Adsorption of Mercury Ion From Aqueous Solutions Onto Bentonite Clay

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Abstract:
In this research, the bentonite clay was utilized for the removal of mercury ion from aqueous solutions. Adsorption experiments were conducted under various conditions where the batch method was used to determine the best adsorption ratio and the adsorption capacity for the concentration used of Hg(II) ion between (100-10 mg/L), the results show that the best concentration was (10 mg/L) where the adsorption ratio was 88.7 and the adsorption capacity was 0.444 mg/g. The adsorbent dose was 20 g/L, and the shaking time found that it equal to 140 min and the best pH value between (5-8). The effect of temperature and thermodynamic functions wear also studied, the adsorption capacity was increased with increased the temperature and the reaction was endothermic. The equilibrium isotherm data was analyzed using the Langmuir equation, where found $q_m$ and $b$ are equal to 3.367 mg/g and 0.134 respectively. The rate constant $k_2$ for the adsorption of Hg(II) ion is equal to 0.1067 mg/g.min.

Keywords: The bentonite clay, mercury ion, adsorption, batch method, Langmuir isotherm and the rate constant.

Introduction:
The presence of heavy metals in aqueous solution beyond certain limit creates serious threat to the environment because of their non-degradability and toxicity. Mercury has many negative effects on human beings, such as the disruption of the nervous system, defects in the work and functions of the brain, distorting of DNA and chromosomes, and skin rashes because of allergies. Mercury metal has many uses because of its high density it is used in barometers and manometers, it is extensively used in thermometers and its ease in amalgamating with gold is used in the recovery of gold from its ores. Industry uses mercury metal as a liquid electrode in the manufacture of chlorine and sodium hydroxide by electrolysis of brine. Mercury is still used in some electrical gear, such as switches and rectifiers, which need to be reliable, and for industrial catalysis. Much less mercury is now used in consumer batteries and fluorescent lighting, but it has not been entirely eliminated.

Several methods are available to uptake toxic metals from aqueous solutions such as chemical precipitation, electrolysis (membrane separation), ion exchange resins, solvent extraction, reverse osmosis, photoreduction and adsorption. Adsorption is generally efficient in the removal and recovery of heavy metal ions because of their physical and chemical stabilities, different conventional and non-conventional type of adsorbents have been used for removal of mercury ions, such as, activated carbon, tree fern, montmorillonite clay, Camel bone charcoal, corn cobs, etc.
Bentonite clay is widely applied in many fields of adsorption technology including the removal of metals ions (19,20), phenols (21-23), organic molecules (24,25), polymers (26,27), pesticides (28), radionuclides (29) and dyes (30,31). Bentonite, which is predominantly montmorillonite clay, is characterized by one Al octahedral sheet placed between two Si tetrahedral sheets. The isomorphous substitution of Al$^{3+}$ for Si$^{4+}$ in the tetrahedral layer and Mg$^{2+}$ for Al$^{3+}$ in the octahedral layer results in a net negative surface charge on the bentonite. This charge imbalance is offset by exchangeable cations (Na$^+$ and Ca$^{2+}$, etc.) at the bentonite surface. The layered structure of the clay expands after wetting. Na$^+$ and Ca$^{2+}$ are strongly hydrated in the presence of water, resulting in a hydrophilic environment at the bentonite surface (32).

The aim of the present work was to study the possibility of utilizing bentonite clay for the adsorption of mercury ions from aqueous solutions under various conditions.

Experimental Section:

1- Apparatus:
- 1- Spectrophotometer- PD-303, Japan.
- 3- pH-meter model Ionlop-720, Japan.
- 4- Oven, memmert 30C-220C, W.Germany.
- 5- Centrifuge machine, Hettich EBA35, Japan.

2- Adsorbent preparation:
Bentonite clay used in this study was obtained from the Geological Survey of the Ministry of Industry and Minerals, Baghdad, Iraq. It was washed with an excess amount of distilled water to remove carbonate and remove the soluble materials. Then it was dried in the oven at 105°C for (12h), the chemical analysis of bentonite clay is listed in Table (1) (33).

3- Preparation stock solution of Hg(II) (1000 mg/L):
A standard solution of 1000 mg/L of mercury ion was prepared by dissolving 0.1353 g of HgCl$_2$ in a minimum amount of distilled water in a 100 ml volumetric flask and the volume was made up to the mark with distilled water. Solutions of different concentrations were prepared by serial dilutions for mercury ion between (100-0.1 mg/L).

4- Adsorption studies:
Batch adsorption studies were carried out by adding (0.5 g) of bentonite clay to 25 ml of Hg(II) solution and shaken was done by a shaker bath. The pH of the solution was adjusted by adding dilute HCl or NaOH solution. At regular intervals 5 ml samples were withdrawn and filtered. The residual concentration in the solution was estimated colorimetrically with dithizone as orange-yellow dithizionate which is extractable into CC$_4$ at $\lambda_{\text{max}}$ equal to 485 nm (34). From the Hg(II) concentrations measured before and after the adsorption (C$_i$ and C$_e$, mg/L, respectively) and weight of bentonite clay (m, g), as well as volume of aqueous solution (V, L), the percentage of adsorption (% Adsorption) and the equilibrium adsorption capacity of mercury ion (q$_e$, mg/g) were calculated according to equations (1) and (2):

$$\% \text{Adsorption} = \frac{C_i - C_e}{C_i} \times 100 \quad \ldots \ldots (1)$$

$$q_e = \frac{(C_i - C_e) \times V}{m} \quad \ldots \ldots (2)$$

Results and Discussion:

1- Effect of initial concentration and adsorbent dose:
The effect of initial Hg(II) concentration on the adsorption ratio was studied by varying the initial Hg(II) concentration between (100-10) mg/L. It is observed that the percentage of adsorption increased from 57.4 to 88.7 and the adsorption capacity decreased from 2.87 to 0.444 mg/g when the concentration decreased from 100 to 10 mg/L, the result show that the best concentration of Hg (II) was given the best adsorption ratio was 10 mg/L. From the results, noted the adsorption ratio of
Hg (II) decreased with an increase in initial Hg (II) concentration where as the amount of Hg (II) uptake per unit weight of the adsorbent (mg/g) was found to increase, due to increased surface area, more adsorption sites are available causing higher removal of Hg (II), are shown in the table (2) and figure (1).

Batch experiments were carried out by varying the adsorbent dose between (20-4) g/L at the best initial concentration (10 mg/L) by change the weight of bentonite clay or change the volume of Hg (II) solution. The percentage of adsorption decreases from 88.7 to 68.9 and the adsorption capacity increases from 0.444 to 1.723 mg/g, are illustrated in the table (3). The increase in the percentage of adsorption is due to the increase in amount of free surface available or decreases the amount of Hg (II) in aqueous solution (19).

**2- Influence of the shaken time:**

Removal of mercury ion on the bentonite clay as a function of time at the best initial concentration (10 mg/L) was studied, where shaken it to different times between (20-200) min. From the experimental data, it is observed that the percentage of adsorption increased with increasing contact time up to 140 min. The percentage of adsorption increases from 61.3 to 88.7, because of the surface of bentonite clay contain oxygen atoms which bonded with mercury ion (20), it is shown in the figure (2).

**3- Effect of p**H:

Adsorption experiments were performed over a range of pH (1-10) for the best initial mercury ion concentration (10 mg/L) and shaken time to 140 min. From figure (3) it is observed that the percentage of adsorption increase from pH (5-8). At low pH, i.e., higher hydrogen ion concentration, the negative charges at the surface of clay, become contend between H+ ion and Hg (II) which bonded with oxygen atoms, it occur to decrease the percentage of adsorption. Above pH 8 the adsorption decrease, due to the effect of the hydroxyl ion, (Hg(OH)+) may be formed (15).

**4- Effect of temperature:**

Experiments were performed at different temperatures, from 288 to 328 K° for the best initial mercury ion concentration (10 mg/L) at pH equal to 7 and shaken time to 140 min. The adsorption capacity of Hg (II) increased from 0.398 to 0.444 mg/g when the temperature increased from 288 to 328 K°, are shown in the table (4) and figure (4). The increase in the adsorption capacity showed the endothermic nature of the process.

The change in enthalpy (ΔH) and entropy (ΔS) were calculated from the plot of log (q/Ce) versus 1/T for mercury ion by using the Van’t Hoff equation (38), is shown in figure (5).

\[
\log \frac{q}{C_e} = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad \ldots \quad (3)
\]

Slope = \[ \frac{\Delta H}{2.303R} \] \quad \ldots \quad (4)

Intercept = \[ \frac{\Delta S}{2.303R} \] \quad \ldots \quad (5)

The adsorption enthalpy of the mercury ion calculated from slope of the plot is 19.62 KJ/mol and entropy (ΔS) was also calculated from intercept of the plot is 94.163 J/mol.K°. These values of the heat of adsorption show that the type of adsorption onto bentonite clay is physical adsorption, because the adsorption with the heat that is lower than 20 KJ/mol (35). The change in free energy (ΔG) was calculated from Gibbs equation (36),

\[
\Delta G = \Delta H - T\Delta S \quad \ldots \quad (6)
\]

The increase in the adsorption capacity of bentonite clay with temperature indicates an endothermic process. The positive value of (ΔS) suggested some structural changes in adsorbent and adsorbate and also reflects the affinity of the adsorbent material under consideration towards Hg (II) ions. The negative values of free energy (ΔG) show the spontaneous adsorption of metal ion on the adsorbent,
is illustrated in the table (5). The value of (ΔG) decreases with increasing temperature, demonstrating an increase in the feasibility of adsorption at higher temperatures.

5- Adsorption isotherm:
From the plot of q_e versus C_e of Hg (II) in figure (6), it is obvious that the adsorption isotherm of Hg (II) on bentonite clay is L-type according to the Gilles classification\(^{(37)}\). In this type of isotherm, the initial portion provides information about the availability of the active site to the adsorbate and the plateau signifies the monolayer formation. The initial curvature indicates that a large amount of Hg (II) is adsorbed at a lower concentration as more active sites of bentonite clay are available. As the concentration increases, it becomes difficult for a Hg (II) ion to find vacant sites, and so monolayer formation occurs.

In order to determine isotherm model that described more accurately the experimental data, the model developed by Langmuir is represented by the following linear equation\(^{(38)}\):

\[
\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad \ldots \ldots (7)
\]

Where \(q_e\) is the amount of adsorbate retained per unit weight of the adsorbent (mg/g) at equilibrium, \(C_e\) the equilibrium concentration of Hg(II) (mg/L), \(q_m\) and \(b\) are Langmuir constants related to the maximum saturation capacity of the bentonite clay (mg/g) and energy of adsorption (L/mg), respectively. The Langmuir constants (\(q_m\) and \(b\)) were calculated from the plots of \(C_e/q_e\) versus \(C_e\), using linear least-squares fitting where the slope equal to (1/\(q_m\)) and the intercept equal to (1/\(q_m b\)). The values of the constants of this model with correlation coefficients (R\(^2\)) are given in figure (7) and table (6).

6- Adsorption kinetic studies:
In the present studies, pseudo-first-order, pseudo-second-order equations have been used for modeling the kinetics of Hg(II) adsorption. The pseudo-first-order rate equation is expressed as:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \ldots \ldots (8)
\]

Where \(q_t\) and \(q_e\) are the adsorption capacity at time \(t\) and at equilibrium, respectively, and \(k_1\) is the rate constant of pseudo-first-order (min\(^{-1}\))\(^{(39)}\). The values of \(k_1\) at different adsorption parameters were calculated from the plot of log \((q_e - q_t)\) as a function of the time for the best initial Hg(II) concentration (10 mg/L) at pH equal to 6 and temperature equal to 328 K\(^0\) should give a linear relationship where the slope equal to (-\(k_1/2.303\)) and the intercept equal to (log \(q_e\)), is given by figure (8) and table (7). Although the correlation coefficient values were higher than 0.99, the experimental \(q_e\) did not agree with the calculated \(q_e\), obtained from the linear plots. Therefore, pseudo-first-order kinetic model did not describe the adsorption results of Hg(II) onto bentonite clay.

The pseudo-second-order rate equation is expressed as:

\[
\frac{t}{q_t} = \frac{1}{(q_e)^2 k_2} + \frac{t}{q_e} \quad \ldots \ldots (9)
\]

Where \(k_2\) is the rate constant of pseudo-second-order (g/mg.min), \(q_t\) and \(q_e\) are the adsorption capacity at time \(t\) and at equilibrium, respectively\(^{(40)}\). The values of \(k_2\) were calculated from the plot of \((t/q_t)\) versus \(t\) for the best initial Hg(II) concentration (10 mg/L) at pH equal to 6 and temperature equal to 328 K\(^0\), should give a linear relationship where the slope equal to \((1/q_e)\) and the intercept equal to \([1/(k_2(q_e)^2)]\), is given by figure (9) and table (8). It was noticed that the correlation coefficient value for the pseudo-second-order were found to be higher than that of the correlation coefficient value for the pseudo-first-order. The theoretical \(q_e\) value was closer to the experimental \(q_e\) value. In the view of these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the adsorption of Hg(II) onto bentonite clay in contrast to the pseudo-first-order model.
Conclusion:
The bentonite clay was found to be a good adsorbent for the removal of Hg(II) ion from aqueous solutions. The Hg(II) ion removal efficiency of the adsorbent is found to be increase with the increase in time, temperature and adsorbent dose, when decrease with increase adsorbate concentration. The percentage adsorption increases with increasing temperature, which indicates that, the adsorption mechanism is endothermic. The experimental values were well fitted to the Langmuir isotherm equation, where found \( q_m \) and \( b \) are equal to 3.367 mg/g and 0.134 respectively.

The adsorption kinetic followed a pseudo 2\textsuperscript{nd} order rate equation where \( k_2 \) is equal to 0.1067 g/mg.min.

Table (1) Chemical analysis of Bentonite clay

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>43.568</td>
</tr>
<tr>
<td>BaO</td>
<td>36.394</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>9.245</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>6.321</td>
</tr>
<tr>
<td>CaO</td>
<td>2.655</td>
</tr>
<tr>
<td>MgO</td>
<td>1.368</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>0.449</td>
</tr>
</tbody>
</table>

Table (2). The effect of Hg(II) concentration on the percentage of adsorption and the adsorption capacity

<table>
<thead>
<tr>
<th>( C_i, \text{mg/L} )</th>
<th>( C_e, \text{mg/L} )</th>
<th>% Adsorption</th>
<th>( q_e, \text{mg/g} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>42.6</td>
<td>57.4</td>
<td>2.87</td>
</tr>
<tr>
<td>90</td>
<td>34.74</td>
<td>61.4</td>
<td>2.763</td>
</tr>
<tr>
<td>80</td>
<td>26.8</td>
<td>66.5</td>
<td>2.66</td>
</tr>
<tr>
<td>70</td>
<td>20.93</td>
<td>70.1</td>
<td>2.454</td>
</tr>
<tr>
<td>60</td>
<td>15.42</td>
<td>74.3</td>
<td>2.229</td>
</tr>
<tr>
<td>50</td>
<td>10.35</td>
<td>79.3</td>
<td>1.983</td>
</tr>
<tr>
<td>40</td>
<td>7.12</td>
<td>82.2</td>
<td>1.644</td>
</tr>
<tr>
<td>30</td>
<td>4.56</td>
<td>84.8</td>
<td>1.272</td>
</tr>
<tr>
<td>20</td>
<td>2.56</td>
<td>87.2</td>
<td>0.872</td>
</tr>
<tr>
<td>10</td>
<td>1.13</td>
<td>88.7</td>
<td>0.444</td>
</tr>
</tbody>
</table>

Table (3). The effect of the adsorbent dose on the percentage of adsorption and the adsorption capacity for the best initial concentration (10 mg/L)

<table>
<thead>
<tr>
<th>( m, \text{g} )</th>
<th>( V, \text{L} )</th>
<th>adsorbent dose, ( \text{g/L} )</th>
<th>( C_i, \text{mg/L} )</th>
<th>% Adsorption</th>
<th>( q_e, \text{mg/g} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.025</td>
<td>20</td>
<td>1.13</td>
<td>88.7</td>
<td>0.444</td>
</tr>
<tr>
<td>0.4</td>
<td>0.025</td>
<td>16</td>
<td>1.84</td>
<td>81.6</td>
<td>0.51</td>
</tr>
<tr>
<td>0.3</td>
<td>0.025</td>
<td>12</td>
<td>2.08</td>
<td>79.2</td>
<td>0.66</td>
</tr>
<tr>
<td>0.5</td>
<td>0.025</td>
<td>8</td>
<td>2.24</td>
<td>77.6</td>
<td>0.776</td>
</tr>
<tr>
<td>0.2</td>
<td>0.025</td>
<td>5</td>
<td>2.67</td>
<td>73.3</td>
<td>0.916</td>
</tr>
<tr>
<td>0.5</td>
<td>0.1</td>
<td>5</td>
<td>2.98</td>
<td>70.2</td>
<td>1.404</td>
</tr>
<tr>
<td>0.1</td>
<td>0.025</td>
<td>4</td>
<td>3.11</td>
<td>68.9</td>
<td>1.723</td>
</tr>
</tbody>
</table>

Table (4). The effect of temperature on the adsorption capacity

\[
\begin{array}{|c|c|c|c|c|}
\hline
K' & 1/K'' & C_e, \text{mg/L} & q_e, \text{mg/g} & \log q_e/C_e \\
\hline
288 & 0.00347 & 2.04 & 0.398 & -0.710 \\
298 & 0.00335 & 1.82 & 0.409 & -0.648 \\
308 & 0.00324 & 1.57 & 0.422 & -0.571 \\
318 & 0.00314 & 1.30 & 0.435 & -0.475 \\
328 & 0.00304 & 1.13 & 0.444 & -0.406 \\
\hline
\end{array}
\]
Table (5). The calculate the thermodynamic parameters and effect on the adsorption ratio

<table>
<thead>
<tr>
<th>K°</th>
<th>1/ K°</th>
<th>ΔH, KJ/mol</th>
<th>ΔS, J/mol.K°</th>
<th>ΔG, KJ/mol</th>
<th>% Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>0.00347</td>
<td>13.924</td>
<td>53.614</td>
<td>-1.516</td>
<td>79.6</td>
</tr>
<tr>
<td>298</td>
<td>0.00335</td>
<td></td>
<td></td>
<td>-2.053</td>
<td>81.8</td>
</tr>
<tr>
<td>308</td>
<td>0.00324</td>
<td></td>
<td></td>
<td>-2.589</td>
<td>84.3</td>
</tr>
<tr>
<td>318</td>
<td>0.00314</td>
<td></td>
<td></td>
<td>-3.125</td>
<td>87</td>
</tr>
<tr>
<td>328</td>
<td>0.00304</td>
<td></td>
<td></td>
<td>-3.661</td>
<td>88.7</td>
</tr>
</tbody>
</table>

Table (6). Langmuir isotherm parameters

<table>
<thead>
<tr>
<th>q_m, mg/g</th>
<th>b</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.367</td>
<td>0.134</td>
<td>0.9998</td>
</tr>
</tbody>
</table>

Table (7). Pseudo-first-order kinetic constants for adsorption Hg(II) on kaolinite clay

<table>
<thead>
<tr>
<th>q_e, exp. mg/g</th>
<th>q_e, cal. mg/g</th>
<th>k_1 (min^{-1})</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.444</td>
<td>0.2447</td>
<td>0.082</td>
<td>0.9342</td>
</tr>
</tbody>
</table>

Table (8). Pseudo-second-order kinetic constants for adsorption Hg(II) on kaolinite clay

<table>
<thead>
<tr>
<th>q_e, exp. mg/g</th>
<th>q_e, cal. mg/g</th>
<th>k_2 (g/mg.min)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.444</td>
<td>0.4867</td>
<td>0.1067</td>
<td>0.9959</td>
</tr>
</tbody>
</table>

Figure (1). The effect of initial Hg(II) concentration on the percentage of adsorption

Figure (2). The effect of shaken time on the percentage of adsorption
Figure (3). The effect of pH on the percentage of adsorption

Figure (4). The effect of temperature on the adsorption capacity

Figure (5). The plot of log (q_e/C_e) versus 1/T

Figure (6). The adsorption isotherm of Hg(II) on bentonite clay
$y = 0.297x + 2.2171$
$R^2 = 0.9998$

Figure (7). Linear form of Langmuir equation for adsorption Hg(II) on bentonite clay

$y = -0.0079x - 0.6113$
$R^2 = 0.9342$

Figure (8). Pseudo-first-order kinetic for adsorption Hg(II) on bentonite clay

$y = 2.0544x + 39.531$
$R^2 = 0.9959$

Figure (9). Pseudo-second-order kinetic for adsorption Hg(II) on bentonite clay

References: