Treatment of Polluted Water Resources Using Reactive **Polymeric Hydrogel**

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Received 5 March 2005; accepted 22 August 2005 DOI 10.1002/app.23017 Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: An experimental work was conducted to study the performance of the already prepared polyvinyl pyrrolidone/acrylic acid (PVP/AAc) copolymer hydrogel to chelate heavy metals from bulk solution. Studies of the binding capacity, adsorption isotherm, and adsorption kinetic experiments showed that PVP/AAc copolymer hydrogel has high binding capacities and good adsorption kinetic properties for the metal ions under investigation. The adsorption isotherms of such metal ions on the copolymer exhibit a Langmuir-type equation. The chelated copolymers were characterized by FTIR and XRD. Technical feasibility for the uses of the prepared PVP/AAc hydrogel for the

treatment of polluted samples; collected from different water resources in Helwan area (Egypt) was investigated. The evaluation of the system was performed by a complete analysis of water samples before and after the treatment process. The results showed a promising possibility for producing water of better quality in the area under investigation, using such prepared hydrogel. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3966-3973, 2006

Key words: chelating hydrogel; adsorption isotherms; water treatment

INTRODUCTION

Helwan area is a suburb in south Cairo, on the east bank of the Nile River. The area is characterized by the presence of many water resources such as the River Nile, irrigation canals, the groundwater wells, and the sulfur and mineral springs.^{1–3} These water resources are used for drinking, domestic, agricultural, and industrial purposes as well as for medical treatment. Nowadays, the area is considered one of the industrial forts in Egypt because of some huge industrial projects such as iron and steel, cement, and galvanization industries. With the progressive increase of industrial activities, the area under consideration suffered from deterioration of the quality of surface and ground waters because of heavy metals pollution from the industrial waters.⁴

The removal of such toxic metal ions from industrial wastewaters has received much attention in recent years because they cause health hazards in human beings and animals. Various methods, such as ionexchange, reverse osmosis, and electrodialysis techniques, have been developed for the removal and recovery of heavy metal ions from sewage and industrial wastewater.⁵⁻¹⁰ Traditional chemical precipita-

The search for an effective method of removing such toxic heavy metal ions requires the consideration of unconventional materials and processes. Polymeric hydrogels acquire a great interest in the field of water purification due to the facility of incorporation of different chelating groups into the polymeric networks and their chemical and thermal stability, easy separation from the reaction medium leading to operational flexibility, and their facial regenerability.^{13–15} Hydrogels may be prepared by treating the aqueous solution of hydrophilic polymers and monomers with γ -ray¹⁶ or chemical initiators.¹⁷ Among these methods, γ-ray-induced simultaneous polymerization and crosslinking is advantageous over the others. This technique is generally termed a "clean technique," not requiring extra chemicals and without leaving any unwanted residues.

The aim of the present study was to investigate the applicability of the already prepared¹³ chelating poly-(vinyl pyrrolidone/acrylic acid) (PVP/AAc) copolymer hydrogel for treatment of the polluted water samples collected from Helwan area.

EXPERIMENTAL

Materials

PVP/AAc gels of molar composition (80/20) were prepared by γ -radiation-induced copolymerization

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tion can be envisaged, but the generation of precipitated bulky hydroxides and colloidal particles is a major disadvantage.^{11,12}

Journal of Applied Polymer Science, Vol. 100, 3966-3973 (2006) © 2006 Wiley Periodicals, Inc.

(using ⁶⁰Co gamma rays at a dose rate of 10.28 kGy/h) of PVP of MW 1,300,000 (Acros, Belgium) and AAc of purity 99.9% (Merck, Germany). Details were shown in our pervious work.¹³ All reagents used were analytical reagent grade and used without further purification.

Instruments and methods

FTIR measurements

The dried samples were pressed into pellets with KBr, then analyzed with a Mattson 1000 FTIR spectrometer (wave number 400–4000 cm⁻¹), product of Unicam Ltd., UK.

X-ray diffraction

The XRD patterns of the hydrogel were measured with a Philips model PW 3719 with Ni-filter and Cu-K α radiation (λ = 1.54,178 Å) from fine focus X-ray tube.

Adsorption experiments

Batch adsorption experiments

Batch adsorption experiments were carried out by shaking 0.5 g dried samples of (PVP/AAc) chelating hydrogel with 100 mL aqueous solution of metal ions of various concentrations, pH values, and time intervals. The adsorption experiments were also conducted in the presence of sodium chloride (NaCl), calcium chloride $(CaCl_2)$, and magnesium chloride $(MgCl_2)$. The concentration of metal ions was detected by Plasma Optical Emission-Mass Spectrometer (POEMS III; Thermo Jarrell Ash). Multielement certified standard solution (1000 ppm; 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. The relative standard deviation for triplicate analysis by optical emission spectrometer (OES) technique was 0.11–1%.

Recovery and regeneration experiments

Recovery of adsorbate and regeneration of adsorbent are a key process in wastewater treatment. To achieve these two purposes and to assess the practical utility of the adsorbent, the PVP/AAc-metal hydrogels were stirred with 100 mL HCl (2*M*) at 50°C for 2 h to desorb the metal ions. Thereafter, the hydrogels were neutralized with dilute NaOH, washed with deionized water and again subjected to chelation processes. Sample collection and analysis

Samples were collected from different water points during February, in the area under investigation, and the position of these points (longitude and latitude) was recorded using GPS model Magellan. Two kinds of samples were collected: 1 L samples were collected in clean, deionized water-washed polyethylene bottles, and used for the measurements of their physical and chemical properties. The physical properties of water samples were determined by measuring the specific electrical conductance (EC) by EC meter Model LF 538 (WTW, USA) and were expressed μ S/cm at 25°C, and the measurement of pH by a 3320 pH meter (Jenway, UK). The chemical properties were determined by measuring the concentrations of total dissolved salts (TDS), Ca²⁺, Mg²⁺, Na⁺, K⁺, CO₃²⁻, HCO_3^- , SO_4^{2-} , CI^- , and NO_3^- ions.

Other samples were collected in 100 mL acidwashed polyethylene bottles, followed by *in situ* acidification by nitric acid, brought to the laboratory in iceboxes, and stored at 4°C until analysis for heavy metal content. Samples were analyzed for Al, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, V, and Zn, using POEMS III. All the analyses were done according to the methods adopted by American Society for Testing Materials (ASTM 2002), and the obtained chemical data were expressed as mg/L.

Water treatment process

About 100 mL of each of the polluted samples was equilibrated with 0.5 g of the prepared hydrogel for 24 h at room temperature (25°C), then the remaining solution was reanalyzed.

RESULTS AND DISCUSSION

In our previous work¹³, the preparation, characterization, and metal ion chelation of PVP/AAc copolymer hydrogel were performed. The study revealed the capability of the prepared copolymer hydrogel to remove Fe(III), Cu(II), and Mn(II) metal ions with a maximum uptake of 36, 23, and 14 mg/g, respectively, by optimizing the preparation conditions such as suitable copolymer composition (80/20 mol % PVP/AAc) and irradiation dose (20 kGy/h). The prepared hydrogel possessed high thermal and chemical stability. On the basis of the results, we recommend the use such hydrogel in the purification of water resources (in some Egyptian districts and localities) containing high metal ions concentration, which is the main target of this work.



Figure 1 FTIR spectra of PVP/AAc: (a) blank, (b) chelated with cupper, (c) chelated with iron, and (d) chelated with manganese.

Characterization of (PVP/AAc) copolymer-metal complex

The relation between the nature of polymeric material and the adsorption process is generally complicated with many possible interactions. Oxygen of the carbonyl groups either of PVP or AAc is responsible for the interaction of the metal ion with the copolymer. Since the mobile π -electrons are pulled strongly towards oxygen, carbonyl carbon is electron deficient and carbonyl oxygen is electron rich and metal ion acts as electron acceptor and taken by the coordination to the donor oxygen.^{18–20}

FTIR was used to follow up the changes in the carbonyl characteristic peak. PVP spectrum shows its characteristic peak at 1680 cm⁻¹ whereas the spectrum of PVP/AAc shows the presence of the carbonyl group of AAc in addition to that of PVP, which results in three peaks at 1650, 1690, and 1740 cm⁻¹ (Fig. 1). On the other hand, the FTIR spectrum of PVP/AAc (80/20 mol %) hydrogel complexed with Cu, Mn, and Fe shows that complexation process produces a shift of the carbonyl peaks at 1690 and 1740 cm⁻¹ to 1660 and 1724 cm⁻¹, respectively, giving a good proof that complexation process takes place.^{21,22}

X-ray diffraction (XRD) technique was used to get knowledge on the change of morphological structure and the change in the crystal form of the PVP/ AAc copolymer hydrogel due to the effect of swell-

ing and interaction of pollutant metal ions with the hydrogel polymer matrix. XRD patterns of the PVP/ AAc hydrogel before and after metal adsorption are shown in Figure 2. The diffraction curves of the metal uptake in hydrogel record the same region and that there is no significant change is observed between 2θ for PVP/AAc before and after metal uptake. The integrated intensity (counts) is taken as an indication of the amorphous and crystallinity percent of the polymer, according to the area under peak in the charts of XRD patterns. It is well known that the increase in the integrated intensity is an indication of the crystallinity increment.²³ It can be seen from the figure that the integrated intensity decreased in hydrogel-metal complexes than that in the blank hydrogel. The PVP/AAc crystallinity results from strong intermolecular interaction between the PVP/AAc chains due to intermolecular hydrogen bonding. The integrated intensity of the diffraction and also the size of the crystals in PVP/ AAc are determined by the number of PVP/AAc chains packed together.²⁴ After being complexed with metal ions, the integrated intensities of the hydrogel peaks are further decreased. This is due to the interaction of PVP/AAc hydrogel with iron and manganese, which leads to a decrease of the intermolecular interaction between the PVP/AAc chains and, as a result, the degree of crystallinity reduced.

Figure 2 XRD patterns of (a) blank PVP/AAc, (b) PVP/ AAc copolymer chelated with iron, and (c) PVP/AAc chelated with manganese.

Adsorption and equilibrium isotherms

Although the Langmuir and Freundlich isotherms were the first introduced, in the beginning of the last century, they still remain the two most commonly used adsorption isotherm equations that can be transformed to a linear form and so their adjustable parameters can be easily estimated either by graphical means or by linear regression. The most promising extension to Langmuir and Freundlich isotherms is based on the generalized Langmuir and generalized exponential isotherms.^{25,26}

Effect of time on the adsorption process

In case of heterogeneous complex formation between the insoluble crosslinked macromolecular ligand and a metal ion in aqueous medium, the following fundamental processes have to be considered: (i) diffusion of metal ions into the polymer matrix, (ii) adsorption on the surface, and (iii) the reaction, which may or may not be followed by desorption. It is useful to study the effect of time on the adsorption process which may help us to estimate the adsorption and desorption rates.²⁷ According to Langmuir, who assumed that the hydrogel is almost homogeneous and of uniformly distributed isoenergetic active sites, the reversible sorption-desorption can be described by the following equation:



$$\ln c_t - c_e = -kt + \text{constant}$$

where c_t is the concentration of the adsorbate in solution at time t; c_e is the concentration of the adsorbate in solution at equilibrium.

Plotting $\ln c_t - c_e$ against time (Fig. 3), produced good linear plot of slope equal to -k. The reaction rate constants, rate of sorption (k_s) and rate of desorption (k_d) , were calculated from the following equations:

$$k_d = k(c_e/c_0)$$
 and $k_s = k - k_d$

where c_0 is the concentration of the adsorbate in solution at time (0).

Table I shows the values of k_s and k_d , from which it can be seen that although the chelated hydrogel with iron has the lowest k_s value, it has much lowest k_d , while Mn, which has almost similar k_s to that of Fe, has the highest k_d , which explain the high affinity of the hydrogel towards iron and its low affinity towards Mn.

Effect of metal ion concentration

The Langmuir isotherm can be used also to estimate the capacity of the PVP/AAc copolymer for different metal ions. The distribution of the metal ions between the copolymer and the metal ion solution, at equilib-

TABLE I Adsorption Rate Constant of Fe, Cu, and Mn on PVP/ AAc Copolymer Hydrogel

Metal	$k (s^{-1})$	c_e/c_0	$k_d \; ({ m s}^{-1})$	$k_{s} ({ m s}^{-1})$
Fe	0.82×10^{-4}	0.194	0.16×10^{-4}	0.66×10^{-4}
Cu Mn	1.8×10^{-4} 3.3×10^{-4}	0.57 0.78	1.0×10^{-4} 2.6×10^{-4}	0.8×10^{-4} 0.7×10^{-4}







Figure 4 Equilibrium adsorption isotherms for the adsorption of Fe, Cu, and Mn.

rium, is important to estimate the tendency of the copolymer towards such metal ion. Figure 4 shows the relation between metal ion concentration c_e (mg/L) and the adsorbed metal ion per unit mass of the PVP/ AAc copolymer q_e (mg/g). The adsorption isotherms of Fe, Cu, and Mn were calculated using Langmuir linear form as

$$\frac{c_e}{q_e} = \frac{1}{k_L} + \left(\frac{a_L}{k_L}\right)c_e$$

where c_e is the equilibrium concentration of the metal ion solution (mg/L); q_e is the amount of adsorbed metal ion per gram of PVP/AAc copolymer at equilibrium (mg/g); k_L and a_L are the Langmuir isotherm constants.

Plotting $\left(\frac{c_e}{q_e}\right)$ against c_e (Fig. 5) produces a linear

TABLE II Langmuir Model

Metal	Langmuir equation	a_L	k_L	$\left(\frac{k_L}{a_L}\right)$	r ²
Fe	$\left(\frac{c_e}{q_e}\right) = 0.53 + 0.025 c_e$	0.047	1.88	39.9	0.99
Cu	$\left(\frac{c_e}{q_e}\right) = 1.64 + 0.039 c_e$	0.024	0.61	25.4	0.98
Mn	$\left(\frac{c_e}{q_e}\right) = 5.87 + 0.067 c_e$	0.011	0.17	15.4	0.99

relationships of slope $\left(\frac{a_L}{k_L}\right)$ and intercept $\left(\frac{1}{k_L}\right)$. The ratio

 $\left(\frac{\kappa_L}{a_L}\right)$ is known as the capacity factor, which is the maximum adsorption capacity of the PVP/AAc copolymer for particular metal ion. The estimated Langmuir parameters and capacity factors for each metal ion are shown in Table II.

On the other hand, Freundlich isotherm constant could be estimated if the adsorption of Fe(III), Cu(II), and Mn(II) onto PVP/AAc fits Freundlich isotherm which is expressed as

$$\log q_e = \log A + (1/n) \log c_e$$

The plot of log q_e against log c_e (Fig. 6) also produces a linear relationship of slope (1/n) and intercept log A, where A and n are empirical constants (Freundlich parameters), indicates the capacity and intensity of adsorption, respectively. The estimated Freundlich constants for each metal ion are shown in Table III. From the experimental data, the numerical value of 1 < n < 10 indicating that the adsorption for the metal ions under investigation was unhindered and the isotherm does not predict any saturation of the copolymer surface.²⁸



Figure 5 Langmuir isotherms for the adsorption of metals.



Figure 6 Freundlich isothermal adsorption curve.

Freundlich Model							
Metal	Freundlich equation	Α	п	r^2			
Fe Cu Mn	$\begin{array}{l} \log q_{\rm e} = 0.23 + 0.69 \log c_{\rm e} \\ \log q_{\rm e} = -0.10 + 0.69 \log c_{\rm e} \\ \log q_{\rm e} = -0.61 + 0.73 \log c_{\rm e} \end{array}$	1.7 0.79 0.24	1.45 1.44 1.37	0.98 0.98 0.99			

TABLE III Freundlich Model

Recyclability of the chelated hydrogel

The possibility of recycling the PVP/AAc-metal hydrogels was investigated (Fig. 7). On recycling, the hydrogels adsorbed almost the same amounts of metal ions even after 10 cycles. These points to the possibility of reusing the hydrogels several times.

Water treatment

In recent years, there has been considerable interest in the chelation of metal ions by insoluble crosslinked polymeric substrate.^{29,30} Such substrates have advantages over soluble materials of easy separation from the reaction medium, leading to operational flexibility of their facial regenerability and of higher stability.

Several parameters such as pH of the medium, metal ions concentration, and the presence of dissolved salts may affect the uptake process. The effect of pH and initial feed solution concentration were discussed in a pervious work.¹³ Polluted water may contain dissolved salts, like NaCl, MgCl₂, CaCl₂, in addition to heavy metal ions, which may also affect the chelation process. Adsorption of Fe ions, as an example of polluting metal ion, on PVP/AAc hydrogel was studied in the presence of various concentrations of inorganic salts such as NaCl, CaCl₂, and MgCl₂ to investigate the effect of their presence on Fe



Figure 7 Recyclability of the chelated hydrogel.



Figure 8 Effect of different concentration of dissolved salts on Fe uptake.

adsorption (Fig. 8). In case of NaCl, there is no effect on the adsorption of Fe ions even at high NaCl concentrations. Also, Fe adsorption is not affected by low concentrations of $CaCl_2$ and $MgCl_2$, but at higher concentrations a small decrease in adsorption was observed and this may be attributed to the affinity of the reactive polymers towards alkaline earth metals as transition metal ions.⁵

So, the results suggest that the adsorption capacity of the adsorbent is slightly affected by the presence of such inorganic salts.

Analysis of nine water samples representing all water resources in Helwan area (groundwater, irrigation canal) as well as some samples collected from industrial and irrigation wastes are presented in Table IV. The results reveal that, surface and ground waters are locally contaminated by heavy metals. The presence of such heavy metals in the water resources is of major concern due to their toxicities. For this reason, these polluted water samples were chosen to be treated using PVP/AAc copolymer hydrogel. After treatment, another chemical analysis of these water samples was performed (Table IV).

Generally, the treatment must provide water of better quality, and the data achieved reveal the following:

- The (PVP/AAc) hydrogel was capable of removing 98–99.9% of total Fe, 84–100% of Al(III), 64– 99% of Mn(II), and 78–97% of Zn(II), resulting in a satisfactory removal of heavy metals in the water samples under investigation.
- A decrease in the percent removal of total iron and zinc was noticed in sample 2, due to the higher concentration of those metal ions originally found in the feed solution. However, recycling of water samples several times with the hydrogel may result in a higher percent removal.
- The analysis also showed a decrease in Ca²⁺ and Mg²⁺ concentrations.

 TABLE IV

 Chemical Analysis Data of Water Samples Before and After the Treatment Process

Sample source	Groundwater sample									
Analytical	Sample no. 7		Samp	Sample no. 14 Sample		no. 18 Sample no. 33		io. 33	Sample no. 35	
parameter	Before	After	Before	After	Before	After	Before	After	Before	After
pН	6.9	4.2	7.4	4.8	7.4	5.3	7.2	4.5	7.2	4.9
$EC (\mu S/cm)$	3250	2740	1050	540	2750	2100	2590	2200	1120	710
TDS (mg/L)	1782.6	1608.3	532.4	319.2	1586.5	1309.8	1346.3	1072.1	596.6	371.2
Ca^{2+} (mg/L)	165.81	131.26	59.22	20.15	98.7	32.18	296.1	195.99	75.01	29.05
Mg^{2+} (mg/L)	65.95	47.85	34.76	7.56	107.92	68.94	71.95	58.85	59.96	31.49
Na^+ (mg/L)	370	370	90	80	310	310	90	90	55	55
K^+ (mg/L)	17	17	17	12	4	4	5	5	4	4
CO_{3}^{2-} (mg/L)	38.7	0	46.4	0	27.1	0	19.3	0	0	0
HCO_3^- (mg/L)	204.59	39.34	310.82	139.87	330.48	41.1	346.23	62.95	380.48	78.69
SO_4^{2-} (mg/L)	300.33	300	75	75	461	461	210.3	210.3	117.3	117.3
Cl^{-} (mg/L)	722.49	722.49	54.64	54.64	412.4	412.4	480.5	480.5	95.03	95.03
NO_3^- (mg/L)	51.9	51.8	45	45	51.03	51.02	33.03	33	35.23	35.2
Al^{3+} (mg/L)	< 0.07	< 0.07	0.17	< 0.07	0.34	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07
Total Fe (mg/L)	8.11	0.09	1.21	0.02	5.31	0.04	1.42	0.01	0.32	< 0.005
Mn^{2+} (mg/L)	0.05	< 0.002	0.15	< 0.002	0.05	< 0.002	0.03	0.01	0.02	< 0.002
Zn^{2+} (mg/L)	0.1	0.01	2.54	0.13	11.2	0.26	7.0	0.42	0.6	0.13
Sample source]	ndustrial	waste		Irrig	ation Canal		Irrigation	n Waste
Analytical	Sample no. (2)		Sample no. (28)		Sample no. (19)		-	Sample no. (5)		
parameter	Before	А	fter	Before	After	Before	After	•	Before	After
pН	6.0		3.1	8.1	4.9	6.6	4.8		7.5	4.2
EC (μ S/cm)	2610	2	500	600	406	578	370		3200	2800
TDS (mg/L)	1137.8	10	09.5	336.9	218.1	294.9	187.1		1706.8	1604.3
Ca^{2+} (mg/L)	296.1	1	84.6	55.7	24.04	51.32	20.51		157.9	116.3
Mg^{2+} (mg/L)	23.94	1	5.42	21.58	8.51	16.78	6.52		77.94	47.85
Na^+ (mg/L)	80		80	36	36	30	30		380	380
K^+ (mg/L)	10		10	5	5	8	8		19	19
CO_3^{2-} (mg/L)	0		0	15.4	0	7.74	0		30.9	0
HCO_3^- (mg/L)	15.73		0	173.1	55.08	173.11	55.08		212.46	39.34
SO_4^{2-} (mg/L)	40.35		40	67.16	67.16	57.02	57.02		490.25	480
Cl^{-} (mg/L)	679.5	6	79.5	49.89	49.89	37.51	37.51		550.69	541.7
NO_3^- (mg/L)	8.25		8.2	35.05	35.02	2.59	2.58		47.13	47.1
Al^{3+} (mg/L)	0.4	().06	1.43	0.18	5.04	0.19		0.53	< 0.07
Total Fe (mg/L)	57.36	6	5.06	0.65	0.01	1.42	0.01		1.34	< 0.005
Mn^{2+} (mg/L)	1.13	().26	0.2	0.01	0.32	< 0.002	2	0.12	0.01
Zn^{2+} (mg/L)	203.6	1	88.8	0.18	0.02	0.42	0.05		0.29	0.02

- A drop in the pH of the water samples was also observed leading to a decrease in the bicarbonate concentration in the samples. The drop in the pH may be explained by the exchange between metal ions Mⁿ⁺ and H⁺ of the carboxylic group (COOH) in the hydrogel, resulting in an excess proton in solution, leading to a drop in the pH.
- As a result of the decrease in the concentration of heavy metal, calcium, magnesium, and bicarbonate ions, a decrease in the TDS of the water samples ranging from 6 to 40% was observed.

So, it can be concluded that, the prepared (PVP/AAc) hydrogel is somewhat effective in treating the polluted water and decreases water salinity.

CONCLUSIONS

The results reported here demonstrate the applicability of using PVP/AAc hydrogel for water treatment. The characterization of the hydrogel reveals that it has a high binding capacity, good adsorption kinetic properties, and a strong field ligand. The study also showed that, metal–copolymer adsorption isotherms exhibit a Langmuir-type equation.

The analysis of nine water samples representing water resources in Helwan area showed that trace metals contents are very high. The hydrogel treatment resulted in a satisfactory removal of polluted heavy metals especially iron, manganese, and aluminum. Also, a drop of pH and a decrease in Ca²⁺, Mg²⁺, and TDS concentrations in the water samples were achieved.

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