Synthesis and Characterization of a Molecularly Imprinted Polymer for Pb^{2+} Uptake Using 2-vinylpyridine as the Complexing Monomer

(Sintesis dan Pencirian Polimer Cetak Molekul untuk Pengambilan Pb^{2+} Menggunakan 2-vinilpiridina Sebagai Monomer Pengkompleks)

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ABSTRACT

Molecularly imprinted polymer (MIP) particles for selective extraction of Pb^{2+} from aqueous media were prepared using non-covalent molecular imprinting methods. 2-vinylpyridine was chosen as the complexing monomer. The imprinted polymer was synthesised by radical polymerisation. The template (Pb^{2+}) was removed by leaching with 0.1 M HCl. The polymer particles (imprinted and non-imprinted) were characterised by IR spectroscopy. The effect of different parameters such as pH, kinetic, adsorption isotherm and selectivity were evaluated. The maximum adsorption capacity is 150 µg Pb^{2+}/mg MIP. The adsorption efficiently occurred at pH 6. The selectivity coefficients of the imprinted polymer particles for Pb^{2+}/Zn^{2+} and Pb^{2+}/Al^{3+} were 13.55 and 1.71, respectively.

Keywords: Ion imprinting; metal extraction; molecular recognition; Pb^{2+} removal

ABSTRAK

Partikel polimer cetak molekul (MIP) untuk pengekstrakan selektif Pb^{2+} daripada media akuas telah disediakan menggunakan kaedah cetakan molekul bukan kovalen. 2-vinilpiridina telah dipilih sebagai monomer pengkompleks. Polimer cetak telah disintesis menggunakan pempolimeran radikal. Templat (Pb^{2+}) telah disingkirkan menerusi peluturan dengan 0.1 M HCl. Partikel polimer (cetakan dan bukan cetakan) telah dibuat pencirian menggunakan spektroskopi IR. Kesan bagi pelbagai parameter seperti pH, kinetik, isotem jerapan dan selektiviti telah dinilaikan. Kebolehan jerapan maksimum adalah 150 µg Pb^{2+}/mg MIP. Jerapan adalah cekap pada pH 6. Pekali selektiviti bagi partikel polimer cetak bagi Pb^{2+}/Zn^{2+} dan Pb^{2+}/Al^{3+} adalah masing-masing, 13.55 dan 1.71.

Kata kunci: Cetakan ion; pengecaman molekul; pengekstrakan logam; penyingkiran Pb^{2+}

INTRODUCTION

Pb is a toxic metal of continuing occupational and environmental concern with a wide variety of adverse effect. Pb is a general protoplasmic poison that is cumulative, slow acting and subtle, and produces a variety of symptoms. Like other heavy metals, it has an affinity for sulfur. Though it exerts much of its activity through sulfohydryl inhibition, Pb also interacts with carboxyl and phosphoryl groups. The element interferes with heme synthesis (Elinde & Friberg 1980).

Numerous studies have been carried out on ion imprinting polymers involving various metal ions (Andac et al. 2004; Araki et al. 2005; Birlik et al. 2007; Khajeh et al. 2007; Nishide et al. 1977; Say et al. 2003; Yavuz et al. 2005) but no studies concerning removal of Pb^{2+} were reported in the literature.

Imprinted polymerisation is a process in which monomers are polymerised in a solution containing the specific analyte producing imprinted polymer which is selective towards the target analyte. The selectivity of an ion imprinted polymer is based on the coordination geometry and coordination number of the ions also on their charges and sizes (Mayes & Whitcombe 2005).

The principles of molecular imprinting are as follows: (1) specific complex formed based on non-covalent bonding interactions between template molecule and polymerisable functional monomer in an apolar and aprotic solvent before polymerisation by assembling the functional monomers around the template molecule; (2) yield of a rigid and porous copolymer in the presence of cross linker and initiator and (3) the distinct cavities remain in the copolymer with the removal of the target template complementary to the template molecule in size, shape and functionality.

The ability to selectively recognise a target molecule in a pool of similar molecules is essential to biological and chemical processes. Molecular recognition is an event that occurs everywhere in nature. It occurs when two molecules are both geometrically and chemically complementary to each other using non-covalent forces including hydrogen bonds, electrostatic interactions, hydrophobic interactions and weak metal coordination. Imprinted polymers are

highly cross-linked molecules bearing 'tailor-made' binding sites for target analyte. Imprinted polymers are easy to prepare, stable, inexpensive and can be reused. There are many methods for the preparation of MIP, such as bulk polymerisation (Milojkovic et al. 1997), suspension polymerisation (Zhang et al. 2003), emulsion polymerisation, two step polymerisation (Moral & Mayes 2004), electropolymerisation (Blanco-Lopez et al. 2003) and precipitation polymerisation (Andac et al. 2007). Among them, bulk polymerisation appears to be the simplest and produced a bulk polymer which can be crushed and sieved to get uniform size particles.

In this study, ion imprinted polymer were used for Pb^{2+} uptake in aqueous environment. 2-vinylpyridine was chosen as the complexing monomer. The imprinted polymer was prepared by bulk polymerisation method. The template (Pb^{2+}) was removed using 0.1 M HCl. After removal of Pb^{2+}, the imprinted polymer was evaluated for the binding capability towards Pb^{2+} in aqueous environment and compared with non imprinted polymer. Study on different factors such as pH, kinetic, adsorption isotherm and selectivity were also carried out. Study on the interaction between the template (Pb^{2+}) and the polymer was carried out using FTIR.

EXPERIMENTAL DETAILS

MATERIALS

2-vinylpyridine, Ethylene glycol dimethacrylate acid (EGDMA) and Benzoylperoxide (BPO) were obtained from Fluka (Switzerland). All other chemicals were of reagent grade and purchased from Merck (Germany). Dionised water was used throughout the experiment.

PREPARATION OF Pb^{2+}- IMPRINTED POLYMER

Radical polymerisation was used for the preparation of the Pb^{2+}- imprinted polymer $Pb(NO_3)_2$ (1 mmol) was dissolved in a mixture of water:ethanol (1:3). 4.0 mmol of 2-vinylpyridine was added followed by 20.0 mmol of EGDMA. After that, 50 mg of BPO was added and the mixture was bubbled with N_2 for 10 minutes. Polymerisation was conducted for 24 hours in water bath at 70°C with constant stirring. The obtained imprinted polymer was washed with ethanol and water to remove unreacted monomer or diluent. The polymer was also crushed, ground and sieved prior to storage. Non-imprinted polymers (NIP) were made with the same procedure except with the absence of the template molecules.

To remove the templates, the MIP were treated with 0.1 M HCl and the excess amount of HCl were washed by methanol. This procedure was repeated several times until the template (Pb^{2+}) could not be detected in the filtrate using ICPAES.

ADSORPTION STUDIES

Adsorption of Pb^{2+} ions from aqueous solutions was investigated in batch experiments. The effects of the initial Pb^{2+} ion concentration, pH of the medium on the adsorption rate and adsorption capacity were studied. The suspensions were brought to the desired pH by adding sodium hydroxide and nitric acid. The concentration of the metal ions in the aqueous phases after the desired treatment periods was measured by using an ICPAES. The experiments were performed in replicates of three. Binding capacity of the imprinted polymer towards Pb^{2+} was calculated from the following equation:

$$\text{Binding capacity} = \frac{C_A - C_B}{C_A} \times 100, \qquad (1)$$

where C_A and C_B are the concentration of Pb^{2+} ion before and after extraction in the solution, respectively.

CHARACTERIZATION OF THE IMPRINTED POLYMER

FTIR spectra of imprinted and non-imprinted polymer were obtained by using FTIR spectrophotometer. The polymer particles (about 0.1 g) were thoroughly mixed with KBr and pressed into a pellet and FTIR spectrum was recorded. The average size was determined by using particle size analyser (Nanophox).

SELECTIVITY EXPERIMENT

In order to show Pb^{2+} specificity of the imprinted polymer, competitive adsorptions of other metal ions (Zn(II) and Al(III)) were also studied. Twenty five milliliter of 20 ppm of each metal ion were poured into a 50 mL centrifuge tube (10 mg). The imprinted polymer (10 mg) was added and adjusted to pH 6 by adding 0.01M NaOH and 0.1M nitric acid. The mixture was centrifuged for 1 h at 130 rpm followed by filtration. The remaining metal ions in the filtrate were measured by using ICPAES. Selectivity of the imprinted polymer over the interferent metal ion can be evaluated by using the following equation (Andac et al. 2004):

$$K_d = \{(C_i - C_f)/C_f\} \{V/m\}, \qquad (2)$$

where K_d is selectivity coefficient, C_i is the initial concentration of metal ion, C_f is the final concentration of metal ion, V is the volume used and M is the weight of MIP.

The selectivity for the binding of a metal ion in the presence of interferent metal can be estimated by using the following equation:

$$k = K_{\text{template metal}}/K_{\text{interferent metal}} \qquad (3)$$

where k is relative selectivity coefficient.

RESULTS AND DISCUSSION

CHARACTERISATION OF THE IMPRINTED POLYMER

Cross linked imprinted and non-imprinted particles were spherical in shape with a size range 1.5-1.7 μm in diameter as analysed by particle size analyser. FTIR spectra (Figure 1) of imprinted and non-imprinted polymer were recorded by using KBr pellet method. No band is present in the region of 1648-1638 cm^{-1} indicating the absence of vinyl groups in the polymers. This confirmed the complete polymerization of vinyl pyridine. FTIR spectrum for Pb^{2+}–imprinted polymer has a strong characteristic stretching of around 3400 cm^{-1} indicating an electrostatic interaction between Pb^{2+} and pyridine group.

EFFECT OF pH

Metal ion adsorption onto specific adsorbents is pH dependent. The Pb^{2+}-imprinted polymer exhibited a low affinity in acidic concentrations (pH < 5.0) and a high affinity at pH 7.0 (Figure 2). Ion imprinted beads for molecular recognition based mercury removal from human serum also exhibited a low affinity in acidic concentrations (pH < 5.0) and a high affinity at pH 7.0 (Andac et al. 2007). In acidic pH, the lower adsorption proved that the H$^+$ ion can be considered as competitor of Pb^{2+}cations since the nitrogen in pyridine group in the MIP which is responsible for binding site of Pb^{2+} are predominantly protonated. At high pH values, the adsorption of $Pb^{2+}$is high, since the protonation process decreases and the number of negatively charged sites increases. Testing was not carried out at pH higher than 7.0 due to formation of precipitate between a high concentration of hydroxide ion and Pb^{2+} ion.

EFFECT OF TIME

Figure 3 shows the time dependence of the adsorption capacities of Pb^{2+} ions towards imprinted polymer as a function of time. As seen here, Pb^{2+} adsorption increased with the time during the first 20 min and then levels off as equilibrium was most probably due to high complexation between Pb^{2+} ions and Pb^{2+}cavities in the imprint polymer structure. The removal of the template (Pb^{2+}) from the
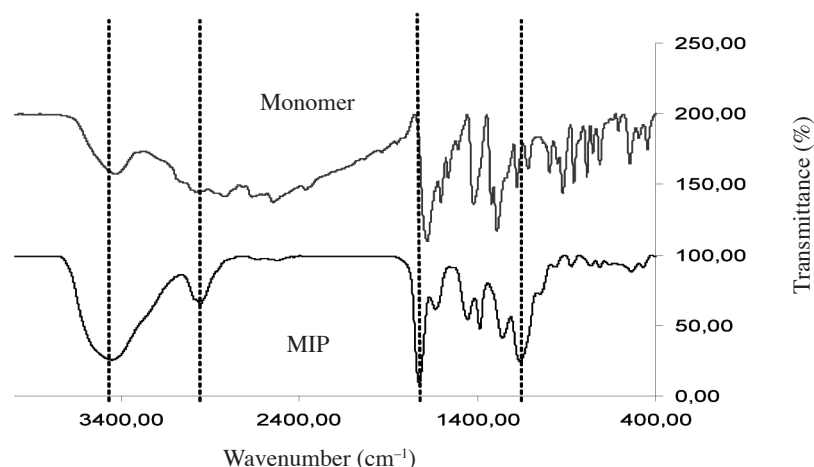

FIGURE 1. FTIR spectra for Pb^{2+} -imprinted polymer (MIP) and monomer (2-vinylpyridine
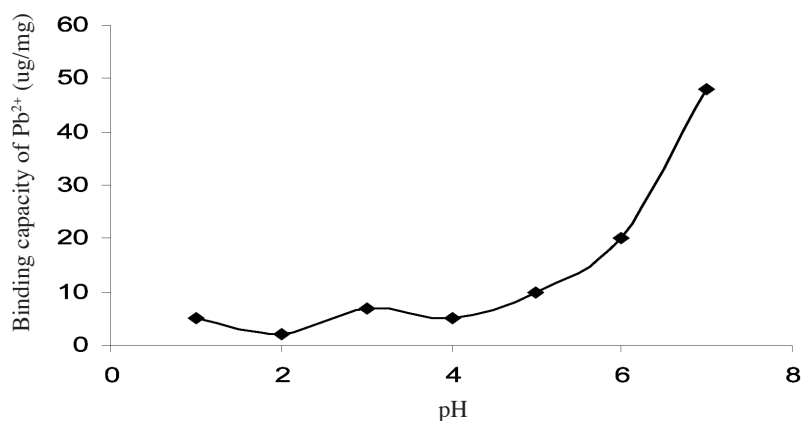

FIGURE 2. Effect of pH on Pb^{2+} sorption; initial concentration 50 ppm, sorption time 60 min.

polymeric matrix leaves cavities of complementary size, shape and chemical functionality to the template. Maximum adsorption capacity is 150 μg Pb^{2+}/mg MIP.

EFFECTS OF INITIAL CONCENTRATION OF Pb^{2+} ION

Figure 4 shows the dependence of the initial concentration of Pb^{2+}on the adsorbed amount of Pb^{2+} ions into the imprinted polymer. The adsorption values increased with increasing concentration of Pb^{2+} ions, and saturation was achieved at Pb^{2+} ion initial concentration of 150 μg/mL. The level off represents saturation of the active binding cavities on the imprinted polymer.

The equilibrium isotherm plays an important role in predictive modeling for analysis and design of adsorption systems. The adsorption isotherm is also an invaluable tool for the theoretical evaluation and interpretation of thermodynamic parameters. An adsorption isotherm is used to characterise the interactions of each molecule with adsorbents. This provides a relationship between the concentration of the molecules in the solution and the amount of ion adsorbed on the solid phase when the two phases are at equilibrium. The Langmuir adsorption model assumes that the molecules are adsorbed at a fixed number of well-defined sites, each of which is capable of holding only one molecule. These sites are also assumed to be energetically equivalent and distant from each other so that there are no interactions between molecules adsorbed on adjacent sites (B"uy"uktiryaki et al. 2007).

During the batch experiments, adsorption isotherms were used to evaluate adsorption properties. For the systems considered, the Langmuir model was found to be applicable in interpreting Pb^{2+} ion adsorption on the Pb^{2+}-imprinted polymer. The Langmuir isotherm is based on the assumption that: (1) the solid surface presents a finite number of identical sites which are energetically uniform; (2) there is no interaction between sorbed species, meaning that the amount of sorbate molecules sorbed has no influence on sorption rate; (3) monolayer is formed when the solid surface reaches saturation.

The Langmuir model is probably the best known and most widely applied sorption isotherm. It has produced good agreement with a wide variety of experiment data and may be represented as follows (Liu et al. 2004):

$$q_e = \frac{q_m \, b \, C_e}{1 + b \, C_e} . \tag{4}$$

The above equation can be rearranged to the following linear form:
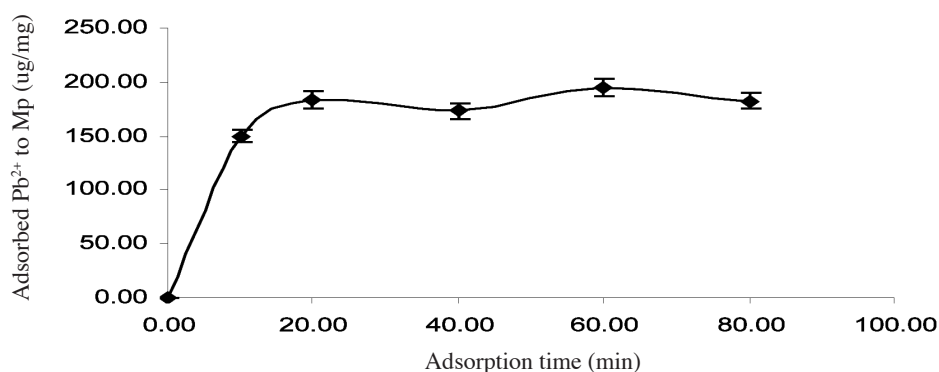

FIGURE 3. Time dependence of the adsorption capacities of Pb^{2+} towards imprinted polymer; Pb^{2+} concentration: 200 μg/ml.
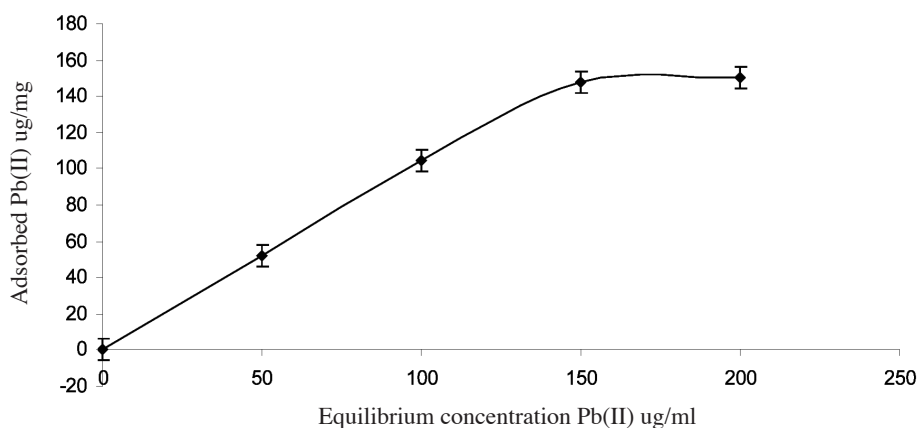

FIGURE 4. Adsorption isotherm of Pb^{2+}-imprinted polymer

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m}, \qquad (5)$$

where C_e is the equilibrium concentration, q_e the amount of Pb^{2+} adsorbed at equilibrium, q_m is amount of Pb^{2+} adsorbed for a complete monolayer, b is a constant related to the energy or net enthalpy of sorption. The sorption data were analysed using the linear form Eq. (5) of the Langmuir isotherm. The plots of specific sorption, C_e/q_e, against the equilibrium concentration, C_e, for Pb^{2+}-imprinted polymer are shown in Figure 5.

The Langmuir adsorption model can be applied in this affinity system. The maximum adsorption capacity (Qmax) data for the adsorption of Pb^{2+} ions were obtained from experimental data. The correlation coefficient (R^2) is 0.9931. It can be confirmed that the Pb^{2+} sorption by Pb^{2+}-imprinted polymer follow the Langmuir Model with the maximum sorption capacity of 150 μg Pb^{2+}/mg MIP.

In order to examine the controlling mechanism of adsorption process such as mass transfer and chemical reaction, kinetic models were used to test experimental data. The kinetic models (pseudo first order and second order equations) can be used assuming that the measured concentrations are equal to adsorbent surface concentration. The first order rate equation of Lagergren is one the most widely used for the adsorption of solute from a liquid solution (Liu et al. 2004).

Kinetics in adsorption depends on the surface area of particles. Kinetics is the description of reaction rates. The order of the reaction defines the dependence of reaction rates on the concentration of reacting species. Order is determined only empirically but not related to the stoichiometry of the reaction. Rather, it is governed by the mechanism of the process, that is, by the number of species that collided for the reaction to occur. Besides that, the kinetics is also the speed with which adsorption takes place and determines the portion of the equilibrium capacity that may be utilised in a practical dynamic situation. Overall adsorption rates may be influenced by a change in solvent nature and content, particle size and temperature. Adsorption rates are most rapid in water systems and become increasingly slow with less polar solvents. The kinetics of adsorption reactions also depends on the type of functional group and its concentration. The kind of functional group and its degree of dissociation under a given set of condition greatly affects adsorption rates. A high degree of substitution of the functional groups on the inert polymer matrix directly enhances overall reaction rates (Allen et al. 2004).

The sorption kinetics data of Pb^{2+} were analysed using the Langergen first order rate model:

$$\frac{dq_t}{d_t} = k1 \, (q_e - q) \qquad (6)$$

where k_1 (min^{-1}) is the rate constant of pseudo-first-order sorption, q_t denotes the amount of Pb^{2+} adsorption at time, t (min) and q_e denotes the amount of Pb^{2+} adsorption at equilibrium. After definite integration and applying the initial conditions $q_t = 0 \; at \; t = 0$ and $q_t = q_t \; at \; t = t$, Eq. (6) becomes

$$\ln(q_e - q_t) = ln \, (q_e) - k_1 t \, . \qquad (7)$$

In addition, a pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the form:

$$\frac{dq_t}{dt} = k_2 \, (q_e \text{-} q_t)^2 \qquad (8)$$

where k_2 is the rate constant of pseudo-second-order sorption. Integrating Eq. 8 and applying the initial conditions,

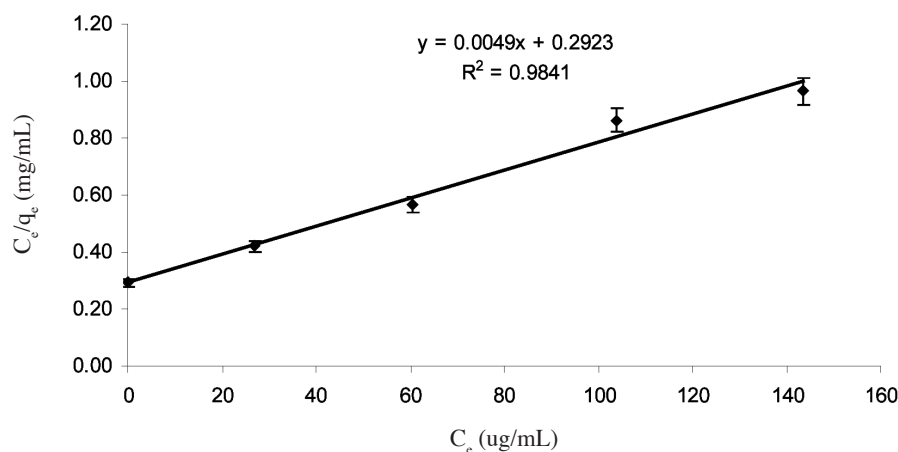$$\frac{1}{(q_e \text{-} q_t)} = \frac{1}{q_e} + k_2 t \qquad (9)$$

FIGURE 5. Langmuir adsorption isotherm of Pb^{2+}-imprinted polymer.

or equivalently

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (10)$$

The plot t/q versus t should give a straight line if second order kinetic is applicable and the values q_e and k_2 can be calculated from the slope and the intercept of the plot, respectively.

The plots of ln $(q_e$-$q)$ versus t is shown in Figure 6. The data does not fall on straight lines and having a low correlation coefficient indicating that the first order kinetic

model is less appropriate. In addition the q_e estimated by this model differs substantially from those measured experimentally as shown in Table 1. On the other hand the plot of t/q against t was high correlation coefficient (Figure 7). The data in Table 1 shown that the q_e values calculated were similar with the experimental values. This shows that the Pb^{2+} adsorption using Pb^{2+}- imprinted polymer is second order kinetics reaction.

SELECTIVITY EXPERIMENTS

Competitive adsorption of Pb^{2+}/Zn^{2+} and Pb^{2+}/Al^{3+} were also studied in a batch system. The ionic radius of Zn^{2+} (74 pm) is
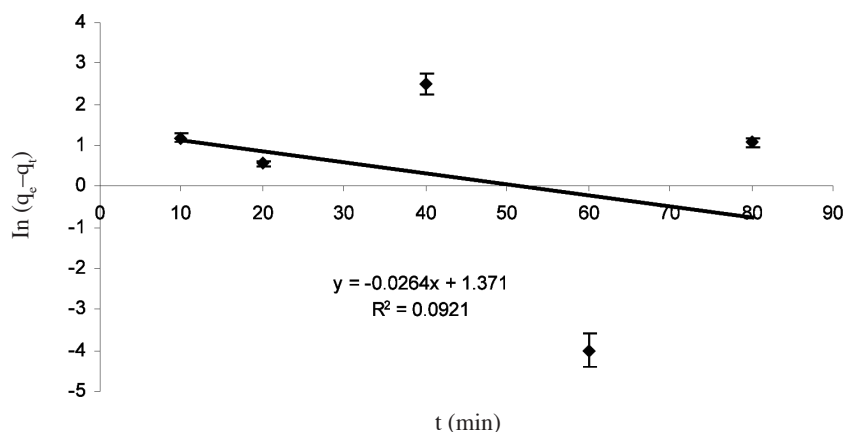

FIGURE 6. Seudo first order kinetic of the experimental data for Pb^{2+}-imprinted polymer

TABLE 1. Kinetic constants for the Pb^{2+}-imprinted polymer

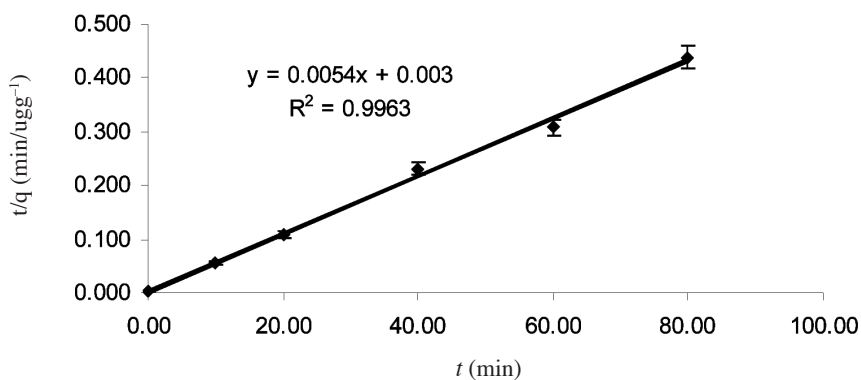| Experimental q_e (μg/mg) = 181.90		
First Order		
R^2	q_e (μg/mg)	k
0.0921	3.94	-0.0264
Second order		
R^2	q_e (μg/mg)	k
0.9942	185.185	1143118.42

FIGURE 7. Second order kinetic of the experimental data for Pb^{2+}-imprinted polymer

smaller than Pb^{2+} (119 pm) whereas Al^{3+} has larger oxidation number compared to Pb^{2+}. Table 2 summarizes K_d and k values for Zn^{2+} and Al^{3+} with respect to Pb^{2+}. K_d values for the Pb^{2+}–imprinted polymer shows an increase in K_d for Pb^{2+} while K_d decrease for Zn^{2+} and Al^{3+}. The relative selectivity coefficient (k) is an indicator to express an adsorption affinity of recognition sites to Pb^{2+}. The k value for Pb^{2+}/Zn^{2+} and Pb^{2+}/Al^{3+} are 13.55 and 1.71, respectively.

TABLE 2. K_d and k values of Zn^{2+} and Al^{3+} with respect with to Pb^{2+}

Metal ion	K_d	k
Pb^{2+}	4.44	-
Zn^{2+}	0.33	13.55
Al^{3+}	2.59	1.71

CONCLUSION

Molecularly imprinted beads spherical in shape were prepared by radical polymerization. The average size of the beads was controlled to be between 1.5 and 1.7 μm in diameter. The adsorption was relatively fast and the time required to reach equilibrium conditions was about 20 min. The maximum adsorption capacity for Pb^{2+} ions was 150 μg/mg dry weight of imprinted polymer. The fast adsorption equilibrium is most probably due to high complexation and geometric affinity between Pb^{2+} ions and Pb^{2+} cavities in the beads structure. The adsorption values increased with increasing concentration of Pb^{2+} ions, and a saturation value is achieved at ion concentration of 150 μg/mL, which represents saturation of the active binding cavities on the Pb^{2+}-imprinted polymer. Langmuir model was found to be applicable in interpreting Pb^{2+} ion adsorption on the Pb^{2+}-imprinted polymer. Results also indicate that the Pb^{2+}-imprinted polymer system was described by the pseudo-second-order kinetic model.

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