Adsorption of cadmium(II) from aqueous solutions by thiol-functionalized activated carbon
Doyoon Kim, Young Wook Jung, Seokjoon Kwon and Jae-Woo Park

ABSTRACT
Thiol groups of adsorbent surfaces offer strong affinities for heavy metal ions, such as Hg(II), Pb(II), Cd(II), and so on. In this study, thiol group was impregnated to activated carbon by a series of treatments of oxidation and chlorination followed by 1,2-ethanedithiol introduction in order to investigate the adsorption properties of Cd(II) in aqueous solution. Batch sorption experiments were carried out to study kinetics, and the effect of Mg(II) and different pH conditions on Cd(II) sorption. Sequential extraction experiments were performed to understand binding characteristics. In general, thiol-functionalization improved the removal of Cd(II) by activated carbon in aqueous solution. Compared to untreated activated carbon, over a factor of four of the maximum sorption capacity enhancement was achieved. The presence of Mg(II) interfered Cd(II) sorption, but the degree of the sorption interference was alleviated significantly. Cd(II) sorption occurred more rapidly due to more involvement of ion exchange by thiol-functionalization.

Key words | activated carbon, adsorption, Cd(II), functionalization, thiol groups

INTRODUCTION
Adsorption on porous media with high surface area and porosity is environmentally important as it is the method of choice for the removal of organic and inorganic contaminants due to its operational simplicity and low cost (Chingombe et al. 2005; Nadeem et al. 2008). Quite a few researches focused on modification of their surface properties to develop stronger affinities for certain target contaminants (Yin et al. 2007). For example, introduction of surface oxygen groups onto activated carbon with nitric acid was proven to be effective in adsorbing heavy metal ions (Jia & Thomas 2000).

Thiol-functionalization has been intensively studied as a promising method of heavy metal ion adsorption (Vidic & Siler 2001; Aguado et al. 2005; Ladhe et al. 2008). The reaction between thiol group present in the adsorbents and heavy metal ions such as Cd(II), Hg(II), Zn(II), Cu(II), and Ag(I) explains its high adsorption capacity (Krishnan & Anirudhan 2003; de Mello Ferreira Guimarães et al. 2009). Some researchers have suggested methods of functionalizing thiol group onto silica and the results have been successful (Aguado et al. 2005; Blitz et al. 2007; Burke et al. 2008; de Mello Ferreira Guimarães et al. 2009). As a further application, activated carbon functionalization by thiol group was used to disperse precious metals onto carbon surface. For example, Kim et al. introduced a route for the dispersion of Pt nanoparticles for electrocatalysts using thiol group (Kim & Mitani 2006).

While synthesis of thiol-functionalized activated carbon may not be considered as cost effective due to the involvement of costly pre-treatment, e.g., oxidation and chlorination (Vidic & Siler 2001; Rios et al. 2003), the strong affinity of thiol-functionalized activated carbon for heavy metal ions holds promise for the remediation of metal-contaminated environment. In particular, thiol-functionalized activated carbon could be applied to remediation of contaminated sediments (Jo et al. 2008) by limiting the mobility of heavy metal ions through the food-web by sorption under in-situ
conditions, which could be less energy intensive, less expensive, and less environmental destructive than conventional technologies such as dredging and capping (Mulligan et al. 2001).

Cadmium (Cd(II)) was selected as the target contaminant for this study. Cadmium accumulates in organisms and causes serious health problems, even in low concentration (Nadeem et al. 2008). Discharged mainly from industries, it is frequently present in wastewater and subsurface and thus is of a great environmental concern (Yoo et al. 2004; Özer & Pirinciçi 2006).

In this study, thiol contents on activated carbon surface were enhanced by a series of treatments and the adsorption characteristics of Cd(II) were evaluated under different experimental conditions, such as initial pH of the solution, Mg(II) concentration, and contact time. Langmuir isotherm model was used to understand sorption properties and sequential extraction procedure was followed to understand its binding characteristics.

METHODS

Adsorbent preparation

Commercially available coconut-based activated carbon was used in this study. Five grams of 50-80 mesh activated carbon was washed with distilled water and refluxed in 5 M nitric acid solution for 12 hours to increase the surface oxygen groups onto carbon surface. The oxidized carbon was washed with distilled water until the pH of washed solution was constant and then dried under vacuum at 80 °C for 12 hours to remove residual nitric acid. Chlorination and thiol-functionalization were followed using thionyl chloride and 1,2-ethanedithiol (Rios et al. 2003). The washed, oxidized, and thiol-functionalized activated carbons were denoted as AC-U, AC-O, and AC-T, respectively. Sulfur contents were obtained with infrared adsorption method. Physical properties, such as surface area, of each adsorbent were determined using ASAP 2010 (MICROMETRICS).

Adsorption and desorption studies

Batch adsorption experiments were conducted in vials with 0.1 g of each adsorbent and 30 mL of Cd(II) solution in a rotary shaker (40 rpm) at room temperature. Desired Cd(II) concentrations and pH were obtained by adjustment with CdCl₂, HCl, and NaOH. Kinetic studies were carried out at an initial pH of 7 with an initial Cd(II) concentration of 50 mg/L. Sorption isotherm experiments were carried out at initial pH levels of 3 and 7, and Langmuir model was fit to the experimental data. To evaluate the effect of Mg(II) on Cd(II) sorption, MgCl₂ was added at a molar ratio of 1:1 and 1:2 (Cd(II):Mg(II)).

Sequential extraction procedure

To investigate binding characteristics of Cd on activated carbon, a sequential extraction procedure suggested by Tessier et al. (1979) was employed in this research. This method was originally developed to evaluate the particular metal partitioning among the various forms in sediments, which can be divided by sequential use of different agents. This method can be used to evaluate binding characteristics of heavy metals adsorbed on activated carbon, especially for whose main sorption mechanism is ion-exchange. In this study, Cd(II) was fully adsorbed onto each adsorbent with an initial concentration of 1 g/L at an initial pH of 7, then each extraction agent was added to 1 g of activated carbon after filtered and dried. Detailed information of extraction agents and conditions for each fraction, such as exchangeable, carbonate, Fe-Mn oxides, organic matter, and residual, are described in Chou et al. (2009).

Measurements and analysis

The concentration of Cd(II) in the solution was measured by Atomic Absorption Spectrometer (Analytik jena AAS Vario 6) after the solution was filtered through a 0.45 syringe filter (PVDF). The adsorbed mass of Cd(II), q (mg/g) and the Langmuir equation may be written as:

\[ q = \frac{(C_o - C_t)V}{W} \]

\[ q_e = \frac{q_{max}bC_e}{(1 + bC_e)} \]

where \(C_o\) and \(C_t\) (mg/L) are the concentrations of Cd(II) of the solution at initial and time t, V (L) is the volume of the solution, and W (g) is the weight of the carbon. The \(q_e\) (mg/g)
and $C_e$ (mg/L) are the adsorbed concentrations of Cd(II) at equilibrium. The $q_{\text{max}}$ and $b$ are the Langmuir constants referring to the capacity and energy of adsorption.

### RESULTS AND DISCUSSION

**Adsorbent properties**

Physical properties of each activated carbon are summarized in Table 1. Nitric acid oxidation creates surface oxygen groups on the surface of activated carbon and carboxyl groups play an important role in adsorption heavy metals (Jia & Thomas 2000; Sato et al. 2007). A thiol group is impregnated on carbon surface by replacing a chloride exchanged from a hydroxide ion of a carboxyl group by the treatment with thionyl chloride (Liu et al. 1998; Rios et al. 2003; Hu et al. 2005). More than 2% of sulfur content was obtained with the decreases in pore volume and surface area.

**Isotherm studies**

The Langmuir isotherm parameters for AC-U, AC-O, and AC-T at initial pH 3 and 7 are reported in Table 2 and the experimental adsorption isotherms are shown in Figure 1.

### Table 1 | Physical properties of the activated carbons

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BET surface area (m²/g)</th>
<th>Mesopore volume (cm³/g)</th>
<th>Average Pore Diameter (Å)</th>
<th>Sulfur content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-U</td>
<td>1406.3</td>
<td>0.3447</td>
<td>34.56</td>
<td>0.06</td>
</tr>
<tr>
<td>AC-O</td>
<td>1156.3</td>
<td>0.2853</td>
<td>33.76</td>
<td>0.04</td>
</tr>
<tr>
<td>AC-T</td>
<td>1137.8</td>
<td>0.2272</td>
<td>39.88</td>
<td>2.10</td>
</tr>
</tbody>
</table>

At initial pH 7 AC-O shows the lowest adsorption capacity, contrary to our original expectation and previous studies showing enhanced Cd(II) sorption capacities (Jia & Thomas 2000; Sato et al. 2007; Yin et al. 2007). Significant pH decrease (from 7 to 3.9) after sorption with AC-O may be ascribed to decrease in sorption, while pH was slightly increased to 8 with AC-U (Griffin & Shimp 1976). It appears that surface oxygen groups on AC-O do not adsorb Cd(II) at pH below 4 due to the competition with protons (Xiao & Thomas 2004). The AC-T, however, shows the most sorption despite the lowest pH. Therefore, thiol groups are stronger sorbents of Cd(II) than oxygen groups in the proton rich environment. Reduction in porosity and surface area by oxidation of activated carbon surface could be another reason for the reduced Cd(II) sorption capacity of AC-T (Jia & Thomas 2000; Chingombe et al. 2005; Yin et al. 2007). As listed in

### Table 2 | Langmuir isotherm parameters

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Initial pH</th>
<th>$q_{\text{max}}$ (mg/g)</th>
<th>$b$ (L/mg)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-U</td>
<td>7</td>
<td>23.3</td>
<td>0.0153</td>
<td>0.9578</td>
</tr>
<tr>
<td>AC-O</td>
<td>7</td>
<td>36.4</td>
<td>0.0009</td>
<td>0.9706</td>
</tr>
<tr>
<td>AC-T</td>
<td>7</td>
<td>27.0</td>
<td>0.0138</td>
<td>0.9294</td>
</tr>
<tr>
<td>AC-U</td>
<td>3</td>
<td>2.11</td>
<td>0.1135</td>
<td>0.8355</td>
</tr>
<tr>
<td>AC-T</td>
<td>3</td>
<td>8.86</td>
<td>0.0532</td>
<td>0.9442</td>
</tr>
</tbody>
</table>

Figure 1 | Langmuir isotherm for Cd(II) adsorption at initial pH 7 (a) and 3 (b).
Table 1, surface area and mesopore volume reduced about 17% after oxidation process. Thus, enhanced sorption capacity of AC-T could be more noticeable considering the further decrease in surface area and pore volume during functionalization process. More than 99.9 percent of cadmium exists as Cd(II) at pH 8 as simulated by visual MINTEQ, and the results indicated that there was no removed fraction by precipitation of Cd(OH)₂. The isotherm curve for AC-O was omitted at initial pH 3 due to the negligible sorption of Cd(II).

In all cases, Cd(II) sorption followed the Langmuir model. The highest Cd(II) sorption could be observed with AC-T while the difference in sorption at high aqueous concentration regimes was more significant under conditions of low initial pH. The steeper slopes at the beginning indicate that thiol-functionalized activated carbon could provide additional sorption sites for Cd(II) with the stronger binding energy.

It would be meaningful to compare the enhanced Cd(II) sorption capacity of thiol-functionalization with other modification processes. Recent research on modified carbon surfaces for removal is arranged. Functional groups such as weakly acidic groups and sulphur surface complexes created on carbon surface were proved to be effective in enhancing sorption capacity (Yin et al. 2007). For example, it can be increased up to 70.3% by heat treatment at 900°C in SO₂ (Gomez-Serrano et al. 1998; Jia & Thomas 2000). In this study, however, it is difficult to compare the sorption capacity of thiol groups with others because of differences in experimental conditions.

**Effect of contact time and Mg(II)**

Figure 2 shows the % removal of Cd(II) by AC-U, AC-O, and AC-T as a function of contact time with an initial Cd(II) concentration at 50 mg/L. The highest removal efficiency and fastest kinetics were observed with AC-T, indicating that impregnated thiol group provided additional sorption sites with ion exchange which occurred faster than C₆-cation interaction (Sato et al. 2007). Note that the least Cd(II) removal efficiency could be observed with AC-O, which was in a good agreement with the previous isotherm study.

The effect of Mg(II) on Cd(II) adsorption by AC-U, AC-O, and AC-T at an initial pH 3 and an initial Cd(II) concentration 50 mg/L was shown in Figure 3. For AC-U and AC-O, added Mg(II) with the molar ratio of 2 (Mg(II)/Cd(II)) decreased adsorption capacities by 81% and 50%, respectively. However, AC-T maintained its capacity at more than 70% with the same mass of added Mg(II), indicating that additional sorption sites created by thiol-functionalization were durable from sorption hindrance caused by competing ions in solutions.

**Cadmium fraction in activated carbon**

The result from the sequential extraction procedure is shown in Figure 4, which indicates the bonding types of adsorbed
Cd(II) onto activated carbon. The main fraction of Cd(II) bound to AC-T was exchangeable. The fraction of exchangeable Cd(II) increased from 27% to 71% after thiol-functionalization. It was in a good agreement with the results from the effect of contact time that showed more immediate reaction. However, the exchangeable fraction does not increase significantly after the oxidation process, reaffirming that acidic groups formed by oxidation did not strongly affect the Cd(II) adsorption at lower pH range.

Carbonate fraction mainly decreased as exchangeable fraction increased by thiol-functionalization while organic matter and residual fractions remained almost constant. These bindings were less than 2.5% of total fraction. The Fe-Mn oxide fraction decreased from 36% to 17% after thiol-functionalization but changes were minimal after oxidation.

CONCLUSIONS

The Cd(II) adsorption capability of activated carbon can be increased by introducing thiol groups onto its surface. In spite of a decrease in pH by acidity of thiol groups and blockage effect by the intermediate procedure of impregnation, AC-T exhibited more enhanced adsorption capacity than unmodified and oxidized activated carbons especially at lower pH range. Thiol modification reduced interference with Cd(II) sorption by competing ions in the environment. Compared to untreated activated carbon, Cd(II) sorption equilibrium was more rapidly reached with thiol-functionalization. Sequential extraction results supported that thiol-functionalization created additional sorption sites where exchange was the dominant mechanism in binding Cd(II). These results suggested that thiol-functionalization is an effective way to increase Cd(II) sorption capacity.

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