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Adsorptions of Cd(II) and Pb(II) in aqueous solution by rice-straw char

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ABSTRACT

In this study, a low-cost adsorbent was prepared from rice straw without any activation process and studied for the adsorption capacities and mechanisms of Cd and Pb ions in water. The adsorption of these metal ions on rice-straw char (RSC) was fast and reached equilibrium within 24 h. The adsorption isotherms exhibited the L-type and the adsorption capacities of Pb(II) and Cd(II) at pH 4 were determined to be 68 and 26 μmol g^{-1}, respectively. The difference between the adsorption capacities of these two metal ions implied different adsorption mechanisms. The adsorptions of Pb(II) and Cd(II) both increased with increasing pH. The adsorption of Pb(II) was insensitive to ionic strength, and the adsorption edge was significantly lower than the PZC of RSC. On the contrary, the adsorption of Cd(II) was affected by changing ionic strength, and the adsorption edges was close to the PZC of RSC. Based on these results, the adsorption mechanism of Pb(II) was determined to be inner-sphere complexation, whereas Cd(II) interacted with the RSC surface through electrostatic attraction and formed outer-sphere complexes on RSC.

Keywords: Cd; Pb; Adsorption; Rice straw; Low-cost adsorbent; Water treatment

1. Introduction

Wide utilization of heavy metals has resulted in their frequent occurrences in the environment through intentional or non-intentional discharges of industrial wastes. After entering the environment, heavy metals can accumulate in food chains and be consumed via the intake of contaminated drinking water and food [1,2]. Some heavy metals, such as Cu and Zn, are essential nutrients but become toxic once their accumulation reaches a critical level; others, such as Cd and Pb, are non-essential and toxic even at low concentrations [2–4]. The toxic effects of heavy metals on human health can become more severe after long-term exposure and can ultimately lead to avoidable premature death [2]. One example is itai–itai disease, which was first observed in Japan [5]. It is caused by Cd poisoning arising from the continuous consumption of Cd-contaminated drinking water and rice [5]. Thus, the contamination of surface and ground waters by heavy metals can restrict their usage as drinking water and irrigation water. For water conservation,

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heavy metals must be removed from wastewater before it is discharged into the environment.

Activated carbons (ACs) have been extensively studied for application in water treatment due to their high efficacy in removing a wide variety of contaminants, including heavy metals [6]. ACs produced with different precursors and activation processes have exhibited a wide range of removal capacities of heavy metals [6–8]. For example, Ferro-Garcia et al. [9] found that the adsorption capacities of three ACs for Cd(II), Cu(II), and Zn(II) at pH 5 and 20°C were 22–52 μmol g^{-1}, 114–145 μmol g^{-1}, and 76–102 μmol g^{-1}, respectively [9]. Machida et al. [10] reported the adsorption capacities of a commercial AC for Cu(II) and Pb(II) at pH 6 as 56 and 52 μmol g^{-1}, respectively. The surface areas of ACs used in these two studies ranged from 876 to 1,316 m^2 g^{-1}. Because the content of the surface functional groups and the associated surface properties of ACs determine the adsorption capacities of ACs for heavy metals, different activation processes have been applied to enhance the content of surface functional groups of ACs [7]. For example, in Wilson et al. [11], various ACs were produced using different pyrolysis and activation processes and were tested for the adsorption of heavy metal ions at pH 4.8. The surface areas of the ACs were 542–815 m^2 g^{-1}, and the metal adsorption capacities ranged from 96 to 1,016 μmol g^{-1}. The adsorption capacities of heavy metals were enhanced by the activation process, even though the corresponding surface areas were about the same as those used in other studies. They suggested that the metal adsorption capacities depend on the contents of functional groups and surface charge properties, which are determined by the activation process of the ACs [11].

For real-world applications, cost is an important factor that needs to be considered. Because the high price of ACs are considered disadvantageous in their application to water treatment, extensive studies have been conducted to produce ACs using low-cost precursors in order to develop cost-effective methods for water treatment [6,12–17]. In particular, selected agricultural wastes such as sugarcane bagasse, coconut shells, and maize cobs have been used to produce low-cost ACs, which were subsequently tested for removal efficiencies of heavy metals [13,14,17,18]. For example, Tong et al. [19] report that crop-straw chars exhibited adsorption capacities of 0.58–1.40 μmol g^{-1} for Cu(II) at pH 5. In Inyang et al. [20], sugarcane-bagasse char exhibited an adsorption capacity of 31.3 μmol g^{-1} for Pb(II). These adsorption capacities were comparable with those of commercial ACs at the same pH, but the price of the adsorbent was estimated to be one-fifth to one-third that of commercial ACs. The low cost of the adsorbents produced from agricultural wastes increases the economic feasibility of applying these materials to solve real-world problems.

The goal of this study was to investigate the adsorptions of toxic Cd(II) and Pb(II) in water using a carbon material derived from rice straw. Rice straw is a by-product of rice production. The annual production of rice straw worldwide is estimated to be 600 million tons or more, which could potentially be converted to a large quantity of carbon materials. If a rice-straw char (RSC) is proven to be an effective scavenger for heavy metals, it would provide wastewater industries with an abundant source of low-cost adsorbents for the treatment of water containing heavy metals. Moreover, although many activation processes have been applied to develop carbon materials with high adsorptive properties for heavy metals, previous studies have shown that direct burning or low-temperature pyrolysis can convert lignocellulosic materials (such as rice straw and coconut shell) into carbons with a higher content of oxygen-containing functional groups, compared with their high-temperature counterparts [18]; the difference in the surface functionality of different materials subsequently affects their adsorptions of pollutants, such as chlorophenol [21] and Cr(VI) [22]. Oxygen-containing surface functional groups are attached to peripheral aromatic units in the carbon structure [7,23]. Some oxygen-containing functional groups, such as carboxylic and phenolic groups, are Lewis bases and can potentially serve as the binding sites for metal ions [23–25]. The key role of surface functional groups in the adsorption of heavy metals on ACs has been confirmed by the enhanced adsorption capacities of ACs due to wet oxidation or chemical activation [7]. Accordingly, RSC prepared by low-temperature pyrolysis is expected to have good adsorptive properties for heavy metals, even though no activation or surface modification is performed for the material. This simple process of preparing RSC without additional activation processes may reduce the cost of the product. In this study, adsorption experiments were conducted to determine the adsorption kinetics and isotherms of Cd(II) and Pb(II) for RSC. The influences of pH and ionic strength on the adsorptions of Cd(II) and Pb(II) were also studied and interpreted in terms of the adsorption mechanisms. This knowledge is essential for further improving the removal efficiency of RSC for Cd(II) and Pb(II) and other heavy metals, and recovering heavy metals from the used adsorbent. The results provide a good reference for developing new adsorbents using other crop residues.

2. Materials and methods

2.1. Preparation and characterization of RSC

Rice straw was collected and dried at 60℃ for 24 h. To obtain RSC, rice straw was heated at 300℃ for 1 h with supply of N_2 gas (flow rate = 100 mL min^{-1}). The resulting material was ground, passed through a 0.25-mm sieve, and washed with 1 M HCl solution to remove soluble salts. Subsequently, the material was dialyzed in a cellulose-ester tube to remove excessive acid and salt. The suspension in the dialysis tube was centrifuged, and the collected solids were then freeze-dried and stored in a plastic bottle prior to use.

The C, O, H, and N contents in the organic fraction of RSC were analyzed using a Heraeus Elemental Analyzer. The contents of metal ions were analyzed using ICP-AES (Spectro Genesis) after RSC was digested in 1 M HF solution. The BET surface area was determined using the N_2 adsorption method with a Micrometritics ASAP 2000 surface area analyzer. The point of zero charge (PZC) was measured using the pH drift method [24].

The Boehm titration method was used to determine the contents of the surface acidic and basic sites on RSC [26,27]. The RSC samples of 0.5 g were first immersed in 25 mL HCl, $NaHCO_3$, Na_2CO_3, and NaOH solutions of 0.05 M for 48 h, and then the suspensions were filtered using 0.22-μm (pore size) membrane filters to collect the filtrates. The filtrate after equilibration with the 0.05 M HCl solution was titrated using a 0.05 M NaOH solution to determine the content of surface basic groups on RSC. The filtrates equilibrated with the $NaHCO_3$, Na_2CO_3, and NaOH solutions were titrated using 0.05 M HCl solution. The contents of the acidic groups were derived based on the assumption that NaOH neutralizes phenolic, lactone, and carboxyl groups; Na_2CO_3 neutralizes lactone and carboxyl groups; $NaHCO_3$ neutralizes carboxyl groups [26].

2.2. Adsorption kinetics of Cd(II) and Pb(II)

The stock solutions of 5 mM Cd(II) and Pb(II) were prepared by dissolving 1.543 g $Cd(NO_3)_2{\cdot}4H_2O$ and 1.656 g $Pb(NO_3)_2$, respectively, in 1 L of 0.01 M KNO_3 solution at pH 4. These stock solutions were then used to prepare all of the heavy metal solutions in the subsequent adsorption experiments.

The batch method was used to determine the adsorption kinetics of Cd(II) and Pb(II) on RSC. RSC of 2.5 g was added into 250 mL of 0.01 M KNO_3 solution at pH 4 in a water-jacked reaction vessel, which was connected to a water bath in order to maintain a constant temperature of 25℃ in the vessel. The suspension under stirring was purged with N_2 gas (flow rate = 50 mL min^{-1}), and the pH of the suspension was frequently adjusted to 4.0 using 0.01 M HNO_3 or KOH solution. After equilibration for 24 h, the suspension was added to 250 mL of 0.6 mM Cd(II) or Pb(II) solution in 0.01 M KNO_3 at pH 4 to initiate the reaction. To determine the initial metal concentration in each system, a separate set of samples were prepared using the same procedure without adding RSC into the reaction vessel. During the reaction, the suspension was continuously purged with N_2 gas (flow rate = 50 mL min^{-1}), and the pH of the suspension was maintained constant by adding 0.01 M KOH or HCl solution whenever the change in pH exceeded ±0.1. At given time intervals, 10 mL of the suspension in each reaction vessel was withdrawn with a glass syringe and passed through a 0.22-μm (pore size) cellulose-acetate membrane filter to collect the filtrate. The concentration of Cd or Pb in the filtrates was then analyzed using ICP-AES. The amount of a heavy metal adsorbed by RSC was calculated from the difference between the initial and measured concentrations of the metal.

2.3. Adsorption isotherms of Cd(II) and Pb(II)

The adsorption isotherms of Cd(II) and Pb(II) by RSC were obtained using the batch method. The initial concentrations of Cd or Pb ions ranged from 0.1 to 1.4 mM, and the solids concentration was 5 g L^{-1}. The samples of each concentration of a metal ion were in triplicate. The centrifuge tubes containing the samples were then shaken under 100 rpm at 25℃ for 24 h, and the pH was constantly adjusted to pH 4. The samples were filtered using 0.22-μm (pore size) cellulose-acetate membrane filter to collect the filtrates, and the equilibrium concentrations of Cd or Pb in the filtrates were analyzed using ICP-AES.

2.4. Effects of pH and ionic strength

The effects of ionic strength on the adsorptions of Cd(II) and Pb(II) were investigated using the abovementioned experimental setup. The initial concentrations of Cd or Pb ions ranged from 0.1 to 1.4 mM, and the solids concentration was 5 g L^{-1}. To evaluate the pH effect, the suspensions with an initial concentration of 1 mM Cd or Pb were adjusted for their pH values in the range of 2–10. The samples of each pH value were in triplicate. The samples were shaken under 100 rpm at 25℃ for 24 h, and the pH was constantly adjusted to the desired values. The suspensions were then filtered for the analysis of heavy metal concentration as described above. The amount of a heavy metal adsorbed by RSC was calculated as the difference between the initial and equilibrium concentrations of the heavy metal in filtrate.

3. Results and discussion

3.1. Characterization of RSC

The chemical composition of RSC is listed in Table 1. The C and O contents in the organic fraction of RSC accounted for 49% of RSC (wt.%). Only small amounts of nitrogen (1.3%) and hydrogen (2.2%) were detected. The O content in RSC was contributed by functional groups (e.g. hydroxyl and carbonyl) and C–O–C bonds in RSC. Si (21%) and K (1.0%) were the major constituents while the other metals were trace. In particular, Si is present as silica in RSC, since silica is a natural constituent in rice straw and remains after rice straw pyrolysis.

The N_2-BET surface area of RSC was determined to be $40\ m^2\ g^{-1}$ (Table 2). The surface area in the micropores measured by the *t*-plot analysis was $12\ m^2\ g^{-1}$. The surface area of RSC was smaller than those of ACs reported in the literature. The oxygen content of RSC indicates that oxygen-containing functional groups were present on the RSC surface and therefore determined the surface charge property. According to the result of the Boehm titration [26], the concentrations of the carboxyl, lactonic, and phenolic groups on RSC were 0.07, 0.49, and $0.20\ mmol\ g^{-1}$, respectively (Table 2). The total surface acidity and basicity were 0.76 and $0.26\ mmol\ g^{-1}$, respectively. The sum of all acidic and basic functional groups acting on the surface of RSC gave rise to the surface charge property of RSC, which was described by the PZC value. Using the pH drift method [24], the PZC of RSC was determined to be 6.5 (Table 2), at which the positive charge is equal to the negative charge leading to a net zero charge. The PZC of RSC was lower than those of ACs (often >7). As the surface charge property of a material is determined by its surface functionality, the lower PZC value of RSC was attributed to the higher surface acidity [23].

3.2. Adsorption kinetics

Fig. 1 shows the adsorption kinetics of Cd(II) and Pb(II) by RSC at pH 4. This pH was selected, because no hydrolytic species and precipitates of these metal ions occur, while the adsorption of these ions is relatively significant for observation. Based on our preliminary thermodynamic calculation using Visual Minteq (Version 3.0; [28]), the predominant forms of these heavy metals in water at pH 4 are all divalent cations (i.e. Cd^{2+} and Pb^{2+}), and their hydrolytic ions and precipitates are negligible. Regardless of the type of heavy metals, the adsorption rates were fast in the first 30 min and then gradually slowed down. The curves leveled off within 24 h, after which no significant changes were observed. Because the equilibriums of Cd(II) and Pb(II) were both established within 24 h under the selected condition, adsorption under other conditions was presumed to reach equilibrium within a similar period of time. The agitation time was therefore chosen to be 24 h when adsorption isotherms were obtained.

3.3. Adsorption isotherms

Fig. 2 shows the adsorption isotherms of Cd(II) and Pb(II) on RSC in 0.01 M KNO_3 at pH 4. Each isotherm represents the amount of a metal ion adsorbed on RSC (expressed as $\mu mol\ g^{-1}$) as a function of equilibrium concentration of the metal ion in solution (expressed in mM). The adsorption isotherms all exhibited the *L*-shape [29], characterized by a steep initial slope that gradually leveled off with increasing equilibrium concentration of the metal ions. The isotherms of *L*-shape indicate that limited binding sites on the RSC surface are available for adsorbing metal ions, and the affinity of the RSC surface toward the metal ions decreases as the surface coverage of the metal ions increases. Eventually, maximum adsorptions of metal ions on RSC were established as the concentrations of the metal ions were progressively increased.

To determine the adsorption maximums for the metal ions, the adsorption isotherms were fitted with the linear form of the Langmuir model (Eq. (1)). The resulting parameters are listed in Table 3.

Table 1
Elemental composition of RSC

C (%)	O (%)	N (%)	H (%)	Si (%)	K (%)	Na (%)	Mg (%)	Ca (%)	Fe (%)
38	11	1.3	2.2	21	1.0	ND	ND	ND	ND

Table 2
Surface properties of RSC

Surface area ($m^2 g^{-1}$)		Acidic groups ($mmol g^{-1}$)					
BET	Micropore	Carboxyl	Lactonic	Phenolic	Total	Basic group ($mmol g^{-1}$)	PZC
40	12	0.07	0.49	0.20	0.76	0.26	6.5

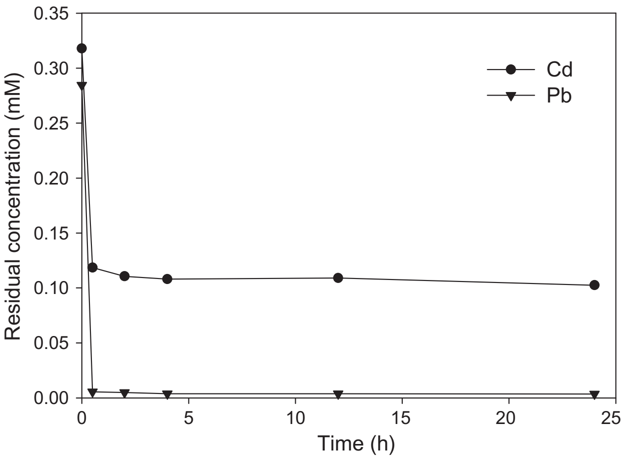

Fig. 1. Adsorption kinetics of Cd(II) and Pb(II) on RSC at pH 4.

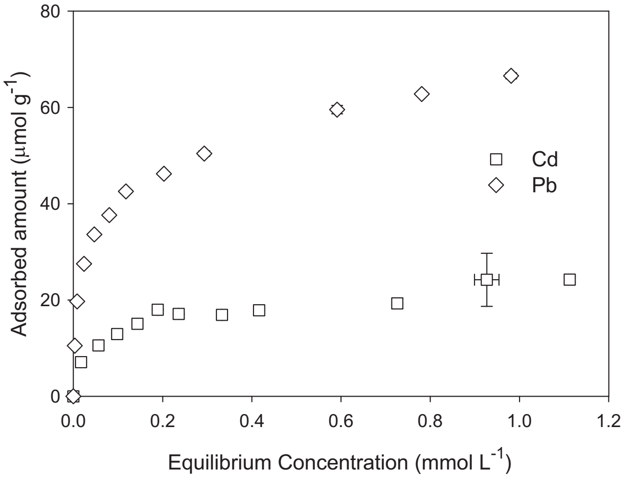

Fig. 2. Adsorption isotherms of Cd(II) and Pb(II) on RSC at pH 4.

Table 3
Coefficients of Langmuir model for the adsorption of Cd (II) and Pb(II) on RSC at pH 4

Adsorbate	S_m (μmol g^{-1})	K	R^2
Cd(II)	26	8.3	0.9749
Pb(II)	68	16.3	0.9931

$$\frac{C_e}{S} = \frac{C_e}{S_m} + \frac{1}{KS_m} \quad (1)$$

where C_e and S are the equilibrium concentrations of heavy metal in the aqueous and adsorbed phases; S_m and K are the adsorption capacity and energetic coefficient, respectively. As indicated by the coefficients of determination (R^2), the adsorption of heavy metals by RSC can be described using the Langmuir model. The Langmuir adsorption maximums were determined to be 68 and 26 μmol g^{-1} for Pb(II) and Cd (II), respectively (Table 3). Although the surface area of RSC is lower than those of ACs and crop-residue-derived carbons, the adsorption capacities of RSC for different heavy metals are comparable to those of ACs and crop-residue-derived carbons, ranging from 0.29 to 146 mg g^{-1}, as reviewed in [12,14]. The relatively high adsorption capacities of RSC for Cd(II) and Pb(II) were attributed to the surface acidity of RSC, which was determined to be 0.76 mmol g^{-1} and provided binding sites for Cd and Pb ions.

3.4. Effects of ionic strength

Fig. 3 shows the adsorption isotherms of different heavy metals in 0.001 and 0.01 M KNO_3 solutions at pH 4 and 25˚C. The change in ionic strength had no significant effect on the adsorption of Pb(II), while that of Cd(II) decreased with the increasing ionic strength. By studying the effects of ionic strength on the adsorption of metal ions, it is possible to distinguish the bonding configurations of the adsorbed ions between inner-sphere and outer-sphere complexes. The increase of ionic strength has a negative effect on the outer-sphere complexation because of the compression of the electric double layer [30–32]. On the contrary, an inner-sphere complex of adsorbed ion has a direct bonding to the adsorbent surface, which is not affected by an increase in ionic strength. Accordingly, adsorbed Pb(II) ions form inner-sphere complexes with the RSC surface, while adsorbed Cd(II) ions form outer-sphere complexes.

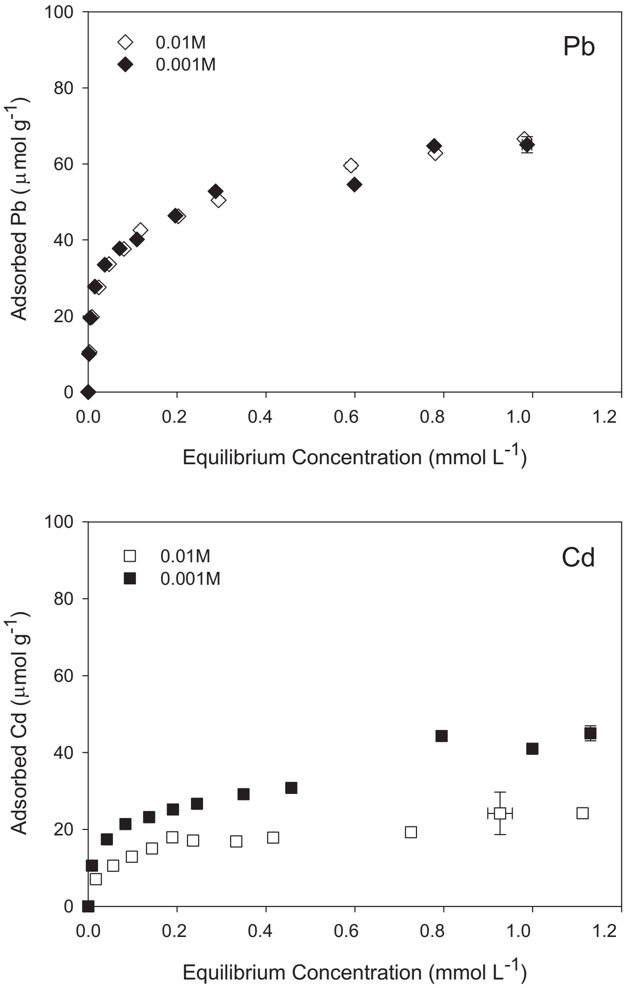

Fig. 3. Effects of ionic strength on the adsorptions of Cd(II) and Pb(II) on RSC.

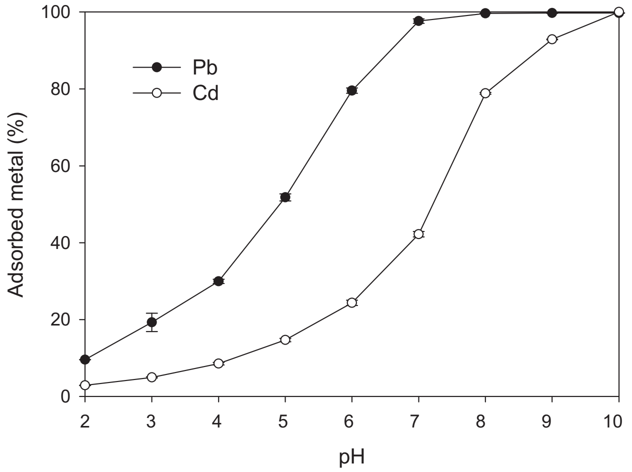

Fig. 4. Adsorptions of Cd(II) and Pb(II) on RSC as a function of pH.

3.5. Effects of pH

Fig. 4 shows the adsorption of heavy metals on RSC as a function of solution pH. Regardless of metal type, their adsorptions were low at low pH and increased with increasing pH. The reasons for the positive effects of pH on the adsorptions of metal ions are twofold. First, RSC has functional groups that are subjected to protonation/deprotonation depending on the solution pH. An increase in pH results in a buildup of net negative charges on the RSC surface, because the surface functional groups are partially (or fully) deprotonated. The increase in the net negative charges on the RSC surface consequently facilitated the adsorption of positively charged metal ions due to the enhanced electrostatic attraction between the adsorbent and adsorbate. Second, the hydrolysis of metal ions leads to the formation of hydrolytic species, such as $Cd(OH)^+$ [33–36]. Such a hydrolytic species has a lower charge than the counterpart of free metal ion (e.g. Cd^{2+}) and therefore has a higher adsorption density on the same adsorbent surface. At high pH values, the adsorptions of metal ions reached 100%, which is attributed to the precipitation of metal hydroxides (Fig. 4).

An abrupt increase in metal ion adsorption occurred in a narrow pH range, which is referred to as the adsorption edge. Here, the adsorption edges were designated to the pH value at which 50% of the metal ions were in the adsorbed form. The adsorption edges of Pb(II) and Cd(II) were determined to be 4.9 and 7.2, respectively. The adsorption edge of Pb(II) occurred at the pH level that was lower than the PZC of RSC (i.e. 6.5). This significant shift of the adsorption edge is attributed to the formation of inner-sphere complex of Pb(II) ions with the oxygen-containing groups on RSC. Because the oxygen-containing groups act as a Lewis base to bind metal ions, the activation energy for the exchange of hydration water around adsorbed Pb(II) ions by OH^- ligand is reduced; thus, the adsorption edge shifts to a lower pH value. Comparatively, the adsorption edge of Cd(II) was higher than the PZC of RSC, indicating that the increases in the absorption of these metal generally followed the surface charge property of RSC due to the electrostatic attraction between the adsorbate and adsorbent. Thus, adsorbed Cd(II) ions formed outer-sphere complexes when they were adsorbed on RSC. These results are consistent with those observed with the effects of ionic strength.

4. Conclusions

RSC exhibited adsorption capacities of Pb(II) and Cd (II) comparable to those of ACs, because the surface functional groups of RSC remained during the pyrolysis of rice straw at a low temperature. Thus, RSC may be used as a low-cost substitute for AC to remove heavy metals from water and wastewater. The adsorptions of Cd(II) and Pb(II) on RSC both increased with increasing pH. The positive effect of pH on the metal adsorptions is attributed to the increasing net negative charges on the RSC surface and the hydrolysis of the metal ions. The adsorptions of different metal ions exhibited different extents of dependence on pH and ionic strength, which were applied to distinguish the adsorption mechanisms between inner- and outer-sphere complexes. The adsorption of Pb(II) was insensitive to ionic strength, and the adsorption edge was significantly lower than the PZC of RSC as the surface of RSC was positively charged. The strong affinity of Pb(II) to the RSC surface is attributed to the formation of inner-sphere complexes on the RSC surface. On the other hand, the adsorption of Cd(II) depended on ionic strength, and the adsorption edge was close to the PZC of RSC. This indicates that Cd(II) ions were bound to the RSC surface through electrostatic attraction, giving rise to the formation of outer-sphere complexes on RSC. This work provides a fundamental understanding of the adsorption mechanism of Cd(II) and Pb(II) ions on RSC. This knowledge can be extended to understand the adsorption of other heavy metals on carbon adsorbents derived from crop residues.

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