Modelling of Single and Binary Adsorptions of Heavy Metals Onto Activated Carbon - Equilibrium Studies

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ABSTRACT

A series of batch laboratory studies were conducted to investigate the suitability of activated carbon SA2 for the removal of cadmium ions and zinc ions from their aqueous solutions. The single component equilibrium data were analyzed using the Langmuir and Freundlich isotherms. Overall, the Langmuir isotherm showed a better fitting for all adsorptions under investigation in terms of correlation coefficient and error analysis (SSE only 18.2 for Cd\textsuperscript{2+} and 47.95 for Zn\textsuperscript{2+}). As the binary adsorption is competitive, extended Langmuir models could not predict the binary component isotherm well. The modified extended Langmuir models were used to fit the binary system equilibrium data. The binary isotherm data could be described reasonably well by the modified extended Langmuir model, as indicated in the error analysis.

Keywords: Activated carbon, adsorption, binary isotherm, cadmium, zinc

NOMENCLATURES

\[ a_F = \text{Freundlich constant (L/mg)} \]
\[ a_L = \text{Langmuir constant for energy of the sorbent (L/mg)} \]
\[ C_e = \text{residue metal ions concentration remaining after adsorption (mg/L)} \]
\[ C_o = \text{initial dye concentration (mg.L)} \]
\[ K_F = \text{Freundlich constant for adsorption capacities (L/mg)} \]
\[ K_L = \text{Langmuir constant (L/mg)} \]
\[ 1/n = \text{Freundlich exponent (surface heterogeneity)} \]
\[ m = \text{Amount of activated carbon used for metal ions adsorption during equilibrium (g)} \]
\[ N = \text{Number of points in data set} \]
\[ q_e = \text{Amount of metal ions adsorbed by activated carbon at equilibrium (mg/g)} \]
\[ q_m = \text{Monolayer capacity of the Langmuir isotherm (mg/g)} \]
\[ V = \text{Initial volume of metal ions used (L)} \]
\[ \eta_i = \text{Langmuir correction coefficients of component} \]

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INTRODUCTION

Heavy metals have been known as having very toxic elements and their discharge into receiving water can cause detrimental effects on human health and the environment. Heavy metal contamination exists in aqueous waste streams of many industries such as metal plating, mining, and agricultural fields. Zinc and cadmium are among the harmful heavy metal wastes produced by these industries, and they pose a risk of contaminated groundwater and other water resources. The removal of cadmium and zinc from water has become a great concern because of their uses in many industries.

Effluents from metallurgical and chemical industries, ceramics, electroplating, and textile industries are potential sources of water pollution by Cd$^{2+}$ ions (Hizal and Apak, 2006). Cd$^{2+}$ ions cause serious cases of acute toxicity and diseases such as lung cancer and kidney failure. In Japan, a bone disease named ‘itai-itai’ emerged in the mid-fifties especially in children (Hizal and Apak, 2006) as a result of the consumption of cadmium-contaminated rice as food, because the rice plant was watered with effluents from Cd–Ni battery factories.

Elevated levels of zinc may come from a variety of sources such as effluents from manufacturing of batteries, pharmaceuticals, and agricultural chemicals. Other sources of metallic zinc traces in drinking water are water treatment processes and pickup of metallic ions during storage distribution. These toxic metals can cause cumulative poisoning, cancer, brain damage, etc. when they are found above the tolerant levels (Berman, 1980). According to some surveys from the public health services of different countries, significant numbers of people have been exposed to the hazards of excess metals in the municipal water supplies (Chuah et al., 2005; WHO, 1971).

Table 1 shows the Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979 in Malaysia with selected parameter limits of effluent of Standards A and B (Department of Environment, DOE, Malaysia).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>A'</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury (Hg)</td>
<td>mg/L</td>
<td>0.005</td>
<td>0.05</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>mg/L</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>mg/L</td>
<td>0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>mg/L</td>
<td>0.10</td>
<td>0.50</td>
</tr>
<tr>
<td>Chromium (Cr), Trivalent</td>
<td>mg/L</td>
<td>0.20</td>
<td>1.0</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>mg/L</td>
<td>0.20</td>
<td>1.0</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>mg/L</td>
<td>0.20</td>
<td>1.0</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>mg/L</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>mg/L</td>
<td>1.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

* This standard applies to the industrial and development projects which are located within catchment areas (areas upstream of surface or above sub-surface water supply intakes, for the purpose of human consumption including drinking).
alternative technologies or sorbents for the treatment of metals contaminated waste streams. Some examples are summarised in Table 2.

Activated carbons have been used as adsorbents with promising results. The potential and capability of activated carbon for the removal of heavy metals from water have been very well documented in the literature. Many studies have reported removal of toxic Cd\(^{2+}\) and Zn\(^{2+}\) from aqueous solutions using biomass (Bailey et al., 1999) or inorganic materials such as calcite (Yavuz et al., 2007).

Unlike organic pollutants which are mostly susceptible to biological degradation, heavy metals will not degrade. Thus, the treatment of aqueous wastes containing soluble heavy metals requires concentration of the metals into a smaller volume, followed by a recovery or a secure disposal. The removal of heavy metals using activated carbons and other adsorbents still remains a topic of most recent investigations (Marzal et al., 1996; Martin et al., 2004).
Several studies have been carried out and reported on cadmium and zinc as a binary system using various sorbents (Liu et al., 2006; Hajialigol et al., 2006; Horsfall et al., 2006). However, only a few researchers have reported on the binary system modelling which deals with the competitive adsorption of cadmium and zinc ions onto activated carbon. For instance, Srivastava et al. (2006) studied individual and competitive adsorption of Cd$^{2+}$ and Zn$^{2+}$ metal ions from aqueous solution onto bagasse fly ash (BFA). Equilibrium isotherms for the binary adsorption of Cd$^{2+}$ and Zn$^{2+}$ ions on BFA were analyzed using non-modified Langmuir, modified Langmuir, extended-Langmuir, Sheindorf-Rebuhn-Sheintuch (SRS), non-modified R-P, and modified R-P adsorption models. The researchers found that the SRS model could fit most of the adsorption equilibrium data of Cd$^{2+}$ and Zn$^{2+}$ ions well onto BFA with low SSE values. Meanwhile, Fagundes-Klen (2007) studied the equilibrium data of the binary system of Cd$^{2+}$ and Zn$^{2+}$ ions by the biomass of Sargassum filipendula species using six adsorption isotherms models of the Langmuir type. Based on the regression analysis, the neural network could adjust to the equilibrium data of the binary system much as compared to the conventional sorption isotherm models. Mohsen et al. (2009) reported the work on the adsorption of two reactive dyes, Reactive Black 5 and Reactive Red E onto palm kernel shell-activated carbon (PKSAC). Their experimental data showed that competitive adsorption for active sites on the carbon surface resulted in a reduction of the overall uptake capacity of the reactive dyes, whereas the equilibrium was successfully described by the Modified Extended Freundlich model for the binary system.

In this study, the equilibrium experiments were performed to evaluate the effectiveness of the Norit coal based activated carbon for both single and binary adsorptions. Single component adsorption equilibrium was modelled using two isotherms, namely the Langmuir and Freundlich. Meanwhile, the binary component adsorption equilibrium was modelled using the extended Langmuir (EL) and modified extended Langmuir (MEL) models. The applications of these mathematical models provide a quantitative measure of their evaluation and optimize their operational conditions.

**MATERIALS AND METHODS**

**Materials**

In this study, analytical grade Cd (NO$_3$)$_2$.4H$_2$O and Zn (NO$_3$)$_2$.6H$_2$O and Norit activated carbon grade SA2 used in the experiments were supplied by Fisher Scientific, Malaysia. These activated carbons are commonly used in treating drinking water and are relatively cheaper than the others. Stock solutions of metal ions were prepared using deionised water. All solutions were adjusted to pH 7.0 using diluted NaOH and HNO$_3$.

**Procedures**

Batch sorption studies were performed at different concentrations of 5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 mg/L to obtain the equilibrium isotherms. The metals chosen for the investigation in the single component studies were Cd$^{2+}$ and Zn$^{2+}$. As for the isotherm studies, a series of 1000 ml conical flasks were employed. Each conical flask was filled with 500 ml of metal ion solution of varying concentrations and adjusted to pH 7.0. For the binary isotherms studies, a 1:1 ratio of cadmium-zinc solution was prepared. The conical flask with heavy metal ions solution was then shaken using an orbital incubator shaker, which was operated at 150 rpm and 30±1°C. When the desired temperature was reached, a pre-determined amount of norit activated carbon was added into each conical flask and mechanical shaking agitated the solutions. Equilibrium was reached after six hours (from contact time studies). To ensure equilibrium was attained, 96 hours of shaker
time were used for all the equilibrium experiments for both the single and binary systems. After this period, the solution was filtered using the Whatman filter paper (Grade 2, diameter 110mm) and analyzed for the concentration of the metal ions remaining in the solution using atomic absorption spectrophotometer (Hitachi Model Z-8100, Japan.) at the maximum wavelength ($\lambda_{\text{max}}$) of 228.8 nm for cadmium and 213.9 nm for zinc, respectively (Jumasiah et al., 2005).

The adsorption isotherms for the binary-component systems were obtained at pH 7.0. Meanwhile, a 1:1 ratio was used to determine the effect of other metal ions on the adsorption of Cd$^{2+}$ and Zn$^{2+}$ onto activated carbon. The metal ions concentration at equilibrium, $q_e$ (mg/g), can be calculated from:

$$q_e = \frac{V(C_0 - C_e)}{m}$$

where $C_0$ (mg/L) is the initial metal ions concentration in the liquid phase, $C_e$ (mg/L) is the metal ions concentration in the liquid phase at equilibrium, $V$ (L) is the total volume of metal ions solution, and $m$ (g) is mass of adsorbent.

RESULTS AND DISCUSSION

Effect of Initial pH

The pH of the solution affects the surface charge of the adsorbents, as well as the degree of ionization and speciation of different pollutants. A change in pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. The adsorption of various anionic and cationic species on such adsorbents has been explained on the basis of the competitive adsorption of $H^+$ and ions with the adsorbates (Allen, 2004). It is a common observation that the surface adsorbs anions favourably at lower pH due to the presence of $H^+$ ions, whereas, the surface is active for the adsorption of cations at higher pH due to the deposition of ions. The effect of initial pH on the adsorption equilibrium was studied by varying the initial pH of the solution, with a fixed initial concentration of 10 mg/L.

Fig. 1 indicates the effect of pH on the removal of Cd$^{2+}$ and Zn$^{2+}$ onto activated carbon from aqueous solutions. In strong acidic condition, the adsorption capacity was found to be very low. Overall, the maximum uptake percentage of cadmium and zinc removal was observed at pH 7.0.

Single Component Isotherms

Non-linear optimisation techniques have been applied to determine the isotherm parameters. The isotherm parameters were determined by minimising error function using Microsoft Excel Solver. The error function used in this work is the sum of the square of the errors (SSE), as defined in equation [2] (Chen et al., 2001):

$$SSE = \sum_{i=1}^{N} (q_{i,\text{cal}} - q_{i,\text{exp}})^2$$

where the subscripts ‘exp’ and ‘cal’ indicate the experimental and calculated values and $N$ is the number of measurement.

The equilibrium established between the adsorbed component on the adsorbent and unadsorbed component in solution can be represented by the adsorption isotherms. The most widely used isotherm equation for modelling equilibrium is the Langmuir equation which is valid for monolayer sorption onto a surface with a finite number of identical sites which are homogeneously distributed over the sorbent surface, as given in equation [3].
where $K_L$ indicates the solute adsorptivity, $a_L$ is related to the energy of adsorption and $C_e$ is the residue metal ions concentration remaining after adsorption (mg/L). The Langmuir isotherm is characterized by a “plateau”. The monolayer capacity of the Langmuir isotherm, $q_m$ is given as:

$$q_m = \frac{K_L}{a_L}$$

where $a_L$ is Langmuir constant for energy of the sorbent (L/mg), $K_L$ is Langmuir constant (L/mg) and $q_m$ is the monolayer capacity of the Langmuir isotherm (mg/g). The Langmuir and Freundlich models were used to describe the adsorption systems of Cd$^{2+}$ and Zn$^{2+}$ onto the norit activated carbon. The SSE and isotherm parameters for Cd$^{2+}$ and Zn$^{2+}$ adsorption are presented in Table 3.

The determination of the isotherm parameters for cadmium and zinc by the non-linear regression appears to give acceptable fits to the experimental data, as shown in Fig. 2.

The monolayer of adsorption capacity ($q_m$) of the Cd$^{2+}$ and Zn$^{2+}$ systems on the activated carbon were 46.88 mg/g and 45.41 mg/g, respectively. This finding showed that the activated carbons used in this study had a slightly higher adsorption capacity on Cd$^{2+}$ and Zn$^{2+}$.

The Freundlich isotherm describes the equilibrium on a heterogeneous surface where, the energy of adsorption is not equivalent for all the adsorption sites, and thus allowing multi-layer adsorption. The Freundlich equation is given as follows (Schay, 1982):

$$q_e = a_F C_e^{1\over n_f}$$

where $a_F$ is the Freundlich constant and $n_f$ is the Freundlich exponent. The larger the value of the adsorption capacity, $a_F$, the higher the adsorption capacity is. The more heterogeneous the surface, the closer $1\over n_f$ is to zero. The results presented in Table 3 show that the heterogeneity factor, from the Freundlich model $1\over n_f$, are 0.36 for cadmium and 0.51 for Zn$^{2+}$, respectively.
The non-linear correlation obtained from Fig. 2 shows that the experimental data also obeyed the Freundlich isotherm model, but they are not as good as the Langmuir isotherm especially for Cd$^{2+}$.

**Binary Component Isotherms**

One of the difficulties in describing the adsorption of heavy metals from wastestreams is that wastewaters contain more than one type of heavy metals. When several components are present, interference and competition phenomena for adsorption sites occur and may lead to a complex mathematical formulation of the equilibrium.

The modelling of binary adsorption equilibrium is still a challenging task. Several isotherms have been proposed to describe the equilibrium of such system. These isotherms could broadly be divided into (a) predictive models (where only individual isotherm parameters are used), and (b) correlative models (where individual isotherm parameters and correction factors are used).

The single-component adsorption Langmuir isotherm can be extended to describe the adsorption for multi-sorbate solution, as follows (Chen et al., 2001):

\[
q_{e,i} = \frac{K^0_{L,i} C_{e,i}}{1 + \sum_{j=1}^{N} a^0_{L,j} C_{e,j}}
\]

where \(i\) is the number of components, \(C_{e,i}\) is the equilibrium concentration of the component \(i\) in the multi-component solution (mg/L), \(q_{e,i}\) is the equilibrium uptake of the component \(i\) (mg/g), and \(K^0_{L,i}\) and \(a^0_{L,i}\) are the single component Langmuir parameters for the component \(i\).
The extended Langmuir (a predictive model) model assumes a homogeneous surface with respect to the energy of adsorption, no interaction between adsorbed species, and that all sites are equally available to all adsorbed species. The single-component parameter sets for the two heavy metals (as obtained in sub-section 3.2) were substituted into equation (6) to enable prediction of the binary component isotherms using the extended Langmuir (EL) isotherm. A comparison of the EL isotherm predictions and the experimentally measured values is presented in Fig. 3. Meanwhile, the SSE values for the EL isotherm for both heavy metals are given in Table 4. From the SSE values, the quality of fit using the EL isotherm for zinc was rather good, but the quality of fits for Cd\(^{2+}\) was very poor. The failure of the EL model suggested that the binary adsorption might be competitive.

For competitive adsorption, Schay (1982) introduced the modified extended Langmuir (MEL) by incorporating interaction parameters (Pagnanelli et al., 2001):

\[
q_{c,i} = \frac{k_i^d (C_{c,i}/\eta_{L,i})}{1 + \sum_{j=1}^{c} a_{i,j} (C_{c,j}/\eta_{L,j})}
\]

where is the Langmuir correction coefficients of the component \(i\) extracted from the competitive adsorption data.

The MEL models for the adsorption of cadmium and zinc onto activated carbon are plotted in Fig. 4. The model parameters of the MEL model, which were estimated from the binary adsorption data and their respective SSE, are given in Table 4. Based on the information presented in Fig. 4, the isotherm parameters for cadmium and zinc which were obtained using the non-linear regression method appeared to have given acceptable fits to the experimental data. Cd\(^{2+}\) and Zn\(^{2+}\) will compete with each other in the binary adsorption system, and more Zn\(^{2+}\) is being adsorbed in this system as compared to Cd\(^{2+}\). The maximum uptakes for Cd\(^{2+}\) and Zn\(^{2+}\) in the binary system are 43.096 and 19.214 mg/g, respectively.
Fig. 4: Application of modified extended Langmuir for simultaneous sorption of Cd$^{2+}$ and Zn$^{2+}$ onto norit activated carbon

<table>
<thead>
<tr>
<th>Models</th>
<th>Cadmium (II)</th>
<th>Zinc (II)</th>
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<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_m$(mg g$^{-1}$)</td>
<td>46.88</td>
<td>45.41</td>
</tr>
<tr>
<td>$K_L$(L mg$^{-1}$)</td>
<td>64.62</td>
<td>9.78</td>
</tr>
<tr>
<td>$a_L$(L mg$^{-1}$)</td>
<td>1.38</td>
<td>0.22</td>
</tr>
<tr>
<td>SSE</td>
<td>18.26</td>
<td>47.95</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_F$(mg g$^{-1}$)</td>
<td>23.79</td>
<td>9.65</td>
</tr>
<tr>
<td>$1/n_F$(L mg$^{-1}$)</td>
<td>0.36</td>
<td>0.51</td>
</tr>
<tr>
<td>SSE</td>
<td>96.31</td>
<td>28.83</td>
</tr>
</tbody>
</table>
CONCLUSIONS

Single component equilibrium data for both cadmium and zinc were studied and the adsorption data were found to be fitted best using the Langmuir model. The combined effects of the two metals onto Norit activated carbon are competitive. A predictive model, namely the Extended Langmuir model, described the adsorption equilibrium of zinc in a binary mixture rather well. However, it did not accurately predict the adsorption equilibrium of cadmium in a binary mixture. A correlative model, namely the modified extended Langmuir model, was found to be able to describe the binary components adsorption equilibrium well using single component parameters and additional correction factors. The maximum uptakes of Cd$^{2+}$ and Zn$^{2+}$ in binary system are 43.096 and 19.214 mg/g, respectively.

REFERENCES


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**TABLE 4**

Comparison of the SSE for each component evaluated from the modified extended Langmuir (MEL) and extended Langmuir (EL) models for simultaneous sorption of Cd$^{2+}$ and Zn$^{2+}$

<table>
<thead>
<tr>
<th>Component</th>
<th>Modified Extended Langmuir</th>
<th>Extended Langmuir</th>
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<tbody>
<tr>
<td></td>
<td>$\eta_{L1}$</td>
<td>$\eta_{L2}$</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>9.179</td>
<td>1.546</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>13.413</td>
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