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Adsorption of heavy metals from industrial wastewater by using polyacrylic acid hydrogel

Naim Sezgin*, Nilgun Balkaya

Faculty of Engineering, Department of Environmental Engineering, Istanbul University, Avcilar, Istanbul 34320, Turkey, Tel. +90212 473 70 70/17721; email: nsezgin@istanbul.edu.tr (N. Sezgin)

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ABSTRACT

In this study, the removal of heavy metals (Cu(II), Ni(II), Zn(II), and total Cr) from real industrial wastewater (IWW), being taken from galvanotechnic industry, by means of polyacrylic acid (Aac) hydrogel was investigated. The effects of adsorbent dosage, contact time, and shaking speed on heavy metal removal from wastewater were monitored using real wastewater. In addition, adsorption isotherm and kinetics studies for adsorption of heavy metals were studied in this study. The adsorption capacities of Aac hydrogel for Cu(II), Ni (II), Zn(II), and total Cr were achieved as 2.74, 1.91, 6.83, and 6.61 mg/g, respectively. The removal of heavy metals using Aac hydrogel was fitted with Freundlich isotherm and pseudo-second-order kinetic models. Thermodynamic studies indicated that the process was exothermic and spontaneous. According to these results, Aac hydrogel is suitable adsorbents for removing heavy metals from IWW.

Keywords: Acrylic acid; Hydrogel; Heavy metal; Adsorption; Wastewater treatment

1. Introduction

The discharge of untreated industrial wastewater (IWW) to the environment is a major source of environmental pollution. Wastewater that contains heavy metals is especially dangerous for the environment and biological organisms [1]. Heavy metals show toxic effect even at low concentrations and also have potential to accumulate. Heavy metals are defined as a group of more than 40 elements with mass greater than 5 g/cm^3 [2,3]. Heavy metals are discharged to receiving environments from various industrial production processes or auxiliary processes such as battery production, paint industry, printing facilities, coal firing, domestic wastewater, vehicle emissions, mining operations, metal coating, and the use of fossil fuels [1,4].

Removal and recovery of heavy metals that have severe negative effects on the environment, especially on living organisms, are of great importance to minimize environmental hazards, to control pollution, and in terms of economic factors. Chemical precipitation, filtration, reverse osmosis, adsorption, electrochemical methods, and ion exchange are common methods to remove heavy metals from wastewater [5,6]. There is ongoing research on the use of adsorption methods and adsorbents in removal of heavy metals from wastewater. These adsorbents can include natural or

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*Corresponding author.

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synthetic zeolites, hydrogels, and nanoparticles [7–10]. Table 1 shows the advantages and disadvantages of various processes used for the removal of heavy metals from wastewater [11].

Hydrogels can be defined as a cross-linked, insoluble network of polymeric structures consisting of homo- or copolymers with the capability to absorb a large volume of water [12]. Hydrogels can be natural such as gelatin, alginate, starch and cellulose based, or acrylamide 2-hydroxyethylmethacrylate, acrylic acid, 2-acrylamido 2-methylpropane sulfonic acid-based synthetic polymers [13,14]. Hydrogels have many advantages over conventional methods of heavy metal removal, including having a hydrophilic structure, being lighter than water, appropriateness of monomer functional groups for direct synthesis, further penetration into pollutants due to their three-dimensional structures, synthesizability at controllable dimensions, changeability of functional groups, environmentally benign due to easy biologic decomposition, and the possibility of reuse due to desorption processes [12].

In this study, the removal of Cu(II), Ni(II), Zn(II), and total Cr from real IWW was studied. The adsorption ability of Aac hydrogel was investigated for the removal of Cu(II), Ni(II), Zn(II), and total Cr from single (non-competitive) and multi (competitive) aqueous systems. Samples of real IWW were used to investigate the effect of adsorbent amount, contact time, and shaking speed on heavy metal removal. The experimental isotherm data were analyzed using Langmuir and Freundlich isotherms. The adsorption kinetics was investigated for the pseudo-first-order and pseudo-second-order kinetic models. The thermodynamic parameters were also evaluated from the adsorption measurements.

2. Materials and methods

2.1. Wastewater samples

Two different types of wastewater were used in the study: real IWW and synthetic wastewater (SWW), which was prepared single (non-competitive) and multi (competitive) aqueous solution containing Cu (II), Ni(II), Zn(II), and total Cr. The real IWW was collected from the inflow of a treatment plant of galvanotechnic industrial site in Istanbul. The properties of the real IWW are presented in Table 2.

Table 1
Comparisons of various processes used for the removal of heavy metals from wastewater [11]

Technology	Advantages	Disadvantages
Chemical precipitation	Process simplicity Not metal selective Inexpensive capital cost	Large amount of sludge containing metals Sludge disposal cost High maintenance cost
Ion exchange	Metal selective Limited pH tolerance High regeneration	High initial capital cost High maintenance cost
Membrane filtration	Low solid waste generation Low chemical consumption Small space requirement Possible to be metal selective	High initial capital cost High maintenance and operation costs Membrane fouling Limited flow rates
Coagulation/ flocculation	Bacterial inactivation capability Good sludge settling and dewatering characteristics	Chemical consumption Increased sludge volume generation
Flotation	Metal selective Low retention times Removal of small particles	High initial capital cost High maintenance and operation costs
Electrochemical treatment	No chemical required can be engineered to tolerate suspended solids Moderately metal selective Treat effluent > 2,000 mg/ dm^3	High initial capital cost Production of H_2 (with some process) Filtration process for flocs
Adsorption	Wide variety of target pollutants High capacity Fast kinetics Possibly selective depending on adsorbent	Performance depends on type of adsorbent Chemical derivation to improve its sorption capacity

Table 2
Heavy metal concentrations of the IWW

Cations	Value	Unit
Cu^{+2}	86.12	mg/L
Ni^{+2}	83.99	mg/L
Zn^{+2}	178.30	mg/L
Total Cr	302.80	mg/L
Total Fe	77.74	mg/L
Na^{+1}	822.88	mg/L
NH_4^+	181.23	mg/L
K^+	146.81	mg/L
Mg^{+2}	59.01	mg/L
Ca^{+2}	212.22	mg/L

2.2. Preparation of polyacrylic acid hydrogel (Aac)

Polyacrylic acid (Aac) hydrogel was synthesized by free radical participation polymerization of acrylic acid monomer. Aac hydrogel was 60% neutralized by sodium hydroxide solution prior to synthesis. Neutralized Aac was polymerized in the presence of 1 mol% monomer cross-linker [N,N methylenebisacrylamide (NMBA)]; 1 mol% monomer initiator [potassium persulfate ($K_2S_2O_8$)] and an equal weight of accelerator [potassium bisulfite ($KHSO_3$)] and nitrogen atmosphere for 2 h at 7˚C. The obtained Aac hydrogel was purified and dried in a vacuum for 24 h at 40˚C. The polymerization reaction was given in Fig. 1. All chemicals used to prepare the hydrogel were obtained from Merck.

In addition, the hydrogel sample was analyzed using a Perkin Elmer Precisely Spectrum One Fourier transform infrared (FTIR) spectrophotometer in the region of 450–4,000 cm^{-1} with KBr disc technique. Prior to the measurement, the hydrogel sample was dried under vacuum overnight until they reached a constant weight.

2.3. Experimental procedures

The real IWW was filtered with a mesh size of 0.45 μm before experimental studies. In batch tests,

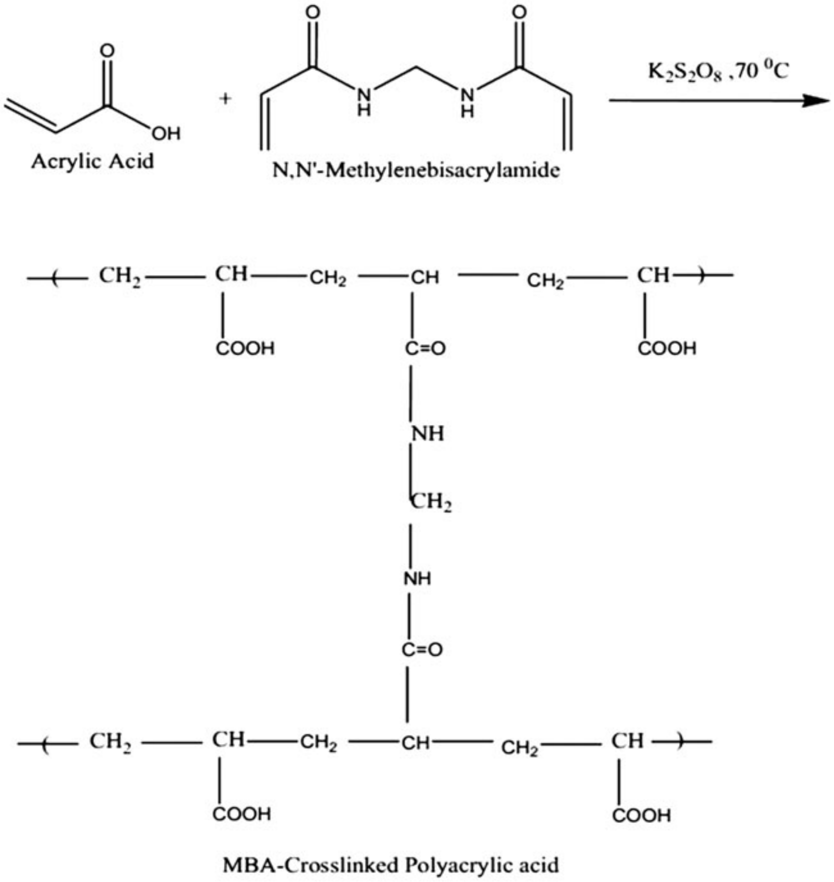

Fig. 1. Synthesis of N,N methylenebisacrylamide (MBA) polyacrylic acid.

100 mL synthetic and IWW samples were placed in 250 mL erlenmeyer flasks; adsorbent was added and the flasks were shaken at 150 rpm in a shaker (Gallenkamp orbital incubator). The samples were then transferred to glass tubes for analysis. Cu(II), Ni (II), Zn(II), and total Cr concentrations of solutions before and after adsorption were measured using atomic absorption spectroscopy (Perkin Elmer A Analyst 400, AAS).

The heavy metal removal and adsorption capacities of Aac hydrogel were calculated using Eqs. (1) and (2), respectively.

$$\text{Removal effiency}\,(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

$$q = \frac{(C_0 - C_e) \times V}{m} \tag{2}$$

where C_0 represents initial concentration of metals in the wastewater (mg/L), C_e represents metal concentrations in the solution after the experimental study (mg/L), q represents the equilibrium adsorption capacity (mg/g), V represents sample volume (L), and m represents amount of hydrogel used (g).

Experimental studies used various amounts of adsorbent (1.0–3.0 g/100 mL), contact times (1–24 h), shaking speeds (80–200 rpm), and temperatures (293–323 K).

2.4. Theory

2.4.1. Adsorption isotherm

Langmuir and Freundlich equations are widely used in adsorption processes [15]. The linear form of the Langmuir isotherm is as follows [16]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{3}$$

where C_e is the equilibrium concentration of the adsorbate (mg/L); q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g); q_m is the theoretical maximum monolayer adsorption capacity of the adsorbent (mg/g); K_L is the Langmuir isotherm constant related to the adsorption energy (L/mg), the relationship between the adsorbent and the adsorbate. The values of q_m and K_L can be determined from the slope and intercept of the linear plot of C_e/q_e vs. C_e.

The linear form of the Freundlich isotherm is expressed as follows [17]:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \tag{4}$$

where K_f is Freundlich isotherm constant related to the adsorption capacity of the adsorbent (mg/g). The values of K_f and $1/n$ were calculated from the intercept and slope of the plot of ln q_e vs. ln C_e.

2.4.2. Adsorption kinetics

Pseudo-first-order and pseudo-second-order kinetic model equations developed by Lagergren are generally used as the kinetic model to determine reaction degrees of adsorption systems [14,18,19]. The linear form of pseudo-first-order kinetic model equation is expressed as follows [20,21]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

where q_e and q_t are the adsorption amounts of heavy metal ions per gram of adsorbent at time t (min) and at equilibrium (mg/g), respectively; k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}); t is time (min). The adsorption rate constant k_1 and equilibrium adsorption capacity $q_{e,cal}$, calculated from the slopes and intercepts of plots of log $(q_e - q_t)$ vs. t.

The linear form of the pseudo-second-order kinetic model equation is as follows [20,21]:

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \tag{6}$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (min^{-1}). The adsorption rate constant k_2 and equilibrium adsorption capacity $q_{e,cal,}$ calculated from the slopes and intercepts of plots of t/q_t vs. t.

When q_e values calculated by experimental data are consistent with theoretical values and according to correlation coefficient (R^2) values adsorption rate is deemed to fit the pseudo-first or second-order kinetic models.

On the other hand, the adsorption data were subjected to piecewise linear regression analysis to understand the mechanism of adsorption. The information of adsorption mechanism can be used to optimize the design of adsorbents and adsorption conditions [22]. The overall rate of adsorption can be described by the following three steps [23]: (1) film or surface diffusion where the sorbate is transported from the bulk solution to the external surface of sorbent, (2) intraparticle or pore diffusion, where sorbate molecules move into the interior of sorbent particles, and (3) adsorption on the interior sites of the sorbent. Since the adsorption step is very rapid, it is assumed that it does not influence the overall kinetics. The overall rate of adsorption process, therefore, will be controlled by either surface diffusion or intraparticle diffusion. The Weber–Morris intraparticle diffusion model has often been used to determine as below equation if intraparticle diffusion is the rate-limiting step [24,25] (Eq. (7)):

$$q_t = k_i t^{0.5} + C \tag{7}$$

where k_i is the intraparticle diffusion rate constant (mg/g $h^{0.5}$) and C is the intercept. According to this model, a plot of q_t vs. $t^{0.5}$ should be linear if intraparticle diffusion is involved in the adsorption process and if the plot passes through the origin then intraparticle diffusion is the sole rate-limiting step [26]. It has also been suggested that in instances when q_t vs. $t^{0.5}$ is multilinear two or more steps governs the adsorption process [27,28].

2.4.3. Thermodynamics

Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) thermodynamic parameters were calculated using Eqs. (8) and (9).

$$\Delta G = -RT \ln K_\mathrm{c} \tag{8}$$

$$\ln K_\mathrm{c} = \Delta S/R - \Delta H/RT \tag{9}$$

where R is the universal gas constant (8.314 J/mol K), T is the temperature (K). ΔH and ΔS are calculated from the slope and intersection point of the graph of $1/T$ against ln K_c, respectively. The adsorption equilibrium constant is expressed as $K_\mathrm{c} = C_\mathrm{ads}/C_\mathrm{e}$. C_ads is the concentration of the adsorbate that is adsorbed at the equilibrium (mg/L); C_e is the concentration of the adsorbate remaining in solution at the equilibrium (mg/L).

2.4.4. The removal of heavy metals from single (non-competitive) and multi (competitive) aqueous systems

SWW samples containing single and multi-component types of heavy metals were prepared. Concentrations in samples containing multi-component metals were prepared in a similar procedure to the initial concentrations of real IWW. Experiments of SWW with multi-component metals were conducted under the same experimental conditions as IWW experiments. Samples of 100 mL wastewater containing 2.5 g Aac hydrogel were placed in the shaker. The samples were shaken at 150 rpm for 24 h and were taken at the different contact times from the shaker.

SWW samples containing single-component metals were prepared at five different initial concentrations ranging from 30 to 100 mg/L for Cu(II); 20–100 mg/L for Ni(II); 40–200 mg/L for Zn(II); and 50–300 mg/L for total Cr. Isotherm curves were drawn according to the results obtained from wastewater samples containing a mono-component metal.

2.5. Scanning electron microscope and EDS

Surface morphology of the Aac hydrogel before and after the adsorption was determined using a FEI Quanta FEG 450 scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) analysis.

3. Result and discussion

3.1. FTIR spectroscopy results

In order to confirm the network structure of prepared hydrogel, FTIR study was used. It is a sensitive technique to detect the shift in the position of bonds, which confirms the interaction. The FTIR spectra of Aac hydrogel is shown in Fig. 2. The main peaks of Aac hydrogel are –OH stretch at 3,467 cm^{-1}, –CH stretch at 2,928 cm^{-1}, and –C=O stretch at 1,616 cm^{-1}.

3.2. Effect of hydrogel dosage

The dosage of adsorbent used in the removal of heavy metal is of great importance for design. It should be determined equilibrium of the system between the used adsorbent and adsorbate [29]. The effect of Aac hydrogel dosage on heavy metal removal is presented in Fig. 3. As can be seen Fig. 3, the removal of heavy metal was increased with the increase in adsorbent dosage. This can be explained due to the fact that the higher the dose of adsorbent in the solution, the greater the availability of exchangeable sites for metal ions [30,31]. Beyond the certain amount (25 g), the percentage removal of heavy metal reaches almost a constant value. Cu(II), Ni(II), Zn(II), and total Cr removal in the presence of 25 g/L hydrogel were 86.68, 53.76, 66.64, and 55.30%, respectively. Adsorption capacities were 3.10, 1.64, 6.43, and 6.94 mg/g, respectively.

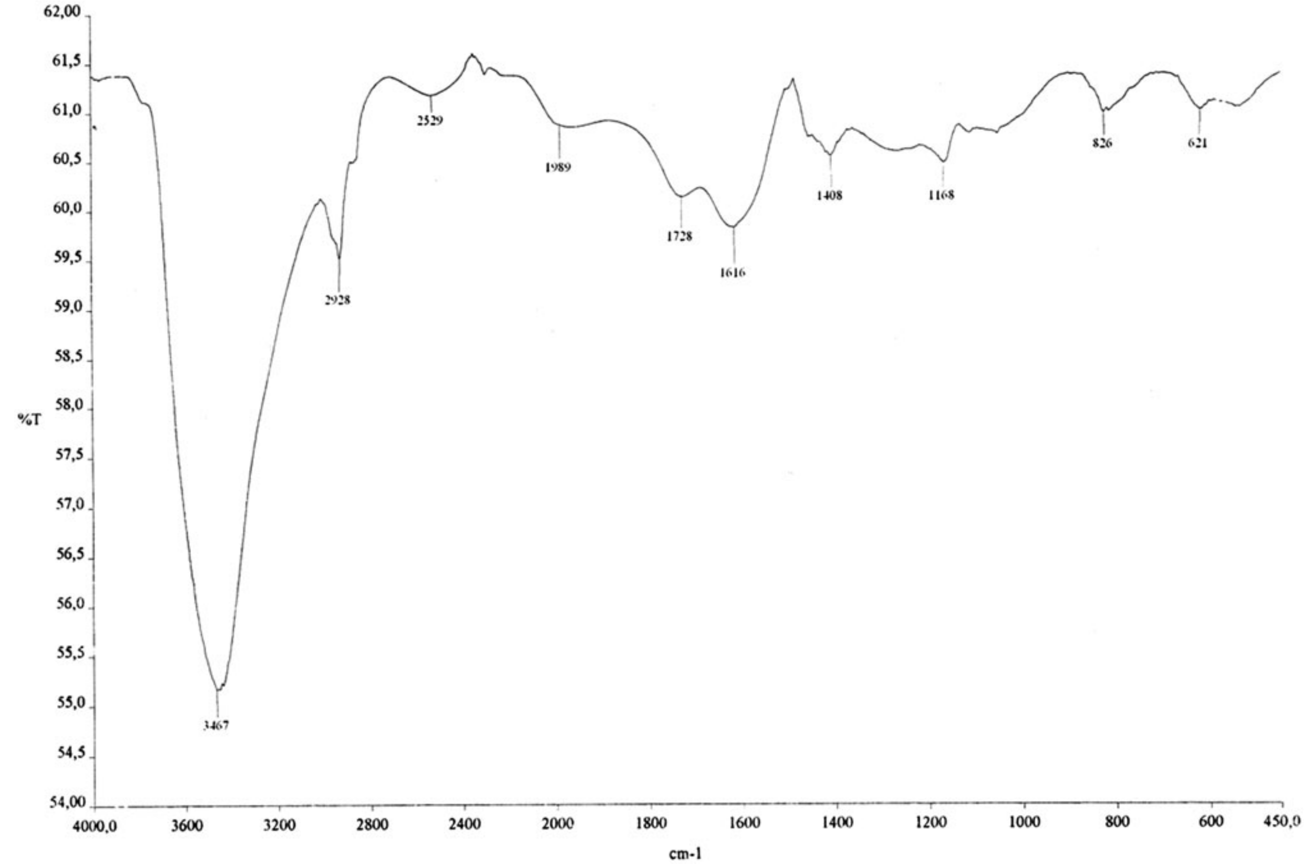

Fig. 2. FTIR spectra of polyacrylic acid.

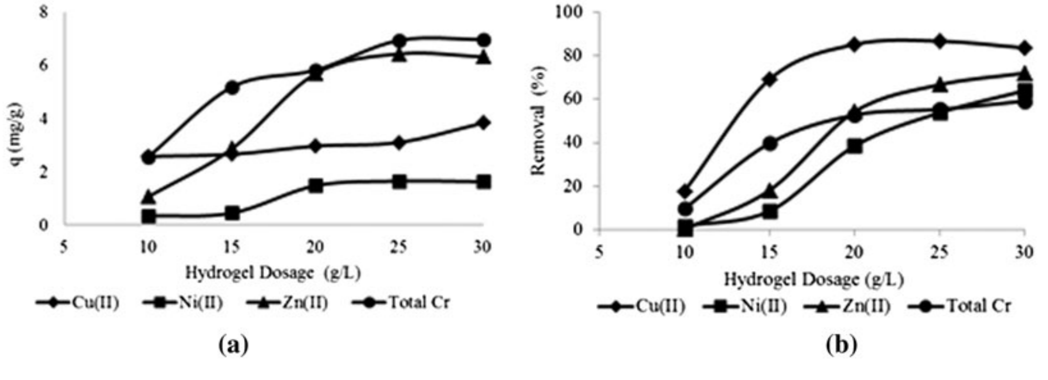

Fig. 3. Effect of adsorbent dosage on (a) adsorption capacity, *q* (mg/g), for Aac hydrogel and (b) heavy metal removal (%) (pH 2.08, *t* = 4 h, shaking speed = 150 rpm).

3.3. Effect of contact time

Contact time is important to determine the adsorption kinetics and feasibility of the system in practice [32,33]. The effect of contact time on heavy metal removal is presented in Fig. 4. Adsorption capacity and heavy metal removal increased in the first 3 h and no significant change occurred after 4 h, indicating that the adsorption system equilibrated at the 4 h.

3.4. Effect of shaking speed

Low shaking speeds will fail to produce the energy required to move heavy metal ions into the pores of the

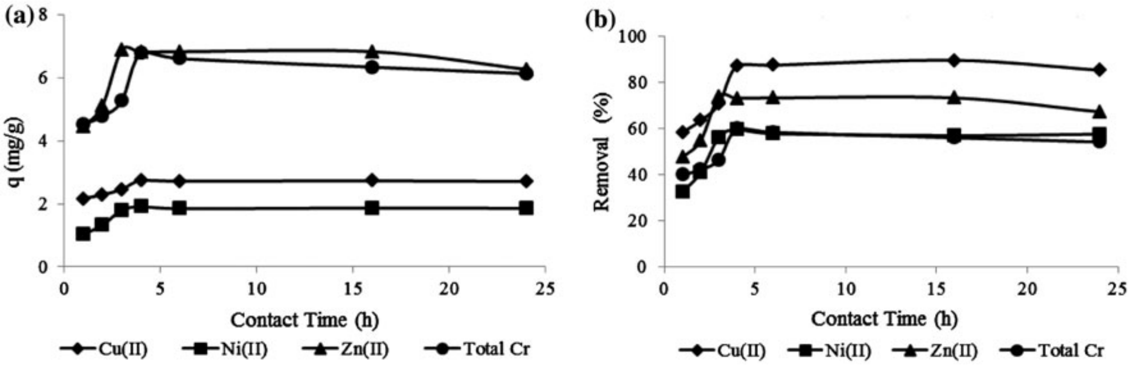

Fig. 4. Effect of contact time on (a) adsorption capacity, q (mg/g), for Aac hydrogel and (b) heavy metal removal (%) (pH 1.96, hydrogel dosage = 25 g/L, shaking speed = 150 rpm).

adsorbent and to induce adsorption. If the shaking speed is very high heavy metal ions that were adsorbed at adsorbent surface will repass into the solution. Determining the appropriate shaking speed is therefore an important factor in adsorption processes [29].

The effect of shaking speed on heavy metal removal is shown in Fig. 5. Increased shaking speed increased adsorption capacity and heavy metal removal. The heavy metal removal and adsorption capacity were increased with the increase in shaking speed. It can be said that this indicates that heavy metal ions are easily and rapidly diffused from the hydrogel surface and pores [34].

3.5. Adsorption isotherms

The adsorption data were applied to both the Freundlich and the Langmuir equations. The coefficients for the linearized forms of the Langmuir and Freundlich isotherms and correlation coefficients of Cu(II), Ni(II), Zn(II), and total Cr on Aac hydrogel are presented in Table 3. Adsorption isotherm plots of Cu (II), Ni(II), Zn(II), and total Cr onto Aac hydrogel are shown in Fig. 6.

According to the correlation coefficients shown in Table 2, adsorption of Cu(II), Ni(II), Zn(II), and total Cr is fitted well by the Freundlich isotherm. Accordingly, it is assumed that adsorption sites on the adsorbent surface are heterogeneous and that there was no interaction between the molecules adsorbed onto the surface [15]. Furthermore, K_f and n values in the Freundlich isotherm provide information about the suitability of adsorbent/adsorbate system and adsorption system [35–37]. If $n < 1$, the adsorption system is more heterogeneous, and that adsorption is more efficient at high concentrations. If n is equal to unity, the adsorption is linear. When $n > 1$ this indicates that the system is more efficient at low concentrations. Greater K_f value indicates that adsorption capacity is high [30,36–38].

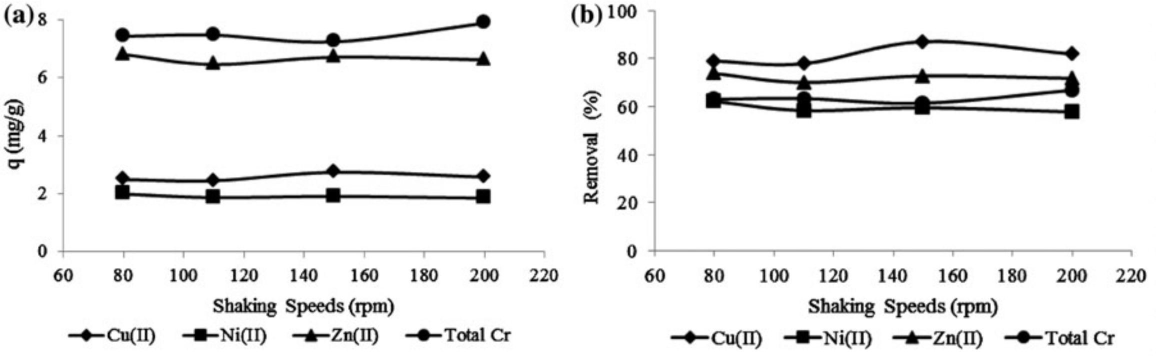

Fig. 5. Effect of shaking speed on (a) adsorption capacity, q (mg/g) and (b) heavy metal removal (%) for Aac hydrogel (pH 2.14, hydrogel dosage: 25 g/L, t = 4 h).

Table 3
Langmuir and Freunlich Isotherm parameters

	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	R[a]	K_f (mg/g)	n	R[a]
Cu(II)	1.410	0.069	0.966	0.018	0.440	0.981
Ni(II)	5.850	0.054	0.882	0.543	0.660	0.945
Zn(II)	14.310	43.48	0.865	0.210	0.820	0.989
Total Cr	16.500	0.011	0.923	0.097	0.750	0.998

[a] Correlation coefficient.

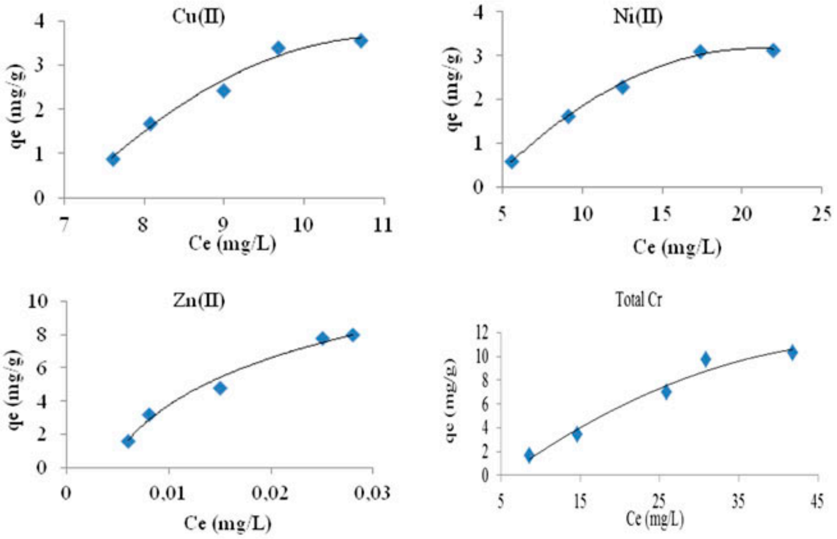

Fig. 6. Equilibrium curve for the adsorption of Cu(II), Ni(II), Zn(II), and total Cr on Aac hydrogel.

3.6. Adsorption kinetics

The pseudo-first-order and pseudo-second order kinetic models were used to explain adsorption mechanisms in heavy metal removal with Aac hydrogel. The values of the parameters and the correlation coefficients are presented in Table 4. As can be seen in Table 4, the correlation coefficients calculated from the pseudo-second-order model were high (0.995–0.971) for all heavy metals, and the calculated q_e values from the pseudo-second-order model were in good agreement with the experimental q_e values. The adsorption of Cu(II), Ni(II), Zn(II), and total Cr with Aac hydrogel followed a pseudo-second-order kinetic model. According to Table 4, the high total Cr adsorption capacities with respect to the other metals may be explained on the basis of its size. The ion radius of Cr(III) and Cr(VI) are lower than the other heavy metals [39].

The adsorption capacities of different adsorbents and hydrogels for some heavy metals are given in Table 5. In addition, there are many studies related to the reuse of hydrogels in the literature e.g. Kaşgöz et al. [50] were found hydrogels with acid groups which were desorbed three times for heavy metals removal.

Intraparticle diffusion plot q_t vs. $t^{0.5}$ was given in Fig. 7. According to Fig. 7, the adsorption Cu(II), Ni(II), Zn(II), and total Cr on Aac hydrogel occurred in two phases. The initial linear section represents a gradual adsorption stage where intraparticle or pore diffusion is rate limiting and the second section plot is final equilibrium stage. As the plots did not pass through the origin, intraparticle diffusion was not the only rate-limiting step on the adsorption process. So that, multiple diffusion model was determined to be effective in adsorption [22]. In additional, the intraparticle diffusion rate k_i and plot intercept value C were found 0.551 mg/g h$^{0.5}$ and 1.569 for Cu(II), 0.931 mg/g h$^{0.5}$ and 0.087 for Ni(II), 3.248 mg/g h$^{0.5}$ and 0.987 for Zn(II), and 2.087 mg/g h$^{0.5}$ and 2.128 for total Cr.

Table 4
Kinetic parameters for the adsorption of Cu(II), Ni(II), Zn(II), and total Cr

	Pseudo-first order				Pseudo-second order			
	R^2	k_1 (L/min)	$q_{e,cal}$	$q_{e,exp}$	R^2	k_2 (mg/g.min)	$q_{e,cal}$	$q_{e,exp}$
Cu(II)	0.933	0.880	2.06	2.74	0.995	0.746	2.94	2.74
Ni(II)	0.896	0.574	1.34	1.91	0.973	0.391	2.28	1.91
Zn(II)	0.802	0.967	4.44	6.83	0.983	0.160	7.91	6.83
Total Cr	0.847	0.789	6.83	6.61	0.971	0.130	7.72	6.61

Table 5
Adsorption capacities of different adsorbents and hydrogels for heavy metals

	Adsorption capacity (mg/g)				
Adsorbents	Cu(II)	Ni(II)	Zn(II)	Total Cr	References
Hydrogels					
PVP/Aac (mol%, 30/70)	2				[40]
Crosslinked starch gel	135				[41]
C-g-AA hydrogels		380.1			[42]
An/AAx/AMPS	0.87		1.00		[43]
CMC/ECH hydrogel bead	6.49	4.06			[44]
Aac hydrogel	2.74	1.91	6.83	6.61	In this work
Other adsorbents					
Zeolite, clinpotilolite	1.64	0.4	0.5		[45]
Kaolinite	0.76	0.003	1.80		[46]
Sawdust	1.79				[47]
Na-Montmorillonite	3.04	3.63	3.61		[48]
Coal	1.62		1.20		[49]

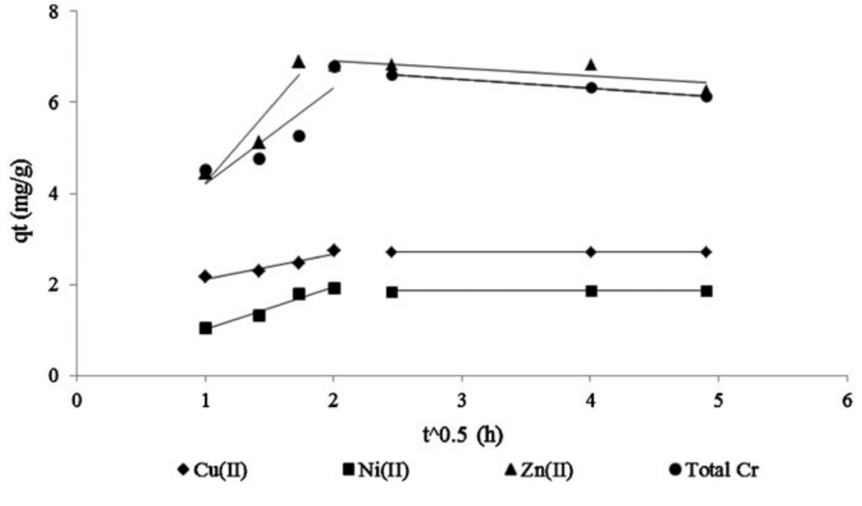

Fig. 7. Intraparticle diffusion plots for the adsorption of Cu(II), Ni(II), Zn(II), and total Cr on Aac hydrogel.

3.7. Thermodynamic study

Various thermodynamic parameters, such as ΔG, ΔH, and ΔS have been calculated. As known, thermodynamic parameters are indicators of feasibility of adsorption processes in practice [32]. The feasibility of the adsorption procedure can be understood by negative Gibbs free energy (ΔG) and enthalpy (ΔH). On the other hand, a positive ΔS value indicates greater randomness in the solid/solution interface. Negative ΔG indicates spontaneous adsorption, while positive ΔG indicates that energy is needed for adsorption. On the other hand, ΔS is the measure for irregularity in adsorption. As the relationship between the adsorbent and the adsorbate increased during adsorption, the

Table 6
Thermodynamic parameters for the adsorption of metal ions from real IWW

	ΔG (J/mol)					
	293 K	303 K	313 K	323 K	ΔH (J/mol)	ΔS (J/mol/K)
Cu(II)	−2,170.48	−2,151.90	−2,584.54	−2,413.21	−6,546.86	33.76
Ni(II)	−1,471.60	−1,561.43	−2,086.06	−2,197.88	−6,483.67	26.99
Zn(II)	−2,134.84	−3,137.88	−3,289.42	−3,334.46	−8,964.15	38.76
Total Cr	−2,640.92	−3,208.46	−3,678.34	−3,889.93	−9,774.77	42.63

Table 7
Thermodynamic parameters for the adsorption of metal ions from SWW

	ΔG (J/mol)					
	293 K	303 K	313 K	323 K	ΔH (J/mol)	ΔS (J/mol/K)
Cu(II)	−6,082.81	−6,290.41	−6,777.52	−8,108.35	−12,955.71	64.19
Ni(II)	−6,060.35	−6,339.87	−6,493.97	−8,010.98	−12,796.29	64.08
Zn(II)	−6,095.46	−6,080.84	−6,666.21	−8,381.55	−15,431.62	72.20
Total Cr	−7,435.33	−9,164.09	−10,726.90	−9,872.94	−19,056.52	92.07

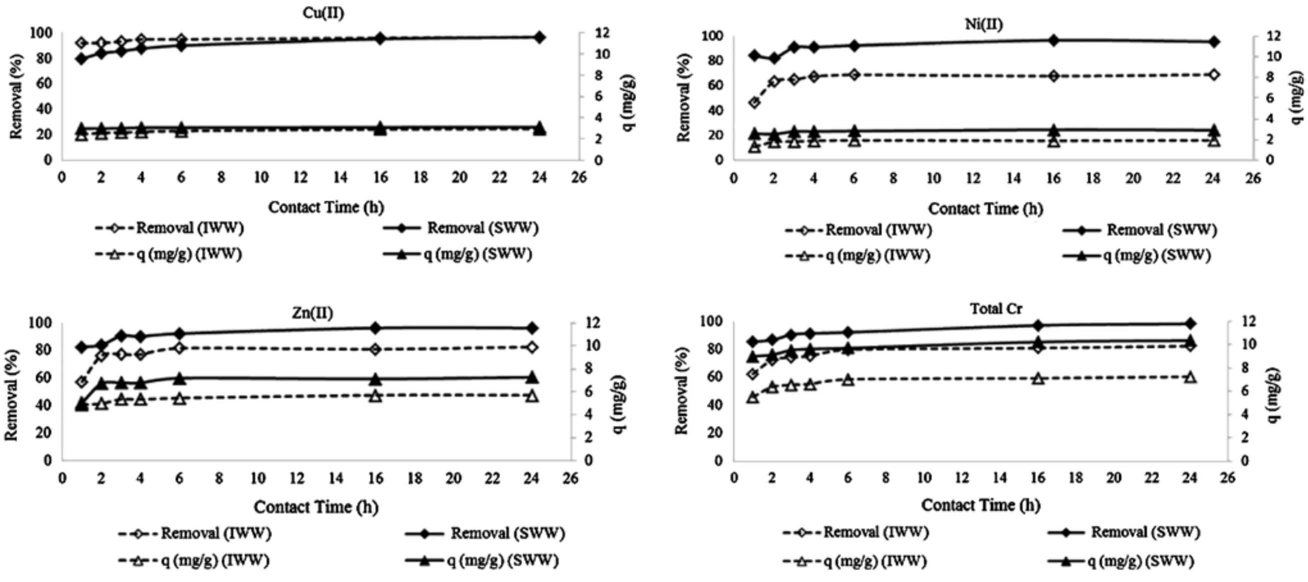

Fig. 8. Effect of contact time on heavy metal removal (%) and adsorption capacity, q (mg/g), for real IWW, and SWW in multi-aqueous system (hydrogel dosage = 25 g/L, shaking speed = 150 rpm).

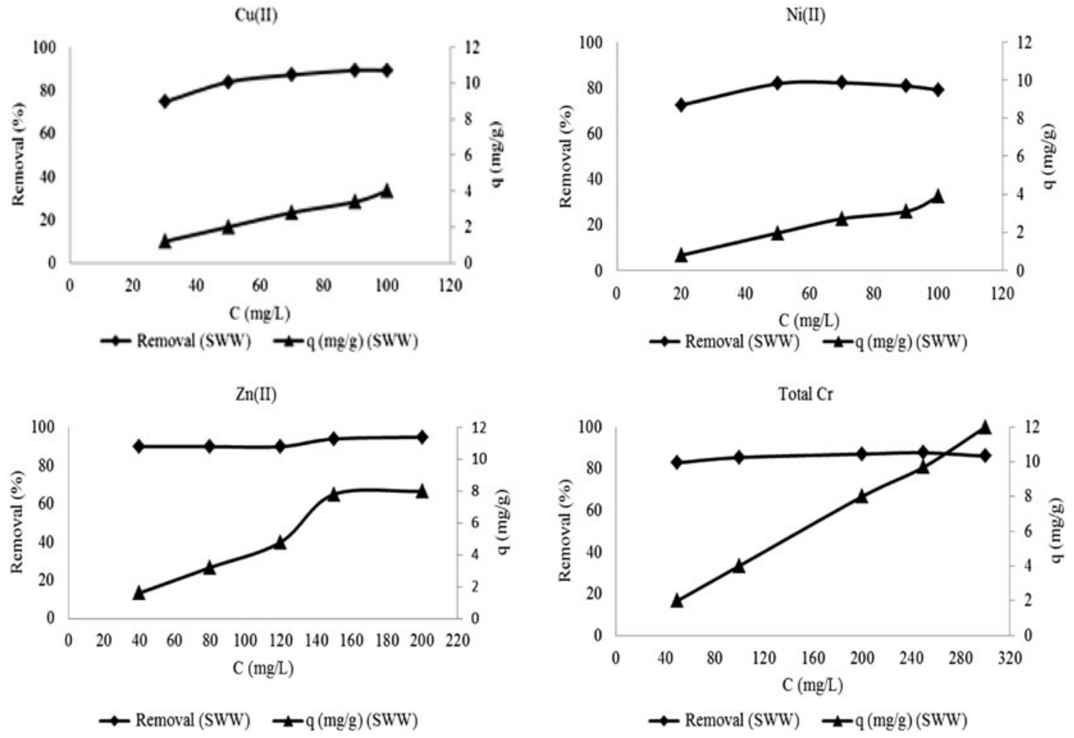

Fig. 9. Effect of initial concentration on heavy metal removal (%) and adsorption capacity, q (mg/g), for real IWW and SWW in single aqueous system (hydrogel dosage = 25 g/L, t = 4 h, shaking speed = 150 rpm).

irregularity of the adsorbent–adsorbate interface also increased [51,52].

According to data obtained from thermodynamic studies on industrial and SWW using Aac hydrogel, the Gibbs free energy (ΔG) and adsorption enthalpy (ΔH) were negative. Negative values for adsorption free energy (ΔG) and adsorption enthalpy (ΔH), which is also known as adsorption heat, indicate that the process was exothermic and spontaneous [53]. Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) values obtained from thermodynamic studies of the real IWW and SWW are presented in Tables 6 and 7, respectively.

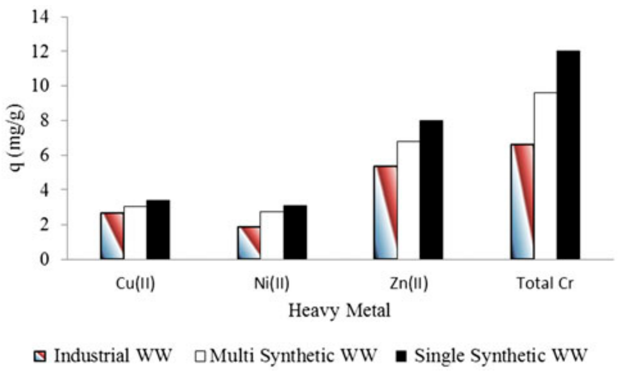

Fig. 10. Adsorption capacities of heavy metals for real IWW, and SWW in single and multi-aqueous systems (hydrogel dosage = 25 g/L, t = 4 h, shaking speed = 150 rpm).

A ΔG value to –20.000 J/mol indicates that adsorption occurred due to electrostatic interactions (physical adsorption), whereas values more negative than –40.000 J/mol indicate that metal ions are kept on the surface by coordination bond [54]. Furthermore, an ΔG value between –8,000 and –6,000 J/mol indicates that adsorption occurred by ion exchange [37,55]. In SWW, ΔG values varied between −10,726.9 and −6,060.35. ΔG values between −10,726.9 and −6,060.35 indicate that ion exchange can play an important role in adsorption process. This supports the view that heavy metal removal using Aac hydrogel occurred by ion exchange. Calculations found that ΔH values were negative at all temperatures, indicating that adsorption was exothermic. On the other hand, positive values of ΔS indicate that heavy metal ions were strongly adsorbed onto the adsorbent surface [56]. The finding of positive ΔS values at all temperatures indicates that the Aac hydrogel used in experimental studies was a suitable adsorbent for removal of heavy metals from wastewater.

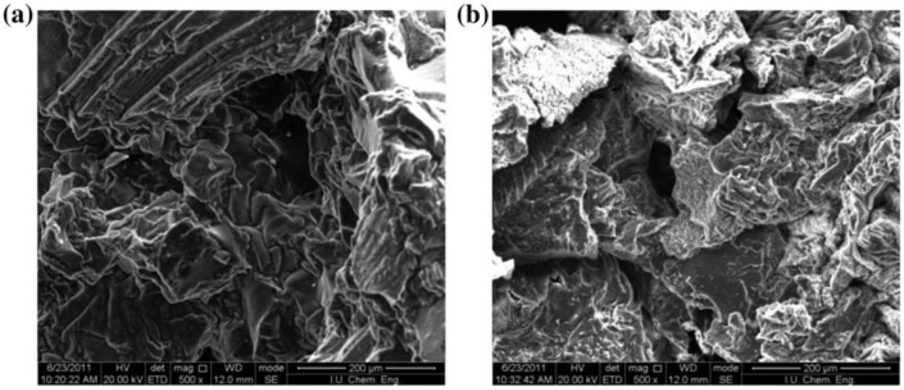

Fig. 11. SEM micrography of Aac hydrogel before (a) and after (b) adsorption (200 μm).

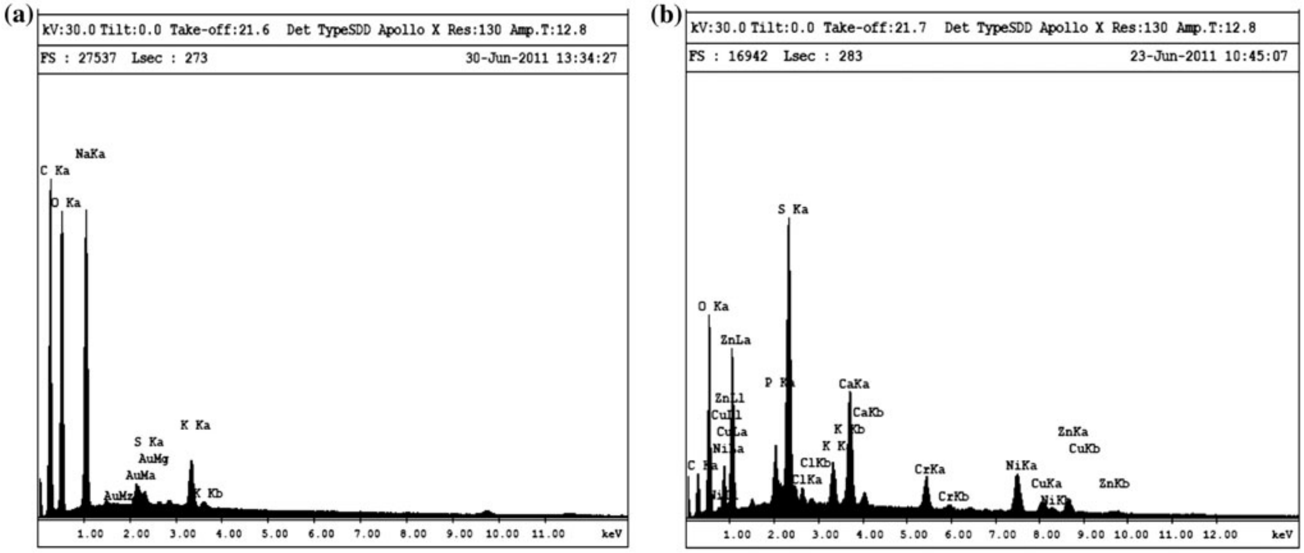

Fig. 12. Results of EDS before (a) and after (b) adsorption.

The finding that ΔG and ΔH values for total Cr were more negative than those of other metals, and that ΔS values were higher than other metals both in real IWW and SWW, indicated that chromium is more readily adsorbed that adsorption rate is greater, and that chromium it will be better adsorbed onto the hydrogel compared to other metals. This is supported by the experimental finding of higher adsorption capacities for total Cr compared to other metals (Zn (II), Cu(II), and Ni(II)).

3.8. The removal of heavy metals from single (non-competitive) and multi (competitive) aqueous systems

This section presents experimental results for the removal of heavy metals from single and multi-aqueous systems. Heavy metal concentrations in multi-aqueous systems were prepared similarly to those in real IWW. The experimental results for multi-aqueous systems and real IWW using Aac hydrogel are presented in Fig. 8.

Single aqueous system was prepared at different initial concentrations. The results are presented in Fig. 9, which indicates that adsorption capacities increased with increase in metal concentrations up to a certain threshold. The results for IWW and SWW containing single and multi-metals are presented in Fig. 10. The lowest adsorption capacity occurred in real IWW, as expected, due to the presence of anions and cations in real IWW in addition to Cu(II), Ni(II), Zn(II), and total Cr. Fig. 10 shows that q values for SWW were lower in multi-aqueous systems than in single ones. This is attributed to the absence of a competitive media and also the absence of other anions and cations in the media.

3.9. SEM results

A SEM was used to analyze changes in the morphology of hydrogels used in experimental studies. SEM images before and after the use of Aac hydrogel to remove heavy metals from wastewater are presented in Fig. 11. The results obtained by EDS are presented in Fig. 12.

Analysis of SEM images showed that while the hydrogel had a generally smooth and porous surface before adsorption. The surface roughness increased after the adsorption. Increased roughness shows the capture of heavy metals on the surface of the adsorbent. These findings were supported by the EDS results, which showed no heavy metals on the surface of the hydrogel at first; however, Cu(II), Ni(II), Zn(II), and total Cr metals were later detected on hydrogel surfaces. The EDX spectra of adsorbent before and after adsorption are illustrated in Fig. 12(a) and (b). The qualitative EDX spectra for Aac hydrogel (Fig. 12(a)) indicated that oxygen, carbon, potassium, sulfur, sodium, and magnesium are the main constituents. From the qualitative EDX spectra after adsorption, copper, nickel, zinc, and chromium can be also seen (Fig. 12(b)).

4. Conclusion

In this study, heavy metals removal was investigated using Aac hydrogel, which is as a novel adsorbent for the removal heavy metals, from galvanotechnic industry real wastewater. The adsorption process of heavy metals onto Aac hydrogel was observed as efficiently, quickly, and affordable method for the removal of heavy metals. The pseudo-second-order model was the most suitable kinetic model, and intraparticle diffusion was not the only rate-limiting step on the adsorption process. The isotherm analysis indicated that the sorption data could be well represented by the Freundlich model. The parameters of thermodynamic experiments were indicated that the adsorption process was spontaneous and exothermic. Comparison between synthetic and IWW samples showed that—as expected—both heavy metal removals and adsorption capacities were higher for SWW containing multi-component metals than for IWW.

In conclusion, the findings of this study showed that Aac hydrogel can provide an alternative method of removing heavy metals from IWW, thereby reducing the problems associated with treating sludge derived from chemical precipitation processes.

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