Heavy Metal Removal from Aqueous Solution by using Bentonite Clay and Activated Carbon

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Abstract— Heavy metal ions contained in the industrial waste water are one of the most common pollutants found in textile finishing manufacturing. The heavy metal is highly toxic and can affect human, plant and animal lives and aquatic systems. Therefore the removal of these ions from waste water becomes a critical issue from environmental point of view. In this study, three types of heavy metal, cadmium (Cd), lead (Pb) and copper (Cu) were used as pollutants in water while the adsorbents used were unmodified and modified bentonite clays and activated carbon derived from tamarind shell. The comparison of batch and packed bed adsorption of metal ions at ambient temperature was investigated in this paper. It was found that the modified bentonite clay can adsorb the ions better than the unmodified bentonite clay. This is due to the effects of high energy sites on the modified clay. Amount of lead can be adsorbed by the adsorbent greater than those of cadmium and copper, respectively: this may be due to the diffusion effects of heavy metal. The kinetic adsorption data were tested with the pseudo first-, second-order kinetic models and Langmuir model. The pseudo second-order kinetic model can describe the adsorption behavior of ions in these adsorbents quite well. The results show that the modified bentonite clay is effective for removing the heavy metal from textile waste water.

Keywords—adsorption; activated carbon; bentonite clay; heavy metal; waste water

I. INTRODUCTION

The number of textile industries in Thailand has increased rapidly since 2006 especially silk industries in the northeast area of Thailand. The synthetic dyes are generally used for the dyeing of silk because of their cheap price and ease of buying in the market. However, the problem concerning silk dyeing is the release of residual heavy metal ions and coloration of the effluent generated from wastage and washing during the silk dyeing process [1]. Since a large amount of water is used in the process, a great deal of waste water that caused unpleasant appearances to surface water and highly toxic to aquatic systems is produced [2]. Therefore the removal of dyes and heavy metals from this waste water is a challenge issue for environmental sciences and engineers. However in this study, we will focus on the removal of heavy metals especially, cadmium (Cd), lead (Pb) and copper (Cu) which present mostly in the textile industrial waste water.

There are several methods to remove dye and heavy metals from waste water such as ion-exchange, ultra-filtration, electrodialysis, reverse osmosis, precipitation and coagulation and adsorption processes [3]. Adsorption is an effective separation process due to its low operating cost and low energy consumption. Activated carbon is widely used as an adsorbent for removal a variety of pollutant species from waste water, particularly metal ions, organic compounds and dyes due to its large surface area, suitable pore size distribution and presence of surface functional groups [1, 4-6]. Bentonite clay is a low cost adsorbent mostly found in the northern part of Thailand and its adsorption capacity is quite high [7]. Bentonite clay was also modified using hydrochloric acid, sulfuric acid and sodium hydroxide in order to change its surface chemistry. Therefore the activated carbon derived from tamarind shell, unmodified and modified bentonite clays are used in this study to investigate the removal of heavy metal from waste water synthesized in our laboratory. The adsorption process was carried out in both batch adsorber and fixed bed column.

II. EXPERIMENTALS

A. Preparation and characterization of Activated carbon

In this study, tamarind shell was used as a precursor for preparing activated carbons. The preparation of tamarind shell activated carbon using chemical activation was as follows, the pre-dried tamarind shell was crushed and sieved to obtain average size 0.5 mm and then mixed with starch solution as a binder before pressing to form granular. After that the granular tamarind shell was impregnated in phosphoric acid 50% by wt. for 1 hour and then carbonized in a horizontal tube furnace for 1 hour under a constant flow of nitrogen 200 ml/min. Next, the char was activated in the same tube furnace under a constant flow of 400 ml/min of nitrogen and carbon dioxide with equal proportion, at 773K for 1 hour, followed by cooling down to room temperature under nitrogen atmosphere. The carbon samples were characterized for the structural porous properties (BET surface area, micropore volume and total pore volume) by nitrogen adsorption at 77K, and the proximate analysis (fixed carbon, volatile matter, ash content and moisture
content) by thermogravimetric analyzer. The pore size distribution was determined with the density functional theory (DFT). This method also gave the micropore volume which was calculated from the cumulative volume of the pores smaller than 2 nm. The activated carbon used in this study is in the granular form of 5 mm in diameter and in the length of 15 mm as shown in Fig. 1.

**B. Preparation and characterization of Bentonite clay**

The unmodified bentonite clay was supplied by Thai Nippon Chemical Industry LTD. in Thailand. To increase the functional group concentration, the bentonite clay was treated with hydrochloric acid, sulfuric acid and sodium hydroxide 1 M in the ratio of 1:50 by weight. The mixture was shaken at speed of 120 rpm for 24 hours by Orbital Shaker, and then washed with water until its pH about 6-7. The modified clay then was separated from water by vacuum filtration and dried at room temperature, after that it was milled and sieved to obtain the average size of 0.074 mm in powder form. The modified and unmodified clays were characterized for their porous properties by nitrogen adsorption at 77K.

**C. Adsorption study in batch adsorber**

The adsorption isotherms were carried out using a batch equilibrium technique in a conical flask. Each flask was filled with 50 ml of a specific type of heavy metal solution and 1 g of adsorbent at a known concentration, depending on each experiment. The flask was then closed and shaken for 72 hours at room temperature using Orbital Shaker. The sample was centrifuged to separate the adsorbent from the slurry and then the supernatant was analyzed for adsorbate concentration. The heavy metal content in waste water was determined using Atomic absorption spectroscopy.

**D. Adsorption study in fixed bed column**

The glass column used in this study was 2 cm in a diameter and 40 cm in length with a porous glass sieve support at the bottom. In all set of experiments, the column was loaded with the mixture of sand and clay. The mixtures were prepared by mixing dry adsorbent clays with quartz sand as described in the literature [8]. The feed solution with concentration of 100 mg of metal/l was gently pumped into the column which was operated in the downward flow. The valve below the column was gently opened to allow the effluent solution to pass through the bed slowly with a constant flowrate of 4 ml/min and every 10 ml of effluent samples were collected and analyzed for their solute content in order to obtain the breakthrough curve. The effluent collection time was recorded in order to evaluate the liquid flow rate. The similar procedure was applied for activated carbon, however only activated carbon was used instead of the mixture of sand and clay.

**III. RESULTS AND DISCUSSIONS**

We will start our discussion by presenting the physical properties of all adsorbents used in this study, and then the adsorption behavior of heavy metals in these three types of adsorbent for batch process will be presented. Finally, the adsorption isotherms of metal ions in all adsorbent using fixed bed column will be discussed.

**A. Porous properties of the adsorbent**

The structural properties of activated carbon, original and modified bentonite clays determined from nitrogen adsorption isotherms at 77K are shown in Table 1, while the proximate analysis of activated carbon is shown in Table 2. The adsorption isotherms of nitrogen at 77K in activated carbon, unmodified clay and modified bentonite clays with sodium hydroxide, hydrochloric acid and sulfuric acid, denoted as NaOH Bentonite, HCl Bentonite and H$_2$SO$_4$ Bentonite, respectively are presented in Fig. 1.

As seen from Fig. 2 and Table 1, the adsorption of nitrogen in activated carbon is greater than that in bentonite clays and this is due to the greater surface area and pore volume of activated carbon. Activated carbon contains micropore about 72% and larger pores about 28%, while bentonite clays are composed of 15% of micropore and 85% of mesopore and macropore. The activated carbon used in this study having widths varying from 1 to 7.5 nm and average pore size of 2.4 nm, which is typical pore size found for activated carbon. In the case of clays, pore sizes are varied from 1.5 to 50 nm, and it is found that the surface area and micropore volume for modified clays increase from the original clay while the opposite is true for the average pore size, and this is due to the replacement of aluminum ion and magnesium ion of clay’s structure by hydrogen ion from acid and the ion size of aluminum and magnesium are greater than that of hydrogen [9].

**Figure 1** the granular activated carbon used in this study.

**Figure 2** Nitrogen adsorption isotherms at 77K for activated carbon, unmodified and modified bentonite clays.
TABLE 1 POREOUS PROPERTIES OF ADSORBENTS USED IN THIS STUDY

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET area (m²/g)</th>
<th>Micropore volume (cm³/g)</th>
<th>Meso- and macropores volume (cm³/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>484</td>
<td>0.21 (72%)</td>
<td>0.08 (28%)</td>
<td>0.29</td>
<td>2.4</td>
</tr>
<tr>
<td>Bentonite</td>
<td>47</td>
<td>0.02 (15%)</td>
<td>0.11 (85%)</td>
<td>0.13</td>
<td>10.9</td>
</tr>
<tr>
<td>NaOH Bentonite</td>
<td>106</td>
<td>0.04 (25%)</td>
<td>0.12 (75%)</td>
<td>0.16</td>
<td>6.1</td>
</tr>
<tr>
<td>HCl Bentonite</td>
<td>74</td>
<td>0.03 (20%)</td>
<td>0.12 (80%)</td>
<td>0.15</td>
<td>8.1</td>
</tr>
<tr>
<td>H₂SO₄ Bentonite</td>
<td>83</td>
<td>0.03 (20%)</td>
<td>0.12 (80%)</td>
<td>0.15</td>
<td>7.2</td>
</tr>
</tbody>
</table>

TABLE 2 PROXIMATE ANALYSIS FOR ACTIVATED CARBON USED IN THIS STUDY (% WT.)

<table>
<thead>
<tr>
<th>Component</th>
<th>Fixed carbon</th>
<th>Volatile matter</th>
<th>Ash content</th>
<th>Moisture content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>65.4</td>
<td>21.4</td>
<td>4.0</td>
<td>9.2</td>
</tr>
</tbody>
</table>

B. Study of adsorption kinetics

The kinetics of heavy metal adsorption by tamarind based activated carbon and bentonite clay was investigated and the plot between adsorbed amount of each heavy metal and time was presented in Fig. 3. The initial concentration of each ion was 1000 mg/l for carbon and 2000 mg/l for clay, and it was found that the amount adsorbed increased with time and reached the equilibrium at time about 36 hours. The time of 36 hours was then used as a suitable time for heavy metal adsorption to achieve the equilibrium condition. The longer time to reach equilibrium may be due to the slow diffusion rate of heavy metal inside the pore which its molecular size is quite large compared to the adsorbent pore size.

The kinetic data were then analyzed by applying pseudo-first-order, pseudo-second-order, and intra-particle diffusion models to gain a better understanding of the adsorption dynamic behavior. The amount of heavy metal adsorbed at time t, \( q_t (\text{mg/g adsorbent}) \), was obtained by a mass balance as the following equation,

\[
q_t = (C_0 - C_t)V/W
\]

where \( C_0 \) (mg/l) and \( C_t \) (mg/l) are the concentration of metal ion in the solution at time \( t = 0 \) and at any time \( t \), respectively, \( V \) is the volume of the solution (l), and \( W \) is the weight of adsorbent used (g).

Pseudo-first order kinetic model can be described well at the beginning of adsorption process. If the rate of adsorbate diffusion across the boundary layer is a limiting step, the kinetic data is well fitted to the Pseudo-first order model [10]. It is generally expressed as follows:

\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]

where \( k_1 (\text{min}^{-1}) \) is the rate constant of first-order adsorption. and \( q_e \) (mg/g) is the adsorbed amount at equilibrium condition. The Pseudo-second-order kinetic model proposed by Ho [11] can be used in the case of that the chemical sorption is the rate-limiting step, and expressed as:

\[
t/q_e = 1/(k_2 q_e^2) + t/q_e
\]

where \( k_2 (\text{min}^{-1}) \) is the rate constant of second-order adsorption. If the diffusion of adsorbate molecules into internal surfaces of pores and capillaries of the adsorbent is the rate-limiting step, the adsorption data can be presented as:

\[
q_t = k_p t^{1/2} + C
\]

where \( C \) is a constant (mg/g) and \( k_p \) represents intraparticle diffusion rate constant \((\text{mg g}^{-1} \text{min}^{-1/2})\) which gives information about the thickness of boundary layer.

The three kinetic models were used to fit the experimental data and the values of kinetic parameters derived by applying
a regression analysis along with the correlation coefficients ($R^2$) are listed in Table 3 and 4 for tamarind based activated carbon and unmodified bentonite clay, respectively. From our analysis, the values of correlation coefficient are close to unity; however the kinetic adsorption data fitted well to the pseudo-second-order model. The equilibrium adsorbed capacities for each ion onto bentonite clay is greater than that onto activated carbon, and this is due to that the bentonite clay has amount of mesopore and macropore greater than activated carbon about 40% as shown in Table 1. This implies that the adsorbent with large amount of meso- and macro pores is suitable for the adsorption of heavy metal. Bentonite clay also contains magnesium and aluminum ions in its structure which can cause the greater interaction between adsorbate and adsorbent; as a result it increases adsorption capacity inside the pore. The difference in the maximum adsorption capacity is may be due to the effects of diffusion mechanism and the size of metal ion which can be packed perfectly inside the pore.

It is interesting that lead was the fastest metal adsorbed in both carbon and clays. However copper can be adsorbed faster than cadmium in the case of carbon while the opposite was true in the case of bentonite clays. This may be due to the effect of electronegativity of each metal, it is reported that the electronegativity of Pb (2.33) > Cu (1.90) > Cd (1.69) and the higher electronegativity of metal is, the greater adsorption onto the surface can be observed. Therefore the adsorption of heavy metal in activated carbon corresponded to this hypothesis, however in the case of clays, the formation of complex compound between heavy metal and solid surface may be dominated. This lead to the adsorption of Cd is greater than that of Cu for clays.

### C. Study of adsorption isotherm

It is known that pH of solution can influence the adsorption ion on an adsorbent; the effects of initial pH on the adsorption of metal ion in activated carbon are shown in Fig. 4.

The adsorption of lead and copper ions first increased dramatically with pH from 2 to 3, followed by a slow increase before attaining a plateau for pH values in the range from 3 to 6, and the decreased by increasing pH value. However the initial pH does not affect the adsorption of cadmium ion. In the case of modified and unmodified bentonite clays, the initial pH does not influence the adsorption capacity of heavy metal ion onto the adsorbent.

In this study the experimental adsorption isotherm were tested against the Langmuir equation which is suitable for monolayer adsorption on a homogeneous surface. The equation contains two parameters, the maximum monolayer capacity ($q_m$), and the Langmuir constant ($K_L$), and the fitting parameters obtained by regression analysis for all adsorbents are shown in Table 5. The comparison between experimental data and Langmuir model for activated carbon are presented in Fig. 5, the experiment were carried out at room temperature with the initial concentration of heavy metal varied from 100 to 5,500 mg/l and the adsorption time is 36 hours.
Figure 4 Effects of solution pH on heavy metal ion adsorption efficiency for activated carbon at room temperature, (initial concentration of metal in solution = 1000 mg/l with adsorption time of 36 hours.)

The Langmuir isotherm can describe the experimental data quite well as one can see from the figure and the correlation coefficients ($R^2$) are greater than 0.96. This can be implied that the adsorption of heavy metal ion is the monolayer behavior.

The adsorption of metal in the modified bentonite is greater than that in the original clay and the order of adsorption capacity is NaOH Bentonite ~ Activated carbon > HCl Bentonite ~ H$_2$SO$_4$ Bentonite > Bentonite for lead and copper adsorption while in the case of cadmium, the order becomes HCl Bentonite > NaOH Bentonite > H$_2$SO$_4$ Bentonite > Bentonite. This is due to the stronger interaction between the surface heterogeneity of modified clays and adsorbate. The activated carbon derived from tamarind shell in our laboratory can adsorb heavy metal very well and better than some commercial activated carbons. Therefore the tamarind based activated carbon and modified bentonite clay with NaOH is the useful materials for the environmental treatment.

Table 5 Parameters of Langmuir Isotherm for Heavy Metal Adsorption in Activated Carbon and Bentonite Clays for Batch Tests.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Heavy Metal</th>
<th>$q_m$ (mg/g)</th>
<th>$K_L$ (l/mg)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>Lead</td>
<td>125.88</td>
<td>0.00146</td>
<td>0.987</td>
</tr>
<tr>
<td></td>
<td>Cadmium</td>
<td>68.94</td>
<td>0.00028</td>
<td>0.980</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>104.32</td>
<td>0.00050</td>
<td>0.982</td>
</tr>
<tr>
<td>Bentonite</td>
<td>Lead</td>
<td>83.02</td>
<td>0.021</td>
<td>0.988</td>
</tr>
<tr>
<td></td>
<td>Cadmium</td>
<td>48.20</td>
<td>0.005</td>
<td>0.982</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>30.99</td>
<td>0.003</td>
<td>0.988</td>
</tr>
<tr>
<td>NaOH Bentonite</td>
<td>Lead</td>
<td>102.83</td>
<td>0.023</td>
<td>0.961</td>
</tr>
<tr>
<td></td>
<td>Cadmium</td>
<td>55.43</td>
<td>0.002</td>
<td>0.976</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>74.97</td>
<td>0.003</td>
<td>0.982</td>
</tr>
<tr>
<td>HCl Bentonite</td>
<td>Lead</td>
<td>92.85</td>
<td>0.023</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>Cadmium</td>
<td>57.88</td>
<td>0.003</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>56.30</td>
<td>0.004</td>
<td>0.976</td>
</tr>
<tr>
<td>H$_2$SO$_4$ Bentonite</td>
<td>Lead</td>
<td>92.17</td>
<td>0.035</td>
<td>0.960</td>
</tr>
<tr>
<td></td>
<td>Cadmium</td>
<td>53.10</td>
<td>0.004</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>52.85</td>
<td>0.004</td>
<td>0.971</td>
</tr>
</tbody>
</table>

D. Adsorption in fixed-bed column

The data presented in this section are the results for the uptake of metal ions onto activated carbon, the initial concentration of metal ion is 100 mg/l and the solution was passed through the bed with flowrate of 4 ml/min. The ratio between the effluent concentration and initial concentration were plotted against the effluent collection time as shown in Fig. 6, and the information from the breakthrough curves can be obtained as follows. Activated carbon can remove the heavy metal ion in a fixed-bed-column, initially there was a few amount of metal ions in the effluent samples until the breakthrough occurred. After that, an increasing amount of ions was detected in the effluent. The order of adsorbed amount of metal per amount of activated carbon in fixed bed was lead (1.56 mg/g) > copper (1.52 mg/g) > cadmium (1.32 mg/g) which was similar to the order of metal adsorption capacity onto carbon in batch system. The operating time for lead, copper and cadmium were 53, 50 and 48 min, respectively while the ideal breakthrough time for lead, copper and cadmium were 39, 38 and 33 min, respectively. The reason was the same as those described in batch process.

CONCLUSIONS

Due to the environment concern of heavy metal contained in the textile waste water discharged to the public sewage, the removal of these metals from waste water becomes an important issue for environmental study. In this study, activated carbon derived from tamarind shell, bentonite and
modified bentonite clays are used to study in both kinetics and equilibrium mechanism. Three types of heavy metal found in waste water are used as a sample study; they are cadmium, copper and lead. For the kinetic study, the pseudo-second-order model can describe the adsorption kinetic for metal adsorption on the adsorbate quite well while the adsorption isotherm corresponds to that of Langmuir equation. This suggests that the adsorption of heavy metal on activated carbon and clays is monolayer mechanism. Both activated carbon and modified bentonite clays should be a promising material to adsorb the heavy metal from textile waste water.

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