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Swelling and metal ion uptake characteristics of kaolinite containing poly [(acrylic acid)-co-acrylamide] hydrogels

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ABSTRACT

Hydrogels of poly [(acrylic acid)-co-acrylamide], with N,N′-methylene bisacrylamide (MBA) crosslinker and different compositional ratios of kaolinite were prepared and investigated. The swelling characteristics of the hydrogels were investigated in distilled water as a function of clay content. The clay–hydrogel composite of 5.3% clay percentage showed a higher swelling property in distilled water relative to clay-free hydrogel. The swelling ratio was found to be affected by the change in contact time, pH, salt solution and temperature. The adsorption properties of the hydrogels towards Mn(II), Cu(II) and Zn(II) in aqueous solutions were also studied at different conditions. The rate of adsorption followed the pseudo-second-order kinetics. Elution behavior of loaded hydrogel (P3) was also studied in EDTA solution.

Keywords: Hydrogels; Acrylamide polymers; Swelling; Kaolinite; Adsorption; Metal ions

1. Introduction

Hydrogels have great applications in different fields such as medicine as drug delivery devices, absorbent pads, hydrometallurgy and water purification [1–4]. In agriculture, they are used as soil conditioners to reduce irrigation, water consumption, run off and soil erosion [5–8] and as controlled release fertilizers [9–11]. Hydrogel polymers are capable of swelling and retaining huge volumes of water (sometime about thousand-fold water compared with the dry mass of polymer) in the swollen state [12,13]. This property is related to the flexibility and hydrophilicity of the polymer network that depend on the chemical composition of the hydrogel [14]. Layered silicates-containing hydrogels are characterized by good swelling, mechanical, and thermal properties [15]. Therefore, clay-based hydrogel composites have a greater demand due to their low cost and high water absorbing capacity.

Swellability of the hydrogels is affected by the salt solutions and their ionic strength, pH and temperature. The ability to partition an ionic species by a hydrogel can be further enhanced by the proper selection of its hydrophilic components. For example, the uptake of metal ions by a hydrogel is affected by hydrophilic-hydrophobic balance that is related to the nature of chelating sites, the nature of monomer and the extent of crosslinking [16,17]. Weian et al [18] prepared nanocomposite hydrogels from organophilic montmorillonite and poly (vinylpyrrolidone/acrylic acid that showed swelling ratio $S = 45$. Tong et al. [19] presented a hydrogel of polyvinyl alcohol incorporating carbon nanotubes that showed $S = 5$. Li et al. [20] cited a hydrogel composed of poly (acrylamidoglycolic acid–co–acrylamide) that gave $S \approx 500$.

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Polymeric hydrogels are promising materials in the field of hydrometallurgical applications and water purification due to their chemical stability and facility of incorporation of different chelating groups into the polymeric network. Hydrogels have been used as membranes in water purification. These materials have advantages over the conventional ion exchangers and chelating resins due to their high wettability and swellability that might be advantages to improving adsorption of target metals. Hydrogels are commonly used in the diffusive gradient thin film technique that provides a means of measuring labile metal species in natural water. They separate labile metal species *in situ*, eliminating the need for sample collection and storage. The technique relies on the diffusion of metal species through hydrogel followed by their complexation by a chelating agent. Thus, preconcentration of the labile metal occurs allowing the detection of very low concentrations of metal in solution [21,22].

In the present work, a number of kaolinite-containing hydrogels of an acrylic acid/acrylamide copolymer have been prepared. Swelling characteristics of the hydrogels obtained and their adsorption behavior towards some selected metal ions were investigated.

2. Experimental

2.1. Preparation of hydrogels

2.1.1. Preparation of the poly(acrylic/acrylamide) hydrogel

The preparation was carried out following a modified method of the early reported method [9]. Acrylic acid (AA) (Merck) in the amount of 7.5 mL was placed in a round bottom flask and partially neutralized (neutralization degree 63%) by 4.1 mL (33%) ammonia solution (Merck) (ratio of acrylic acid:acrylamide (AA:AAm) is 1:1.7). An aqueous solution containing 0.3947 g of N,N′-methylene bisacrylamide (MBA) (Aldrich) was added with continuous stirring for 30 min. A Fisher Scientific balance (0.1 mg accuracy) from Denver Instrument (USA) was used. An amount of 0.0789 g of each initiator [extra pure ammonium persulphate, Laboratory Rasayan, Boisar,. and sodium sulphite, Na_2SO_3 (Merck)] was dissolved in distilled water and added to the reaction mixture. The mixture was heated on a water bath at a temperature of 75–80°C. After 1 h, the formed hydrogel was filtered off, washed with distilled water several times and dried in air. The dried hydrogel was stored in the desiccators before use and is referred to as P1.

2.1.2. Preparation of kaolinite-containing hydrogel

Kaolinite (Merck) of cation exchange capacity (CEC) = 12.9 mmol/100 g was used in this study. Kaolinite was characterized by X-ray diffraction (XRD) using an X-ray diffractometer (XRD), Scientag (USA), FN: AGKU.RD, with Ni-filtered Cu K_α radiation.

The above method of preparation of the gel was repeated in the presence of kaolinite at weight percentages of 1.3, 5.3, 7.3, 10.3 and 13.3% relative to the monomer. The hydrogels obtained are referred to as P2, P3, P4, P5 and P6, respectively.

FT-IR measurements were used to characterize the hydrogel prepared. A portion of the hydrogel was air dried for several days and then was further dried in an oven for 2 h at 70°C. The oven-dried sample was ground with KBr and then compressed as pellets under hydraulic pressure. The pellets obtained were again dried in oven at 70°C for 1 h and used for FT-IR measurments using the Nicolet IR200 FT-IR.

2.2. Swelling studies

2.2.1. Effect of time

Air-dried hydrogel samples in the amount of 0.25 g of P1 or P3 were placed in 25 mL distilled water at 25°C for different time intervals. The swollen samples were then removed, blotted with a filter paper to remove non-absorbed water and weighed. All experiments were carried out in duplicate and the swelling values were the average of two data points. The swelling ratio S (g/g) was calculated using the formula [18]:

$$S = \frac{W_t - W_o}{W_o} \qquad (1)$$

where W_o is the weight (g) of the dried hydrogel at 70°C and W_t is the weight (g) of swollen gel at time t.

2.2.2. Effect of clay content

An amount of 0.25 g of each air-dried hydrogel (P1–P6) was placed in 25 mL distilled water for 18 h at 25°C. The swollen samples were blotted and weighed. The swelling ratio was calculated using Eq. (1) (W_t is the weight of the hydrogel at $t = 18$ h).

2.2.3. Effect of pH

An amount of 0.25 g of air-dried hydrogel samples—P1 or P3—was placed in 25 mL distilled water. The samples were subjected to solutions of different pH using 0.1 M NaOH or 0.1 M HCl for 18 h at 25°C. The values of S were calculated for the swollen samples.

2.2.4. Effect of salt solution

1. Sodium salt solutions: An amount of 0.25 g of air-dried samples of P1 or P3 was immersed in 25 mL

aqueous solution of EDTA-disodium salt (2×10^{-3} M), NaCl (4×10^{-2} M) or Na_2SO_4 (4×10^{-2} M) for 1 h at 25°C. The swelling ratio (*S*) for samples was calculated.

2. Heavy metal salt solutions: An amount of 0.25 g of air-dried hydrogel samples of P1 or P3 was immersed in 25 mL aqueous sulphate solution of some divalent metal ions ($MnSO_4.H_2O$, $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$) with an initial concentration of 5×0^{-3} M for 10 min at 25°C. Then the *S* values were obtained.

2.2.5. Effect of concentration of metal ion

An amount of 0.25 g of air-dried hydrogel samples of P1 or P3 was immersed in aqueous copper sulphate solutions with two different concentrations (5×10^{-3} M or 2×10^{-2}M) for 10 min at 25°C. The *S* values of samples were calculated.

2.2.6. Effect of temperature

An amount of 0.25 g of air-dried hydrogel samples of P1 or P3 was immersed in 25 mL distilled water. The samples were placed in a thermostated water bath at different temperatures (25°C, 40°C, 50°C, 60°C and 70°C) for 18 h. The swelling ratio was calculated for each sample.

2.3. Metal ion uptake studies

2.3.1. Effect of pH

Uptake experiments of metal ions at different pHs were carried out by placing portions of 0.25 g of air-dried samples of P1 or P3 in a series of flasks containing 25 mL aqueous solutions of Mn(II), Cu(II) or Zn(II) with an initial concentration of 5×10^{-3} M. The pH was adjusted using 0.1 M NaOH and 0.1 M HCl. The flasks were shaken on a Vibromatic-384 at 300 rpm at 25°C for 1 h for Zn(II) and Mn(II) and for 18 h in the case of Cu(II) till reaching equilibrium. The residual concentration of metal ions was measured using a Perkin-Elmer 2380 atomic absorption spectrometer (AAS). The amount of metal ion adsorbed by the hydrogel (q_e, mmol g^{-1}) was calculated according to the following equation [23]:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \qquad (2)$$

where C_0 and C_e are the initial and equilibrium concentration of metal ion (M), respectively, *V* is the volume of solution (mL) and *m* is the mass of hydrogel dried at 70°C.

2.3.2. Effect of contact time

Portions of 0.25 g of air-dried hydrogel samples of P1 or P3 were placed in a series of flasks. To each flask, 25 mL aqueous solution (5×10^{-3} M) of Mn(II), Cu(II) or Zn(II) at natural pH was added and shaken at 25°C. Five milliliters of the solution were taken at different time intervals (from 2.5 min to 24 h). The residual concentration of metal ions was determined using AAS. The amount adsorbed of metal ion (q_e, mmol g^{-1}) was calculated according to Eq. (2).

2.3.3. Effect of initial concentration of metal ions

Portions of 0.25 g air-dried samples of P1 or P3 were placed in a series of flasks containing 25 mL of metal ion solution with different concentrations at natural pH of each metal ion. The contents of the flasks were shaken at 300 rpm and 25°C for 1 h for Zn(II) and Mn(II) and for 18 h for Cu(II). After equilibration, 5 mL of the solution was taken for the determination of residual concentration of metal ions by AAS. The adsorbed amount of metal ion by the hydrogel (q_e, mmol g^{-1}) was then calculated.

2.4. Elution studies

Portions of 4 g of the P3 air-dried sample were placed in the same volume of solutions from $MnSO_4$, $CuSO_4$ or $ZnSO_4$ at a concentration of 5×10^{-3} M overnight. The metal-loaded hydrogel was filtered off, washed thoroughly by distilled water to remove the excess of non-adsorbed metal ions, dried at 70°C and ground for elution studies in EDTA solution.

2.4.1. Effect of EDTA

An amount of 0.02 g of dry metal-loaded gel was soaked for 12 h in 10 mL EDTA-disoduim salt with different concentrations (1×10^{-4} M to 0.1 M). The ions of Mn(II), Cu(II) or Zn(II) released in the EDTA solution were measured by AAS. The release percent of metal ions was calculated from the following equation [24]:

$$\text{Release (\%)} = \frac{\text{Released amount of metal ion in EDTA solution } (C_r)}{\text{Total amount of loaded metal ion on gel } (C_t)} \times 100 \qquad (3)$$

2.4.2. Effect of time

An amount of 0.02 g of dry metal-loaded gel was placed in 10 mL EDTA-disoduim salt with an initial concentration of 0.1 M for different time intervals. The concentration of the released Mn(II), Cu(II) or Zn(II) was measured by AAS and the release percent (%) of metal ions was calculated. The same experiment was repeated at a lower concentration of EDTA (5×10^{-3} M).

3. Results and discussion

3.1. Characterization of hydrogels

FT-IR spectra of kaolinite clay mineral showed characteristic bands of kaolinite at ~3696.2, 3620.7, 1100, 1032.6, 1007.3, 913.4, 698.6, 537.5, 469.7 and 428.8 cm^{-1}. Bands of large intensity at the region 3690–3620 cm^{-1} represent well-crystallized kaolinite. XRD patterns of kaolinite showed diffraction lines at 2θ = 12 and 24.5° and the width of the 002 diffraction peak (d = 3.62 Å) at half the maximum height, which confirms well-crystallized kaolinite [25].

FT-IR spectra of P3 are characterized by a number of peaks at 3445(m), 2886(m), 1700(m), 1694(s) 1647(s), 1401 and 1170, and 1067 cm^{-1}. These peaks are assigned to υNH, υCH, υC=O of carboxylic acid, υC=O (amide I), δNH (deformation-amide II), υC-N (amide III) and/or in plane OH bending and υC-O of carboxylic acid and/or the carboxylate group, respectively. These assignments confirm the formation of the polymer as well as the presence of COOH/COO$^-$ and CONH$_2$ groups in the hydrogel. The observed slight changes between the spectrum of P1 and that of P3 may be attributed to the presence of kaolinite in P3 [4,9,11,12].

3.2. Swelling studies

It is well known that the swelling properties of the hydrogel are affected by the nature of the medium, ionic strength, pH, temperature and its ability to interact with different chemical species [16]. The swellability of the prepared hydrogels was investigated in terms of kaolinite content and at different experimental conditions of time, pH, salt solution, ionic strength and temperature.

3.2.1. Effect of kaolinite content

The swellability of kaolinite containing hydrogels (P2–P5) in distilled water was found to be greater than that of free kaolinite (P1). The values of swelling ratio (S) are 97.83, 220.62, 282.80, 157.02, 138.99 and 86.81 g/g for P1, P2, P3, P4, P5 and P6, respectively. It is seen that as the kaolinite content increases, the swellability increases up to the compositional ratio of 5.3% (w/w) and then decreases in the range 7.3–13.3%. This behavior may be explained as follows: (1) In the lower range of kaolinite content (P1–P3), kaolinite particles become highly dispersed throughout the hydrogel; (2) the electrostatic repulsion between the negatively charged –COO$^-$ of the polymer. Both factors lead to the increase of the free space of the hydrogel; (3) In the higher range of kaolinite content (>5.3%), the observed decrease in the swellability may be attributed to the aggregation of kaolinite fine particles and to the shielding of the carboxylate groups with large number of Na$^+$ ions lowering the repulsion forces between them. The shielding effect along with the higher content of kaolinite results in the decrease of the free volume inside the gel and therefore lowers the swellability [12,15].

3.2.2. Effect of time

The swelling ratio of both kaolinite-free gel (P1) and kaolinite-containing composite (P3) in distilled water as a function of time is given in Fig. 1. Obviously, the kaolinite-containing composite shows a higher rate of swelling relative to that of kaolinite-free hydrogel in the initial time periods of swelling (~2 h). Equilibrium water absorbency was achieved within 6 h with swelling values of 95 and 275 (g/g) for both P1 and P3, respectively (sample pre-dried at 70°C). This indicates that P3 is characterized by good swelling properties relative to P1.

The water absorption data in Fig. 1 were treated according to pseudo-second-order kinetics (Eq. 4) [26,27]:

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

where q_e and q_t refer to the amount of water absorbed at equilibrium and at time t, respectively (mol g^{-1}), k_2 (g mol^{-1} min^{-1}) is the overall rate constant of the pseudo-second-order kinetics. The values of q_e and k_2 were obtained from the slope and intercept of the straight line obtained by plotting t/q_t against t. The values of k_2 were found to be 9.43×10^{-3} and 9.72×10^{-4} g mol^{-1} min^{-1} for P1 and P3, respectively. Values of q_e were found to be 5.45 and 17.67 mol g^{-1} for P1 and P3, respectively. A satisfactory agreement was found between calculated and experimental values of q_e (5.44 and 17.57 mol g^{-1} for P1 and P3, respectively). This indicates the validity of the pseudo-second-order model for water absorption.

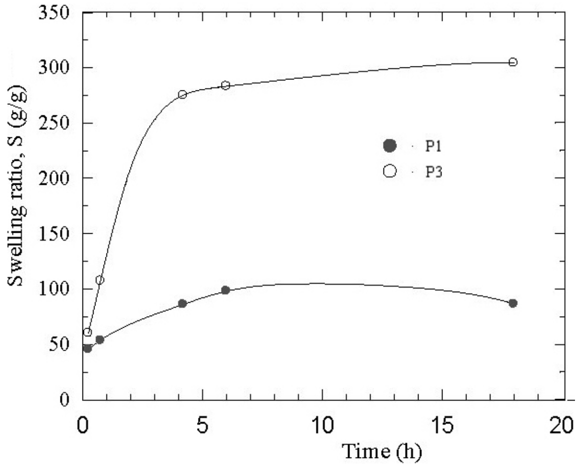

Fig. 1. Swelling of the hydrogels P1 and P3 in distilled water as a function of time at natural pH and 25°C.

The above kinetic behavior gives an indication for the effective role of the textural properties of the hydrogel on the rate of water absorption. This can be confirmed by treating the uptake-time data according to the following pore diffusion model [28–30]:

$$q_t = X + K_{dif}\, t^{0.5} \qquad (5)$$

where q_t represents the quantity of water absorbed at time t (mol g^{-1}), X represents the boundary layer diffusion effects (external film resistance), and K_{dif} is the diffusion rate constant (mol g^{-1} min$^{-0.5}$). The plot of q_t against $t^{0.5}$ gives a straight line with slope and intercept equal K_{dif} and X, respectively. As the value of X decreases, the effect of external film resistance on the reaction rate decreases. The values of K_{dif} were found to be 0.193 and 0.867 mol g^{-1} min$^{-0.5}$ for P1 and P3, respectively. The values of X were found to be 1.724 and 0.161 for P1 and P3, respectively. The positive values of X confirm the effect of boundary layer on the rate of water absorption. Therefore, the rate of water absorption is controlled by the pore diffusion and the boundary layer resistance [28]. The observed higher values of K_{dif} as well as the lower values of X (external film diffusion) of P3 relative to P1 may be related to the higher hydrophilic nature of kaolinite.

3.2.3. *Effect of pH*

The effect of pH on the swelling behavior of the hydrogels (P1 and P3) is represented in Fig. 2. Obviously, the swelling ratio increases as the pH increases from 2 to 7 (for P3) or from 2 to 5 (for P1) using NaOH. This may be explained on the basis of the increased dissociation of carboxylic groups of the gel that leads to a higher repulsion increasing the internal free volume of the gel. On the other hand, the presence of free Na$^+$ ions increases the osmotic pressure inside the gel which enhances the diffusion of water molecules into the gel. Further addition of NaOH will increase both pH of the medium as well as the shielding effect of Na$^+$ ions on the carboxylate groups. This effect again lowers the repulsion between carboxylate groups and therefore, lowers the free volume inside the gel giving a lower swellability. The observed lower swellability value (~ zero) at pH 2 for both investigated gels may be related to higher extent of undissociated carboxylic groups. The undissociated carboxylic groups are characterized by a lower degree of hydrophilicity and a higher capability of H-bond formation giving a rigid network with a small internal free volume. These reasons synergistically resist the diffusion of water into the gel and therefore lead to a lower degree of swellability [17,18, 20,31].

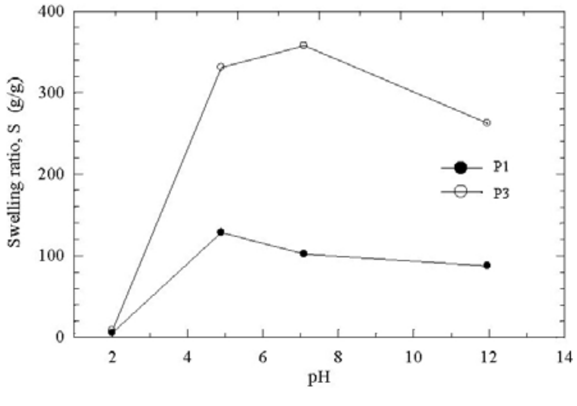

Fig. 2. Effect of pH on the swellability of P1 and P3 in distilled water at 6 h and 25°C.

3.2.4. *Effect of salt solution*

The effect of salt solution on the swellability of the investigated hydrogels (P1 and P3) was investigated and the results are given in Table 1. Generally, it is seen that the swellability of hydrogel decreased in the salt solution (except EDTA-disodium salt) relative to distilled water. The swellability in the heavy metal salt solutions of Mn(II), Cu(II) and Zn(II) was sharply decreased (within 10 min) relative to sodium salt solutions (60 min). The observed decrease of swellability in sodium salt solutions (NaCl or Na_2SO_4) relative to distilled water can be explained on the basis of osmotic pressure difference due to Na$^+$ concentration gradient between inside and outside the gel. The decrease in concentration gradient of Na$^+$ from the bulk of the solution towards the inside of the gel causes the diffusion of water out of the gel giving a lower swellability. This effect along with the shielding of carboxylate groups by Na$^+$ reduces the free volume inside the gel [20–22]. The observed increase in the swellability in the case of EDTA-disodium salt may be attributed to the

Table 1
Swelling ratio of P1 and P3 in distilled water and metal ion salts

	Hydrogels	
	S (g/g), P1	*S* (g/g), P3
Dist. water	56	145
EDTA-disodium[a]	75	175
NaCl[b]	40	70
Na_2SO_4[b]	43	65
$MnSO_4$[c]	26.53	53.49
$ZnSO_4$[c]	6.37	13.94
$CuSO_4$[c]	35.42	42.88
$CuSO_4$[d]	16.38	22.59

Initial concentration: a = 2×10^{-3} M; b = 4×10^{-3} M; c = 5×10^{-3} M; d = 2×10^{-2} M.

presence of the hydrophilic carboxylate groups of EDTA which enhance the diffusion of water towards the inside of the gel.

The effect of metal ion concentration on the swellability was tested for Cu^{2+} as an example. As shown in Table 1, the swellability decreases as the metal ion concentration increases. In the case of heavy metal salt solution, the observed fast and sharp decrease (Fig. 3) in the swellability can be explained on the basis of complex formation. The interaction between metal ions and both carboxylate and amino- (of amide) groups through coordination gives a highly crosslinked network with small free volume inside the gel [32].

3.2.5. *Effect of temperature*

Fig. 4 shows the effect of temperature on the swelling ratio of P1 and P3 in distilled water at natural pH of hydrogels. Generally, the swellability increases as the temperature increases. This may be attributed to the expansion of the internal volume of the hydrogel as a result of weakening and/or destruction of internal bonds (especially H-bond) as the temperature increases giving a soft hydrogel [12].

3.3. *Metal ion uptake studies*

3.3.1. *Effect of pH*

Table 2 shows the effect of pH on the uptake of metal ions by hydrogels (P1 and P3). Generally, it is seen that as the pH increases the uptake of metal ions increases. The maximum uptake was obtained at natural pH [5 for Mn(II) and Zn(II); 5.5 for Cu(II)]. The uptake measurements in the basic medium were avoided due to the precipitation of metal hydroxides. The observed decrease in the uptake value in the pH range 2.0–4.5 for all metal ions may be attributed to the protonation of amino groups as well as the lower dissociation extent of carboxylic groups. This behavior along with shrinking of hydrogel in acidic medium hinders the diffusion of metal ions inside the gel as well as the complex formation. Inverse behavior was obtained as the pH increases (proir the precipitation of metal ions).

For all metal ions under study, the slightly higher uptake values of P3 relative to that of P1 may be attributed to the higher swellability ratio of P3 which enhances the diffusion of metal ions inside the gel [23,33,34].

3.3.2. *Kinetics*

The uptake of the studied metal ions by P3 as a function of time is shown in Fig. 5. Generally, P3 displayed a higher uptake values towards the studied metal ions than that of P1. As shown in Fig. 5, the maximum uptake of P3 was obtained after 10–15 min for Mn(II), 30 min for Zn(II) and 60-120 min for Cu(II). On the other hand, the investigated hydrogels display different maximum uptake values towards the investigated metal

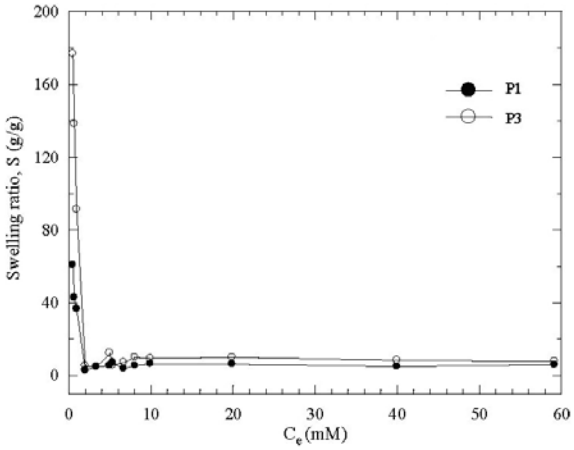

Fig. 3. Swelling of the hydrogels P1 and P3 in $CuSO_4$ solution as a function of concentration at equilibrium time, natural pH and 25°C.

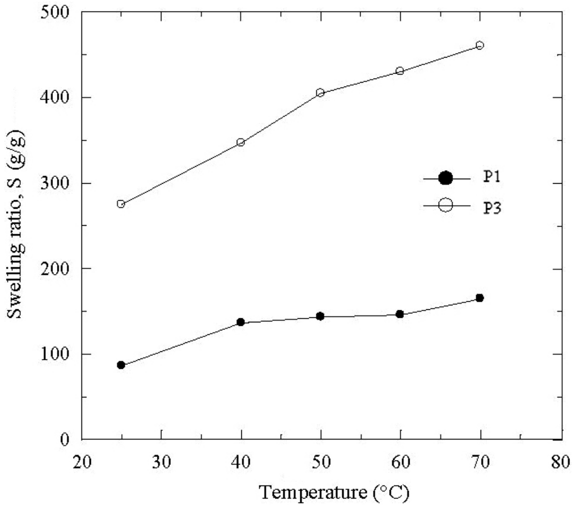

Fig. 4. Effect of temperature on the swelling ratio of P1 and P3 in distilled water for 6 h at natural pH (P1: 7.95, P3: 7.24).

Table 2
Effect of pH on the uptake of different metal ions by P1 and P3

pH	Mn(II)		Cu(II)		Zn(II)	
	P1	P3	P1	P3	P1	P3
1.0	0.39	0.50	0.00	0.00	0.00	0.00
2.0	0.98	1.26	-	-	-	-
2.5	—	—	0.27	0.34	0.28	0.29
4.0	1.37	1.76	—	—	0.83	0.89
4.5	—	—	0.79	1.02	—	—
5.0	3.86	4.92	—	—	1.73	1.86
5.5	—	—	1.67	2.24	—	—

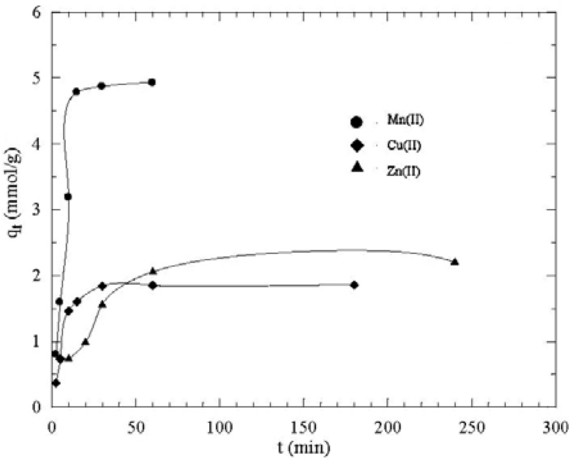

Fig. 5. Effect of time on the adsorption of studied metal ions by P3 at initial concentration of 5×10^{-3} M, natural pH and 25°C.

ions. The above behavior may be related to the nature of metal ions, nature of interaction between metal ion and hydrogel's active sites and the swelling behavior of hydrogel in the metal ion solution. It is noteworthy that the uptake of metal ions by kaolinite is expected to be minimal due to its low cation exchange capacity (12.9 mmol/100 g) as well as its low content (5.3%) in the hydrogel.

The adsorption data in Fig. 5 were treated according to pseudo-second-order kinetics [Eq. (4)]. A satisfactory agreement was found between calculated and experimental values of q_e for the studied metal ions. This indicates the validity of pseudo-second-order model for adsorption of these metal ions (Table 3) [26].

The above kinetic behavior confirms the effective role of the textural properties of the hydrogel on the rate of uptake reaction. This role was confirmed by treating the uptake-time data according to the intraparticle diffusion [Eq. (5)]. The values of K_{dif} and X for all investigated metals were obtained and are reported in Table 4. The observed negative values of X indicate that the boundary layer diffusion does not affect the rate of metal ions adsorption and the reaction is mainly controlled by the intraparticle diffusion [35]. This may be attributed to the higher affinity of the hydrogel towards the metal ion solution.

3.3.3. Isotherm studies

Fig. 6 shows the adsorption isotherm of Mn(II), Cu(II) and Zn(II) on hydrogel P3. It is seen that as the concentration of the metal ion increases, the uptake of metal ions increases till reaching the plateau. As indicated in Table 5, the maximum uptake capacities follow the order Mn(II) > Cu(II) > Zn(II). The hydrogel P3 generally displays slightly higher uptake capacities relative to P1. The uptake data in Fig. 6 were treated according to the Langmuir model [23,26,28]:

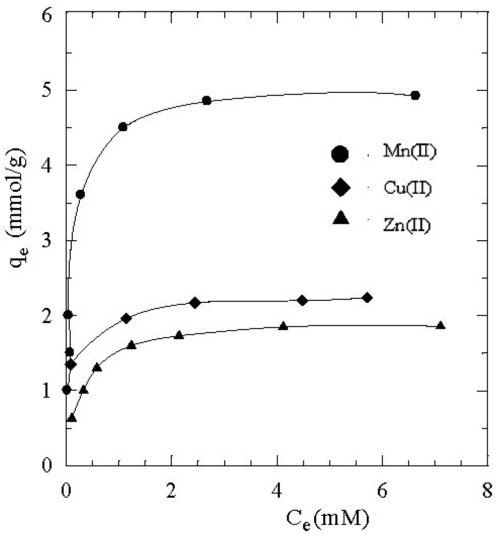

Fig. 6. Effect of the concentration on the adsorption of studied metal ions by P3.

Table 3
Kinetic data for the adsorption of metal ions by P1 and P3

Metal ion	Exp. $q_{\max}$ (mmol/g)		Pseudo-second-order kinetics			
			k_2, g/mmol.min		q_e, mmol/g	
	P1	P3	P1	P3	P1	P3
Mn(II)	3.86	4.92	3.94×10^{-1}	3.01×10^{-2}	3.79	5.20
Cu(II)	1.87	2.24	1.11×10^{-2}	2.95×10^{-1}	2.00	2.31
Zn(II)	1.72	1.86	1.55×10^{-1}	1.49×10^{-1}	1.77	1.90

Table 4
Intraparticle diffusion parameters for the adsorption of metal ions by P1 and P3

Metal ion	K_{dif}, mmol g^{-1} $min^{-0.5}$		X	
	P1	P3	P1	P3
Mn(II)	1.81	1.74	-1.99	-2.13
Cu(II)	0.13	0.29	- 0.34	-0.23
Zn(II)	0.54	0.57	-0.46	-0.51

$$\frac{C_e}{q_e}=\left(\frac{C_e}{Q_{\max}}\right)+\left(\frac{1}{K_L Q_{\max}}\right) \tag{6}$$

where C_e is the equilibrium concentration of metal ions in solution (mmol L^{-1}), q_e is the amount adsorbed of metal ions at equilibrium concentration (mmol g^{-1}), and K_L is the Langmiur binding constant which is related to the energy of adsorption (L $mmol^{-1}$). Plotting of (C_e/q_e) against C_e gives a straight line with slope and intercept equal to $1/Q_{\max}$ and $1/(K_L\,Q_{\max})$, respectively. The value obtained of $Q_{\max}$ and K_L is given in Table 5. The observed consistence between the calculated and the experimental values of $Q_{\max}$ indicates that the uptake process is in agreement with the Langmuir hypothesis. The observed variation in the values of K_L with the type of metal ions may be related to their binding with the active sites ($-NH_2$ and/or $-COO^-$ groups). It is also seen that the clay-containing hydrogel P3 is characterized by lower K_L values relative to P1. This may be attributed to: (1) relative rigidity of clay-containing hydrogel (P3) and (2) higher internal strain inside P3 (relative to P1) due to the absorption of large quantity of water (or aqueous metal ions). These two factors cause the formation of stretched weak coordinate/covalent bonds between metal ions and active sites and therefore lower values of K_L [36].

4. Elution studies

The elution behavior of metal ion-loaded hydrogel (P3) was investigated for Mn(II), Cu(II) and Zn(II) using EDTA-disodium salt solutions. Generally, it is seen that as the concentration of EDTA solution increases the released percentage of metal ion increases (Fig. 7). As indicated in Fig. 7, the release percentage (in 2×10^{-2} M EDTA for 12 h at 25°C) of the studied metal ions was found to be 35%, 60% and 67% for Mn(II), Cu(II) and Zn(II), respectively. Complete release percentage (100%) for Cu(II) and Zn(II) was achieved in 0.1 M EDTA and at the same conditions of time and temperature. The observed incomplete release of Mn(II) may be related to the lower stability constant value ($K_1 = 3.63\times10^{13}$ mol^{-1} L^{-1}) of its complex with EDTA relative to those of Cu(II) and Zn(II) ($K_1 = 6.31\times10^{18}$, 3.16×10^{16} mol^{-1} L^{-1}) [37]. Release percentage as a function of time was also studied at two different concentrations of EDTA. In dilute concentration of EDTA (5×10^{-3} M), a maximum release percentage of 9.5–28% was obtained during 6 h (Fig. 8). Afterwards, no increase in the release percentage was observed unless the EDTA solution is replaced by another fresh one. In the concentrated solution of EDTA (0.1 M), the release takes place at faster rate. For example, about 92% [except for Mn(II), 70%]

Table 5
Langmuir parameters for the adsorption of metal ions by P1 and P3

Metal ion	Q_{max} (mmol/g)		K_L (L.mmol^{-1})	
	P1	P3	P1	P3
Mn(II)	3.91	5.02	12.12	7.23
Cu(II)	1.69	2.16	16.09	5.84
Zn(II)	1.77	1.90	7.01	5.43

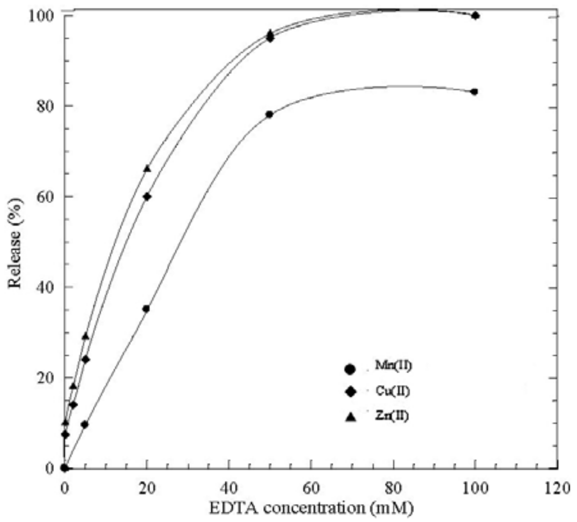

Fig. 7. Effect of EDTA concentration on the release (%) of Mn(II), Cu(II) and Zn (II) from P3 for 12 h at 25°C.

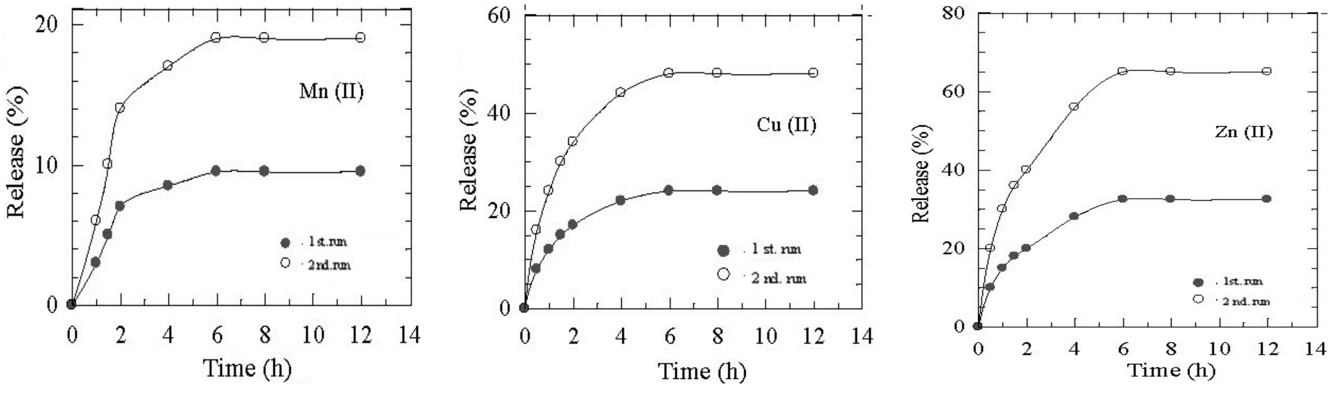

Fig. 8. Release (%) of Mn(II), Cu(II) and Zn(II) from P3 as a function of time at low concentration of 5×10^{-3} M EDTA at 25°C.

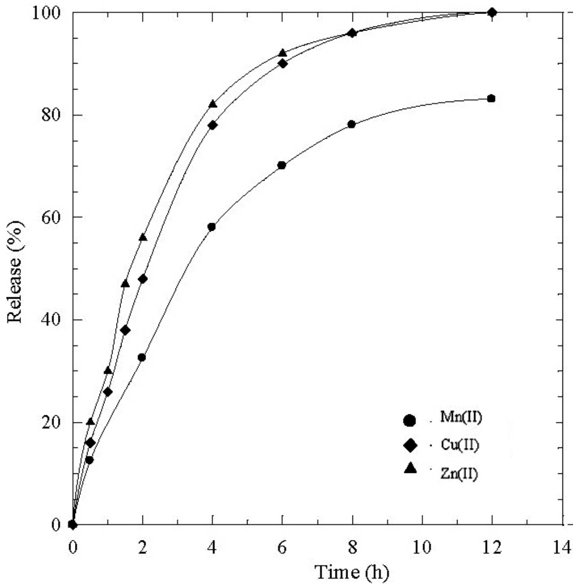

Fig. 9. Release (%) of Mn(II), Cu(II) and Zn(II) from P3 as a function of time at high concentration of 0.1 M EDTA at 25 °C.

release percentage was obtained within 6 h (Fig. 9) relative to 9.5–28% in dilute solutions.

It is noteworthy that, the adsorption as well as the easy elution characteristics of the investigated hydrogel towards metal ions makes it promising in the fields of pollution control.

5. Conclusions

Kaolinite-containing hydrogels with different compositional ratios were prepared. Clay containing hydrogel with a compositional ratio of 5.3% displayed a higher swelling ratio in distilled water. The results indicated that a kaolinite-polymer composite is characterized by good swelling properties relative to hydrogel free of kaolinite. The hydrogels are characterized by reasonable uptake capacity towards Mn(II), Cu(II) and Zn(II). The adsorption was found to be limited to monolayer capacity and proceeds according to pseudo-second-order. The elution data indicated that the studied hydrogels are characterized by dual functions: slow as well as fast release, depending on the concentration of EDTA solution in contact.

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