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Removal of heavy metal ions from electroplating wastewater

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ABSTRACT

Polyacrylic acid diallyl dimethyl ammonium chloride (AAC-Dadmac) hydrogel was used as adsorbent for the removal of heavy metals (Cu(II), Ni(II), Zn(II) and total Cr) from electroplating wastewater. The effects of hydrogel dosage, contact time and shaking speed on heavy metal removal from electroplating wastewater were studied in a batch system. The equilibrium adsorption isotherm of heavy metals on the AAC-Dadmac hydrogel was studied using Langmuir and Freundlich isotherm models. The adsorption equilibrium data fitted well to the Langmuir isotherm model. The maximum adsorption capacities, q_m (mg/g), of the AAC-Dadmac hydrogel for Cu(II), Ni(II), Zn(II) and total Cr were 2.336, 0.960, 5.319, and 4.608 mg/g, respectively. Kinetics of adsorption was found to follow the pseudo-second-order rate equation. The results showed that the AAC-Dadmac hydrogel can be used as an alternative adsorbent for the removal of heavy metal ions from electroplating wastewater.

Keywords: Adsorption; Diallyl dimethyl ammonium chloride; Electroplating wastewater; Heavy metal; Hydrogel; Wastewater treatment

1. Introduction

Nowadays, heavy metal pollution is one of the most serious environmental problems. Heavy metals are the major environmental contaminants. They are dangerous for humans and the other organisms, often even at low concentrations. Contrary to the organic contaminants, heavy metals are not biodegradable. They tend to accumulate in living organisms. It is known that numerous heavy metal ions are toxic or carcinogenic. Zinc, copper, nickel, mercury, cadmium, lead and chromium are toxic heavy metals of particular importance in the treatment of industrial wastewaters [1]. They are released into the environment from battery industry, paint industry, metal finishing industry (e.g. electroplating), printing facilities, coal firing, domestic wastewater, vehicle emissions, mining operations, and the use of fossil fuels, etc. [2,3]. Metal finishing industry produces significant quantities of metal-contaminated wastewater that contain heavy metal ions such as copper, nickel, zinc and cadmium ions.

In order to decrease their impact on the environment, there are various methods for the removal of heavy metals from wastewaters. Chemical precipitation, coagulation-flocculation, adsorption, reverse osmosis, ultra-filtration, electro-dialysis flotation and ion exchange are the used methods to remove heavy metals from wastewaters. The availability of various adsorbents and the simplicity of operation make adsorption a suitable water treatment method. However, adsorption has certain limitations. It could not attain a commercially good status because of the absence of suitable adsorbents of high adsorption capacity and commercial scale columns, and the lack of a single adsorbent that can be used for all kinds of pollutants [4]. Activated carbon is the most widely used adsorbent in water and wastewater treatment. However, it is an expensive adsorbent.

In the last decades, various alternative adsorbents such as hydrogels were applied for heavy metal removal from wastewaters [5–10]. The development and application of novel hydrogels in water and wastewater treatment is an increasing research interest. In the adsorptive removal of many aqueous pollutants (e.g., heavy metals), hydrogels have been reported to show excellent performance [11].

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Hydrogels, which are polymeric materials, mostly remove pollutants from aqueous solution through electrostatic interactions. The presence of specific functional groups (e.g., –OH, $–NH_2$, $–SO_3H$, –COOH, $–CONH_2$) in hydrogel networks enables the adsorptive removal and recovery of aqueous pollutants [12]. Depending on the nature of the pollutant to be removed, specifically functionalized hydrogels can be prepared. For instance, the functional groups on polyacrylamide can be converted to sulfonate groups by sulfomethylation reaction, to amine groups by Hofmann reaction, to carboxylate groups by hydrolysis, or to hydroxyl groups by reacting with formaldehyde [13,14]. Hydrogels have many advantages over the 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, being environmentally benign due to easy biologic decomposition, and the possibility of re-use due to desorption processes [15]. On the other hand, in order to evolve hydrogel based treatment systems from the lab-scale to practical applications, certain challenges should be addressed [11].

In our previous study, the removal of heavy metals (Cu, Ni, Zn, and total Cr) from electroplating wastewater collected from a galvanotechnique industrial site was studied using polyacrylic acid (AAC) hydrogel. AAC hydrogel is a homopolymer where the repeating unit is acrylic acid. As known, a homopolymer is obtained from a single type of monomer and there is one repeating unit. In previous study, it was revealed that the AAC hydrogel is a suitable adsorbent for removing heavy metals from electroplating wastewater [16].

In the present study, a hydrogel (AAC-Dadmac hydrogel) prepared by adding diallyl dimethyl ammonium chloride to the AAC hydrogel was used as an adsorbent for heavy metal removal from electroplating wastewater. The electroplating wastewater was collected from a galvanotechnique industrial site in Istanbul. The effects of adsorbent dosage, contact time and shaking speed on heavy metal removal were studied in a batch system. Langmuir and Freundlich isotherms were used to analyze the equilibrium data. Kinetics of adsorption of heavy metals with the AAC-Dadmac hydrogel was analyzed using pseudo first-order, pseudo second-order, and intra-particle diffusion models. Polyacrylic acid diallyl dimethyl ammonium chloride (AAC-Dadmac) hydrogel is a cross-linked copolymer. When there are two types of monomers joining to make a polymer, that type of polymer is known as a copolymer. This is also known as heteropolymer. Two monomers can join in any fashion to make a polymer.

2. Materials and methods

2.1. Wastewater

The samples of electroplating wastewater used in this study were collected from the inflow of the treatment plant located in a galvanotechnique industrial site in Ikitelli, Istanbul, Turkey. The characteristics of the wastewater are given in Table 1. Before the experimental studies, the electroplating wastewater was passed through a filter having a mesh size of 0.45 µm.

2.2. Preparation of polyacrylic acid diallyl dimethyl ammonium chloride (AAC-Dadmac) hydrogel

Polyacrylic acid diallyl dimethyl ammonium chloride (AAC-Dadmac) hydrogel was prepared by the addition of 10% mole diallyl dimethyl ammonium chloride (Dadmac) monomers to acrylic acid (AAC) in the Analysis Laboratory of Chemical Engineering Department of Istanbul University, Istanbul, Turkey. AAC-Dadmac was polymerized in the presence of 1 mole% monomer cross-linker [N,N methylenebisacrylamide (NMBA)]; 1 mole% 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 70°C. The obtained AAC-Dadmac hydrogel was purified and dried in a vacuum for 24 h at 40°C. All the chemicals used were all analytical-grade and used as received without further purification. Preparation process for the AAC-Dadmac hydrogel is shown in Fig. 1.

2.3. Adsorption studies

In batch tests, 100 mL of electroplating wastewater samples were placed in 250 mL Erlenmeyer flasks and then the desired amount of hydrogel was added into the Erlenmeyer flasks. The Erlenmeyer flasks were shaken with a temperature-controlled water bath (Gallenkamp orbital incubator). In the experimental studies, to determine the effects of hydrogel dosage, contact time and shaking speed on heavy metal removal, different dosages (1.0–3.0 g/100 mL) of hydrogel, different contact times (1–24 h), and different shaking speeds (80–200 rpm) were used. At the end of the experiments, the samples were transferred to glass tubes and then analyzed for Cu (II), Ni (II), Zn (II) and total Cr. All the measurements were done in duplicate and the results were averaged.

The heavy metal removal (%) and adsorption capacity, q (mg/g) of AAC-Dadmac hydrogel were calculated using Eqs. (1) and (2), respectively.

Table 1
Characteristics of the electroplating wastewater taken from a galvanotechnique industrial site (in Ikiteli, Istanbul, Turkey)

Cations	Concentration (mg/L)
Cu(II)	86.12
Ni(II)	83.99
Zn(II)	178.30
Total Cr	302.80
Total Fe	77.74
Na	822.88
Ammonium	181.23
K	146.81
Mg (II)	59.01
Ca (II)	212.22

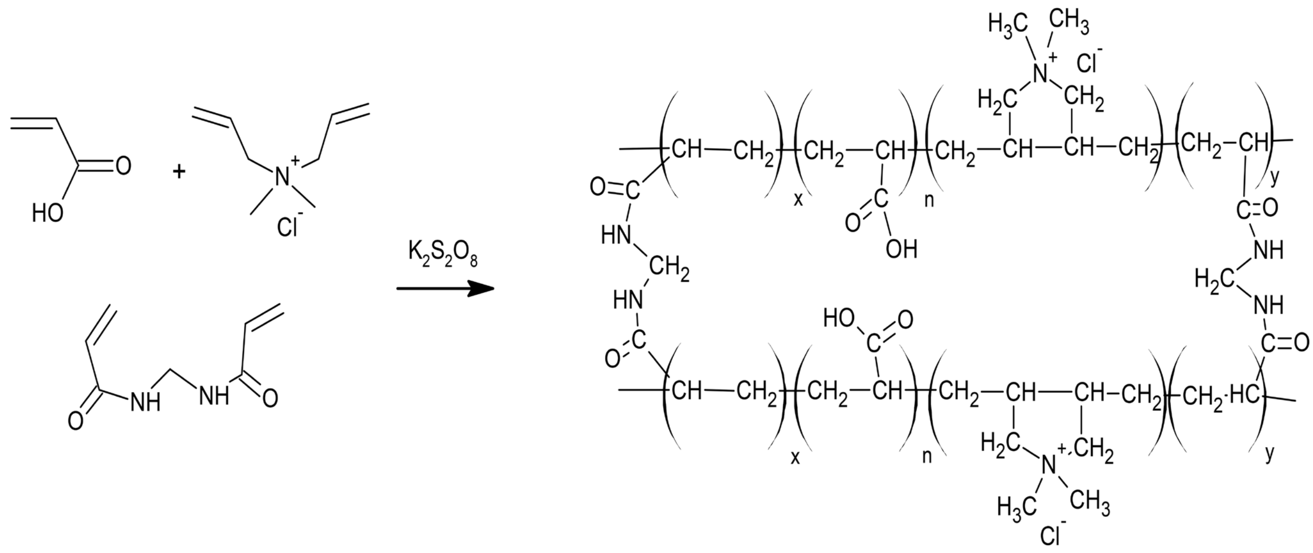

Fig. 1. Preparation process for the polyacrylic acid diallyl dimethyl ammonium chloride (AAC-Dadmac) hydrogel.

$$\text{Heavy metal removal (\%)} = \frac{\left(C_o - C_e\right)}{C_o}100 \tag{1}$$

$$q\,(\text{mg/g}) = \left(C_o - C_e\right)\frac{V}{m} \tag{2}$$

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

2.4. Instrumentation

The heavy metal concentrations in the samples were estimated by atomic absorption spectrophotometer (Perkin-Elmer A Analyst 400, AAS). The organic functional groups in the AAC-Dadmac hydrogel were examined by a Perkin Elmer Spectrum One Fourier Transform Infrared (FTIR) spectrophotometer. FTIR analyses were performed at the Detailed Analysis Laboratory of Istanbul University, Istanbul, Turkey. The surface morphology and chemical constitution of the hydrogel before and after the adsorption were analyzed using a FEI Quanta FEG 450 scanning electron microscope (SEM) combined with energy dispersive X-ray (EDS) technique.

2.5. Theoretical approach

2.5.1. Adsorption Isotherms

Langmuir and Freundlich equations are widely used in the adsorption processes [17]. The linear form of the Langmuir isotherm is as follows [18]:

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

where C_e is the equilibrium concentration of the adsorbate (mg/L); q_e is the amount of adsorbate adsorbed per unit mass of the 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 the intercept of the linear plot of C_e/q_e vs. C_e.

The linear form of the Freundlich isotherm is expressed as follows [19]:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{4}$$

where K_f is the 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 the slope of the plot of *ln* q_e vs. *ln* C_e.

2.5.2. Adsorption kinetics

The pseudo first-order and pseudo second-order kinetic model equations developed by Lagergren are generally used as the kinetic model to determine the reaction degrees of the adsorption systems [20–22]. The linear form of the pseudo first-order kinetic model equation is expressed as follows [23,24]:

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

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 the pseudo-first-order adsorption (1/min); t is the time (min). The adsorption rate constant k_1 and equilibrium adsorption capacity q_e are calculated from the slopes and the intercepts of the plots of $log\ (q_e - q_t)$ vs. t.

The linear form of the pseudo second-order kinetic model equation is as follows [23,24]:

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

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

The information of the adsorption mechanism can be used to optimize the design of the adsorbents and the adsorption conditions [25]. The overall rate of adsorption can be described by the following three steps [26]: (1) the film or surface diffusion where the sorbate is transported from the bulk solution to the external surface of the sorbent, (2) the intra-particle or pore diffusion, where the sorbate molecules move into the interior of the sorbent particles, and (3) the 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 the adsorption process, therefore, will be controlled either by the surface diffusion or the intra-particle diffusion. If the intra-particle diffusion is the rate-limiting step, the Weber-Morris intra-particle diffusion model has often been determined using the equation given below [27,28] [Eq. (7)]:

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

where k_i is the intra-particle diffusion rate constant ($mg/gh^{0.5}$) and C is the intercept. According to this model, a plot of q_t vs. $t^{0.5}$ should be linear if the intra-particle diffusion is involved in the adsorption process, and if the plot passes through the origin then the intra-particle diffusion is the sole rate-limiting step [29]. It has also been suggested that in instances when q_t vs. $t^{0.5}$ is multi linear, two or more steps govern the adsorption process [30,31].

3. Results and discussion

3.1. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectrum of the AAC-Dadmac hydrogel is shown in Fig. 2. The main peaks of the AAC-Dadmac hydrogel are –OH stretch at 3436 cm^{-1}, –CH stretch at 2929 cm^{-1}, and –C=O stretch at 1627 cm^{-1}.

3.2. Effect of hydrogel dosage

The adsorbent dosage is very important for design, and determines the equilibrium of the system between the adsorbent and the adsorbate used in heavy metal removal from aquatic environment [28]. Fig. 3 shows the effect of hydrogel dosage on heavy metal removal from electroplating wastewater. As can be seen from Fig. 3, the adsorption capacity (q) and heavy metal removal (%) from wastewater were increased with the increase in hydrogel dosages. This can be explained due to the fact that the higher the dosage of the adsorbent in the solution, the greater the availability of the exchangeable sites for metal ions [33,34].

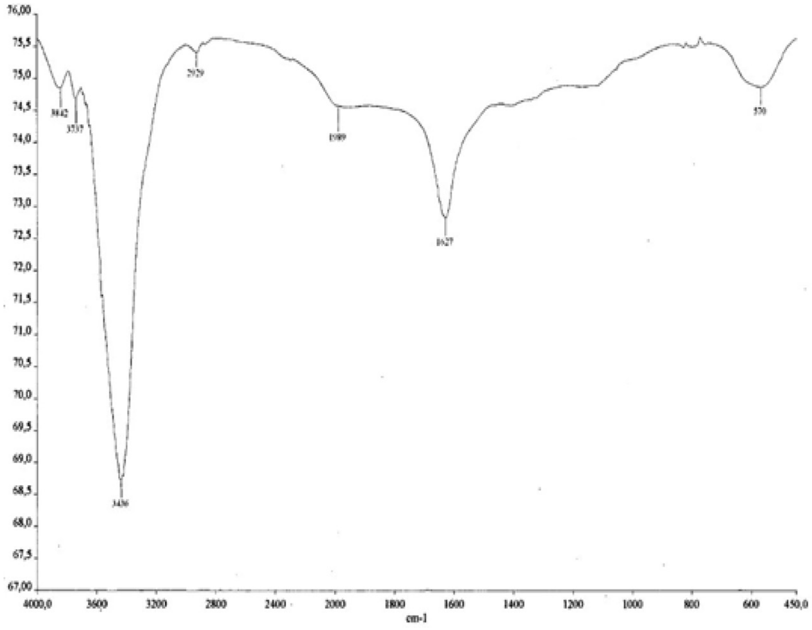

Fig. 2. FTIR spectrum of the AAC-Dadmac hydrogel.

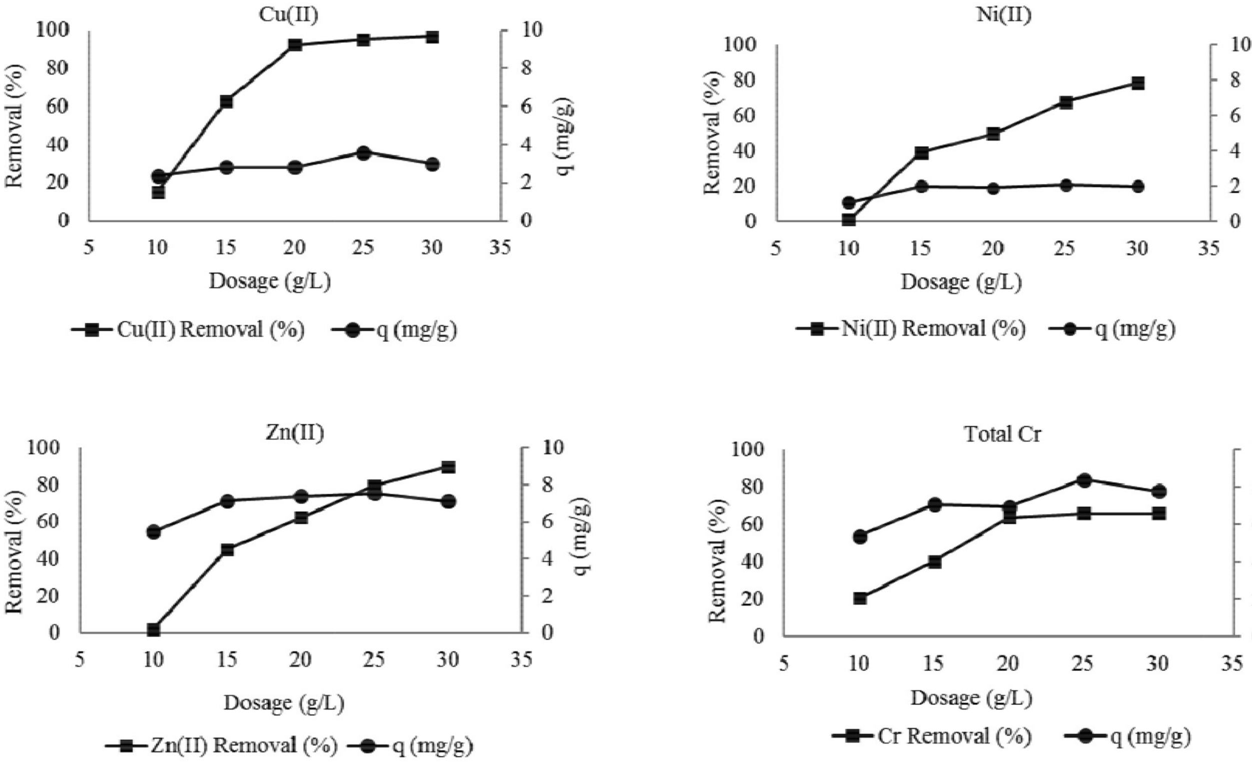

Fig. 3. The effects of adsorbent dosage on adsorption capacity, *q* (mg/g), and heavy metal removal (%) for the AAC-Dadmac hydrogel (pH: 2.08, *t*: 4 h, shaking speed: 150 rpm).

3.3. Effect of contact time

The effect of contact time, that is important for the determination of adsorption kinetics and feasibility of the system in practice, is presented in Fig. 4. As can be seen from Fig. 4, the adsorption capacity (*q*) and the heavy metal removal (%) increased in the first 4 h. Thereafter no remarkable changes in the adsorption capacity (*q*) and heavy metal removal were observed, indicating that the adsorption equilibrium was reached in 4 h.

3.4. Effect of shaking speed

The effect of shaking speed on heavy metal removal from electroplating wastewater is shown in Fig. 5. The adsorption capacity (*q*) and heavy metal removal (%) were increased by the increased shaking speed (Fig. 5). This indicates that the heavy metal ions are easily and rapidly diffused from the hydrogel surface and the pores [35].

3.5. Adsorption isotherms

The equilibrium adsorption isotherm was studied using the two widely used isotherm models, which are Freundlich and Langmuir isotherm models. The Langmuir and Freundlich parameters for the adsorption of Cu (II), Ni (II), Zn (II), and total Cr on the AAC-Dadmac hydrogel are shown in Table 2. According to the correlation coefficient values shown in Table 2, it can be said that the adsorption of Cu(II), Ni(II), Zn(II) and total Cr is fitted well by the Langmuir isotherm. It may be concluded that the lower proportion of adsorption took place as multilayer adsorption, while the Langmuir isotherm confirms that monolayer adsorption is the predominant mechanism.

3.6. Adsorption kinetics

Three adsorption kinetics models; the pseudo-first-order, pseudo-second order and intra-particle diffusion models, were used to explain the adsorption mechanisms of heavy metal removal on the AAC-Dadmac hydrogel. The parameters and the correlation coefficient values are given in Table 3. For all the studied heavy metals, the pseudo-second-order kinetic model showed correlation coefficients ($R^2 \geq 0.998$) higher than the pseudo-first-order kinetic model (Table 3). Also, the values of the calculated adsorption capacity ($q_{e,cal}$) were very close to the values of the experimental equilibrium adsorption capacity ($q_{e,exp}$) for the pseudo-second-order kinetic model than the pseudo first-order kinetic model. Therefore, it can be said that the adsorption of Cu(II), Ni(II), Zn(II) and total Cr followed the pseudo-second-order kinetic model. The multi metal adsorption capacities of different adsorbents reported in the literature are given in Table 4.

The intra-particle diffusion plots are shown in Fig. 6. As can be seen from Fig. 6, the adsorption processes follow two steps. The first linear portion is attributed to the boundary layer diffusion and the second linear portion is the gradual

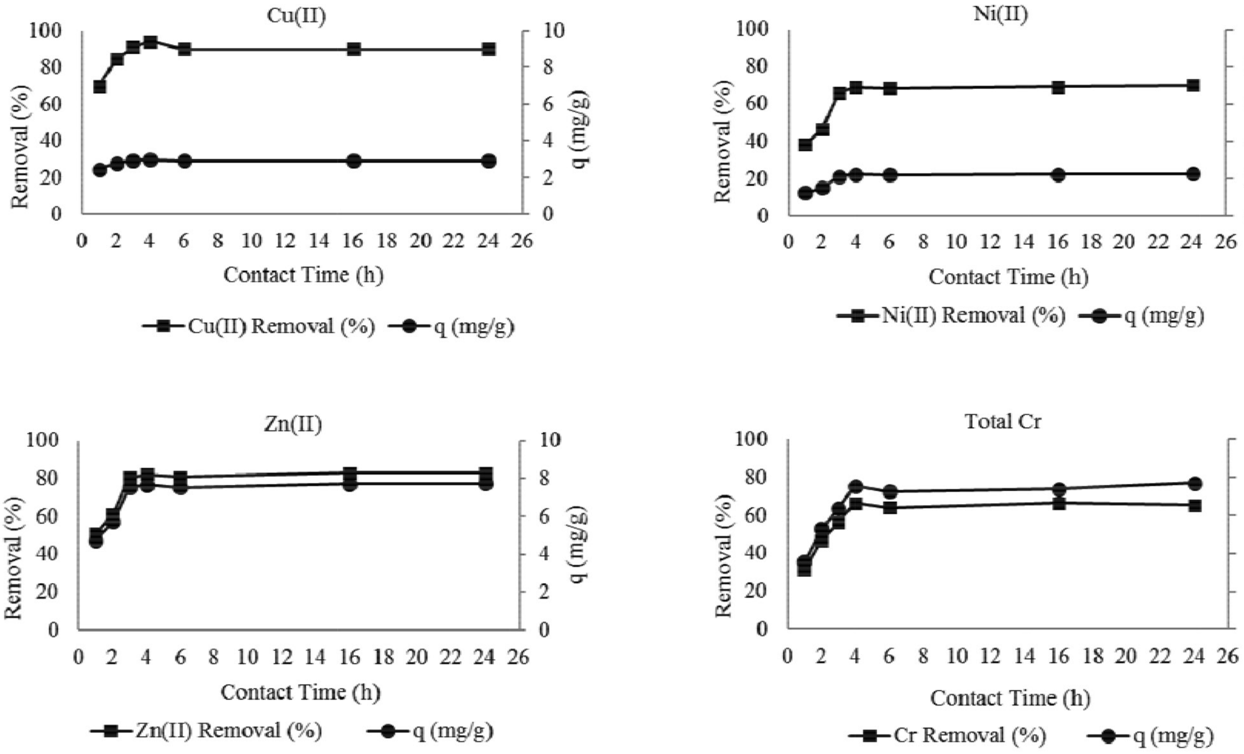

Fig. 4. The effects of contact time on adsorption capacity, *q* (mg/g), and heavy metal removal (%) for the AAC-Dadmac hydrogel (pH: 1.96, hydrogel dosage: 25 g/L, shaking speed: 150 rpm)..

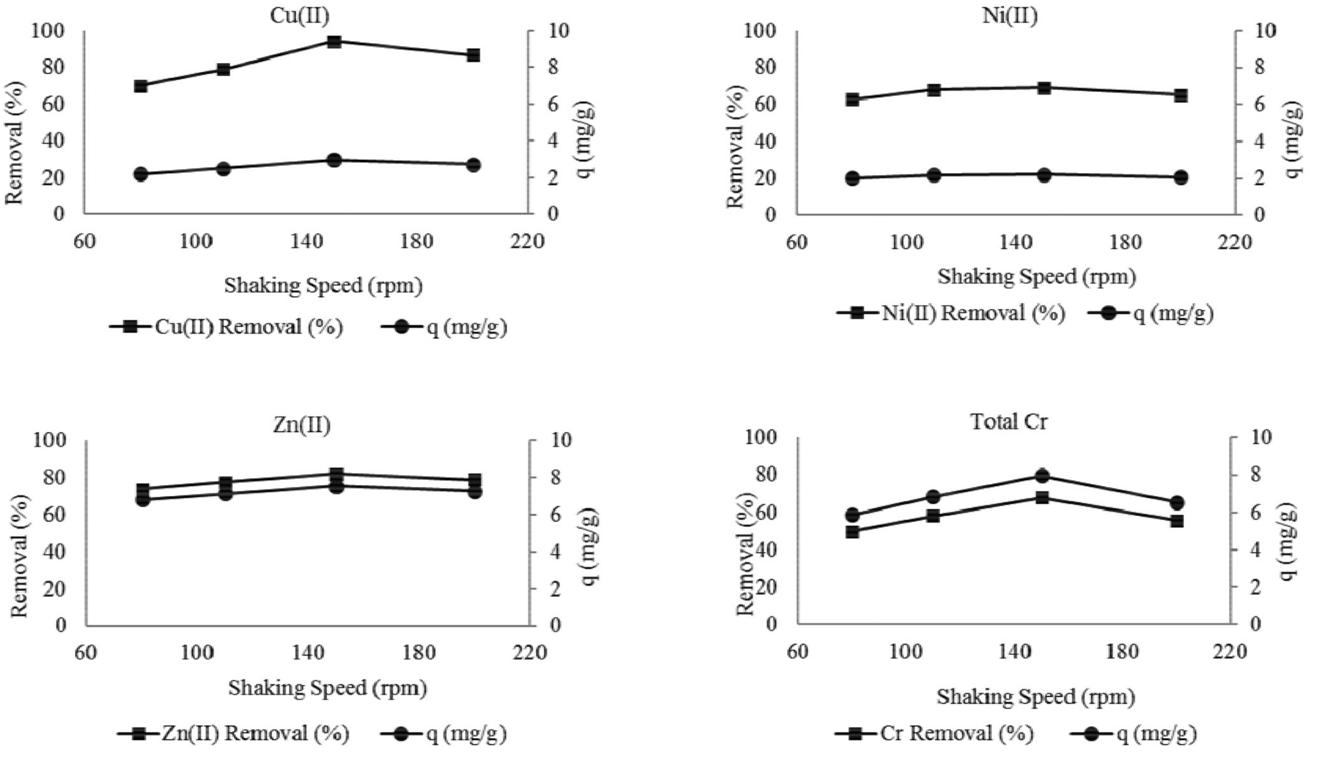

Fig. 5. The effects of shaking speed on adsorption capacity, *q* (mg/g) and heavy metal removal (%) for the AAC-Dadmac hydrogel (pH: 2.14, hydrogel dosage: 25 g/L, *t*: 4 h).

Table 2
Isotherm parameters values for the removal of Cu(II), Ni(II), Zn(II) and total Cr by AAC-Dadmac hydrogel

	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	n	R^2
Cu(II)	2.336	0.580	0.995	3.723	9.433	0.718
Ni(II)	0.960	0.069	0.918	6.109	2.857	0.569
Zn(II)	5.319	0.058	0.976	10.592	10.204	0.434
Total Cr	4.608	0.025	0.967	41.686	2.695	0.739

Table 3
Kinetic model parameters for the adsorption of Cu(II), Ni(II), Zn(II) and total Cr on the AAC-Dadmac hydrogel

	Pseudo first-order				Pseudo second-order				Intra-particle diffusion			
	R^2	k_1 (L/min)	$q_{e,cal}$	$q_{e,exp}$	R^2	k_2 (mg/g.min)	$q_{e,cal}$	$q_{e,exp}$	$k_{i\text{-}1}$ mg/g.min$^{1/2}$	R^2	$k_{i\text{-}2}$ mg/g.min$^{1/2}$	R^2
Cu(II)	0.052	0.028	0.105	2.979	0.999	6.502	2.923	2.979	0.689	0.983	0.012	0.437
Ni(II)	0.482	0.092	0.391	2.301	0.998	0.775	2.304	2.301	1.186	0.906	0.013	0.715
Zn(II)	0.482	0.095	1.069	7.905	0.999	0.305	7.936	7.905	3.712	0.940	0.051	0.535
Total Cr	0.595	0.095	1.977	7.917	0.998	0.158	7.936	7.917	3.910	0.998	0.177	0.866

Table 4
Comparison of multi metal adsorption capacities of different adsorbents reported in the literature

Adsorbents	Adsorption capacity, q_m				
	Cu(II)	Ni(II)	Zn(II)	Total Cr	Reference
Hydrogels					
Poly(AMPS)	118 mg/g	115 mg/g			[12]
Poly(hEA-co-MALA)	0.16 mmol/g	0.16 mmol/g			[36]
An/AAx/AMPS	0.87 mg/g		1.00 mg/g		[37]
CMC/ECH hydrogel bead	6.49 mmol/g	4.06 mmol/g			[38]
Acrylic acid hydrogel	1.41 mg/g	5.85 mg/g	14.31 mg/g	16.50 mg/g	[16]
AAC-Dadmac hydrogel	2.34 mg/g	0.96 mg/g	5.32 mg/g	4.61 mg/g	This work
Other adsorbents					
Zeolite, Clinoptilolite	1.64 mg/g	0.48 mg/g	0.50 mg/g		[39]
Kaolinite	0.76 mg/g	0.003 mg/g	1.82 mg/g		[40]
Na-Montmorillonite	3.04 mg/g	3.63 mg/g	3.61 mg/g		[41]
Coal	1.62 mg/g	1.20 mg/g			[42]

adsorption stage, where the intra-particle diffusion is rate-controlled. As the plots did not pass through the origin, it can be said that the intra-particle diffusion was not the only rate limiting step.

3.7. SEM/EDS

Changes in the surface morphology of the AAC-Dadmac hydrogel before and after adsorption were studied by scanning electron microscopy (SEM) and the images were displayed in Fig. 7. EDS spectra are shown in Fig. 8.

The analysis of the SEM images showed that while the AAC-Dadmac hydrogel had a generally smooth and porous surface before adsorption, its surface roughness increased after the adsorption. The increased roughness shows the ability to capture heavy metals on the surface of the hydrogel. These findings were supported by the EDS results. The EDS

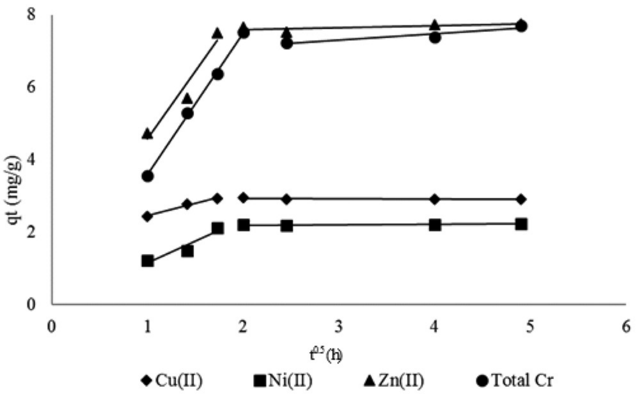

Fig. 6. Intra-particle diffusion plots for the adsorption of Cu(II), Ni(II), Zn(II) and total Cr on the AAC-Dadmac hydrogel.

spectra of the hydrogel before and after adsorption are illustrated in Fig. 8a and 8b. The EDS spectra for the AAC-Dadmac hydrogel (Fig. 8a) indicated that oxygen, carbon, potassium, sulfur, sodium, and magnesium are the main constituents of the AAC-Dadmac hydrogel. From the EDS spectra after adsorption, it can be seen that there is copper, nickel, zinc and chromium in the chemical constitution of the AAC-Dadmac hydrogel (Fig. 8b).

4. Conclusion

In this study, the removal of toxic heavy metal ions (Cu(II), Ni(II), Zn(II) and total Cr) from electroplating wastewater using the AAC-Dadmac hydrogel is reported. The optimum adsorbent dosage and the contact time for the

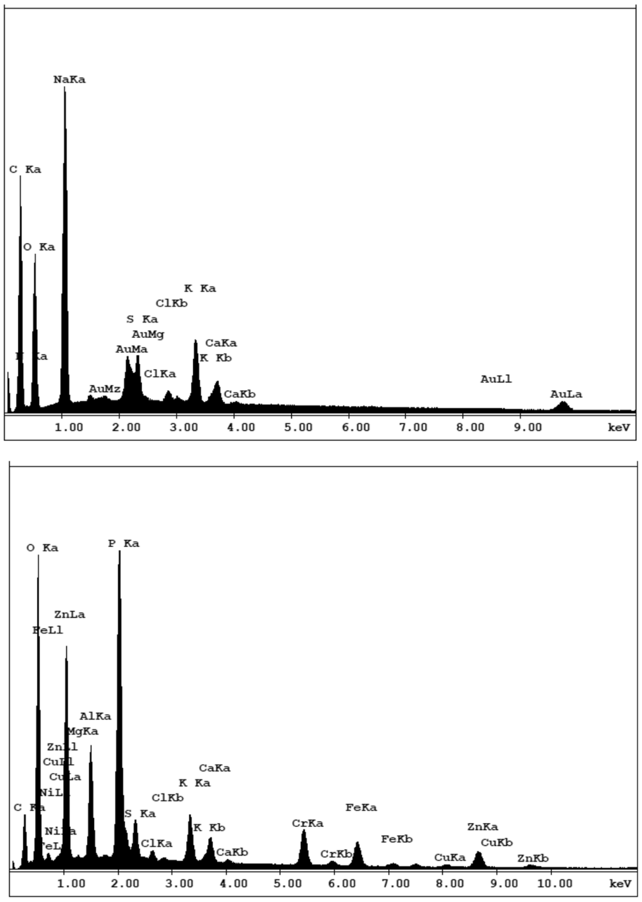

Fig. 8. EDS spectra of the AAC-Dadmac hydrogel before (a) and after (b) adsorption.

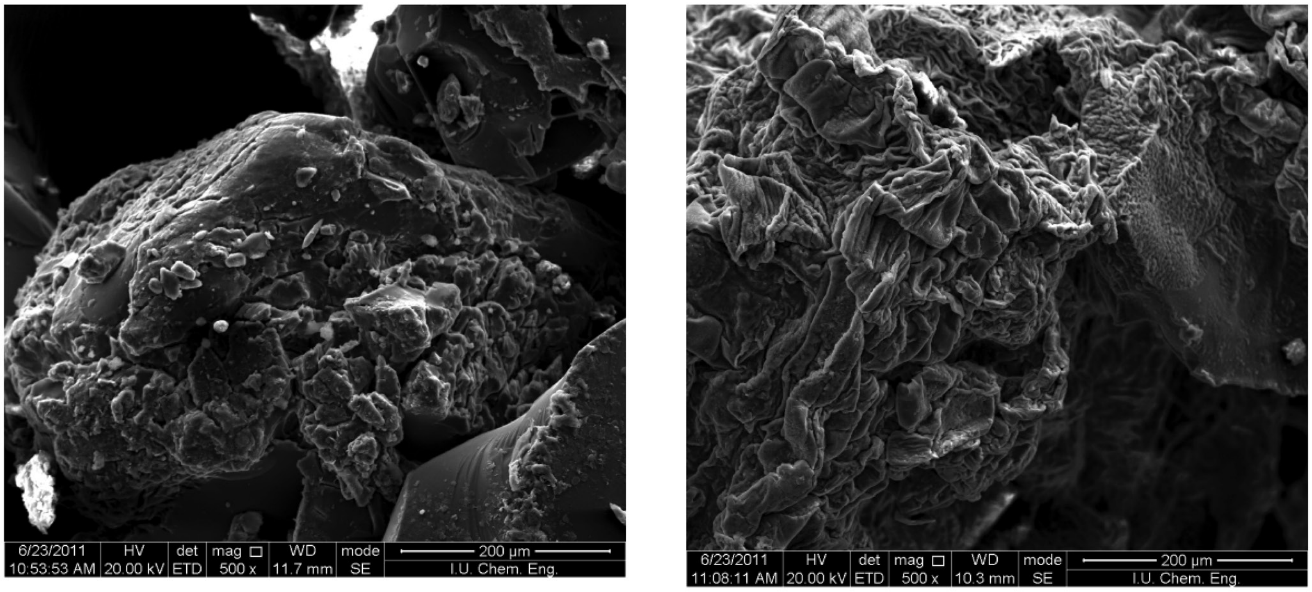

Fig. 7. SEM micrograph of AAC-Dadmac hydrogel before (a) and after (b) adsorption.

removal of heavy metal ions by the AAC-Dadmac hydrogel were 25 g/L and 4 h, respectively. Adsorption of Cu(II), Ni(II), Zn(II) and total Cr followed Langmuir isotherm. The value of the maximum adsorption capacity, q_m (mg/g), was found to follow the sequence Zn (II) > total Cr > Cu(II) > Ni(II), which were 5.319, 4.608, 2.336, and 0.960 mg/g, respectively. The maximum adsorption capacities were found to be lower (except Cu(II)) than the AAC hydrogel which was used in the previous study. The experimental data fitted well to the pseudo-second-order kinetic model. Besides, the kinetic studies showed that the intra-particle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption. From this study, it can be concluded that the AAC-Dadmac hydrogel seems to be an efficient and promising adsorbent for the removal of heavy metal ions from electroplating wastewater.

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