

Effect of Modification of Granular Activated Carbon on Pb(II) Adsorption

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In these days, lead (Pb) contamination in water and wastewater, which discharged from many industries such as metal plating, mining and tanneries, is a serious problem due to the poisoning on humans. Specially, the heavy metals of lead and mercury are considered to be most harmful to the environment.¹ Their high toxicity and the more severe regulations of new environmental legislation have demanded the advanced technologies to treat water bodies or industrial effluents contaminated with the heavy metals.^{2,3} A number of techniques have been developed for removing lead pollutant from aqueous effluents to minimize its impact. Activated carbons (ACs) have been proven to be effective adsorbents for the removal of a wide variety of organic and inorganic pollutants. ACs are widely used to treat waters contaminated with heavy metals because of their well developed porous structures, large surface area and a wide spectrum of surface functional. This capacity is mainly derived from (i) their porous texture, which gives them a large surface area, and (ii) their chemical nature, which can be appropriately modified by physical or chemical treatments to increase their adsorption capacity. The surface chemistry of ACs has a major influence on their capacity to adsorb inorganic compounds, especially metallic cations.^{4,5} The objective of the present work is to enhance the adsorption capacity of Pb ion from solution with NaOH-modified granular activated carbons (GACs). The changes of physicochemical properties of NaOH-modified GACs are investigated in terms of the change of surface and pore properties of ACs during modification.

The mass titration result for GACs are shown in Fig. 1.

These graphs plot pH values as a function of the mass fraction of GACs in the solution. They also demonstrate that a plateau is found in the plot of pH versus mass fraction. It is noted that there are some deviations in the asymptotic values of the curves for different initial pH conditions. By measuring the mass titration, the chemical nature of the used GACs surface are basicity because the pH of point of zero charge (PZC) were around 10. Therefore the GACs will be modified by NaOH, which will enhance the adsorption process because of the greater attractive electrostatic interactions between the surface of the modified GACs and the Pb(II) species present at the pH of the experiments. It is clear that the nature of surface chemical functionalities is significantly altered by the NaOH treatment.

Fig. 2 shows the SEM micrographs of the pristine and NaOH-modified GACs. There are small cavities, cracks

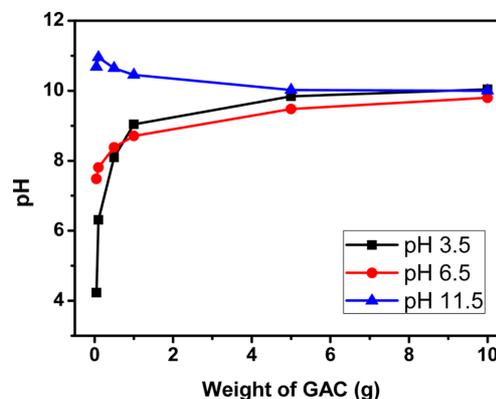


Fig. 1. Variation of pH as a function of the weight of GACs.

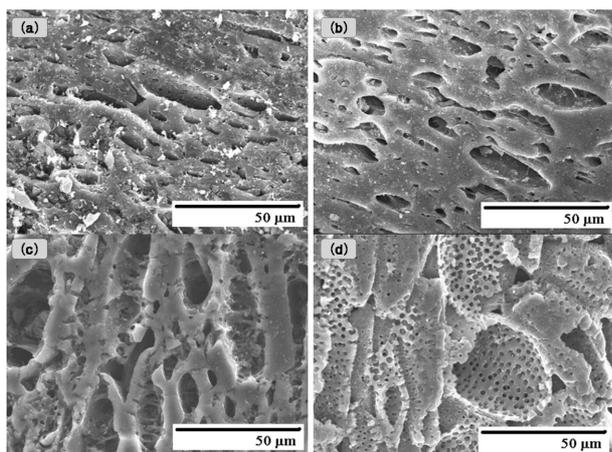


Fig. 2. SEM images of as received (a) GAC; modified (b) NaGAC1 (c) NaGAC2 (d) NaGAC3.

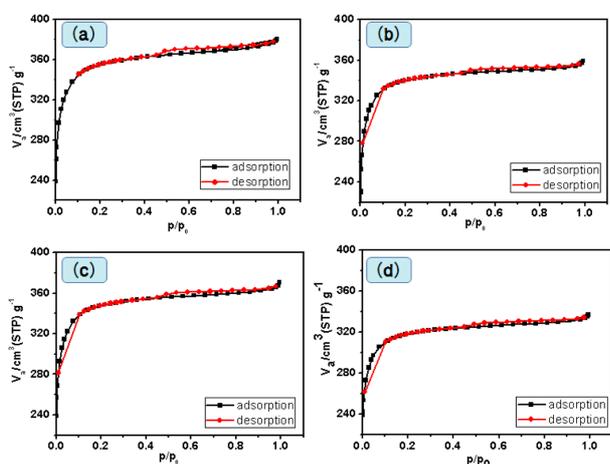


Fig. 3. Nitrogen adsorption-desorption isotherms of (a) GAC; modified (b) NaGAC1 (c) NaGAC2 (d) NaGAC3.

and attached fine particles over the activated carbon surface, forming a system of complicated pore networks.

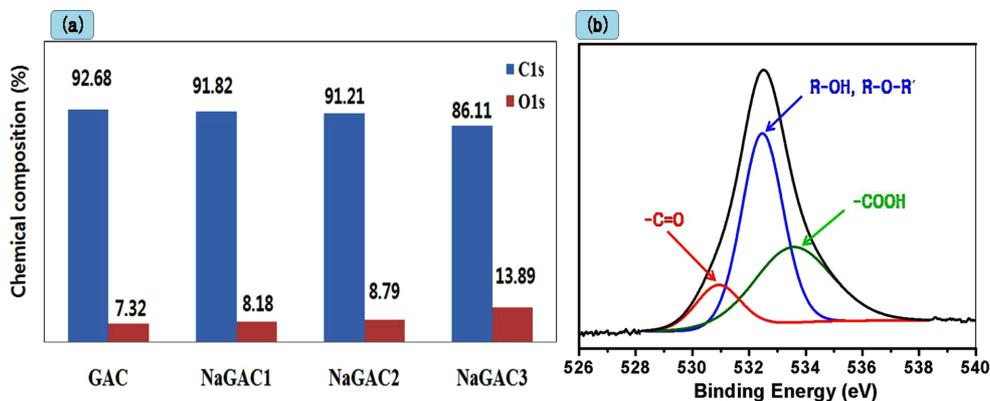


Fig. 4. (a) Chemical compositions of unmodified and base-modified GACs and (b) Deconvolution of O1s of NaGAC3, measured from XPS analysis.

Table 1. Pore characteristics of the used A-GACs

| | S_{BET}^a (m^2/g) | V_t^b (cm^3/g) | V_m^c (cm^3/g) | APD ^d |
|--------|----------------------------|-------------------------|-------------------------|------------------|
| GAC | 1360.0 | 0.58 | 0.55 | 1.72 |
| NaGAC2 | 1327.4 | 0.56 | 0.54 | 1.71 |
| NaGAC3 | 1216.5 | 0.52 | 0.50 | 1.70 |

^a S_{BET} =BET surface area; ^b V_t =Total pore volume, ^c V_m =micropore volume by the t-method, ^dAverage pore diameter (nm)

After modification, relatively regular pore structures, which are mesoporous and/or microporous, are found in Fig. 2(b-c).

The nitrogen adsorption-desorption isotherms of unmodified and modified GACs are shown in Fig. 3, and the porous structure of the GACs is summarized in Table 1. According to BDDT (Brunauer-Deming-Deming-Teller) classification,⁶ the isotherms are of Type I, indicating that GACs are microporous materials. It is evident that most of the pore volumes of samples are filled below $P/P_0 \approx 0.1$, indicating that these samples are highly microporous. However, the specific surface areas of GACs are decreased by the chemical modification. In this work, the isotherms and porosities of modified GACs assure that some of the pores were blocked by oxide functional groups introduced by the chemical treatment.⁷ The decrease of surface area was mainly ascribed to the decrease of the micropore volume.

Quantitative peak analyses were also carried out to determine the concentrations of the surface elements by XPS, which are showed in Fig. 4(a). It was found that the chemical composition of C and O of modified GACs increased with an increase concentration of NaOH. As a result, the NaOH treatment led to an increase of oxygen-containing polar functional groups and total acidity as

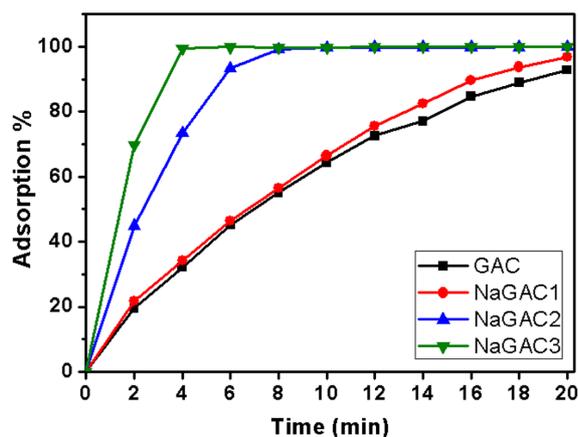


Fig. 5. Adsorption percentage of Pb(II) ions with respect to contact time.

well. The deconvolution of the O1s XPS spectrum (Fig. 4b) revealed three Gaussian curves centered at 531.0, 532.0 and 533.1 eV, which can be assigned to $\text{COO}^-/\text{O}=\text{C}-\text{O}$ and $\text{C}-\text{OH}/\text{O}=\text{C}$ and $\text{O}=\text{C}-\text{OH}/\text{R}-\text{O}-\text{R}$, respectively.⁸

Fig. 5 shows the effect of contact time on Pb(II) adsorption onto GACs. Pb ion removal efficiency of GACs was almost completed within 2 min. the Pb(II) adsorption of modified GACs is superior to that of untreated GACs, due to the increased oxygen-containing functional groups, more adsorption sites are available, causing higher removal of Pb(II). This result is interesting because time to equilibrium is one of the parameters for economical wastewater treatment plant applications.

Meanwhile, the specific surface areas or micropore volumes were slightly decreased after the chemical treatment due to the micropore filling or blocking. Nevertheless, the total Pb(II) adsorption of modified GACs was increased with increasing of the NaOH concentration, attributed to the good interaction between Pb(II) ions and polar functional groups on the GACs. This indicates that the functional groups introduced by NaOH treatment improve the ion-exchange capabilities of the GACs and thus make Pd(II) adsorption capacities increase correspondingly (Fig. 6).

In conclusion, GACs are sensitive toward NaOH mod-

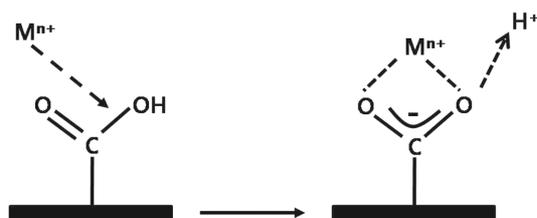


Fig. 6. Possible mechanism of ion exchange between Pb(II) ion and carboxyl group on GACs.

ification, which results in a decrease of pore volume/surface area and increase of functional groups. The decrease of surface area is mainly due to decreased micropore volume resulting from pore blocking by surface oxide groups existing in some of the micropores. However, this treatment gives rise to a large increase in the amount of total acidity rise to a large increase in the amount of total acidity. The total Pb(II) ions adsorption of GACs was increased with increasing of NaOH concentration for modification of GACs, attributed to the good interaction between Pb(II) ions and polar functional groups on the GACs.

EXPERIMENTAL

Materials and characterizations

The base adsorbent used in the study was commercially available GAC made from coconut shell (A-GAC), whose mesh size ranges 12*30. The surface morphology of the GAC were analyzed by Scanning electron micrograph (SEM) using the S-4700 (Hitachi, Tokyo, Japan) and surface area and pore size distributions for the sample were measured by the Brunauer-Emmett-Teller (BET) method using Micrometrics (ASPS2020, USA). The surface functional groups of the samples were characterized by a mono-chromatized Al K_{α} X-ray from X-ray photoelectron spectroscopy (XPS) (VG Scientific ESCALAB 250 Spectrometer). Inductively coupled plasma-atomic emission spectroscopy (ICP) was used to analyze heavy metal absorption using OPTIMA 4300 DV (perkin elmer, USA).

Point of zero charge (PZC)⁹

To measure the PZC of the A-GAC sample, three different initial pH solutions were prepared using 0.1 M HNO and 0.1 M NaOH; for example, pH=3.5, 6.5, and 11.5. NaNO₃ was used as the background electrolyte. For each initial pH, six containers were filled with 100 ml of the solution, and different amounts of carbon sample were added (0.05%, 0.1%, 0.5%, 1%, 5%, and 10% by weight). The equilibrium pH was measured after 24 h.

Modification of GAC

The GACs were deposited in a three-necked flask, equipped with stirrer, condenser, dropping funnel and heating mantle. The GACs (5 g) in 20 ml distilled water were treated with 1, 2, 3 N NaOH (5 g), respectively at 80 °C for 1 h to increase the formation of functional groups and porosity. The modified GACs were washed with deionized water and dried overnight at 80 °C in vacuum oven to produce modified ACs such as NaGAC1, NaGAC2, and NaGAC3.

Adsorption measurements

Adsorption isotherms of the Pb ion were carried out in batches as follow. Salts used were $\text{Pb}(\text{NO}_3)_2$ for Pb(II) with a high degree of purity. Experiments were carried out using 250 mL of Pb ion aqueous solution containing 10 mg l^{-1} concentration and a constant modified GACs, in 300 mL Teflon bath at 20 ± 1.5 °C. At a given intervals, samples were filtered using $0.45 \mu\text{m}$ cellulose acetate filters and the content of remaining Pb ion was analyzed every 2 min by using ICP.

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