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Removal of Zinc Ions from Aqueous Solutions by Adsorption on Virgin and Calcined Lignin

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We prepared virgin (Lig) and calcined lignin at 200–1000 °C (Lig200, Lig400, Lig600, Lig800, and Lig1000) and evaluated their adsorption capability for zinc ions from the water phase. The properties (morphology, specific surface area, pore volume, mean pore diameter, and functional groups) of adsorbents were characterized by scanning electron microscopy, specific surface area analysis, and FT-IR analysis. The specific surface area and pore volume of Lig800 was greater than those of the other adsorbents. In addition, -OH and -COOH groups were detected on Lig, Lig200, and Lig400, but those functional groups were not confirmed by calcination treatment over 600 °C. Amount of zinc ions adsorbed on Lig800 was greater than that on other adsorbents. We also evaluated the adsorption mechanism of zinc ions with adsorbents. The result showed that the amount of zinc ions adsorbed was related to ion-exchange with proton (correlation coefficient: 0.817) or physical property (mesopore volume; correlation coefficient: 0.867) for Lig, Lig200, and Lig400 or Lig600, Lig800, and Lig1000, respectively. These results indicate that the adsorption mechanism is changed with calcination treatment. Moreover, we elucidated the effect of temperature on the adsorption of zinc ions, and evaluated the adsorbent surface before and after zinc ion adsorption. We confirmed the zinc existed on the adsorbent surface after adsorption. Finally, as per the thermodynamic parameters, the negative value of ΔG indicates the spontaneous nature and feasibility of the zinc ion adsorption. These findings provide significant information that can be useful for removal of zinc ions from aqueous solution.

Key words lignin, calcination, zinc ion, adsorption

INTRODUCTION

The presence of heavy metals in the water environment has been of great concern to researchers because of their increased discharge, toxic nature, and other adverse effects on receiving water media.[1)] Zinc is one of the most important heavy metals, and it is released into the water environment from various natural sources. Zinc ions are not biodegradable and can get accumulated easily in living tissues.[2)] High zinc concentrations can cause health problems such as lethargy, anemia, growth retardation, stomach cramps, vomiting, skin irritations, nausea, etc.[2-4)] Therefore, various removal technologies have been employed for the purification of wastewaters contaminated with zinc ions in the water phase.

In developing countries, removal of heavy metals from wastewater is normally achieved using advanced technologies such as advanced oxidation processes, biological methods, ultrafiltration, extraction, ion exchange, electrochemical methods, and adsorption.[1,5)] However, these technologies do not seem to be economically feasible because of their relatively high cost, and developing countries may not be able to afford such technologies.[1)] Therefore, there is a growing requirement for cost-effective, efficient, and novel technologies for the treatment of wastewaters including heavy metals before their discharge into receiving water bodies. Recently, biosorption has shown considerable potential for metal removal from aqueous media. In this approach, natural raw materials or wastes from industrial and agricultural activities are used to remove metals from aqueous solutions.[5,6)]

Lignin is a natural polymer that is present in large quantities in the cell walls of plants and serves as the main binding agent for fibrous plant components.[7)] In addition, lignin is a natural amorphous cross-linked resin with an aromatic three-dimensional polymer structure containing a number of functional groups.[7)] Interest in the possible uses of lignin is currently growing, chiefly due to the availability and low cost of these biopolymers, as well as the fact that they are structurally interesting renewable materials.[7-10)] Previous studies have discussed the mechanisms of heavy metal (including zinc ions) removal from aqueous solutions using lignin. The results suggested that no single mechanism could explain the process of metal adsorption by lignin. Several adsorption mechanisms were reported, and further studies are required to confirm the adsorption mechanism.[5,7,11)] Biomass is often pyrolyzed or carbonized to remove volatile organic constituents, leaving behind a highly porous carbonaceous residue. Biomass pyrolysis induces changes in physicochemical properties. In general, calcination treatment increases the specific surface area, pore volume, and mean pore diameter of biomass. These reports indicate that the carbonaceous materials obtained by calcina-

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tion treatment can be used as an adsorbent for purification of wastewater.[12] Therefore, calcination is one of the most useful treatments for producing adsorbents with high adsorption capacity. However, no study reported on the calcination treatment of lignin. Thus, if zinc ion adsorption using calcined lignin could be developed, the value and applicability of these materials would increase drastically and help elucidate the relevant adsorption mechanism. Therefore, in this study, we prepared virgin and calcined lignin, and used these materials as adsorbents for zinc ions in the water phase. The properties of the adsorbents, adsorption isotherms, and effect of temperature were investigated. Moreover, the adsorption mechanism of zinc ions was evaluated. The results provide new insights into the development of high-potential adsorbents for removal of zinc ions from aqueous solutions.

MATERIALS AND METHODS

Materials Lignin was purchased from Tokyo Chemical Industries, Ltd. (Japan). Calcined lignin samples were prepared by treating lignin in a muffle furnace at temperatures of 200, 400, 600, 800, and 1000 °C for 2 h (the calcined samples are denoted as Lig200, Lig400, Lig600, Lig800, and Lig1000). Standard zinc ion solution was prepared using zinc chloride obtained from Wako Pure Chemical Industries, Ltd., Japan. The characteristics of adsorbents were measured by the following methods. Electron microscope images were analyzed by scanning electron microscopy (SEM, SU-1510, JEOL, Japan). The specific surface area and pore volume were measured by a NOVA4200*e* specific surface analyzer (Yuasa Ionics, Japan), and the functional groups on the adsorbents were measured by FT-IR–460Plus (JASCO, Japan). Elemental analysis was carried out using an electron microanalyzer (EPMA, JXA-8530F, JEOL, Japan) at an accelerating voltage of 15.0 kV and a beam diameter of 5 µm.

Amount of Zinc Ions Adsorbed The adsorbent (0.05 g) was added to zinc ion solution at 100 mg/L (50 mL). The suspension was shaken at 100 rpm for 2 h at 25 °C. The sample solution was filtered through a 0.45 µm membrane filter, and the filtrate concentration was measured by an inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo Fisher Scientific, USA). The amount of zinc ions adsorbed was calculated using Eq. (1).

$$q = (C_0 - C_e)V/W \qquad (1)$$

where q is the amount of zinc ions adsorbed (mg/g), C_0 is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the solvent volume (L), and W is the weight of the adsorbent (g).

Adsorption Isotherms The adsorbent (0.05 g) was added to a zinc ion solution at 5–100 mg/L (50 mL). The suspension was shaken at 100 rpm for 2 h at 10, 25, and 50 °C. The sample solution was filtered through a 0.45 µm membrane filter, and the filtrate concentration was measured by ICP-OES. The amount of zinc ion adsorbed was calculated using Eq. (1).

RESULTS AND DISCUSSION

Properties of Adsorbent Figure 1 shows the SEM images of virgin and calcined Ligs. We could confirm the surface roughness of the adsorbents. However, we could not observe the adsorbent configuration changes owing to calcination treatment in this study. The characteristics of the adsorbents are shown in Table 1. Specific surface area increased in the order Lig (0 m²/g) < Lig200 (0.2 m²/g) < Lig400 (11.7 m²/g) < Lig1000 (82.7 m²/g) < Lig600 (176.5 m²/g) < Lig800 (306.3 m²/g). In addition, the mesopores (20 < d < 500 Å) in Lig800 were developed compared to the other adsorbents. Previous studies reported that the specific surface area of lignin and virgin or modified paper and pulp sludge ranges from

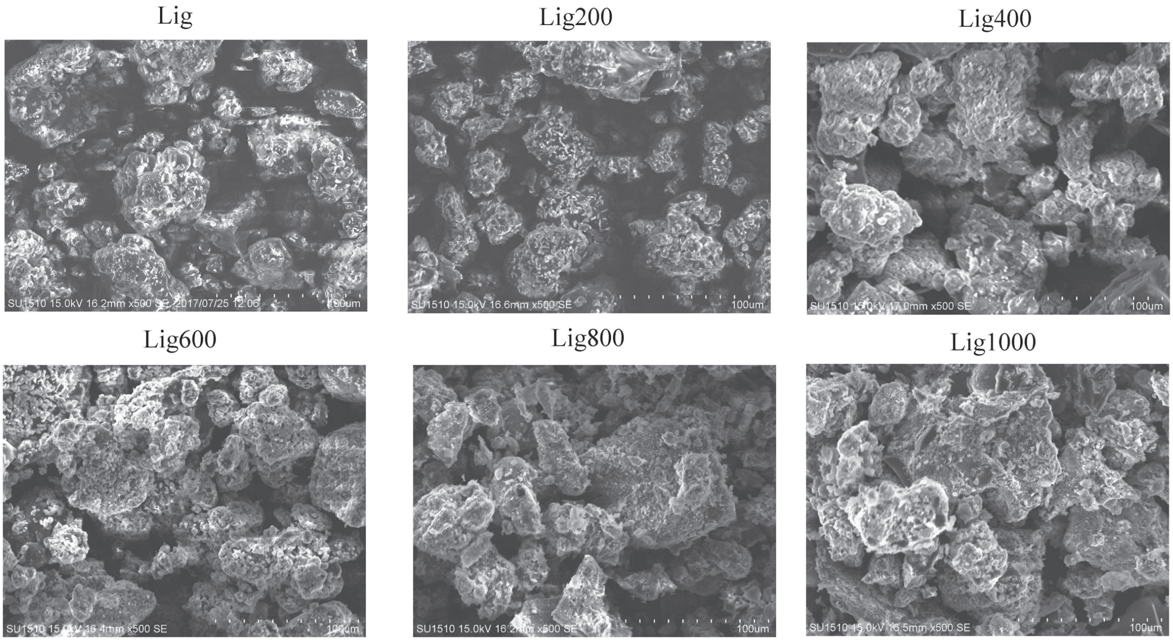

Fig. 1. SEM Images of Ligs

Lig200, Lig400, Lig600, Lig800, and Lig1000 were prepared by calcination at 200, 400, 600, 800, and 1000 °C, respectively. SEM images were analyzed by scanning electron microscopy SU-1510.

Table 1. Properties of Ligs

Adsorbents	Specific surface area (m^2/g)	Pore volume (μL/g)		
		$d \leq 20$Å	$20 < d \leq 500$Å	Total
Lig	0.0	0.0	0.8	1.8
Lig200	0.2	0.0	0.2	0.2
Lig400	11.7	0.2	2.6	2.8
Lig600	176.5	1.1	9.1	10.3
Lig800	306.3	1.4	21.1	22.5
Lig1000	82.7	0.3	10.8	11.1

Physical properties, the specific surface area and pore volume, were obtained by first determining the adsorption isotherms at liquid nitrogen temperature (-195.8 °C) with high-purity nitrogen gas (99.999%) as the adsorption gas on a NOVA4200*e* specific surface analyzer. Next, curve fitting to the nitrogen adsorption isotherm at a relative pressure of 0.05–0.30 was carried out using the Brunauer-Emmett-Teller (BET) equation.

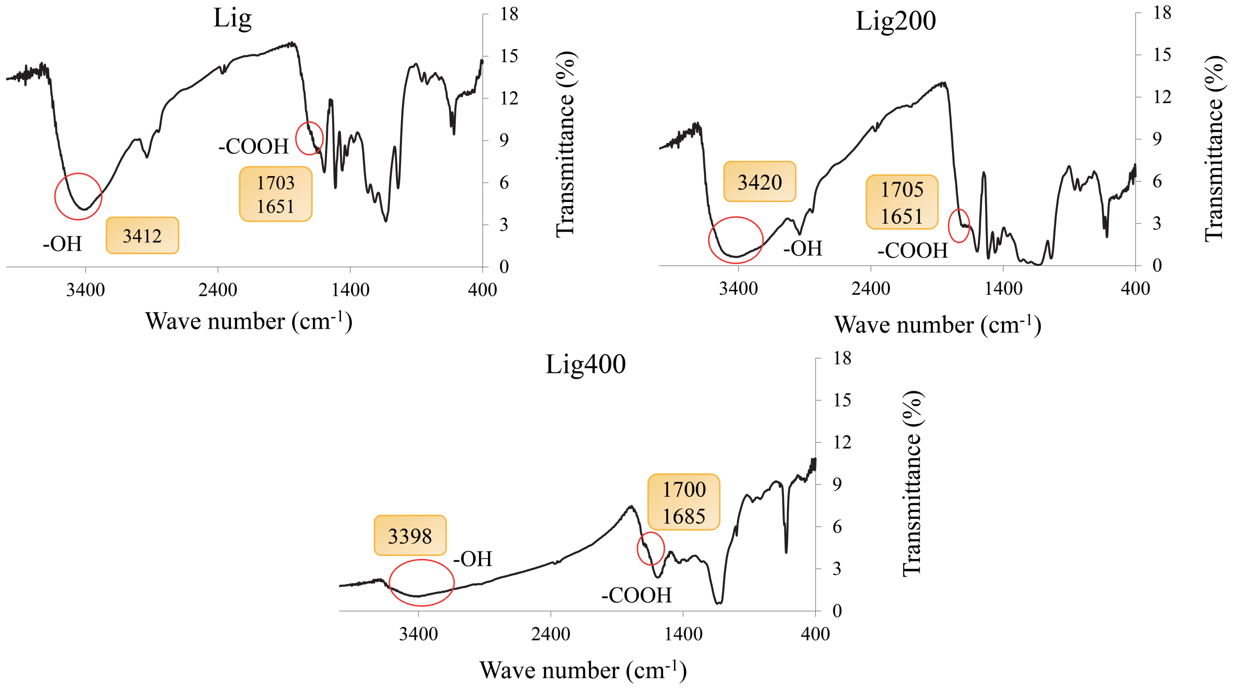

Fig. 2. FT-IR of Ligs

The functional groups (hydroxyl groups and carboxyl groups) on the adsorbents were measured by FT-IR–460Plus. The bands of 3398, 3412, and 3420 cm^{-1} show hydroxyl groups and those of 1651, 1685, 1700, 1703, and 1705 show carbonyl groups.

1.0–21.7 m^2/g.[3,7] The FT-IR spectra of the adsorbents are shown in Fig. 2. For Lig, the broad band at 3412 cm^{-1} was dominated by the stretching vibrations of aromatic and aliphatic O–H groups. The peaks at 2938 and 2849 cm^{-1} predominantly arose from C–H stretching in the methyl and methylene groups of side chains and aromatic methoxyl groups. Moreover, two shoulders, at about 1703 and 1651 cm^{-1}, originated from conjugated carboxyl and carbonyl stretching. Three strong peaks at 1597, 1513, and 1425 cm^{-1} could be assigned to typical aromatic skeletal vibrations. The peak at 1459 cm^{-1} suggests aromatic methyl group vibrations. Similar trends were observed in a previous study.[7] Regarding Lig200 and Lig400, the signal associated with the aromatic and aliphatic O–H and carboxyl groups showed low intensity, indicating that these units were lower compared to Lig.[13-15] In addition, the broad bands were not shown for Lig600, Lig800, and Lig1000 (data not shown). These results suggest that the carbonaceous material was produced from Lig by calcination treatment. Therefore, the specific surface areas of Lig600, Lig800, and Lig1000 were greater than those of Lig, Lig200, and Lig400.

Adsorption Capability of Zinc Ions onto Lig The amounts of zinc ions adsorbed on the adsorbents are shown in Fig. 3. The amount adsorbed on Lig800 was greater than that on other adsorbents. The results of the above section show that Lig, Lig200, and Lig400 have abundant aromatic hydroxyl (-OH) and carboxyl (-COOH) groups. On the other hand, Lig600, Lig800, and Lig1000 are characterized by high surface area. Therefore, the adsorption mechanisms of zinc ions are different. Firstly, the amount of zinc ions adsorbed is related to the aromatic OH and carboxyl groups in Lig, Lig200, and Lig400. We evaluated the relationship between the amount adsorbed and the proton (H$^+$) concentration after adsorption. The result indicated good linearity (correlation coefficient: 0.817) for this experimental condition (Fig. 4). These findings indicate that the suggested mechanism is based on ion-exchange with positive zinc ions for the phenolic, -COOH, and -OH functional groups.[5]

Next, the relationship between the amounts adsorbed using Lig400, Lig600, Lig800, and Lig1000 and mesopore volumes was investigated. We confirmed a good correlation coefficient (0.867), which suggests that the amounts adsorbed were related to the physical characteristics (Fig. 4). Previous studies have reported that activated carbon shows adsorption capability of zinc ions from aqueous solution, and specific surface area is an important factor for adsorption or removal of zinc ions.[16] Similar trends were observed in this study. From the abovementioned, we elucidated that the adsorption mechanism of zinc ions by lignin changed after calcination treatment. We selected Lig and Lig800 as adsorbents in the following experiments.

Comparison of Adsorption Capacities The reported adsorption capabilities of various types of adsorbents are shown in Table 2.[5,7,17-24] The amount of zinc ion adsorbed on Lig800 was greater than those of most other adsorbents. Particularly, among the lignins, Lig800 shows considerable potential for the adsorption of zinc ions in aqueous solutions.

Adsorption Isotherms of Zinc Ions on Lig and Lig800 Figure 5 shows the adsorption isotherms of zinc ions on Lig and Lig800. The amounts adsorbed using Lig decreased with increasing temperatures (10 °C–25 °C). On the other hand, the opposite trend was observed using Lig800. These trends depend upon the different adsorption mechanisms of Lig or Lig800 (as mentioned in Adsorption Capability of Zinc Ions onto Lig). However, the detailed adsorption mechanism of zinc ions could not be elucidated in this study. Therefore, we need to evaluate the adsorption process of zinc ions using lignin.

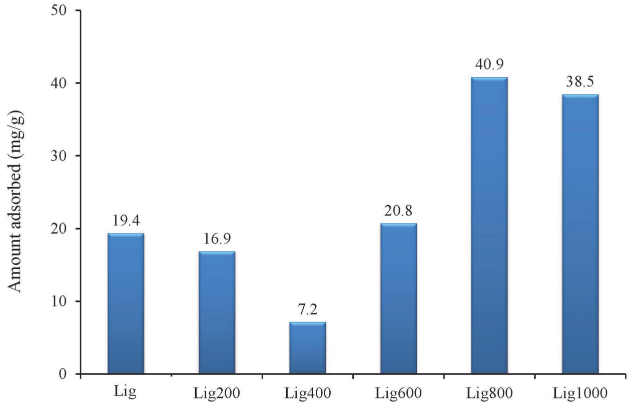

Fig. 3. Amount of Zinc Ion Adsorbed onto Ligs

Amount of zinc ion adsorbed was calculated using the concentration of zinc ion before and after adsorption. The concentration was measured by ICP-OES. Initial concentration: 100 mg/L, Solvent volume: 50 mL, Adsorbent: 0.05 g, Temperature: 25 °C, Stirring: 100 rpm, pH in solution: 6.0~6.1

The Langmuir and Freundlich equations were used to evaluate the adsorption isotherm. The Langmuir equation is defined as

$$C_e/q_e = 1/aW_s + C_e/W_s \quad (2)$$

where q_e is the adsorption capacity at equilibrium (mg/g), C_e is the equilibrium concentration of zinc ions (mg/L), and W_s and a are the maximum adsorption capacity (mg/g) and the equilibrium adsorption constant (L/mg), respectively.

The Freundlich equation is defined as

$$\log q_e = \log K + 1/n \log C_e \quad (3)$$

where K is a constant indicative of the relative adsorption capacity of the adsorbent, and n is a constant indicative of the intensity of the adsorption and varies with surface heterogeneity.[17]

The Langmuir and Freundlich constants for adsorption of zinc ions onto adsorbents are shown in Table 3. The Langmuir adsorption isotherm model (the correlation coefficients of Lig and Lig800 are 0.810–0.990 and 0.997–1.000, respectively) provides a better fit to the experimental data than the Freundlich adsorption isotherm model (correlation coefficients of Lig and Lig800 are 0.758–0.859 and 0.549–0.677, respectively). The Langmuir-type isotherm hints toward surface homogeneity. Therefore, the adsorption process is strongly related to the adsorbent surface. The Langmuir constant W_s tends to decrease for Lig or increase for Lig800 with increasing temperatures. These results are in agreement with the adsorption isotherm data.[25] When the value of $1/n$ ranges from 0.1–0.5, the adsorbate is easily adsorbed. However, if $1/n > 2$, adsorp-

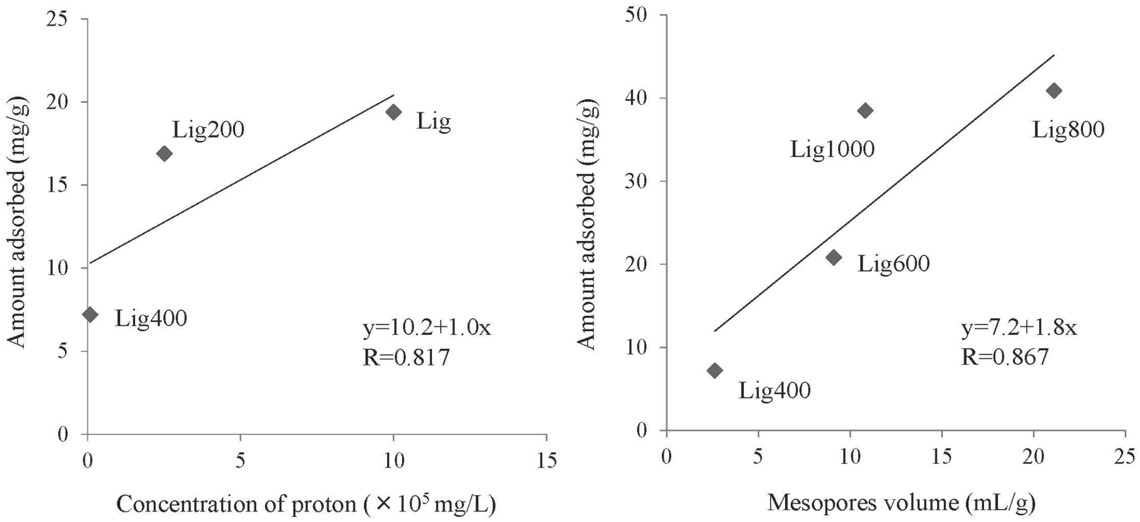

Fig. 4. Relationship between the Amount Adsorbed and Concentration of Proton or the Mesopores Volume

Amount adsorbed and mesopores volumes were obtained from Fig. 3 and Table 1, respectively and the concentration of proton was calculated using the pH data before and after adsorption.

Table 2. Comparison of the Zinc Ion Adsorption Capacities of the Various Adsorbent

Samples	Adsorption capability (mg/g)	References
Lignin	11.18	1
Modified lignin	73.2	13
Amino-functionalized $Fe_3O_4@SiO_2$ magnetic nano-adsorbent	169.5	8
Activated carbon from bagasse	31.11	7
Cashew nut shell	24.98	9
Lignocellulosic substrate	16.02	10
Bagasse fly ash	7.03	11
Cork biomass	6.80	12
Chitin/lignin adsorbent	82.41	6
Kraf lignin	1.77	14
Lig	18.8	This study
Lig800	37.3	This study

Table 3. Langmuir and Freundlich Constants for Adsorption of Zinc Ion onto Ligs

Sample		Langmuir constants			Freundlich constants		
		Ws (mg/g)	*a* (L/mg)	*r*	log*K*	1/*n*	*r*
Lig	10°C	30.3	0.04	0.810	0.1	0.7	0.859
	25°C	18.8	1.2	0.990	1.0	0.2	0.834
	50°C	10.9	0.7	0.990	0.6	0.3	0.758
Lig800	10°C	35.7	5.4	1.000	1.3	0.2	0.677
	25°C	40.8	9.1	1.000	1.4	0.2	0.549
	50°C	56.8	1.1	0.997	1.4	0.3	0.607

The values of W_s and a were obtained from the Langmuir equation, and those of log K and $1/n$ were obtained from the Freundlich equation. The W_s and a are the maximum adsorption capacity (mg/g) and the equilibrium adsorption constant (L/mg), respectively. In addition, K is a constant indicative of the relative adsorption capacity of the adsorbent, and n is a constant indicative of the intensity of the adsorption and varies with surface heterogeneity.

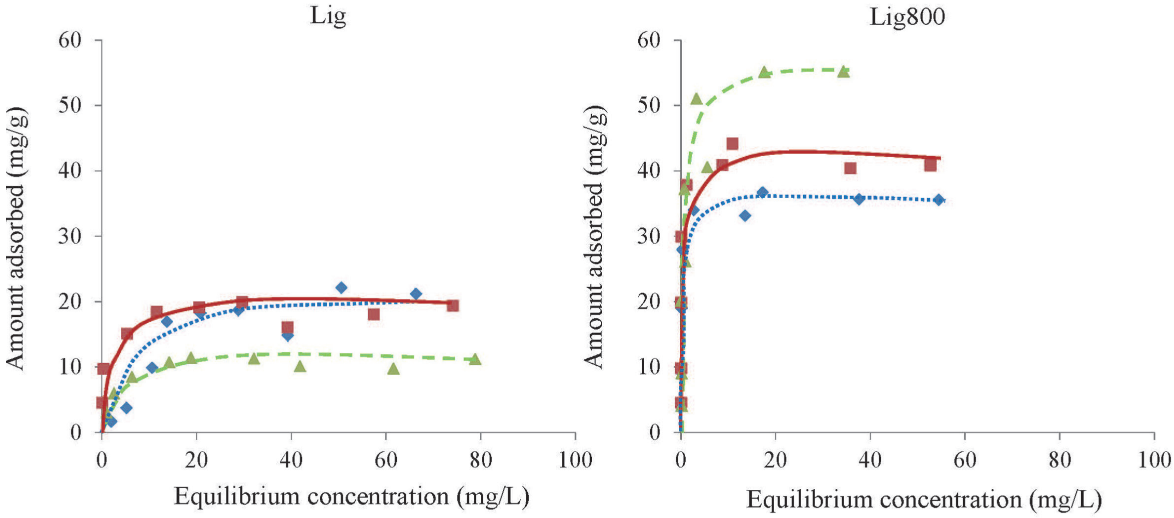

Fig. 5. Adsorption Isotherms of Zinc Ion onto Ligs at Different Temperatures

Adsorption isotherm data was calculated using the concentration of zinc ion before and after adsorption. The concentration was measured by ICP-OES. Initial concentration: 5~100 mg/L, Solvent volume: 50 mL, Adsorbent: 0.05 g, Temperature: 25 °C, Stirring: 100 rpm, pH in solution: 5.8~6.4. ♦10 °C, ■ 25 °C,▲: 50 °C

tion may not be as efficient.[26,27] Our results (1/*n*: 0.2–0.7) indicated that zinc ions are easily adsorbed on Lig and Lig800.

As mentioned above, the adsorbent surface is a very important factor in the adsorption of zinc ions from aqueous solutions. Therefore, we evaluated the adsorption surface after the adsorption of zinc ions (Fig. 6; the warm and cold colors show high and low concentrations, respectively. The sample was crushed to pieces). We could confirm that zinc ions existed on the adsorbent surface after adsorption.

Thermodynamic Parameters Thermodynamic parameters for the adsorption of zinc ions on the lignin sorbent at different temperatures were calculated using the following equations:

$$\Delta G = -RT \ln K \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

$$\ln K = \Delta S/R - \Delta H/RT \quad (6)$$

where R (8.134 J/mol K) is the gas constant, T (K) is the absolute temperature, and K is the standard thermodynamic equilibrium constant defined as q_e/C_e. In the plot of ln K versus $1/T$, ΔH and ΔS can be estimated from the slopes and intercept, respectively. Using the K values determined from the adsorption isotherms, the corresponding adsorption values of ΔG can

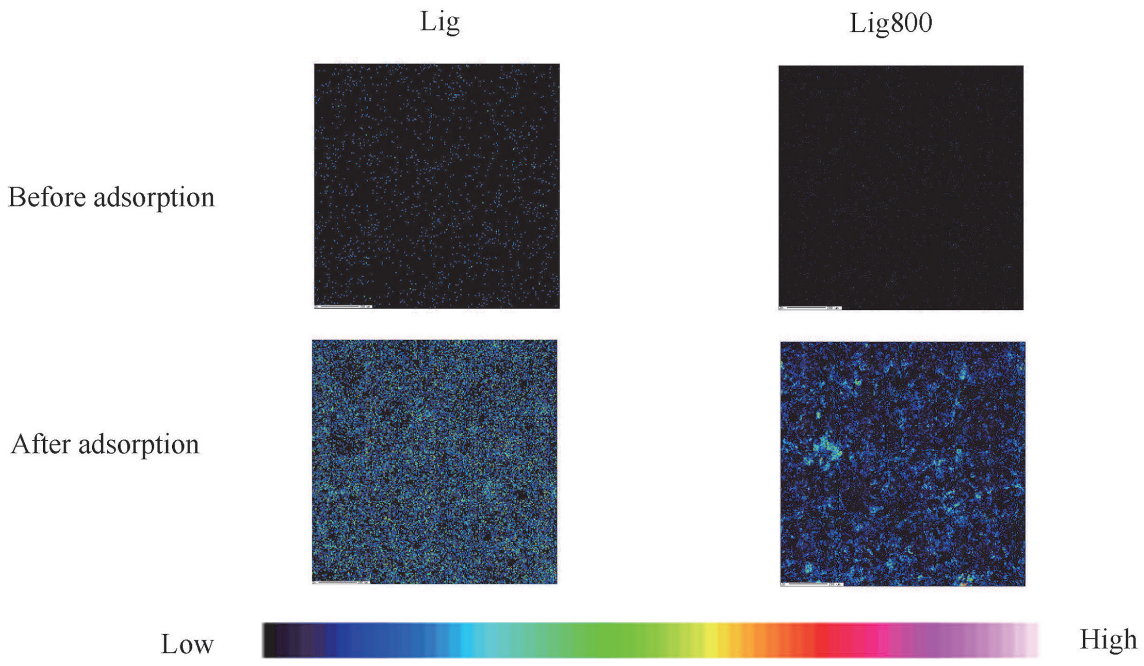

Fig. 6. Qualitative Analysis of Ligs Surface Before and After Adsorption of Zinc

Lig and Lig800 before and after adsorption of zinc ion were prepared and the elemental distribution on adsorbent was carried out using an electron microanalyzer JXA-8530F at an accelerating voltage of 15.0 kV and a beam diameter of 5 µm. Initial concentration: 50 mg/L, Solvent volume: 100 mL, Adsorbent: 0.1 g, Temperature: room temperature, Stirring: 250 rpm

Table 4. Thermodynamic Parameters for Adsorption of Zinc Ion on Adsorbent

Sample	*ΔH* (kJ/mol)	*ΔS* (J/(mol K))	*ΔG* (kJ/mol) at temperature		
			283K	298K	323K
Lig	-52.9	-190.8	1.0	-4.1	-2.2
Lig800	3.3	-27.5	-4.5	-5.0	-4.4

Thermodynamic parameters for the adsorption of zinc ions were obtained by Gibbs free energy (*ΔG*, kJ/mol), enthalpy (*ΔH*, kJ/mol), and entropy changes (*ΔS*, J/(mol K)).

be determined at different experimental temperatures.[5]

Table 4 shows thermodynamic parameters for adsorption of zinc ions on the adsorbent. The negative value of *ΔG* (except for Lig at 283 K) indicates the spontaneous nature and feasibility of the zinc ion adsorption.[12] The changes in *ΔS* describe the randomness in the interactions between the adsorbent and adsorbate. The negative value of *ΔS* indicates that the randomness of the adsorption systems decreases at the solid–solution interface.[28] The value of *ΔH* for the adsorption process is negative, which indicates that the process is exothermic in nature.[29] Generally, the magnitude of *ΔH* for absolute physical adsorption is less than 20 kJ/mol, whereas for chemisorption, *ΔH* = 80–200 kJ/mol.[30] In this study, the enthalpies implied by the temperature dependence ranged from -52.9–3.3 kJ/mol, suggesting that the adsorption of zinc ions onto Lig and Lig800 should be characterized as partly physical and chemical adsorption, but dominated by the former, because the enthalpy change is less the 20 kJ/mol.[31]

Lignin (Lig) and calcined lignin at 200–1000 °C (Lig200, Lig400, Lig600, Lig800, and Lig1000) were prepared and their characteristics were investigated. The SEM image of Lig did not change with calcination treatment. Specific surface area and pore volume of Lig increased with calcination treatment, and those of Lig800 was the highest compared to other adsorbents. Lig, Lig200, and Lig400 have functional groups such as -OH and -COOH groups. However, these functional groups were lost after calcination treatment over 600 °C. These results suggest that calcination treatment affected the characteristics of lignin. Next, the adsorption capability of zinc ion was evaluated, and the amount adsorbed on Lig800 was the highest compared to other adsorbents. The amount adsorbed was related to ion-exchange with protons released from functional groups or mesopore volume for Lig calcined under the 400 °C or over the 600 °C, respectively, which suggests that adsorption mechanism was changed by calcination treatment. The amounts of zinc ions adsorbed using Lig or Lig800 decreased or increased with increasing temperatures. In addition, adsorption isotherms were better fitted to the Langmuir equation (correlation coefficient: 0.810–1.000) compared to the Freundlich equation (correlation coefficient: 0.549–0.859). Finally, the decrease in *ΔG* with temperature revealed that zinc ion adsorption onto lignin became more favorable at higher temperatures. Taken together, the results obtained in this study illustrate that calcined lignin has potential for zinc ion removal from aqueous solutions.

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Conflict of interest The authors declare no conflict of interest.

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