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Synthesis and Evaluation of a Molecularly Imprinted Polymer for Pb(II) Ion Uptake

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ABSTRACT

A molecularly imprinted polymer (MIP), with the ability to bind Pb(II) ion, was prepared using the non-covalent molecular imprinting methods and evaluated as a sorbent for the Pb(II) ion uptake. 4-vinylbenzoic acid was chosen as the complexing monomer. The imprinted polymer was synthesized by radical polymerization. The template (Pb(II) ions) was removed using 0.1 M HCl. As a result, the efficient adsorption was found to occur at pH 7. The result also showed the applicability of the Langmuir model for the sorption, with the maximum sorption capacity of 204.08 μg/mg.

Keywords: Ion imprinting, molecular recognition, Pb(II) removal, metal extraction

INTRODUCTION

Imprinted polymerization is a process in which monomers are polymerized in a solution containing the specific analyte to produce imprinted polymer, which is selective towards the target analyte. Imprinted polymers are highly cross-linked molecules, which are bearing 'tailor-made' binding sites for the target analyte. Imprinted polymers are easy to prepare, stable, inexpensive and can be reused. The selection of an ion imprinted polymer was done based on the coordination geometry and coordination number of the ions, as well as their charges and sizes (Mayes and Whitcombe, 2005). A number of studies have been carried out on ion imprinting polymers involving various metal ions (Ebru *et al.*, 2006; Handan *et al.*, 2005; Hiroyuki *et al.*, 1977; Mostafa *et al.*, 2007; Muge *et al.*, 2004; Ridvan *et al.*, 2007, Kosuke *et al.*, 2005), but no studies have so far reported on the removal of Pb(II) in the literature.

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

In this study, ion imprinted polymer was used to study on the Pb^{2+} uptake in aqueous environment. For this purpose, 4-vinylbenzoic acid was chosen as the complexing monomer. The imprinted polymer was synthesized by radical polymerization. The template (Pb(II) ions) was removed using 0.1 M HCl. After removing Pb^{2+}, the imprint polymer was evaluated for its binding capability towards Pb^{2+} in the aqueous environment, and compared with the non-imprinted polymer. A study on the pH for the binding to occur was also carried out.

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Meanwhile, the study on the interaction between the template (Pb^{2+}) and the monomer was carried out using the FTIR.

EXPERIMENTAL

Materials

4-Vinylbenzoic acid (4VBA), 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). Deionised water was used throughout the experiment.

(a) The preparation of Pb^{2+}- imprinted polymer

Radical polymerization was used for the preparation of the Pb^{2+}- imprinted polymer. For this purpose, 1.00 mmol of $Pb(NO_3)_2$ was dissolved in a mixture of water:ethanol (1:3), and 4.0 mmol of 4VBA was added, and this was 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. Polymerization 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 diluents. The polymer was also crushed, ground and sieved prior to storage.

(b) Adsorption studies

The adsorption of Pb(II) ions from the aqueous solutions was investigated in the batch experiments. The effects of the initial Pb(II) ion concentration, pH of the medium on the adsorption rate, and the 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 using an ICP-AES. The experiments were performed in three replicates.

The adsorption values were calculated as the differences in the Pb(II) ion concentration of the pre- and post-adsorption solutions divided by the weight of the dry imprinted polymer. The adsorbed Pb(II) ions were desorbed by treating them with HCl solution. The Pb(II) adsorbed imprinted polymer were placed in the desorption medium and stirred continuously at 600 rpm at room temperature for 2 hours. The final Pb(II) ion concentration, in the aqueous phase, was determined by the ICP-AES.

(c) The characterization of the imprinted polymer

The FTIR spectra of 4VBA and the imprinted polymer were obtained using the FTIR spectrophotometer. The imprinted polymer particles (about 0.1 g) were thoroughly mixed with KBr, pressed into a pellet and the FTIR spectrum was recorded.

RESULTS AND DISCUSSION

The Characterization of the Imprinted Polymer

Cross-linked imprinted and non-imprinted particles were spherical in shape, with a size ranged from 63-90 μm in diameter. The FTIR spectrum (*Fig. 1*) of 4VBA has the characteristic of carbonyl band at 1724 cm^{-1} and weak O-H stretching at 3300 cm^{-1}. The FTIR spectrum (*Fig. 1*) for Pb^{2+}– imprinted polymer has a strong characteristic stretching of

hydrogen bonded alcohol, and O-H around 3400 cm^{-1}, indicating an interaction between Pb^{2+} and the O-H group. There is also a shift for carbonyl band, which indicates an interaction of coordinate covalent between Pb^{2+} and the carbonyl group.

Adsorption Rate

Fig. 2 shows the time dependence of the adsorption capacities of the Pb(II) ions towards imprinted polymer as a function of time. As can be seen here, Pb^{2+} adsorption increased with the time during the first 20 min, and the levels off as equilibrium was most probably due to geometric shape memory between Pb^{2+} ions and Pb^{2+}cavities in the imprinted polymer structure. The removal of the template (Pb^{2+}) from the polymeric matrix created several cavities of complementary size, shape and chemical functionality to the template.

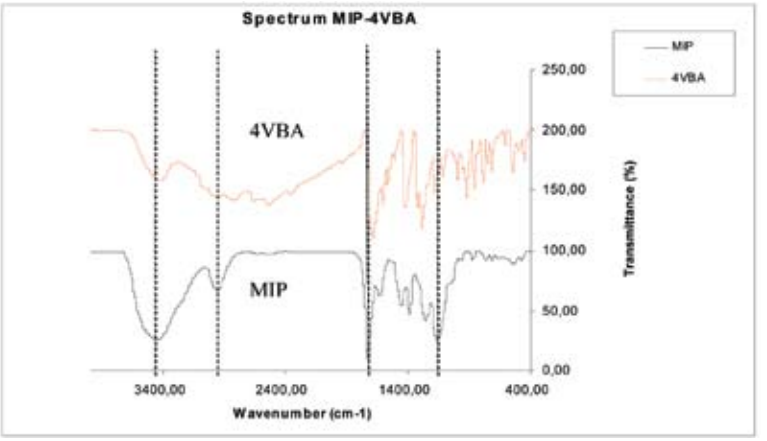

Fig. 1: FTIR Spectra for monomer (4VBA) and Pb^{2+}-imprinted polymer

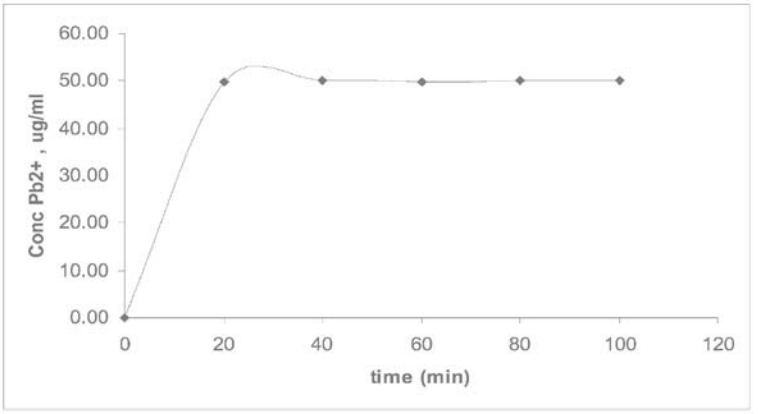

Fig. 2: Time dependence of the adsorption capacities of lead ions towards imprinted polymer

The Effects of the Initial Concentration of the Pb(II) Ion

Fig. 3 shows the dependence of the equilibrium concentration on the adsorbed amount of the Pb^{2+} ions into the imprinted polymer. The adsorption values were found to increase with the increasing concentration of Pb^{2+} ions, and a saturation value was achieved at Pb^{2+} ion concentration of 250 µg/ mL. The level off represented the saturation of the active binding cavities on the imprinted polymer. Meanwhile, the maximum adsorption capacity for Pb^{2+} ions was 150 µg/ mg dry weight of Pb^{2+}-imprinted polymer.

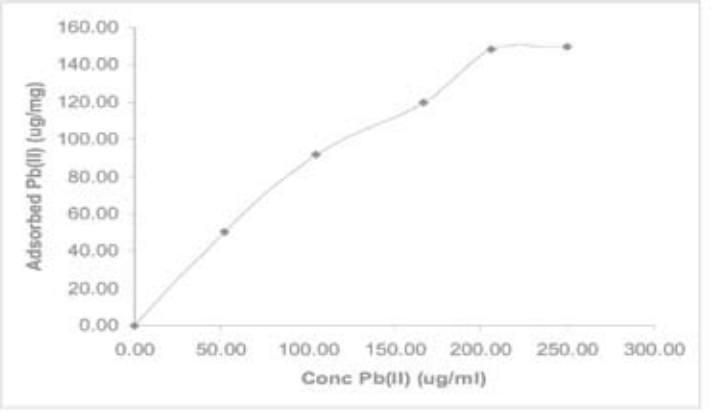

Fig. 3: Effects of the initial concentration of lead(II) ion

Adsorption Isotherm

An adsorption isotherm was used to characterize the interactions of each molecule with the adsorbents. This provided a relationship between the concentration of the molecules in the solution and the amount of ions adsorbed on the solid phase when the two phases were 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 (Sibel *et al.*, 2007).

During the batch experiments, the adsorption isotherms were used to evaluate the adsorption properties. For the systems considered, the Langmuir model was found to be applicable in interpreting Pb(II) ion adsorption on the Pb^{2+}-imprinted polymer. As a result, the Langmuir adsorption model was found to fit better as compared to the Freundlich model for this system. The correlation coefficient (R^2) was 0.9931. The maximum adsorption capacity and the Langmuir constant were calculated to be 204.08 µg/mg and 0.02 mL/µg, respectively. Both the Langmuir and Freundlich plots are respectively displayed in *Fig. 4* and *5*. The constants are summarized in Table 1.

The Effects of pH

Metal ion adsorption onto specific adsorbents is pH dependent. The effect of the pH on the Pb^{2+} ion adsorption of Pb^{2+}-imprinted polymer is shown in Table 2. The Pb^{2+}-imprinted

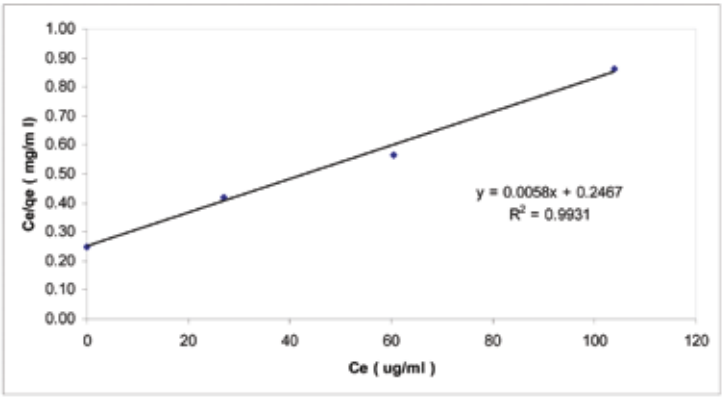

Fig. 4: The Langmuir plot for the adsorption of Pb(II) by fabricated MIP

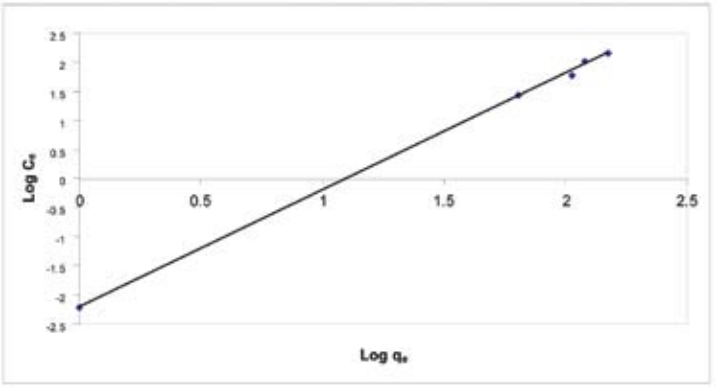

Fig. 5: The Freundlich plot for the adsorption of Pb(II) by fabricated MIP

polymer exhibited a low affinity in acidic concentrations (pH < 5.0) and a high affinity at pH 7.0. Muge *et al.* (2007), who fabricated ion imprinted beads for molecular recognition based mercury removal from human serum, also discovered a low affinity in acidic concentrations (pH < 5.0) and a high affinity at pH 7.0. This is due to the protonation of the carboxyl group in the polymer at low pH, indicating the inhibition of the complex formation between the recognition site (carboxyl group) and Pb(II) ion. pH higher than 7.0 was not tested due to the formation of precipitate between a high concentration of hydroxide ion and Pb(II) ion.

TABLE 1
Calculated value of Langmuir and Freundlich constants

	Experimental, q (ug/mg)	Langmuir constants			Freundlich constants		
		q_m(ug/mg)	b	r^2	K_F	n	r^2
MIP	148.78	204.08	0.02	0.993	0.006	0.496	0.979

TABLE 2
The effect of pH on the Pb^{2+} ion adsorption of Pb^{2+}-imprinted polymer

pH	Binding Capacity,ug/mg (MIP)
1	0.00
2	0.00
3	0.00
4	9.56
5	15.52
6	26.88
7	46.88

CONCLUSIONS

Molecularly imprinted beads, which were spherical in shape, were prepared using the radical polymerization. The average size of the beads was controlled to be between 63 and 140 μm in diameter. The adsorption was relatively fast and the time required to reach the equilibrium condition was about 20 min. The maximum adsorption capacity, for Pb^{2+} ions, was 150 μ/g dry weight of the imprinted polymer. The fast adsorption equilibrium was most probably due to the high complex and geometric affinity between the Pb^{2+} ions and Pb^{2+} cavities in the beads structure. The adsorption values was increased with the increasing concentration of Pb^{2+} ions, and the saturation value was achieved at the ion concentration of 250 μg/mL. This represented the saturation of the active binding cavities on the Pb^{2+}-imprinted polymer. The adsorption time was found to be 30 min. Therefore, Pb^{2+}-imprinted polymer can be used a number of times, without decreasing their adsorption capacities significantly.

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