proposed scheme of hydrogel preparation.

The same procedure was repeated during the preparation of the AAm gelatin-based hydrogel ( $\text{HG}_{\text{AAm}}$ ) and the HPMA gelatin-based hydrogel ( $\text{HG}_{\text{HPMA}}$ ) with single monomers that is, AAm in  $\text{HG}_{\text{AAm}}$  and HPMA in  $\text{HG}_{\text{HPMA}}$ . The proposed scheme of the hydrogel preparation is shown in Scheme 1.

### Characterization of the hydrogels

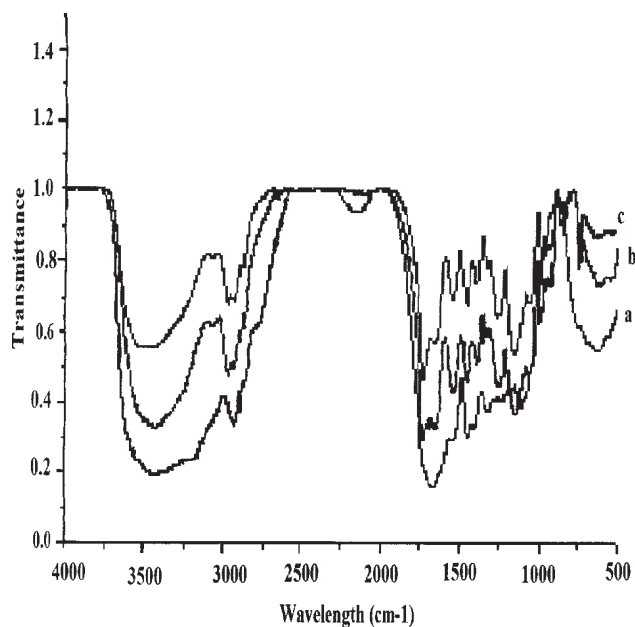
Characterization of the hydrogels was carried out by scanning electron microscopy (SEM; JEOL StereoScan-150 microscope, Cambridge, U.K.) and Fourier transform infrared (FTIR) spectroscopy (Nicolet 5700, Madison, WI). The swelling behaviors of the hydrogels were studied as functions of time, temperature, and pH by the immersion of 0.1 g of the crushed monolith in water, and the water uptake was studied as a function of time (30–480 min), pH (2.0, 4.0, 5.4, 6.6, 6.8, 7.0, or 9.2), and temperature ( $25\text{--}45^\circ\text{C}$ ), including at  $37^\circ\text{C}$ . Swollen polymers were taken out from the solution, wiped off, and then weighed immediately to calculate the percentage water uptake ( $P_s$ ) as follows:<sup>18</sup>

$$P_s = \frac{\text{Weight of the swollen hydrogel} - \text{Weight of the dry hydrogel}}{\text{Weight of the dry hydrogel}} \times 100$$

### Sorption of $\text{Cu}^{2+}$

The hydrogels (0.1 g) were separately immersed in a 10 ppm solution of  $\text{Cu}^{2+}$  ions that was prepared in

deionized water and placed in a water bath (accuracy  $\pm 0.01^\circ\text{C}$ ) at  $37^\circ\text{C}$ . The percentage uptake was studied as a function of time from 10 to 240 min,



**Figure 1** FTIR spectra of different hydrogels: (a)  $HG_{AAm/HPMA}$ , (b)  $HG_{AAm}$ , and (c)  $HG_{HPMA}$ .

and equilibrium was reached within 120 min. The concentration of the rejected  $Cu^{2+}$  ions was determined with a DR 2010 spectrophotometer (Hach, Co., Loveland, Colorado), as reported elsewhere.<sup>28</sup> The effects of the  $Cu^{2+}$  concentration (1–20 ppm) and the pH (2.0, 4.0, 7.0, and 9.2) were studied at 37°C for 120 min. The highest uptake was exhibited by  $HG_{AAm}$ , and its maximum retention capacity (MRC) was determined by the repeated treatment of the hydrogel at a  $Cu^{2+}$ -ion concentration of 10 ppm under the conditions obtained for the maximum uptake. To evaluate the reusability of the hydrogel,  $Cu^{2+}$ -loaded hydrogels were treated with 0.1N ethylene diamine tetraacetic acid for 2 h to leach out the adsorbed  $Cu^{2+}$  ions, and  $Cu^{2+}$  uptake by these hydrogels was studied at 37°C with a  $Cu^{2+}$ -ion concentration of 10 ppm for 120 min. The sorption results were evaluated with the following expressions:

$$(P_u) = \frac{\text{Amount of } Cu^{2+} \text{ ions sorbed}}{\text{Total } Cu^{2+} \text{ ions in the feed solution}} \times 100$$

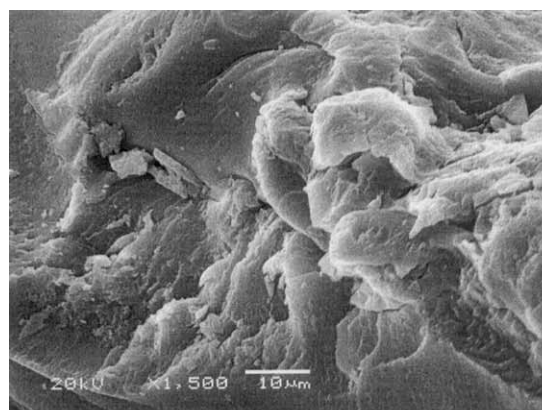
$$(q) \text{ (mg/g)} = \frac{(C_o - C_t)V}{m}$$

where  $P_u$  is the percentage uptake and  $q$  is the amount of  $Cu^{2+}$  ions adsorbed onto the unit dry mass of the hydrogels (mg/g);  $C_o$  and  $C_t$  are the concentrations of ions in the feed solutions and in the aqueous phase after treatment for a certain period of time  $t$ , respectively (mg/L);  $V$  is the volume of the aqueous phase (L); and  $m$  is the weight of the dry hydrogel (g).

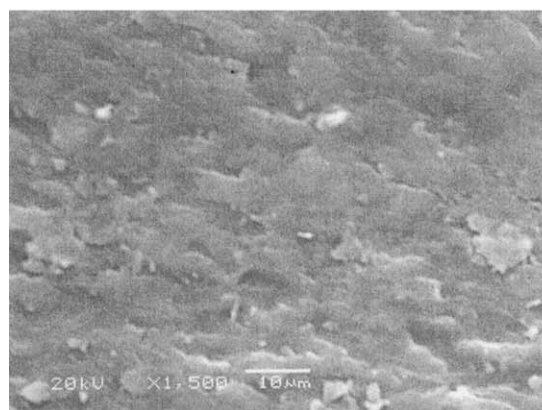
## RESULTS AND DISCUSSION

### Characterization of the hydrogels

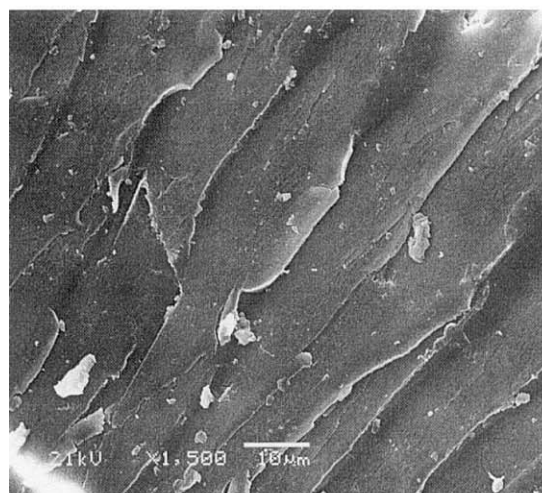
The hydrogels were characterized by FTIR spectroscopy and SEM to obtain evidence of the incorporation of gelatin, monomer(s), and crosslinker. The FTIR spectra of the synthesized hydrogels provided



(a)

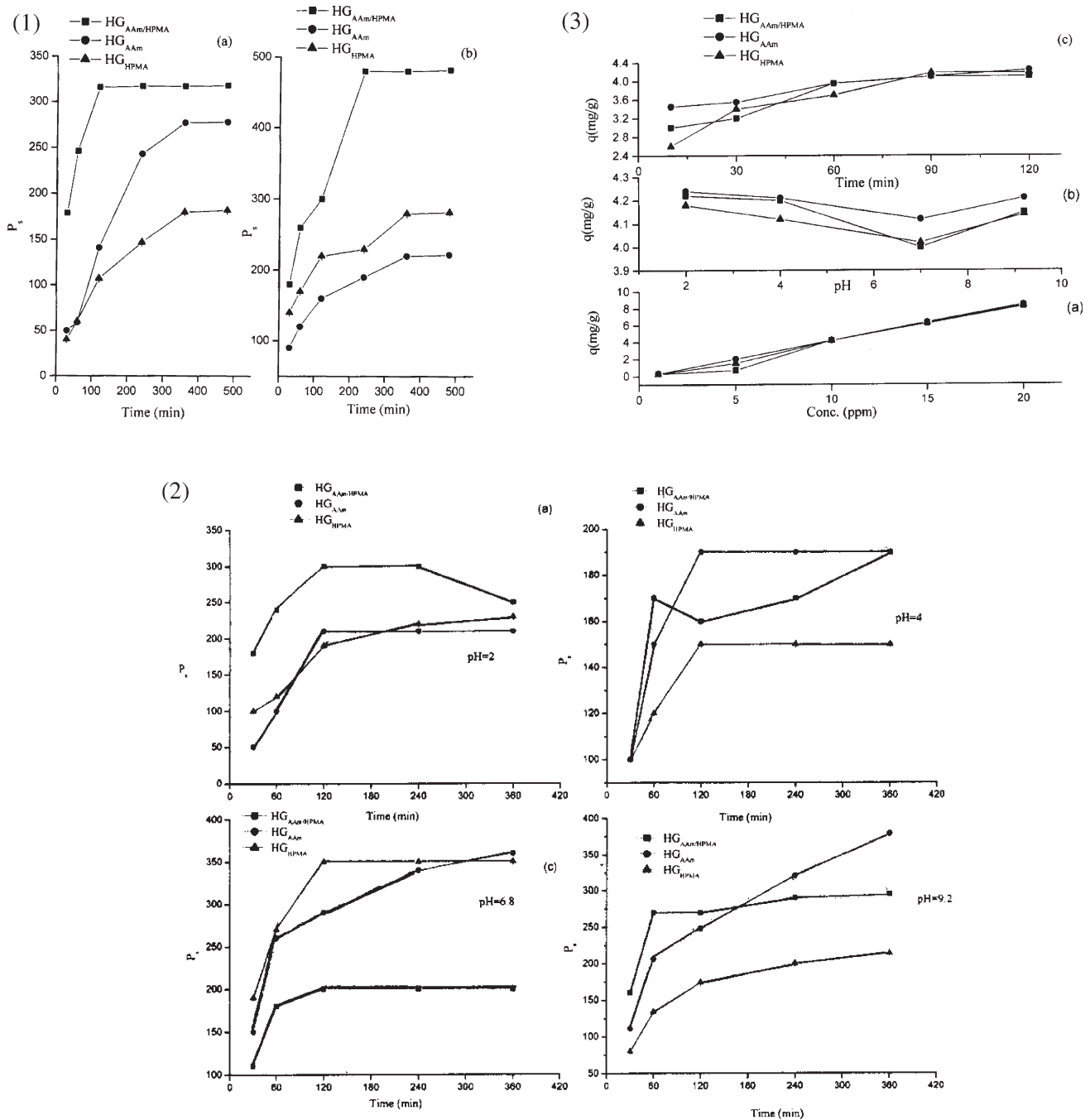


(b)



(c)

**Figure 2** SEM micrograph of the hydrogels: (a)  $HG_{AAm/HPMA}$ , (b)  $HG_{AAm}$ , and (c)  $HG_{HPMA}$ .



**Figure 3** (1) Percentage swelling of the hydrogels as a function of time at (a) 25 and (b) 35°C. (2) Percentage swelling of the hydrogels as a function of time at different pH's: (a) 2.0, (b) 4.0, (c) 6.6, and (d) 9.2 (temperature = 37°C). (3)  $q_e$  of the hydrogels for  $\text{Cu}^{2+}$  as a function of the (a) concentration, (b) pH, and (c) time (temperature = 37°C). (4) Langmuir isotherm plot for the adsorption of  $\text{Cu}^{2+}$  ions on (a)  $\text{HG}_{\text{AAm}}$  and (b)  $\text{HG}_{\text{HPMA}}$ . (5) Freundlich isotherm plot for the adsorption of  $\text{Cu}^{2+}$  ions on (a)  $\text{HG}_{\text{AAm/HPMA}}$ , (b)  $\text{HG}_{\text{AAm}}$ , and (c)  $\text{HG}_{\text{HPMA}}$ . (6) Pseudo-second-order kinetics for the adsorption of  $\text{Cu}^{2+}$  ions on (a)  $\text{HG}_{\text{AAm/HPMA}}$ , (b)  $\text{HG}_{\text{AAm}}$ , and (c)  $\text{HG}_{\text{HPMA}}$ .

evidence of the network formation, as the additional characteristic peaks of the functional groups of different components appeared in the resulting networks. The pure gelatin absorbed at 3426.9, 2926.3, and 1100  $\text{cm}^{-1}$  because of  $-\text{OH}$ ,  $-\text{CH}$ , and  $-\text{COC}-$  stretching, respectively. The spectrum of  $\text{HG}_{\text{AAm/HPMA}}$  had important additional peaks at 1654.8  $\text{cm}^{-1}$

( $\text{C}=\text{O}$  stretching in secondary amide), 1544.9  $\text{cm}^{-1}$  ( $-\text{NH}$  bending), and 1740  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$  stretching in ester groups), as shown in Figure 1. The spectrum of  $\text{HG}_{\text{AAm}}$  had important additional peaks at 1654.8  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$  stretching in secondary amide) and 1544.9  $\text{cm}^{-1}$  ( $-\text{NH}$  bending), and  $\text{HG}_{\text{HPMA}}$  had additional peaks at 1740  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$  stretching in

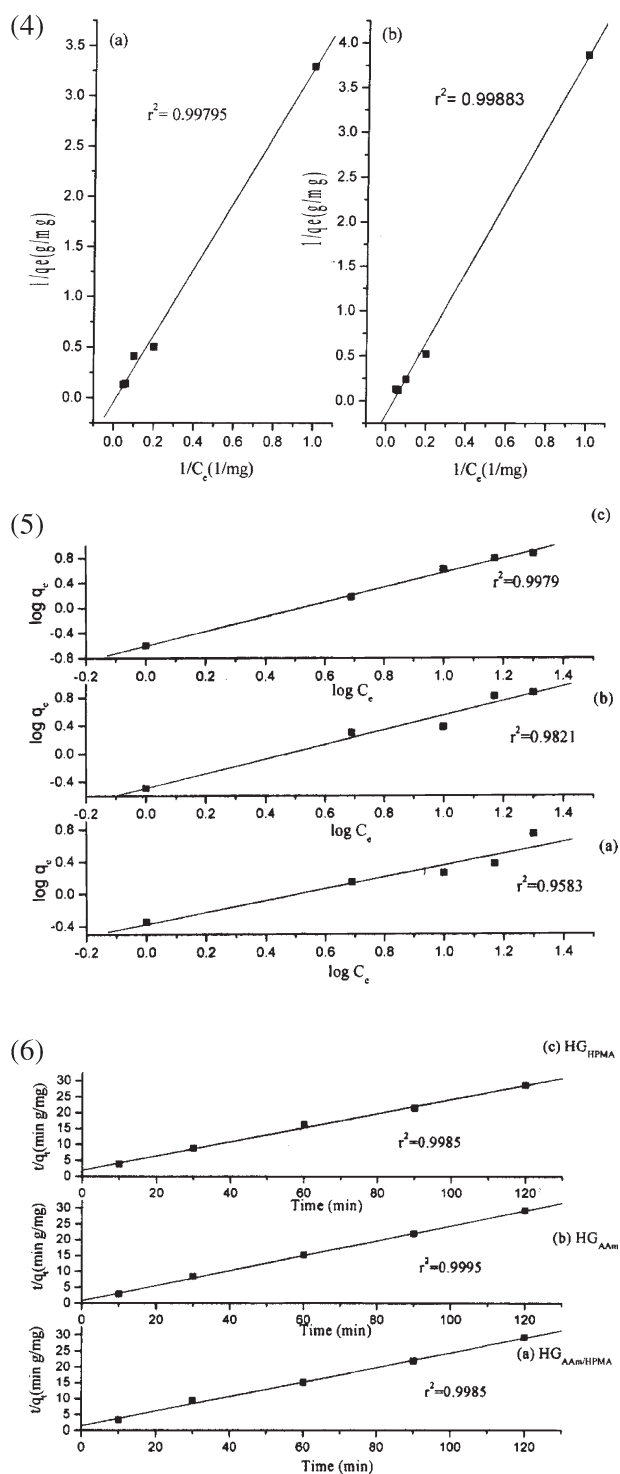


Figure 3 (Continued from the previous page)

ester group) in Figure 1. The SEM micrographs of different polymeric networks are shown in Figures 2(a–c). These reveal the surface morphology of polymeric structures. They provide evidence of the changes affected in the surface morphology after crosslinking reactions. These hydrogels showed good thermal stability, as reported for analogous hydrogels elsewhere.<sup>29</sup>

The swelling behavior of the hydrogels was observed to be affected both by the hydrogel structure and by external environmental factors, such as pH, temperature, and ion concentration. All of the hydrogels exhibited an increase in  $P_s$  with time up to 360 min, with  $HG_{AAm}$  reaching the equilibrium swelling [Fig. 3(1)]. The swelling behavior of the hydrogels as a function of temperature revealed that  $HG_{AAm}$  and  $HG_{HPMA}$  exhibited a maximum, yet comparable,  $P_s$  at 37°C. However, in the case of  $HG_{AAm/HPMA}$ , the maximum swelling was observed at 30°C; this showed that the combination of the hydrophilic and hydrophobic monomers in this hydrogel made it more temperature-sensitive than the other hydrogels. The swelling behavior of these hydrogels as a function of pH at 37°C for 360 min is presented in Figure 3(2).

### Sorption of the $Cu^{2+}$ ions

The  $P_u$  and  $q$  values as a function of time are presented in Table I and Figure 3(3). The  $P_u$  values increased with time, and after an initial rapid adsorption process, equilibrium was reached within 120 min. The temperature variation resulted in increases in the  $P_u$  and  $q$  values from 25 to 37°C and, thereafter, decreased with further increases in temperature. With an increase in temperature, the hydrogel structure opened up, and more active sites became accessible to the  $Cu^{2+}$  ions. At high temperature, as the ionic mobility increased, the ions had a tendency to desorb, and hence, a decrease in the adsorption capacity ( $q_e$ ) after the optimum temperature was observed.<sup>30</sup> These hydrogels exhibited some good performances, even at the low ion concentration (1 ppm). Increases in their  $P_u$  values from 50 to 84.8% and  $q$  values from 0.25 to 8.4 mg/g were observed with  $Cu^{2+}$ -ion concentration variation from 1 to 20 ppm within 120 min at 37°C and pH 7.0, as presented in Table I and Figure 3(3). The equilibrium was reached at a  $Cu^{2+}$  ion concentration of 10 ppm. On variation of pH, the performance of these hydrogels in the ion uptake was significant, as even in the acidic media, quite high  $q_e$  values were observed (Table I). The  $P_u$  values of these hydrogels as a function of pH are shown in Figure 3(3b). The highest  $P_u$  was observed in the acidic pH, which made these hydrogels of special interest in the ion uptake studies. The ion uptake decreased with increasing pH to neutral pH and then increased in the medium of pH 9.2. At low pH, the hydrogels swelled appreciably and partitioned the ions effectively to the active sites on the hydrogels. We suggest that in the acidic pH, the carboxylic ends of the constituent amino acids of the gelatin acquired  $H^+$ , which acted as exchangeable sites for the  $Cu^{2+}$ . In the basic medium, the number of the negatively

**TABLE I**  
**Adsorption of Cu<sup>2+</sup> on the Hydrogels with Various Values of Time, pH, and Concentration**

Polymer	Adsorption of Cu <sup>2+</sup> on the hydrogel (mg of Cu <sup>2+</sup> sorbed/g of xerogel)					<i>P<sub>u</sub></i>				
	10	30	60	90	120	10	30	60	90	120
	Time (min)					pH				
HG <sub>AAm</sub> /HPMA	3.00	3.2	3.95	4.10	4.10	60.0	64.0	79.0	82.0	82.0
HG <sub>AAm</sub>	3.45	3.55	3.95	4.10	4.24	69.0	71.0	79.0	82.0	84.8
HG <sub>HPMA</sub>	2.60	3.40	3.70	4.18	4.18	52.0	68.0	74.0	83.6	83.6
	pH					ppm				
	—	2	4	7	9.2	—	2	4	7	9.2
HG <sub>AAm</sub> /HPMA	—	4.22	4.20	4.00	4.15	—	84.5	84	80.0	83.0
HG <sub>AAm</sub>	—	4.24	4.21	4.12	4.21	—	84.8	84.3	82.5	84.2
HG <sub>HPMA</sub>	—	4.18	4.12	4.02	4.14	—	83.6	82.5	80.4	82.9
	ppm					ppm				
	1	5	10	15	20	1	5	10	15	20
HG <sub>AAm</sub> /HPMA	0.27	0.70	4.20	6.18	8.2	55.0	72.0	82.0	82.0	82.0
HG <sub>AAm</sub>	0.32	2.0	4.20	6.36	8.44	65.0	80.0	84.8	84.8	84.4
HG <sub>HPMA</sub>	0.25	1.50	4.18	6.27	8.30	50.0	60.0	83.6	83.6	83.0

Temperature = 37°C.

charged sites increased on the surface of the adsorbent; as a result, it showed more affinity toward the positively charged Cu<sup>2+</sup> ions.<sup>31,32</sup> The uptake and  $q_e$  of all of the synthesized hydrogels for Cu<sup>2+</sup> decreased in the presence of imidazole buffer at pH 7 because Cu<sup>2+</sup> ions also interacted with the imidazole ring.<sup>33</sup> The structure–property relationships were exhibited by these hydrogels in the Cu<sup>2+</sup>-ion uptake because HG<sub>HPMA</sub>, being hydrophobic in nature, showed the least uptake of the three hydrogels, although the differences were not significant.

The maximum  $P_u$  (84.8) was observed for HG<sub>AAm</sub> at the technologically important temperature, 37°C, and within a short time interval of 120 min and with a 10 ppm concentration of Cu<sup>2+</sup> ions. In view of the results discussed in the preceding paragraph, we evaluated MRC of HG<sub>AAm</sub> by subjecting it to four feeds each of a 10-ppm solution of Cu<sup>2+</sup> ions at 37°C and 120 min (Table II). An MRC of 14.9 mg/g was obtained after the fourth feed. The reusability of all three hydrogels was studied at a 10-ppm feed of the ions at 37°C and pH 7.0 after treatment with the Cu<sup>2+</sup>-loaded hydrogels with 0.1N ethylene diamine tetraacetic acid. All of the sorbed ions were eluted.

The regenerated hydrogels, HG<sub>AAm</sub>/HPMA, HG<sub>AAm</sub>, and HG<sub>HPMA</sub>, exhibited comparative uptake. This showed that these hydrogels were reusable.

### Mechanism and kinetics of Cu<sup>2+</sup> adsorption

To investigate  $q_e$  as a function of ion concentration, different sorption isotherms, that is, the Langmuir and Freundlich isotherms, were applied to the obtained experimental values. The linearized Langmuir isotherm allowed the calculation of  $q_e$  values and Langmuir constants and was equated by the following equation:

$$1/q_e = 1/q_{\text{mon}} + 1/K_L q_{\text{mon}} \times 1/C_e \quad (1)$$

where  $K_L$  is the Langmuir constant related to the energy of adsorption (L/mg),  $C_e$  is the equilibrium concentration (ppm) of Cu<sup>2+</sup> ions after a time period of 2h and  $q_{\text{mon}}$  is the maximum amount of adsorption corresponding to the complete monolayer coverage on the surface. The linear plots of  $1/q_e$  versus  $1/C_e$  showed good fit of the  $q_e$  values with the Langmuir adsorption isotherm model. The high

**TABLE II**  
**Adsorption of Cu<sup>2+</sup> on HG<sub>AAm</sub> with Repeated Treatments**

Polymer	Feed				<i>P<sub>u</sub></i>				MRC
	Adsorption of Cu <sup>2+</sup> on HG <sub>AAm</sub> (mg of Cu <sup>2+</sup> sorbed/g of xerogel)								
	First	Second	Third	Fourth	First	Second	Third	Fourth	
HG <sub>AAm</sub>	4.20	3.56	3.54	3.60	84.8	71.2	70.9	72.0	14.9

Cu<sup>2+</sup> = 10 ppm, temperature = 37°C, and time = 2 h.

**TABLE III**  
Langmuir Constants,  $r_2$  Values for the Freundlich Isotherm, and Pseudo-Second-Order Kinetics for the Adsorption of  $\text{Cu}^{2+}$  Ions on the Hydrogels

Polymer	Langmuir isotherm				Freundlich isotherm	Pseudo-second-order kinetics
	$r^2$	$q_{\text{mon}}$	$K_L$	$R_L$	$r^2$	$r^2$
HG <sub>AAm</sub> /HPMA	0.9587	5.43	0.05	0.66	0.9583	0.9985
HG <sub>AAm</sub>	0.9979	25.0	0.01	0.90	0.9821	0.9995
HG <sub>HPMA</sub>	0.9988	6.57	0.03	0.76	0.9979	0.9985

correlation coefficient ( $r^2$ ) values (0.9979, 0.9988) showed that the experimental data fit reasonably well in the linearized form of the Langmuir isotherm [Table III and Fig. 3(4)]. Similar results were also reported elsewhere.<sup>34</sup> The values of  $q_{\text{mon}}$  and  $K_L$  were calculated from the intercept and slope of the linear plots, respectively, and are presented in Table III. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter ( $R_L$ ), which is defined as follows:

$$R_L = 1/(1 + K_L C_0) \quad (2)$$

where  $C_0$  is the initial concentration of  $\text{Cu}^{2+}$ . The  $R_L$  value indicates the shape of isotherm, which predicts whether an adsorption system is favorable or unfavorable. The calculated  $R_L$  values were between 0 and 1, which indicated a favorable adsorption system, and these confirmed that the hydrogels were suitable candidates for  $\text{Cu}^{2+}$  adsorption (Table III).

The Freundlich equation presents a nonideal sorption that involves heterogeneous adsorption over the active sites. The linearized form of the Freundlich adsorption isotherm was used to evaluate the sorption data, and it is represented as follows:

$$\log q_e = \log K_F + (1/n) \log C_e \quad (3)$$

where  $K_F$  is an indicator of  $q_e$  and  $1/n$  is the adsorption intensity. The values of  $n > 1$ , as in the case of HG<sub>AAm</sub>/HPMA ( $n = 1.371$ ), signified favorable adsorption conditions.  $r^2$  indicated a lower match of the experimental values with the Freundlich adsorption isotherm [as shown in Table III and Fig. 3(5)]. The predominance of the Langmuir isotherm in this case was obvious from the nature of the absorbent groups, which led to the predominantly adsorption process.

The linear pseudo second-order equation is given as follows:<sup>35,36</sup>

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \quad (4)$$

where  $k_2$  is the equilibrium rate constant of the

pseudo second-order sorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ). Figure 3(6) shows a typical plot of the pseudo second-order equation  $t/q_t$  versus  $t$ . This shows that these hydrogels followed pseudo-second-order kinetics. The  $r^2$  values, as shown in Table III, were greater than 0.99.

From the perusal of the isotherm and the kinetics treatment of the experimental data, it follows that the removal mechanism was mainly by chemisorption and involved valency forces through the sharing or exchange of electrons between copper and active sites, such as  $-\text{OH}$ ,  $-\text{COO}^-$ , and  $-\text{CONH}_2$ , present on the surface of the hydrogels. The same mechanism was also reported elsewhere for the adsorption of  $\text{Cu}^{2+}$  on the guar gum hydrogels.<sup>30</sup> The Langmuir isotherm and pseudo-second-order kinetics model provided the best correlation with the experimental data for the adsorption of copper ions onto the hydrogel surface. Both assume the homogeneous surface of adsorbent for adsorption. Some contribution to the overall mechanism was also due to the ion exchange<sup>37</sup> of  $\text{Cu}^{2+}$  with the  $-\text{NH}_3^+$  of lysine or glutamic or aspartic acid present on the gelatin. The surface of the hydrogel provided multisites for  $\text{Cu}^{2+}$ . The pseudo-second-order equation, which was applicable for chemisorption onto the homogeneous surface, fit well in this case.<sup>38</sup>

### Adsorption thermodynamics

To study the nature of adsorption, the thermodynamic parameters for adsorption process, such as the standard Gibbs free energy change ( $\Delta G^\circ$ ), the standard enthalpy change ( $\Delta H^\circ$ ), and the standard entropy change ( $\Delta S^\circ$ ), were calculated with the following equations:<sup>39,40</sup>

$$\ln k = \Delta S^\circ/R - (\Delta H^\circ/R) \times (1/T) \quad (5)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

where  $k$  is the thermodynamic constant,  $R$  is the universal gas constant ( $\text{J/K/mol}$ ) and  $T$  is the temperature in Kelvin. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated from the slope and intercept of the plot of  $\ln k$  versus  $1/T$ .  $k$  for the sorption reaction was

**TABLE IV**  
**Thermodynamic Parameters for the Adsorption of Cu<sup>2+</sup> Ions on the Hydrogels**

Hydrogel	$\Delta H^{\circ}$ (J/mol)	$\Delta S^{\circ}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^{\circ}$ (J/mol) at			
			298 K	303 K	308 K	310 K
HG <sub>AAM</sub> /HPMA	55936	191.22	-1047	-2000	-2959	-3342
HG <sub>AAM</sub>	65722	224.5	-1179	-2301	-3424	-3873
HG <sub>HPMA</sub>	53409	182.9	-1095	-2009	-2924	-3290

calculated by the method described by Khan and Singh<sup>41</sup> by the plot of  $\ln(q_e/C_e)$  versus  $q_e$  and the extrapolation to zero  $q_e$ . The calculated values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  are presented in Table IV. The positive values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$ , respectively, indicated the endothermic nature of the adsorption interaction and the positive affinity of the hydrogels for Cu<sup>2+</sup> with a favorable increase in the randomness at the solid-solution interface during the adsorption process.<sup>39</sup>

### CONCLUSIONS

A series of the gelatin-based hydrogels were synthesized by a clean and simple method with biocompatible components. These hydrogels were effective sorbents for Cu<sup>2+</sup> ions. Despite the fact that all of the hydrogels exhibited good Cu<sup>2+</sup> uptake, a structure-property relationship was observed, as the hydrogel (HG<sub>AAM</sub>) with gelatin and polyacrylamide as components exhibited the best performance with an MRC of 14.9 mg/g and a  $P_u$  of 84.8%. The equilibrium isotherms obtained were close to the Langmuir isotherm; this showed that the adsorbent surface contained adsorption sites suitable for the operation of the monolayer adsorption. The experimental data followed pseudo-second-order kinetics. These hydrogels are suitable candidates for use as Cu<sup>2+</sup> sorbents for use in bioseparation and water purification technologies.

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