



## Fabrication and Characterization of Molecularly Imprinted Polymer for Hg(II) Ion

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A molecular imprinted polymer for Hg(II) has been fabricated using free radical polymerization method. The selectivity and binding capability of the fabricated molecular imprinted polymer towards Hg(II) ions in aqueous environment has been carried out. Molecular imprinted polymer was prepared using mercury(II) nitrate dihydrate as the template molecule and vinylcarbazole as the functional monomer. Free template polymer was then used in metal uptake study at different pH, timing and equilibrium concentration. The molecular imprinted polymer shows highest adsorption at pH 6 for 135 min at 40 ppm Hg<sup>2+</sup> solution. The kinetic order of the adsorption is second order with equilibrium rate constant  $9.0 \times 10^{-4} \text{ min ppm}^{-1}$ . The adsorption obeys the Langmuir isotherm with maximum adsorption of 10.13 mg g<sup>-1</sup> and Langmuir constant 0.032 gm g<sup>-1</sup>. In selectivity study, the distribution coefficient of Hg<sup>2+</sup> is much higher than Cd<sup>2+</sup> and Zn<sup>2+</sup> that is 10443.31, 73.74 and 28.66, respectively.

**Keywords:** Molecular imprinted polymer, Mercury, Free radical polymerization.

### INTRODUCTION

Mercury is a global contaminant and a potent neurotoxin which would affect human health and wildlife reproductive potential. The pollution caused by mercury is difficult to control as it high volatility and low solubility<sup>1</sup>. There are various ways where mercury can enter the human body such as through inhalation of its vapour, ingestion, injection or absorption through skin<sup>2</sup>. Nowadays, human's health is threatened by mercury due to the extensive contamination of water and fish and also the increase of consumption of fish in human diet. Mercury would cause toxic to kidney and colon, it is also a cytotoxic<sup>3</sup>. 70 -80 % of the mercury found in environment are come from anthropogenic source<sup>4</sup>, which is mainly cause by burning of coal, inappropriate disposal from batteries, paints and lights. When coal is incinerated, mercury is released to environment.

Various methods are available to determine and remove mercury in water such as adsorption<sup>5,6</sup>, ion exchange resins<sup>7</sup>, open chain ligands<sup>8</sup>, mossy tin filters<sup>9</sup>, electrochemical method<sup>2</sup>. This study is concerned with the removal of Hg<sup>2+</sup> from water using molecular imprinted polymer. Several works using common functional monomer such as 4-vinylpyridine<sup>2,10</sup> had been reported previously. However, using 4-vinylpyridine may lead to low selectivity<sup>2,10-12</sup>. Due to that reason, vinylcarbazole is used as functional monomer in this study in order

to improve the selectivity of the ion. The parameters studied in this research include pH study, sorption kinetics and selectivity study.

### EXPERIMENTAL

Chemicals used in this study are mercury(II) nitrate dihydrate were supplied by Merck. Tetrahydrofuran, hydrogen peroxide, hydrochloric acid were supplied by R&M Chemical. Vinylcarbazole, ethylene glycol dimethacrylate, thiourea, copper(II) sulphate and zinc(II) sulphate were supplied by Sigma-Aldrich Chemical.

Instrument used in this study are Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) for metal uptake experiments and Fourier Transform Infrared (FT-IR) to characterized molecular imprinted polymer.

**Synthesis of molecular imprinted polymer:** The molecular imprinted polymer for Hg(II) was prepared by free radical polymerization technique. In this process, 400 mg of vinylcarbazole monomer was dissolved in 14 mL tetrahydrofuran. Next, 504 mg of Hg(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O was dissolved in the solution. 8 mL of ethylene glycol dimethacrylate (EDGMA) is added together with 60 mg of hydrogen peroxide into the mixture. The mixture is then heated in 60 °C water bath and stirred with magnetic stirrer at 600 rpm for 2 h. The polymer obtained is washed with deionized water to remove any unreacted

monomer, initiator and solvent. Finally the polymer is dried, grinded and sieved with Standard Test Sieves.

**Extraction of the template:** After the molecular imprinted polymer is grinded and washed, the template was removed from the polymer. Molecular imprinted polymer was added into acidic thiourea solution. The mixture was stirred by using magnetic stirrer for 48 h. The mixture was filtered to separate the beads and the filtrates. The beads were left dried while the filtrates were filtered to analyze for  $\text{Hg}^{2+}$  content by using ICP-AES. This procedure was repeated several times until the template molecule ( $\text{Hg}^{2+}$ ) in the filtrates was in a very low concentration or could not be detected with ICP-AES. The beads were washed with distilled water, dried in an oven and weighed. The molecular imprinted polymer used in metal uptake process.

**Metal uptake:** After extraction procedure, the beads that have been dried in the oven will be used in metal uptake study.

**Effect of pH study:** Buffer solution from pH 1 to pH 8, 10 mg of extracted molecular imprinted polymer and 2.5 mL of 100 ppm  $\text{Hg}^{2+}$  solution was added together followed by 22.5 mL buffer solution (pH 1-8). All test tubes were labeled clearly. The test tubes were stirred for 1 h before filtration. The filtrates were analyzed for  $\text{Hg}^{2+}$ .

**Kinetic study of adsorption capacity of  $\text{Hg}^{2+}$  by molecular imprinted polymer beads:** 10 mg of extracted molecular imprinted polymer was added into 25 mL 20 ppm  $\text{Hg}^{2+}$  solution at optimum pH. The mixture was stirred for 15 min before filtered. The filtrates were analyzed for  $\text{Hg}^{2+}$  content. The steps were repeated until the concentration of  $\text{Hg}^{2+}$  become constant. The time required for the concentration of  $\text{Hg}^{2+}$  become constant is the optimum duration. The binding capacity is calculated and the kinetic order was determined.

**Selectivity study:** 25 mL of 20 ppm  $\text{Cd}^{2+}$  solution at optimum pH was prepared. 10 mg of extracted molecular imprinted polymer was added into a test tube follow by the  $\text{Cd}^{2+}$  solution. The mixture was stirred for the optimum duration filtration. The steps were repeated by using 25 mL of 20 ppm  $\text{Zn}^{2+}$  solution. The filtrates were analyzed for metal content.

## RESULTS AND DISCUSSION

FTIR spectra for molecular imprinted polymer and vinylcarbazole monomer were shown in Fig. 1. The IR spectra were recorded by using KBr method. Fig. 1a shows the FTIR spectrum for molecular imprinted polymer. From the spectrum, the peaks at 3438, 2960, 1726, 1456, 1158 and 946  $\text{cm}^{-1}$  were observed. From the spectra, a broad peak appears in the range of 3500-3200  $\text{cm}^{-1}$  suggested the hydrogen bonding occurs in the polymer. This can be a proof that the polymer synthesized consists of hydrogen bonding. This peak is not found in the monomer (Fig. 1b). In molecular imprinted polymer, it is discovered that the  $\text{Hg}^{2+}$  are bind with the O-H functional group. The stretching of O-H occurs at the recognition site and the surface of the polymer. The broad and strong band ranging from 3500 to 3000  $\text{cm}^{-1}$  should be attributed to the overlapping of O-H and N-H stretching vibration which was consistent with the peaks at 1158.00 and 946  $\text{cm}^{-1}$  assigned to C-O and C-N stretching vibration, thus showing the presence of hydroxyl and amide groups on molecular imprinted polymer.

At 1726  $\text{cm}^{-1}$ , the H-bonded C=O peak was found but the peak intensity are not very sharp. This is reasonable because hydrogen bonds not only lower the frequency but also cause peak broadening. The band at 1456  $\text{cm}^{-1}$  represents the amide absorption bands. On the other hand, the monomer shows a splitting pattern in the range of 2000-1000  $\text{cm}^{-1}$ , while the imprinted polymers show a broad peak in the same region, indicating the absence or negligible carboxylic acid contents. In addition, at peaks 3000-2850  $\text{cm}^{-1}$  the  $sp^3$  C-H functional group appears. This functional group appears in both molecular imprinted polymer and methacrylamide spectra indicating that C-H also occur when the polymer are prepared.

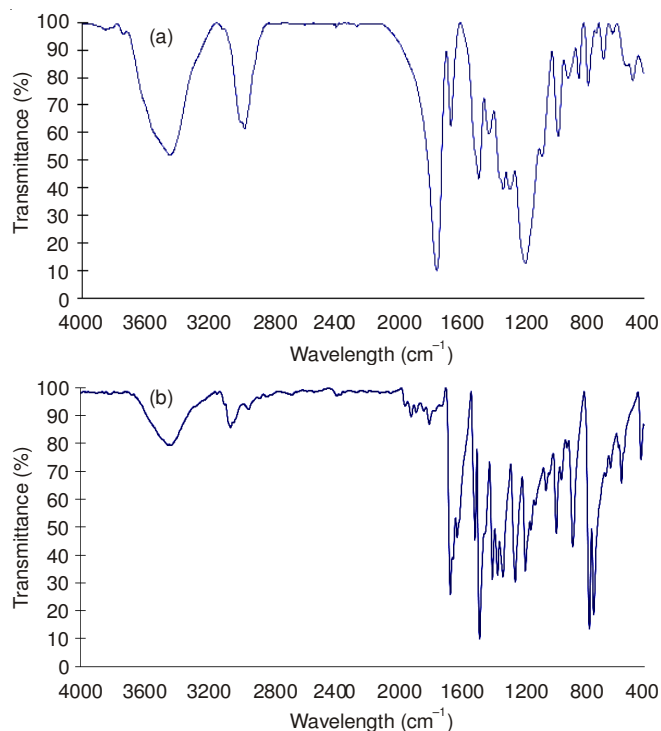


Fig. 1. (a) FTIR spectra for molecular imprinted polymer; (b) FTIR spectra for monomer

**Metal uptake:** Metal uptake for  $\text{Hg}^{2+}$  ions was carried out to evaluate the selectivity and the binding capability of molecular imprinted polymer towards  $\text{Hg}^{2+}$ .

**Effects of pH study:** Metal ion adsorption onto specific adsorbents is pH dependent. The effect of pH on the  $\text{Hg}^{2+}$  ion adsorption of imprinted polymer is shown in Fig. 2. From the figure, we found that the  $\text{Hg}^{2+}$  imprinted beads exhibited a low affinity in acidic concentrations (pH < 5) and a high affinity at pH 6. The result obtained was in contrast with the previous research where they found that the adsorption capacity in  $\text{Hg}^{2+}$  is increase with increasing of pH value<sup>10,11,13</sup>.

**Kinetic study of adsorption capacity of  $\text{Hg}^{2+}$  by molecular imprinted polymer beads:** Fig. 3 shows the time dependence of the adsorption capacity of  $\text{Hg}^{2+}$  ions on the molecular imprinted polymer beads. It can be seen that the adsorption of  $\text{Hg}^{2+}$  ions is initially fast with the most mercury being adsorbed within the first 90 min. In line with previous research<sup>10,13</sup>, this fast adsorption equilibrium is most probably due to high complexation and geometric shape affinity between  $\text{Hg}^{2+}$  ions and the  $\text{Hg}^{2+}$  cavities in the molecular imprinted

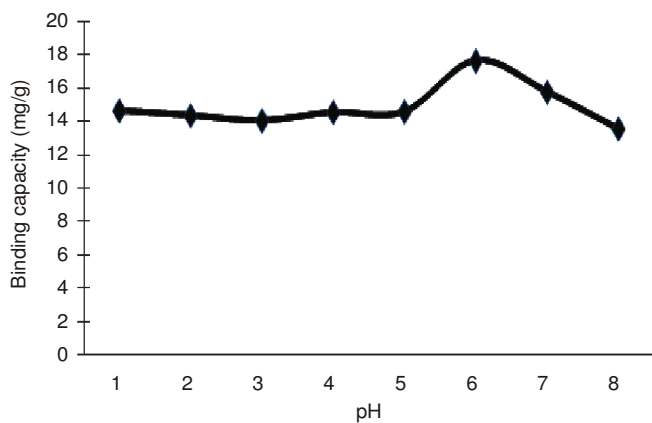


Fig. 2. Effect of pH on the Hg<sup>2+</sup> ion adsorption; Hg<sup>2+</sup> ion concentration: 10 ppm

polymer beads structure. It is well known that the removal of the template from the polymeric matrix leaves cavities of complementary size, shape and chemical functionality to the template. The maximum adsorption for Hg<sup>2+</sup> ions was 15.3675 mg g<sup>-1</sup>.

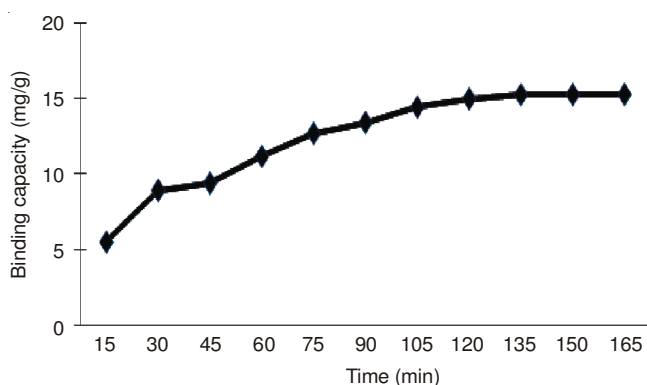


Fig. 3. Adsorption capacity of Hg<sup>2+</sup> ions on molecular imprinted polymer; Hg<sup>2+</sup> ion concentration: 10 ppm; pH 6

In order to examine the controlling mechanism of adsorption process, kinetic models were used to test experimental data (Table-1). The kinetic models (pseudo-first and second order equations) can be used in this case assuming that the measured concentrations are equal to adsorbent surface concentrations. The pseudo-first equation is given as follows:

$$\ln [A] = -k_1 t + \ln [A]_0 \quad (1)$$

where A is the final concentration of Hg<sup>2+</sup> in the solution (ppm), A<sub>0</sub> is the initial concentration of Hg<sup>2+</sup> in the solution (ppm), t is the duration for the adsorption (min) and k<sub>1</sub> is the equilibrium rate constant of the first order adsorption (min<sup>-1</sup>). From this eqn. (1), a graph ln [A] versus t was plotted and showed in Fig. 4.

The rate constant for the pseudo-second-order adsorption model could be obtained from the following equation:

$$\frac{1}{[A]} = \frac{1}{k_2 t} + \frac{1}{[A]_0} \quad (2)$$

where k<sub>2</sub> is the equilibrium rate constant of pseudo-second-order adsorption (min ppm<sup>-1</sup>). From eqn. (2), a graph 1/[A] vs. t was plotted and showed in Fig. 5.

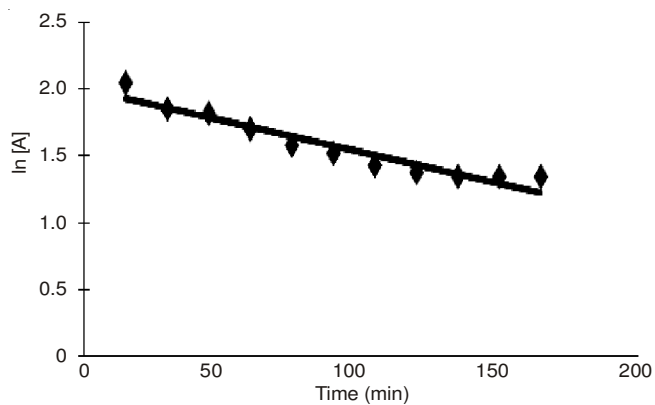


Fig. 4. Pseudo-first-order adsorption; Hg<sup>2+</sup> ion concentration: 10 ppm; pH 6

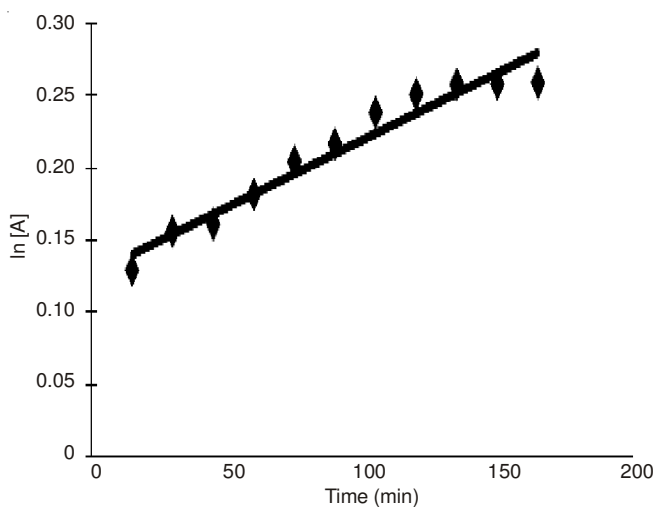


Fig. 5. Pseudo-second-order adsorption; Hg<sup>2+</sup> ion concentration: 10 ppm; pH 6

TABLE-1 FIRST AND SECOND ORDER KINETIC CONSTANT FOR THE MOLECULAR IMPRINTED POLYMER BEADS			
First order kinetic		Second order kinetic	
K <sub>1</sub> (min <sup>-1</sup> )	R <sub>2</sub>	K <sub>2</sub>	R <sub>2</sub>
4.3 × 10 <sup>-3</sup>	0.8241	9.0 × 10 <sup>-4</sup>	0.9463

**Effect of selectivity:** Competitive adsorptions of Cd<sup>2+</sup>/Hg<sup>2+</sup> and Zn<sup>2+</sup>/Hg<sup>2+</sup> from their mixture were also studied in a batch system. Cd<sup>2+</sup> and Zn<sup>2+</sup> were chosen as competitive metal ions as their similar ionic radii. Table-2 summarizes K<sub>d</sub> and k, values of Cd<sup>2+</sup> and Zn<sup>2+</sup> with respect to Hg<sup>2+</sup>. From the table, we can say that the K<sub>d</sub> for the Hg<sup>2+</sup> is much higher than the Cd<sup>2+</sup> and Zn<sup>2+</sup>.

TABLE-2 K <sub>d</sub> AND k VALUES OF Cd <sup>2+</sup> AND Zn <sup>2+</sup> WITH RESPECT TO Hg <sup>2+</sup>		
Metal ion	K <sub>d</sub>	k
Hg <sup>2+</sup>	10443.31	-
Cd <sup>2+</sup>	73.74	141.62
Zn <sup>2+</sup>	28.66	315.15

Fig. 6 shows adsorbed template and competitive ions in molecular imprinted polymer. A significant increase is observed in the selectivity of beads when the adsorbent is prepared in the presence of the target ion.

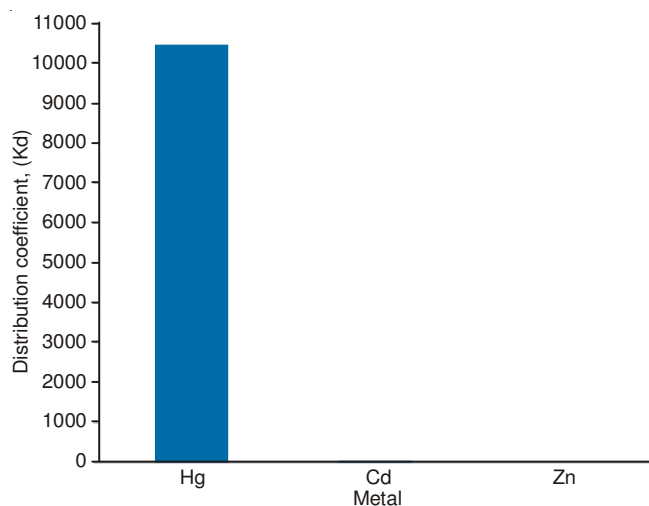


Fig. 6. Adsorbed template and competitive ions in molecular imprinted polymer beads;  $\text{Hg}^{2+}$  ion concentration: 10 ppm; pH 6

### Conclusion

The molecular imprinted polymer was successfully fabricated with selectivity towards  $\text{Hg(II)}$  with  $\text{Hg(NO}_3)_2 \cdot 2\text{H}_2\text{O}$  as a template, vinylcarbazole as a monomer and ethylene glycol dimethacrylate (EGDMA) used as crosslinker. molecular imprinted polymer has been demonstrated to possess a very high degree of selectivity towards the template which is  $\text{Hg}^{2+}$  ions. Molecular imprinted polymer has been characterized by Fourier transformed infrared spectroscopy. In metal uptake

study, it is found that the optimum condition for a 10 ppm  $\text{Hg}^{2+}$  at pH 6 is 135 min. The adsorption mechanisms obey the pseudo-second-order with the rate constant  $9 \times 10^{-4} \text{ min ppm}^{-1}$ . For selectivity study, it is found that  $\text{Hg}^{2+}$  ions is much more adsorbed compare to the  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions. This shows that the molecular imprinted polymer form is highly sensitive in selectivity. Lastly, the adsorptions obey the Langmuir isotherm with the maximum adsorption capacity at  $10.13 \text{ mg g}^{-1}$  and Langmuir constant  $0.032 \text{ gm g}^{-1}$ .

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