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**Biosorption of Pb and Cd onto *Polygonum sachalinense***

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## Abstract

Adsorption of Pb and Cd onto a biosorbent, carbonized *Polygonum sachalinense* (CPS) was investigated. The carbonization condition was 1 hour at 350°C. The adsorption behaviors of Pb and Cd onto CPS could be explained by a proposed adsorption model based on the monodentate binding of the divalent metal ions with two types of adsorption sites. The adsorption sites were considered as carboxylic and phenolic groups based on the results of Boehm titration and FT-IR analysis. The maximum adsorption capacity of CPS for the divalent metal ions was determined as 1.22 mmol/g, and it was much larger than the values reported in the previous reports. The binding affinities of Pb of the adsorption sites were considered as much higher than those of Cd based on the adsorption constants. The adsorption constants of Pb and Cd with carboxylic group were about 200-2000 times larger than those of the adsorption constants with phenolic group. The kinetics of Pb and Cd onto CPS were also investigated. It was found that the adsorption of the divalent metal ions onto the phenolic group was a rate limiting step.

Keywords: Biosorption; Plant-derived adsorbent; Metal ion removal; Adsorption model

## **1. Introduction**

The concentration of heavy metals in natural water is generally very low, however, they become concentrated throughout the food chain to the extent of posing a serious health hazard to higher predators [1]. Among them, Pb and Cd have been very harmful to the human body. Pb affects hematopoietic function and can have adverse effects on the nervous, digestive, and reproductive systems. Cd can cause diseases such as skeletal deformities, cancer, and liver damage, which have been accumulated in the body. Therefore, the removal of heavy metals from aqueous environments is very important. For these reasons, The World Health Organization (WHO) has set the effluent limit in drinking water for Pb at 0.01 mg/L and Cd at 0.003 mg/L, respectively [2,3].

Recently, various methods have been employed to remove heavy metals, for example, membrane techniques [4,5], chemical precipitation method [6-8], adsorption [9-11], electrochemical treatment [12-14], solvent extraction [15,16], and so on. Among them, adsorption technique is considered one of the simplest methods to remove heavy metals from dilute solutions because of its low cost, convenient operation, and high removal efficiency [17]. Various adsorbents have been attempted to remove heavy metals, i.e., ion-exchange resin [9-11], activated carbon [18-20], zeolite [21-23],

hydrogel [24,25], etc. In the last two decades, adsorbents using biomaterials (biosorbent) and adsorption method using them (biosorption) have been attracting much attention [26].

Since biosorbents can be prepared in huge quantities at lower cost than commercial adsorbents, biosorption should be suitable for usage in areas where low-cost environmental remediation processes are required. Therefore, various biosorbents have been studied, for example, bacteria [27,28], yeast [29], biopolymers [30], microalgae [31-33] and so on. However, these have required complex pretreatment (centrifugation, immobilization, or modification), resulting in become costly and impractical. On the other hand, plant-derived biosorbents have not required complex pretreatments and are available at a lower cost. For these reasons, many studies have been reported, such as seaweed [34,35], wheat straw [36-38], pinecone [39,40], fruit peels [41-43], corn [44-46], sugarcane [47,48], olive [49,50], peanut husk [51,52], and other plants [53-56].

*Polygonum sachalinense* is a large perennial herb found in the mountains and riverside of Northeast Asia. In Japan, it has been mainly treated as a weed. Moreover, due to its stout and vigorously growing, *P. sachalinense* has rapidly expanded in Europe and North America and has become an invasive alien plant [57-59]. However, until now, there are few studies on the effective utilization of *P. sachalinense*. Therefore, the

effective utilization of *P. sachalinense* as a biosorbent would be an economical and environmentally friendly way to remove heavy metal ions.

In this study, carbonized *P. sachalinense* (CPS) is used as a biosorbent, and the adsorption experiments were carried out to remove Pb and Cd from an aqueous phase in a batch system. CPS was not done many pretreatments, but only carbonization and grinding were done as pretreatment. In many previous studies on biosorbents, regeneration of the adsorbents has been considered. However, regeneration of biosorbents is costly in terms of acid reagents, treatment process, and their retrieval after the adsorption process. In addition, it is necessary to consider the treatment of the acidic solution containing toxic substances produced after regeneration. These problems could prevent the biosorbent from practical use. Therefore, it will be less costly to use the adsorbent as a disposable type than to reuse it. Although it is practically impossible to use CPS as a packing layer because of its small size, it is expected that CPS could be used as a disposable adsorbent at low cost by quickly recovering the adsorbent by foam separation or flocculation after adsorption operation in a dispersed system. For these reasons, in this study, we assumed that CPS is used as a disposable type of biosorbent, so the regeneration of CPS was not considered.

The purpose of this study is to evaluate the adsorption performance of CPS on the

removal of Pb and Cd and to investigate the possibility of using CPS as a low-cost biosorbent for heavy metal removal. To estimate the amount adsorbed of Pb and Cd, we proposed an adsorption model considering multiple types of adsorption sites and analyzed the adsorption behavior of Pb and Cd onto CPS.

## 2. Materials and methods

### 2.1. Chemicals

Nitric acid, sodium hydroxide, lead (II) nitrate, methyl orange, phenolphthalein, were purchased from FUJIFILM WAKO Pure Chemical Corporation (Japan). Hydrochloric acid, sodium bicarbonate, sodium carbonate, zinc chloride, cadmium nitrate tetrahydrate, were purchased from KANTO CHEMICAL Co., INC. (Japan). These chemicals were analytical reagent grade. They were used without further purification. Deionized water was used for all experiments.

### 2.2. Preparation of biosorbents

The stems of *P. sachalinense* was collected from Hakodate campus of Hokkaido university (Hokkaido prefecture, Japan). *P. sachalinense* was cut into about 3 cm in size and was washed several times with deionized water to remove surface dirt and inorganic matter. It was dried in a dryer at 80°C for 24 hours. This will be referred as PS. Carbonization of PS was carried out in a muffle furnace (Burn Out Furnace 007-Plus,



KDF, Japan) at a desired temperature and time under air atmosphere (temperature rise rate was 15°C/min). Hereafter, carbonized PS will be abbreviated as CPS.

Generally, commercially activated carbon is often prepared by an operation called activation, which pores are introduced into the carbon materials. In this study, to compare the adsorption performance with or without this activation, PS-derived activated carbon was also prepared according to the activation method using ZnCl<sub>2</sub> [60]. First, the dried PS was immersed in ZnCl<sub>2</sub> solution (20 mL, 1.0 mol/L) at 80°C for 4 hours. Then, it was separated from the solution using a nylon filter (0.27 mm) and was dried at 80°C for 24 hours to remove the remaining water. The impregnated PS was set in a stainless container filled with nitrogen gas and heated at 500°C for 1 hour using a muffle furnace (temperature rise rate was 10°C/min). After cooling, the activated carbon prepared with ZnCl<sub>2</sub> was washed with dilute HCl solution and was further washed with warm water until the pH was stabilized. Then, it was dried in a dryer at 80°C for 24 hours.

PS and CPS were ground in a mill mixer and were sieved through 80 mesh (0.177 mm) sieves. CPS with the particle size less than 0.177 mm was used in the experiment. All the adsorbents were dried in a dryer at 80°C for 24 hours before being used in the experiments.

### 2.3. Adsorption experiments of Pb and Cd onto PS and CPS

All adsorption experiments were conducted in a batch system. A certain concentration of the metal solution containing PS (0.1 L) was stirred at 60 rpm for 48 hours at 25°C using a mixed rotor (VMRC-5, AS ONE, Japan). A certain concentration of the metal solution containing CPS (0.5 L) was stirred at 350 rpm for 24 hours at 25°C using a magnetic stirrer (REXIN RS-4DN, AS ONE, Japan). The mass of PS and CPS was set to 0.1 g for all adsorption experiments. The pH of the solution was adjusted with HNO<sub>3</sub> or NaOH solutions. After stirring, the adsorbent was separated from the solution by standing. And then, the pH and metal ion concentration of the supernatant solution were measured. The equilibrium pH of the solution was measured with a pH meter (InLab®410, METTLER TOLEDO, Switzerland). The concentrations of Pb and Cd in the liquid phase was determined with an atomic absorption spectrophotometer (AAAnalyst 200, Perkin Elmer, U.S.). The amount adsorbed of Pb and Cd was evaluated by the following equation.

$$q_e = \frac{(C_{m0} - C_{me})V}{m} \quad (1)$$

where  $q_e$  (mol/g) represents the experimental value of the amount adsorbed of Pb or Cd.  $C_{m0}$  and  $C_{me}$  (mol/L) represent the initial and the equilibrium concentration of the adsorbate, respectively.  $V$  (L) represents the volume of the solution.  $m$  (g) represents the mass of the adsorbent. The effect of contact time (0-24 hours) was also studied by varying contact time while keeping all other parameters fixed. Almost experiments were repeated at least twice. The repeatability of the experimental results has been confirmed. Infrared spectra of adsorbent were measured using Fourier transfer infrared spectrophotometer (FT/IR-4600AC, JASCO co., Japan).

#### *2.4. Boehm titration of PS and CPS*

The amount of oxygen functional groups (phenolic, lactone, and carboxyl group) included PS and CPS were determined by the Boehm titration method [61-63]. PS and CPS (0.05 g) were added to 30 mL of NaOH (0.05 mol/L), Na<sub>2</sub>CO<sub>3</sub> (0.01 mol/L), and NaHCO<sub>3</sub> (0.01 mol/L) solutions, respectively, and were shaken at 25°C for 48 hours using a mixed rotor (VMRC-5, AS ONE, Japan). Then, the suspension was then filtered. The filtrated solution (5.0 mL) was titrated with HCl solution (0.01 mol/L) for

neutralization. Methyl orange and phenolphthalein were used as an indicator for titration.

It is thought that NaOH neutralizes all Brønsted acid sites (phenolic, lactone, and carboxyl groups) and  $\text{Na}_2\text{CO}_3$  neutralizes carboxyl and lactone groups, and  $\text{NaHCO}_3$  neutralizes only carboxyl groups. The difference in the uptake of each base was used to quantify the type of oxygen surface groups included PS and CPS.

### 3. Results and discussion

#### 3.1. Influence of carbonization on number of acidic adsorption sites

Adsorption isotherms of Pb onto PS and CPS (carbonized at 350°C for 1 hour) are shown in Fig. 1. The experiments were conducted at pH 5.1. The initial concentration of Pb was set to 0.05-0.35 mmol/L. The amount adsorbed of Pb onto CPS was larger than that onto PS. The main metal binding sites of biosorbents are dissociative acidic functional groups such as phenolic and carboxyl groups. Boehm titration was applied to PS and CPS to quantify acidic functional groups. The results are listed in Table 1. It was reported that phenylpropanoid glycosides and flavonoids were the main types of compounds in *P. sachalinense* [64,65]. Thus, PS mainly contained lactone and phenolic groups with 1.25 and 1.03 mmol/g, respectively. In CPS, the number of carboxyl, lactone, and phenolic groups were 0.27, 1.38, and 2.07 mmol/g, respectively. The number of the total acidic functional groups of CPS increased compared to PS. Bardestani et al. [66] reported that carbonization of plant-derived biomass at medium or low temperatures under an air atmosphere leads to oxidation reactions on the surface of the adsorbent. As the result, the number of acidic functional groups increases compared

to that before carbonization. Thus, it is considered that the carbonization treatment in this study also increases the number of acidic functional groups, resulting in that the amount adsorbed of Pb onto CPS is larger than that onto PS. Moreover, Rahim et al. [67] reported that when plant-derived biomass is carbonized at temperatures above 300°C, cellulose and some lignin are decomposed into volatile components. This leads to forming pores on the adsorbent surface. In this study, the formation of pores on CPS could also increase the number of available adsorption sites compared to PS. For these reasons, it is suggested that the carbonization treatment improves the adsorption performance of the adsorbent prepared from *P. sachalinense*.

### 3.2. Influence of carbonization conditions on amount adsorbed of Pb

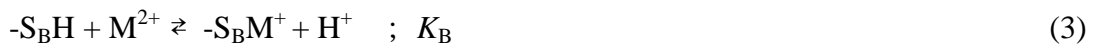
In the preparation of biosorbents, it is important to determine the optimal carbonization conditions. Fig. 2 shows the pH dependence of the amount adsorbed of Pb onto CPS carbonized under various conditions. The initial concentration of Pb was set to 0.20 mmol/L. Firstly, the amount adsorbed of Pb onto CPS activated with ZnCl<sub>2</sub> was much lower than that of other carbonization conditions. Figs. 3a and 3b show the FT-IR spectra of CPS activated with ZnCl<sub>2</sub> and CPS, respectively. Sharp peaks at 1625 cm<sup>-1</sup>

and  $3370\text{ cm}^{-1}$  were observed in CPS, whereas these peaks completely disappeared in CPS activated with  $\text{ZnCl}_2$ . These results indicate that the number of carboxyl and phenolic groups in CPS decreased after the activation treatment [41, 47]. Abe [60] reported that  $\text{ZnCl}_2$  dehydrates the side chains of lignin (mainly phenolic groups), and it has the effect of promoting polycyclic aromatization of lignin above  $200^\circ\text{C}$  to form a porous carbon structure. Yagmur et al. [68] also reported that the activation process using  $\text{ZnCl}_2$  decreases the number of hydroxy groups in lignin on the results of FT-IR analysis. For these reasons, it was found that the number of phenolic and carboxyl groups of CPS decreases because of this activation treatment, and the amount adsorbed of Pb decreases. Secondly, the amount adsorbed of Pb onto CPS carbonized at  $350^\circ\text{C}$  for 1 hour,  $350^\circ\text{C}$  for 3 hours, and  $500^\circ\text{C}$  for 1 hour, were all similar. The weight loss before and after carbonization was 76% for the CPS carbonized at  $350^\circ\text{C}$  for 1 hour, while it was about 94% for the CPS carbonized at  $500^\circ\text{C}$  for 1 hour. Therefore,  $350^\circ\text{C}$  for 1 hour was selected for carbonization of CPS, and unless otherwise noted, it was used in further adsorption experiments.

### *3.3. pH dependence of amount adsorbed of Pb and Cd onto CPS*

The pH dependences of the amount adsorbed of Pb and Cd onto CPS are shown in Figs. 4a and 5a. The initial concentrations of Pb and Cd were set to 0.20 mmol/L. The amount adsorbed of Pb increased abruptly from pH 4 to 5. On the other hand, the amount adsorbed of Cd increased gradually from pH 5 to 7 and increased abruptly over pH 7. These results suggest that the adsorption of Pb and Cd onto CPS is considered to involve at least two types of adsorption sites, which dissociate at different pH. Hereafter, these adsorption sites will be referred to as the site A and the site B.

The estimation of the pH dependence of the amount adsorbed of metal ions is important for the optimal operation of the adsorption and desorption process. Thus, we propose an adsorption model as a function of pH. Considering that the adsorption of the divalent metal ion is a monodentate binding to the acidic functional groups, the adsorption reactions are as follows,



where,  $-S_A$  and  $-S_B$  represent the two adsorption sites, site A and site B of CPS.  $M^{2+}$



represents the divalent metal ion, and  $K_A$  and  $K_B$  represent the adsorption equilibrium constants of the adsorption reactions. From Eqs. (2) and (3), the amount adsorbed of the metal ion onto CPS at equilibrium can be derived as follows,

$$q_{e\text{-cal}} = Q_A \frac{K_A C_{me}}{K_A C_{me} + C_h} + Q_B \frac{K_B C_{me}}{K_B C_{me} + C_h} \quad (4)$$

where  $Q_A$  and  $Q_B$  (mol/g) represent the maximum adsorption capacity of site A and site B, respectively.  $C_h$  (mol/L) represents the concentration of hydrogen ion at equilibrium. By fitting of the data to Eq. (4) using a least-squares method, the values of  $K_A$ ,  $K_B$ ,  $Q_A$ , and  $Q_B$  can be determined. In the right side of Eq. (4), the first and the second terms correspond to the amount adsorbed onto site A ( $q_{Ae}$ ) and site B ( $q_{Be}$ ), respectively.

The solid lines in Figs. 4a and 5a represent the values of  $q_{e\text{-cal}}$  for CPS calculated from Eq. (4). Since both Pb and Cd exist in the same form (divalent metal ion) in the liquid phase, the values of  $Q_A$  and  $Q_B$  should be the same for Pb and Cd. Thus, in this calculation, the same values of  $Q_A$  and  $Q_B$  were used for Pb and Cd. The correlation coefficients were 0.93 for Pb and 0.97 for Cd. The evaluated adsorption parameters of CPS are summarized in Table 2. The maximum adsorption capacity of CPS ( $Q_T = Q_A + Q_B$ ) was 1.22 mmol/g. By comparison with characteristics of other biosorbents reported

in the literature (Table 3), it is recognized that CPS possess considerable large adsorption capacity for Pb and Cd, suggesting that CPS would be a very potential adsorbent for Pb and Cd removal. The values of  $Q_A$  and  $Q_B$  were 0.26 mmol/g and 0.96 mmol/g, respectively. The dotted lines in Figs. 4 and 5 represent the amount adsorbed of Pb and Cd on site A. Compared with the results summarized in Tables 1 and 2, the value of  $Q_A$  is almost the same as the number of carboxyl groups on CPS. In general, the carboxyl groups on biosorbents dissociate in the weak acidic region. Seki et al. [34] reported that the acid dissociation constant ( $pK_a$ ) of the carboxyl groups in seaweeds is around 3, based on the results of potentiometric titration. Huizenga [69] also reported that the  $pK_a$  of the carboxyl groups of humic compounds is in the range of 3-4. Judging from the results in Figs. 4a and 5a, the site A is a functional group that dissociates around pH 3-5. Thus, the site A could be regarded as a carboxyl group. In this study, we assume that the adsorption sites for divalent metal ions are acidic groups. From the results summarized in Table 1, site B could be regarded as a phenolic group. These discussions can also be explained by the results of FT-IR analysis. Figs. 3c and 3d show the infrared spectra of CPS after the Pb and Cd adsorption experiments. The peak of the hydroxyl group shifted from  $3370\text{ cm}^{-1}$  to  $3424\text{ cm}^{-1}$  and  $3438\text{ cm}^{-1}$  before and after adsorption. Moreover, the peak of the carboxyl group shifted slightly from  $1625\text{ cm}^{-1}$  to

1614  $\text{cm}^{-1}$ . These results indicate that phenolic and carboxyl groups are mainly attributed to the Pb and Cd adsorption onto CPS. This result agrees with the reports that hydroxyl or phenolic groups can be the adsorption site for divalent metal ions [41, 44, 47,54].

Furthermore, the adsorption equilibrium constants for Pb and Cd of the site A ( $K_{A-Pb}$ ,  $K_{A-Cd}$ ) were 58.9 and 0.48, and those for site B ( $K_{B-Pb}$ ,  $K_{B-Cd}$ ) were 0.26 and  $2.18 \times 10^{-4}$ , respectively. The values of  $K_{A-Pb}$  and  $K_{B-Pb}$  are about 100-1000 times larger than  $K_{A-Cd}$  and  $K_{B-Cd}$ . These results suggest that Pb is more selective than Cd for the adsorption sites on CPS. Moreover, the values of  $K_A$  are about 200-2000 times higher than  $K_B$  for the Pb and Cd adsorption. This result indicates that the site A binds Pb and Cd more strongly than the site B.

We verified whether the estimated adsorption equilibrium constants and the maximum adsorption capacity were appropriate for the different initial metal concentrations. Fig. 6 shows the comparison between the experimental values and the calculated values of the amount adsorbed of Pb and Cd. The initial concentrations of Pb and Cd were 0.10 and 0.30 mmol/L. The dotted lines in Fig. 6 indicate an error of 15 %. The calculated values mostly agreed with the experimental values.

In addition, we considered that the adsorption equilibrium constants should be the

same even if the size of the adsorbent and the carbonization conditions are different. Thus, we estimated the values of  $Q$  of the PS-based adsorbent prepared under the different sizes of CPS (Figs. 4b and 5b) and carbonization conditions (Fig. 2) using the  $K$  values presented in Table 2. The values of  $Q$  were estimated by a least-squares method using Eq. (4). The solid lines in Figs. 4b and 5b represent the calculated values of the amount adsorbed of Pb and Cd in the case of CPS larger than 0.177 mm in size (CPS-L). The solid lines in Fig. 2 represent the calculated values of the amount adsorbed of Pb in the case of CPS prepared under different carbonization conditions. The experimental and the calculated values of the amount adsorbed of Pb and Cd onto CPSs mostly agreed well. The correlation coefficients ranged from 0.98 to 0.99. These results indicate that the estimated adsorption parameters and the proposed adsorption model are valid. Table 4 shows the comparison of the maximum adsorption capacity of CPS for Pb, and in some cases Cd. CPS carbonized at 350°C for 1 hour has the highest maximum adsorption capacity. The value of  $Q_A$  (carboxyl groups) increased, and the value of  $Q_B$  (phenolic groups) decreased as the carbonization temperature and time increased. These results could be caused by the decomposition of lignin and further oxidation of CPS caused by high temperature [66]. Also, the value of  $Q_T$  for CPS-L was lower than that of CPS. From the result, it is considered that Pb and Cd ions could not

diffuse into the interior of CPS-L, and the acidic groups inside CPS-L could not be contributed to the adsorption reaction.

#### 3.4. Kinetics of the Pb and Cd adsorption onto CPS

Fig. 7 shows the typical results of the time course of the Pb and Cd adsorption for CPS at 25 °C. The initial concentrations of Pb and Cd were set to 0.20 mmol/L, and the pH conditions were at pH 4.6 for Pb and pH 5.6 for Cd. The adsorption kinetics of the divalent metal ion onto biosorbents has been often reported to follow the pseudo-second order kinetic model [18,44,51,70]. From the results in section 3.3, we considered that there are at least two types of adsorption sites on CPS. Therefore, we applied the pseudo-second order kinetic model considering two types of adsorption sites as follows,

$$\frac{dq_A}{dt} = k_A (q_{Ac} - q_A)^2 \quad (5)$$

$$\frac{dq_B}{dt} = k_B (q_{Bc} - q_B)^2 \quad (6)$$

by solving Eqs. (5) and (6) with the initial conditions ( $q = 0$  at  $t = 0$ ), the following

equations are obtained,

$$q_A = q_{Ae} \frac{k_A q_{Ae} t}{1 + k_A q_{Ae} t} \quad (7)$$

$$q_B = q_{Be} \frac{k_B q_{Be} t}{1 + k_B q_{Be} t} \quad (8)$$

where,  $q_A$  and  $q_B$  (mol/g) represent the amount adsorbed of the metal ion to the adsorption site A and site B at time  $t$ , respectively.  $k$  (g/mol·s) represents the pseudo-second order rate constant,  $q_{Ae}$  and  $q_{Be}$  (mol/g) represent the amount adsorbed of the metal ion at the equilibrium state. The total amount adsorbed of the metal ion ( $q$ ) can be defined by Eq. (9),

$$q = q_A + q_B \quad (9)$$

the values of  $k_A$ ,  $k_B$ ,  $q_{Ae}$ , and  $q_{Be}$  were determined by fitting the experimental data to Eq. (9) using a least-squares method. The solid and dotted lines in Fig. 7 represent the amount adsorbed of Pb and Cd calculated from Eq. (9). The correlation coefficients were 0.99, indicating that the kinetics of Pb and Cd adsorption onto CPS follows well

the pseudo-second order kinetic model. The amount adsorbed of Pb at pH 4.6 reached an equilibrium state within 12 hours. On the other hand, the amount adsorbed of Cd at pH 5.6 reached an equilibrium state within 2 hours. The evaluated  $k_A$  and  $k_B$  values for Pb and Cd are summarized in Table 5. The values of  $k_A$  are about 1000 times higher than  $k_B$ . Judging from these results, the adsorption of Pb and Cd to site B is considered as a rate-limiting step of the Pb and Cd adsorption onto CPS.

#### 4. Conclusions

In this study, adsorption of Pb and Cd ions onto *Polygonum sachalinense* was investigated using the carbonized or uncarbonized *P. sachalinense* (CPS and PS) as adsorbents. The adsorption behaviors of Pb and Cd onto CPS were also investigated by applying the proposed adsorption model based on the binding between two types of adsorption sites and Pb/Cd. Consequently, the followings were clarified.

- (1) The adsorption behaviors of Pb and Cd onto CPS were explained well by the proposed adsorption model.
- (2) Two types of adsorption site suggested by the proposed model were considered as carboxylic and phenolic groups, which was supported by Boehm titration and FT-IR analysis.
- (3) The maximum adsorption capacity of CPS was 1.22 mmol/g, which was much higher than that of biosorbents reported in literature.
- (4) The adsorption equilibrium constants of Pb and Cd for the carboxyl group ( $K_{A-Pb}$ ,  $K_{A-Cd}$ ) were 58.9 and 0.48, and those for the phenolic group ( $K_{B-Pb}$ ,  $K_{B-Cd}$ ) were 0.26 and  $2.18 \times 10^{-4}$ , respectively. The values of  $K_{A-Pb}$  and  $K_{B-Pb}$  were about 100-1000 times higher than  $K_{A-Cd}$  and  $K_{B-Cd}$ . This result suggested that Pb was adsorbed much selectively than



Cd for each adsorption site of CPS. Moreover, the values of  $K_A$  were about 200-2000 times higher than  $K_B$  in the Pb and Cd adsorption. This result indicated that the carboxyl group binds divalent metal ions more strongly than the phenolic group.

Based on above described, the carbonized CPS is a very potential adsorbent for the removal of toxic heavy metals from aqueous environment, especially in terms of adsorption capacity. In addition, it is suggested that CPS can be used for the fractionation of Pb and Cd. The vegetation of *P. sachalinense* seems to indicate that CPS can be widely prepared and used globally. In a further study, the adsorption performance will be improved.

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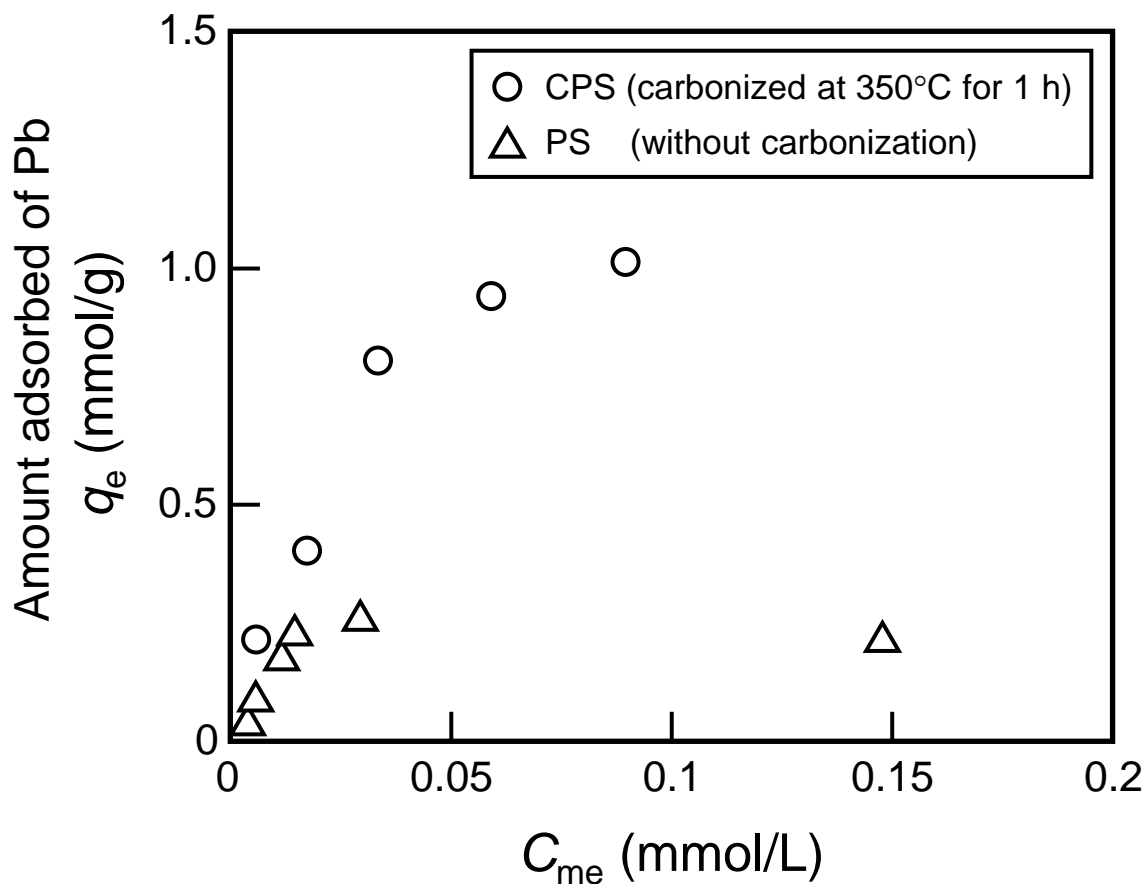
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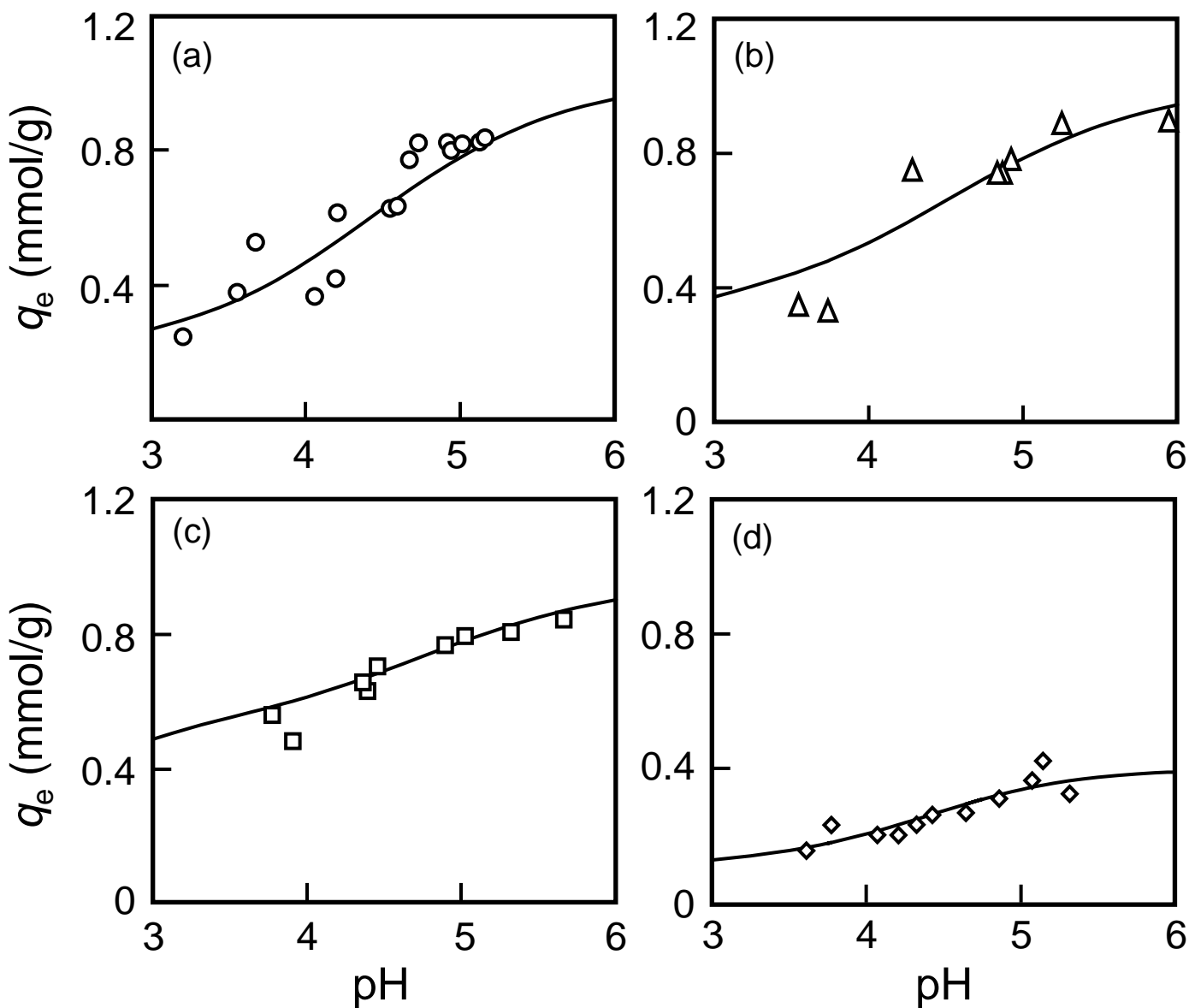
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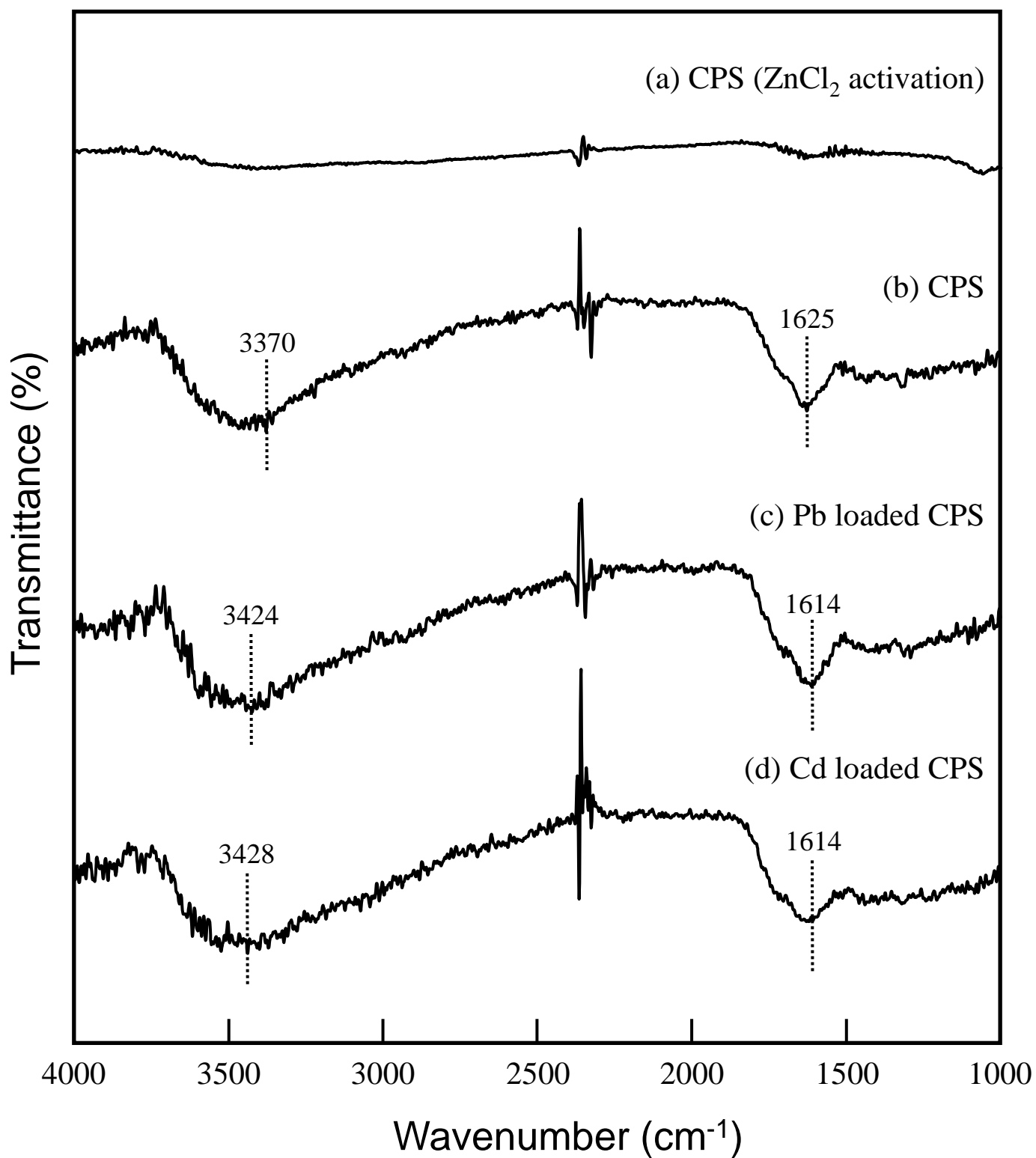




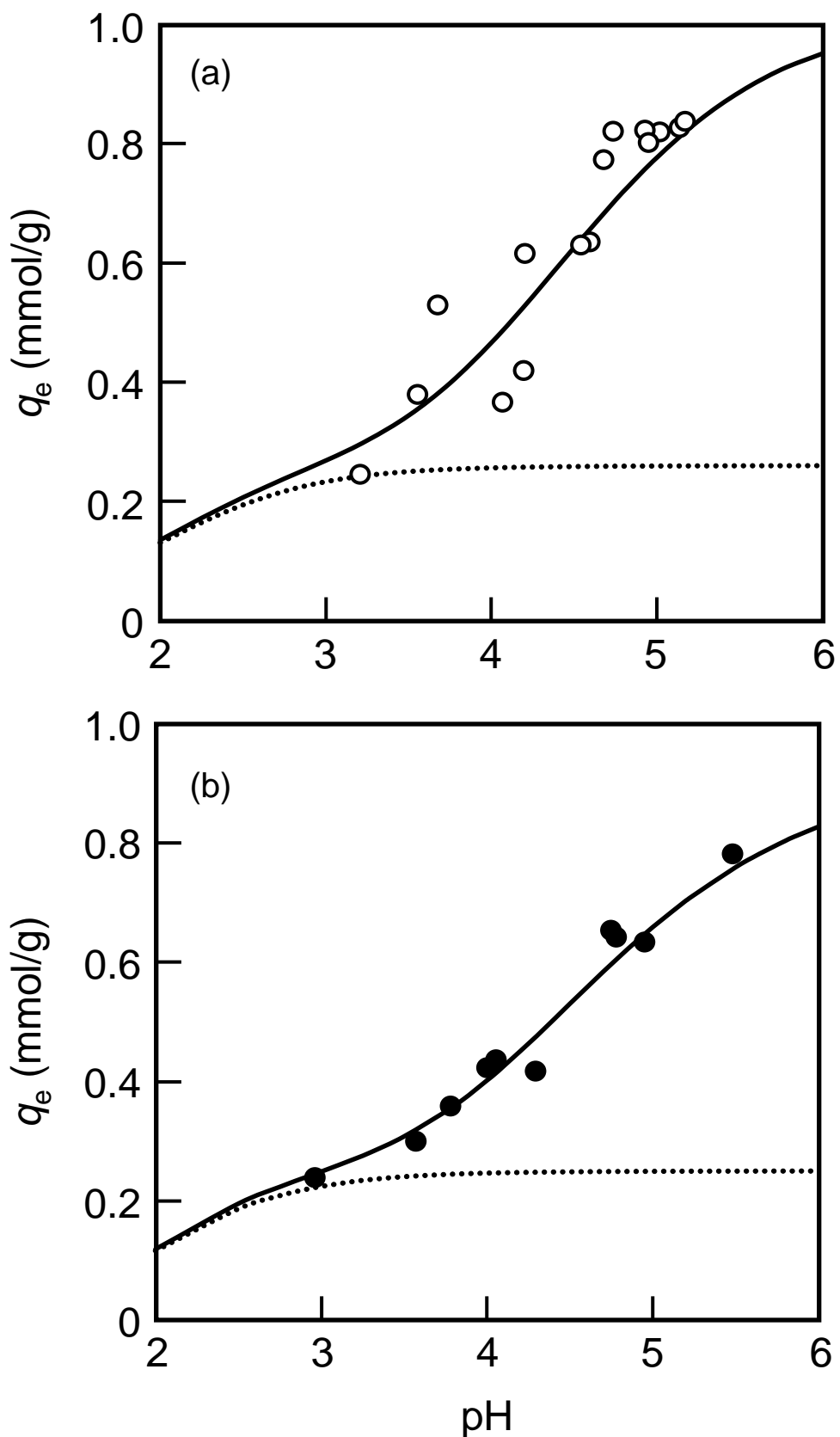
**Fig. 1.** Adsorption isotherms of Pb onto CPS (open circle) and PS (open triangle) at 25 °C. The initial concentration of Pb was set to 0.05-0.35 mmol/L, and the pH condition was at pH 5.1. The size of PS was less than 0.177 mm.



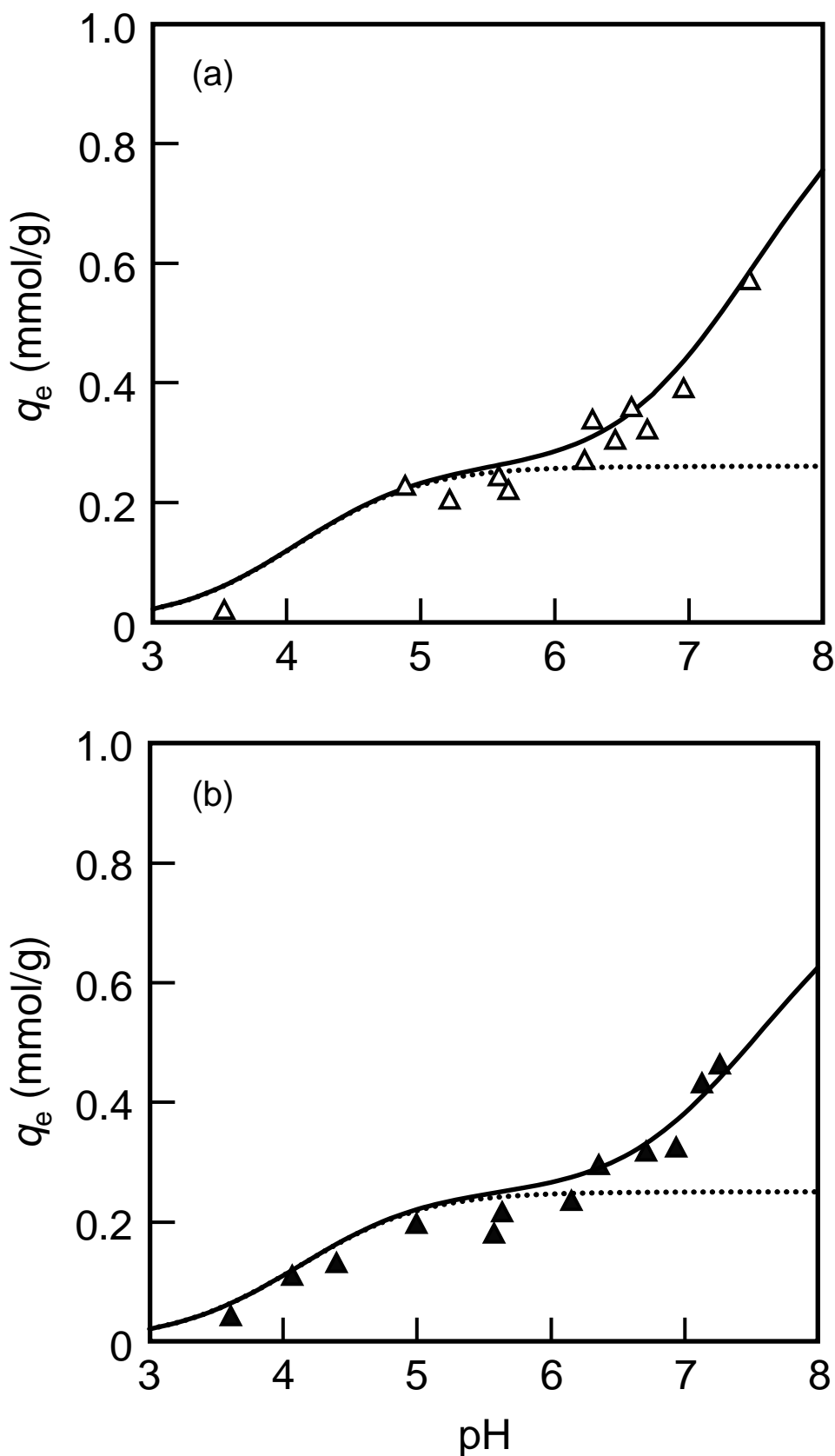
**Fig. 2.** pH dependence of the amount adsorbed of Pb onto CPS under various carbonized conditions. The carbonized conditions were 350°C for 1 hour (a), 350°C for 3 hours (b), 500°C for 1 hour (c), and activation with  $ZnCl_2$  at 500°C for 1 hour (d). The initial concentration of Pb was set to 0.20 mmol/L. The solid lines represent the calculated value from Eq. (4).



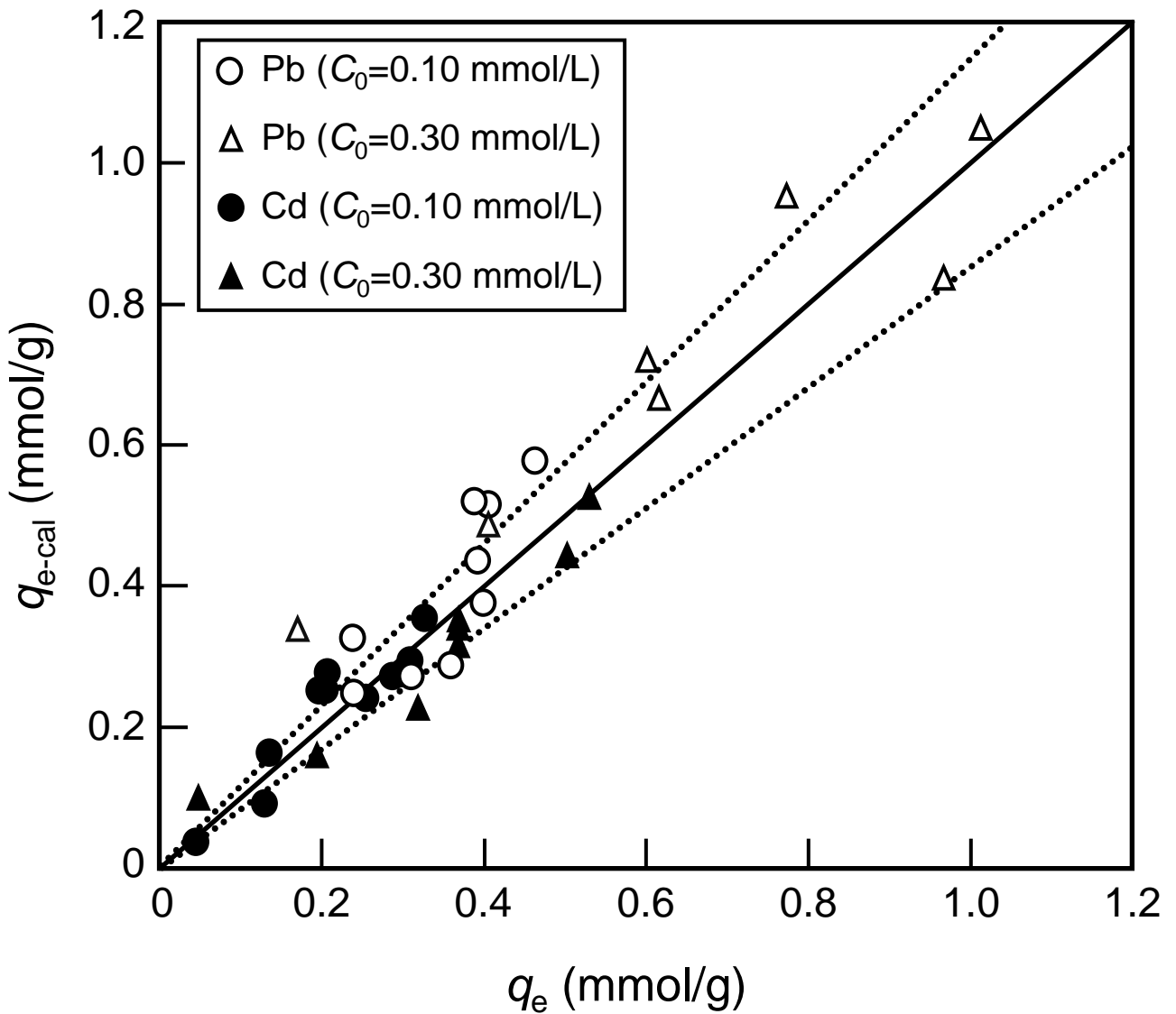
**Fig. 3.** FT-IR spectra of (a) CPS ( $\text{ZnCl}_2$  activation), (b) CPS ( $350^\circ\text{C}$ , 1 hour), (c) Pb loaded CPS, and (d) Cd loaded CPS, respectively.



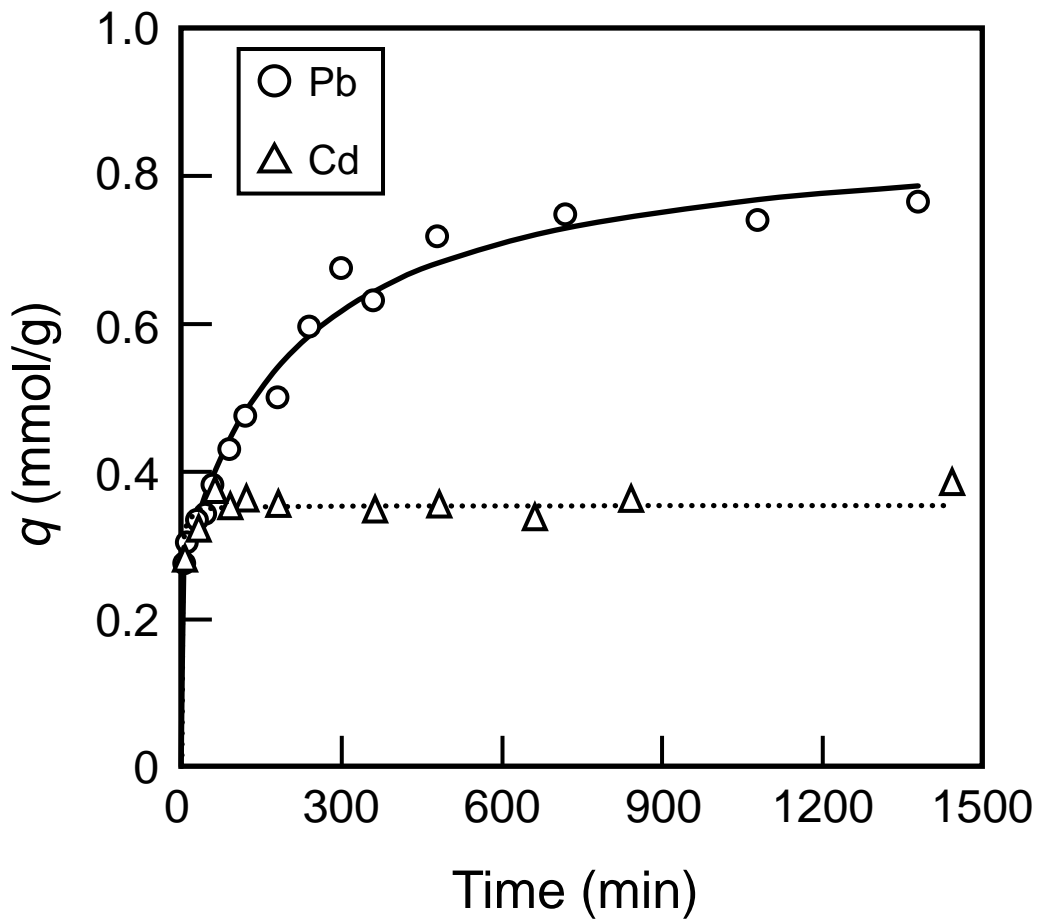
**Fig. 4.** The amount adsorbed of Pb onto CPS (a) and CPS-L (b) as a function of pH. CPSs were carbonized at 350°C for 1 h. The initial concentration of Pb was set to 0.20 mmol/L. The solid lines represent the calculated values from Eq. (4). The dotted lines represent the value of  $q_{Ae}$ .



**Fig. 5.** The amount adsorbed of Cd onto CPS (a) and CPS-L (b) as a function of pH. CPSs were carbonized at 350°C for 1 h. The initial concentration of Cd was set to 0.20 mmol/L. The solid lines represent the calculated values from Eq. (4). The dotted lines represent the value of  $q_{Ae}$ .



**Fig. 6.** Comparison of the experimental and the calculated values of the amount adsorbed of Pb (open symbols) and Cd (solid symbols) onto CPS. CPS carbonized at 350°C for 1 hour was used. The initial concentrations of the metal ions were set to 0.10 mmol/L (circles) and 0.30 mmol/L (triangles). The dotted lines represent the error of 15 %.



**Fig. 7.** The time course of the amount adsorbed of Pb (open circles) and Cd (open triangles) onto CPS at 25 °C. The initial concentrations of Pb and Cd were 0.20 mmol/L, and the pH conditions were at pH 4.6 and pH 5.6 for Pb and Cd, respectively. The solid and dotted line represent the calculated values from Eq. (9).

**Table 1**

The number of acidic functional groups on PS and CPS.

Adsorbent	Functional groups (mmol/g)		
	Carboxyl	Lactone	Phenolic
PS	0	1.25	1.03
CPS	0.27	1.38	2.07



**Table 2**

Adsorption parameters for CPS (carbonized at 350 °C for 1 h) estimated by Eq. (4).

Adsorption parameters					
$Q_A$ (mmol/g)	$Q_B$ (mmol/g)	$K_{A-Pb}$ (-)	$K_{A-Cd}$ (-)	$K_{B-Pb}$ (-)	$K_{B-Cd}$ (-)
0.26	0.96	58.9	0.48	0.26	$2.18 \times 10^{-4}$

**Table 3**

Comparison of the maximum Pb and Cd adsorption capacity with other reported biosorbents

Adsorbent	Maximum Pb adsorption capacity (mg/g)	Maximum Cd adsorption capacity (mg/g)	Reference
CR-11 (chelate resin)	381.8	229.3	[71]
Cys-chitin	351.5	214.6	[72]
CPS	252.2	136.8	This study
Marine bacterium	250.0	–	[70]
<i>Bacillus badius</i>	–	131.6	[73]
Corn silk	90.0	–	[44]
Peanuts husk	29.1	26.9	[51]
Activated carbon	20.3	27.3	[18]
Wheat straw	–	14.6	[36]

**Table 4**

Comparison of the maximum adsorption capacity of CPS prepared by different carbonized conditions and sizes.

Carbonization conditions	Size (mm)	Adsorbate	Maximum adsorption capacity (mmol/g)		
			$Q_A$	$Q_B$	$Q_T$
350 °C, 1 hour	$\leq 0.17$	Pb, Cd	0.26	0.96	1.22
350 °C, 1 hour	0.17-0.25	Pb, Cd	0.25	0.68	0.93
350 °C, 3 hours	$\leq 0.17$	Pb	0.39	0.74	1.13
500 °C, 1 hour	$\leq 0.17$	Pb	0.56	0.42	0.98
ZnCl <sub>2</sub> activation	$\leq 0.17$	Pb	0.12	0.27	0.39

**Table 5**

Adsorption kinetic parameters of CPS for Pb (pH 4.6) and Cd (pH 5.6) estimated by Eq. (9).

Adsorbate	Adsorption kinetic parameters				
	$q_{Ae}$ (mmol/g)	$q_{Be}$ (mmol/g)	$k_A$ (g/mmol·s)	$k_B$ (g/mmol·s)	$r^a$ (-)
Pb	0.26	0.61	0.234	$1.31 \times 10^{-4}$	0.99
Cd	0.25	0.09	0.180	$1.21 \times 10^{-4}$	0.99

a ;  $r$  represents the correlation coefficient