Lead Adsorption onto Various Solid Surfaces

Handojo Djati Utomo¹²

¹School of Architecture and The Built Environment, Division of Civil Engineering, Singapore Polytechnic, Singapore
²Department of Chemistry, Marine and Freshwater Chemistry Laboratory, University of Otago, Dunedin, New Zealand
Email: han@sp.edu.sg, handojo_djatiutomo@yahoo.com

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Abstract

Adsorption is becoming an important method in water and wastewater treatment technology at low concentrations. Pb²⁺ adsorption at low concentration onto various solid surfaces using either nano metal oxide of MnO₂, or granulated activated carbon (GAC) or agricultural by-products such as tea leaves and coffee residue are considered promising. In this adsorption study the measurements were conducted by equilibratingLead solutions at different concentrations range 19 - 291 µmol·L⁻¹ with various adsorbent suspensions in the concentration range 0.388 - 8.738 g·L⁻¹. Comparing all the adsorption capacities calculated using Langmuir equation Pb²⁺ adsorption by MnO₂ shows the highest adsorption capacity with the estimated Γ₀ = 528.0 µmol·g⁻¹ at a fixed equilibrium constant K = 0.0119 L·µmol⁻¹. In addition, the Pb²⁺ adsorption by coffee residue is subject to a particle concentration effect in which the adsorption density decreases as the concentration of solid adsorbent Cₛ is increased. The Pb²⁺ adsorption by tea leaves, MnO₂ and GAC shows less dependency to the concentration of solid adsorbent Cₛ, especially at lower metal ion concentrations. In the particular case of Pb²⁺ adsorption on MnO₂ there appears to be no dependence on Cₛ.

Keywords

Adsorption, Coffee Residue, GAC, Pb²⁺, Particle Concentration Effect, Tea Leaves, Nano Metal Oxide of MnO₂

1. Introduction

Lead is among the most toxic heavy metal ion affecting the environment [1]. It may come into waterways through the combustion of fossil fuels and the smelting of sulphide ore, and into lakes and streams by acid mine drainage. Process industries, such as battery manufacturing and metal plating and finishing are also prime source
of lead pollution.

Lead accumulates mainly in bones, brain, kidney and muscles and may cause many serious disorders like anaemia, kidney diseases, nervous disorders and sickness even death. In 2001, EPA published Identification of Dangerous Levels of Lead [2] and Identifying Lead Hazards in Residential Properties [3]. The World Health Organization (WHO) stated a legal limit of 50 ppb level for lead in 1995, which is decreased to 10 ppb level in 2010. The stringent requirement for lead in aquatic environment has triggered some wastewater engineer to work harder in searching for inexpensive material and technology to uptake lead pollutants from water and wastewater.

At low concentration of heavy metal concentration adsorption process is becoming an important pollutant removal method in water and wastewater treatment technology. After the revelation that activated carbon can adsorb organic and inorganic contaminants the advent of new technology is shifting towards sustainable technology that use more economic and environmentally friendly materials as a replacement of activated carbon.

The re-use of natural waste materials that arise through various industrial processes for additional purposes, rather than simple disposal, makes both environmental and commercial sense [4]. There also has been a recent focus on agricultural and food industry wastes such as tea, coffee grounds and rice hull as alternatives to membrane filtration, synthetic ion-exchange resins or activated carbon for treating heavy metal-containing waste waters [5] [6]. Tannin-containing materials such as exhausted coffee contain metal-binding polyhydroxy polyphe-nol functional groups and they are available in large quantities from the manufacture of instant coffee [4] [7]. While there have been several studies of metal ion adsorption by tea and coffee the detailed chemistry causing their affinity for different metal ions is not yet well-known [8] [9].

Adsorption of metal ions and other solutes on solid surfaces can be described by simple isotherms such as the Langmuir or Freundlich equations [9] [10]. In this approach, the extent of adsorption of lead ion (Pb\(^{2+}\)) per unit mass of solid adsorbent is described by simple isotherm equations that are based on conceptual models similar to those used for homogeneous equilibria. For this study the experimental data was applied to Langmuir isotherm model only due to the consistency in explaining the existence of particle concentration effect in the previous study [11]. In the Langmuir model the adsorption of a solute M by a surface S– is considered to be a result of the equilibrium surface reaction

\[
M + S\overset{\leftrightarrow}{\rightarrow} MS
\]

where \([M – S]\) is the concentration of adsorbed solute M, \(C_e\) is the concentration of unadsorbed M and \([S–]\) is the concentration of free surface sites, all at equilibrium. This formalism gives rise to the Langmuir adsorption isotherm

\[
\Gamma = \Gamma_m \frac{KC_e}{(1 + KC_e)}
\]

where \(\Gamma = [M – S]\) is the adsorption density, \(\Gamma_m\) is the maximum concentration of adsorbed M per unit mass of solid and \(\Gamma_m\) is the maximum concentration of adsorbed M.

In Equation (2), the adsorption properties are inherently described by the equilibrium constant in Equation (1) which may be identified with the free energy of adsorption of M by the solid. Normally, \(K\) and \(\Gamma_m\) may be determined simultaneously from measurements of \(\Gamma\) and \(C_e\) under different conditions.

This batch adsorption study was meant to be a comparison study set up using different concentration of adsorbents at various concentration of Pb\(^{2+}\). Granulated Activated Carbon (GAC) and nano metal oxide of MnO\(_2\) were used as comparisons to agricultural by-product materials of tea leaves and coffee residues.

2. Materials and Methods

2.1. Chemicals

All chemicals including MnO\(_2\) and GAC used in this study were of analytical grade obtained from Merck, Germany. Stock solution of Pb\(^{2+}\) was prepared using Lead nitrate (Pb(NO\(_3\))\(_2\)) in deionised water. Purified water was prepared using a Millipore Milli-Q (Bedford, MA, USA) water purification system. Standard solution of Pb\(^{2+}\) (1000 mg/L) for flame atomic absorption spectrometry analysis was obtained from Merck, Germany. Pb\(^{2+}\) solutions of different concentrations were obtained by diluting the stock solution. Standard acid of 0.1 M HNO\(_3\) and base solutions of 0.1 M NaOH were used for pH adjustments.
2.2. Preparation of Tea and Coffee Adsorbents

Exhausted coffee ground used was obtained from a local coffee manufacturer using steam extraction (Cerebos Gregg Ltd.). This material resulted from various coffee sources. The solid was dried in a stainless steel pan at 105°C for about 2 days to remove moisture, then ground and sieved through an ASTM 18 stainless steel sieve (1 mm mesh size). The solid was then repeatedly extracted with 0.1 M NaOH solution to remove soluble materials, neutralized with 0.1 M HNO₃ and then rinsed extensively with deionized water base (Millipore Milli-Q) as reported earlier [6]. The material was then dried again at 105°C before ready to use for the batch experiment.

A Sri Lankan black tea variety known commercially as English Breakfast was obtained from a local supermarket. Tea leaves were removed from tea bags after Milli-Q pretreatment and drying at 105°C before being used as reported earlier [6].

2.3. Batch Adsorption and Methods of Analysis

Adsorption measurements were conducted by equilibrating Pb²⁺ solutions at different concentrations range 19-291 µmol·L⁻¹ with various adsorbent suspensions in the concentration range 0.388 - 8.738 g·L⁻¹. Due to strong adsorptive properties found in preliminary experiment lower concentration of manganese dioxide (MnO₂) with range 0.388 - 1.214 g·L⁻¹ was used rather than higher concentration range 2.913 - 8.738 g·L⁻¹, which used for other adsorbents. Equilibration took place at room temperature (21°C) using a rotating turntable overnight at 30 rpm. The suspensions were then filtered through a Whatman 114 filter and the concentrations of metal ion remaining in solution were determined by flame atomic absorption spectrometry using matrix-matched standards (Perkin Elmer AA 3100 series). From this the amount adsorbed was calculated by difference. For a given value of Γ the data were fitted to the linearized form of Langmuir isotherm, Equation (2), using non linear least-squares regression. This method, which differs from the more classical linearized fitting in a previous study, was carried out using the software NLReg [6][12]. It involves varying the values of K and Γₘ from initial guesses until the sum of squared deviations of the calculated Γ from the experimental value for each data point is minimized.

3. Results and Discussions

In most experiments each set of Pb²⁺ concentrations ranging from 19 to 291 µmol·L⁻¹ were equilibrated with 3 (three) different concentrations of adsorbent Cₛ except for coffee residue which used a wider range of concentration as detailed in Table 1.

More variations of coffee grounds concentration were used to clearly discuss a particle concentration effect found in this particular adsorption study. In this case coffee ground concentration used was extended from the concentrations of 0.971, 2.913, 4.369, 5.825 and 8.738 g·L⁻¹. The result was expected in such cases that different concentrations of adsorbent Cₛ equilibrated with Pb²⁺ ranging from 19 to 291 µmol·L⁻¹ fit into a single Langmuir model, i.e. single values of K and Γₘ for each type of adsorbent.

Figure 1 shows the adsorption result at different MnO₂ solid concentration Cₛ. The calculated curves of Γ versus Cₛ that resulted from this fitting are also shown in the figure. The curve was calculated using a fixed value of K = 0.0119 L·µmol⁻¹ and a fixed value of Γₘ = 528.0 µmol·g⁻¹ for all Cₛ. The result shows that a single Langmuir equation adequately describes the data for the 3 different solid concentrations Cₛ. This implies that Pb²⁺ adsorption on MnO₂ does obey the Langmuir Equation (2).

Adsorption of Pb²⁺ on GAC in aqueous solution was investigated using the procedure described above for MnO₂ at the same concentration of solid Cₛ as used for tea leaves in the range 2.913 - 8.738 g·L⁻¹. The result is shown in Figure 2 with the curve was calculated using a fixed value of K = 0.0158 L·µmol⁻¹ and a fixed value of Γₘ = 134.0 µmol·g⁻¹ for all Cₛ. Again in this case, the results are reasonably well-described by a single Langmuir equation for different values of the solid concentrations Cₛ. This implies that Pb²⁺ adsorption on GAC does obey the Langmuir Equation (2).

Figure 3 shows the adsorption results for Pb²⁺ at different coffee solid concentrations Cₛ. The results are presented as the adsorption density Γ as a function of the measured concentration of unadsorbed metal ion Cₑ. For a given value of solid concentration Cₛ, the data were fitted to the linearized form of Langmuir isotherm, Equation (2), using least-squares regression; the calculated curves are shown in the figure. Separate estimates of K and Γₘ values were obtained for each Cₛ value, with results shown in Table 2.
Figure 1. Adsorption density $\Gamma$ as a function of the measured equilibrium concentration $C_e$ of metal ion Pb$^{2+}$ for 3 different concentrations of manganese dioxide $C_s$, i.e. 0.388, 0.583 and 1.214 g L$^{-1}$.

Figure 2. Adsorption density $\Gamma$ as a function of the measured equilibrium concentration $C_e$ of metal ion Pb$^{2+}$ for 3 different concentrations of GAC $C_s$, i.e. 2.913, 5.825 and 8.738 g L$^{-1}$.

Table 1. Adsorbent concentration used to equilibrate Pb$^{2+}$ solutions at concentrations range 19 - 291 µmol L$^{-1}$.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>GAC (g L$^{-1}$)</th>
<th>Tea leaves (g L$^{-1}$)</th>
<th>MnO$_2$ (g L$^{-1}$)</th>
<th>Coffee residue (g L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration ($C_s$)</td>
<td>2.913, 5.825, 8.738</td>
<td>2.913, 5.825, 8.738</td>
<td>0.388, 0.583, 1.214</td>
<td>0.971, 2.913, 4.369, 5.825, 8.738</td>
</tr>
</tbody>
</table>

Table 2. Adsorption results for Pb$^{2+}$ at different solid concentrations $C_s$ for which separate estimates of $K$ and $\Gamma_m$ were obtained for each $C_s$ value [11]. The values in parentheses are the standard errors for each parameter obtained from the non-linear regression fitting.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Concentration ($C_s$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$ (L·µmol$^{-1}$)</td>
<td>0.0748 (0.0069)</td>
</tr>
<tr>
<td>$\Gamma$ (µmol·g$^{-1}$)</td>
<td>72.4 (1.3)</td>
</tr>
<tr>
<td>$C_s$ (g L$^{-1}$)</td>
<td>2.913</td>
</tr>
<tr>
<td>$C_s$ (g L$^{-1}$)</td>
<td>4.369</td>
</tr>
<tr>
<td>$C_s$ (g L$^{-1}$)</td>
<td>5.825</td>
</tr>
<tr>
<td>$C_s$ (g L$^{-1}$)</td>
<td>8.738</td>
</tr>
</tbody>
</table>

The results shown in Figure 3 were very different from the previous two results, when using GAC and MnO$_2$ as adsorbents. The results revealed that while the Langmuir Equation (2) adequately describes the adsorption equilibrium for a given $C_s$ value, the best-fit values of both $K$ and $\Gamma_m$ vary with $C_s$. This is not consistent with the simple Langmuir equation, which should give the same values of both parameters at different adsorbents concentrations.
A number of authors had reported that the parameters $K$ and/or $\Gamma_m$ could vary when measurements were made at different concentrations of solid. Examples included quinoline adsorption by calcium montmorillonite [12], 2,2-bipyridine onto Na⁺-kaolinite [13], phosphate by hydrous aluminium oxides [14] and zinc by goethite [15] [16]. This dependence on $C_s$ violates the simple assumptions of the Langmuir theory.

Macchi [10] reported that the adsorption of Hg²⁺ by coffee grounds shows anomalous behaviour when the solids concentration $C_s$ is varied. However, they did not attribute this to an effect of $C_s$ on adsorption, but on the competitive effect of soluble organic substances leached out of the coffee. In fact the particle concentration effect on coffee grounds, when adsorbing heavy metal ions, was affected by particle aggregation [11].

The adsorption results using tea leaves adsorbent show different behaviour from that showed with coffee residue in Figure 3. There is very much less dependence of the adsorption curve on the concentration of solid. As shown in Figure 4, a single Langmuir model using fixed values of $K = 0.0119$ L·μmol⁻¹ and $\Gamma_m = 5.0$...
μmol·g⁻¹ for all $C_s$ values fitted the data reasonably well, given the scatter of the points at 2.913 g/L. This suggests that lead adsorption on tea leaves approximately follows the simple Langmuir equation.

4. Conclusions

Pb²⁺ adsorption at low concentration onto various solid surfaces using either nano metal oxide of MnO₂, or granulated activated carbon (GAC) or agricultural by-products such as tea leaves and coffee residue is unarguably promising.

Comparing all the adsorption capacities calculated using single Langmuir equation the Pb²⁺ adsorption using nano metal oxide of MnO₂ shows the highest adsorption capacity with the estimated $\Gamma_m = 528.0 \mu\text{mol} \cdot \text{g}^{-1}$ at a fixed equilibrium constant $K = 0.0119 \text{L} \cdot \mu\text{mol}^{-1}$. This could be due to the largest surface area per mass of MnO₂.

The Pb²⁺ adsorption by coffee residue is subject to “particle concentration effect” in which the adsorption density decreases as the concentration of solid adsorbent $C_s$ is increased. The Pb²⁺ adsorption onto tea leaves, MnO₂ and GAC shows less dependency to the concentration of solid adsorbent $C_s$, especially at lower metal ion concentrations. In the particular case of Pb²⁺ adsorption on MnO₂ there appears to be no dependence on $C_s$ and the single Langmuir equation is followed.

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References


