

Short communication

## Prediction of simultaneous adsorption of Cu(II) and Pb(II) onto activated carbon by conventional Langmuir type equations

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### Abstract

Removal of Cu(II) and Pb(II) by adsorption onto activated carbon was examined in single- and binary-component aqueous solutions representative of contaminated solutions containing heavy metals. Reversibility of adsorption of the heavy metals on the activated carbon was evaluated by desorption experiments. The number of the maximum adsorption sites and adsorption equilibrium constants of Cu(II) and Pb(II) were estimated by the results of single-component systems assuming the Langmuir adsorption model. The adsorption sites per gram of activated carbon resulted in similar values for Cu(II) and Pb(II) from the isotherms. The adsorption constant for Pb(II) was nearly 1.8 times greater than that of Cu(II). Rate constants of adsorption and desorption were also estimated from the kinetic analysis. Using the single set of common parameters obtained from the single-component systems, the experimental results for a binary-component system were quantitatively predicted. Competitive adsorption of Cu(II) and Pb(II) on the same adsorption sites was confirmed by both experimental and predicted results of adsorption in the binary mixture.

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**Keywords:** Competitive adsorption; Langmuir model; Heavy metal; Binary mixture; Activated carbon

### 1. Introduction

High concentrations of toxic heavy metals have been observed in river sediments [1], agricultural soil [2] and acidic leachate [3] in Japan as well as many other regions in the world. Such contamination has generally been caused by mining [2] and landfills [4]. For example, more than two to three hundred milligrams of zinc, lead and copper per kilogram were found in agricultural soil in Japan, because chemical properties of these metals are similar to each other [5].

Numerous studies have been conducted to eliminate toxic heavy metals from the aqueous solutions. Precipitation by controlling pH in the solution [6,7] and ion exchange [8,9] are widely used for reducing the level of contamination.

Adsorption is also an attractive option for heavy metal removal. Activated carbon [10–14], polymers [15,16], metal oxides [17,18] and other low-cost adsorbents, such as agricultural byproducts [19,20], have been used as adsorbents. Most studies, however, were conducted using aqueous solutions containing a single-component of heavy metals. A relatively small number of studies have examined the adsorption of two- or multi-component solutions of heavy metals [13,21–24]. However, studies of multi-component systems will be required to apply the use of adsorbents to treat solutions containing more than a single heavy metal. In this study, Cu(II) and Pb(II) were employed as heavy metals to examine the adsorption kinetics onto activated carbon for both single- and multi-component systems, because Cu(II) and Pb(II) exhibit relatively strong adsorption affinity for activated carbon [11] and metal oxides [25]. The Langmuir model has been widely applied to describe the adsorption of heavy metals on adsorbents. Therefore, the same model was

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used to evaluate the adsorption and desorption of Cu(II) and Pb(II) in both single- and binary-component systems.

## 2. Experimental materials, methods and kinetic analysis

Granular activated carbon (GAC) derived from coconut shell (Mitsubishi Chemical DIASORB W10-30) was used for the adsorption of Cu(II) and Pb(II) from aqueous solutions. The activated carbon was boiled twice with de-ionized water and dried in an oven at 110 °C for 6 h prior to use. The properties of the activated carbon include a specific surface area of 1000 m<sup>2</sup> g<sup>-1</sup>, a methylene blue decolorizing activity of 180 mL g<sup>-1</sup>, an iodine adsorption capacity of 1100 mg g<sup>-1</sup>, and a pH of 6.0 at 20 °C in de-ionized water.

Stock solutions of Cu(II) and Pb(II) were prepared by dissolving reagent grade CuCl<sub>2</sub>·2H<sub>2</sub>O and PbCl<sub>2</sub> in de-ionized water, respectively. The influence of solution pH on the removal of Cu(II) and Pb(II) was examined by adding HCl aqueous solution to Cu(II) and Pb(II) solutions. Adsorption of the heavy metals was carried out by batch experiments. The 50 mL aqueous solutions of the heavy metals bearing 100 mg of the activated carbon in 100 mL conical glass flask were agitated for a week to examine pH dependency for the adsorption. One liter aqueous solutions bearing 2 g activated carbon were used for the measurement of the rate of adsorption. The initial concentrations of Pb(II) and Cu(II) in the solution were varied from 0.05 to 0.3 mmol L<sup>-1</sup>. All experiments were carried out at 100 rpm in agitation at 20 °C. Desorption was also observed by adding 50 mL de-ionized water to 100 mg of the activated carbon onto which Cu(II) and Pb(II) was previously adsorbed. The pH of the solutions was always less than 6.1 throughout the experiments to prevent precipitation of metal hydroxides [10,21,26]. The specific surface area of the activated carbon was measured by a surface area analyzer (BECKMAN COULTER Model 3100) using the B.E.T. method [27]. The pH of the aqueous solutions was measured using a pH meter (HORIBA Model D-21). The concentrations of the heavy metals in the solution were determined by an atomic absorption spectrometer (HITACHI Model 180-30) after the solution was separated from the GAC with a decantation technique. The amounts Cu(II) and Pb(II) adsorbed onto the GAC were calculated by difference.

The Langmuir isotherms were employed to evaluate the adsorption equilibrium between metal ions and the surface adsorption sites. Our preliminary kinetics study showed that adsorption rate for Pb(II) was found not to be limited by diffusion but to be controlled by binding heavy metal ions onto adsorption sites under the imposed conditions [28]. For the kinetic analysis, the conventional Langmuir model was also used to predict the adsorptions of single- and binary-mixture of Cu(II) and Pb(II) by making the following assumptions according to the previous kinetics study, pH dependency experiment, and the Langmuir isotherms obtained in the present study:

- the adsorption conditions, especially pH that strongly affects the adsorption, are the same for Cu(II) and Pb(II);
- adsorption rate is controlled by binding Cu(II) or Pb(II) onto adsorption sites;
- adsorption and desorption occur at the same time; and
- both Cu(II) and Pb(II) adsorb in a mono layer onto the GAC as a first-order reaction with respect to metal concentrations.

Based on the assumptions, the rate of adsorption for Cu(II) can be represented as follows [29]:

$$\frac{d[S_{Cu}]}{dt} = k_{ADS,Cu}C_{Cu}[S] - k_{DES,Cu}[S_{Cu}] \quad (1)$$

where  $[S]$  and  $[S_{Cu}]$  are the concentrations of available and occupied surface sites by the Cu(II) ion in mmol g<sup>-1</sup> on the activated carbon, respectively,  $C_{Cu}$  is the metal ion concentration in the aqueous solutions in mmol L<sup>-1</sup>, and the  $k_{ADS,Cu}$  and  $k_{DES,Cu}$  are the adsorption and desorption rate constants on the adsorption sites of the activated carbon in L mmol<sup>-1</sup> h<sup>-1</sup> and h<sup>-1</sup>, respectively. The adsorption equilibrium constant of Cu(II),  $K_{Cu,e}$ , can be represented as follows [29]:

$$K_{Cu,e} = \frac{k_{ADS,Cu}}{k_{DES,Cu}} \quad (2)$$

When the system attains an equilibrium state, adsorption rate becomes zero, and Eq. (1) can be converted to Eq. (3), which is widely known as the Langmuir equilibrium equation:

$$\frac{C_{Cu,e}}{[S_{Cu}]_e} = \frac{C_{Cu,e}}{X_{m,Cu}} + \frac{1}{K_{Cu,e}X_{m,Cu}} \quad (3)$$

where  $C_{Cu,e}$  and  $[S_{Cu,e}]$  are the equilibrium concentration and the equilibrium amount on the GAC, respectively, and  $X_{m,Cu}$  is the number of the maximum available adsorption sites for copper. The relationship between the aqueous concentration and the concentration on the occupied surface sites of activated carbon can be written as follows [29]:

$$C_{Cu} = C_{Cu,0} - [S_{Cu}] \frac{M}{V} \quad (4)$$

where  $C_{Cu}$  and  $C_{Cu,0}$  are the concentration at a given time and the initial concentration in mmol L<sup>-1</sup>,  $M$  is the amount of activated carbon in grams, and  $V$  is the volume of the solution in liters. The  $K_e$  values were calculated from the following equation, which was derived from Eqs. (1), (2) and (4) using experimental rate data for the single-component systems.

$$K_{Cu,e} = \frac{C_{Cu,0} - C_{Cu,e}}{C_{Cu,e}\{X_{m,Cu}M/V - (C_{Cu,0} - C_{Cu,e})\}} \quad (5)$$

The concentration of available surface sites for Cu(II) adsorption,  $[S]$ , is related to concentration of occupied surface sites by Cu(II),  $[S_{Cu}]$ , as follows:

$$[S] = X_{m,Cu} - [S_{Cu}] \quad (6)$$

Eq. (1) can be written as a function of  $[S_{Cu}]$ , based on Eqs. (2), (3) and (5), as follows:

$$\frac{d[S_{Cu}]}{dt} = k_{DES,Cu}K_{Cu,e} \left( C_{Cu,0} - [S_{Cu}] \frac{M}{V} \right) \times (X_{m,Cu} - [S_{Cu}]) - k_{DES,Cu}[S_{Cu}] \quad (7)$$

Integration of Eq. (7) gives the aqueous concentration of the heavy metal at a given time,  $t$ , as follows:

$$C_{Cu} = C_{Cu,0} - \frac{(B^2 - D^2)(1 - e^{-Dt})M}{2A\{(B + D) - (B - D)e^{-Dt}\}V} \quad (8)$$

where  $A$  is the  $k_{DES,Cu}K_{Cu,e}M/V$ ,  $B$  the  $k_{DES,Cu}(K_{Cu,e}C_{Cu,0} + K_{Cu,e}X_{m,Cu}M/V + 1)$ ,  $C$  the  $k_{DES,Cu}K_{Cu,e}C_{Cu,0}X_{m,Cu}$ , and  $D$  the  $(B^2 - 4AC)^{1/2}$ .

Since  $k_{DES,Cu}$  (or  $k_{ADS,Cu}$ ) was the only parameter that could not be determined from the isotherms,  $k_{DES,Cu}$  was determined by iterating Eq. (8) until the best fit was obtained to the experimental results. The kinetic parameters for the Pb(II) adsorption were also determined in the same way as for the Cu(II) adsorption. The adsorption of Cu(II) and Pb(II) onto the activated carbon in the binary mixture was predicted by using the kinetic parameters obtained from the single-component systems. Changes in Cu(II) and Pb(II) concentrations on the activated carbon in the binary mixture as functions of  $[S_{Cu}]$  and  $[S_{Pb}]$  were represented as shown in Eqs. (9a) and (9b), respectively, in which the Langmuir adsorption sites of  $X_{m,Cu}$  and  $X_{m,Pb}$  were assumed to be identical for the binary mixture experiment:

$$\frac{d[S_{Cu}]}{dt} = k_{ADS,Cu}C_{Cu}(X_{m,Cu} - [S_{Cu}] - [S_{Pb}]) - k_{DES,Cu}[S_{Cu}] \quad (9a)$$

$$\frac{d[S_{Pb}]}{dt} = k_{ADS,Pb}C_{Pb}(X_{m,Pb} - [S_{Cu}] - [S_{Pb}]) - k_{DES,Pb}[S_{Pb}] \quad (9b)$$

Since the above equations could not be converted to an integral form by numerical analysis, the changes in concentrations of Cu(II) and Pb(II) as a function of time were calculated by the fourth-order Runge–Kutta routine [30].

### 3. Results and discussion

Fig. 1 shows changes in removal rates of Cu(II) and Pb(II) as a function of solution pH measured after adsorption equilibrium was attained. The resulting data for metal removal at pH around 6.0 were accumulated in a narrow pH range in the adsorption equilibrium state, although the initial pH ranged from 5.1 to 5.8. Metal removal was enhanced from pH 5.0 to 6.0 in which Pb(II) was always adsorbed onto the GAC to a greater extent than Cu(II) for metal concentrations

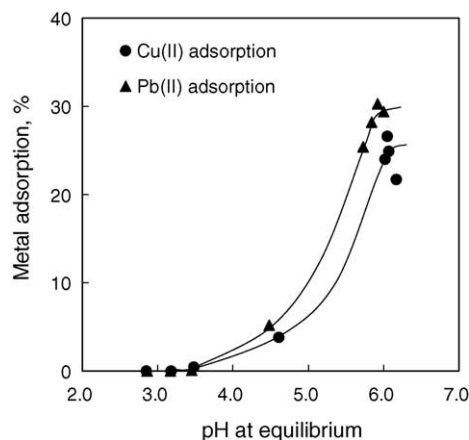


Fig. 1. Adsorption of Cu(II) and Pb(II) onto activated carbon as a function of pH at 20 °C. Initial metal concentrations, 0.28 mmol L<sup>-1</sup> for Cu(II) and Pb(II). Solution volume, 50 mL; GAC, 100 mg.

of 0.28 mmol L<sup>-1</sup>. Up to pH 6.0, metal adsorption also approached saturation of the adsorption sites of the GAC for the conditions described in the kinetic experiments. However, the metal adsorption rate does not change much even if the pH drifts between 5.5 and 6.0, i.e., as long as hydrochloric acid is not added to the solution from our previous study [28].

Fig. 2 shows that the Langmuir isotherms exhibit good linearity. The Langmuir parameters for  $K_e$  and  $X_m$  tabulated in Table 1 correspond to the adsorption affinity onto the acti-

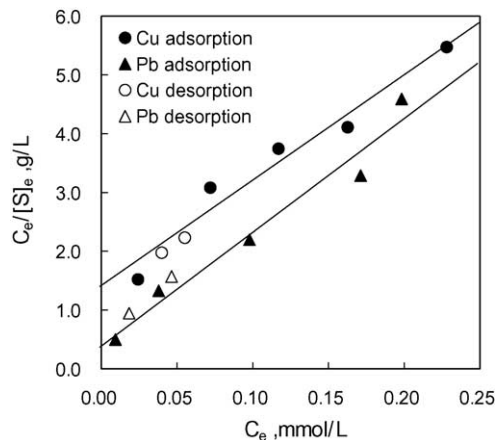


Fig. 2. Langmuir isotherms of the single-component adsorption and desorption of Cu(II) and Pb(II) onto activated carbon at 20 °C. Solution volume, 50 mL; GAC, 100 mg. Solid lines: adsorption isotherm by a least square method.

Table 1  
Langmuir parameters for adsorption of Cu(II) and Pb(II)

| Metal ion   | Cu(II) | Pb(II) |
|---|--------|--------|
| Isotherms   |        |        |
| $X_m$ (mmol g <sup>-1</sup> )                                   | 0.056  | 0.052  |
| $K_e$ (L mmol <sup>-1</sup> )                                   | 12     | 21     |
| Kinetics  |        |        |
| Adsorption; $k_{ADS}$ , (L mmol <sup>-1</sup> h <sup>-1</sup> ) | 0.20   | 0.20   |
| Desorption; $k_{DES}$ , (h <sup>-1</sup> )                      | 0.017  | 0.0096 |

vated carbon and the maximum concentration of adsorption site, respectively. The adsorption affinity for Pb(II),  $K_{\text{Pb(II),e}}$ , is about 1.8 times greater than that for Cu(II),  $K_{\text{Cu(II),e}}$ . The maximum concentration of adsorption sites for Cu(II) and Pb(II) are approximately the same, indicating that the number of adsorption sites per gram of the activated carbon is close for both Cu(II) and Pb(II) [31–33]. Furthermore, it can be assumed that the Cu(II) and Pb(II) are adsorbed on the same sites as described in the binary mixture experiment.

The experimental plots of the desorption data for Cu(II) and Pb(II) are linear plots for the range in metal ion concentrations considered as also shown in Fig. 2, indicating that adsorption of Cu(II) and Pb(II) onto activated carbon is reversible. Hence, the surface adsorption sites are assumed to be energetically homogeneous under the conditions used, although two-site [28,29,34] or multi-site models [35] also have been proposed for the adsorption of heavy metals onto activated carbons. The adsorption of Pb(II) and Cu(II) is in the form of a mono layer, and the adsorption sites are proposed to exist on the relatively external surface of the GAC. Based on the Langmuir isotherm fits, the Cu(II) and Pb(II) ions, which are assumed to exist as  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions, respectively [10,21,36], covered less than 0.5% of the B.E.T. surface area of the activated carbon even at maximum adsorption.

Fig. 3 shows changes in aqueous concentrations of Cu(II) and Pb(II) as a function of time in the single-component system. The initial rates of adsorption were fast and then gradually decreased toward the equilibrium concentration. The adsorption equilibrium was achieved within a few days. The prediction of the experimental results for the single-component adsorption was conducted using Eq. (8). An average value of  $0.054 \text{ mmol g}^{-1}$  was used as the maximum number for the adsorption sites,  $X_m$ , to predict the Cu(II) and Pb(II) adsorption, since the  $X_{m,\text{Cu}}$  and  $X_{m,\text{Pb}}$  values are close to each other. The differences between the initial and the equilibrium concentrations of Cu(II) and Pb(II) were 0.20 and 0.23  $\text{mmol L}^{-1}$ ,

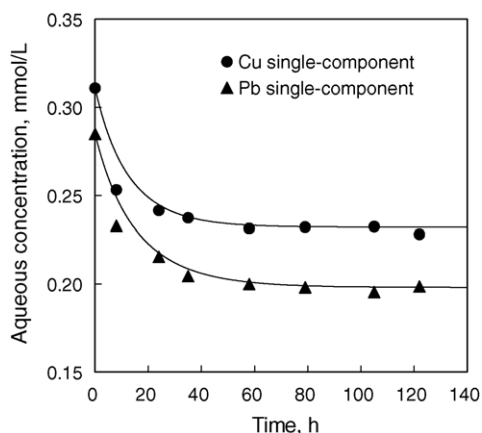


Fig. 3. Changes in aqueous concentrations of Cu(II) and Pb(II) in single-component adsorption as a function of time. Solution volume, 1.00 L; GAC, 2.00 g. Solid lines: predicted by Eq. (8) for Cu(II) or Pb(II).

which corresponds to 0.040 and 0.045  $\text{mmol g}^{-1}$  on the GAC, respectively. The results indicate that more than 70% of the adsorption active sites were occupied by Cu(II) or Pb(II) under the conditions of the study.

The  $K_e$  values were calculated using Eq. (5) and the experimental data in Fig. 3. As previously mentioned, since  $k_{\text{DES}}$  (or  $k_{\text{ADS}}$ ) was the only parameter that can not be determined from the isotherms, the  $k_{\text{DES}}$  was determined by iterating in increments of  $0.0001 \text{ h}^{-1}$  until the best fit was obtained. For the kinetic analysis, the adsorption rate constant for  $k_{\text{ADS}}$  was assumed to be the same for both Cu(II) and Pb(II), because no significant difference in behavior between Cu(II) and Pb(II) in the solutions is expected, although the ionic radii for  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  in the solution are 1.12 and 0.70 Å, respectively [10]. The  $k_{\text{ADS}}$  should not be influenced by the properties of activated carbon surface, whereas the desorption rate constant,  $k_{\text{DES}}$ , is strongly influenced by the surface properties [37]. The resulting values of  $k_{\text{ADS}}$  and  $k_{\text{DES}}$  are shown in Table 1; the rate constant for desorption for Pb(II) is nearly 1.8 times smaller than that for Cu(II).

Fig. 4 shows changes in aqueous concentrations of Cu(II) and Pb(II) as a function of time. Competitive adsorption between Cu(II) and Pb(II) is apparent for the binary mixture. In comparison with the results for the single-component system shown in Fig. 3, the adsorption rates for Cu(II) and Pb(II) in the binary mixture are slower than those in single-component system. The equilibrium concentrations of Cu(II) and Pb(II) in the binary system are also lower than those in the single-component systems, as expected.

The Langmuir equations given by (9a) and (9b) were used to quantitatively predict the experimental results for Cu(II) and Pb(II) in the binary mixture using the parameters obtained from the kinetic analysis in the single-component systems. An average value for  $X_m$  of  $0.054 \text{ mmol g}^{-1}$  was used for these predictions. As shown by the solid lines in Fig. 4,

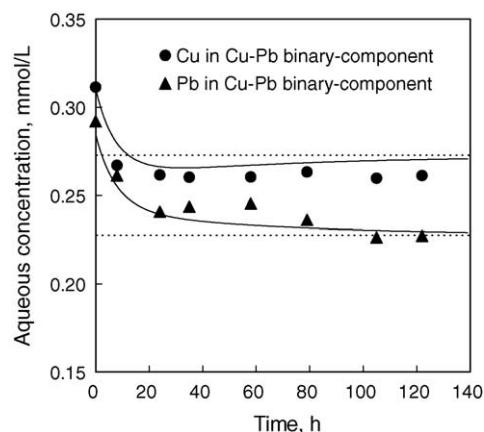


Fig. 4. Changes in aqueous concentration of Cu(II) and Pb(II) in binary mixture as a function of time. Solution volume, 1.00 L; GAC, 2.00 g. Solid lines: the aqueous concentration predicted by Eqs. (9a) and (9b), dotted lines: aqueous concentration at adsorption equilibrium calculated from the  $K_{e,\text{Cu}}$  and  $K_{e,\text{Pb}}$  obtained in single-component systems.



the experimental results for the binary mixture can be predicted although a slight deviation of  $0.005 \text{ mmol g}^{-1}$  from the experimental results is observed for Cu(II) at equilibrium [38]. The excess Cu(II) adsorption may be attributed to a slightly larger  $X_m$  for Cu(II) than that for Pb(II), resulting in Cu(II) adsorption onto the sites not occupied by Pb(II).

#### 4. Conclusions

The simultaneous adsorption of Cu(II) and Pb(II) onto activated carbon was examined by employing the conventional Langmuir equation in which the parameters obtained from the adsorption of Cu(II) and Pb(II) in the single-component systems were used. The following conclusions were obtained from the study.

1. The activated carbon is covered by a mono layer of Cu(II) and Pb(II) ions, and the number of maximum adsorption site for Cu(II) on the activated carbon is as great as that of Pb(II) from the Langmuir isotherms.
2. The adsorption of Cu(II) and Pb(II) onto the activated carbon is reversible from the desorption experiments.
3. The adsorption affinity of Pb(II) onto adsorption sites is nearly 1.8 times as great as that of Cu(II) due to the smaller desorption rate constant of Pb(II).
4. The simultaneous adsorption of Cu(II) and Pb(II) can be quantitatively predicted using a single set of parameters obtained from the isotherms and kinetic analysis in the single-component systems. Hence, it is proposed that the Cu(II) and Pb(II) competitively adsorb onto the same adsorption sites on the activated carbon.

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