Lead (II) Adsorption on Chemically Modified Activated Carbon in Aqueous Solution

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In the present study, we developed modified activated carbon (KL) for the adsorption of Pb (II). Chemically modified activated carbons (KL-A and KL-B) were prepared by nitric acid and ethylenediamine treatments, respectively. The properties (specific surface area, pore volume, mean pore diameter, acidic or basic functional groups, and pH) of KL, KL-A, and KL-B were investigated by various methods. Contact time, adsorption isotherms, and recovery of Pb (II) were evaluated. Equilibrium adsorption on KL and KL-B or KL-A was reached in about 12 h and 5 h, respectively. The experimental data was fitted to pseudo-second order model and compared with the pseudo-first order model. The optimal pH conditions for the adsorption of Pb (II) was pH = 5.1-5.5. These data were fitted to Freundlich and Langmuir models. Moreover, the adsorption mechanism of Pb (II) on KL-A was related to the ion exchange with acidic functional groups. It would be possible to recover Pb (II) by using nitric acid. The results suggest that KL-A would be useful in the adsorption of Pb (II). [DOI: 10.1380/ejsnt.2013.93]

Keywords: Lead; Adsorption; Activated carbon; Chemical modification

I. INTRODUCTION

Heavy metals are discharged from various industries, such as electroplating, metal finishing, textile, storage batteries, mining, ceramic, and glass industries [1]. Lead poisoning or exposure can cause hypertension, nephritis, abdominal pain, constipation, cramps, nausea, vomiting, behavioral changes, learning disabilities, reading problems, development defects, and language difficulties [2, 3]. The maximum permissible limit assigned by World Health Organization (WHO) for Pb (II) in drinking water is 0.05 mg/L [4]. A number of techniques have been developed for removing lead pollutants from aqueous effluents to minimize their impact. Although traditional treatment methods, such as precipitation, oxidation, reduction, electrochemical treatment, reverse osmosis, solvent extraction, adsorption, ion exchange, and evaporation, can be used for metal-containing effluents, most of these methods are expensive and difficult to apply [5, 6]. Among these methods, adsorption is an attractive process, in view of its efficiency and ease of use [7].

Activated carbons are the major adsorbents used in water treatment plants because the large specific surface area of activated carbon provides adsorption sites for contaminating organic compounds, especially for aromatics, such as phenol and nitrobenzene [8–11]. In contrast, heavy metal adsorption on activated carbon has been considered to take place mainly at acidic functional groups, such as carboxylic and lactonic groups [12, 13]. It is well known that the surface properties and physical and chemical properties of activated carbons have significant effect on the adsorption performance. Zhenhua *et al.* reported the metal ion adsorption capacity of activated carbon modified with ethylenediamine [14]; however, the properties of the modified activated carbon were not investigated in detail. Moreover, the concentration of metal ions in the adsorption experiments was very low, and the relationship between the adsorbed amount and the properties of activated carbon was not discussed. The object of this study is therefore to reveal the properties of activated carbon

FIG. 1: Schematic illustration of activated carbon functionalization.

treated with nitric acid or ethylenediamine, and then elucidate the adsorption mechanism of Pb (II) on chemically modified activated carbon.

II. EXPERIMENTAL METHODS

A. Materials

Activated carbon (KL, Shirasagi series) was purchased from Japan EnviroChemicals, Ltd. KL was washed with distilled water, and subsequently filtered using a 0.45- μ m membrane filter. Filtered KL was used for the experiments. A standard solution of Pb (II) and all other reagents were purchased from Wako Pure Chemical Industries, Ltd. KL was first purified by treating with 10% (v/v) hydrochloric acid solution for 24 h to remove metal ions and other impurities. Then, 10 g of KL was suspended in 300 mL of 32.5% (v/v) nitric acid solution under stirring and heated for 5 h at 60°C. The mixture was filtered, and the residue was washed with deionized water until the washings were neutral, and dried at 70°C for 24 h. The product was a carboxylic acid derivative of activated carbon (KL-A).

For the synthesis of ethylenediamine-modified activated carbon (KL-B), 10 g of KL-A was suspended in 150 mL of ethylenediamine. Then, 10 g of *N,N'*-dicyclohexylcarbodiimide (DCC) was added into the suspension and refluxed at 120°C for 48 h [14]. The product (KL-B) was filtered off, washed with ethanol, and dried at 70°C for 24 h. The synthetic routes for KL-A and KL-B

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FIG. 2: SEM images of KL, KL-A, and KL-B.

are illustrated in Fig. 1.

B. Methods

Scanning electron microscopy (SEM) was carried out using a JSM-5500LV system (JEOL, Japan). The specific surface area, mean pore diameter, and pore volume of KLs were measured using a NOVA4200e surface area analyzer (Yuasa Ionic, Japan). The number of surface functional groups was measured by a titration method [15]. The pH of the solution after the addition of KLs was measured by an activated carbon test method (JIS K1474).

C. Effect of contact time on the adsorption of Pb (II)

Adsorbent (0.015 g) was added to 50 mL of 10 mg/L Pb (II) solution. The suspensions were shaken at 25°C for 0.05-18 h at 100 rpm, and then filtered using a 0.45-μm membrane filter. The concentration of the solution was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Shimadzu). The adsorbed amount was calculated from the concentrations before and after the adsorption using Eq. (1):

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

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

D. Adsorption isotherms of Pb (II) on KLs

Adsorbent (0.015 g) was added to 50 mL of Pb (II) solution at different concentrations (pH ranges 3.0-3.8,

3.9-4.8, and 5.1-5.5), and the suspensions were shaken at 100 rpm for 24 h at 25°C. The solution was then filtered using a 0.45-μm membrane filter, and the concentration of Pb (II) was determined by ICP-AES. The amount of the adsorbed Pb (II) was calculated using Eq. (1).

E. Recovery of Pb (II) using nitric acid solution

Adsorbent (0.1 g) was added to 50 mL of 20 mg/L Pb (II) solution, and the suspensions were shaken at 100 rpm for 24 h at 25°C. The solution was then filtered using a 0.45-μm membrane filter, and the concentration of Pb (II) was determined by ICP-AES. The amount of adsorbed Pb (II) was calculated using Eq. (1). The filtered adsorbent was dried at room temperature, and added to 50 mL of 10 or 100 mmol/L nitric acid solution. The suspensions were shaken at 100 rpm for 24 h at 25°C. The solution was then filtered using a 0.45-μm membrane filter, and the concentration of Pb (II) was determined by ICP-AES. The amount of desorbed Pb (II) was calculated using Eq. (2).

$$d = C_e V/W, \quad (2)$$

where d (mg/g) is the desorbed amount, C_e (mg/L) is the equilibrium concentration, V (L) is the solvent volume, and W (g) is the weight of the adsorbent.

III. RESULTS AND DISCUSSION

A. Properties of KLs

SEM images of KL, KL-A, and KL-B are shown in Fig. 2. The particle diameters decreased in the order: KL-B < KL-A < KL. The surface of KL and KL-A was observed to be uneven, whereas the surface of KL-B was observed to be smooth. The physical and chemical properties of the activated carbons are listed in Tables I and

TABLE I: Physical properties of ACs.

ACs	Specific surface area (m ² /g)	Pore volume (mL/g)			Mean pore diameter (Å)
		$r \leq 10$ Å	$10 < r \leq 250$ Å	Total	
KL	1542	0.05	0.86	0.91	23.6
KL-A	1267	0.06	0.54	0.60	18.9
KL-B	771	0.04	0.66	0.70	21.1

TABLE II: Chemical properties of ACs.

ACs	Acidic functional groups (mmol/g)				Basic functional groups (mmol/g)	pH
	Total	Phenolic	Lactonic	Carboxyl		
KL	1.04	0.43	0.00	0.61	0.00	4.86
KL-A	2.39	0.99	0.07	1.33	0.01	2.95
KL-B	0.94	0.43	0.21	0.30	1.21	7.86

II. The specific surface areas decreased in the order: KL-B (771 m²/g) < KL-A (1267 m²/g) < KL (1542 m²/g). In contrast, the mean pore diameters followed the order KL-A (18.9 Å) < KL-B (21.1 Å) < KL (23.6 Å). The pore volumes showed a trend similar to that observed for mean pore diameters. These results indicate that specific surface area of activated carbon decreased with chemical modification.

The number of phenolic functional groups (0.99 mmol/g) and carboxyl functional groups (1.33 mmol/g) on KL-A were higher after the nitric acid treatment of KL. The number of basic functional groups (1.21 mmol/g) on KL-B increased following the DCC treatment. These results suggest that carboxyl and basic functional groups were generated on the surface by the treatments above (see Section II.A). The pH of the solution for KL, KL-A, and KL-B were 4.86, 2.95, and 7.86, respectively.

B. Effect of contact time on Pb (II) adsorption on KL, KL-A, and KL-B

Effect of contact time on the Pb (II) adsorption on KL, KL-A, and KL-B is shown in Fig. 3. The amounts of adsorbed Pb (II) followed the order: KL $\cong$ KL-B < KL-A. Equilibrium adsorption times for KL and KL-B or KL-A were about 12 h and 5 h, respectively. Hence, the adsorption rate of Pb (II) was higher on KL-A than on KL.

Lagergren pseudo-first order rate equation is widely used for describing the adsorption in liquid/solid system based on solid capacity [16]. The pseudo-first order rate equation is given by:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (3)$$

where k_1 is the Lagergren rate constant of adsorption (1/h), q_e is the amount of solute adsorbed at equilibrium (mg/g), and q_t is the amount of solute adsorbed on the surface of the adsorbent at time t (mg/g).

FIG. 3: Effect of contact time for adsorption of Pb(II) onto KL, KL-A, and KL-B. $\diamond$: KL, $\bullet$: KL-A, $\circ$: KL-B.

Pseudo-second order rate equation, derived by Ho and McKay, is one of the most widely used kinetic expressions [17]. In this equation, adsorption capacity is assumed to be directly proportional to the number of occupied active sites on the adsorbent [16]. The pseudo-second order rate equation could be expressed as:

$$t/q_t = 1/\{k_2 q_e^2\} + t/q_e, \quad (4)$$

where k_2 is the pseudo-second order rate constant of adsorption (g/mg h), q_e is the amount of solute adsorbed at equilibrium (mg/g), and q_t is the amount of solute adsorbed on the surface of the adsorbent at time t (mg/g).

The correlation coefficient (r) and pseudo-first or pseudo-second order constant (k_1 or k_2) for these models are summarized in Table III. The correlation coefficient r for pseudo-second order kinetic model is much higher than that for the pseudo-first order model, and the adsorption capacities calculated by the former model are close to the experimental results. Therefore, it can be concluded that the pseudo-second order adsorption model is more suitable for describing the adsorption kinetics of Pb (II) on

TABLE III: Constants of kinetics model for adsorption of Pb(II) onto ACs.

ACs	$q_{e,exp}$ (mg/g)	PFOM			PSOM		
		k_1 (1/hr)	$q_{e,cal}$ (mg/g)	r	$k_2 \times 10^{-2}$ (g/mg/hr)	$q_{e,cal}$ (mg/g)	r
KL	9.50	0.38	4.41	0.261	2.49	10.45	0.990
KL-A	17.77	1.51	6.11	0.532	1.77	17.10	0.989
KL-B	9.89	3.00	4.38	0.478	4.82	8.94	0.930

FIG. 4: Adsorption isotherms of Pb(II) adsorbed by KL-A and KL-B. ●: pH 3.0-3.8, □: pH 3.9-4.8, ◇: pH 5.1-5.5.

KLs.

C. Adsorption isotherms of Pb (II) on KL-A and KL-B

Adsorption isotherms of Pb (II) on KL-A and KL-B are shown in Fig. 4. The values of maximum adsorption of Pb (II) on KL-A and KL-B in the pH range 5.1-5.5 were 24.7 mg/g and 18.4 mg/g, respectively. The amount adsorbed on KL-A and KL-B increased with pH. The Langmuir and Freundlich isotherm models are generally used to simulate the adsorption isotherms. The Langmuir model assumes that adsorption occurs on a monolayer where all adsorption sites are identical and energetically equivalent [18]. The model can be described by the following equation:

$$q_e = aW_s C_e / (1 + aC_e), \quad (5)$$

where C_e is the equilibrium concentration of Pb (II) remaining in the solution (mg/L), q_e is the amount of Pb (II) adsorbed after equilibrium, W_s , the maximum adsorption capacity, is the amount of adsorbate at complete monolayer coverage (mg/g), and a (L/mg) is a constant that is related to the heat of adsorption.

The Freundlich isotherm model applies to several kinds of adsorption sites on the solid surface, and represents the adsorption at low and intermediate concentrations on heterogeneous surfaces [19]. The model is represented by the following equation:

$$\log q_e = \log K + \{1/n\} \log C_e, \quad (6)$$

where K is the adsorption capacity when Pb (II) equilibrium concentration is equal to 1, and n is the degree of the dependence of adsorption on equilibrium concentration.

FIG. 5: Relationship between amount of Pb(II) adsorbed by KL-A and amount of proton released from KL-A. ●: pH 3.0-3.8, □: pH 3.9-4.8, ◇: pH 5.1-5.5.

The values calculated from the two models are listed in Table IV. The correlation coefficients (r) of Freundlich and Langmuir equations using KL-A (pH = 5.1-5.5) are 0.952 and 0.914, respectively, which indicates that the experimental data of adsorption isotherms fitted well to both Freundlich and Langmuir equations. The optimal pH conditions for the maximum adsorption (W_s) of Pb (II) was pH = 5.1-5.5. These results show a trend similar to the amount of adsorbed Pb (II). Moreover, when the Freundlich constant, $1/n$, is in the range 0.1-0.5, the adsorption occurs easily. On the other hand, if $1/n > 2$, the adsorption is considered to be difficult [20]. The Freundlich constant $1/n$ for Pb (II) is in the range of 0.05-0.53 (except for KL and KL-B at pH = 3.0-3.8). These results show that Pb (II) was easily adsorbed on KL-A.

D. Adsorption mechanism of Pb (II) on KL-A

Previous reports have shown that the adsorption mechanism of Pb (II) on different acidic functional groups (carboxyl and lactonic groups) on activated carbon is ion exchange [21]. In this study, we investigated the adsorption mechanism of Pb (II) on KL-A. The relationship between the amount of Pb (II) adsorbed by KL-A and the amount of protons released from KL-A is shown in Fig. 5. The amount of protons released was calculated from the proton concentration before and after the adsorption of Pb (II). The amount of Pb (II) adsorbed on KL-A was

TABLE IV: Freundlich and Langmuir constants for adsorption of Pb(II) onto ACs.

ACs	pH	Freundlich model			Langmuir model		
		$\log K$	$1/n$	r	$\overline{W}_s$ (mg/g)	a (L/mg)	r
KL	3.0-3.8	1.15	-1.21	0.978	0.7	-0.4	0.860
	3.9-4.8	0.97	0.53	0.961	3.0	-1.1	0.990
	5.1-5.5	1.01	0.11	0.944	8.6	-35.3	0.854
KL-A	3.0-3.8	0.91	0.05	0.524	8.8	71.9	0.756
	3.9-4.8	1.18	0.20	0.894	18.2	7.3	0.771
	5.1-5.5	1.28	0.21	0.952	22.0	9.0	0.914
KL-B	3.0-3.8	-2.89	2.82	0.724	-0.1	-0.1	0.742
	3.9-4.8	0.99	0.07	0.320	11.7	7.1	0.607
	5.1-5.5	1.27	0.05	0.832	19.4	109.2	0.738

FIG. 6: Adsorption mechanism of Pb(II) by KL-A and KL-B.

TABLE V: Recovery percentage of Pb(II) using nitric acid.

ACs	Concentration of HNO ₃ (mmol/L)	Amount adsorbed (mg/g)	Amount desorbed (mg/g)	Recovery percentage (%)
KL-A	10	9.28	3.93	42.3
	100	8.94	4.72	52.8
KL-B	10	9.96	3.73	37.4
	100	9.96	3.97	39.8

strongly correlated to the amount of protons released from KL-A (except for pH = 3.0-3.8). At pH values 5.1-5.5 and 3.9-4.8, the ratio of the amounts of adsorbed Pb (II) and protons released from KL-A was about 1:2 (correlation coefficients: 0.979 (pH = 3.9-4.8) and 0.984 (pH = 5.1-5.5)). These results indicate that ion exchange occurred in this study. (The adsorption mechanism of Pb (II) by KL-A and KL-B is shown in Fig. 6 [14].) In acidic solution at pH = 3.0-3.8, the protons were not easily released from KL-A and thus, the adsorbed amount was lower than at higher pH values.

E. Recovery of Pb (II) using nitric acid solution

The percent recovery of Pb (II) from KL-A and KL-B is shown in Table V. The percent recoveries of Pb (II) from KL-A and KL-B were 42.3-52.8% and 37.4-39.8%, respectively. The percent recovery of Pb (II) increased with the concentration of nitric acid, which suggests that using nitric acid would be useful in the recovery of Pb (II).

IV. CONCLUSIONS

KL-A and KL-B were prepared by nitric acid and DDC treatments, respectively. Specific surface areas followed the order: KL-B (771 m²/g) < KL-A (1267 m²/g) < KL (1542 m²/g). The numbers of acidic functional groups of KL-A or basic functional groups of KL-B were higher than for KL. The experimental data for the contact time required for the adsorption of Pb (II) were fitted to the pseudo-second order model. Moreover, the adsorption isotherms of Pb (II) were fitted to both Freundlich and Langmuir models. Pb (II) was adsorbed onto KL-A by ion exchange with the protons of the surface functional groups on KL-A. It would be possible to recover Pb (II) from KL-A using nitric acid solution. These results suggest that KL-A would be useful for the adsorption of Pb (II).

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