

Study of the Adsorbent-Adsorbate Interactions from Cd(II) and Pb(II) Adsorption on Activated Carbon and Activated Carbon Fiber

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ABSTRACT. The adsorption characteristics of Cd(II) and Pb(II) in aqueous solution using granular activated carbon (GAC), activated carbon fiber (ACF), modified ACF (NaACF), and a mixture of GAC and NaACF (GAC/NaACF) have been studied. The surface properties, such as morphology, surface functional groups, and composition of various adsorbents were determined using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) measurements. The specific surface area, total pore volume, and pore size distribution were investigated using nitrogen adsorption, Brunauer-Emmett-Teller (BET), and Barrett-Joyner-Halenda (BJH) methods. In this study, NaACF showed a high adsorption capacity and rate for heavy metal ions due to the improvement of its ion-exchange capabilities by additional oxygen functional groups. Moreover, the GAC and NaACF mixture was used as an adsorbent to determine the adsorbent-adsorbate interaction in the presence of two competitive adsorbents.

Key words: Activated carbon, Activated carbon fiber, Surface functional group, Adsorption, Interaction

INTRODUCTION

The presence of the heavy metals in the environment is a major concern because of their toxicity to humans and the environment, especially at high levels.¹ Heavy metals can be classified as toxic pollutants because they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain.² Industrialists are seeking effective measures to comply with the stringent contamination limits set by the World Health Organization (WHO).³⁻⁵

A number of techniques have been developed for removing lead from aqueous effluents to minimize its health impact. Adsorption is the preferred physico-chemical technique for heavy metal remediation due to its simplicity, low cost, easy scaling and, most importantly, its ability to remove low concentrations, even part per million levels, with high efficiency.⁶ Activated carbon (AC) is an effective adsorbent for the removal of a wide variety of organic and inorganic pollutants because of its high specific surface area, chemical stability and durability. Activated carbon fibers (ACFs), a relatively recent development, are highly microporous carbons with large surface areas and pore volumes, conferring a superior ability to rapidly and effectively adsorb and desorb gases and metals relative to ACs.⁷ The surface

chemistry of ACFs involves both hydrophobic graphite layers and hydrophilic functional groups. Organic compounds are adsorbed on the former, whereas polar species are adsorbed on the latter.⁸ The objective of the present work is to study the interaction of adsorbent-adsorbate and the effect of surface oxygenated groups on the adsorption of Cd(II) and Pb(II) on the ACs and ACFs. Experimental results will be analyzed to provide an understanding of the adsorption mechanism.

MATERIAL AND METHODS

ACF Modification

The ACFs were deposited in a three-necked flask equipped with a stirrer, condenser, dropping funnel and heating mantle. The ACFs (2 g) were dissolved in 100 mL of distilled water and treated with 1 N NaOH (25 g) at 80 °C for 3 h to increase the number of functional groups formed and the porosity. The modified ACFs were washed with deionized water and dried overnight at 80 °C in a vacuum oven to produce modified ACFs, such as NaACF.

Adsorption Measurements

The adsorption isotherms of the Cd(II) and Pb(II) ions were measured in batches as follows. The adsorption iso-

therms of Cd(II) and Pb(II) in aqueous solution on the AC samples were obtained using CdCl_2 and $\text{Pb}(\text{NO}_3)_2$ (Merck), respectively, as precursor salts. The experiments were carried out using an aqueous metal ion solution (250 mL , 10 mg l^{-1}) with a constant GAC concentration in a 300 mL Teflon bath at $20 \pm 1.5 \text{ }^\circ\text{C}$. At a given interval, samples were filtered using $0.45 \text{ }\mu\text{m}$ cellulose acetate filters. The content of the remaining metal ions was analyzed every 2 min using an inductively coupled plasma-atomic emission spectroscopy (ICP). GAC, ACF, NaACF, and a mixture of GAC and NaACF (GAC/NaACF, 90/10 w/w) were used as the adsorbents.

Materials and Characterizations

The base adsorbent used in the study was commercially available GAC made from coconut shell with a mesh size ranges of 12×30 . The as-received petroleum-pitch based-ACFs were purchased from Osaka Gas. The GAC and ACF surface morphologies were analyzed by an S-4700 model SEM (Hitachi, Tokyo, Japan). The specific surface area and mesopore size distribution for the samples were measured using the BET and BJH methods using a Micrometrics apparatus (ASPS2020, USA). The surface functional groups of the samples were characterized with monochromatized AlK_{α} X-rays via XPS (VG Scientific ESCALAB 250 Spectrometer). ICP was used to analyze heavy metal absorption (OPTIMA 4300 DV, Perkin Elmer, USA).

RESULTS AND DISCUSSION

SEM photographs of two adsorbents are shown in Fig. 1. The SEM micrographs of the pristine GACs in Fig. 1a–b reveal small cavities, cracks and attached fine particles

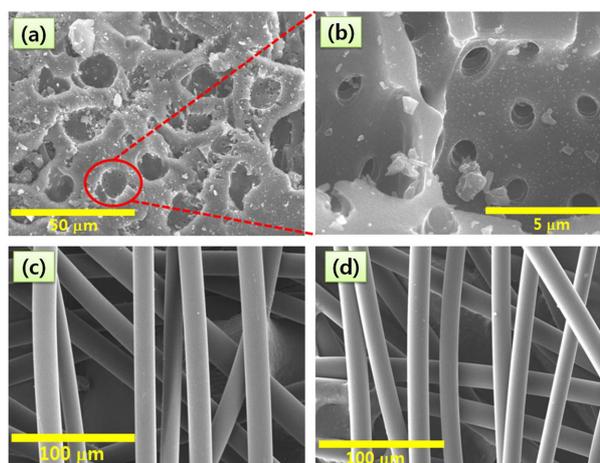


Fig. 1. SEM images of (a) GAC at magnifications of $1 \text{ K}\times$ and (b) $10 \text{ K}\times$, (c) ACF, and (d) NaACF

on the activated carbon surface, forming a complicated network of pores. The ACF and NaACF surfaces look smooth, with the average fiber diameter decreasing from $19.35 \text{ }\mu\text{m}$ for ACF to $17.07 \text{ }\mu\text{m}$ after its modification to NaACF, which indicates that the ACF surface is not destroyed by modification with NaOH, as shown in Fig. 1c–d.

Fig. 2 shows the nitrogen adsorption isotherms at 77 K and the pore size distributions of GAC, ACF, and NaACF. According to the BDDT (Brunauer-Deming-Deming-Teller) classification,⁹ the isotherms are of Type I, indicating that GAC, ACF, and NaACF are microporous materials. Additionally, no hysteresis curve is observed either before or after modification. The nitrogen isotherms were planar at relative pressures above 0.1 , indicating that these samples are highly microporous. The BJH pore size distributions of the GAC, ACF, and NaACF samples (Fig. 2b) are calculated using the desorption curve. ACF and NaACF mainly

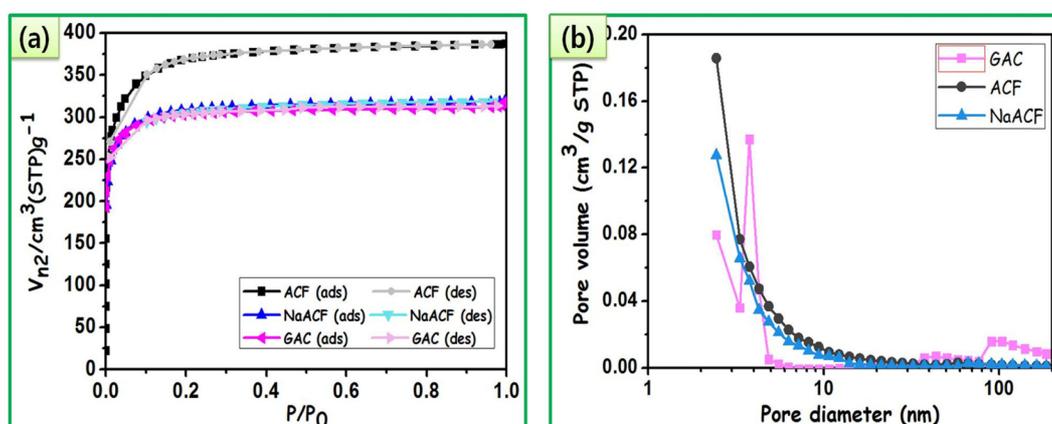


Fig. 2. (a) Nitrogen adsorption-desorption isotherms and (b) differential pore volume of GAC, ACF, and NaACF as a function of pore diameter.

Table 1. Pore characteristics of GAC, ACF, and NaACF

Sample	S_{BET}^a (m ² /g)	V_t^b (cm ³ /g)	APD ^c	Pore volume fraction (%) ^d	
				Micropore	Mesopore
GAC	1170.4	0.48	1.66	97.05	2.95
ACF	1390.1	0.59	1.72	99.45	0.55
NaACF	1174.4	0.50	1.67	96.17	3.83

^a S_{BET} = BET surface area, ^b V_t = Total pore volume, ^cAverage pore diameter (nm), ^dPore volume fraction by the t-method.

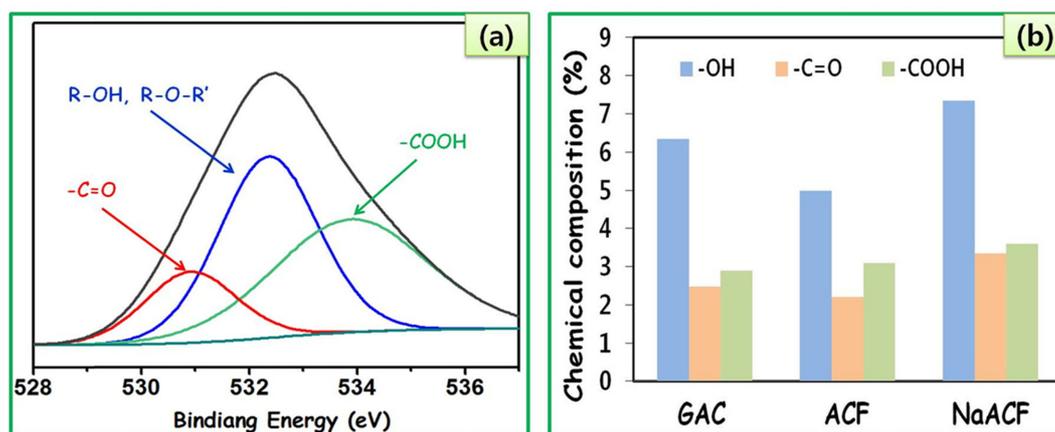


Fig. 3. (a) Deconvolution of O1s of ACF and (b) chemical compositions of GAC, ACF, and NaACF based on XPS analysis.

possess micropores, whereas GAC exhibits mesopores in the range of 3–5 nm. The BET surface area, total pore volume, and micropore volume determined from the *t*-plot method decrease after the chemical modification of ACF to NaACF, as shown in Table 1, due to the blocking of the narrow pores by the surface complexes. The mean pore size is 1.6–1.7 nm, indicating that the decreased pore volume was not due to the destruction of the basal planes and instead due to pore blocking by newly developed oxide functional groups at the unreacted edges of the basal planes.¹⁰

The deconvolution of the O1s XPS spectrum (Fig. 3a) revealed three Gaussian curves centered at 531.0, 532.0, and 533.1 eV, which can be assigned to $\text{C}\underline{\text{O}}\text{O}^-/\underline{\text{O}}=\text{C}-\text{O}$, $\text{C}-\underline{\text{O}}\text{H}/\underline{\text{O}}=\text{C}$, and $\text{O}=\text{C}-\underline{\text{O}}\text{H}/\text{R}-\underline{\text{O}}-\text{R}$, respectively.¹¹ The XPS data were carefully analyzed to identify the acid-oxygenated groups on the carbon surface most responsible for the adsorption capacity. Fig. 3b presents the proportions of the different oxygen contributions obtained from the deconvolution of the O1s peak. The carbon-oxygen functional groups on NaACF, such as phenol-type hydroxyl, lactone, and carbonyl groups, increased in number after the modification of ACF.^{12,1} Carbon-oxygen surface groups are generally considered to be responsible for the adsorption of heavy metal ions.^{13,14} The oxygen-containing groups behave as acids or bases, possessing ion-exchange properties.

The adsorption curves of Cd(II) and Pb(II) ions on the four activated carbon samples (GAC, ACF, NaACF, and GAC/NaACF) are presented in Fig. 4. ACF and NaACF show the lowest and highest adsorption capacities, respectively, for the Cd(II) and Pb(II) ions, which suggests that not only the pore structure but also the surface chemical groups affect the adsorption. As shown in Fig. 3b, ACF, which has fewer oxygen functional groups than do NaACF and GAC, also has fewer adsorption sites, resulting in low removal of Cd(II) and Pb(II) via the ACF surface. The equilibrium on NaACF and GAC was reached within 2 min for all metal ion concentrations due to the greater number of oxygen-containing functional groups, which was attributed to the strong interaction between the ions and the polar functional groups. In particular, the Cd(II) and Pb(II) adsorption of NaACF is superior to that of the other samples because the micropores on the carbon surface exposed to the adsorbates are mostly uniform, which minimizes diffusion limitations and allows more rapid adsorption/desorption compared with GACs.¹⁵

Although NaACF has an excellent adsorption capacity for Cd(II) and Pb(II) ions, low-cost adsorbents are becoming increasingly studied. Therefore, the GAC and NaACF mixture was studied as an adsorbent, and the adsorbent-adsorbate interaction for the competition of the two adsorbents was determined. All adsorption experiments were

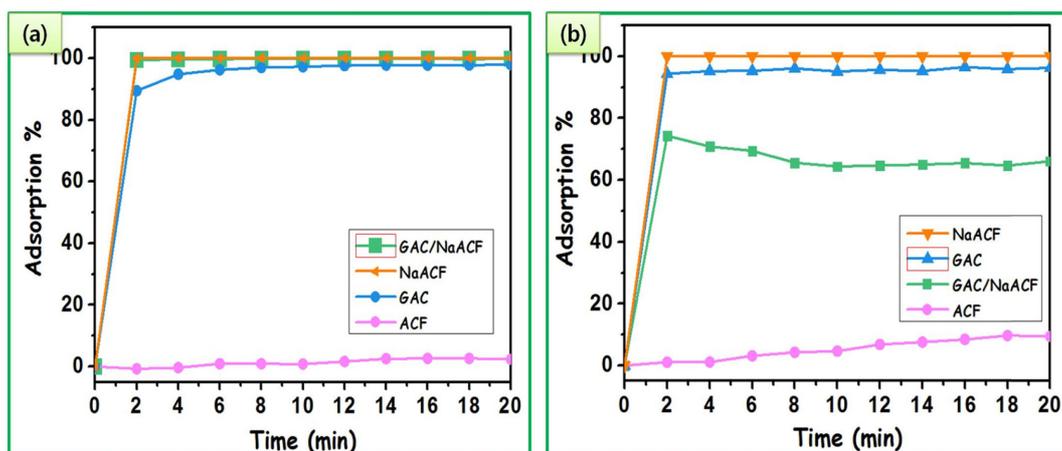


Fig. 4. Adsorption percentage of (a) Cd(II) and (b) Pb(II) ions with respect to contact time.

performed at pH 9. As shown in Fig. 4, the adsorption of Cd(II) increased due to the addition of NaACF, whereas that of Pb(II) decreased. All Cd(II) species present a positive sign increased regardless of the pH used in the calculated distribution of Cd(II) species.¹⁶ Synergistically, the addition of NaACF in GAC induces predominantly electrostatic-type interactions between the Cd(II) species and the carbon surface by increasing the number of oxygenated groups on the NaACF surface because the main species is $\text{Cd}(\text{OH})^+$ at pH value above 8.¹⁷ In contrast to the case of Cd(II), Pb(II) adsorption was impeded by the repulsive electrostatic interactions in this process because the Pb(II) species at pH 9, $\text{Pb}(\text{OH})_2$, presents no charge.¹ In the case of Pb(II), dispersion interactions between the activated carbon surface and the $\text{Pb}(\text{OH})_2$ play a more important role in the adsorption process than do electrostatic interactions. In general, the delocalized p electron system ($-\text{C}_p$) of the activated carbon surface can act as Lewis base as well as a reduction center.¹⁸ The electron withdrawing functional groups decrease the basicity and reductive properties of activated carbon, decreasing its surface electronic density and weakening the dispersion interactions between the activated carbon surface and nonionic species.¹⁷ Therefore, NaACF with a greater number of oxygenated functional groups would reduce the adsorption capacity because $\text{Pb}(\text{OH})_2$ may be competitively adsorbed on GAC and NaACF. The mechanism of the adsorption action for the GAC and NaACF mixture requires further study.

CONCLUSION

The carbon-oxygen functional groups on ACF, such as phenol-type hydroxyl, lactone, and carbonyl groups, were

increased in number by the modification with NaOH, without leading to a significant change in the surface and pore structures. The NaACF with a large number of oxygen functional groups and uniform micropores exposed directly to adsorbates provides more adsorption sites, resulting in the highest adsorption capacity and fastest adsorption of Cd(II) and Pb(II) ions. The use of the GAC and NaACF mixture as an adsorbent at pH 9 revealed that the high adsorption capacity of Cd(II) ion is due to the electrostatic-type interactions between the $\text{Cd}(\text{OH})^+$ species and the carbon surface with the more numerous oxygenated groups on the NaACF. In contrast, the adsorption of Pb(II) is diminished by the addition of NaACF with more numerous oxygenated functional groups in GAC because the $\text{Pb}(\text{OH})_2$ may be adsorbed on GAC and NaACF competitively. The electron withdrawing functional groups decrease the basicity and reductive properties of activated carbon, decreasing its surface electronic density and weakening the dispersion interactions between the activated carbon surface and nonionic species, $\text{Pb}(\text{OH})_2$. Therefore, adsorbent-adsorbate interactions, in addition to the textural characteristics and surface functional groups of each adsorbent, are relevant to adsorption performance.

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