Preparation and Characterization of Innovative Selective Imprinted Polymers for the Removal of Hazardous Mercury Compounds From Aqueous Solution

Ayman H. Kamel

1 Chemistry Department, College of Science, Qassim University, Bujairah, KSA
2 Chemistry Department, Faculty of Science, Ain Shams University, Abbasia, Cairo, Egypt
ahkamel76@yahoo.com

Abstract: The presence of organic and inorganic mercuric compounds in surface waters is a health concern worldwide. The present study deals with the feasibility of removal both dissolved Hg\(^{2+}\) and CH\(_3\)Hg\(^+\) ions from aqueous solutions by using a mimicking receptor for these hazardous pollutants. A molecularly imprinted polymer (MIP), with special molecule recognition properties of 3-methyl-5-(methylthio)-4-vinylthiophene-2-carboxylic acid (VTCA) and methylmercury chloride or Hg\(^{2+}\), was prepared by thermal polymerization in which either CH\(_3\)Hg\(^+\) or Hg\(^{2+}\) ions acted as the template molecule, (VCTA) acted as the functional monomer and ethylene glycol dimethacrylate (EGDMA) acted as the crosslinker. Batch adsorption studies for methylmercury and mercury adsorption were conducted to evaluate various experimental parameters such as, contact time, initial concentration of the adsorbate, adsorbent dosage, pH and temperature. Selectivity studies of mercury versus other metal ions which Cu\(^{2+}\), Zn\(^{2+}\), Pb\(^{2+}\) and Cd\(^{2+}\) was reported and distribution and selectivity coefficients of these ions with respect to methylmercury and mercury were calculated here. The findings seem to be important for application of the introduced mimicking receptor as an efficient new nonconventional adsorbent in hazardous pollutants removal technology.

Key words: Methylmercury, Removal, Mimicking receptor, Molecular imprinting polymer, Hazardous waste.

1. Introduction

Mercury is recognized as one of the most hazardous pollutants introduced into the environment. The majority released into the aquatic environment is inorganic mercury but can be converted to the more toxic organic MeHg\(^+\) in sediments as well as water columns, which is readily bio-accumulated in fish through the food chain (Craig, 1982). Human health hazards from environmental mercury were tragically realized during the severe pollution incidents of Minamata and Niigata in Japan owing to consumption of fish contaminated by MeHg\(^+\) which was discharged from acetaldehyde manufacturing plants. After these tragic events, considerable efforts have been expended on monitoring mercury in the aquatic environment, and limits on mercury levels in seafood have been established in various countries (Rapsomanikis et al., 1991). So it is very important to decrease the residual mercury concentration below the safety limit for organic and inorganic mercury from industrial wastewater, especially from drinking water. Conventional methods for the removal of mercury from waste streams include adsorption (Herrero et al., 2005; Melamed et al., 2006 and Velicu et al., 2007), biosorption (Green-Ruiz et al., 2006), ion exchange (Chiarle et al., 2000), membrane filtration (Vieira et al., 2006), chelate precipitation (Ying et al., 2006), precipitation/adsorption (Liu et al., 2008 and Sajidu et al., 2008), and photoreduction (Khalil et al., 2002 and Miranda et al., 2009). Polymer adsorbents immobilizing S-contained functional groups were conveniently used for the removal of mercury in water (Randall et al., 2004). However, most of these methods require either high energy or large quantities of chemicals. Conventional precipitation methods do not always provide a satisfactory removal rate to meet pollution control limits; moreover, synthetic ion-exchange resins are often expensive (Unlu et al., 2006), and adsorbents have low mechanical strength, weak hydrothermal stability, or a weak chemical bond with the metals (Wu et al., 2007). These methods are ineffective when the mercury concentration was low (Choong et al., 2005). Furthermore, most of the researches were limited to the removal of inorganic mercury.

Mercury exists in two major forms in aqueous solutions: inorganic mercury and organic mercury, in particular, methyl mercury (Ito et al., 2008). The treatment method that could be used for the removing of both inorganic and organic mercury from aqueous solutions has not been reported until now. Therefore, in order to meet the demand of residual concentration lower than 1µgL\(^{-1}\) in drinking water purification, it is necessary to explore adsorptive materials with low cost, high adsorption speed, and good removal
Molecular imprinted polymers (MIP) are new high selective synthetic receptors with molecular recognition sites designed for a particular analyte. MIP technology has been developed as a method for the preparation of synthetic receptors by polymerization of self assembled complexes, formed by functional monomers and a template in the pre-polymerization mixture (Moreira et al., 2010; Kamel et al., 2012; Kamel et al., 2013; Kamel et al., 2011 and Kamel et al., 2009). This technology can also be used for the preparation of polymers containing inorganic cation selective sites as the so-called ion imprinted polymers (IIP) (Guo et al., 2009; Singh et al., 2009 and Abd-Rabboh et al., 2012). Different kinds of imprinted polymers have so far been reported for the recognition of mercury ions (Andac et al., 2007; Singh et al., 2010; Dakova et al., 2009 and Liu et al., 2005).

In this work, novel mercury selective imprinted polymer based on the use of 5-methyl-5-(methylthio)-4-vinylthiophene-2-carboxylic acid (VTCA) as a functional monomer will be synthesized and characterized. The obtained mercury imprinted polymer will be used as a new adsorbent for both inorganic and organic mercury.

2. Experimental
2.1. Materials
All chemicals were of analytical grade and de-ionized water (conductivity < 0.1 µS cm⁻¹) was employed. Ethylene glycol dimethacrylate (EGDMA) were purchased from Fluka A.G. (Buchs, Switzerland). Benzoyl peroxide (BPO), 5-methyl-5-(methylthio)-4-vinylthiophene-2-carboxylic acid (VTCA), methylmercury chloride and mercuric chloride were supplied by Sigma-Aldrich and used as received.

2.2. Instrumentation
The concentration of mercury and other ions in the aqueous phase, were measured using an inductive coupled plasma-atomic emission spectrometer (ICP-AES) (Perkin-Elmer). The working wavelengths for mercury, cadmium, copper, zinc and lead were 223.652, 228.802, 327.393, 206.200 and 220.353 nm, respectively. An Orion pH/mV meter (model SA 720) in combination to Ross glass pH electrode (Orion 81–02) was used for all pH measurements.

2.3. MIP preparation
The procedure for MIP synthesis used in this research work was based on a previous work (Kamel et al., 2008). The template (HgCl₂ or methylmercury chloride, 0.02 mmol) was first added into a bottle containing a mixture of solvent (acetonitril, 4 mL) and 5-methyl-5-(methylthio)-4-vinylthiophene-2-carboxylic acid (VTCA) as a functional monomer (0.1 mmol), and sonicated for 5min at ambient temperature. The cross-linker (24.5 mmol) and initiator (80 mg) were then added into the solution. This was followed by purging with N₂ gas for 5 min in order to get rid of oxygen in solution, which would retard the synthesis process due to the annihilation of free radicals generated from the decomposition of the initiator. Thereafter, the bottle was sealed to prevent air from entering the bottle. Finally, the solution was cured at 70 °C for 1 h. The resulting polymers were grounded and sieved to particle sizes ranging from 50 to 150 µm. The polymers were washed with a mixture of methanol and acetic acid (volume ratio of 9:1) for 4 times, and each at duration of 1.5 h. The total volume of the eluting solution for the first extraction was 10 and 5mL for each of the subsequent elutions. Then, the polymer was washed with methanol for 24 h. This was followed by another two extractions with methanol for 1.5 h each. The powder collected after centrifugation was finally dried overnight in a vacuum desiccator. The NIP was synthesized and treated in the same way.

2.4. Experiments of adsorbing performance
Adsorption of methylmercury and mercury ions from aqueous solutions was investigated in batch experiments. Effects of the initial CH₃Hg⁺ /Hg²⁺ ion concentrations, pH of the medium on the adsorption rate and adsorption capacity were studied. Adsorption isotherms were obtained with different initial concentrations of either Hg²⁺ or CH₃Hg⁺ while maintaining MIP dosage at a constant level (0.5 gm). In order to correct for any adsorption of mercury ions on the container surface, control experiments were carried out in the absence of the MIP particles. These experiments indicated that no adsorption by the container walls was detected.

Adsorption experiments for CH₃Hg⁺ or Hg²⁺ were conducted by using 50 mL aliquots of a test solution containing 10.0 mg L⁻¹ CH₃Hg⁺ or Hg²⁺. The solutions were adjusted to pH 5 and placed in 250 mL reagent bottles. A known quantity (0.1–2.0 g) of either MIP or NIP microbeads was added to each bottle and the pH was adjusted to 5 using 0.1N of either nitric acid or sodium hydroxide solution. The solutions were agitated at a speed of 150 rpm for 5–120 min at 25±1 °C in a shaking incubator. The polymer microbeads were separated by filtration and mercury content of the filtrate was determined using inductive coupled plasma-atomic emission spectrometer (ICP-AES). Percentage removal (R, %) was calculated according to the following equation:

\[ R = \left( \frac{C_o - C_f}{C_o} \right) \times 100 \]  

……(1)
where \( R \) is the percent removal of mercury, \( C_0 \) and \( C_e \) are the initial and residual concentrations (mg L\(^{-1}\)) CH\(_3\)Hg\(^+\) or Hg\(^{2+}\)), respectively. In all experiments, the difference between the initial mercuric concentration (\( C_0 \)) and the equilibrium concentration (\( C_e \)) was calculated and used to determine the adsorptive capacity (\( q_e \)) as follows:

\[
q_e = \frac{V}{m} (C_0 - C_e) \quad \text{(2)}
\]

where \( V \) is the total volume of mercury solution (mL), \( m \) is the mass of adsorbent used (g), \( C_0 \) is the initial concentration of mercury solution (mg L\(^{-1}\)), and \( C_e \) is the residual mercury concentration (mg L\(^{-1}\)). The linear model, which describes the accumulation of solute by sorbent as directly proportional to the solution concentration is presented by the relation:

\[
q_e = K_D C_e \quad \text{(3)}
\]

The constant of proportionality or distribution coefficient \( K_D \) is often referred to as the partition coefficient.

The Langmuir isotherm equation is given by the equation:

\[
q_e = \frac{q_{\text{max}} b C_e}{1 + b C_e} \quad \text{(4)}
\]

where \( q_e \) is the solid phase adsorbate concentration in equation (mg g\(^{-1}\)), \( q_{\text{max}} \) is the maximum adsorption capacity corresponds to complete monolayer coverage on the surface (mg g\(^{-1}\)) and \( b \) is the Langmuir constant (g mL\(^{-1}\)) which related to the energy of adsorption.

Equation (4) can be rearranged to the following linear form:

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{q_{\text{max}} b} \frac{1}{C_e} \quad \text{(5)}
\]

The Freundlich isotherm is the most widely used non-linear sorption model and is given by the general form:

\[
q_e = K_F C_e^{1/n} \quad \text{(6)}
\]

where \( K_F \) relates to sorption capacity and \( n \) to sorption intensity.

The logarithmic form of Eq. (6) given below is usually used to fit data from batch equilibrium studies:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{(7)}
\]

### 2.5. Selectivity experiments

The batchwise selective adsorption experiments of Cd\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\) and Pb\(^{2+}\) ions with respect to CH\(_3\)Hg\(^+\) and Hg\(^{2+}\) were conducted using imprinted and non-imprinted polymer. A 50.0 mL solution containing 10.0 mg L\(^{-1}\) from each metal ion was treated with 0.5 gm of the CH\(_3\)Hg\(^+\)-imprinted microbeads at pH 5.0 at room temperature and stirred magnetically at 600 rpm. After adsorption equilibrium, the concentration of each metal ion in the remaining solution was measured by an ICP-AES.

The selectivity factor (\( \alpha \)) for the binding of a specific metal ion in the presence of competitor species can be obtained from equilibrium binding data according to

\[
\alpha = \frac{q_{\text{template}}}{q_{\text{interferent}}} \quad \text{(8)}
\]

Where, \( q_{\text{template}} \) and \( q_{\text{interferent}} \) are the adsorption capacity of either CH\(_3\)Hg\(^+\) or Hg\(^{2+}\) by the prepared MIP microbeads.

### 2.6 Analytical Applications

A synthetic sea water samples were prepared as described (Spiegler, 1962), and spiked with various Hg\(^{2+}\) or CH\(_3\)Hg\(^+\) concentrations (5.0-20.0 mg L\(^{-1}\)). 0.5 gm of MIP beads was added to a 50.0 mL flask containing 50.0 mL of the spiked sea water sample. After being shaken for 1 h at room temperature, the samples were centrifuged and filtered. The free Hg\(^{2+}\)/CH\(_3\)Hg\(^+\) concentration in the filtrate was detected by ICP-AES. All the experiments were performed in triplicate.

### 3. Results and Discussion

Molecular imprinting is a process where the target molecule (or a derivative thereof) acts as a template around which interacting and cross-linking monomers are arranged and copolymerized to form a cast-like shell (Fig. 1) (Arshady et al., 1982 and Haupt, 2003). Initially, the monomers form a complex with the template through covalent or non-covalent interactions. After polymerization and removal of the template, binding sites are exposed that are complementary to the template in size, shape, and position of the functional groups, which are held in place by the cross-linked structure. In essence, a molecular memory is imprinted in the polymer, which is now capable of rebinding the template selectively. Thus, molecularly imprinted polymers (MIPs) possess the most important feature of biological receptors – the ability to recognize and bind specific target molecules. In this study, we aimed to establish a simple and sensitive analytical system based on MIPs for the removal of CH\(_3\)Hg\(^+\) as a hazardous waste.

#### 3.1. Effect of contact time

The effect of contact time on the adsorption capacity of either CH\(_3\)Hg\(^+\) or Hg\(^{2+}\) by the prepared MIP microbeads is shown in Fig. 2. The removal of mercuric ions was rapid in the initial stages of contact time and gradually decreased with lapse of time until equilibrium. The equilibrium time is the time taken for the maximum adsorption of the species onto the adsorbent surface, above which the adsorption remains constant. It is one of the important parameters for economical wastewater treatment applications. The curves were shown in Fig. 2; the initial portion of the curve rises linearly and is change in to a curve and levels of 25 and 120 min of contact time for 10 mg L\(^{-1}\) Hg\(^{2+}\) or CH\(_3\)Hg\(^+\) concentration. At later times the available adsorption sites became fewer which decrease the rate of adsorption and an equilibrium state was attained (Kadirvelu et al., 2000). The removal curves were single, smooth and continuous indicating mono-layer coverage of mercuric ions on
the surface of the adsorbent (Namasivayam et al., 1996 and Namasivayam et al., 1998).

![Chemical structure]

**VTCA (functional monomer)** + **HgCl₂ or CH₃HgCl** (Template) → **EGDMA (cross linker)**

**Figure 1:** Protocols for preparation of the MIP micro beads and their recognition towards mercury compounds.

![Graph and diagram]

**Figure 2:** The removal efficiency of Hg²⁺/CH₃Hg⁺-imprinted polymers microbeads. Other conditions: 0.5 g of sorbent (MIP), 50 mL of 10 mg L⁻¹ either Hg²⁺ or CH₃Hg⁺ adsorbate, pH5, temperature 25 °C.

### 3.2. Effect of pH

The pH value of the solution is an important parameter for the adsorption experiments. The effect of varying pH values on either Hg²⁺ or CH₃Hg⁺ uptake was investigated using the batch procedure (Fig. 3). The lowest metal uptake values were determined at pH 2.0 for methyl mercury. At lower pH, more protons will be available to protonate the active functional groups in the imprinted polymer, and then the adsorption would be depressed by the electrical repulsion. The optimal adsorption initial pH values of the solutions were taken to be 5.0 for mercuric ions, because more negative charge could be developed from COOH groups in the MIP and would favour the surface electrostatic interactions with aqueous mercury cations or surface mercury adsorption. These optimal pH values were chosen for the subsequent experiments.
3.3. Sorption isotherm

Sorption isotherm is used to characterize the interactions of each molecule with adsorbents. This provides 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 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.

Equations (3), (5) and (7) are used for the analysis of equilibrium batch experiment data assuming linear, Langmuir and Freundlich isotherms, respectively. Figs. 4-6 present the linear, Langmuir and Freundlich isotherm plots of CH₃Hg⁺ and Hg²⁺ adsorption on MIP microbeads. The equilibrium data are fitted very well to Langmuir isotherm. Calculation of the isotherm parameters using these plots gives the data presented in Table 1. The fact that the Langmuir isotherm is in agreement with the experimental data very well may be due to homogenous distribution of caves on the MIP surface.
values for the MIP samples with the control samples shows an increase in adsorption affinity of recognition sites to the imprinted CH polymer for CH ions against matrix elements. The applicability of the method was tested to the sea water sample. The standard addition method was applied to check the selectivity of the ion imprinted polymer for CHHg ions against matrix elements. The synthetic sea water sample was prepared as described (Spiegler, 1962). The MIP beads showed higher (97.6 % and 98.2%) removal efficiency than NIP (66.5% and 61.5%) beads under similar conditions for Hg²⁺ and CHHg⁺ ions, respectively.

### 3.4. Selectivity studies

Competitive adsorption of CHHg⁺/Hg²⁺, CHHg⁺/Cd²⁺, CHHg⁺/Cu²⁺, CHHg⁺/Zn²⁺, CHHg⁺/Pb²⁺, Hg²⁺/Cd²⁺, Hg²⁺/Cu²⁺, Hg²⁺/Zn²⁺, Hg²⁺/Pb²⁺ from their couple mixture was investigated in a batch system. Table 2 summarizes竞争性吸附的CHHg⁺/Hg²⁺, CHHg⁺/Cd²⁺, CHHg⁺/Cu²⁺, CHHg⁺/Zn²⁺, CHHg⁺/Pb²⁺, Hg²⁺/Cd²⁺, Hg²⁺/Cu²⁺, Hg²⁺/Zn²⁺, Hg²⁺/Pb²⁺从其混合物的等温吸附。表2总结了竞争性吸附的CHHg⁺/Hg²⁺, CHHg⁺/Cd²⁺, CHHg⁺/Cu²⁺, CHHg⁺/Zn²⁺, CHHg⁺/Pb²⁺, Hg²⁺/Cd²⁺, Hg²⁺/Cu²⁺, Hg²⁺/Zn²⁺, Hg²⁺/Pb²⁺从其混合物的等温吸附。

Table 2: The Selectivity Parameters of CHHg⁺-Ion Imprinted Polymer for CHHg⁺ Ions.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>CHHg⁺ imprinted polymer</th>
<th>Hg²⁺ imprinted polymer</th>
<th>Non imprinted beads</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kₐ (mL g⁻¹)</td>
<td>α</td>
<td>α'</td>
</tr>
<tr>
<td>CHHg⁺</td>
<td>6.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>2.52</td>
<td>2.40</td>
<td>2.18</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>0.921</td>
<td>6.57</td>
<td>3.32</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.643</td>
<td>9.41</td>
<td>3.13</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>0.592</td>
<td>10.22</td>
<td>2.82</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>0.723</td>
<td>8.38</td>
<td>2.79</td>
</tr>
</tbody>
</table>

### 3.5. MIP reuse

The regeneration of the adsorbent is likely to be a key factor in improving process economics. Desorption of Hg⁻² or CHHg⁺ ions from their corresponding MIP beads was performed in a batch experimental set-up. An adsorption–desorption cycles were repeated five times by using the same MIP beads. The adsorption capacity of the recycled MIP beads can still be maintained at 80% of its original value at the fifth cycle. The reason for that may be probably related to the loss of some memory cavities during regeneration process. It can be seen concluded that the MIP beads can be used many times without decreasing their adsorption capacities significantly. The removal percent of either Hg²⁺ or CHHg⁺ ions was not significantly changed with increasing reuse number. It decreased from 23% to 18% with the increase of the reuse number from 1 to 5. In general, the MIP beads had certain regeneration adsorption efficiency, and could be used repeatedly.

### 3.6. Application to removal of Hg²⁺ and CHHg⁺ ions

The applicability of the method was tested to the sea water sample. The standard addition method was applied to check the selectivity of the ion imprinted polymer for CHHg⁺ ions against matrix elements. The synthetic sea water sample was prepared as described (Spiegler, 1962). The MIP beads showed higher (97.6 % and 98.2%) removal efficiency than NIP (66.5% and 61.5%) beads under similar conditions for Hg²⁺ and CHHg⁺ ions, respectively.

### 4. Conclusions

This study demonstrated the potential of CHHg⁺/MIP synthesized by thermal polymerization for the selective removal of CHHg⁺ from sea water samples. The results of binding experiments indicated that the prepared MIP exhibited outstanding selectivity and adsorption ability for CHHg⁺. The adsorption of CHHg⁺ was very rapid and the binding equilibrium was achieved within 40 min. The removal efficiency of either CHHg⁺ or Hg²⁺ ions by MIP and NIP remained unchanged at pH 5. The selectivity and adsorption capacity of MIP exhibited better selectivity and higher removal efficiency than that of NIP beads in spiked deionized water. The MIP developed in this study has excellent regeneration characteristics and can be reused at least 5 times without significant loss of loading capacity.

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### Corresponding author

Ayman H. Kamel

1Chemistry Department, College of Science, Qassim University, Burayida, KSA
References


materials for the potentiometric measurement of oxytetracycline. Biosens. & Bioelect., 26:566-574


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