Adsorption Characteristics of Pb(II) and Cd(II) Ions on Dithizone-loaded Natural Zeolite

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(Manuscript submitted May 21, 2007; accepted June 13, 2007)

Abstract
Adsorption characteristics of Pb(II) and Cd(II) on natural zeolite loaded with dithizone have been examined. The parameters studied includes effect of pH, contact time and initial concentrations of Pb(II) and Cd(II). Results of study show that adsorption of Pb(II) and Cd(II) reaches its maximum values at pH 5 and 6, respectively. First-order adsorption rate of Pb(II) and Cd(II) on dithizone-loaded zeolite is larger than that on original zeolite. Comparison between Pb(II) and Cd(II) shows that adsorption rate and capacity for Cd(II) is larger than that for Pb(II) but the equilibrium constant and thus adsorption energy for Cd(II) is smaller than that for Pb(II). In general, the ability of dithizone-loaded zeolite to adsorb the two metals is better than does the unmodified one.

Key words: adsorption, lead, cadmium, dithizone, zeolite

1 Introduction
The pollution of the environment by heavy metals including lead (Pb) and Cadmium (Cd) has received considerable attention in recent years. These elements can accumulate in living organisms and have high toxic potential. Their wide technological use such as in fertilizers, mining and pigments, as well as their production from burning fossil oil and coal, and incineration of waste, bring about an extensive anthropogenic contamination of soil, air and water [1]. Furthermore, human activities often mobilize and redistribute natural substances in the environment so much so that they can cause adverse affect to ecosystem. On the otherhand, high levels of heavy metals in sediments, sludges and soil and through leaching/transfer process, also in ground water and plants, may have a negative effect on animals and human health [2].

Many efforts have been done to reduce the level of heavy metals such as Cd and Pb in the environment. The techniques include ion-exchange, adsorption onto specific sorbents, electrolytic methods, phytoremediation, and many others. Among the mentioned techniques, adsorption on specific sorbents is more promising because it is cheaper and the sorbents may be regenerated. It is already well known that natural zeolite has a high capability to adsorb metal ions from the aqueous solution because it has permanent negative charges on their surfaces [3]. However, their adsorption towards metal ions is not selective because it is mainly based on electrostatic attraction. Therefore, modification of the zeolite surface should be carried out using a specific and sensitive ligand [4,5].
Dithizone (diphenylthiocarbazone) is a suitable ligand for such purposes because it contains many N donor atoms, -NH as well as -SH groups which is very specific for transition metal ions including Pb, Cd and Hg [6].

In our previous report, we have described the immobilization of dithizone onto the surface of natural zeolite and characterized the result using various chemical methods [7]. As the extension of our previous work, here we further investigate the adsorption characteristics of Pb(II) and Cd(II) ions on dithizone-loaded natural zeolite. The parameters examined including effect of pH, adsorption kinetics and isotherm adsorption.

2 Experimental

2.1 Materials

Metal salts and dithizone (1,5-diphenylthiocarbazone) were purchased from Merck, Germany. Natural zeolite was obtained from Wonosari, Yogyakarta, Indonesia. Zeolite activation and dithizone immobilization were prepared and characterized according to previously reported procedure [7]. Organic solvents were of reagent grade and used as received. For all solutions, double distilled water was used and the buffer solutions were prepared from sodium hydrogen phosphate to which different volume of hydrochloric acid were added and the pH-value of the resulting solution was adjusted with the use of pH-meter.

2.2 Effect of pH on the Cd(II) and Pb(II) adsorption

The experiment was done by batch system. The adsorbent (20 mg, 200 mesh) was interacted with 10 cm$^3$ of Cd$^{2+}$ ion (15 µg cm$^{-3}$) or Pb$^{2+}$ ion (50 µg cm$^{-3}$) solutions and the pH of the solution was varied from 3.0 to 7.0. The mixture was stirred using horizontal shaker for 60 minutes. The mixtures were then filtered and the concentration of Pb(II) or Cd(II) ions in the filtrate was determined by AAS. For a control solution, the same solution of corresponding metal ion at each evaluated pH was treated in the same procedure but without addition of adsorbent.

2.3 Effect of contact time on the Cd(II) and Pb(II) adsorption

This experiment was carried out to evaluate kinetical aspects of the zeolite adsorption towards Cd(II) and Pb(II) ions. A similar procedure to that described in the section 2.2 was applied but the stirring time was varied in the range 10-60 minutes for Cd(II) ion and 10-180 minutes for Pb(II). The obtained data were evaluated by modified Langmuir-Hinshelwood equation [8]:

\[
\ln\left(\frac{C_0}{C_A}\right) = k_1 \left(\frac{t}{C_A}\right) + K
\]

Where C$_0$ is initial concentration of metal ion and C$_A$ is concentration of metal ion at equilibrium. Plot of ln(C$_0$/C$_A$)/C$_A$ versus t/C$_A$ gives the slope and Y-intercept equal to first-order adsorption rate (k$_1$) and adsorption equilibrium constants (K), respectively.

2.4 Effect of initial concentration of metal ions on the adsorption capacity

The effect of initial concentration of metal ions on the adsorption of modified zeolite adsorbent was examined by conducting metal ion adsorption experiment in various concentration of Cd(II) or Pb(II) ion. The same procedure as in section 2.2 was employed with various concentration of metal ions. The obtained data were evaluated by Langmuir isotherm adsorption model (eq. 2) to deduce adsorption capacity (b) and equilibrium constant (K).

\[
\frac{C}{m} = \frac{1}{bK} + \frac{1}{b}
\]

Where C is concentration of metal ion at equilibrium, m is mole of metal ion adsorbed by 1 g of adsorbent. The
value of $K$ was then used to calculate the adsorption energy ($E$) based on the equation derived from Standard Gibbs-Helmholtz relation (Eq. 3).

$$E = -\Delta G^0 = RT \ln K$$

(3)

Where $R$ is gas constant (8,314 J/mol K) and $T$ is an absolute temperature (K).

Fig. 1 Effect of pH of the solution on the adsorption of Pb(II) ion (left) and Cd(II) ion (right). Initial concentration and contact time are kept constant.

3 Results and Discussion

3.1 Effect of pH on the adsorption of metal ions

Adsorption of Pb(II) and Cd(II) metal ions onto the surface of an adsorbent is influenced by active site (species) available on the surface of the adsorbent. The charge of active sites of the adsorbent is normally affected by the pH of the solution. This situation is also applied for dithizone-zeolite adsorbent, therefore in this study the effect of pH on the adsorption of Pb(II) and Cd(II) by dithizone-zeolite adsorbent has been investigated and the results are illustrated in Fig. 1 (right and left), respectively.

It is clearly shown in Fig. 1 that the absorbed metal ions by both adsorbents increase with pH of the solution and reach its maximum value at pH = 5 for Pb(II) ion and pH = 6 for Cd(II) ion. This trend is easily understood because at lower pH the active sites of the adsorbents are protonated by H$^+$ ion to yield partially positive charge of the sites which is similar to those of metal ions. As a result adsorption of metal ions by both adsorbents is retarded. Further increase in pH of the solution, however, results in the decrease of the adsorbed metal ions, probably due to the precipitation of metals as hydroxide species or the formation of other negative species (metal complexes) involving hydroxide ion. At higher pH, the active sites of the adsorbents are deprotonated and tend to posses negative charge. This condition electrostatically hinders the adsorption of positively charged metal ions by the adsorbents. Thus, it is not surprising to observe the decrease in the metal adsorbed by both adsorbents as the pH of the solution is elevated. Furthermore, it is also observed that dithizone-zeolite adsorbs more metal as compared to those adsorbed by active zeolite. This may be due to the addition of various types of active site (N, –NH and –SH) obtained from the immobilization of dithizone on to the surface of zeolite which are specific for soft and medium acid like Cd(II) and Pb(II). Therefore, for further experiment, pH = 5 and pH = 6 has been selected for the adsorption study of Pb(II) and Cd(II) respectively.
3.2 Adsorption kinetics of metal ions

Adsorption kinetics of metal ions has been examined by contacting each metal ion with two kinds of adsorbent at fixed concentration of metal ion and at various contact times, i.e. in the range 10-180 min for Pb(II) (50 μg/ml) and 10-60 min for Cd(II) (15 μg/ml). Figure 2 gives the profile of the effect of contact time on the adsorbed Pb(II) and Cd(II) ions. In general, the metal adsorbed by two kinds of adsorbents increases with the increase of contact time up to the certain value of contact time where the absorbed metal reaches its maximum value and then the absorbed metal becomes constant. However, the adsorption rate of Pb(II) ion by two kinds of adsorbents is faster than that of Cd(II) ion. The adsorption equilibrium for Pb(II) has been reached within 10 min while that for Cd(II) takes at least 40 min. Evaluation of the data using Eq. 1 gives the kinetic parameters for Pb(II) and Cd(II) ions as summarized in Table 1.

Table 1 Adsorption kinetic parameters of Cd(II) and Pb(II) ion as evaluated by Eq. (1)

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Adsorbent</th>
<th>Adsorption rate constant, k (first order, min⁻¹)</th>
<th>Equilibrium constant, K (mol⁻¹L)</th>
<th>Linearity of the model, r</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II)</td>
<td>AZ</td>
<td>5.3 x 10⁻³</td>
<td>2.460</td>
<td>0.879</td>
</tr>
<tr>
<td></td>
<td>DZ</td>
<td>8.8 x 10⁻³</td>
<td>508.2</td>
<td>0.965</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>AZ</td>
<td>5.0 x 10⁻⁴</td>
<td>519.9</td>
<td>0.964</td>
</tr>
<tr>
<td></td>
<td>DZ</td>
<td>8.0 x 10⁻⁴</td>
<td>710.2</td>
<td>0.983</td>
</tr>
</tbody>
</table>

AZ= active zeolite, DZ= dithizone-loaded zeolite

From the data in Table 1, it is observed that dithizone-loaded zeolite (DZ) gives significantly higher adsorption rate (k) than active zeolite does (AZ) for both metal ions, indicating that loading dithizone onto surface of zeolite enhances the affinity of the adsorbent to these two metal ions. The increase in adsorption rate may be due to the availability of additional active sites originated from dithizone which is a specific ligand for both Pb(II) and Cd(II) ions. The data of adsorption equilibrium constants (K) for both metals are also in agreement with such explanation where K values for dithizone-loaded zeolite are larger than those for unmodified zeolite.
It is also revealed from Table 1 that adsorption rate for Cd(II) ion is slightly higher than that for Pb(II) ion. This may be explained with respect to the ionic size of metal ions because the charge as well as hydration number of the two metal ions are the same. The hydrated Cd(II) ion has smaller size as compared to Pb(II) ion, thus Cd(II) ion can move faster in the solution to reach the surface of adsorbent. In contrast, the K values for the adsorption of Pb(II) ion is arger than those for Cd(II), indicating that Pb(II) ion is thermodynamically favourable to interact with adsorbents. This probably due to fact that Pb(II) ion, according to Hard-Soft Acid-Base (HSAB) theory by Pearson [9], is classified as medium (borderline) acid which is able to interact with both soft base (such as -NH and -SH groups of dithizone) and hard base (-Si-OH, Si-O-Al and -Al-OH of zeolite), while Cd(II) ion is a soft acid which may interact very well with soft base only. Therefore, It is easily understood that the K value for Pb(II) ion is larger than that for Cd(II) ion.

Fig. 3 Effect of initial concentration of metal ions on the adsorption capacity of active and dithizone-loaded natural zeolite: Pb(II) ion (left) and Cd(II) ion (right). pH and contact time are kept constant at certain value

3.3 Isotherm adsorption of metal ions

Isotherm adsorption of Pb(II) and Cd(II) ions by active and dithizone-loaded zeolites was examined by conducting adsorption experiment at various concentration of metal ions and the data were evaluated by Langmuir model using Eq. 2, while their energy adsorption was calculated based on Eq. 3. Figure 3 gives the profile of isotherm adsorption of Pb(II) and Cd(II) ions by active and dithizone-loaded zeolites and Table 2 summarizes the results of parameter evaluation for isotherm adsorption of the two metal ions, except those of Cd on active zeolite.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Adsorbed Pb(II) (μmol/g)</th>
<th>Adsorbed Cd(II) (μmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>Zeolite-dithizone</td>
<td>Activated zeolite</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>1.0</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>1.5</td>
<td>20</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 2 Parameters of Langmuir isotherm adsorption for Pb(II) and Cd(II) by active and dithizone-loaded zeolites

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Adsorbent</th>
<th>Adsorption capacity, b (mol/g)</th>
<th>Equilibrium constants, K (mol^-1*L)</th>
<th>Adsorption Energy, E (kJ/mol)</th>
<th>Linearity of the model (r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>AZ</td>
<td>1.11 x 10^-6</td>
<td>1.24 x 10^4</td>
<td>23.51</td>
<td>0.9928</td>
</tr>
<tr>
<td></td>
<td>DZ</td>
<td>2.08 x 10^-6</td>
<td>2.26 x 10^4</td>
<td>25.00</td>
<td>0.9930</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>AZ</td>
<td>2.87 x 10^-6</td>
<td>1.62 x 10^4</td>
<td>24.17</td>
<td>0.9517</td>
</tr>
<tr>
<td></td>
<td>DZ</td>
<td>2.87 x 10^-6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Langmuir parameters for Cd(II) adsorption on AZ were not given because the adsorption pattern does not fit Langmuir model (gives very low r value).
Again it is clearly seen from Table 2 that adsorption capacity (b) and equilibrium constant (K) for dithizone-loaded zeolite (DZ) is larger than that for active zeolite (AZ), especially for Pb(II) ion. The same comparison as for Pb(II) ion is not possible for Cd(II) ion because only the isotherm adsorption parameters for Cd(II) ions using dithizone-loaded zeolite (DZ) can be evaluated. In the case of metal adsorption using active zeolite (AZ), its parameters can not be determined because the adsorption seems to not follow Langmuir model. Furthermore, unlike the adsorption of Pb(II) ion, it is also observed that the adsorption of Cd(II) ion by both active and dithizone-loaded zeolites occurs in two steps. The first adsorption is possibly the chelation of Cd(II) ion to loaded dithizone ligand, while the second step is the interaction of Cd(II) with –Al-OH, Si-O-Al and/or Si-OH of the zeolite. If such assumption is correct, it means that dithizone which has been successfully loaded to zeolite surface is not so much. From Table 2, it is also consistently found that Pb(II) ion is thermodynamically favourable for adsorption as indicated by its K value and adsorption energy which are larger as compared to those for Cd(II) ion. A similar explanation to what has been elaborated in section 3.2 may also be applied here. In terms of the amount of absorbed metals and the adsorption affinity between Pb(II) and Cd(II) ions, our results presented here are comparable to those have been reported by other workers who have been used dithizone-anchored poly(EGDMA-HEMA) microbeads [4] and silica-loaded dithizone [5] to adsorb Pb(II), Cd(II) as well as other metal ions. The value of E, which is slightly > 20 kJ/mol, suggests that the adsorption mechanism is mixed between physisorption and chemisorption [10], meaning that the physical and electrostatic interaction still play an essential role as a driving force for the adsorption.

As a conclusion, it has been demonstrated that the capacity and affinity of natural zeolite in adsorbing Pb(II) and Cd(II) ions is greatly improved by loading dithizone onto the surface of the zeolite. The modified zeolite may be used as selective adsorbents for the removal of heavy metals such as Pb(II), Cd(II), Hg(II) and other metal ions that react specifically with dithizone ligand.

Acknowledgement

This study was supported by the Ministry of Research and Technology, The Republic of Indonesia through RUT XII Research Project, contract No. 02/Perj/Dep.III/RUT/PPKI/II/2005 (1 February 2005) and contract No. 02/BA/Dep.III/RUT-T/PPKI/II/2006 (1 February 2006).

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