Adsorption of Zinc(II) onto Zn(II)-Ionic Imprinted Polymer

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Abstract. A new Zn(II)-ionic imprinted polymer via precipitation polymerization using 8-hydroxyquinoline (8HQ) as a ligand, methacrylic acid (MAA) as functional monomer, and ethylene glycol dimethacrylate (EGDMA) as a cross-linker has been prepared. The benzoyl peroxide and ethanol/acetonitrile (2:1) mixture were used as initiator and porogen, respectively. The template Zn(II) ion was removed from the polymer by leaching with a solution of 1 M HNO₃. The experimental parameters for adsorption, such as pH of a solution, contact time, and initial zinc concentration, have been optimized. The optimum conditions of zinc adsorption onto the ionic imprinted polymer (IIP) was at pH 5.5 and contact time 15 min. The equilibrium data could be better described by the Langmuir isotherm model. The maximum adsorption capacity of IIP was 20.833 mg/g.

1. Introduction

Zinc is an important food element. Zinc is a transition metal with the highest concentration in the brain and second in the body [1,2]. Zinc plays a role in biochemical processes in a number of physiological functions including normal immune function, sexual function, and neurosensory function. Zinc affects the function of proteins, enzymes, and transcription factors, and its also an important component of hundreds of proteins and metalloenzymes [3,4]. Zinc is considered relatively non-toxic, compared to other metals having similar chemical properties. Only high-dose exposure has a toxic effect on toxicity symptoms such as nausea, vomiting, epigastric pain, lethargy, and fatigue [5]. Zinc is widely used in mining, galvanization, metal coating, and some industries such as batteries, brass, ceramics, paint, wood, fabric, sunblock, deodorants, and medicines [6-8].

Several approaches have been employed to remove heavy metal ions from wastewater such as the chemical precipitation [9,10], electrochemical precipitation [11], coagulation [12,13], flotation [14,15], electrochemical [16,17], filtration [18,19], cation-exchange [20], reverse osmosis [21], electrodialysis [22], and adsorption.
Adsorption is considered an effective, efficient, and economical method for water purification [23]. Since the performance of an adsorptive separation is directly dependent on the quality and cost effectiveness of the adsorbent, the last decade has seen a continuous improvement in the development of effective noble adsorbents in the form of activated carbon [24,25], carbon nanotubes [26], zeolites [27,28], kaolinite [29], clay minerals [30], and chitosan [31]. However, most of these adsorbents are either not effective (due to diffusion limitation or the lack of enough active surface sites) or have shown problems like high cost, difficulties of separation from wastewater, or generation of secondary wastes [32].

The Ionic-imprinted-polymer is the most promising new type of adsorbent. This adsorbent is synthesized by starting the formation of a complex between metals (templates) with a ligand. The complex is immobilization in a cross-linked polymeric matrix. The template is then removed from the polymer matrix to produce a selective ion mold for the metal ion used as the template in the polymerization [33].

Recently, there are some reports on the application of imprinted technique for adsorbent of heavy metal ions, such as lead [34,35], arsen [36], chromium [37], mercury [38], and cadmium [39,40].

In this study, a new ion imprinted polymer has been synthesized. IIP is synthesized using zinc metal ions as templates and 8-hydroxyquinoline (8HQ) as complex ligands. The complex was immobilized in a polymer with methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), and benzoyl peroxide as functional monomers, cross-linking agents, and initiators, respectively. Polymerization was carried out by precipitation polymerization method in porogen ethanol-acetonitrile (2:1). This novel imprinted polymer has been studied for its adsorption of zinc using a batch procedure. The effect of adsorption parameter, i.e. pH solution, contact time, and initial concentration, on the adsorption capability of the IIP were studied. Furthermore, isotherm adsorption process of zinc on the IIP was also evaluated.

2. Experimental Section

2.1. Materials

A Zinc atomic spectroscopy standard solution in HNO₃ (1 g L⁻¹, Merck, Germany) was used. Nitric acid (Merck, Germany) was used as a desorption agents, leached zinc, and adjusted pH. Ethanol (Merck, Germany) and acetonitrile (Merck, Germany) were used as porogen. Zinc sulphate hydrate, ZnSO₄.7H₂O (Merck, Germany) and 8-hydroxyquinoline (8HQ) (Sigma Aldrich, US) were used for the preparation of Zn(II) complexes. Methacrylic acid (MAA) (Sigma Aldrich, US), ethylene glycol dimethacrylate (EGDMA) (Sigma Aldrich, US) and benzoyl peroxide (Merck, Germany) were applied for the synthesis of polymers.

2.2. Instrrumentation

The Fourier Transform Infrared Spectrophotometer (Perkin Elmer Frountier-89485) was used characterization of functional groups among adsorbent. The Atomic Absorption Spectrophotometer (Perkin Elmer, AA 700) was used to analyzed concentration of zinc. A pH-meter (Mettler Toledo) was used for the pH adjustments.

2.3. Procedure

2.3.1. Preparation of IIP. The ionic imprinted polymer (IIP) was prepared according to the following procedure: 0.1 mmol (0.0287 g) of ZnSO₄.7H₂O and 0.25 mmol (0.0363 g) of 8-hydroxyquinoline (8HQ) were dissolved in 60 mL of ethanol-acetonitrile (2:1) and stirred for 30 min. Then 4 mmol (0.34 mL) of methacrylic acid (MAA), 0.2 mmol (0.0485 g) of benzoyl peroxide, and 20 mmol (3.77 mL) of ethylene glycol dimethacrylate (EGDMA) were added to the solution. The glass tube was flowed with nitrogen for 5 min and sealed. The reaction temperature of precipitation polymerization
was kept constant at 60°C for 8 h while stirred. The resultant solid polymer was filtered, washed, and dried at 60°C for 2 h. The zinc ions were removed from polymer by introducing in the 100 mL of 1 M nitric acid for 30 min. Finally, the IIP was filtered, washed, and dried at 100°C for 24 h. The control polymer was synthesized in a similar procedure, but in the absence of ZnSO₄·7H₂O and 8-hydroxyquinoline. The polymer and IIP were characterized by FTIR.

2.3.2. Experiment. Batch adsorption experiments were conducted to investigate the influence of physiochemical parameters such as pH solution, contact time, and initial zinc concentration on zinc adsorption.

Effect of pH
The effect of solution pH was tested by shaking 0.01 g IIP and 20 mL of the 10 mg/L Zn(II) standard solution at various pH for 10 min. The pH of the sample solutions was varied from pH 4 to 8. The IIP was separated by filtration and concentration of Zn(II) in the filtrate was determined by FAAS.

Effect of contact time
The effect of contact time was tested by shaking 0.01 g IIP and 20 mL of the 10 mg/L Zn(II) standard solution at pH 6 for various contact time. The contact time was varied from 0 to 90 minutes. The IIP was separated by filtration and concentration of Zn(II) in the filtrate was determined by FAAS.

Effect of initial Zn(II) concentration
The effect of initial Zn(II) concentration was tested by shaking 0.01 g IIP and 20 mL of the Zn(II) standard solution with a various concentration of Zn(II) at pH 6 for 15 minutes. The concentration of Zn(II) was varied from 5 to 25 mg/L. The IIP was separated by filtration and concentration of Zn(II) in the filtrate was determined by FAAS.

The amount of zinc adsorbed per weight of IIP, Q (mg/g) can be calculated using the following equation:

\[
Q = \frac{V(C_o - C_e)}{m}
\]

where \(C_o\) is the initial zinc concentration (mg L⁻¹), \(C_e\) is the zinc concentration after adsorption (mg L⁻¹), \(V\) is the volume of zinc solution (L), and \(m\) is the weight of IIP (g).

3. Result and discussion
New adsorbents were synthesized using zinc, 8-hydroxyquinoline (8HQ), methacrylate acid (MAA) and ethylene glycol dimethacrylate (EGDMA) as consecutive templates, complexing monomers, and cross-linking agents. The Ionic imprinted polymer was synthesized by precipitation polymerization technique, with the following steps (Fig. 1): (1) Complexation of zinc ions with 8HQ (2) copolymerization of MMA in the presence of zinc ions, and (3) removal of zinc ions after copolymerization of the polymer.
Figure 1. Schematic representation of the synthesis of Zn$^{2+}$-imprinted polymer and its role in the adsorption and desorption process of the Zn$^{2+}$ ions.

3.1. Characterization of IIP

The FTIR spectra of polymer (Fig. 2a) showed the characteristics stretching vibration bands 1631.67 cm$^{-1}$ indicates the presence of a C=O and the strong band at 1269.07 cm$^{-1}$ indicates the presence of a C-O group. The polymer compound was formed from the polymerization reaction of methacrylic acid with ethylene glycol dimethacrylate as a crosslinker. The spectrum of the polymer compound contains the groups present in the methacrylic acid compound and the ethylene glycol dimethacrylate, except in the absence of the C=C group. The polymerization reaction was the addition polymerization. The FTIR spectra of IIP (Fig. 2b) showed the characteristics stretching vibration bands near 3502.49 cm$^{-1}$ indicate the presence of hydroxyl groups. The presence of a strong band of 1728.1 cm$^{-1}$ indicates the presence of a C=O. The band at 1639 cm$^{-1}$ indicates the presence of a C=C group. The band at 1265.22 cm$^{-1}$ indicate the presence of a C-O group. Bands near 3000 cm$^{-1}$ and about 1600 cm$^{-1}$ and 1500 cm$^{-1}$ indicate the presence aromatic group. The IIP formed indicated by the appearance of a peak at 1492.8 cm$^{-1}$ (C=C aromatic) of IIP spectra (Fig. 2a) compared with the spectra of polymers.
3.2. Effect of pH

The effect of varying pH values on Zn(II) adsorption was investigated using the batch procedure. The adsorption experiments were triplicated. The adsorption of Zn(II) as a function of the pH is shown in Fig. 3. The adsorption of Zn(II) increased greatly between pH 4.5 to 5.5, almost constant from 5.5 to 6, and then gradually decrease from 6 to 8. So pH 5.5 was chosen as optimum for further experiments. The activity of the adsorbent’s functional groups is strongly affected by solution pH. In a highly acidic environment, several functional groups become protonated and act as positively charged species, resulting in reduced attraction between the metals and the minerals. Deprotonation of functional groups occurs at increasing pH and these behave as negatively charged moieties, attracting heavy metals [8]. At pH above 7, adsorption decreases because there are a large amount of OH’ ligands in the solution [41]. Zinc ions react with OH’ ligand to form Zn(OH)$_2$ precipitate.
3.3. Effect of contact time

Determination of optimum contact time in the adsorption process on an adsorbent is very important because it is needed to develop cost-effective procedures [42]. Fig. 4. shows the typical results of the time-dependent adsorption zinc on IIP. The adsorption capacity for zinc ions onto IIP rapidly increased in the first 15 min and then slowly augmented. The absorption equilibrium has been achieved after 15 min, indicating that IIP has saturated.

3.4. Effect of initial zinc concentration

The effect of initial zinc concentration on the amount of adsorbed zinc was done by a batch method with 0.01 g of adsorbent, 20 mL initial solution volume with pH of solution 5.5, and contact time 15 min. The treatment was performed on IIP. The plot between the initial zinc concentration against the
adsorbed zinc is presented in Fig. 5. There was an increase in zinc initial concentration followed by an increase in the amount of adsorbed zinc. Increasing concentration gradient acts as increasing driving force, and in turn leads to increasing equilibrium sorption until sorbent saturation was achieved [43].

![Graph showing effect of initial zinc concentration on zinc adsorption onto IIP.](image)

**Figure 5.** Effect of initial zinc concentration on zinc adsorption onto IIP.

### 3.5. Isoterm adsorption

Isoterm adsorption is fundamental in describing interactive behavior between adsorbate and adsorbent. It is important to predict adsorbent adsorption capacity, which is the main parameter necessary to design the adsorption system. In this study, the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherms model were used to describe zinc adsorption onto IIP.

Langmuir isotherms apply to monolayer adsorption on surfaces with a limited number of identical sides. This model assumes the same energy on adsorption on the surface. Langmuir isotherm model is expressed by the equation [44]:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e
\]

where \( q_m \) is the maximum adsorption capacity (mg/g), \( K_L \) is the coefficient associated with the adsorption energy (L/mg), \( C_e \) is the metal ion concentration in the solution (mg/L), and \( q_e \) is the adsorption capacity (mg/g) calculated using the formula \( q_e = \frac{C_0 - C_e}{V} \). By plotting \( C_e/q_e \) versus \( 1/C_e \) the curves (Fig. 6a), \( q_m \) and \( K_L \) can be obtained.

The Freundlich model evaluates the phenomenon of multilayer adsorption and heterogeneous surfaces on the surface of the adsorbent. Freundlich isotherm model is expressed by the equation [44]:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

where \( K_F \) is Freundlich’s constant (L/g). By plotting \( \ln C_e \) versus \( \ln q_e \) the curves (Fig. 6b), \( n \) and \( K_F \) can be obtained. The \( n \) value indicates surface heterogeneity, if the value of \( n \geq 1 \) indicates a homogeneous system, and if \( n < 1 \) then the system is heterogeneous.

Isotherm Temkin assumes that the adsorption heat decreases linearly with an increase in adsorption. The Temkin isotherm equation is given by the equation [42]:

\[
q_e = \frac{RT}{b_t} \ln \alpha_t + \frac{RT}{b_t} \ln C_e
\]
where \( R \) is the ideal gas constant (8.314 \( \text{J.mol}^{-1}.\text{K}^{-1} \)), \( K \) is the absolute temperature (K), \( b_t \) is the constant associated with the adsorption heat (\( \text{J/mol} \)), and \( a_t \) is the isotherm of the Temkin constant (L/g). By plotting \( \ln C_e \) versus \( q_e \) the curves (Fig. 6c), \( a_t \) and \( b_t \) can be obtained.

Dubinin-Radushkevich isotherms can be applied to study the properties, free energy, and porosity of the adsorbent. Dubinin-Radushkevich isotherm equation is given by the equation [42]:

\[
\ln q_e = \ln q_m - B \varepsilon^2
\]  

(5)

where \( \varepsilon \) is the Polanyi potential \( (\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)) \) (\( \text{mol}^2 \text{J}^2 \)) and \( Q_m \) is the saturated adsorption capacity (mg/g). By plotting \( \ln C_e \) versus \( q_e \) the curves (Fig. 6d), \( \varepsilon^2 \) and \( \ln q_e \) can be obtained.

| Models                  | \( R^2 \) | Constants                |
|-------------------------|-----------|--------------------------|
| Langmuir                | 0.9726    | \( q_{max} = 20.833 \text{ mg/g} \) |
|                         |           | \( K_L = 0.608 \text{ L/mg} \) |
| Freundlich              | 0.9502    | \( n = 0.305 \)          |
|                         |           | \( K_F = 0.001 \text{ L/g} \) |
| Temkin                  | 0.8987    | \( a_t = 12.439 \text{ L/g} \) |
|                         |           | \( b_t = 696.338 \text{ J/mol} \) |
| Dubinin-Radushkevich   | 0.7309    | \( B = 6 \times 10^8 \text{ mol}^2\text{J}^2 \) |
|                         |           | \( Q_m = 14.3392 \text{ mg/g} \) |

Fig. 6 presents the plots of Langmuir, Dubinin-Radushkevich, Freundlich, and Temkin isotherm models for the adsorption of zinc onto the IIP. The \( R^2 \) and constants for those four different adsorption kinetic models were calculated and summarized in Table 1. From the correlation coefficient (\( R^2 \)) values, the adsorption process of zinc onto the IIP was found to follow the Langmuir isotherm model. The maximum monolayer adsorption capability of IIP was 20.833 mg/g. These results indicate that zinc adsorption on IIP forms a monolayer layer which is homogeneous. The KL value (the energy constant associated with heat adsorption) is 0.608 L/mg.

![Figure 6. Plots of Langmuir](image-url)
Figure 7. Plots of Freundlich

Figure 8. Plots of Temkin
Figure 9. Plots of Dubinin-Radushkevich isotherm models for the adsorption of zinc onto IIP.

4. Conclusion
New adsorbents for zinc ions (Zn (II) -ion-imprinted polymers) have been synthesized using zinc, 8-hydroxyquinoline, methacrylate acid, and ethylene glycol dimethacrylate ions, respectively as templates, complexing ligands, monomers, and cross-agent linked. As a porogen and ionisator, ethanol-acetonitrile (2:1) and benzoyl peroxide are used. IIP synthesis using precipitation polymerization techniques. The optimum condition of zinc adsorption in IIP occurs at pH 5.5 and the contact time is 15 minutes. The process of adsorption follows the Langmuir isotherm model. The maximum capacity of adsorption zinc onto the IIP was 20.833 mg/g.

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