Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.983176

57 (2016) 2787–2798
February

Taylor & Francis
Taylor & Francis Group

Adsorption of Cd(II) ions onto polyamine-polyurea polymer modified with pyromellitic dianhydride

Cigdem Ozer[a], Fusun Boysan[a,*], Mustafa Imamoglu[b], Salih Zeki Yildiz[b]

[a]*Faculty of Engineering, Environmental Engineering Department, Sakarya University, 54187 Sakarya, Turkey, Tel. +90 264 295 57 19; email: cozer@sakarya.edu.tr (C. Ozer), Tel. +90 264 295 56 40; Fax: +90 264 295 54 54; email: fboysan@sakarya.edu.tr (F. Boysan)*
[b]*Faculty of Arts & Sciences, Chemistry Department, Sakarya University, 54187 Sakarya, Turkey, Tel. +90 264 295 60 53; email: imamoglu@sakarya.edu.tr (M. Imamoglu), Tel. +90 264 295 61 36; email: szy@sakarya.edu.tr (S.Z. Yildiz)*

Received 26 December 2013; Accepted 24 October 2014

ABSTRACT

In this study, polyamine-polyurea polymer was synthesized using toluendiisocyanate and polyethyleneimine. It was then modified using pyromellitic dianhydride. The polymer so obtained (PMPPP) was used for the adsorption of Cd(II) metal ions from aqueous solutions using a batch adsorption system to simulate the adsorption characteristics of wastewater applications. The effects of pH, dosage, contact time, initial concentration, and temperature were investigated. The optimum pH value was found to be 6.0, and the contact time required to reach equilibrium was 120 min. The Cd(II) adsorption equilibrium data were found to be more in line with the Langmuir equation than the Freundlich model. The maximum adsorption capacity of PMPPP for Cd(II) was calculated to be 94.3 mg g^{-1}. Kinetics studies showed that Cd(II) adsorption followed the pseudo-second-order equation. Thermodynamic investigations revealed endothermicity, spontaneity, and an increased randomness of Cd(II) adsorption onto PMPPP. Polymer was characterized by Fourier transform infrared spectroscopy, thermogravimetric–differential thermal analysis, scanning electron microscopy, and nitrogen adsorption/desorption isotherms.

Keywords: Cd(II); Polyamine-polyurea polymer; Adsorption; Removal; Heavy metal; Wastewater treatment

1. Introduction

Heavy metal pollution in the environment has been increasing as a result of industrial production, especially in developing countries. Heavy metal pollution is of great importance because of its toxicity for human and other living organisms [1,2]. Cd(II) metal is one of the most toxic heavy metals, and is mainly absorbed by the human body nutrition. The human metabolism cannot destroy the Cd(II) ions, so it accumulates them in various parts of the body, especially in the kidneys and liver, and also creates long- or short-term metabolic diseases [3–7]. Therefore, the removal of heavy metals from industrial wastewater is of great importance in order to protect the environment.

Many methods such as ion-exchange [8], membrane process [9], electrochemical techniques [10], precipitation [11], magnetic separation process [12], and reverse osmosis [13] have been developed for the removal of heavy metals [14–16]. Adsorption is an effective method for the treatment of wastewater

---

*Corresponding author.

containing heavy metal ions at low concentrations (<100 ppm) [1,17]. The selection of the adsorbent is important as part of the adsorption procedure in that the effectiveness of this technique directly depends on the chemical and physical properties of the adsorbent. Its re-use ability after regeneration, its selectivity to the target metal ion, and its cost are also important for commercial adsorbents [18,19].

Although activated carbon has a high surface area—accepted as the main parameter of a good adsorbent—its main drawback is its high cost [20,21]. Some natural adsorbents could be obtained cheaply, but their adsorption capacities are very low [22,23]. Those polymers with chelating functional groups provide a higher yield in terms of metal adsorption [24–26]. A number of polymer adsorbents, including melamine formaldehyde and salicylic acid-modified polymer [27], the magnetic chelating resin having iminodiacetate functional group [28], poly(ethylene amine acrylo-amidino) resin [29], amidoxime chelating resin [30], poly(2-acrylamido glycolic acid-co-acrylamide) [31], melamine–formaldehyde–diethylenetriamine pentaacetic acid resin [32], and 1,3,5-triazine-triethylenetetramine polymer [33] have been reported in the literature.

The purpose of this study was to synthesize new chelating polymers having functional groups, and to examine the efficiency of the prepared adsorbent for the removal of Cd(II) ions from aqueous solutions. For this purpose, polyamine-polyurea polymer was synthesized and then was modified with pyromellitic dianhydride. The adsorption characteristics of the modified polymer with regard to Cd(II) metal ions were studied batchwise by investigating the Cd(II) concentration, temperature, contact time, and pH effects on the Cd(II) adsorption. Cd(II) adsorption kinetics, equilibrium data, and the thermodynamics were evaluated using several models.

2. Experimental

2.1. Chemical reagents

The chemicals used in the synthesis of the polymer and adsorption studies were of analytical-reagent grade. Polyethyleneimine (Lupasol FG) was purchased from BASF (Ludwigshafen, Germany). Toluendiisocyanate (TDI), dimethylformamide (DMF), and pyromellitic dianhydride (PMDA) were obtained from Merck KGaA (Darmstadt, Germany). Synthetic solutions of Cd(II) were diluted daily from a 1,000 mg L^{-1} stock solution prepared by solving a required quantity of $CdCl_2{\cdot}H_2O$ purchased from Merck KGaA (Darmstadt, Germany). The pH values of the solutions were adjusted by adding 0.1 M HCl and NaOH.

2.2. Instruments

Infrared spectra were recorded on a Shimadzu FTIR IRPrestige-21 spectrophotometer equipped with PIKE MIRacle™ diamond ATR and corrected by applying IR-solution software's atr-correction function. An atomic absorption spectrometer (Shimadzu AA-6200, Shimadzu Corporation, Kyoto, Japan) was used for the measurement of Cd(II) concentrations at a wavelength of 228.8 nm. A temperature-controlled orbital shaker (KS4000i, IKA-Werke GmbH, Germany) and a magnetic stirrer were used for stirring the suspension. The pH values of Cd(II) solutions were measured using a digital pH meter (WTW pH 720).

2.3. Synthesis and modification of polyamine-polyurea polymer

For this synthesis, 4 mL of TDI was dissolved in 55.0 mL of DMF and then slowly added dropwise to Lupasol FG^{TM} (5.50 g) which was dissolved in 40.0 mL of DMF. The solution was then continuously stirred at room temperature for four and a half hours. The solid polymer (PPP) thus obtained was filtered and washed with distilled water, alcohol, and ether, respectively. Then, it was dried at 40°C in a vacuum oven. The reaction scheme is shown in Fig. 1.

For the modification of PPP, 1.0 g of PPP was put into 30 mL of DMF, while the suspension was mechanically stirred, and 2.5 g of PMDA was added. The reaction was carried out for 4 h at 50°C. The resulting PMDA-modified polyamine-polyurea polymer (PMPPP) was washed with the DMF, then with the NaOH solution (0.1 mol L^{-1}), and finally with distilled water until the pH of the washings reached the pH of 6.5–7 range. Finally, the PMPPP were dried at 40°C for 24 h.

2.4. Adsorption experimental procedure

Adsorption experiments were conducted with PMPPP (0.05 g) in 50 mL of Cd(II) solutions at various initial concentrations and pH values, by shaking at 200 rpm and 25°C for 120 min. After filtration of the polymer, the residual concentrations of Cd(II) were analyzed with AAS.

The adsorption % was calculated by applying the following equation:

$$\text{Adsorption }(\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

where C_0 is the initial Cd(II) concentration (mg L^{-1}), and C_t is the residual Cd(II) concentration (mg L^{-1})

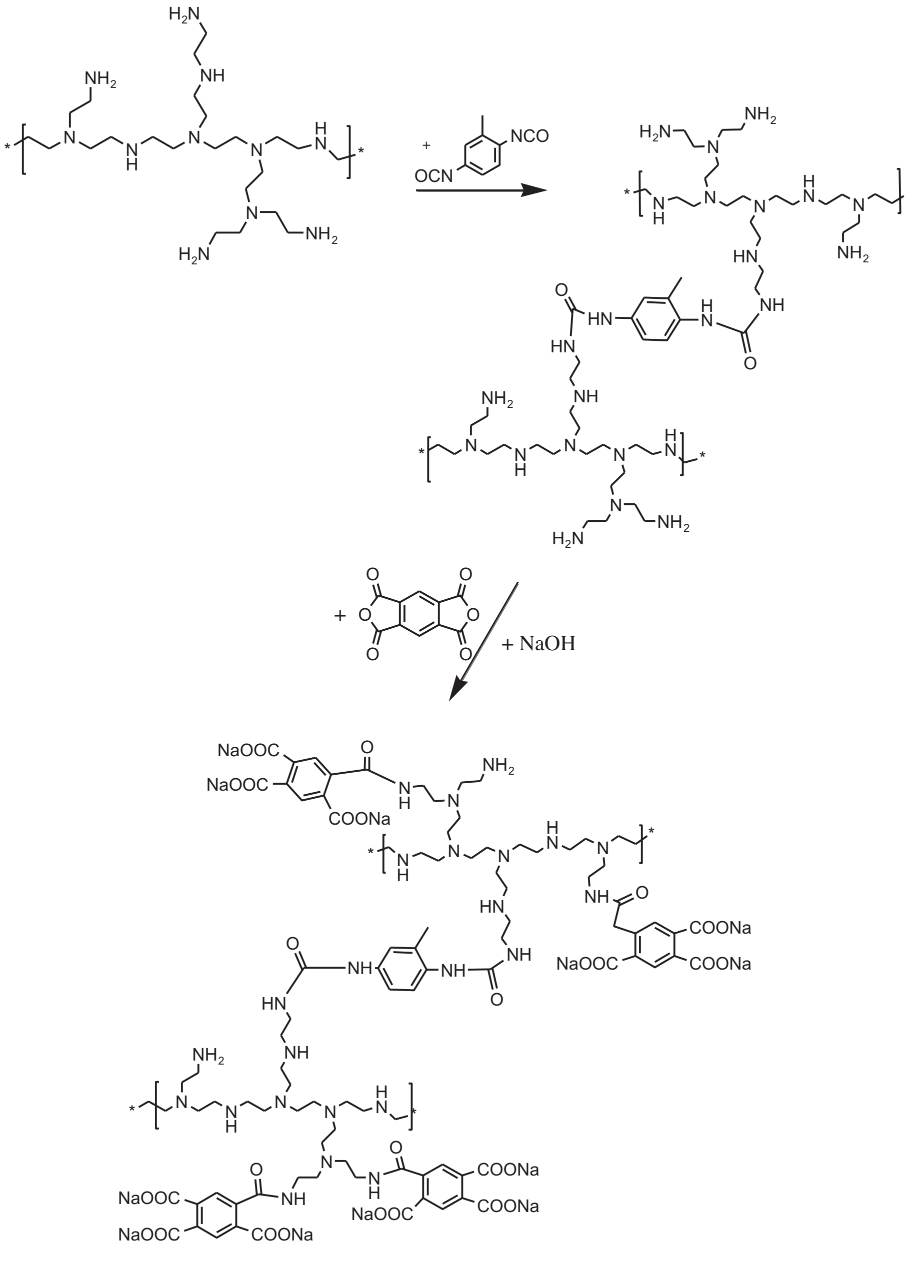

Fig. 1. Preparation procedure of polyamine-polyurea polymer and its modification with pyromellitic dianhydride.

after the batch adsorption at time t. The amount of Cd (II) up taken by PMPPP at time t (min) was calculated using the following equation:

$$q_t = (C_0 - C_t)\frac{V}{m} \tag{2}$$

where q_t is the amount of Cd(II) up taken by the PMPPP (mg g^{-1}), m is the mass of PMPPP (g), and V is the volume of Cd(II) solution in contact with the PMPPP.

3. Results and discussion

3.1. Characterization of PPP and PMPPP

The characterization of the prepared PPP was performed by FTIR spectroscopy. In the spectrum, N–H stretching vibrations appeared at around 3,305 cm^{-1} as a strong broth band to characterize the aliphatic NH and amide NH of urethane groups. The aromatic C–H stretching vibration of the phenyl moieties of TDI were observed at 3,063 cm^{-1}. The stretching of the aliphatic hydrocarbons of the prepared PPP was recorded at the 2,932–2,845 cm^{-1} range as two peaks. The C=O vibration of the urethane groups appeared at 1,645 cm^{-1} and the aromatic C=C stretching at 1,601 cm^{-1}. The strong band at 1,531 cm^{-1} was attributed to the in plane N–H bend of the amine and amide groups. The aliphatic C–H deformation bands appeared at around 1,415 cm^{-1} and the CON stretching of the urethane groups at 1,227 cm^{-1}. In the FTIR spectra of PMPPP, the strong and broth peak at 3,298 cm^{-1} was attributed to the N–H stretching vibrations of the amine and amide groups. The aromatic C–H stretching vibrations belong to the phenyl groups of TDI and PMDA segments appeared at 3,055 cm^{-1}. The aliphatic C–H stretching bands of the polymer backbone were shown at 2,949–2,864 cm^{-1}. The deformation between 3,500–2,500 cm^{-1} can be attributed to the slightly acidic nature of the polymer and to the intramolecular hydrogen bonds. Due to this, the C=O stretching of the amide groups shifted to the lower wave number and appeared at 1,634 cm^{-1}. The C–H deformation bands of the aliphatic hydrocarbons showed at 1,591 and the N–H bending deformation at 1,531 cm^{-1}. The bands at 1,371 and 1,232 cm^{-1} can be attributed to C–N and CON vibrations, respectively.

The thermal characterization of the prepared functional polymer PMPPP was examined by TG/DTA measurements which were performed under a nitrogen atmosphere in the range of 25–900˚C. A very low mass loss (approximately 10% of the weight) at around 100˚C was observed, which can be attributed to the moisture content of the polymer. The thermal decomposition of the PMPPP started at 277.9˚C which was shown in the DTA graphic of PMPPP (Fig. 2). The main weight loss was observed after the decomposition start point to 410.0˚C which was assigned as the decomposition end point. Beyond this temperature, only a few percentage weight loss was noted up to 900˚C. However, a 20% residue still remained after the thermal examination. This consisted of the inorganic part of the prepared polymer as Na_2O.

The surface morphology of PMPPP can be observed by SEM as shown in Fig. 3. It is clear from the photographs that PMPPP showed an irregular surface, and after the adsorption of Cd(II), the morphology of the material has not been changed significantly. The surface area of PMPPP is 1.45 m g^{-1} that was determined by nitrogen physisorption (single point BET) at P/Po = 0.30928.

3.2. Effect of pH

The pH value of the solution is an important parameter for the uptake of metal ions by several adsorbents [34–36]. The effect of the initial pH of the Cd(II) solution on the removal of Cd(II) by PMPPP is illustrated in Fig. 4. As can be seen, the Cd(II) adsorption was quickly increased by increasing the pH from 2.0 to 4.0 and then was not changed due to increasing the pH to 7.0 for both two initial Cd(II) concentrations, namely 50 and 100 mg L^{-1}. The subsequent experiments were conducted at a pH of 6.0.

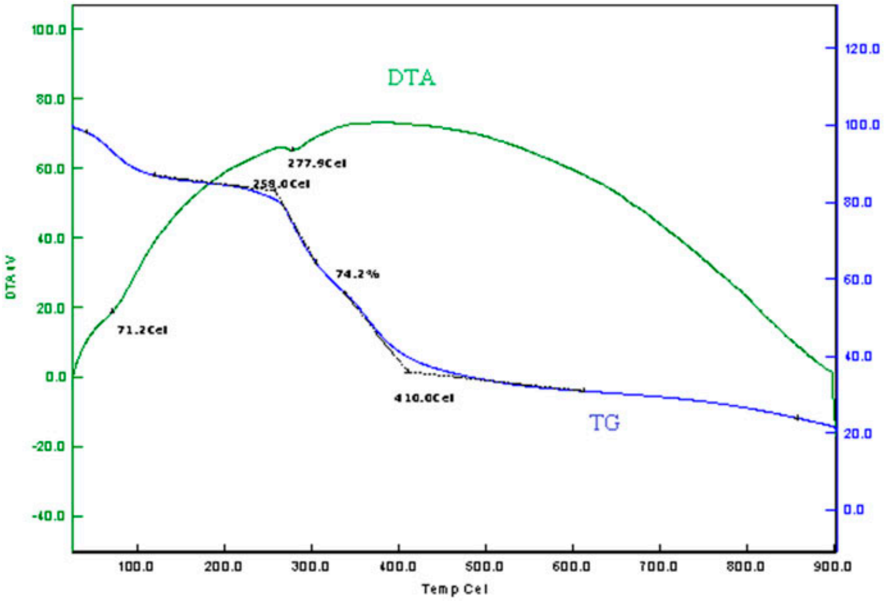

Fig. 2. TG and DTA curves of PMPPP.

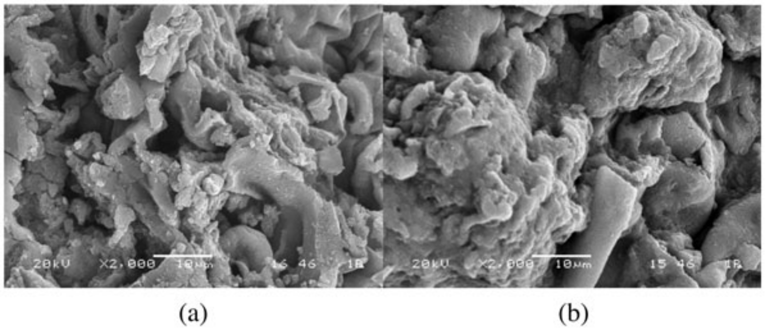

Fig. 3. SEM morphology of PMPPP, (a) before and (b) after adsorption at the magnification of 2,000×.

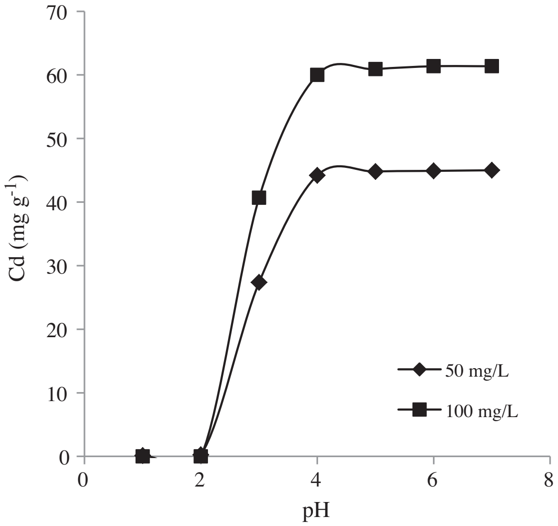

Fig. 4. Effect of pH on the adsorption of Cd(II) onto PMPPP.

The observed increase in Cd(II) adsorption as a result of increasing the pH can be explained as follows: at acidic pH values, the functional groups such as COOH groups of pyromellitic acid and free NH and NH_2 groups of polyethyleneimine segments on PMPPP are protonated. This is a competition reaction between protons and Cd(II) ions for the binding sites, resulting from lower the adsorption capacity of PMPPP at low pH values. With an increase in pH with regard to the solution, the carboxylic acid group deprotonated to form COO^-, and the NH and NH_2 groups became free. The Cd(II) ions coordinate to free amine and carboxylate groups directly on the other sides in that condition. This results in the increase in the Cd(II) adsorption capacity of PMPPP at higher pH values [37].

3.3. Effect of contact time

The contact time effects on Cd(II) adsorption were investigated in the time range 5–240 min at various initial concentrations (100, 150, 200 mg L^{-1}), optimum pH 6.0 and 50 mg fixed dosage per 50 mL of the solution. Fig. 5 shows the effect of the contact time for the adsorption of the Cd(II) metal ions on PMPPP. The adsorption of Cd(II) increased sharply in the first 40 min and slowly increased up to 120 min for three initial concentrations. Equilibrium was achieved at 120 min. Thus, the subsequent studies were carried out at a contact time of 120 min.

3.4. Effect of dosage

To determine the effect of PMPPP dosage, PMPPP in a range of 20 and 50 mg was added to a series of Cd(II) solutions (50 mL) at various concentrations (50, 100, 150 mg L^{-1}). The obtained results are showed in Fig. 6. The amount of Cd(II) adsorbed per unit mass of PMPPP was decreased by increasing of the amount of PMPPP from 20 to 50 mg. This decrease can be

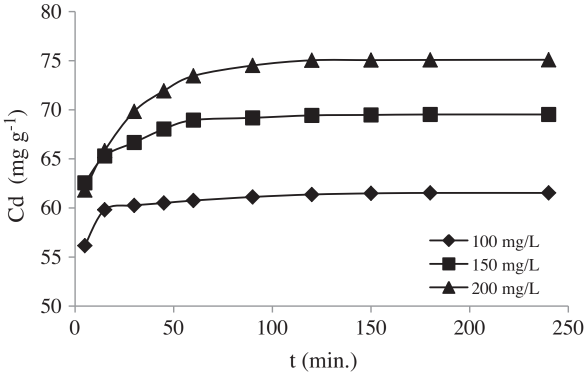

Fig. 5. Effect of contact time on the adsorption of Cd(II) onto PMPPP.

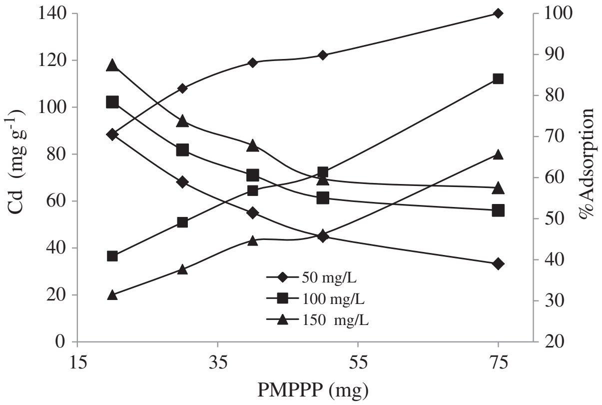

Fig. 6. Effect of PMPPP dose on the adsorption of Cd(II).

explained by an inverse relationship between metal removal and the PMPPP dose. Otherwise, as the dosage of PMPPP was increased, the adsorption percentage of Cd(II) increased. This increase can be explained by increases in sorption sites in the PMPPP surface that causes an enhancement in the number of adsorption zones [38–41].

3.5. *Effect of initial Cd(II) concentration*

The effect of the initial concentration in the range of 50 and 300 mg L^{-1} was studied at PMPPP doses of 40, 50, and 75 mg. The results are demonstrated in (Fig. 7). As can be seen from the figure, due to the direct proportion between the amount of adsorbed ions and the initial concentration, adsorption began to increase gradually with increasing Cd(II) concentrations, until a balance was achieved. Finally, the curves flattened out at a high concentration, which indicates repletion of the active binding sites.

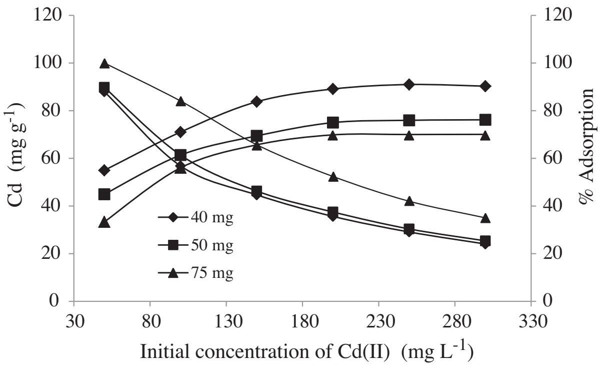

Fig. 7. Effect of initial Cd(II) concentration on the adsorption of Cd(II).

3.6. *Cd(II) adsorption isotherms*

The equilibrium data of Cd(II) were analyzed by Langmuir and Freundlich's isotherm equations. The Langmuir isotherm model is valid for single-layer adsorption on a homogeneous adsorbent surface [42] and can be expressed by Eq. (3)

$$q_e = \frac{K_L q_{\max} C_e}{1 + KC_e} \tag{3}$$

where C_e is the amount of Cd(II) left out in the supernatant (mg L^{-1}), q_e is the amount of Cd(II) adsorbed at equilibrium on the surface, $q_{\max}$ is the maximum

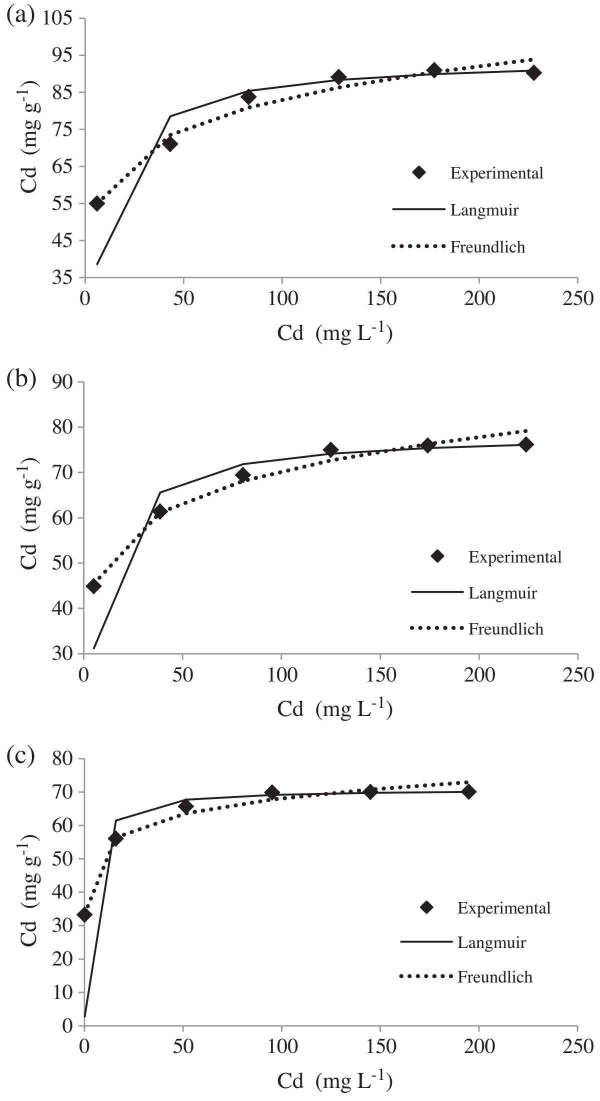

Fig. 8. Experimental, Langmuir, and Freundlich isotherms for the adsorption of Cd(II) onto PMPPP at various dose (a) 40 mg, (b) 50 mg, and (c) 75 mg.

adsorption capacity, K_L is the adsorption constant and the binding energy of adsorption (L mg^{-1}).

The Freundlich adsorption equation is a special case for heterogeneous surface energies of multilayer adsorption [43]. The Freundlich equation can be written as shown in formula (4).

$$q_e = K_F C_e^{\frac{1}{n}} \tag{4}$$

where K_F and n are Freundlich constants which are related to the adsorption capacity and the adsorption intensity, respectively.

The experimental, Langmuir and Freundlich isotherms are shown in Fig. 8, and the calculated constants are summarized in Table 1. According to the results obtained, the adsorption data were compatible with the Langmuir model, as evidenced by the very high values of the correlation coefficient (r^2). The maximum Cd(II) adsorption capacity of PMPPP was found to be 94.3 mg g^{-1} and compared with other adsorbents reported in the literature. Table 2 lists the maximum adsorption capacity of Cd(II) using various adsorbents of different origins. As can be seen from the list, PMPPP has a high adsorption capacity compared to some precedents in the literature.

3.7. Kinetics of Cd(II) adsorption by PMPPP

To examine the controlling mechanism of the adsorption processes, adsorption kinetics were studied using pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetic models. The pseudo-first-order model [54] and the pseudo-second-order model [55] can be represented in linear form in Eqs. (5) and (6), respectively.

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

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

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of Cd(II) adsorbed per unit mass of the PMPPP at equilibrium and time t, respectively. k_1 (min^{-1}) and k_2

Table 1
Parameters of Langmuir and Freundlich isotherms at different dosage of PMPPP for Cd(II) adsorption

	Langmuir constants			Freundlich constants		
Dosage (mg/50 mL)	$q_{\max}$ (mg g^{-1})	K_L (L mg^{-1})	r^2	K_F (mg g^{-1})	n	r^2
40	94.3	0.115	0.9983	42.2	6.8	0.9752
50	78.7	0.129	0.9989	35.8	6.8	0.9860
75	70.9	0.406	0.9996	42.4	9.7	0.9913

Table 2
Comparison of Cd(II) adsorption capacity ($q_{\max}$) of different sorbents reported in the literature

Adsorbent	$q_{\max}$ (mg g^{-1})	Ref.
Fe_3O_4@PAA@TSH MNPs	107.5	[25]
Soy protein hollow microspheres	120.83	[44]
Solyaspartyl polymer and chitosan	3.25	[45]
TiO_2 nanoparticles	7.9	[46]
Fe/Sn mixed-oxides	4.07	[47]
Polymer-modified Fe_3O_4 nanoparticles	29.6	[48]
Silica-supported dithiocarbamate	40.32	[49]
DNPH modified γ-Al_2O_3	83.33	[50]
Salicylic acid type chelate adsorbent	44.9	[51]
Semi-interpenetrating polymer network	19.27	[52]
Marine algal biomass *Sargassum* sp.	85.43	[53]
Poly(methylmethacrylate) Beads	28.2	[4]
PMPPP	94.3	This study

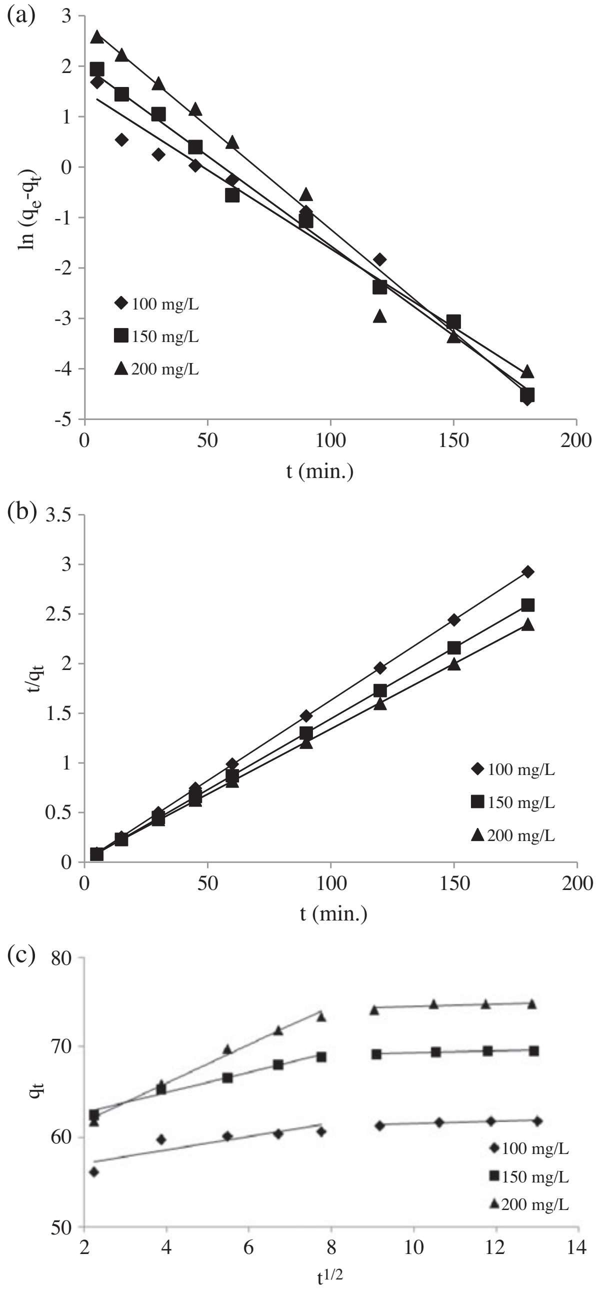

Fig. 9. Various kinetic plots for the removal of Cd(II) by adsorption on PMPPP. (a) plots of pseudo-first-order kinetic models, (b) plots of pseudo-second-order kinetic models, and (c) plots of intraparticle diffusion model.

($g\ mg^{-1}\ min^{-1}$) are the pseudo-first-order and pseudo-second-order rate constants, respectively.

If the first-order kinetic model is applicable, the linear plot of $\ln(q_e - q_t)$ vs. t should give the linear plot, and the value of k_1 and q_e can be calculated from the slope and intercept of the plot, respectively. For the pseudo-second-order model, the plot of t/q_t against t gives a linear plot if the model is applicable, and the values of q_e and k_2 can be computed from the slope and intercept of the plot shown [56]. The plots of the pseudo-first-order and pseudo-second-order model are illustrated in Fig. 9(a) and (b), respectively. Also, the calculated parameters of these models are as listed in Table 3. The correlation coefficient values of the second-order kinetic model are greater than 0.999 for all Cd(II) concentrations, and the experimental q_e values agree with the experimental values obtained from the linear plots. These facts indicate that the adsorption process of Cd(II) onto the PMPPP fits the second-order kinetic model.

The intra-particle diffusion model can be represented by Eq. (7)

$$q_t = k_{id}\, t^{\frac{1}{2}} + c \tag{7}$$

where q_t is the amount of Cd(II) adsorbed at time t; c is the intercept that provides us with estimates about the state of the boundary layer, and k_{id} is the intra-particle diffusion rate constant ($mg\ g^{-1}\ min^{-1/2}$) that provides information about the impact of the mass transfer forces on the adsorption system [40]. The intra-particle diffusion plots of Cd(II) adsorption onto PMPPP are shown in Fig. 9(c). The values of q_{t} were found to be linearly correlated with the values of $t^{1/2}$. The k_{id} values were calculated using correlation analysis. The calculated values of the kinetic model were reported in Table 4. Fig. 9(c) indicates that the Cd(II) adsorption process consists of two steps. It can be anticipated that the instantaneous or external surface adsorption and intra-particle diffusion occur in the first step and in the second step, respectively. The linear lines did not pass through the origin, accordingly, it is obvious that intra-particle diffusion is not the dominating mechanism for the adsorption of the Cd(II) on PMPPP [57].

3.8. Effect of temperature and thermodynamic study

The effect of temperature on the Cd(II) adsorption onto PMPPP are shown in Fig. 10. The fact that Cd(II) adsorption was increased as a result of an increase in temperature revealed that the process was endothermic.

Thermodynamic constants such as the standard Gibbs free energy change (ΔG), the standard entropy change (ΔS), and the standard enthalpy change (ΔH) were calculated in order to evaluate the thermodynamics and nature of the adsorption mechanism [58].

Table 3
Parameters of pseudo-first-order and pseudo-second-order kinetic models for Cd(II) adsorption onto PMPPP

		Pseudo-first-order			Pseudo-second-order		
C_0 (mg L^{-1})	$q_{e\ exp}$ (mg g^{-1})	$k_1 \times 10^2$ (min^{-1})	$q_{e\ cal}$ (mg g^{-1})	r^2	$k_2 \times 10^2$ (g mg^{-1} min^{-1})	$q_{e\ cal}$ (mg g^{-1})	r^2
100	61.5	3.1	4.5	0.9652	2.3	61.7	1
150	69.5	3.6	7.4	0.9917	1.4	69.9	1
200	75.1	4.1	17.1	0.9780	0.6	75.8	0.999

Table 4
Parameters of intraparticle diffusion model for Cd(II) adsorption onto PMPPP

C_o (mg L^{-1})	k_{id} (mg g^{-1} $min^{-1/2}$)	c (mg g^{-1})	r^2
100	0.3564	57.474	0.6653
150	0.5663	63.138	0.8035
200	1.1298	62.337	0.8291

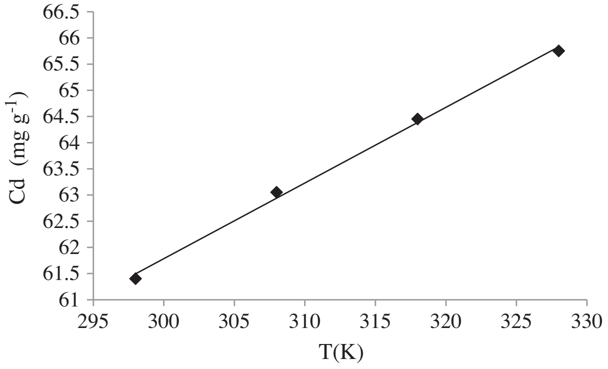

Fig. 10. The temperature-dependent change in the adsorbed amount of Cd(II) ions by PMPPP.

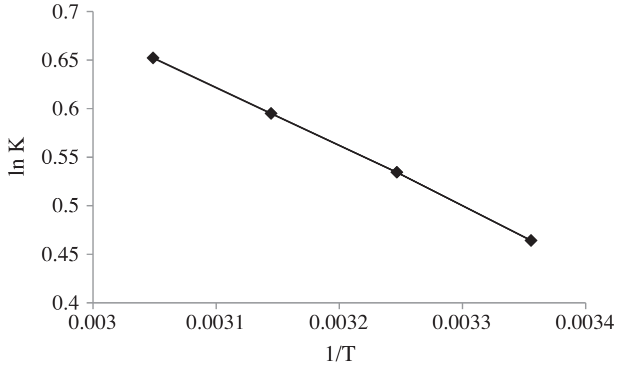

Fig. 11. Variation of equilibrium constant (K) as a function of temperature ($1/T$) for Cd(II) adsorption onto PMPPP.

ΔG was calculated using the Eq. (8)

$$\Delta G = -RT \ln K \tag{8}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), and K is the equilibrium constants of the adsorption process which were calculated from the following Eq. (9)

$$K = \frac{q_e}{C_e} \tag{9}$$

where q_e and C_e are the equilibrium concentration of Cd(II) on PMPPP (mg L^{-1}) and in the solution (mg L^{-1}), respectively.

The change in ΔH and ΔS were calculated using the Van't Hoff equation Eq. (10)

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{10}$$

where T is temperature in Kelvin and R is universal gas constant (8.314 J mol^{-1} K). ΔH and ΔS values can be obtained from the slope and intercept of the Van't Hoff plot, that is, ln K vs. 1/T (Fig. 11) [59].

The thermodynamic constants of Cd(II) adsorption were reported in Table 5. The positive value of ΔH showed that the adsorption process is endothermic, thus the Cd(II) adsorption to PMPPP increased with increasing temperature from 298 to 328 K. The positive

Table 5
Thermodynamic parameters for Cd(II) adsorption on the PMPPP

T (°C)	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K)[a]	ΔH (kJ mol^{-1})[a]
298	−1.15	20.92	5.08
308	−1.37		
318	−1.57		
328	−1.78		

[a] Measured between 298 and 328 K.

value of ΔS indicates that there was increased randomness at the interface between solid and solution during the adsorption process [60]. The negative values of ΔG indicate the spontaneity of the Cd(II) sorption process [61].

4. Conclusion

In this study, polyamine-polyurea polymer was synthesized and then modified with PMPPP. The Cd (II) adsorption on this polymer was examined using the batch method, the optimum pH value was found to be 6.0, and the contact time required to reach equilibrium was found to be 120 min. The Cd(II) adsorption equilibrium data and the adsorption kinetics were identified as being more in line with the Langmuir equation and the pseudo-second-order equation, respectively. The maximum adsorption capacity for Cd(II) ion adsorption with the PMPPP was found to be 94.3 mg g^{-1}. As a result, the prepared polymer was found to be an effective and efficient adsorbent for the removal of Cd(II) ions from aqueous solutions.

Acknowledgments

This work was supported by Sakarya University Research Fund with Project Number 2010-01-12-009.

References

[1] I. Thornton, Metals. In The Global Environment Fact and Misconceptions, International Council on Metals and the Environment, Ottawa, 1995.
[2] E. Akyuz, M. Imamoglu, H. Altundag, Selective determination of Cr(VI) by FAAS after solid phase extraction on bis(3-aminopropyl)amine-bonded silica gel, At. Spectrosc. 34 (2013) 146–153.
[3] B. Liu, D. Wang, Y. Xu, G. Huang, Adsorption properties of Cd(II)-imprinted chitosan resin, J. Mater. Sci. 46 (2011) 1535–1541.
[4] A. Denizli, N. Sanlı, B. Garipcan, S. Patir, G. Alsancak, Methacryloylamidoglutamic acid incorporated porous poly(methylmethacrylate) beads for heavy-metal removal, Ind. Eng. Chem. Res. 43 (2004) 6095–6101.
[5] H. Serencam, D. Ozdes, C. Duran, M. Tufekci, Biosorption properties of Morusalba l. for Cd (II) ions removal from aqueous solutions, Environ. Monit. Assess. 185 (2013) 6003–6011.
[6] X.W. Peng, L.X. Zhong, J.L. Ren, R.C. Sun, Highly effective adsorption of heavy metal ions from aqueous solutions by macroporous xylan-rich hemicelluloses-based hydrogel, J. Agr. Food. Chem. 60 (2012) 3909–3916.
[7] M. Minamisawa, H. Minamisawa, S. Yoshida, N. Takai, Adsorption behavior of heavy metals on biomaterials, J. Agr. Food. Chem. 52 (2004) 5606–5611.
[8] J. Charles, C. Bradu, N. Morin Crini, B. Sancey, P. Winterton, G. Torri, P.M. Badot, G. Crini, Pollutant removal from industrial discharge water using individual and combined effects of adsorption and ion-exchange processes: Chemical abatement, J. Saudi Chem. Soc, (2013), (in press), doi: 10.1016/j.jscs.2013.03.007.
[9] G. Kalaiselvi, P. Maheswari, S. Balasubramanian, D. Mohan, Synthesis, characterization of polyelectrolyte and performance evaluation of polyelectrolyte incorporated polysulfone ultrafiltration membrane for metal ion removal, Desalination 325 (2013) 65–75.
[10] B.A. Aji, Y. Yavuz, A.S. Koparal, Electrocoagulation of heavy metals containing model waste water using monopolar iron electrodes, Sep. Purif. Technol 86 (2012) 248–254.
[11] F. Fu, L. Xie, B. Tang, Q. Wang, S. Jiang, Application of a novel strategy—Advanced fenton-chemical precipitation to the treatment of strong stability chelated heavy metal containing wastewater, Chem. Eng. J. 189–190 (2012) 283–287.
[12] Y.J. Tu, C.K. Chang, C.F. You, S.L. Wang, Treatment of complex heavy metal wastewater using a multi-staged ferrite process, J. Hazard. Mater. 209–210 (2012) 379–384.
[13] S. Malamis, E. Katsou, K. Takopoulos, P. Demetriou, M. Loizidou, Assessment of metal removal, biomass activity and RO concentrate treatment in an MBR–RO system, J. Hazard. Mater. 209–210 (2012) 1–8.
[14] V.K. Gupta, I. Ali, T.A. Saleh, A. Nayak, S. Agarwal, Chemical treatment technologies for waste-water recycling—An overview, RSC Adv. 2 (2012) 6380–6388.
[15] H. Serencam, A. Gundogdu, Y. Uygur, B. Kemer, V.N. Bulut, C. Duran, M. Soylak, M. Tufekci, Removal of cadmium from aqueous solution by nordmann fir (abies nordmanniana (stev.) spach. subsp. nordmanniana) leaves, Bioresour. Technol. 99 (2008) 1992–2000.
[16] L.X. Zhong, X.W. Peng, D. Yang, R.C. Sun, Adsorption of heavy metals by a porous bioadsorbent from lignocellulosic biomass reconstructed in an ionic liquid, J. Agric. Food Chem. 60 (2012) 5621–5628.
[17] M. Imamoglu, Adsorption of Cd(II) ions onto activated carbon prepared from hazelnut husks, J. Dispersion Sci. Technol. 34 (2013) 1183–1187.
[18] B. Alyüz, S. Veli, Low-cost adsorbents used in heavy metal contaminated waste water treatment, J. Eng. Natural Sci. (Sigma), 3 (2005) 94–105.
[19] Suharso, Sumadi, Buhani, Adsorption kinetics and isotherm of Cd(II) ion on *Nannochloropsis* sp biomass imprinted ionic polymer, Desalination 259 (2010) 140–146.
[20] M. Ghaedi, N. Mosallanejad, Removal of heavy metal ions from polluted waters by using of low cost adsorbents: Review, J. Chem. Health Risks 3 (2013) 7–22.
[21] M. Imamoglu, A. Vural, H. Altundag, Evaluation of adsorptive performance of dehydrated hazelnut husks carbon for Pb(II) and Mn(II) ions, Desalin. Water Treat. (2013), (in press), doi:10.1080/19443994.2013.834515.
[22] M. Jain, V.K. Garg, K. Kadirvelu, Chromium removal from aqueous system and industrial wastewater by agricultural wastes, Biorem. J. 17 (2013) 30–39.
[23] M. Iqbal, A. Saeed, N. Akhtar, Petiolar felt-sheath of palm: A new biosorbent for the removal of heavy metals from contaminated water, Bioresour. Technol. 81 (2002) 151–153.

[24] M. Arslan, Z. Temoçin, M. Yiğitoğlu, Removal of Cadmium(II) from aqueos solutions using sporopollenin, Fresenius Environ. Bull. 13 (2004) 616–619.

[25] K. Zargoosh, H. Abedini, A. Abdolmaleki, M.R. Molavian, Effective removal of heavy metal ions from industrial wastes using thiosalicylhydrazide-modified magnetic nanoparticles, Ind. Eng. Chem. Res. 52 (2013) 14944–14954.

[26] M.P. Kutyreva, M.S. Starikova, N.A. Ulakhovich, R.A. Cherkasov, N.G. Zabirov, F.D. Sokolov, Adsorption recovery and preconcentration of Ni(II), Zn(II) and Cd(II) on nitrocellulose membranes modified with N-acylamidophosphates, J. Anal. Chem. 65 (2010) 140–146.

[27] W.B. Gurnule, H.D. Juneja, L.J. Paliwal, Ion-exchange properties of a salicylic acid–melamine – Formaldehyde terpolymer resin, React. Funct. Polym. 50 (2002) 95–100.

[28] A.A. Atia, A.M. Donia, A.M. Yousif, Removal of some hazardous heavy metals from aqueous solution using magnetic chelating resin with iminodiacetate functionality, Sep. Purif. Technol 61 (2008) 348–357.

[29] D.H. Shin, Y.G. Ko, S. Choiu, W.N. Kim, Synthesis and characteristics of novel chelate fiber containing amine and amidine groups, Polym. Adv. Technol. 15 (2004) 459–466.

[30] B.L. Rivas, H.A. Maturana, S. Villegas, Adsorption behavior of metal ions by amidoxime chelating resin, J. Appl. Polym. Sci. 77 (2000) 1994–1999.

[31] B.L. Rivas, A. Maureira, Poly(2-acrylamido glycolic acid-co-acryloyl morpholine) and poly(2-acrylamido glycolic acid-co-acrylamide): Synthesis, characterization, and retention properties for environmentally impacting metal ions, Eur. Polym. J. 44 (2008) 523–533.

[32] A. Baraka, P.J. Hall, M.J. Heslop, Preparation and characterization of melamine–formaldehyde–DTPA chelating resin and its use as an adsorbent for heavy metals removal from wastewater, React. Funct. Polym. 67 (2007) 585–600.

[33] S. Sivrikaya, E. Cerrahoglu, M. Imamoglu, M. Arslan, 1,3,5-triazine-triethylenetetramine polymer: An efficient adsorbent for removal of Cr(VI) ions from aqueous solution, Toxicol. Environ. Chem. 95(6) (2013) 899–908.

[34] W. Zou, H. Bai, S. Gao, Competitive adsorption of neutral red and Cu^{2+} onto pyrolytic char: Isotherm and kinetic study, J. Chem. Eng. Data 57 (2012) 2792–2801.

[35] E. Akdemir, M. Imamoglu, Solid-phase extraction of trace Ni(II) ions on ethylenediamine silica material synthesized by sol–gel method, Desalin. Water Treat. 52 (2014) 4889–4894.

[36] F. Aydemir, H. Altundag, M. Imamoglu, Removal of Cr(VI) from aqueous solution by hazelnut husk carbon, Fresenius Environ. Bull. 21 (2012) 3589–3594.

[37] G. Mahajan, D. Sud, Application of ligno-cellulosic waste material for heavy metal ions removal from aqueous solution, J. Environ. Chem. Eng. 1 (2013) 1020–1027.

[38] C. Ozer, M. Imamoglu, Y. Turhan, F. Boysan, Removal of methylene blue from aqueous solutions using phosphoric acid activated carbon produced from hazelnut husks, Toxicol. Environ. Chem. 94 (2012) 1283–1293.

[39] J.C.P. Vaghetti, E.C. Lima, B. Royer, J.L. Brasil, B.M. da Cunha, N.M. Simon, N.F. Cardoso, C.P.Z. Norena, Application of Brazilian-pine fruit coat as a biosorbent to removal of Cr(VI) from aqueous solution. Kinetics and equilibrium study, Biochem. Eng. J. 42 (2008) 67–76.

[40] B. Royer, N.F. Cardoso, E.C. Lima, V.S.O. Ruiz, T.R. Macedo, C. Airoldi, Organofunctionalized kenyaite for dye removal from aqueous solution, J. Colloid Interface Sci. 336 (2009) 398–405.

[41] T. Calvete, E.C. Lima, N.F. Cardoso, S.L.P. Dias, F.A. Pavan, Application of carbon adsorbents prepared from the Brazilian-pine fruit shell for removal of procion red MX 3B from aqueous solution—Kinetic, equilibrium, and thermodynamic studies, Chem. Eng. J. 155 (2009) 627–636.

[42] Y. Zhou, X. Hu, M. Zhang, X. Zhou, J. Niu, Preparation and characterization of modified cellulose for adsorption of Cd(II), Hg(II), and acid fuchsin from aqueous solutions, Ind. Eng. Chem. Res. 52 (2013) 876–884.

[43] K. Deepa, P. Chandran, S. Khan, Bioremoval of direct red from aqueous solution by Pseudomonas putida and its adsorption isotherms and kinetics, Ecol. Eng. 58 (2013) 207–213.

[44] D. Liu, Z. Li, W. Li, Z. Zhong, J. Xu, J. Ren, Z. Ma, Adsorption behavior of heavy metal ions from aqueous solution by soy protein hollow microspheres, Ind. Eng. Chem. Res. 52 (2013) 11036–11044.

[45] B. Sun, Z.T. Mi, G. An, G. Liu, J.J. Zou, Preparation of biomimetic materials made from polyaspartyl polymer and chitosan for heavy-metal removal, Ind. Eng. Chem. Res. 48 (2009) 9823–9829.

[46] P. Liang, T. Shi, J. Li, Nanometer-size titanium dioxide separation/preconcentration and FAAS determination of trace Zn and Cd in water sample, Int. J. Environ. Anal. Chem. 84 (2004) 315–321.

[47] E. Borai, E. El-Sofany, T. Morcos, Development and optimization of magnetic technologies based processes for removal of some toxic heavy metals, Adsorption 13 (2007) 95–104.

[48] F. Ge, M.M. Li, H. Ye, B.X. Zhao, Effective removal of heavy metal ions Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+} from aqueous solution by polymermodified magnetic nanoparticles, J. Hazard. Mater. 211–212 (2012) 366–372.

[49] L. Bai, H. Hu, W. Fu, Synthesis of a novel silica-supported dithiocarbamate adsorbent and its properties for the removal of heavy metal ions, J. Hazard. Mater. 195 (2011) 261–275.

[50] A. Afkhami, M. Saber-Tehrani, H. Bagheri, Simultaneous removal of heavy-metal ions in wastewater samples using nano-alumina modified with 2,4-dinitrophenylhydrazine, J. Hazard. Mater. 181 (2010) 836–844.

[51] F. An, B. Gao, X. Dai, Efficient removal of heavy metal ions from aqueous solution using salicylic acid type chelate adsorbent, J. Hazard. Mater. 192 (2011) 956–962.

[52] D.F. Apopei, M.V. Dinu, A.W. Trochimczuk, E.S. Dragan, Sorption isotherms of heavy metal ions onto semi-interpenetrating polymer network cryogels based on polyacrylamide and anionically modified potato starch, Ind. Eng. Chem. Res. 51 (2012) 10462–10471.

[53] P.X. Sheng, Y.P. Ting, J.P. Chen, Biosorption of heavy metal ions (Pb, Cu, and Cd) from aqueous solutions by the marine alga *Sargassum* sp. in single- and multiple-metal systems, Ind. Eng. Chem. Res. 46 (2007) 2438–2444.

[54] S. Lagergren, About the theory of so-called adsorption of soluble substance, Kung Sven. Veten. Hand 24 (1898) 1–39.

[55] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[56] M. Ghaedi, A.M. Ghaedi, M. Hossainpour, A. Ansari, M.H. Habibi, A.R. Asghari, Least square-support vector (LS-SVM) method for modeling of methylene blue-dye adsorption using copper oxide loadedon activated carbon: Kinetic and isotherm study, J. Ind. Eng. Chem. (2013) 1504–1514.

[57] D. Ozdes, C. Duran, H.B. Senturk, Adsorptive removal of Cd(II) and Pb(II) ions from aqueous solutions by using Turkish illitic clay, J. Environ. Manage. 92 (2011) 3082–3090.

[58] W.J. Weber, Physicochemical Process for Water Quality Control, Environmental Science and Technology Series, Wiley-Interscience, New York, NY, 1972.

[59] P. Sampranpiboon, P. Charnkeitkong, Equilibrium isotherm, thermodynamic and kinetic studies of lead adsorption onto pineapple and paper waste sludges, Int. J. Energy Environ. 4 (2010) 88–98.

[60] X. Wang, R. Sun, C. Wang, pH dependence and thermodynamics of Hg(II) adsorption onto chitosan-poly (vinyl alcohol) hydrogel adsorbent, Colloid Sur. A 441 (2014) 51–58.

[61] M. Iram, C. Guo, Y. Guan, A. Ishfaq, H. Liu, Adsorption and magnetic removal of neutral red dye from aqueous solution using Fe_3O_4 hollow nanospheres, J. Hazard. Mater. 181 (2010) 1039–1050.