

## Specific heavy metal ion recovery with ion-imprinted cryogels

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**ABSTRACT:** In this study, the functional monomers, N-methacryloyl-L-aspartic acid and N-methacryloyl-L-cysteine were synthesized through a reaction between appropriate amino acids and methacryloyl chloride. Then, Pb(II) or Cd(II) ion-imprinted 2-hydroxyethyl methacrylate based cryogels were prepared by free radical polymerization method under partially frozen conditions. Following the characterization of matrices, adsorption of heavy metal ions was examined in batch mode from aqueous solution considering several parameters affecting the adsorption performance. The actual adsorption capacities were 44.5, 65.3, and 86.7 mg/g for Cd-1, Cd-2, and Cd-3 cryogels meanwhile those were 41.9, 86.3, and 122.7 mg/g for Pb-1, Pb-2, and Pb-3 cryogels, respectively at optimum pH: 5.5. By increasing temperature, adsorption capabilities of both cryogels were inhibited because of the electrostatic nature of coordinated covalent bonds and collapsing of coordination spheres. The adsorption process was very fast, the equilibrium adsorption was achieved in about 60 min, which was directly related to macroporous structure and interconnected flow-channels of cryogels. Kinetics and adsorption isotherms were also studied. Langmuir isotherms and pseudo-second order kinetic model were well suited to adsorption data, which also indicated that the process occurred without any diffusion restrictions or steric hindrances. Finally, the competitive adsorption studies were performed using multi-ion containing synthetic wastewater to show whether the cryogels developed are suitable for specific heavy metal recycling or not. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43095.

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### INTRODUCTION

Presence of heavy metal ions in water causes several health problems for living organisms and undesirable effects on environment because of the toxic effects and nonbiodegradability.<sup>1–4</sup> To treat wastewater; physical, chemical, or biological refinement techniques or combined techniques can be selected with respect to the content and quantity of waste, process performance and economics, chemicals and energy requirements.<sup>5</sup>

Many traditional methods such as chemical precipitation, adsorption, extraction, membrane processes, ion exchange, etc. have been used for heavy metal removal.<sup>6–11</sup> However, these methods are generally expensive or risky, and need to be modified. Adsorption is a common method for metal ion removal from water. Natural or synthetic, organic or inorganic adsorbents may be used. Modified natural materials, industrial by-products, modified agriculture and biological wastes, biopolymers, and hydrogels were extensively examined.<sup>12–17</sup> Polymer-based adsorbents in cryogel form are highly desirable because of the ease of synthesis, macroporous structure, stability, intercon-

nected flow-channels allowing to study with viscous organic mobile phase even at high flow rates without any pressure drop and diffusion problems.<sup>18</sup> The main disadvantage is the small surface area. Imprinting is also considered as alternative to enhance advantages of adsorption method because of ability to create specific recognition sites. Ion-imprinted polymers (IIPs) are prepared by copolymerization of a base monomer, functional monomer (or ligand-template complex), and cross-linker, and following the polymerization, removal of template to create specific recognition sites.<sup>19</sup>

Peptides, nucleic acids, and macrocyclic chelating ligands can be treated as biological ligands to form the precomplex in synthesis.<sup>20</sup> The most common metal binding units are Cys, His, Asp, Glu, and more rarely Met, Asn, Gln, Ser, Thr, and Tyr. These groups can be attached on the polymer with chemical modification of the ligand or synthesis of sorbents by monomeric ligands. Sulfhydryl groups in cysteine and carboxyl groups in aspartic acid are primarily responsible for metal binding. The polar side chains form hydrogen bond with water while acidic functional groups being charged because of pH changes can

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cause ionic interactions. Cysteine is the only amino acid capable of forming covalent bonds, which they do with their particular side chains.<sup>21</sup>

In present study, amino acid (cysteine and aspartic acid) containing 2-hydroxyethyl methacrylate (HEMA) based, Cd(II) and Pb(II) ions-imprinted cryogels were synthesized by free radical polymerization method. The swelling tests, SEM, EDX, FTIR, and BET studies were utilized to characterize the matrices. Amino acids were included into structure by monomeric ligands, N-methacryloyl-L-cysteine and N-methacryloyl-L-aspartic acid. The heavy metal adsorption performance of resulting matrices from single ion or multi-ion containing synthetic media were investigated in batch mode considering several parameters such as temperature, concentration, incubation time, etc. Desorption, reusability, kinetics, and thermodynamic parameters were studied as well.

## EXPERIMENTAL

### Materials

HEMA, N, N'-methylene bisacrylamide (MBAAm), L-cysteine, L-aspartic acid, hydroquinone, triethyl amine, and nitrates of lead and cadmium were purchased from Sigma (St. Louis, USA). N, N, N', N'-tetramethylethylenediamine (TEMED) and ammonium persulfate (APS) were supplied from BioRad (Hercules, CA, USA). All water used in the experiment was purified using Barnstead (Dubuque, IA, USA) RV Pure LP<sup>®</sup> reverse osmosis unit.

### Ion-Imprinted Cryogels

The selection of amino acid, cysteine for complexing of Cd(II) ions and aspartic acid for complexing of Pb(II) ions, depended on the Pearson acid–base theory which describes the classification of ions according to their Lewis acid–base character. The thiol groups of cysteine and dicarboxylic acid side groups of aspartic acid could specifically interact with targeted heavy metal ions.

**Preparation of Amino Acid Based Functional Monomers.** The synthesis of functional monomers was achieved according to methods reported in literature<sup>22–24</sup> and they were used for complexing heavy metal ions. The methods for their synthesis could briefly be given as follows: 5.0 g of L-Cysteine hydrochloride and 0.2 g of hydroquinone were dissolved in 100 mL of CH<sub>2</sub>Cl<sub>2</sub>, then the solution was cooled down to 0°C in an ice bath. Triethylamine (13.0 g) was included to the solution and 4.0 mL of methacryloyl chloride was then slowly added. The resulting mixture was magnetically stirred for 2 h under nitrogen atmosphere at room temperature. Unreacted methacryloyl chloride was extracted with 10% NaOH solution. The aqueous phase was removed in a rotary evaporator, and functional monomer N-methacryloyl-L-cysteine (MAC) was obtained.

Separately, 1.0 g of L-aspartic was dissolved in 100 mL of 1M NaOH. The solution was slowly added to a solution of methacryloyl benzotriazole (1.03 g) in 25 mL of 1,4-dioxane. The mixture was magnetically stirred for 20 min. After the reaction, 1,4-dioxane was evaporated under vacuum. To remove benzotriazole, the precipitate was dissolved in water and extracted with ethyl acetate (3 × 50 mL). The aqueous phase was neutral-

ized by 10% (v/v) HCl solution. Then, water was removed by rotary evaporator to obtain functional monomer N-methacryloyl-L-aspartic acid (MAAsp).

**Synthesis of Pre-Complexes.** In order to coordinate Cd(II) ions, MAC:Cd(II)(1:1) pre-complex was prepared as follows: 18.9 mg (0.1 mmol) of MAC in ethanol (5.0 mL) was added to 30.8 mg of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.1 mmol) at room temperature. The mixture was magnetically stirred for 3 h, and the resulting complex was separated by filtration. The complex was cleaned by ethanol–water mixture (50 : 50, v/v) and dried under vacuum (12 h, 200 mmHg).

In case of Pb(II) ions, MAAsp-Pb(II) pre-complex was prepared as follows: 53.8 mg (0.1 mmol) of MAAsp in 5 mL of water was added to 66.24 mg of Pb(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (0.1 mmol) at room temperature. The following steps were the same as above.

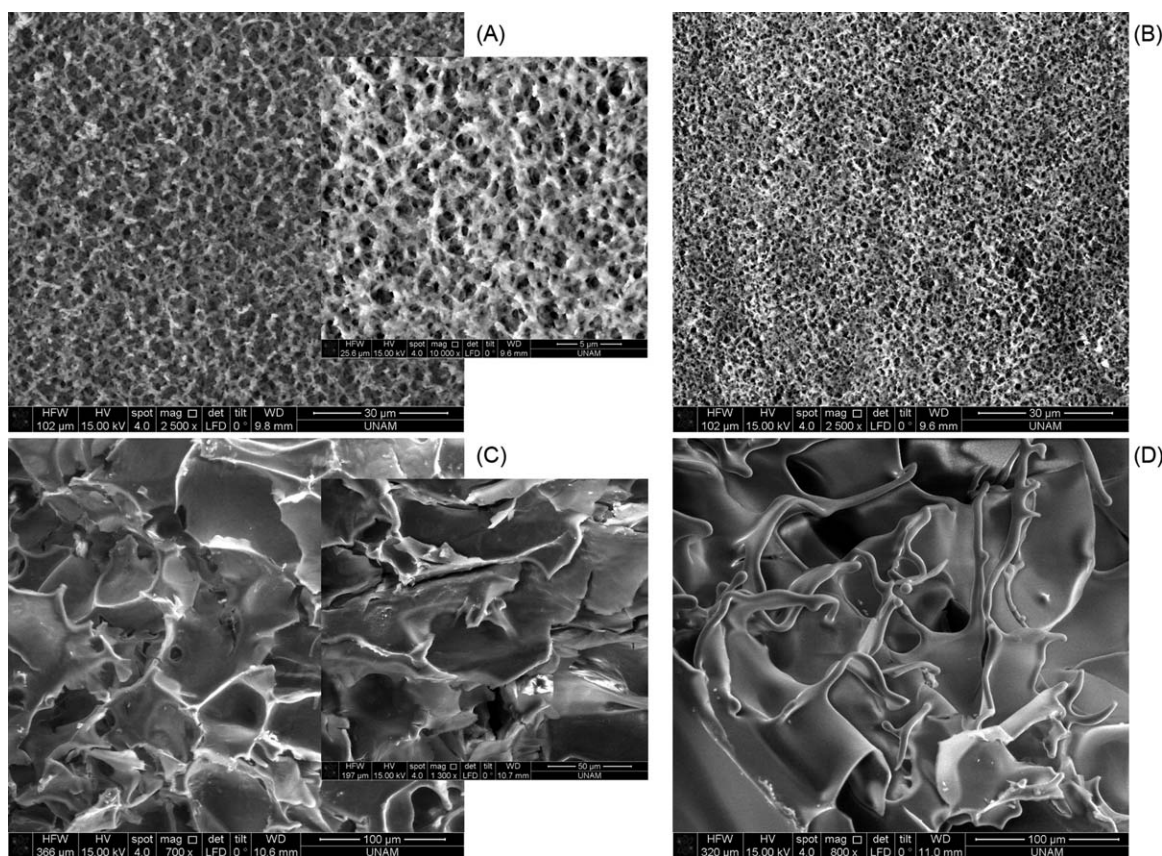
**Preparation of Ion-Imprinted and Nonimprinted Cryogels.** Ion-imprinted cryogels (IICs) having different amounts of pre-complexes (0.05, 0.1, 0.2 mmol) were synthesized, and encoded as Cd-1, Cd-2, Cd-3 and Pb-1, Pb-2, Pb-3 for the reported values above.

About 4.7 mL of HEMA was dissolved in 5.3 mL of deionized water. To remove dissolved oxygen, N<sub>2</sub>(g) was passed through solution for 5 min under vacuum (100 mmHg). The final monomer concentration was adjusted to 18.8% (w/v). The second aqueous phase contained 2.01 mg of methylenebisacrylamide (cross-linker) dissolved in 20.0 mL of deionized water. The two aqueous phases were mixed, and then following the addition of pre-complex in different amounts, it was stirred in an ice-bath until a homogeneous solution was obtained. APS (100 mg) as initiator was included in solution. Following the cooling in an ice bath for 5 min, TEMED (100 μL) was added to solution that was transferred between two electrophoresis plates (25 cm × 25 cm) with closed three edges. Thawing was performed at room temperature after the system was kept at –12°C for 24 h. An extensive cleaning process was applied to resulting cryogels, using dilute HCl solution and water–ethanol mixtures. The imprinted metal ions (templates) were removed by Na<sub>2</sub>(EDTA) solution. The membranes were cut by a perforator in different forms i.e. square and circle. The membranes were stored in 0.02% sodium azide at +4°C until use. In case of nonimprinted cryogel membranes, the same procedure was followed including functional monomer instead of the pre-complex in recipe.

### Characterization Studies

The powdered and completely dried samples (~2 mg) were mixed with KBr (IR-grade, ~98 mg), then pressed into a pellet, and FTIR spectra of samples were obtained by a FTIR spectrophotometer (Nicolet™ iS™10 FT-IR Spectrometer-USA) in the wavenumber range of 400–4000 cm<sup>-1</sup>.

Following the lyophilization, the samples were coated with gold–palladium (40:60) and their surfaces were examined using a Nova Nanosem 430 scanning electron microscope (FEI Company, USA) to monitor surface morphology of IICs.



**Figure 1.** SEM photographs of cryogels: (A) Cd(II) ion imprinted; (B) Nonimprinted; (C) Pb(II) ion imprinted; and (D) Nonimprinted.

By determining the masses of dried membranes ( $m_0$ ) and swollen samples ( $m_s$ ) (incubated in 20 mL water for 2 h) the swelling degree was calculated by using the following equation.

$$\text{Swelling degree \%} = [(m_s - m_0) / m_0] \times 100\%$$

Elemental composition of cryogels was identified by Energy Dispersive X-ray Analysis (EDX) method, system attached to SEM, using lyophilized (for 12 h) samples.

The specific surface areas were measured according to BET, multipoint analysis method by an AutosorpII 6B apparatus from Quantachrome Instruments, USA. To remove oxygen and humidity in pores, lyophilized samples were vacuumed at 35°C for 6 h, and then nitrogen adsorption was studied at room temperature.

#### Adsorption Studies from Singular Aqueous Solutions

Adsorption studies were performed in batch mode. The initial concentration of metal ions was changed over the range of 10–700 ppm. The pH effect was examined for 3.0–6.0 range. The temperature parameter was analyzed for 4.0–40°C range. About 5–180 min time interval was examined for the effect of contact time. The concentration of metal ions was determined by ICP-AAS method (AAAnalyst 800, Perkin-Elmer, USA). The adsorption capacity ( $Q$ , mg/g) was calculated by the following equation:

$$Q = [(C_0 - C) \cdot V] / m$$

where  $C_0$  and  $C$  are the concentrations of heavy metal ions in solution before and after adsorption, respectively (mg/L);  $V$  is

the volume of the solution (L), and  $m$  is mass of cryogel (g). Each reported capacity value was the average of three measurements.

#### Selectivity Studies

The selectivity of all ion-imprinted cryogels was tested for specific metal ions in presence of competitive ions. The selectivity of the Cd(II)-imprinted cryogels for Cd(II) with respect to Cu(II) and Pb(II), and the selectivity of the Pb(II)-imprinted cryogel for Pb(II) with respect to Cu(II), and Cd(II) were examined.

The distribution coefficients ( $K_d$ , L/g) were calculated by the following equation;

$$K_d = [(C_0 - C) / C] \cdot V / m$$

where the terms are the same as above.

The selectivity coefficient ( $k$ ) for binding of specific ions and the relative selectivity coefficient ( $k'$ ) were given by the following equations:

$$k = K_d(\text{template}) / K_d(\text{competing metal ion})$$

$$k' = k_{\text{MIP}} / k_{\text{NIP}}$$

#### Desorption and Reuse

The desorption agent was 20 mL of 100 mmol EDTA solution. Desorption ratio (%) was expressed as the percentage of adsorbed ions, after 1, 2, 3 h of contact time. For examination

of reusability, adsorption–desorption cycle was repeated three times.

### Competitive Heavy Metal Adsorption from Synthetic Wastewater

The Pb(II), Cu(II), and Cd(II) ion-imprinted cryogels were collectively tested for removal of these ions from a solution containing Cd(II), Pb(II), Zn(II), Ca(II), Co(II), Ni(II), and Fe(III) ions. The Cu(II) imprinted cryogels were synthesized using the same experimental procedure choosing the histidine amino acid for pre-complex formation.

## RESULTS AND DISCUSSION

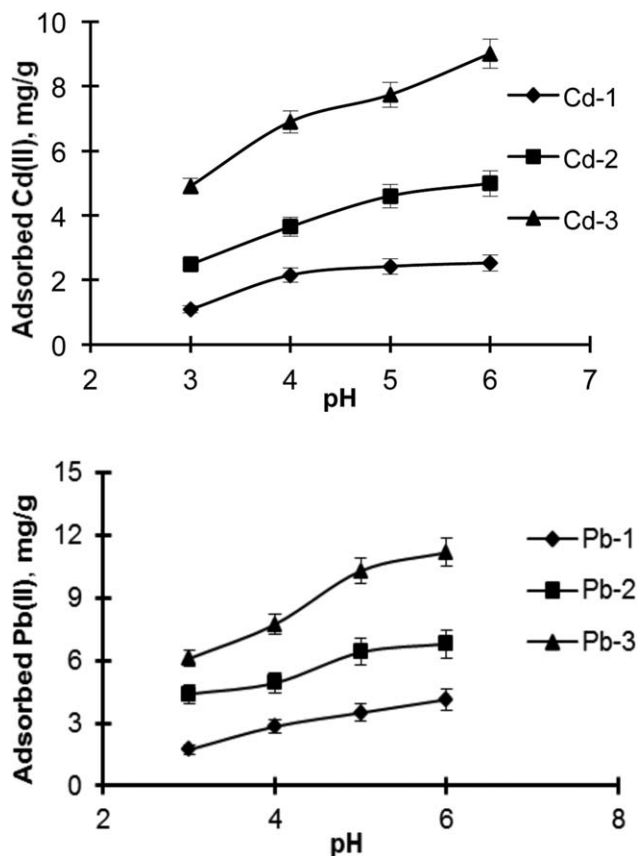
### Characterization

Swelling behaviors are given in Supplementary Materials File (Supporting Information Figure SMF-1) for Cd(II) ion and Pb(II) ion-imprinted and nonimprinted samples. Since additional hydrophilic groups were introduced by pre-complex and because of their distribution during cryogelation, the swelling ratios for IICs were slightly higher than those of their nonimprinted counterparts. Besides, formation of metal ion cavities in structure introduces more hydrodynamic volume into the polymer chain causing to adsorb more water molecules into matrices. The FTIR spectra of Cd(II) IICs and the nonimprinted samples are also given in Supplementary Materials File (Supporting Information Figure SMF-2). The stretching vibration bands of hydrogen bonded alcohol at around  $3200\text{ cm}^{-1}$ , and  $\text{-CONH-}$  at around  $3300\text{ cm}^{-1}$  contributed to the broad peak at  $3200\text{--}3500\text{ cm}^{-1}$ . The same broad peak existed in FTIR spectra of Pb(II) ion-imprinted cryogels (Supporting Information Figure SMF-3). The spectra also involved characteristic amide (I) at  $1653\text{ cm}^{-1}$ , and strong carbonyl stretching vibration at  $1716\text{ cm}^{-1}$ . SEM images of ion-imprinted and nonimprinted cryogels are given in Figure 1. The size of cavities was roughly in the range of  $5\text{--}100\text{ }\mu\text{m}$ . The interconnected flow-channels that form a macroporous structure are clearly seen. This structural property of the cryogels allows to study at high flow rates with viscous mobile phase like wastewaters with heavy metal ions. The ion-imprinted and nonimprinted cryogels contained 4% N, 35% O, 60% C, and 6% N, 36% O, and 56% C (on a mass basis) as determined by EDX analysis.

The surface area of Cd(II) imprinted and nonimprinted cryogels were  $92.0$ , and  $47.0\text{ m}^2/\text{g}$ , respectively, the values being  $78.5$  and  $29.3\text{ m}^2/\text{g}$  for Pb(II) imprinted and nonimprinted cryogels. The pore diameters changed between  $16\text{ }\text{\AA}$  and  $33\text{ }\text{\AA}$ . Total pore volume was  $0.007\text{--}0.05\text{ cm}^3/\text{g}$ .

### Adsorption Studies

**Effect of pH.** Effect of pH is represented in Figure 2 for Cd(II) and Pb(II) imprinted cryogels. Optimum pH value was considered as 5.5 for both heavy metal ion solutions. The adsorption capacities increased with increasing pH. This trend was closely related to the deprotonation of functional groups of amino acid based monomers, which are thiol groups in MAC and carboxylic acid groups in MAAsp. Thus the electrostatic attraction between the cryogels and metal ions was enhanced. The decrease in adsorption capacity with decreasing pH was because of the electrostatic repulsion of the protonated active sites and

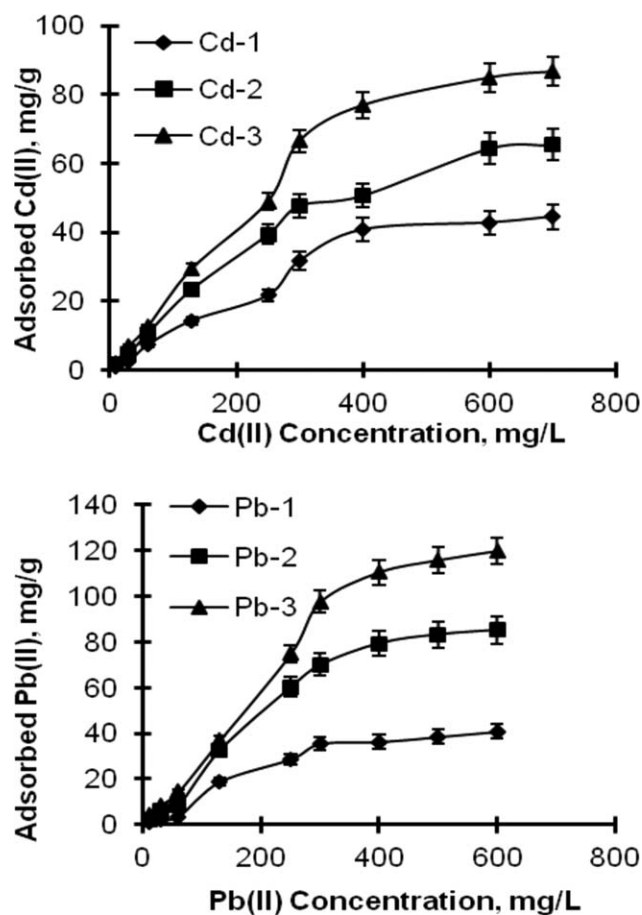


**Figure 2.** The effect of pH on adsorption of Cd(II) and Pb(II) by ion-imprinted cryogels; Concentration:  $60\text{ mg/L}$ ; incubation period:  $120\text{ min}$ ; and  $T:25^\circ\text{C}$ . The capacity values were the average of three repeated measurements.

metal ions. The amount of pre-complex used in synthesis increased the adsorption capacities as the extent of imprinted cavities increased. Adsorption studies were not conducted at higher pH values to avoid the precipitation of heavy metal ions as hydroxide salts.

**Effect of Concentration.** The adsorption capacities increased with increasing metal ion concentration (Figure 3) because of the increased concentration gradient, the driving force for adsorption. Following the saturation of active binding sites, plateau values were obtained around heavy metal ions concentration of  $400\text{ mg/L}$ . The adsorption capacities were  $44.5$ ,  $65.3$ , and  $86.7\text{ mg/g}$  for Cd-1, Cd-2, and Cd-3 cryogels and  $41.9$ ,  $86.3$ , and  $122.7\text{ mg/g}$  for Pb-1, Pb-2, and Pb-3 cryogels, respectively.

**Effect of Temperature.** Heavy metal adsorption studies for evaluating temperature effect on heavy metal adsorption ability were performed at four different temperatures in the range of  $4\text{--}40^\circ\text{C}$ . The decrease in adsorption capacities with an increase in temperature was because of the electrostatic nature of coordinated covalent bonds between the functional monomers that were polymerizable derivatives of amino acids and target metal ions. The disturbance of coordination spheres of those metal ions was also responsible for the change (Figure 4). The maximum adsorption capacities for Cd(II) and Pb(II) ion-imprinted



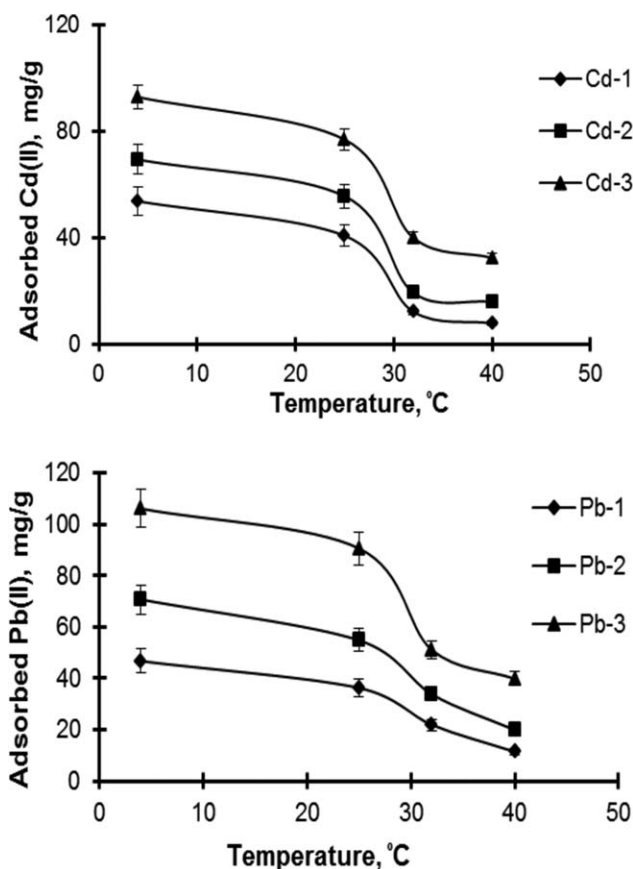
**Figure 3.** The effect of initial concentration on adsorption of Cd(II) and Pb(II) by ion-imprinted cryogels, pH:5.5; incubation period: 120 min; and  $T:25^{\circ}\text{C}$ . The capacity values were the average of three repeated measurements.

cryogels were 92.8 and 106.1 mg/g, respectively at  $4^{\circ}\text{C}$  and for a separate metal ion concentration of 400 mg/L. Herein, it should be noted that the decrease in adsorption capacity of cryogel having highest amount of imprinted cavities was higher than others for both heavy metal ions. This also revealed the electrostatic nature of interaction (coordinated covalent band) between complementary groups.

**Effect of Contact Time.** In order to examine adsorption kinetics, both ion-imprinted cryogels were interacted with heavy metal ion solution while collecting samples at any desired time in the range of 0–180 min. Beyond 90 min of contact time, the adsorption capacities did not change significantly because of almost complete occupation of imprinted cavities. The equilibrium adsorption could be achieved in about 60 min (Figure 5), the time required for movement of analyte molecules towards the pores, diffusion into pores, and interaction with recognition sites. This fast adsorption kinetics is directly related to macroporous structure and interconnected flow-channels of cryogels.

#### Adsorption Isotherms

Langmuir and Freundlich isotherms were treated in their linearized forms to describe the adsorption behavior of ion-imprinted cryogels.



**Figure 4.** The effect of temperature on the adsorption of Cd(II), and Pb(II) by ion-imprinted cryogel membranes; pH:5.5; incubation period: 120 min; and concentration 400 mg/L. The capacity values were the average of three repeated measurements.

Langmuir isotherm was tested using the following equation:

$$1/Q = 1/(Q_{\max} \cdot b \cdot C_{\text{eq}}) + 1/Q_{\max}$$

where  $C_{\text{eq}}$  (mg/g) is the concentration of adsorbate in solution after adsorption,  $b$  (mL/mg) is Langmuir constant,  $Q$  (mg/g) is adsorption capacity and  $Q_{\max}$  (mg/g) is theoretical maximum capacity.

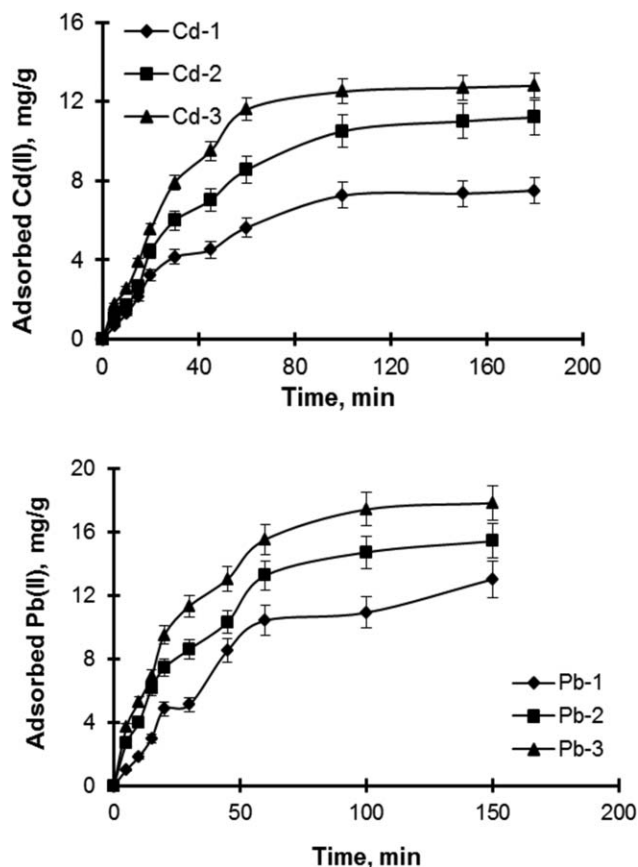
$R_L$ , equilibrium values were also calculated whose values reported the favorability of the adsorption process ( $R_L > 1$  unfavorable,  $R_L = 1$  linear,  $0 < R_L < 1$  favorable).

$$R_L = 1/(1 + b \cdot C_{\text{eq}})$$

$$\ln Q_{\text{eq}} = \ln K_F + (1/n) \cdot \ln C_{\text{eq}}$$

equation was used to test the applicability of Freundlich isotherm. where  $K_F$  and  $1/n$  are Freundlich coefficients.

The related isotherms are given in Supplementary Materials File (Supporting Information Figures SMF-4 and 5) and the parameters calculated are summarized in Table I. In the light of  $R^2$  and  $Q_{\max}$  values calculated from Langmuir isotherms, the adsorption process well suited to Langmuir isotherm, proving the monolayer coverage, the homogeneous distribution of recognition sites and energetically equivalence of these sites. Also,  $R_L$  values ranging between 0 and 1 indicated the favorability of adsorption process



**Figure 5.** The effect of contact time on adsorption of Cd(II), and Pb(II) by ion-imprinted cryogels; Concentration: 60 mg/L; pH:5.5; incubation period: 120 min; and  $T$ : 25°C. The capacity values were the average of three repeated measurements.

as well. The results also indicated that the process occurred without any diffusion restrictions or steric hindrances.

By means of van't Hoff plots,  $\Delta H^\circ$  values (kJ/mol),  $\Delta S^\circ$  values (J/mol.K), and  $\Delta G^\circ$  values (kJ/mol) were calculated using the equation  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ . The values calculated are summarized in Table I. As seen in table, ion-imprinted cryogels adsorb/recognize the template ions spontaneously. The process was energetically favorable with negative Gibbs free energy values for all cryogel samples. In addition,  $\Delta H^\circ$  and  $\Delta S^\circ$  values proved the appropriateness of adsorption process in terms of thermodynamics. The increase in the amount of imprinted cavities also enhanced the favorability of process while causing the increase in entropy values and the decrease in  $\Delta G^\circ$  and  $\Delta H^\circ$  values.

#### Adsorption Kinetics

The pseudo first-order and pseudo second-order kinetic models were examined for kinetic analysis of heavy metal adsorption onto ion-imprinted cryogels. The equations

$$\log(q_{eq} - q_t) = \log(q_{eq}) - (k_1 t)/2.303$$

$$t/q_t = (1/k_2 q_{eq}^2) + (1/q_{eq}) t$$

were used for analysis, where  $k_1$  (1/min) and  $k_2$  [g/(mg.min)] are the rate constants, and  $q_t$  and  $q_{eq}$  are the adsorption capaci-

**Table I.** Thermodynamic Parameters for Adsorption<sup>a</sup> of Cd(II) and Pb(II) by Ion-imprinted Cryogels

Cryogel Codes	$\Delta G^\circ$ @ 25°C kJ/mol	$\Delta H^\circ$ @ 25°C kJ/mol	$\Delta S^\circ$ @ 25°C J/mol K
Cd-1	-14.95	-16.68	10.01
Cd-2	-16.25	-22.40	15.73
Cd-3	-17.86	-24.96	18.11
Pb-1	-16.64	-19.80	13.37
Pb-2	-17.40	-21.72	16.59
Pb-3	-18.74	-23.50	18.03

<sup>a</sup>Parameters for these evaluations: initial concentrations: 0-700 mg/L for Cd(II) and 0-600 mg/L for Pb(II); pH:5.5; incubation period: 120 min; and  $T$ : 25°C.

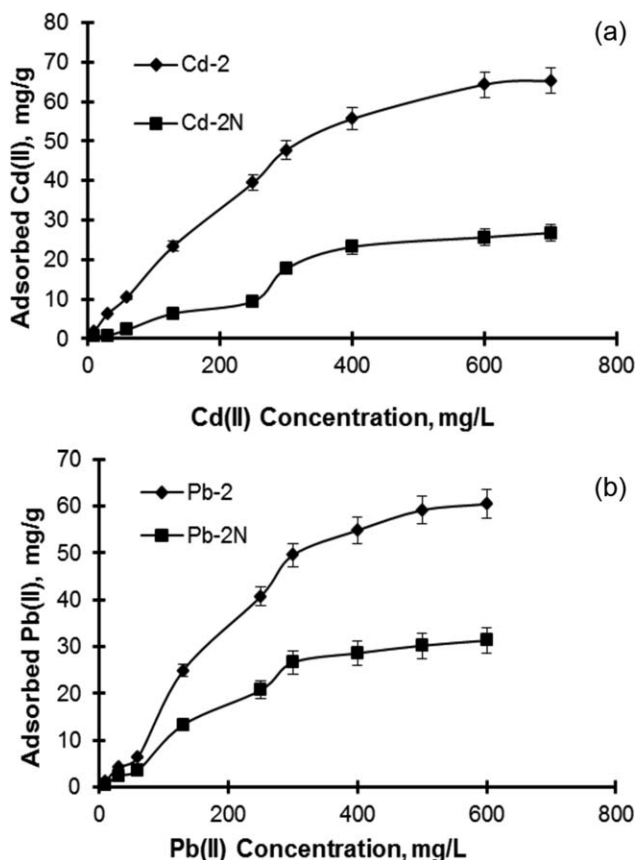
ties (mg/g) at time  $t$  and at equilibrium (Supporting Information Figures SMF-6 and 7). The consistency of the results with second-order model proved that controlling step of process was because of chemical recognition of ions, a chemically controlled reaction without any diffusion restriction for all cryogels samples and for both heavy metal ions. These results proved structural advantages of cryogels and the specificity because of imprinting.

#### Selectivity Studies

In order to compare ion adsorption/recognition capability of ion-imprinted and nonimprinted cryogels, those cryogels were interacted with aqueous template heavy metal ion solution in different concentrations. As seen in Figure 6, the adsorption capacities of both ion-imprinted cryogels were higher than that of their nonimprinted forms. These results depended on the oriented-polymerization of functional monomer around coordination sphere of template heavy metal ions. On the other hand, functional monomers were randomly polymerized in case of nonimprinted ones, which caused multi-point interaction with heavy metal ions. These disordered interactions caused a decrease in adsorption capacities.

Distribution coefficients,  $K_d$ , of Cd(II) ion-imprinted and non-imprinted cryogels were calculated as 0.034 and 0.016 L/g, respectively, which results in a relative selectivity coefficient,  $K'$  of 2.69. The corresponding values for Pb(II) ion-imprinted cryogels were 0.04 and 0.019 L/g which gives the relative selectivity coefficient of 2.1.

In order to show selectivity of both ion-imprinted cryogels against templated ions Cd(II) or Pb(II) with respect to potential competitor heavy metal ions including Pb(II), Cu(II), and Zn(II), heavy metal ion adsorption studies were performed on artificial mixed aqueous solutions of respective heavy metal ions. The results were summarized in following combined table (Table II). As seen in the table, both ion-imprinted cryogels showed lower adsorption capacities for template ion [Cd(II) or Pb(II)] under competition. Cd(II) adsorption capacity decreased from 22.68 to 13.91 mg/g, while Pb(II) adsorption capacity decreased from 28.58 to 17.54 mg/g. The decrease was because of the antagonistic effect of competitor heavy metal ions and



**Figure 6.** Comparison of adsorption capacities of (a) Cd(II) ion-imprinted and nonimprinted cryogels and (b) Pb(II) ion-imprinted and nonimprinted cryogels. pH: 5.5; incubation period: 120 min; and  $T$ : 25°C.

revealed the presence of a competition between heavy metal ions for imprinted cavities.

The distribution ( $K_d$ ) and selectivity ( $k$ ) coefficients of both ion-imprinted cryogels for template heavy metal ions with respect to competitors were also calculated. For Cd(II) ion-imprinted cryogels,  $K_d$  values were calculated as 0.069, 0.010, 0.009, and 0.011 L/g for Cd(II), Cu(II), Pb(II), and Zn(II), respectively. According to these results,  $k$  values were calculated as 6.90, 7.67, and 6.27 for Cd(II):Cu(II), Cd(II):Pb(II), and Cd(II):Zn(II) couples. Meanwhile,  $K_d$  values for Pb(II) ion-imprinted cryogels were calculated as 0.096, 0.016, 0.087 mg/g, and 0.01 for Pb(II), Cu(II), Cd(II), and Zn(II) ions, respectively. Similarly,  $k$  values for these cryogels were calculated as 6.00,

11.03, and 9.60 for Pb(II):Cu(II), Pb(II):Cd(II), and Pb(II):Zn(II) couples, respectively. It is clearly seen that ion-imprinting process has resulted in gaining high selectivity to template heavy metal ions with respect to competitor ions although some antagonistic effect was incurred. In addition, ion-imprinted cryogels showed high selectivity for template ions [Cd(II) or Pb(II)] with respect to the competitors [Cu(II), Zn(II) and Pb(II) or Cd(II)] with selectivity coefficient being in the range of 6.00–11.03. The highest relative selectivity values reported for Cd(II) and Pb(II) IIPs were because of the difference of ionic radii and Lewis acid characters for Pb(II) and Cd(II) ions.

#### Selective Heavy Metal Removal and Specific Recycling from Synthetic Wastewater

In addition to Pb(II) and Cd(II) imprinted ones, Cu(II) ion-imprinted cryogels were synthesized as well (data not given here). A solution containing Cu(II), Cd(II), Pb(II), Zn(II), Ni(II), Ca(II), Co(II), and Fe(III) ions was simultaneously incubated with these three ion-imprinted cryogels (Table III) cut in different shapes to differentiate them.

The selectivity of IIPs for target metal ions was obvious. The decrease in adsorption capacity compared to values for singular solutions was because of antagonistic effects on template ions caused by the competition between template ion and others. The highest adsorption capacity was achieved with respect to template heavy metal ions for each cryogel system. The highest adsorption capacities were determined as 8.70 mg/g for Cu(II) ions with Cu(II) ion-imprinted cryogels, 9.30 mg/g for Cd(II) ions with Cd(II) ion-imprinted cryogels, and 12.40 mg/g for Pb(II) ions with Pb(II) ion-imprinted cryogels. These results indicated that ion-imprinted cryogels have ability to recognize the corresponding heavy metal ions and could be used for selective removal and specific recycling of heavy metal ions even if adsorption process was conducted under competitive conditions like in synthetic wastewater.

#### Desorption and Reuse

Following the contact time (3 h) with desorption agent (EDTA), the desorption ratio was over 96% in all cases. After 3<sup>rd</sup> adsorption–desorption cycles, the adsorption capacities did not change significantly. The results revealed two important features of ion-imprinted cryogels. First, it is possible to create specific cavities into cryogels for selective heavy metal ion adsorption from wastewater even at high flow rate without any diffusion and clogging problems although potential competitor ions were present. Second, specific heavy metal enrichment and recycling are possible with those ion-imprinted cryogels.

**Table II.** Competitive Adsorption of Heavy Metal Ions by Cd(II) and Pb(II) Ion-imprinted Cryogel from Multi-Metal Ions Solution

Ion	$Q$ (mg/g) Cd(II) IIC	$K_d$ (mL/mg)	$k$	$Q$ (mg/g) Pb(II) IIC	$K_d$ (mL/mg)	$k'$
Cd(II)	13.91	0.069	–	17.94	0.096	–
Cu(II)	2.40	0.010	6.90	2.78	0.016	6.00
Pb(II)	2.20	0.009	7.67	2.10	0.0087	11.03
Zn(II)	2.62	0.011	6.27	2.40	0.01	9.60

Concentration of each metal ion, 100 mg/L; pH 5.5; and  $T$ : 25°C. Noncompetitive adsorption capacity for template Pb(II) ion: 28.38 mg/g.

**Table III.** Simultaneous Selective Removal and Specific Recycling of Heavy Metal Ions by Pb(II), Cu(II), and Cd(II) Ion-imprinted Cryogels from Synthetic Wastewater

Ions	Adsorption capacity (mg/g)			
	Total	Cu-2	Cd-2	Pb-2
Pb(II)	18.35	2.30	2.94	12.4
Cd(II)	13.74	1.80	9.30	1.50
Cu(II)	11.58	8.70	1.60	1.10
Zn(II)	3.10	0.60	1.40	0.30
Co(II)	1.96	0.90	0.40	0.30
Ca(II)	2.20	0.60	1.10	0.07
Ni(II)	1.74	0.30	0.70	0.50
Fe(III)	1.38	0.40	0.10	0.60
Total	54.05	15.6	17.54	16.77

### Comparison with Literature Studies

In the literature, different nonimprinted and imprinted polymeric adsorbents (organic-inorganic hybrid polymers, composite cryogels, amino acid containing inorganic matrix, etc.) with a wide range of adsorption capacities for Cd(II) and Pb(II) ions have been reported. We here tried to compile some of relevant studies while reporting adsorption capacities in mg/g unit as well as mentioning original units in brackets. Elmahadi and Greenway used amino acid containing inorganic matrix (cysteine immobilized onto silanized-controlled pore glass) for pre-concentration of heavy metals including Cd(II) and Pb(II). The adsorption capacities were 1397.8 mg/g (12.48 mmol/g) resin for Cd(II), and 1254.4 mg/g (6.06 mmol/g) for Pb(II).<sup>25</sup> Cadmium (II)-imprinted, thiol functionalized silica gel sorbent was prepared by a surface imprinting technique in combination with a sol-gel process, giving a maximum static capacity of 31.8 mg/g (284  $\mu\text{mol/g}$ ) for Cd(II) ions.<sup>26</sup> Tekin *et al.* used composite cryogels containing imidazole group for removal of heavy metal ions such as Pb(II), Cd(II), Zn(II), and Cu(II) from water.<sup>27</sup> The average adsorption capacity values for lead and cadmium ions were 7.62 mg/g (7620  $\mu\text{g/g}$ ) and 5.80 mg/g (5800  $\mu\text{g/g}$ ). Our group synthesized magnetic, ethylene glycol dimethacrylate-co-vinyl imidazole beads by suspension polymerization for removal of heavy metal ions, the capacities being 84.2 mg/g for Cd(II), and 134.5 mg/g for Pb(II).<sup>28</sup> The adsorption capacity was 89.0 mg/g (0.795 mmol/g) at pH: 5.0 at 45°C with equilibrium time 10 h when Cd(II)-imprinted chitosan resin was used.<sup>29</sup> Özkütük *et al.* used Cd(II) complexed chitosan, cross-linked by epichlorohydrin as single imprinted polymer, and polymeric beads synthesized by Cd(II) complexed chitosan with 3-mercaptopropyltrimethoxysilane, cross-linked with tetra-ethoxysilane as the double imprinted polymer for selective recognition of Cd(II) ions in aqueous media.<sup>30</sup> The adsorption capacities were 342 and 172 mg/g for single and double imprinted polymers, respectively. In another study,<sup>31</sup> 64 mg/g capacity was determined for Cd(II) ion with nanosized Cd(II)-imprinted polymer, synthesized by using 4-vinyl pyridine as functional monomer, neocuproine as ligand through precipitation polymerization in acetonitrile as solvent. The radical

initiator was AIBN, and the cross-linker was EGDMA. Free radical polymerization of alginate and NNMBBA-cross-linked polyacrylamide in presence of potassium persulfate (initiator) resulted in ion-imprinted polymer network for Cd(II) ion with a capacity of 48.7 mg/g (0.87 meq/g).<sup>32</sup> 4-vinyl pyridine and acrylate modified spirulina platensis as functional monomers, EGDMA as cross-linker, AIBN (initiator), Fe<sub>3</sub>O<sub>4</sub>, and Pb(II) and Cd(II) as double templates were used to prepare magnetic Pb(II) and Cd(II) ion-imprinted microspheres.<sup>33</sup> The adsorption capacities were 108 and 56 mg/g for lead and cadmium ions, respectively. Two functional monomers (1,12-dodecanediol-*o*, *o'*-diphenylphosphonic acid and 4-vinylpyridine) were used to prepare lead ion-imprinted microbeads by w/o/w polymerization method.<sup>34</sup> The adsorption capacities for cadmium ions were determined as 116.9 and 0.0038 mg/g (3.79  $\mu\text{g/g}$ ) for imprinted poly(1-allyl-2-thiourea-co-ethylene glycol dimethacrylate) and poly(4-vinylpyridine-co-ethylene glycol dimethacrylate) particles, respectively, meanwhile the selectivity factors were nearly 2.3 when lead, cobalt, and nickel ions were treated as competitors.<sup>35</sup> Tabaklı *et al.* developed Cd(II)-imprinted cryogels through particles assisted imprinting approach and reported maximum adsorption capacity as 0.0322 mg/g (32.15  $\mu\text{g/g}$ ) cryogel.<sup>36</sup> As a result, the capacity values reported in this study are comparable to or higher than the values reported in literature.

### CONCLUSIONS

The selective recovery of industrially important and valuable metal ions from wastewater is one of the major concerns for scientific community as well as removing of toxic heavy metal ions from water samples. In this respect, we focused our attention to develop different ion-imprinted cryogels in different physical features, size, shape and magnetic characters, etc. with different affinity against targeted heavy metal ions, Cd(II), Pb(II), and Cu(II), respectively. Herein, we aimed to create a synergy via combining cryogel-based adsorbents with ion-imprinting approach to get excellent adsorbents for selective recycling of template ions. The results emphasized that proposed strategy is very promising and suitable to develop smart adsorbents and the IICs developed here could be used as alternative adsorbent for selective heavy metal ion removal besides recycling of economically important metals.

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