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ORIGINAL PAPER

Removal of Cu^{2+} and Pb^{2+} ions from aqueous solutions by starch-graft-acrylic acid/montmorillonite superabsorbent nanocomposite hydrogels

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Abstract In this study, the removal of copper(II) and lead(II) ions from aqueous solutions by Starch-graft-acrylic acid/montmorillonite (S-g-AA/MMT) nanocomposite hydrogels was investigated. For this purpose, various factors affecting the removal of heavy metal ions, such as treatment time with the solution, initial pH of the solution, initial metal ion concentration, and MMT content were investigated. The metal ion removal capacities of copolymers increased with increasing pH, and pH 4 was found to be the optimal pH value for maximum metal removal capacity. Adsorption data of the nanocomposite hydrogels were modeled by the pseudo-second-order kinetic equation in order to investigate heavy metal ions adsorption mechanism. The observed affinity order in competitive removal of heavy metals was found $Cu^{2+} > Pb^{2+}$. The Freundlich equations were used to fit the equilibrium isotherms. The Freundlich adsorption law was applicable to be adsorption of metal ions onto nanocomposite hydrogel.

Keywords Starch · Nanocomposite hydrogel · Heavy metal ion · Adsorption · Montmorillonite

Introduction

Starch has been the raw material of scientific and industrial studies for many decades, due to its low cost and biodegradability. Chemical modification of starch

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via oxidation, hydrolysis, esterification, etherification, and grafting has been extensively studied [1]. Chemical modification of starch via grafting of vinyl monomers is one of the most effective methods to incorporate desirable properties into starch without sacrificing its biodegradable nature [2]. Grafting of acrylamide [1, 3–5], acrylonitrile [3, 6], methylacrylonitrile [2], alkyl methacrylates [7, 8], vinyl ketones [9], 2-(dimethylamino)ethyl methylacrylate [10], acrylic acid (AA) [11–13] onto starch has been investigated. Starch graft copolymers have been used as hydrogels [12], flocculants [14, 15], and ion exchangers [16].

In recent years, the study of organic–inorganic nanocomposites has become a very important field [17]. Many layered, inorganic mineral micropowders such as mica, attapulgite, and kaolinite have been used in the preparation of polymers to achieve lower production costs and higher properties. Montmorillonite (MMT), a layered aluminum silicate with highly exchangeable cations and reactive groups on its surface, also has been widely used to improve the hydrogel properties of polymers [18]. Traditional superabsorbent network from synthetic polymers, such as poly(sodium acrylate) and polyacrylamide, often have some limitations besides poor biodegradability, and these flaws restrict its application widely [19]. Starch-graft copolymers have greater demand in industry due to their low cost and biodegradable properties and thus environmental friendly. Starch-graft copolymers have become the focus for the preparation inorganic–organic superabsorbent nanocomposite because of the environmental factors. Luo et al. reported the synthesis of starch-grafted poly(acrylamide-*co*-acrylic acid)/MMT with a γ-ray irradiation technique [20]. Li et al. investigated the properties of starch-based attapulgite nanocomposite hydrogels [19, 21].

The removal of toxic and polluting heavy metal ions from aqueous solutions has been given much more attention over the past few years. The removal of heavy metal content of waters because of their toxic effects on living organisms is extremely important. The toxic nature of heavy metals, even at trace level in natural waters has been a public health problem for many years [22]. The contamination of plants, animals, and humans by toxic heavy metals poses a containing and increasing threat to our environment [23]. Various methods exist for the removal of heavy metals from industrial water and natural water such as chemical precipitation, ion-exchange, and reverse osmosis techniques [24]. Graft copolymers of natural polysaccharides such cellulose [25–27] and starch [28–32] have been used in removal of heavy metal ions.

In our previous work [33], we reported the synthesis of superabsorbent composites by graft copolymerization reaction of starch and acrylic acid using *N*,*N*′-methylene-bisacrylamide (NMBA) as a crosslinker and cerium ammonium nitrate (CAN) as an initiator in the presence of MMT micropowder. The effect of MMT content in nanocomposite hydrogels on the swelling behavior was investigated. In addition, we described the removal of safranine T from aqueous solutions using starch-graft-acrylic acid/MMT (S-g-AA/MMT) nanocomposite hydrogels.

In this work, we described the removal of copper(II) and lead(II) ions from aqueous solutions by S-g-AA/MMT nanocomposite hydrogels. For this purpose, various factors affecting the removal of heavy metal ions, such as treatment time, initial pH of the solution, initial metal ion concentration and MMT content were investigated. The Freundlich equation was used to fit the equilibrium isotherms.

Experimental

Materials

A detailed preparation procedure of S-g-AA/MMT hydrogels was given in our previous work [33]. The structures of the polymers (S-g-AA copolymers) (XRD and FT-IR spectra of these hydrogels) and grafting reaction mechanism were also reported in our previous works [28, 33]. The grafting percentages and amount of the MMT of the S-g-AA/MMT nanocomposite hydrogels were shown in Table 1. Copper acetate and lead acetate (Merck, Germany) were analytical grade. Rest of the materials was chemically pure and used without any purification. All solutions and standards were prepared using distilled water.

Removal of heavy metal ions

Stock solution containing Cu^{2+} and Pb^{2+} or both of these ions were prepared by dissolving metal acetate salts in distilled water and by using diluted HNO_3 pH of stock solution was adjusted to 2, 3, and 4. S-g-AA/MMT nanocomposite hydrogels (0.2 g) were added in 50 mL of stock solution (8 mmol metal ion/L), and the mixture was stirred with a magnetic stirrer. The amount of residual metal ions in the aliquots of withdrawn solution was followed by atomic absorption spectrometer (AAS) (Varian SpectrAA FS-220) up to 48 h. Metal ion removal capacities of the copolymers were calculated as follows:

$$\text{Metal ion removal capacity (mmol/g copolymer)} = \frac{(C_i - C_t) \times V}{M_{\text{copolymer}}} \qquad (1)$$

where C_i, initial concentration of metal ions in the solution (mmol/L); C_t, the concentrations of metal ions in the solution after metal ion removal (mmol/L); V, volume of the solution (L); and $M_{\text{copolymer}}$, the weight of S-g-AA/MMT nanocomposite hydrogel (g).

Used S-g-AA/MMT nanocomposite hydrogels were regenerated with 1 M HCl to reemploy in heavy metal ion removal.

Table 1 S-g-AA/MMT nanocomposite hydrogels

Symbols	Graft (%)	MMT (%)
S-g-AA/MMT-0	30	0
S-g-AA/MMT-1	28	1
S-g-AA/MMT-3	27	3
S-g-AA/MMT-5	26	5
S-g-AA/MMT-10	26	10

Determination of mechanical properties

The compressive stress–strain measurements were performed using a tensile-compressive tester equipped with a load cell (Sensotec, Columbus, OH, USA, Model:31/1435-01, Range: 0.5 N, Sensitivity: 0.0001) and displacement transducer (Sensotec, Columbus, OH, USA, Model: D5/300 W LVDT, Range: 15 cm, Sensitivity: 0.001 cm) at 20 °C. To perform the stress–strain measurements the following steps were done; first the dried and powdered hydrogels were pressed by a hydraulic press (10 tons) (Specac Inc., Smyrna, USA) for 5 min to obtain discs of 13 mm in diameter. These disc shape hydrogel samples were put into Cu(II) acetate solutions for 24 h. And after the adsorption, the ion-adsorbed hydrogels used in the mechanical measurements. The shear modulus was calculated according to Eq. 2 [34, 35].

$$\tau = F/A = -G\left(\lambda - \lambda^{-2}\right) \tag{2}$$

where τ, the compressive stress; F, the applied force (N); A, the surface area of the deformed gel (m^2); G, the shear modulus; and $\lambda = h/h_0$ (where h and h_0 are the equilibrium heights of the deformed and original gels in m, respectively).

Results and discussion

Effect of pH

S-g-AA/MMT nanocomposite hydrogel samples were put into the metal stock solutions of pH = 2, 3, and 4 to investigate the effect of pH. The results for removal of Cu^{2+}, Pb^{2+} ions at different pH were shown in Fig. 1. The metal ion removal

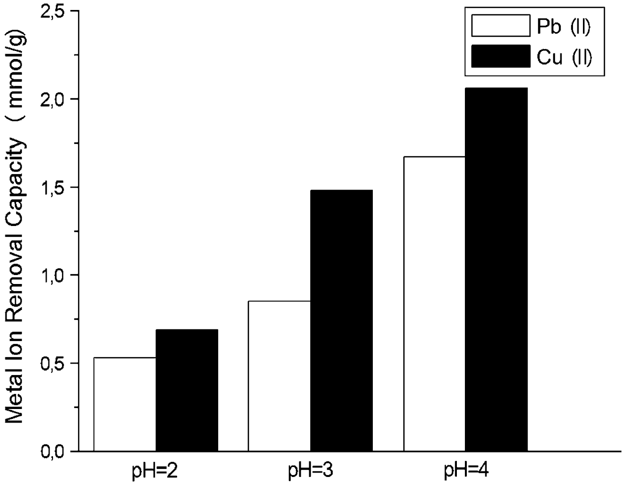

Fig. 1 The effect of the pH on the Cu^{2+}, Pb^{2+} ions removal capacities of S-g-AA/MMT-5 nanocomposite hydrogel

capacities of copolymers increased with increasing pH. When a network has an ionizable group such as carboxyl group, pH has an effective role on the ion removal capacity, because of changing of ionization degree. At low pH, the carboxyl groups are present in mostly nonionized form and a low interaction can occur between the carboxyl groups and the metal ions. Increasing the pH lets the carboxyl groups to be ionized and increases the probability of interaction between the carboxylic groups and the metal ions in the solution [30, 36]. pH 4 was considered to be optimal since lead precipitates as lead hydroxide at pH > 4.5.

Effect of MMT content on metal ion removal capacity of nanocomposite hydrogels

Heavy metal ion removal capacities of the copolymers were determined at pH = 4, at room temperature. S-g-AA/MMT nanocomposite hydrogels were added in stock solution (8 mmol metal ion/L) and the amount of residual metal ions in the aliquots of withdrawn solution was followed by AAS after the 48 h. Used S-g-AA/MMT nanocomposite hydrogels were regenerated with 1 M HCl and then they were reemployed in heavy metal ion removal.

Table 2 shows the influence of MMT content on the metal ion removal capacity of nanocomposite hydrogels.

As seen from Table 2, according to the MMT content there are no significant differences in metal ion removal capacities of nanocomposite hydrogels. The hydrogel that does not contain MMT, (S-g-AA/MMT-0), could not be regenerated because its mechanical properties were poor. On the other hand, the nanocomposite hydrogels that contain MMT could be regenerated with HCl solution. In regeneration processes, S-g-AA/MMT-1-10 hydrogels protected their mechanical properties while the pure hydrogel dissipated and lost its physical form. So, nanocomposite hydrogels (S-g-AA/MMT-1-10) could be regenerated and reemployed in heavy metal ion removal. The results of equilibrium metal ion removal capacities for origin and regenerated hydrogel samples were summarized in Table 2.

After the regeneration process, the ion removal capacities of the hydrogels were lowered. This is probably due to the noncompleted-regeneration process. This

Table 2 Equilibrium metal ion removal capacities of nanocomposite hydrogels

Hydrogels	Equilibrium metal ion removal capacity (mmol/g)			
	Original sample		Regenerated sample	
	Cu(II)	Pb(II)	Cu(II)	Pb(II)
S-g-AA/MMT-0	2.11	1.74	This sample cannot be regenerated	
S-g-AA/MMT-1	2.05	1.64	1.19	0.72
S-g-AA/MMT-3	2.06	1.66	1.17	0.72
S-g-AA/MMT-5	2.06	1.67	1.16	0.70
S-g-AA/MMT-10	2.02	1.59	1.14	0.69

means the regenerated hydrogels still contain heavy metal ions in their backbone, and the re-used hydrogels adsorb less amounts of metal ion than original ones. In our previous similar study [28] regenerated AA-graft-starch copolymers (noncrosslinked) exhibited almost same adsorption capacities with those of original ones. This case indicates almost full-regeneration. However, in this study, the hydrogels are crosslinked and also in nanocomposite type. These two properties cause noncompleted-regeneration process due to the increased difficulties of ion change between H^+ ions of the regeneration media and adsorbed Me^{2+} ions on the polymer backbone during regeneration.

Mechanical properties of nanocomposite hydrogels

For any hydrogel, swelling and mechanical properties are the two major aspects in determining its practical application. In this study, the synthesized hydrogels have excellent swelling values [33], but they are too soft to measure their shear moduli. Thus for getting an idea of their mechanical properties, the shear moduli measurements were carried out after the adsorption studies. Although these data do not give any information about the pristine gels, give some useful information about the used gels. By using these data (Fig. 2), it was clearly informed that using MMT increases the shear moduli of the hydrogels and induces simply removing of the used hydrogels from the adsorption media. As it seen from Fig. 2, increasing MMT content from 0 to 10%, increases the modulus in the range of 5370–14778 Pa. It is well known after the adsorption of a metal ion onto hydrogel sample the rigidity of the hydrogel increases. There is a close relationship between the adsorbed ion amount and rigidity. However, since the adsorption capacities of all hydrogels are very close to each other, it is concluded that MMT acts an important role on the significant increase in shear moduli. This case was also confirmed by the regeneration processes. While the S-g-AA/MMT-0 dissipates in the acid solution

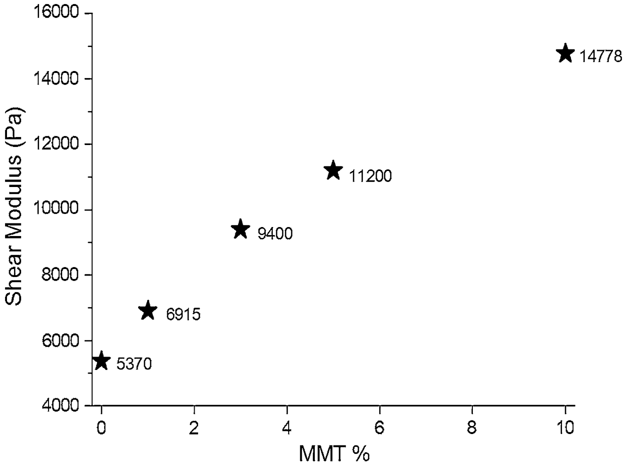

Fig. 2 Dependence of shear modulus on MMT for nanocomposite hydrogels

and could not be regenerated, the all nanocomposite hydrogels could be easily regenerated. Regeneration and re-using are important cases due to environmental aspects; improved mechanical property brings regeneration and re-using ability to hydrogels thus these abilities make these hydrogels considerable.

Kinetic studies

Figure 3 shows the effect of treatment time on the removal of Cu^{2+} and Pb^{2+} ions with S-g-AA/MMT-5 nanocomposite hydrogel. As it seen, the removal capacity of metal ions increased with the treatment time during the 24 h. The metal ion removal capacities of S-g-AA/MMT hydrogels show a rapid increase with increasing treatment time during the 5 h and then slow down and reach an equilibrium value (Fig. 3). The results indicate that the metal ion removal capacities almost reach equilibrium with in 24 h.

To investigate the mechanism of adsorption, the pseudo-first-order and pseudo-second-order equations were used to test the experimental data of adsorption tests. The first-order rate expression of Lagergren [37] is given as:

$$\log(q_\mathrm{e} - q_t) = \log q_\mathrm{e} - (k_1 t/2.303) \tag{3}$$

where q_e and q_t are the amounts of dye adsorbed on adsorbent at equilibrium and at time t, respectively (mmol/g), and k_1 is the rate constant of first-order adsorption (h^{-1}). A straight line of $\log(q_\mathrm{e} - q_t)$ versus t suggests the applicability of this kinetic model to fit the experimental data. In many cases, the first-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes [37, 38]. The second-order kinetic model [38, 39] is expressed as:

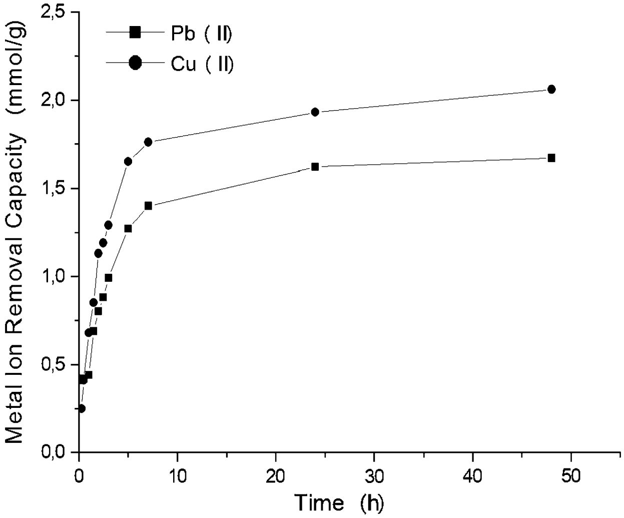

Fig. 3 The effect of the treatment time on the metal ion removal capacity of S-g-AA/MMT-5 nanocomposite hydrogel

$$t/q_t = 1/\left(k_2 q_e^2\right) + t/q_e \tag{4}$$

where k_2 (g/mmol h) is the rate constant of second-order adsorption. If second-order kinetics is applicable, the plot of t/q_t versus t should show a linear relationship. This kinetic model is more likely to predict the behavior over the whole range of adsorption and is in agreement with chemical sorption being the rate-controlling step [38, 39], which may involve valency forces through sharing or exchange of electrons between metal ions and adsorbent.

The slopes and intercepts of plots of $\log(q_e - q_t)$ versus t (Fig. 4) were used to determine the first-order rate constant k_1 and equilibrium adsorption q_e. Table 3 lists the calculated results. A comparison of results with the correlation coefficients (R^2) was also shown in Table 3. The correlation coefficients for the first-order kinetic model are low. Also, the calculated q_e values obtained from the first-order kinetic model do not give reasonable values, which are low compared with experimental q_e values. This suggests that the adsorption of metal ions onto the hydrogel nanocomposite is not a first-order reaction.

Table 3 also lists the computed results obtained from the second-order kinetic model. The correlation coefficients for the second-order kinetic model are very

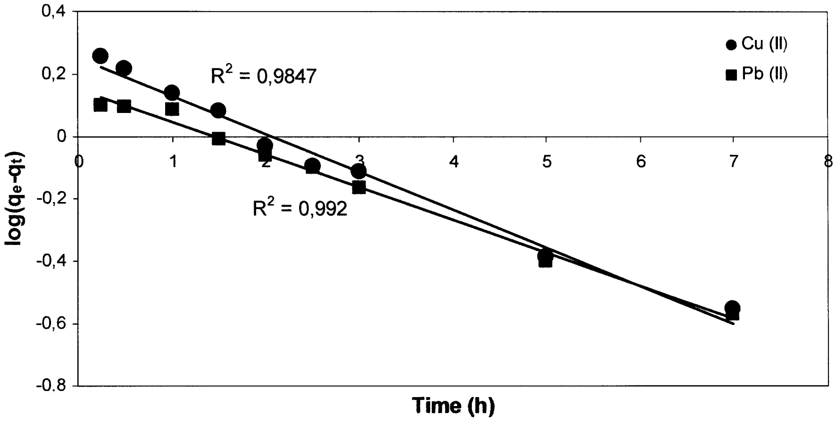

Fig. 4 Pseudo-first-order kinetic plot for the adsorption of Cu^{2+} and Pb^{2+} ions onto nanocomposite hydrogel

Table 3 Kinetic parameters for the adsorption of Cu^{2+} and Pb^{2+} ions onto hydrogels

Hydrogel	Metal ion	$q_{e,exp.}$	First-order kinetic model			Second-order kinetic model			h
			k_1	$q_{e,cal.}$	R^2	k_2	$q_{e,cal.}$	R^2	
S-g-AA	Cu^{2+}	2.11	0.1918	1.0646	0.9843	0.6419	2.14	0.9998	2.9481
	Pb^{2+}	1.74	0.1609	2.9505	0.8229	2.0179	1.74	1.000	6.4516
S-g-AA/MMT-5	Cu^{2+}	2.06	0.2805	1.80	0.9847	0.2410	2.13	0.9995	1.0986
	Pb^{2+}	1.67	0.2415	1.42	0.9920	0.2835	1.74	0.9985	0.8615

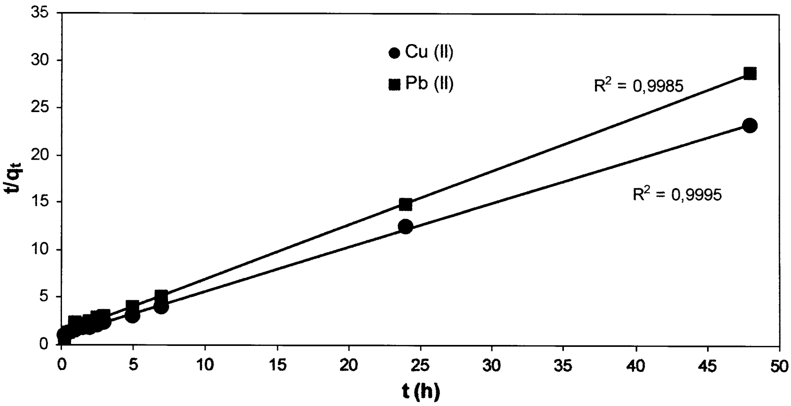

Fig. 5 Pseudo-second-order kinetic plot for the adsorption of Cu^{2+} and Pb^{2+} ions onto nanocomposite hydrogel

close to 1,000 for almost all the cases. Also, the calculated q_e values almost agree with the experimental data. These indicate that the adsorption system we studied belongs to the second-order kinetic model (Fig. 5).

By using pseudo-second-order kinetic model data, the initial sorption rate, h, can be calculated as given below;

$$[t \to 0] \qquad h = k_2 \times q_e^2 \tag{5}$$

As it seen from Table 3, the initial sorption rate for the adsorption of Pb^{2+} onto S-g-AA hydrogel is approximately two times greater than this of Cu^{2+}. However, in case of S-g-AA/MMT-5 hydrogel, Cu^{2+} initial sorption rate becomes faster than this of Pb^{2+}. This case is probably occurred due to the incorporation of MMT into the hydrogel network. MMT may block the entrance of metal ions into the internal faces of the nanocomposite hydrogel and since the Pb^{2+} ions have bigger ion radius than Cu^{2+} ions, the sorption rate of Pb^{2+} is more affected from this hindrance. Similar behavior was observed in case of adsorption capacity findings and discussed in next section.

Noncompetitive and competitive removal of Cu^{2+} and Pb^{2+} ions

In this part, the competitive removal of copper(II) and lead(II) ions from aqueous solutions was described. Since the natural and industrial waters rarely contain a single metal ion, competitive ion removal studies have taken much attention for a long time. In competitive ion removal studies, the concentration of each ion in aqueous solution was fixed to 4 mmol/L. The results for competitive removal of Cu^{2+}, Pb^{2+} ions were shown in Fig. 6.

It is known that several parameters such as pH, initial ion concentration, metal ion–adsorbent interactions, adsorbent's functional groups and surface properties, the competition of metal ions with each other, etc. affect the adsorption rate and capacity. In this study, both of noncompetitive and competitive adsorption properties of Pb^{2+} and Cu^{2+} ions onto nanocomposite hydrogel-type adsorbents were examined. In case

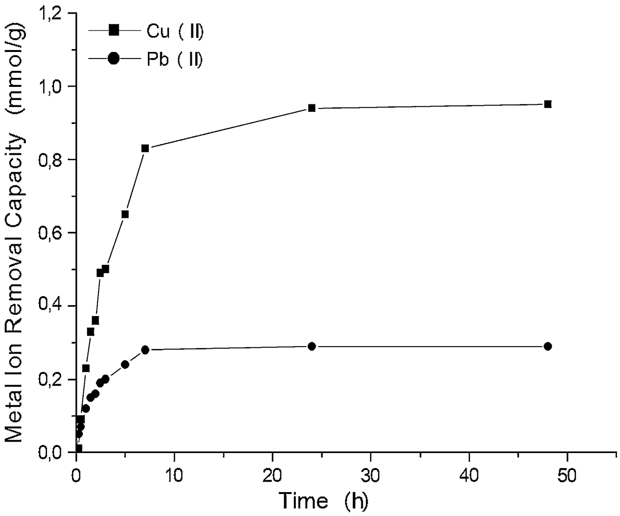

Fig. 6 The competitive removal of Cu^{2+} and Pb^{2+} ions

of noncompetitive adsorption, the adsorption capacity of the hydrogels found to be Cu > Pb. Contrarily, in similar studies [25, 27, 28] the adsorption capacities of the carboxyl group containing hydrogels followed in order Pb > Cu. In these studies, it is concluded that Pb(II) ions have stronger interaction than this of Cu^{2+}. Pb^{2+} ion has bigger ion radius than Cu^{2+} ion, and this property makes Pb^{2+} ions more electropositive, which facilitates electrostatic interaction between metal ion and carboxyl groups of the hydrogel. However, in all these studies the used hydrogels are not nanocomposite (even noncrosslinked [28]). As it said above, in our study the noncompetitive adsorption data showed that the adsorption capacities of the hydrogels followed in order Cu > Pb. We have concluded that this interesting behavior may occur due to the presence of MMT in the crosslinked hydrogel network. As it discussed before, the adsorption process can be affected several parameters such as metal ion–adsorbent interaction and adsorbent surface properties. Although the bigger the ion radius the stronger the metal ion–adsorbent interaction is, but the more difficult the diffusion into the crosslinked hydrogel network is. The presence of MMT in the hydrogel network further prevents the diffusion of Pb^{2+} ions into the internal faces of the hydrogel than Cu^{2+} ions and this case causes a decrease Pb^{2+} adsorption capacity than that of Cu^{2+}.

In case of competitive adsorption studies, total ion adsorption capacity of the S-g-AA/MMT-5 hydrogel was found to be 1.2 mmol/g and according to adsorption data the hydrogel is more selective to Cu^{2+} ions. This selectivity increscent is probably due to the hindrance effect of MMT on hydrogel's affinity for binding of Pb^{2+} ions.

Adsorption isotherms

An adsorption isotherm describes the relationship between the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. The Freundlich equation [40] is the earliest known relationship describing the adsorption equation. Freundlich isotherms were obtained by different initial metal ion concentrations (100–500 mg/L) and 0.1 g nanocomposite hydrogel sample dose for a constant time of 48 h. The adsorption isotherms data were correlated with the Freundlich equations and the Freundlich constants K_f (mg/g) and n (intensity of adsorption) were calculated from the following equations:

$$q_e = K_f \times C_e^{1/n} \tag{6}$$

$$\log q_e = \log K_f + 1/n \log C_e \tag{7}$$

where q_e is the amount of metal ion adsorbed (mg/g) onto nanocomposite hydrogel. The parameters of Freundlich isotherm, K_f and n as well as the regression coefficients R^2 are given in Table 4. Linear plots of log q_e versus log C_e for the different initial metal ion concentrations illustrated that the adsorption follows the Freundlich isotherm (Fig. 7). Such conclusion can be drawn from data R^2 that the Freundlich adsorption law is applicable to be adsorption of metal ions onto nanocomposite hydrogel (Table 4). According to Freundlich adsorption theory, the

Table 4 Freundlich constants of adsorption isotherm for metal ions

Metal ions	K_f	n	R^2
Cu(II)	3.18	1.46	0.9310
Pb(II)	1.47	1.23	0.9588

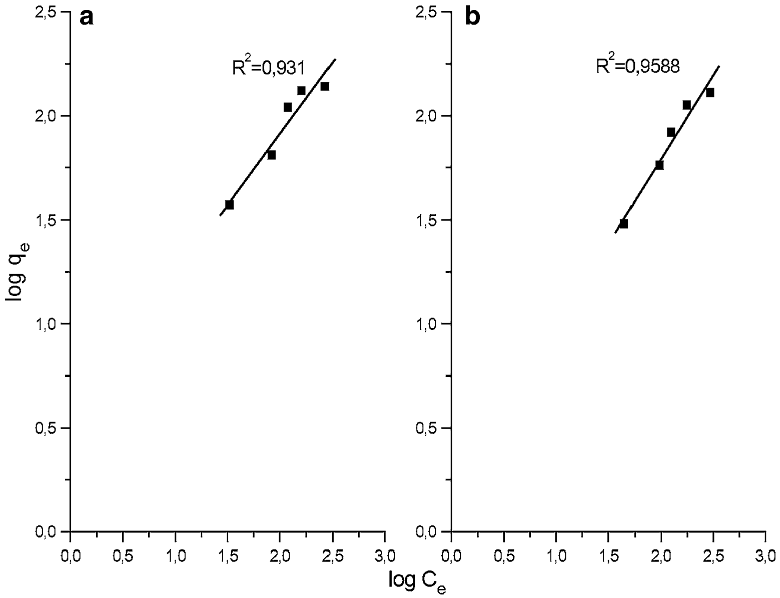

Fig. 7 Freundlich isotherm for the adsorption of **a** Cu^{2+}, **b** Pb^{2+} ions onto nanocomposite hydrogels

n values between 1 and 10 indicate beneficial adsorption [40], and in this study all *n* values are higher than 1 which demonstrate beneficial adsorption.

Conclusions

In this study, we describe the removal of Cu^{2+} and Pb^{2+} ions from aqueous solutions using S-g-AA/MMT nanocomposite hydrogels. Effects of various parameters such as treatment time, initial pH of the solution, initial metal ion concentration and MMT content were investigated. The isotherm data were fitted with Freundlich isotherm. The following conclusions can be drawn:

- Although incorporation of MMT into the hydrogel network did not affect adsorption capacities, it gained high-mechanical properties and increased shear moduli of the hydrogels. Thus, while the pure hydrogel could not be regenerated, all nanocomposite hydrogels could be easily regenerated. Since regeneration and reemploying of the hydrogels are important factors due to environmental and economical aspects, these high-mechanical properties make the nanocomposite hydrogels considerable.
- The metal ion removal capacities of copolymers increased with increasing pH. pH 4 was considered to be optimal since lead precipitates as lead hydroxide at $pH > 4.5$.
- The results indicate that the metal ion removal capacities of nanocomposite hydrogels almost reach equilibrium with in 24 h. Adsorption processes of Cu^{2+} and Pb^{2+} onto the nanocomposite hydrogels followed pseudo-second-order type adsorption kinetic.
- The adsorption capacity for all hydrogels in both noncompetitive and competitive adsorption cases is followed the order $Cu^{2+} > Pb^{2+}$.
- The adsorption isotherms data were correlated with the Freundlich equations. Linear plots of $\log q_e$ versus $\log C_e$ for the different initial metal ion concentrations illustrated that the adsorption follows the Freundlich isotherm.

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