

# Characterization and Adsorption Properties of the Chelating Hydrogels Derived from Natural Materials for Possible Use in the Improvement of Groundwater Quality

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**ABSTRACT:** A new carrageenan based chelating copolymer sorbent was prepared by gamma radiation induced copolymerization and crosslinking of kappa-carrageenan (k-Car) and acrylic acid (AAc). The swelling characteristics of the prepared copolymer were investigated by studying the effect of time, pH, and ionic strength of the swelling medium. The sorption capacities of the chelating copolymer for Fe, Pb, Mn, Zn, Cu, Sr, Cd, and Al were 172, 202, 202, 216, 221, 230, 239, and 244 mg/g respectively. The Freundlich and Langmuir adsorption isotherms were used to validate the metal uptake data and heats of adsorption for the inves-

tigated metal ions were calculated. The re-use experiment showed that the prepared hydrogel could be regenerated upto at least 10 times. Because of the promising data collected from bench scale experiments, the prepared copolymer was examined as chelating sorbent to improve the quality of some groundwater resources. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2904–2912, 2006

**Key words:** K-carrageenan; adsorption; hydrogel; groundwater quality

## INTRODUCTION

The increase of environmental contamination as a consequence of industrial development is a challenge that society must face. The heavy metal contamination of soil, water, and other environments has stimulated the search for soft technologies to remove these pollutants.<sup>1,2</sup> Heavy metals are sometimes naturally found in water resources.<sup>3–5</sup> In Egypt, groundwater is the only water resource for different uses at many localities. El Kharga Oasis is one of the areas that depend on groundwater for water supply. Unfortunately, this groundwater is naturally contaminated with iron and manganese.<sup>6</sup> This contamination affects human health and causes problems with the taste of drinking water, discoloration of clothes, and clogging of water pipes and valves. The search for an effective and economic method of removing toxic heavy metal ions requires the consideration of unconventional materials and processes.<sup>7–11</sup> In this respect, natural polysaccharides and their derivatives containing various functional groups may have some potential. Recently, chitin and its derivatives,<sup>12–14</sup> carrageenan,<sup>15–17</sup> modified cellulose,<sup>18,19</sup> and modified starch ethers,<sup>20,21</sup> have been

studied with respect to their ability to remove heavy metal ions from aqueous solutions. Carrageenan is a collective term for linear sulfated polysaccharides prepared by alkaline extraction (and modification) from red seaweeds.<sup>22</sup> Carrageenans are linear polymers of about 25,000 galactose derivatives with regular but imprecise structures, dependent on the source and extraction conditions.

The presence of hydrophilic sulfate group with high ionization tendency was the main idea for synthesis of carrageenan-based hydrogels. These materials were formed from water soluble polymers by crosslinking them either using radiation or using crosslinker. Acrylic acid forms a hydrogel with high absorbent properties. Carrageenan, on the other hand, forms a mechanically weak gel that undergoes degradation in aqueous medium.<sup>23</sup> However, by using a combination of the two, a more economic hydrogel with good absorbent properties could be produced. The present article represents an optimized synthesis of a novel bi-polymer hydrogel via crosslinking graft polymerization of acrylic acid (AAc) and Kappa-carrageenan (k-Car) under normal atmospheric conditions, by means of  $\gamma$ -rays induced homo and copolymerization as a clean and environment friendly source of initiation. The characterization of the prepared hydrogel will be investigated and the chelating ability of the prepared hydrogel toward different metal ions will be discussed.

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## EXPERIMENTAL

### Materials

k-Carrageenan were obtained from Aldrich Chemical Company, and acrylic acid was purchased from Merck, both were used as received. All other reagents were of analytical grade and used without further purification. Double distilled water was used for the synthesis of hydrogel.

### Preparation of the crosslinked Car/AAC copolymer

The Car/AAC copolymer was prepared from 20 wt % aqueous solution of AAC and carrageenan of composition 1:0.1 wt %. The viscous mixture was exposed to 20 and 40 kGy  $^{60}\text{Co}$   $\gamma$ -irradiation at dose rate 4.8 kGy/h. The prepared copolymer was washed extensively in distilled water for 2 days to remove the un-reacted monomer, and kept at 80°C for 24 h to remove the formed oligomers and entangled polymeric chains that did not join in the copolymer network. Gelation experiments showed that the copolymer under investigation possesses not less than 97%.

### Swelling studies

The Car/AAC copolymer was allowed to swell in distilled water, buffered solution of different pH values, and saline solutions (NaCl) of different ionic strength. The degree of swelling at time intervals and equilibrium swelling was calculated as follows:

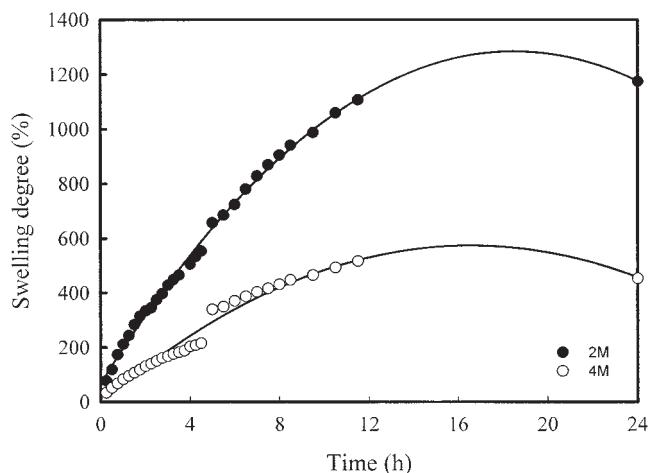
$$\text{Swelling degree (\%)} = \frac{(W_s - W_0)}{W_0} \times 100$$

Where  $W_s$  and  $W_0$  are the weights of the swollen and the dry hydrogels, respectively.

### Adsorption experiments

#### Batch adsorption experiment

Batch adsorption experiments were carried out by shaking a 0.1 g dried sample of the chelating hydrogel with 25 mL aqueous solution for metal ions of various concentrations, pH values, and time intervals. The concentration of metal ions was detected by Plasma Optical Emission-Mass Spectrometer (POEMS III) product of Thermo Jarrell Ash, USA. Thousand ppm multi-element certified standard solution, Merck, Germany, was used as stock solution for instrument calibration. The amount of metal ions adsorbed was calculated by the difference in the concentration of metal ions in solution before and after adsorption.



**Figure 1** Time course swelling of Car/AAC copolymer as a function of the total exposure dose.

### Recovery and regeneration experiments

Recovery of adsorbate and regeneration of adsorbent is a key process in water treatment. To achieve these two purposes and to assess the practical utility of the adsorbent, the metal chelated hydrogels were stirred with 25 mL HCl, 0.1M at 50°C for 2 h to desorb the metal ions. Thereafter, the hydrogel was neutralized with dilute NaOH, washed with de-ionized water and again subjected to chelation processes.

### Groundwater sample collection

Groundwater samples were collected from different points in the area under investigation and the position of these points (longitude and latitude) were determined using GPS model Magellan, Nava 5000 pro.

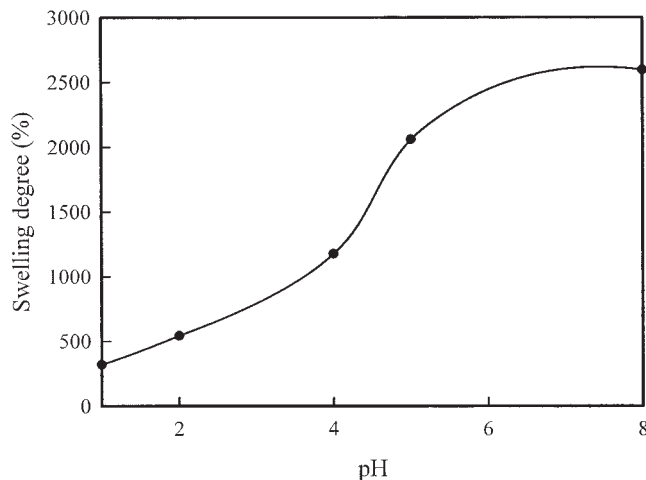
### Water treatment process

About 25 mL of the polluted samples were equilibrated with 0.1 g of the prepared hydrogel for 24 h at room temperature (25°C), and then the remaining solution was re-analyzed.

## RESULTS AND DISCUSSION

### Swelling behavior

Swelling behavior is of great importance for the characterization of chelating polymeric sorbent. Generally, swelling behavior is affected by the preparation conditions, pH, and ionic strength of the swelling medium.<sup>16,24</sup> Figure 1 shows the time course swelling of Car/AAC copolymer as a function of the total exposure dose used during preparation process. It can be seen that hydrogel prepared using 20 kGy possesses higher swelling degree as well as swelling rate than



**Figure 2** The effect of pH value of the medium on the swelling equilibrium of Car/AAC copolymer.

that prepared using 40 kGy. The observed results can be explained in terms of crosslinking density of the prepared copolymer. The copolymer produced by means of higher exposure dose has higher crosslinking density. Such high degree of crosslinking reduces the free spaces available for swelling, which decreases the total absorbed water. Also, the high crosslinking density retards the diffusion process, which consequently slows down the swelling rate.

pH value and ionic strength are parameters of significant influence on the performance of the chelating polymeric sorbent. Figures 2 and 3 show the effect of pH value and ionic strength of the medium on the swelling equilibrium of Car/AAC copolymer. From Figure 3, it was observed that the degree of equilibrium swelling increases as the pH value of the medium increases. The increase in the pH value leads to the dissociation of contained ionic groups (carboxylic and sulfate groups) in the copolymer. Even though, it is well known that p(AAC) has  $pK_a$  value of 4.7 at which it shows a sudden phase transition from collapsed form to the swollen form, the presence of highly hydrophilic carrageenan shifts such  $pK_a$  down, changing the type of the p(AAC) phase transition from sudden or discontinuous to continuous phase transition.

Figure 3 shows that the increase in the ionic strength of the medium reduces the equilibrium swelling of the prepared copolymer. Such decrease in the equilibrium swelling could be attributed to the charge screening effect of the dissociated carboxylic groups, which decrease the repulsion forces between the repulsive carboxylate groups that consequently reduces the free spaces available for swelling, and as a result, the reduction in the equilibrium swelling is obtained.

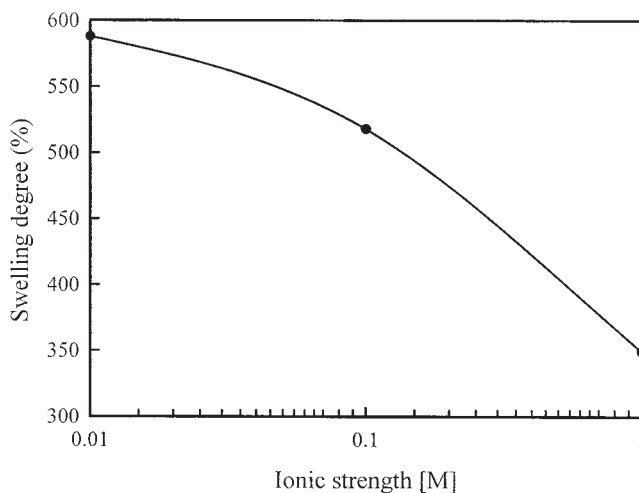
## Adsorption properties

To elucidate the possibility of the practical uses for the prepared hydrogel in the field of water treatment, the adsorption behavior of some selected metals (Al, Cd, Sr, Cu, Zn, Mn, Pb, and Fe) on the hydrogel was studied. Factors affecting the adsorption process such as; pH of the medium, metal concentration, contact time, and temperature were investigated.

### Sorption of metal ions as a function of pH

The solution pH is an important controlling parameter in the adsorption process. Therefore, the sorption behavior of some metal ions on the hydrogel at different pH values ranging from 1 to 5 was examined (Fig. 4). In general, the adsorption of metal ions increased with an increase in pH, reaching a limiting value in each instance. The chelating hydrogel exhibited a drastic decrease in metal ions affinity at low pH conditions due to formidable competition with hydronium ions. Thereafter, increasing the pH of the medium will increase the hydrolysis of the chelating polymer in the aqueous solution. The hydrolysis of  $M^{n+}$  ions also occurs simultaneously in the aqueous solution, and the degree of hydrolysis increases with the increase in the pH of the solution.

Therefore, it can be inferred that the solution pH not only affects the surface charge of the adsorbent (hydrogel), but also infers the degree of ionization and speciation of the adsorbate (metal ion). It was proposed that the adsorption of metal ions at the solid-solution interface is not governed by the 'free' metal concentration, but is instead governed by the much stronger adsorbed hydroxo, sulfato, carbonato, and other metal species.<sup>25</sup>



**Figure 3** The effect of ionic strength of the medium on the swelling equilibrium of Car/AAC copolymer.

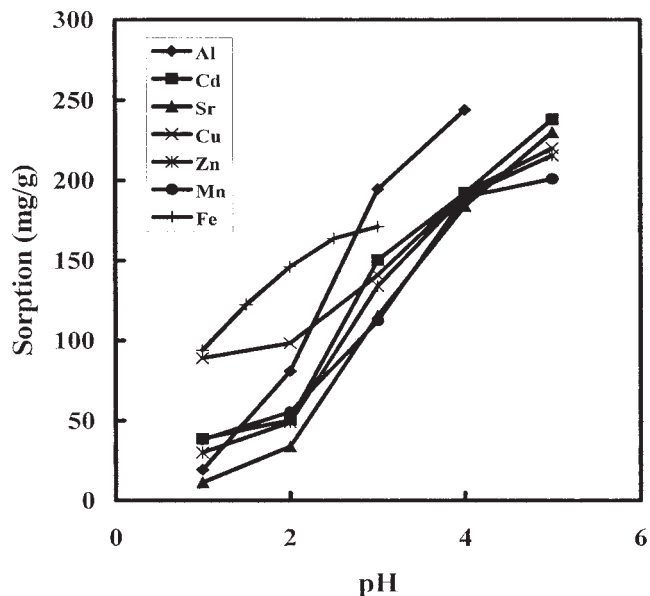


Figure 4 Sorption behavior of Car/AAC copolymer towards metal ions at different pH values.

Hence, the increase in the pH of the solution can promote the chelation of the functional groups in the chelating polymer with metal ions to form the chelates in the adsorption process.

Total sorption capacity

The capacity of the polymer is an important factor for determining the amount of the chelating polymer required for the complete removal of a specific metal ion from a solution.

The total sorption capacity of the chelating polymer was determined by determining the amount of metal ions sorbed per gram of hydrogel by immersing a fixed amount of the polymer in the metal solution at optimum pH, and room temperature. Table I shows the maximum sorption capacity of the chelating Car/AAC hydrogel toward different metal ions.

TABLE I  
Sorption Capacity of the Chelating Hydrogel at the Optimum pH

Metal	Optimum pH	Loading Capacity (mg/g)
Aluminum	4	243.9
Cadmium	5	238.9
Strontium	5	230.3
Copper	5	221.1
Zinc	5	215.6
Manganese	5	202.4
Lead	5	202.2
Iron	3	172

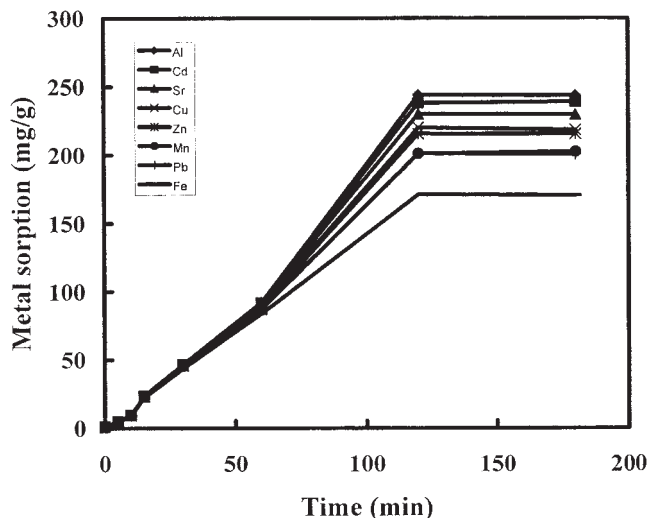


Figure 5 The change in amount of adsorbed metal ions with time for Car/AAC.

Adsorption rate

The rapid adsorption of metal ions by the adsorbent is important for practical use, shortening the treatment time of water during purification. The change in the amount of adsorbed metal ions with time for Car/AAC is shown in Figure 5. It was observed that the adsorption process was fast at first then slowed down until the saturation was reached. The result suggested that, at the beginning of the process, the adsorption occurs on the polymer surface, so, a fast adsorption rate was found.<sup>26</sup> After that; the adsorption takes place at the inner surface of the polymer, so, the adsorption rate was slow due to the pore diffusion of metal ions into the polymer matrix.

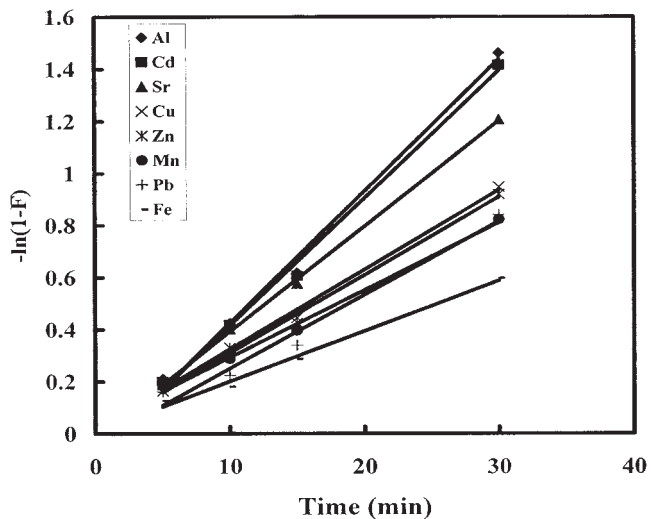


Figure 6 Car/AAC adsorption rate curve.

TABLE II  
Adsorption Rate Constant of Different Metals on Car/AAC Hydrogel

Metal	$K$ ( $s^{-1}$ )	$(C_e/C_0)$	$K_d$ ( $s^{-1}$ )	$K_s$ ( $s^{-1}$ )	$r^2$
Aluminum	$8.43 \times 10^{-4}$	0.0244	$0.2 \times 10^{-4}$	$8.2 \times 10^{-4}$	0.99
Cadmium	$8.16 \times 10^{-4}$	0.048	$0.39 \times 10^{-4}$	$7.7 \times 10^{-4}$	0.99
Strontium	$6.75 \times 10^{-4}$	0.08	$0.54 \times 10^{-4}$	$6.2 \times 10^{-4}$	0.99
Copper	$5.1 \times 10^{-4}$	0.12	$0.6 \times 10^{-4}$	$4.5 \times 10^{-4}$	0.99
Zinc	$5 \times 10^{-4}$	0.13	$0.69 \times 10^{-4}$	$4.3 \times 10^{-4}$	0.99
Manganese	$4.3 \times 10^{-4}$	0.19	$0.84 \times 10^{-4}$	$3.4 \times 10^{-4}$	0.99
Lead	$4.71 \times 10^{-4}$	0.19	$0.92 \times 10^{-4}$	$3.7 \times 10^{-4}$	0.97
Iron	$3.23 \times 10^{-4}$	0.31	$1.01 \times 10^{-4}$	$2.2 \times 10^{-4}$	0.99

### Adsorption kinetics

Sorption kinetics is mainly controlled by various steps including diffusion and reaction processes.<sup>27-29</sup> Four steps can be enumerated and applied to metal ion removal.

1. *Bulk Diffusion*: metal ion transfer from the bulk solution to the boundary film bordering the sorbent surface.
2. *Film diffusion*: metal ion transport from the boundary film to the surface of the sorbent.
3. *Intraparticulate diffusion*: Transfer of the metal ion from the surface to the intraparticulate active sites.
4. *Chemical reaction*: Uptake of the metal ion on the active sites, via chelating, ion-exchange or complexation.

With regard to the first two steps, it has been demonstrated that they could be neglected if a sufficient speed of stirring was used (>400 rpm).<sup>30</sup> For this reason, intraparticulate diffusion or chemical reaction (chelating or ion-exchange) would be the rate-limiting step of sorption kinetics. The adsorption data for heavy metals under investigation were analyzed by a regression analysis to fit the Langmuir and Freundlich models. These data were plotted as a function of, (1) sorption period and (2) the amount of the heavy metal sorbed on the chelating polymer at equilibrium versus the heavy metal concentration of the solution at equilibrium.

### Sorption period

It is important to study the effect of contact time on the adsorption process, which may lead us to an idea about the sorption and desorption rates of the treatment reaction.

According to Langmuir, the reversible sorption-desorption can be described by the following equation:

$$-\ln(1 - F) = Kt + C$$

Where  $K$  is the equilibrium constant, and

$$F(t) = C_0 - C_t / C_0 - C_e$$

Where  $C_0$ ,  $C_t$  and  $C_e$  (all in mg/L) represent the concentration of metal ions initially, in aqueous solution at time  $t$  and at equilibrium, respectively. The experimental results of Figure 5 can be converted into the plots of  $-\ln(1 - F)$  versus  $t$  as shown in Figure 6, and the adsorption rate constants; rate of sorption ( $K_s$ ) and rate of desorption ( $K_d$ ) of the chelating hydrogel can be calculated from the slopes and intercepts of the plots as follow:

$$K_d = k(C_e/C_0) \text{ and } K_s = K - K_d$$

Table II shows the values of  $K_s$  and  $K_d$ , from which the following can be observed; the highest sorption rates ( $K_s$ ) were found in case of the reaction with (Al) revealing the high affinity of the chelating hydrogel for the adsorption of such metal.

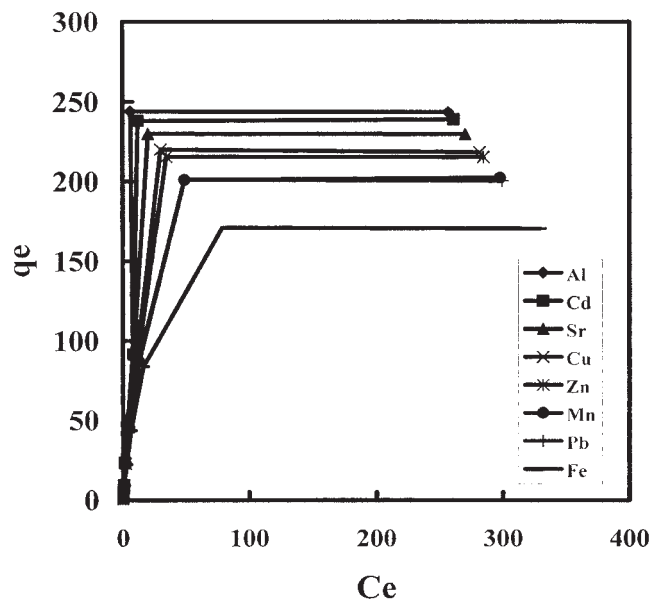


Figure 7 The effect of metal ion concentration on its adsorption.

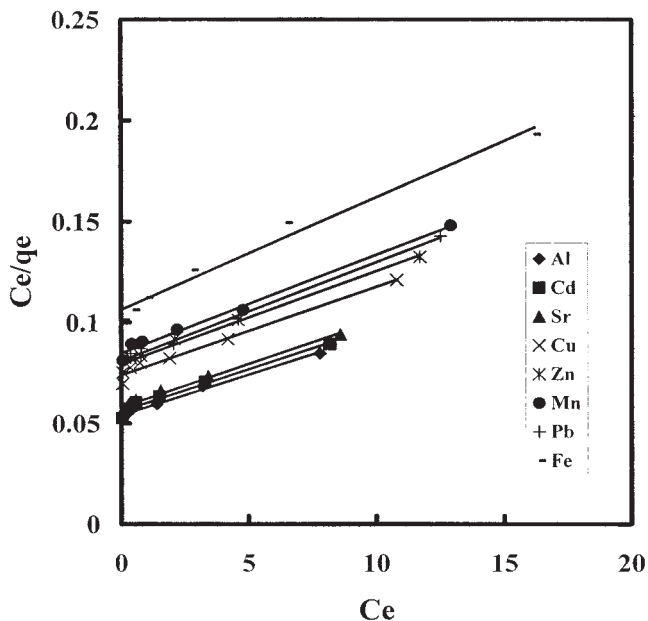


Figure 8 Plot of  $(C_e/q_e)$  against  $C_e$ .

Initial feed concentration

The effect of metal ion concentration on adsorption was shown in Figure 7. It is clear from the figure that as the concentration of the ions increased, adsorption increased first rapidly, and then slowed down, and adsorption saturation values were reached depending on the type of metal ions. The Langmuir model was used to explain the observed phenomenon. The equilibrium data were analyzed with the following linearized equation:

$$C_e/q_e = 1/K_L + [a_L/K_L] C_e$$

Where  $q_e$  is the amount of metal adsorbed at equilibrium (mg/g) and  $K_L$  and  $a_L$  are the Langmuir constants related to the adsorption capacity and the energy of adsorption, respectively. The linear plot of  $(C_e/q_e)$  against  $C_e$  (Fig. 8) for the metal ions under investigation shows that the adsorption obeyed the Langmuir model. The Langmuir constants were eval-

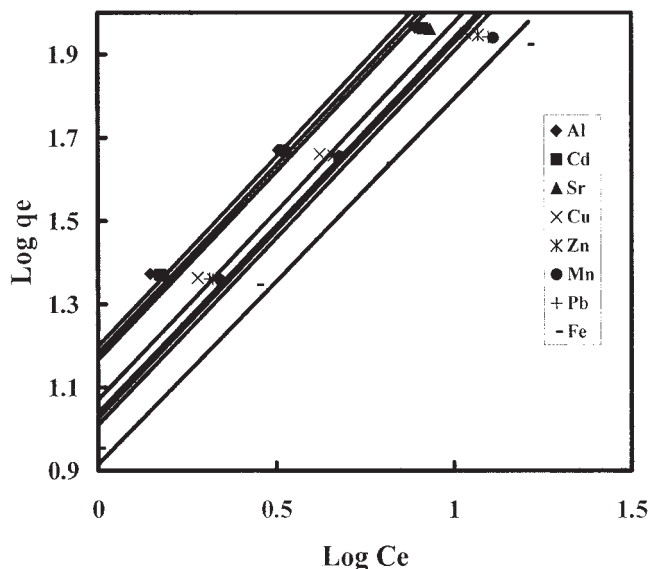


Figure 9  $\text{Log } q_e$  versus  $\text{log } C_e$ .

uated and reported in Table III. The ratio  $[K_L/a_L]$  from the table is known as the capacity factor, which is the maximum adsorption capacity of the hydrogel toward particular metal ion. The adsorption behavior was also confirmed with the Freundlich model:

$$\text{Log } q_e = \text{log } A + (1/n)\text{log } C_e$$

The plot of  $\text{log } q_e$  against  $\text{log } C_e$  (Fig. 9) produces a linear relationship of slope  $(1/n)$  and intercept  $A$ . Where,  $A$  and  $n$  are empirical constants (Freundlich parameters), indicated the capacity and intensity of adsorption, respectively. The Freundlich constants  $A$  and  $n$  were calculated and reported in Table IV. Values of  $1 < n < 10$  show the positive sorption of metal ion.<sup>31</sup>

Also, from the results, it can be seen that the affinity of the chelating hydrogel toward the adsorption of different metal ions following the order;  $\text{Al}^{3+} > \text{Cd}^{2+} > \text{Sr}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Pb}^{2+} > \text{Fe}^{3+}$ .

Effect of temperature

It has been observed that the adsorption of metal ions under investigation from aqueous solution is affected

TABLE III  
Langmuir Model

Metal	Langmuir equation	$a_L$	$k_L$	$(K_L/a_L)$	$r^2$
Aluminum	$(C_e/C_q) = 0.054 + 0.004 C_e$	0.074	18.51	250	0.98
Cadmium	$(C_e/C_q) = 0.056 + 0.0042 C_e$	0.075	17.85	238	0.97
Strontium	$(C_e/C_q) = 0.058 + 0.0043 C_e$	0.074	17.24	232	0.98
Copper	$(C_e/C_q) = 0.074 + 0.0044 C_e$	0.059	13.51	227	0.97
Zinc	$(C_e/C_q) = 0.08 + 0.0046 C_e$	0.057	12.5	217	0.98
Manganese	$(C_e/C_q) = 0.085 + 0.0049 C_e$	0.057	11.76	204	0.98
Lead	$(C_e/C_q) = 0.081 \pm 0.0049 C_e$	0.06	12.34	204	0.99
Iron	$(C_e/C_q) = 0.1 + 0.0056 C_e$	0.056	10	178	0.98

TABLE IV  
Freundlich Model

Metal	Freundlich equation	A	n	r <sup>2</sup>
Aluminum	Log $q_e = 1.19 + 0.87 \log C_e$	15.5	1.15	0.99
Cadmium	Log $q_e = 1.18 + 0.9 \log C_e$	15.1	1.11	0.99
Strontium	Log $q_e = 1.16 + 0.9 \log C_e$	14.5	1.11	0.99
Copper	Log $q_e = 1.07 + 0.9 \log C_e$	11.74	1.11	0.99
Zinc	Log $q_e = 1.03 + 0.89 \log C_e$	10.71	1.12	0.99
Manganese	Log $q = 1.0 + 0.89 \log C_e$	10	1.12	0.99
Lead	Log $q_e = 1.02 + 0.9 \log C_e$	10.4	1.11	0.99
Iron	Log $q_e = 0.91 + 0.87 \log C_e$	8.1	1.15	0.99

by the temperature, with the adsorption being increased remarkably as the temperature increased (Fig. 10). This increase may be due to the enhanced rate of intraparticle diffusion of adsorbate and changes in the size of the pores.<sup>32</sup>

Thermodynamic studies

To explain the effect of temperature on adsorption thermodynamic parameters, free energy  $\Delta G$ , enthalpy  $\Delta H$ , and entropy  $\Delta S$  were calculated according to the following equations:

$$D = q_e/C_e \dots \dots \dots (1)$$

$$\log D = (\Delta H/2.303 RT) + (\Delta S/R) \dots \dots \dots (2)$$

$$\Delta G = \Delta H - \Delta ST \dots \dots \dots (3)$$

Where  $R$  is the gas constant and  $D$  is the distribution ratio between metal ions and the adsorbent in aqueous solution.

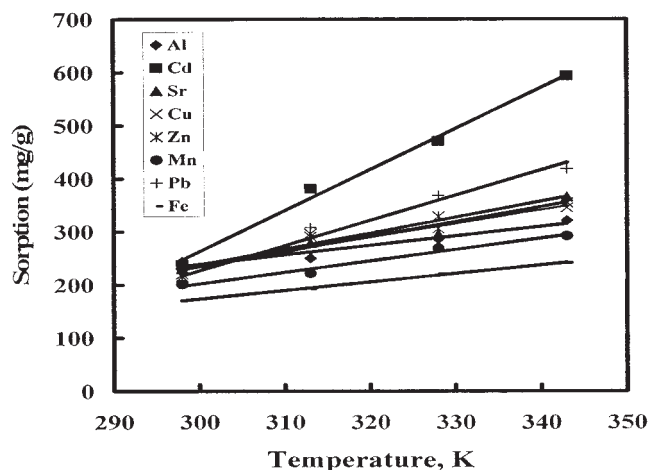


Figure 10 Effect of temperature on the adsorption of metal ions under investigation from aqueous solution.

The relationship between  $\log D$  and  $1/T$  for the prepared chelating hydrogel is shown in Figure 11. According to eqs. (1–3), the slopes and intercepts of linear lines in Figure 11, thermodynamic parameters were calculated, and are shown in Table V. The positive values of  $\Delta H$  reflected that adsorption is an endothermic process and is therefore, responsible for the increase in adsorption as the temperature increased. The higher positive values of  $\Delta H$  suggest the possibility of very strong bonding between the adsorbate and adsorbent. The positive values of  $\Delta S$  suggest some structural changes in the adsorbate and adsorbent. The values of  $\Delta G$  decrease with increasing temperature, demonstrating an increase in the feasibility of adsorption at higher temperatures.<sup>32</sup>

Reusability

Evidently, chelation of the hydrogel with different metal ions is inhibited in strongly acidic conditions. Therefore, the adsorbed metal ions are easily desorbed by treating with 0.1M HCl at room temperature for 2 h. The regenerated hydrogel is again effective for the

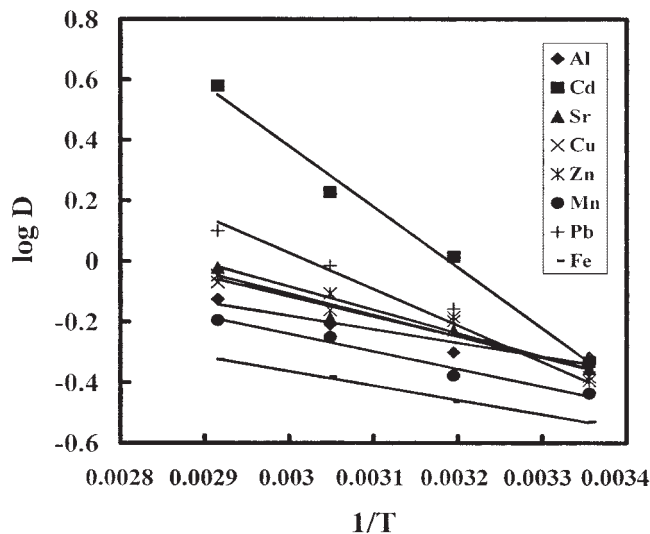


Figure 11 Relationship between  $\log D$  and  $1/T$ .

**TABLE V**  
**Thermodynamic Parameters for Adsorption of Different Heavy Metals on Hydrogel**

Temp. (°C)	Metal	Thermodynamic parameters			<i>r</i> <sup>2</sup>
		Δ <i>G</i> (kj/mol)	Δ <i>S</i> (j/mol)	Δ <i>H</i> (25–70) (kj/mol)	
25	Aluminum	5.62	9.82	8.55	0.95
40		5.61	9.36		
55		5.4	9.57		
70		5.19	9.77		
25	Cadmium	22.51	53.1	38.34	0.99
40		21.65	53.3		
55		21.07	52.6		
70		20.04	53.34		
25	Strontium	8.48	16.64	13.44	0.96
40		8.19	16.74		
55		8.11	16.23		
70		7.66	16.82		
25	Copper	8.15	15.39	12.74	0.94
40		7.72	16.03		
55		7.64	15.51		
70		7.4	15.54		
25	Zinc	9.3	18.17	14.72	0.96
40		8.8	18.88		
55		8.62	18.59		
70		8.46	18.23		
25	Manganese	7.33	12.49	11.06	0.97
40		7.24	12.2		
55		6.94	12.55		
70		6.81	12.38		
25	Lead	14.06	29.83	22.96	0.97
40		13.4	30.53		
55		13.03	30.26		
70		12.7	29.89		
25	Iron	6.44	8.82	9.07	0.99
40		6.33	8.73		
55		6.16	8.84		
70		6.05	8.78		

The relative standard deviation was 0.08–0.64% for triplicate analysis.

readsorption of metal ions. To test the hydrogel stability, it was subjected to several adsorption and desorption operations. The tests revealed that the sorbent was highly stable and could be used repeatedly. There was almost no decrease in the sorption capacity even after 10 cycles of operation (Fig. 12)

**Groundwater treatment**

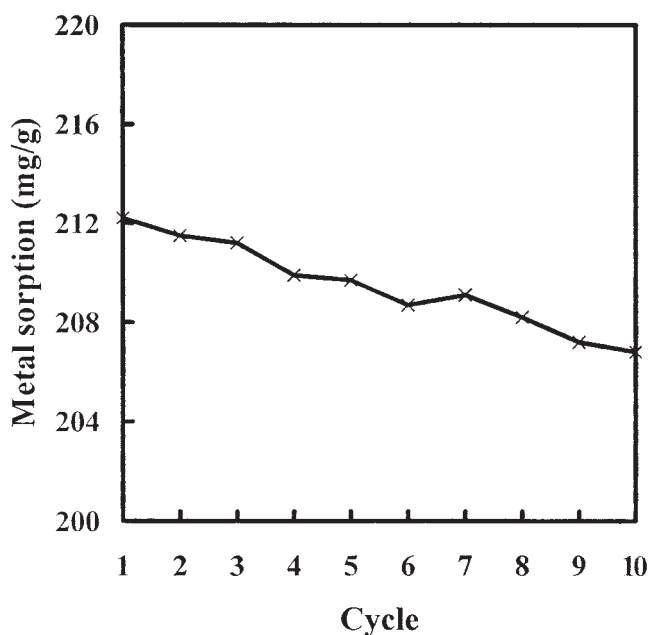
Groundwater is the only source of water in Western Desert of Egypt. So, the development of these localities depends on the presence of good quality water suitable for different uses. Although, most of groundwaters in these areas have a lower salinity values, a higher concentration of iron and manganese are found, and are therefore unsuitable for use as drinking water or any other purposes, without appropriate treatment.

El Kharga depression is one of five oases located in the Western Desert of Egypt, 650 km Southwest Cairo. It is one of these localities that suffer from the problem of high iron and manganese existing in groundwater. So, a simple and widely applicable water treatment procedure is thus needed. For this reason, a trial was made for the treatment of this groundwater, using the prepared Car/AAC hydrogel.

Analysis of 10 water samples collected from the area of study shows that the concentration of iron is varied from 0.71 to 34.48 mg/L; and, the manganese concentration is ranged from 0.07 to 3.7 mg/L. So, the analysis reveals that all samples are unsuitable for different uses with regard to iron and manganese concentrations (according to WHO guideline).<sup>33</sup> For this reason, these groundwater samples were chosen to be treated using the prepared chelated hydrogel. After the treatment process was done, another chemical analysis for the groundwater samples were performed (Table VI).

Generally, a good treatment process must provide water of better quality. From the re-analysis of the water samples after the process, it can be seen that; the chelated hydrogel was able to remove from 97 to 99% of iron, and from 83 to 99% of manganese.

A drop in the pH of the water samples was also observed, which may be explained by the exchange between metal ions Mn<sup>+</sup> and H<sup>+</sup> of the carboxylic group (–COOH) in the hydrogel, resulting in an excess proton in solution, leading to a drop in the pH.<sup>34</sup>



**Figure 12** Reusability and sorption stability of Car/AAC towards Cu ion.



**TABLE VI**  
**Change in Metal Concentration and pH in the Groundwater Samples of Some Localities at El Kharga Oasis upon Treatment by Car/AAC Copolymer**

Serial No.	%			%				
	Before	After	Change	Before	After	Change	Before	After
2	3.266	0.076	98	0.4322	0.0455	90	7.57	6.0
9	34.48	0.245	99	3.729	0.647	83	5.8	3.9
21	3.739	0.0489	99	0.4891	0.0415	92	7.3	3.9
34	3.405	0.0678	98	0.4271	0.0357	92	7.2	3.2
35	2.423	0.026	99	0.4267	0.0376	91	7.3	5.7
50	1.464	0.0156	99	0.2	0.014	93	7.2	5.9
68	0.8893	0.0083	99	0.0468	0.0074	84	8.1	4.5
71	0.7182	0.0046	99	0.0634	0.0085	87	7.7	3.8
81	0.9244	0.0316	97	0.1639	0.0046	97	8.0	3.8
88	1.275	0.015	99	0.1657	0.0023	99	7.2	3.9

### CONCLUSIONS

This article describes the synthesis, characterization, and analytical evaluation of a Car/AAC copolymer hydrogel as an adsorbent. The chelating copolymer hydrogel was prepared by  $\gamma$ -radiation induced copolymerization and crosslinking of kappa-carrageenan and acrylic acid. The prepared hydrogel showed higher swelling characteristics at higher pH, and lower ionic strength of the medium. The sorption capacities of the chelating hydrogel toward some selective elements were studied. The adsorption process was dependent on the pH, time course, initial concentration, and temperature and followed both the Freundlich and Langmuir isothermal adsorptions. Moreover, a higher temperature favored the adsorption, indicating that the process is endothermic. As a case study for application of the Car/AAC chelated hydrogel, it is to be mentioned that groundwater in most localities at the Western Desert of Egypt have higher concentrations of iron and manganese. For example, at El Kharga Oasis the concentration of iron is ranged from 0.7 to 34.5 mg/L; meanwhile, manganese concentration is varied from 0.07 to 3.7 mg/L. The treatment process of such groundwater using the prepared Car/AAC chelated hydrogel showed a removal of 97 to 99% of iron, and 83 to 99% of manganese, resulting in an improvement of the groundwater quality.

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