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**Preparation of adsorbent by mechanochemical reaction based waste seashell with sodium oxalate and its application of Pb ion adsorption**

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## **Abstract**

Waste seashell (scallop shell) based adsorbent was prepared by mechanochemical reaction with sodium oxalate using ball milling. The oxalate modified seashell based adsorbents (OS) were prepared by varying the molar ratio of calcium and oxalate as 0.5, 1, and 2. Sodium oxalate was used as the aqueous solution in ball milling. Lead ion adsorption was conducted with the prepared adsorbent. The adsorption behavior of lead ion was investigated in terms of adsorption kinetics and adsorption equilibrium. Time course of the amount adsorbed of Pb agreed well with Langmuir rate equation. The adsorption equilibrium relationship of OS adsorbent and Pb agreed well Langmuir adsorption isotherm. As increasing with the molar ratio, the saturated amount adsorbed of Pb increased from  $5.45 \times 10^{-3}$  to  $6.23 \times 10^{-3}$  mol/g slightly. Under the present experimental conditions, the maximum equilibrium adsorption was  $5.93 \times 10^{-3}$  mol/g, which is greater than that reported in the literature.

**KEYWORDS:** mechanochemical reaction, waste scallop shell, sodium oxalate, ball milling, adsorption

## 1. Introduction

Mechanochemical reactions using ball milling have the advantage that the new surface created when solid particles are ground is a highly reactive surface, and new bonding states can be easily formed when ions or substances with double bonds are present, but controlling the reaction is a very difficult. However, it is also very difficult to control the reaction. Mechanochemical reactions using ball milling are used in various fields, for examples, metal recovery operations [1], synthesis of metal oxide nanoparticles [2], synthesis of antimicrobial materials [3], pharmaceutical synthesis [4], extraction operations [5, 6], synthesis of catalytic materials [7, 8], and production of functional nanoparticle materials [9, 10].

On the other hand, the removal of harmful toxic heavy metal ions dissolved in water has long been an issue closely related to our daily lives, especially for the preservation of the aquatic environment, the safety of drinking water, and the protection of human health, and continues to attract interest [11]. Various methods are used to remove heavy metal ions from aquatic environments, including chemical precipitation [12], ion exchange resins [13], membrane technology [14], coagulation precipitation [15], electrochemical methods [16], and adsorption. The removal of heavy metal ions is accomplished by using various procedures at the appropriate location and timing, as there is no one-size-fits-all solution.

Among these methods, the separation process by adsorption is used in various fields. Adsorption is widely used because of its simplicity and ease of continuous operation. In recent years, various adsorbents have been developed using inexpensive bio-materials and waste materials. Among them, there have been many reports on the use of waste shells as adsorbents for the recovery of heavy metal ions. The main component of shells is calcium carbonate. Calcium carbonate as a mineral is inexhaustible on the earth and is widely used in various industries. On the other hand, discarded shells are one of the environmental problems

that are generated in large quantities as fishery waste. For example, in Hokkaido, Japan, the total amount of fishery waste in 2021 was 1 million tons, of which 300,000 tons were shells, accounting for 30%. Effective utilization of these discarded shells is one of the most important issues.

Several studies on the adsorption of heavy metal ions using shells have been reported such as, adsorption of Pb and Cu ions using shells (*Anadara inaequalvis*) [17], adsorption of Pb, Ni, and Zn using an adsorbent combined pervious concrete and seashell [18], removal of Sr ion from aqueous solution using clam shell (*Donax trunculus*) [19], adsorption of Pb ion using mussel shell-based adsorbent [20], removal of Cu, Co, and Pb ions using calcined snail shell (*Solamen Vaillanti*) [21], adsorption of Ni ions on sea shells of Mehdiya [22], development of adsorbent combined cement and shells [23], adsorption of Cu, Cd, and Pb ions using calcined golden apple snail shell [24], adsorption of Cu, Zn, Cd, and Ni ions using discarded shells from canning industry [25], adsorption of Cu and Cd ions using indigenous shells (*Macra aequisulcata*) [26] and so on. In addition, the following studies have been reported on the application of mechanochemical reactions by ball milling to discarded shells, for examples, preparation of nanosize calcium carbonate powder from mollusk shells [27].

Preparation of high pure calcite powders from oyster shells by combination of mechanochemical and hydrothermal treatments [28] and so on. However, there are very few reports on the preparation of adsorbents based on waste shells and adsorption experiments using mechanochemical reaction by ball milling, mainly for use as adsorbents.

The author attempted to modify carboxyl groups on the surface of waste shells with an aqueous solution of sodium oxalate, a dicarboxylic acid. It was expected that one of the two carboxyl groups would bind to the reactive surface created by grinding. In this study, the influence on the adsorption behavior of lead ions on shell particles prepared by changing the molar ratio (calcium/oxalate ions) during preparation was experimentally investigated in

terms of adsorption rate and adsorption equilibrium relationship. The influence of preparation conditions (molar ratio, calcium/oxalate ion) on lead ion adsorption was experimentally investigated especially in terms of the adsorption kinetics and the adsorption equilibrium relationship.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1 Scallop shell

Waste scallop shells (*Patinopecten yessoensis*) were obtained from commercial markets in Hakodate city, Hokkaido prefecture, Japan.

#### 2.1.2 Chemicals

Sodium oxalate and nitric acid solution (60 wt.%) were purchased from Kanto Chemical Co. Inc. (Japan). Lead (II) nitrate, nitric acid, sodium hydroxide, and potassium bromide were purchased from Fujifilm Wako Pure Chemical Co. (Japan). Nitric acid and sodium hydroxide were used to adjust pH of the adsorption system. All purchased chemicals were used without further purification.

### 2.2. Preparation of adsorbent

Preparation of the adsorbent was done using grinding in a ball mill pod. The amount of sodium oxalate substance added to 10 g of shells (Ca ion content 0.092 mol) was varied from 0.05, 0.1, and 0.2 mol, and 100 mL of distilled water was added for grinding by ball milling. In most cases, milling was carried out at a speed of 120 rpm and a milling time of 24 hours. The pod used for grinding was 500 mL in volume (outer diameter 10 cm, height 10.5 cm, made of alumina, Takishin Co., Japan), and the mill balls (2 cm in diameter and made of alumina, Hira Co. LTD., Japan). The ball mill stand was used as AV-1 (ASAHI-RIKA SEISAKUSHO CO., LTD., Chiba, Japan). After milling was stopped, the contents of the pods were removed into a 1000-mL beaker, and particles adhering to the balls were washed into the

beaker with distilled water using a washing bottle. The inner wall of the pod was also washed into the beaker with distilled water using a washing bottle. The suspension solution was separated by centrifugation (3000 rpm, 10 min). The collected particles were transferred to a 500-mL beaker, to which 500 mL of distilled water was added and stirred for 10 minutes using a magnetic stirrer. The particles were then transferred to a 500-mL beaker, 500 mL of distilled water was added, and the beaker was stirred for 10 minutes using a magnetic stirrer. The particles were washed twice (three times in total). The particles were then collected by centrifugation and dried in a dryer (60°C). After drying, the particles were dispersed using an agate mortar, placed in polystyrene containers, and the containers were further stored in desiccators. The calcium ion concentration in scallop shells (0.092 mol/g-shell) was determined in a previous study [29]. The molar ratios of calcium ions to sodium oxalate are approximately 0.5, 1.0, and 2.0, and the adsorbents prepared at these molar ratios will be referred to as OS0.5, OS1.0, and OS2.0, respectively.

### *2.3 Characterization of OS adsorbent*

#### *2.3.1 Scanning electron microscopy image*

The particle morphology was observed using a scanning electron microscopy (SEM, JSM6010LA, JEOL Ltd., Japan).

#### *2.3.2 Measurement of particle size distribution*

The particle size distribution was measured using a laser particle size analyzer (HORIBA LA-300, Japan).

#### *2.3.3 Measurement of X-ray diffraction pattern*



The X-ray diffraction (XDR) pattern was recorded a X-ray diffractometer (XRD, MiniFlex, Rigaku co., Japan).

#### *2.3.4 FT-IR measurement*

IR spectra of adsorbents were conducted using a fourier transform infrared spectrometer (FT/IR-4600AC, JASCO co., Japan). Samples for the measurements were prepared by the tablet method using with KBr. KBr was added to the sample (the adsorbent) to make it about 0.5-1.0%, and the powder was mixed well. After fine grinding, pellet discs of 3 mm were made using a pellet forming die. The tablet discs were inserted into the sample chamber for measurement.

#### *2.4. Procedure of adsorption experiment.*

All adsorption experiments (adsorption rate and adsorption equilibrium) were performed in a batch mode. A desired amount of adsorbent was taken in an Erlenmeyer flask, to which a desired amount of distilled water was added. The solution was stirred (300 rpm) with a magnetic stirrer for 10 minutes. Then, the flask was set in a glass bell vacuum chamber, and the suspension was depressurized with an aspirator to degas the surface of the adsorbent for 3 min. The pH of the solution was adjusted by adding HCl or NaOH aqueous solution with stirring using a magnetic stirrer in a 30°C water bath. The adsorption experiment was then started by adding the required amount of lead nitrate solution to achieve the prescribed initial Pb ion concentration. The initial pH of the liquid phase was prepared to be in the range of 4.95-5.05.

After the required adsorption time, the adsorbent was separated from the liquid phase by filtration using a membrane filter (average pore size 0.8 and 0.45  $\mu\text{m}$ , cellulose acetate, Advantec Toyo, Japan). The solution including adsorbents was first filtered by a membrane

filter (0.8 $\mu\text{m}$ ), and then the filtrate was filtered again by a membrane filter (0.45  $\mu\text{m}$ ). Since suction filtration using a 0.45 diameter filter from the beginning causes clogging, filtration was initially performed using a 0.8 $\mu\text{m}$  diameter membrane filter. The filter with a 0.8  $\mu\text{m}$  diameter of was washed with distilled water while suctioning with adsorbent particles still on it, and then placed in a dryer to dry (50°C). The filter was then placed in a dryer for FT-IR measurement of the adsorbent after adsorption. Most experiments were repeated twice. The repeatability of the experimental results has been confirmed.

The equilibrium pH of the liquid phase was measured with a pH meter (model 920A, ThermoOrion, U.S.). The concentration of Pb ions in the liquid phase was measured using an atomic absorption spectrophotometer (AAnalyst 200, Perkin Elmer, U.S.). The amount of Pb adsorbed was calculated from the mass balance expressed by the following equations.

$$X_t = (C_i - C_t)V/m \quad (1)$$

$$X_e = (C_i - C_e)V/m \quad (2)$$

Where  $X_t$  [mol/g] and  $X_e$  [mol/g] are the amount adsorbed at time  $t$  and equilibrium amount adsorbed,  $C_t$  [mol/L] and  $C_e$  [mol/L] are the liquid phase concentration at time  $t$  and equilibrium concentration,  $C_i$  [mol/L] is the initial concentration of the liquid phase,  $V$  [L] is the liquid volume, and  $m$  [g] is the mass of the adsorbent, respectively.

### 3. Results and Discussion

#### 3.1. Characterization of OS adsorbent

Fig. 1 shows SEM images of the OS adsorbent. On the morphological observation by SEM image, most of the OS adsorbent particles were recognized as rectangular in shape. They were found to be partially aggregated. Their surface was also found to be not porous surface. Fig. 2 shows the size distribution of the OS adsorbent particles. Only OS0.5 had one peak (about 3  $\mu\text{m}$ ), while two peaks (about 2 and 40  $\mu\text{m}$ ) were observed for OS1.0 and OS2.0. Under the OS1.0 and OS2.0 preparation conditions, more aggregates are considered to have formed than in the case of OS0.5. The aggregation occurred as the amount of sodium oxalate added increased, but it is unclear how the variation of the sodium oxalate concentration was affected. The specific surface area based on volume was calculated at the same time of the measurement of the particle size distribution by data processing. According to these calculation, these values were  $1.78 \times 10^4$ ,  $3.10 \times 10^4$ , and  $2.45 \times 10^4 \text{ cm}^2/\text{cm}^3$  for OS0.5, OS1.0 and OS2.0, respectively. Based on the average value of the reported scallop shell density ( $2.53 \text{ g}/\text{cm}^3$ ) [30, 31], the specific surface area of OS adsorbents were estimated as 0.703, 1.22, and  $0.966 \text{ m}^2/\text{g}$  for OS0.5, OS1.0, and OS2.0, respectively. These values were considered to be relatively small. Fig. 3a shows typical result of XRD pattern of OS1.0. The XRD patterns of OS0.5 and OS2.0 were mostly same as that of OS1.0, so the data were not shown. The letter C

in fig. 3a indicates the characteristic peak of calcite (JCPDF: 01-078-4614, 04-008-0788). Other characteristic peaks were not observed. No other morphs were observed in the mechanochemical reaction by the addition of sodium oxalate in this study. The XRD pattern was the same as that of crushed shells. Fig. 3b shows the FT-IR spectrum of a waste shell-based adsorbent prepared by ball milling. The FT-IR spectra of the shells (top row) and the reagent sodium oxalate (second from the top) are shown together as reference spectra. The FT-IR spectra of the prepared adsorbents are shown in the third, fourth, and fifth rows of the same figure. The horizontal axis is the wave number and the vertical axis is the transmittance (arbitrary unit). The characteristic absorption peak common to shell and adsorbent OS is 1080(iii), and the characteristic absorption peaks common to sodium oxalate and adsorbent OS are 1317(ii) and 1617(i).

The FT-IR spectra of the crushed shell particles were in good agreement with the measured results of Wang et al. (2021) and Giordano et al. (2022) [20, 32]. In addition, the FT-IR spectrum of sodium oxalate was in good agreement with the IR spectra in the databases (AIST, NIST, and SpectraBase). Lu et al. (2015) reported that the peak at  $1082\text{ cm}^{-1}$  indicated the internal vibrational mode of the carbonate ions in shell powders. [27]. Islam et al. (2013) observed the absorption peak at  $1082\text{ cm}^{-1}$  related to  $\text{CO}_3^{2-}$  in shell powders [33, 34]. Leukel et al. (2018) reported that the ball-milled amorphous calcium carbonate showed the symmetric stretching vibrational mode, which was observed at  $1071\text{ cm}^{-1}$  in the FI-IR spectrum and  $1081\text{ cm}^{-1}$  in Raman spectrum [35]. Ouyang et al. (2003) reported that the main antisymmetric carbonyl stretching band ( $\text{COO}^-$ ) specific to the oxalate family occurs at  $1618\text{ cm}^{-1}$ , and the secondary carbonyl stretching band, the metal carboxylate stretching band,

occurs at  $1317\text{ cm}^{-1}$  [36]. Parekh et al reported that the peak at  $1613\text{ cm}^{-1}$  indicates the presence of more than one C=O bond [37].

Based on previous studies of the absorption peaks mentioned above, it can be inferred that the peak at 1080 is derived from scallop shells, and that the absorption peaks at 1316 and 1617 are carboxyl groups derived from sodium oxalate. In other words, the possibility is suggested that sodium oxalate-derived carboxyl groups on the surface of the shell particles are modified by our preparation method. This also suggests that a mechanochemical reaction occurred by ball milling.

It has been already reported that crushed shell particles alone have the ability to adsorb heavy metal ions. In this study, we experimentally investigated the adsorption capacity of the OS adsorbent prepared in this study by conducting actual adsorption experiments. In the next section, we report on the adsorption behavior of lead ions on the OS adsorbent prepared in this study, especially the adsorption rate and adsorption equilibrium relationship.

### *3.2. Adsorption kinetics of Pb ions onto OS adsorbents*

The adsorption rate experiments were conducted to investigate the adsorption kinetics of Pb ions onto OS adsorbents. Fig. 4 shows the time course of the change in the amount adsorbed of Pb for the prepared adsorbents OS0.5, OS1.0, and OS2.0, respectively. The measurement points shown in Figs. 4a-c are very close to each other, and we have deliberately presented them as separate graphs because we believe that superimposing these graphs would be very difficult to read. In addition, the result of the time course of the amount adsorbed of Pb using non-modified shell particles (control) is also shown in Fig. 4b. The experimental conditions were the liquid volume of 100 mL, the initial Pb ion concentration of ca.  $3\times 10^{-3}$  mol/L, and the OS adsorbent mass of ca. 0.02 g, respectively. At the beginning of each

adsorption experiment, the pH values of the liquid phase were prepared in the range of 4.95-5.05, and the pH values of the liquid phase at each measurement time were in the range of 4.57-4.7. In all adsorption rate experiments, as shown in Fig. 4, the adsorption equilibrium was reached in 180 minutes. As described later, the initial concentration of ca.  $3 \times 10^{-3}$  mol/L is a relatively large value for the initial concentration in this study, judging from the equilibrium concentration. In the case of the initial concentration was set at lower than  $3 \times 10^{-3}$  mol/L, the adsorption equilibrium was also reached in 180 minutes (data were not shown). In the case of using non-modified shell particles, the equilibrium amount adsorbed of Pb was lower than that using OS adsorbents, resulting in the amount adsorbed being 0.11 times of that of OS adsorbents. This difference in the amount adsorbed might be caused that OS adsorbents have the modified adsorption sites where are negatively charged, on the other hand, the pulverized only shell particle also have the adsorption sites negatively charged, however, the number of the adsorption sites was lower than that of OS adsorbents.

The results of the FT-IR measurements shown in Fig. 3b suggest that the carboxyl groups were modified on the surface of the prepared OS adsorbent were modified by mechanochemical reactions in the ball mill grinding field. The majority of the carboxyl groups are expected to be negatively charged based on the pH of the liquid phase in these adsorption rate experiments. Therefore, it is most likely that the adsorption sites for Pb ions are a modified carboxyl group on the surface of the OS adsorbents. Since a plateau region of the amount of Pb ions adsorbed was observed in the range of 180-600 min from the results of the adsorption rate experiment (Figs. 4a-c), the Langmuir type adsorption rate equation was attempted to be applied to the experimental results. The Langmuir type adsorption rate equation is expressed by the following equation.

$$X_t = X_e [1 - \exp(-(k_a C_e + k_d)t)] \quad (3)$$

Where  $k_a$  [L/(mol min)] and  $k_d$  [ $\text{min}^{-1}$ ] represent the adsorption rate constant and the desorption rate constant of the Langmuir rate equation (Eq. (3)). By fitting of the data shown in Figs. 4a-c to Eq. (3),  $k_a$ ,  $k_d$ , and  $X_e$  were determined from a least-squares regression. In this calculation of the least-squares regression, the values of  $k_a$ ,  $k_d$ , and  $X_e$  were determined by giving the average values of the liquid phase concentrations at times 90, 180, and 600 min as the values of  $C_e$  in Eq. (3). The values are  $1.84 \times 10^{-3}$  mol/L,  $1.75 \times 10^{-3}$  mol/L, and  $1.75 \times 10^{-3}$  mol/L for OS0.5, OS1.0, and OS2.0, respectively. The values determined by the least-squares regression by using Eq. (3) are shown in the upper part of Table 1. Table 1 also shows the coefficient of determination  $R^2$ . The solid curves in Figs. 4a-c are calculated values by using Eq. (3) with the adsorption rate constants determined by the least-squares regression. It can be confirmed that the calculation values are in good agreement with the experimental values. The coefficient of determination,  $R^2$  is greater than 0.994 for OS0.5, OS1.0, and OS2.0 adsorbents, which is confirming good agreement between the experimental and calculated values. On the other hand, the results obtained using non-modified shell particles not agreed well with the Langmuir rate model. The values of adsorption rate constants,  $k_a$ , for each adsorbent were not significantly different, but the value of desorption rate constant,  $k_d$ , for OS0.5 was the largest, while those values for OS1.0 and OS2.0 were almost the same. This Tendency will be mentioned again in the explanation of the adsorption equilibrium relationship described below.

### 3.3. Adsorption equilibrium relationship between Pb ions and surface of OS adsorbents

Fig. 5 shows the adsorption isotherms obtained for each adsorbent (OS0.5, OS1.0, and OS2.0), that is, the relationship between the equilibrium concentration and the equilibrium amount of Pb ions adsorbed. The horizontal axis is the equilibrium concentration,  $C_e$  [mol/L],

and the vertical axis is the equilibrium amount of Pb ions adsorbed,  $X_e$  [mol/g]. In the equilibrium concentration range of approximately  $0.6 \times 10^{-3}$  mol/L or higher, a plateau region can be observed where the saturated adsorption amount seems to have been reached experimentally. Judging from the fact that the experimentally obtained adsorption isotherm profiles and the adsorption rate profiles were also well explained by the Langmuir-type adsorption rate equation, it is safe to assume that the adsorption equilibrium relationship is also followed by Langmuir-type isotherm. Langmuir adsorption isotherm is expressed by the following equation.

$$X_e = KX_s C_e / (1 + KC_e) \quad (4)$$

Where,  $K$  and  $X_s$  represent the equilibrium adsorption constant and the saturated amount of Pb ions adsorbed, respectively. By fitting of the data shown in Fig. 5 to Eq. (4), the adsorption parameters,  $K$  and  $X_s$  can be determined by using a least squares regression. The estimated values of the Langmuir's adsorption parameters,  $K$  and  $X_s$  are summarized in the lower part of Table 1. The coefficient of determination,  $R^2$ , was slightly lower than in the case of fitting to the velocity equation, with 0.960 being the lowest value. The solid curves in Figs. 5a-c correspond to the calculated values calculated by using the determined adsorption parameters,  $K$  and  $X_s$ . As seen in the Figs. 5a-c, the experimental and calculated values are in very good agreement for the adsorbents, OS0.5, OS1.0, and OS2.0. Table 1 showed that the saturated adsorption volume,  $X_s$ , increases with increasing molar ratio in the preparation of the adsorbent. By plotting the molar ratio on the horizontal axis and the saturated amount adsorbed,  $X_s$ , on the vertical axis, a linear relationship was obtained, and the equation of the linear relationship determined by a least square regression is as follows (graph not shown).



$$X_s = 5.14 \times 10^{-4} (\text{molar ratio}) + 5.21 \times 10^{-3} \quad (R^2 = 0.997) \quad (5)$$

The coefficient of determination is very high at 0.997, indicating that a very good linear relationship is obtained in the range where the preparation was conducted. The maximum molar ratio of 2:1 employed for the preparation in this study would have been within the range where the carboxyl group modification would not reach the saturated state. It can be seen that the saturated adsorption value estimated from the model, as well as the experimental value, shows an adsorption value of ca.  $5\text{-}6 \times 10^{-3}$  mol/g. Wang et al. (2021) reported that the amount adsorbed of  $\text{Pb}^{2+}$  was in the range of  $1.9 \times 10^{-4}$  -  $3.0 \times 10^{-4}$  mol/g in pH 5.5-6.5 using calcined mussel shell-based adsorbent [20]. Tang et al. (2022) reported that the maximum amount adsorbed of  $\text{Pb}^{2+}$  was  $8.0 \times 10^{-4}$  mol/g using Fe-Mn oxide modified biochar [38]. Ariffin et al. (2017) prepared hydroxyapatite from bulk shells for lead ion adsorption and reported that the adsorption equilibrium relationship followed the Langmuir type and the saturated adsorption capacity was 74.63 mg/g ( $3.6 \times 10^{-4}$  mol/g) [39]. Harripersadth et al. (2020) carried out the adsorption of  $\text{Pb}^{2+}$  with using eggshell and reported that the removal efficiency of Pb was constant (100% removal) in the range of pH 3-7, the equilibrium adsorption isotherm was well fitted to the Langmuir adsorption model, and the maximum adsorption density of Pb was 277 mg/g ( $1.33 \times 10^{-3}$  mol/g) [40]. Okolo et al. (2020) performed Pb ion adsorption using adsorbents prepared from Africa elemi seed (AES), mucuna shell (MS), and oyster shell (OS) and surface modified with phosphoric acid, and showed a maximum adsorption of  $4.83 \times 10^{-4}$  mol/g at 100 mg of adsorbent for all adsorbents [41]. Many previous studies have reported that the adsorption equilibrium relationship for lead ion adsorption on shell-based adsorbents can be explained by the Langmuir type. The amount adsorbed of Pb ions confirmed in this study is considerably larger than that of reported waste shell-based adsorbents and biosorbents made of other materials.

The adsorption equilibrium constant can be regarded as a value that indicates the adsorption strength between the adsorbent and the adsorption sites. The adsorption equilibrium constant is defined as the ratio of the adsorption rate constant to the desorption rate constant ( $k_a/k_d$ ) for the Langmuir adsorption equilibrium. The adsorption site of the adsorbent prepared in this study is likely to be a carboxyl group, and when the liquid phase equilibrium pH is almost the same, the state of the carboxyl group is also almost the same, and the strength of the binding force between the adsorption site (carboxyl group) and the Pb ions can be considered to be almost the same regardless of the adsorbent preparation conditions. However, the adsorption strength of the Pb ions is almost the same regardless of the adsorbent preparation conditions. However, the value of the adsorption equilibrium constant determined by fitting to equation (4) increases with increasing molar ratio in the preparation. The ratio of the adsorption rate constant to the desorption rate constant ( $k_a/k_d$ ) is shown in the adsorption rate parameter orchid. The values are almost equal to the values of the adsorption equilibrium constants determined from adsorption equilibrium experiments. The fact that the values of the adsorption equilibrium constants derived from different experiments are equal suggests that the adsorption mechanism (Langmuir-type adsorption) is not misinterpreted. However, it is very difficult to interpret the fact that the value of the adsorption equilibrium constant increases with the increase of the molar ratio during the preparation. We believe that further detailed studies are needed.

Fig. 6 shows the typical example of the comparison of FT-IR spectra of the adsorbents prepared in this study before and after adsorption of Pb ions. OS1.0 is shown as an example adsorbent. The second chart from the bottom is the FT-IR spectrum of the adsorbent after adsorption of Pb ions, and the others are shown for comparison and are the same data as the spectrum shown in Fig. 3b. Fig. 6 shows that the absorption peak at wave number  $1617\text{ cm}^{-1}$  has shifted to  $1598\text{ cm}^{-1}$ , and similarly, the absorption peak at wave number  $1317\text{ cm}^{-1}$  has

shifted to wave number  $1288\text{ cm}^{-1}$ . The shift widths of both absorption peak shifts are the same at  $29\text{ cm}^{-1}$  in wave number. This phenomenon of shifting of the IR absorption peak of the functional group considered to be the adsorption site when heavy metal ions are adsorbed on the adsorbent has often been reported. Feng et al. (2009) reported that the absorption peak indicating the OH of the adsorbent after Cu(II) adsorption shifted from wave number of  $3400\text{ cm}^{-1}$  to  $3449\text{ cm}^{-1}$  using biosorbent chemically modified with citrus peel [42]. Petrović et al. (2016) performed lead ion adsorption experiments using corn silk (*Zea mays* L.) as an adsorbent and reported that after Pb ion adsorption, the peak representing the OH group of the adsorbent shifted from  $3287\text{ cm}^{-1}$  to  $3331\text{ cm}^{-1}$  [43]. Ezeonuegbu et al. (2021) conducted Ni and Pb ion adsorption experiments using sugarcane bagasse as an adsorbent and reported a shift of all six peaks, including a shift of the absorption peak wave number indicating the carboxyl groups from  $1602\text{ cm}^{-1}$  to  $1636\text{ cm}^{-1}$  [44]. Zhang et al. (2018) conducted Cd adsorption experiments using plant (*Solidago canadensis*) stems as a biosorbent and reported a shift in the absorption peak indicating phenolic group OH [45]. In the case of this study, the absorption peaks at wave numbers of  $1617\text{ cm}^{-1}$  and  $1317\text{ cm}^{-1}$  are peaks involving carboxyl groups, and it can be assumed that Pb ions are probably adsorbed with carboxyl groups derived from sodium oxalate modified on the shell surface.

#### 4. Conclusions

The carboxyl groups on the surface of waste scallop shell particles were modified by a mechanochemical reaction using ball milling with sodium oxalate. The carboxyl group modification was confirmed by FT-IR spectra. Comparison of the FT-IR spectra of the adsorbent particles before and after adsorption confirmed that lead ions were adsorbed on the particle surface, as the absorption peak, which can be considered as originating from the carboxyl group was shifted after adsorption.

The adsorption behavior was well explained by the Langmuir-type model in terms of both adsorption rate and adsorption equilibrium relationship. As the molar ratio in the preparation increased, the saturated adsorption amount estimated by the model also increased slightly from  $5.45 \times 10^{-3}$  mol/g (OS0.5) to  $6.23 \times 10^{-3}$  mol/g (OS1.0). It was also found to be about 8.9 times larger than the equilibrium adsorption amount when unmodified shells were used. The adsorption equilibrium constant also increased with increasing molar ratio in the preparation.

Further studies are required to clarify why this trend is observed, since the adsorption strength of the adsorbate and adsorbate seat is considered to be constant once the substance is determined. Experimental investigations are also needed to determine whether similar results can be obtained with other dicarboxylates.

## **Credit authorship contribution statement**

Hideo Maruyama: Planning the experiments of this research, Conducting the experiments, Analysis of the experimental data, Writing original manuscript.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## **Data Availability**

Data will be made available on request.

## **Acknowledgments**

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## Nomenclature

$C_e$	= equilibrium concentration of Pb ions	[mol/m <sup>3</sup> ]
$C_i$	= initial concentration of of Pb ions	[mol/m <sup>3</sup> ]
$C_t$	= concentration of Pb ions at time, $t$	[mol/m <sup>3</sup> ]
$K$	= equilibrium adsorption constant defined in Eq. (4)	[m <sup>3</sup> /mol]
$k_a$	= adsorption rate constant defined in Eq. (3)	[m <sup>3</sup> /(mol min)]
$k_d$	= desorption rate constant defined in Eq. (3)	[min <sup>-1</sup> ]
$m$	= mass of adsorbent	[kg]
$t$	= time	[min]
$X_e$	= equilibrium amount adsorbed of Pb ions	[mol/kg]
$X_s$	= saturated amount adsorbed of Pb ions defined in Eq. (4)	[mol/kg]
$X_t$	= amount adsorbed of Pb ions at time, $t$	[mol/kg]
$V$	= volume of liquid	[m <sup>3</sup> ]

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## Figures and tables captions

**Fig. 1.** SEM images of the OS adsorbents; OS0.5 (a, b), OS1.0 (c, d), and OS2.0 (e, f).

**Fig. 2.** Particle size distribution of (a) OS0.5, (b) OS1.0, and (c) OS2.0 adsorbents.

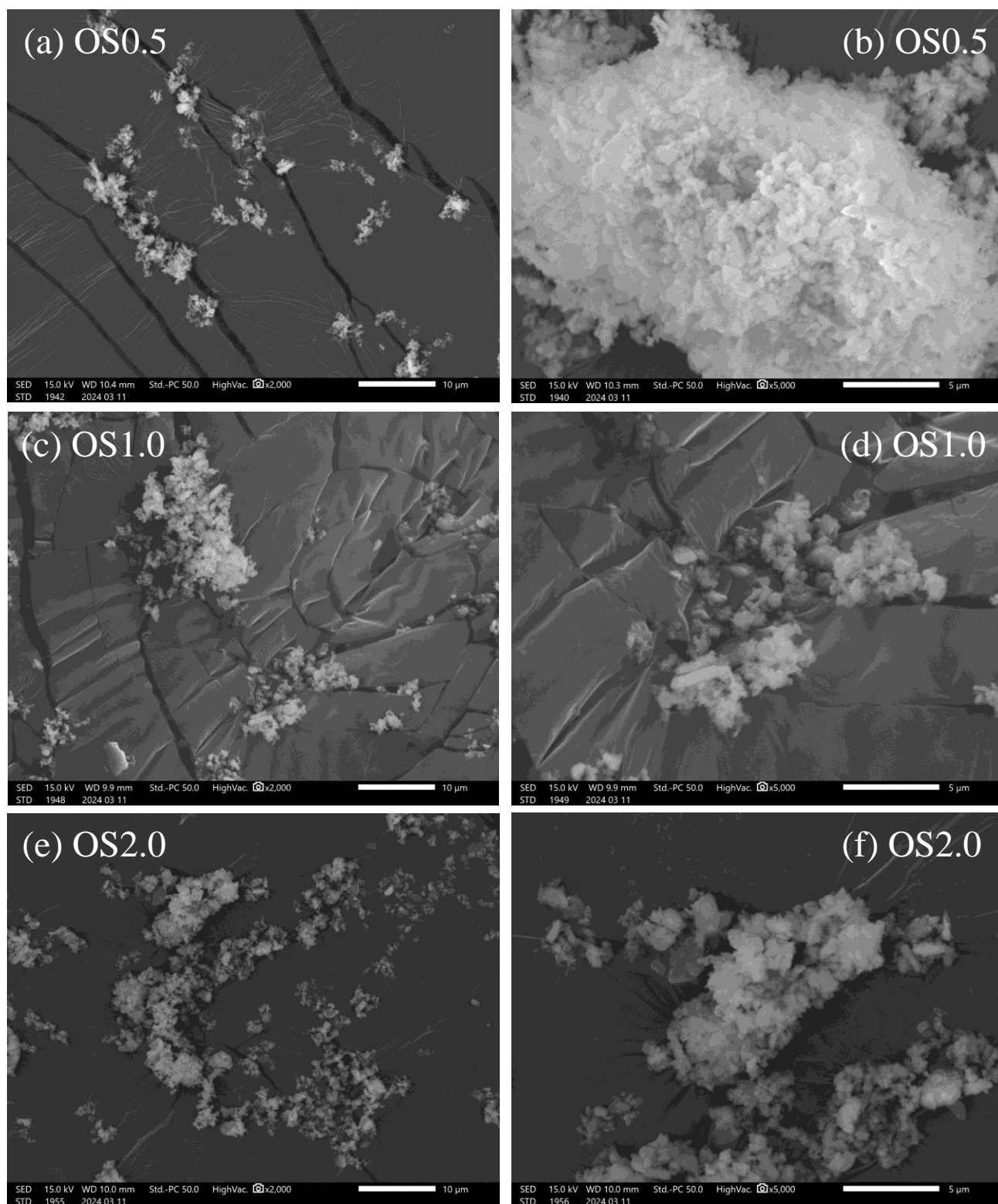
**Fig. 3.** (a) XRD pattern of OS1.0. The character, C, corresponds to characteristic peak of calcite (JCPDF: 01-078-4614, 04-008-0788) and (b) FT-IR spectra of the prepared adsorbent particles varied the molar ratio before using adsorption experiments..

**Fig. 4.** Time course of the amount adsorbed of Pb onto (a) OS0.5, (b) OS1.0, and (c) OS2.0 adsorbents. The solid curves in the figures were the calculated values using adsorption kinetic parameters determined by fitting of the data to Langmuir adsorption rate equation expressed by Eq. (3). The triangle symbol corresponds to the amount adsorbed of Pb onto a non-modified shell particles (control).

**Fig. 5.** The adsorption equilibrium relationships of (a) OS0.5, (b) OS1.0, and (c) OS2.0 adsorbents and Pb, respectively. The solid curves in the figures were the calculated values using adsorption parameters determined by fitting of the data to Langmuir adsorption isotherm expressed by Eq. (4).

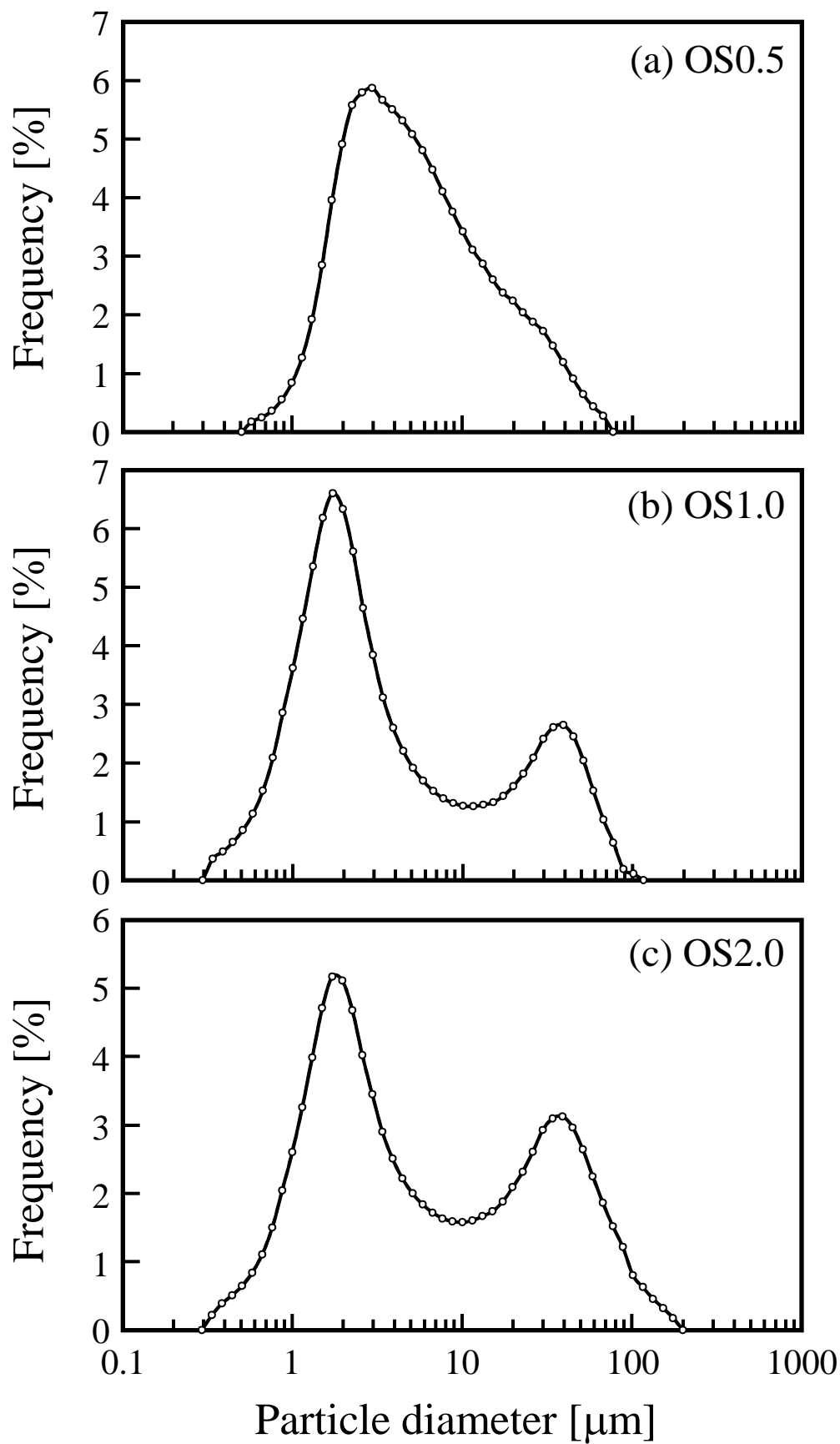
**Fig. 6.** Comparison of FT-IR spectra of before and after the adsorption of lead ions for OS1.0.

**Table 1** Adsorption parameters determined from Eqs. (3) and (4)

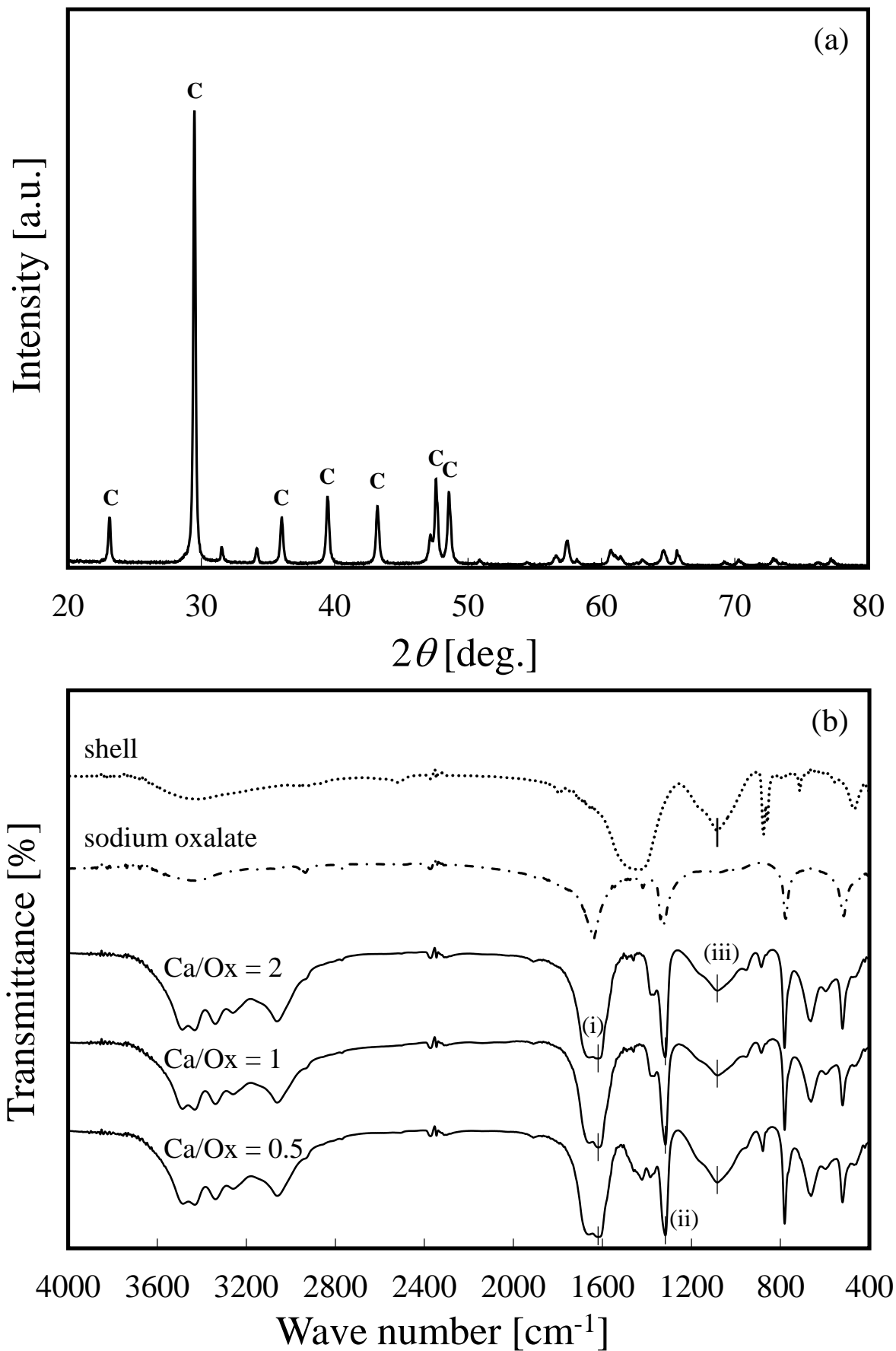


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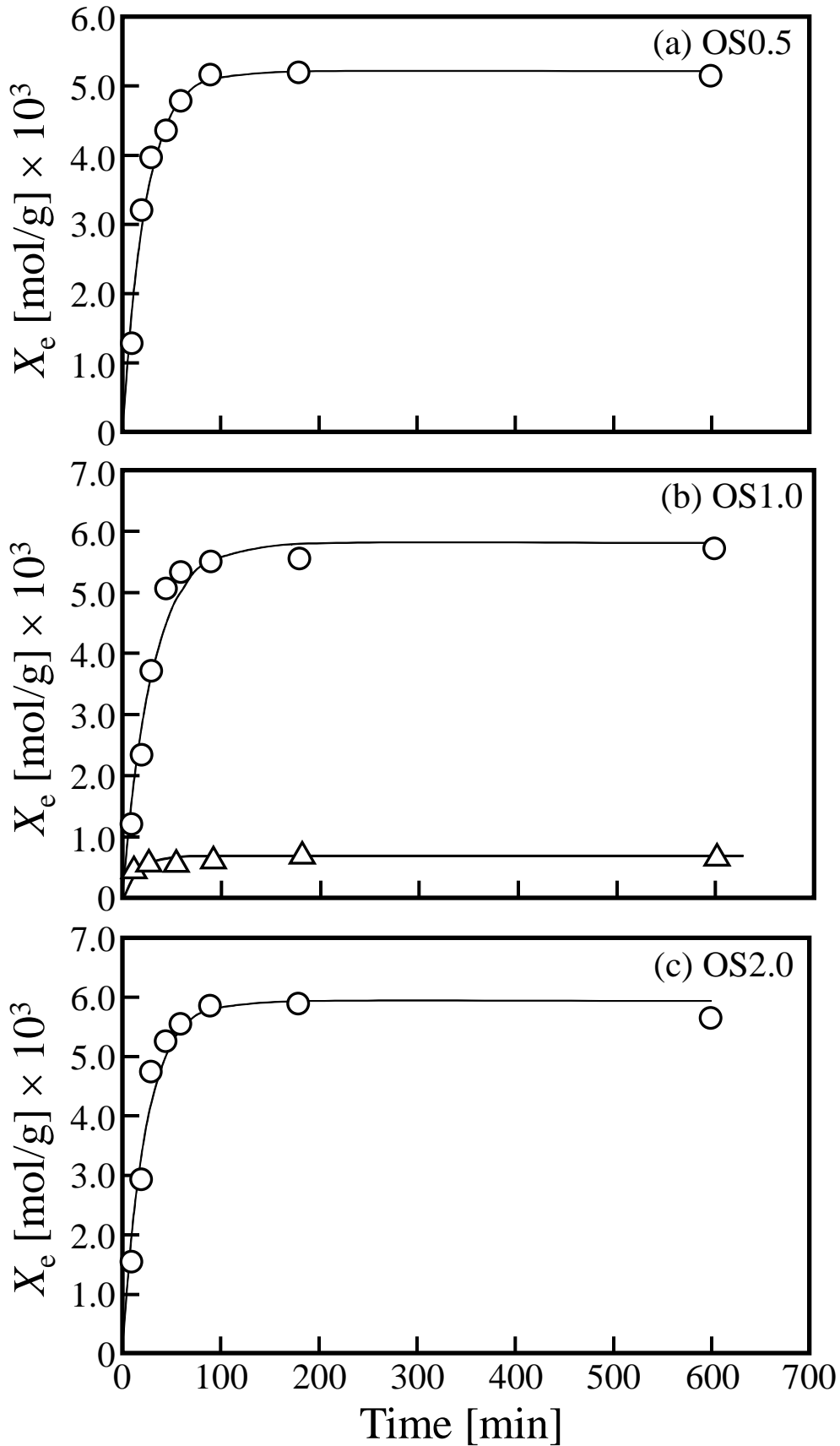




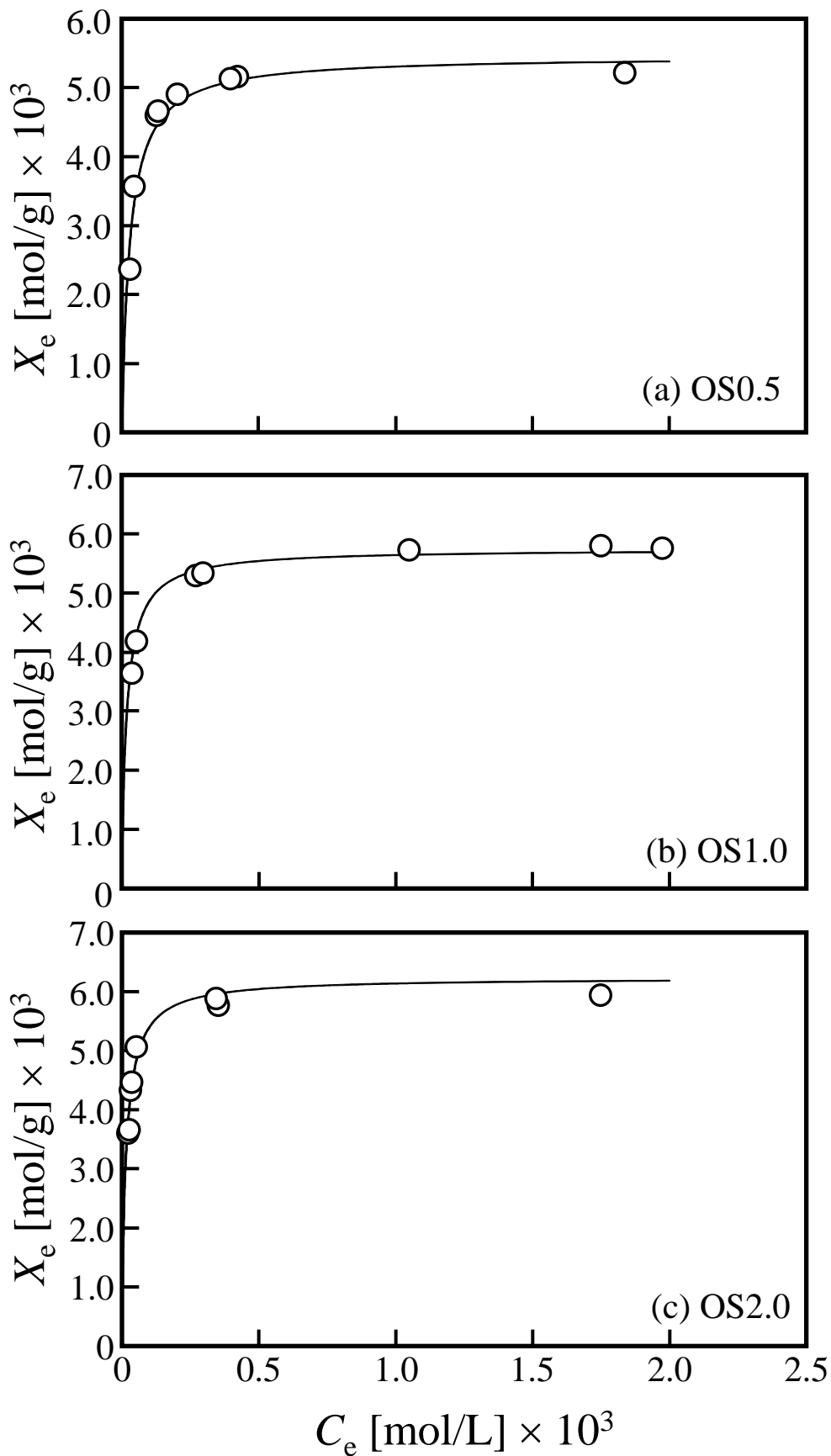
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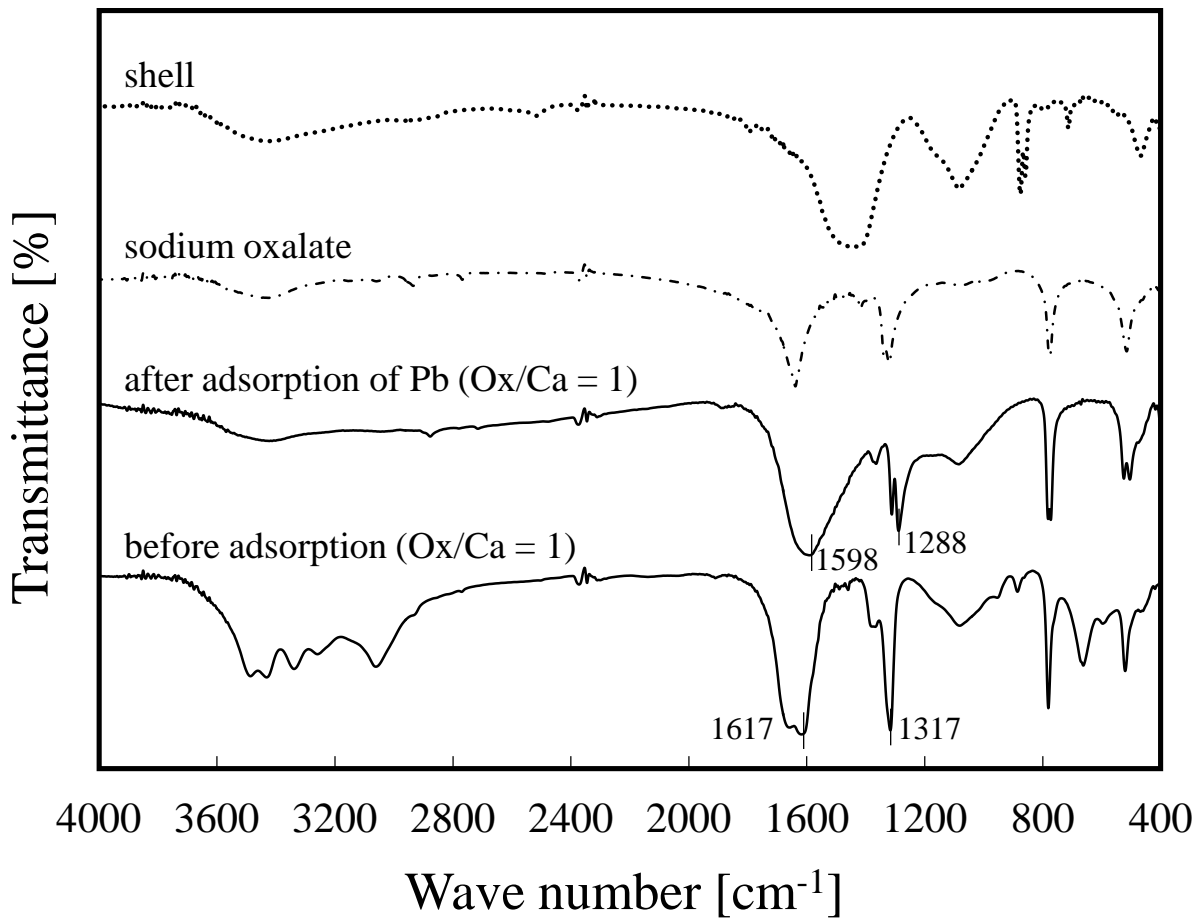
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**Fig. 6.** Comparison of FT-IR spectra of before and after the adsorption of lead ions for OS1.0.

**Table 1** Adsorption parameters determined from Eqs. (3) and (4)

Langmuir adsorption kinetics parameters					
	$k_a$ [L/(mol min)]	$k_d$ [min <sup>-1</sup> ]	$X_e$ [mol/g]	$k_a/k_d$ [L/mol]	$R^2$
OS0.5	22.48	$6.99 \times 10^{-4}$	$5.21 \times 10^{-3}$	$3.21 \times 10^4$	0.997
OS1.0	18.78	$3.50 \times 10^{-4}$	$5.80 \times 10^{-3}$	$5.36 \times 10^4$	0.994
OS2.0	23.43	$3.51 \times 10^{-4}$	$5.93 \times 10^{-3}$	$6.67 \times 10^4$	0.995
shell (control)	12.54	$8.99 \times 10^{-4}$	$6.60 \times 10^{-4}$	$1.40 \times 10^4$	0.579

Langmuir isotherm parameters			
	$K$ [L/mol]	$X_s$ [mol/g]	$R^2$
OS0.5	$3.45 \times 10^4$	$5.45 \times 10^{-3}$	0.991
OS1.0	$5.39 \times 10^4$	$5.75 \times 10^{-3}$	0.961
OS2.0	$6.29 \times 10^4$	$6.23 \times 10^{-3}$	0.960