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Synthesis of Magnetically Separable Activated Carbon from Pineapple Crown Leaf for Zinc Ion Removal

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Keywords: Activated carbon, Adsorption, Magnetite, Metal removal, Pineapple crown leaf

Abstract. Metals removal from wastewater has become a major concern over the years due to the adverse effects of metals on organisms and environment. Adsorption is one of the safest, simplest, and most cost-effective methods for metals removal. The primary purpose of this study was to develop a magnetically separable activated carbon from pineapple crown leaf for zinc removal. Magnetic activated carbon (MAC) were characterized by SEM-EDX and FTIR. The ability of MAC to adsorb zinc ion was studied through variation of initial solution pH, concentration, and contact time. The optimum pH for zinc removal was four, while the equilibrium was reached after 180 min. In this condition, the percentage removal of zinc was 70.5%.

Introduction

Wastewater discharged by industries is one of the heavy metal pollution sources. The hazardous compounds contained in the wastewater (e.g., zinc ion (Zn^{2+})) cause a serious environmental pollution problem if the concentration exceeds the water quality standard. Zn^{2+} can accumulate in organism tissue, causing numerous diseases such as anemia, kidney damage, stomach cramps, and nausea [1]. Several methods have been developed for heavy metals removal from wastewater such as ion-exchange [2], chemical precipitation [3], membrane filtration [4], electrochemical [5], coagulation [6], and adsorption [7]. Among them, adsorption is one of the safest, simplest, and most cost-effective methods for metals removal [1]. In this sense, activated carbon (AC) produced from biomass waste such as pineapple crown leaf [7, 8] is considered an efficient adsorbent due to it has a high adsorption capacity and abundant availability. Pineapple crown leaf (*Ananas comosus*) is composed of 70-80% α cellulose, 5-12% lignin, and hemicellulose, which enable it to act as a precursor in the synthesis of AC [8]. However, operating conditions during AC preparation affect the characteristics and performance of the obtained AC.

Modification of AC using chemical treatment including KOH [9], $ZnCl_2$ [9], H_3PO_4 [10, 11], or K_2CO_3 [12] has been studied. In this sense, conventional heating using an electric furnace was usually adopted [13]. Although AC has been widely used for metal removal in wastewater, the separation of AC from solution is still an important matter. Sedimentation, filtration, and centrifugation, which are usually used after the adsorption process are considered uneconomic and time-consuming [14]. The use of magnetic activated carbon (MAC) becomes a viable alternative to solve the problem. However, the loading of magnetite (Fe_3O_4) in AC requires a detailed investigation to increase its adsorption capacity. Therefore, the aims of this work were to (1) prepare MAC from pineapple crown leaf waste with KOH activation, and (2) investigate zinc (Zn^{2+}) adsorption characteristics by MAC.

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Materials and Methods

Materials. Ferrous sulfate hydrate ($FeSO_4.7H_2O$), ferric chloride hexahydrate ($FeCl_3.6H_2O$), zinc nitrate tetrahydrate ($Zn(NO_3)_2.4H_2O$), potassium hydroxide (KOH) pellets, sodium hydroxide (NaOH), and hydrochloric acid (HCl) were supplied by Merck (Germany).

Activated Carbon (AC) Preparation. Pineapple crown leaf was chopped, washed, dried at 110°C in an electric oven (Memmert type UN55, Germany) for 24 hours, and blended to a powder. The powder was then carbonized in an electric furnace (Model FB1310M-33 Thermolyne, Thermo Scientific, USA) at 500°C for 90 min in limited air [8]. The resulting char was then impregnated with 8.75 g KOH and 10 mL of distilled water for 120 min. The impregnation ratio of 1.75: 1 g/g of KOH to char. Furthermore, the sample was dried at 105°C for 24 hours. The activation process was carried out in a tubular furnace under a flow of nitrogen (0.1 L/min) at a temperature of 500°C for 2 hours. The sample was further washed with 0.1 M HCl and distilled water until the pH was close to seven. The wet sample was then dried at 105°C for 12 h.

Magnetization process. The magnetization process of AC was carried out using co-precipitation method. First, 0.025 mol of $FeSO_4.7H_2O$ and 0.0375 mol $FeCl_3.6H_2O$ were each dissolved in 25 ml of distilled water. The two solutions were then mixed, stirred, and heated at 55°C. Afterward, 15 g of AC was added to the solution and stirred continuously for one hour. Followingly, NaOH solution was slowly dropped until pH reached 12. Then, the magnetite-loaded activated carbon was washed with distillation water until the filtrate pH was around seven, separated from solution by a simple magnetic procedure, and dried in an oven at 65°C for 6 hours.

Characterization of Adsorbents. The char, AC, and MAC were analyzed for the surface morphology using a scanning electron microscope (JSM-6360, JEOL, Japan). The specific surface area was calculated by the Brunauer-Emmet-Teller (BET) method from N_2 adsorption/desorption isotherm at 77K using an automated gas sorption apparatus (NOVA 1200, Quantachrome, USA). The Fourier Transform Infra-red (FTIR) spectroscopy (Spectrum 100, PerkinElmer, USA) was used to analyze surface groups of the adsorbents in a range of 400-4000 cm^{-1}. XRD patterns of MAC were recorded by X-ray diffraction type D8 Advanced (Bruker, UK) to investigate crystal structure.

Adsorption Studies. The aqueous Zn^{2+} solution was prepared by diluting $Zn(NO_3)_2.4H_2O$ with distilled water to a certain concentration. Adsorption experiments were performed using 0.1 g of adsorbents and 50 ml of Zn^{2+} solutions with different concentrations which were placed into 100 ml Erlenmeyers. The adsorption was carried out at different initial solution pH with added HCl or NaOH 0.1 N. The Erlenmeyers were shaken for four hours with a speed of 150 rpm to reach equilibrium. The Zn^{2+} concentration in the residual solution was analyzed using atomic absorption spectrometer (AAS) (Perkin Elmer, Model PinAAcle 900F). While, the contact time influence on the Zn^{2+} adsorption to char, AC, and MAC was investigated by pouring 0.3 g of adsorbent to 50 mL of Zn^{2+} solutions (concentration of 10 mg/L, initial solution pH of 4). The adsorption experiments were carried out at different contact times. The percentage of Zn^{2+} adsorbed was calculated by Eq. 1 [15]:

$$Zn^{2+} adsorbed\ (\%) = \frac{(c_o - c_t)}{c_o} x100 \tag{1}$$

where C_t is the concentration of Zn^{2+} remaining at time t (mg/L).

Results and Discussion

Characterization of Adsorbents. The SEM micrographs of char, AC, and MAC are shown in Fig. 1. The image of char (Fig. 1a) shows the presence of shallow and constricted pores. In addition, some pores appear to be blocked by tarry substances, resulting from the carbonization process. After the KOH treatment process (Fig. 1(b), several pores have been enlarged and opened, resulting in the increase of porosity and specific surface area (from 1.2 m^2/g for char to 325.3 m^2/g for AC). In this sense, potassium (K) can insert into the char pores and functions as a template to widen the existing pores. When magnetite (Fe_3O_4) was embedded to the AC, the pores partially filled and covered by Fe_3O_4 (Fig. 1(c)), leading to a decrease in specific surface area (from 325,3 m^2/g for AC to 230.1 m^2/g for MAC).
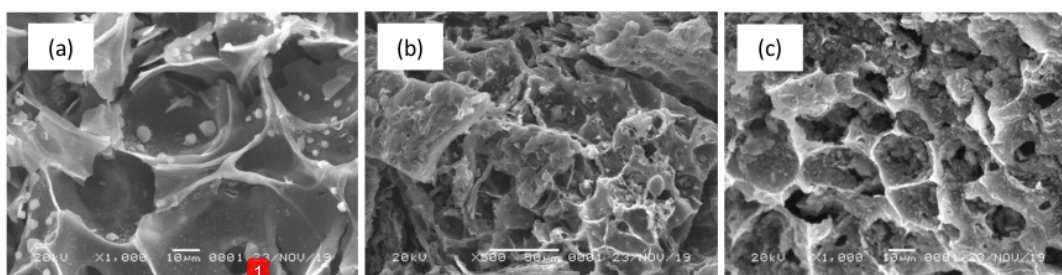
Fig. 1 SEM micrographs of (a) char, (b) activated carbon (AC),
and (c) magnetic activated carbon (MAC).

FTIR spectrum analysis was carried out to identify different surface groups on the char, AC, and MAC surface that function as active sites on the Zn^{2+} adsorption. In Fig. 2, all samples have similar spectra, indicating they have similar surface groups. The absorption peak around 3400-3700 cm^{-1} with a maximum at 3406 cm^{-1} represented -OH stretching vibration of hydroxyl groups [8]. The absorption peak at 2925 cm^{-1} was assigned to the C-H group. The peak observed at 1500-1600 cm^{-1} can be attributed to the C=C stretching vibration of aromatic compounds. The band at 1605 cm^{-1} represented C=O stretching vibration, whereas those at 1060.98 cm^{-1} could be assigned to the C-O stretching of the -OCH$_3$ group [8]. After the carbonization and activation process, the position and intensity of some peaks being changed. The band around 3400-3700 cm^{-1} became shallower, which suggested the decrease -OH group while peaks around 500-750 cm^{-1} belong to the Fe_3O_4 (magnetite) [6]. Magnetite was also identified in the XRD pattern of MAC through the presence of peaks at 2θ of 29°, 35°, 43°, 54°, and 63° which correspond to magnetite peak standards (JCPDS No. 96-900-2321).
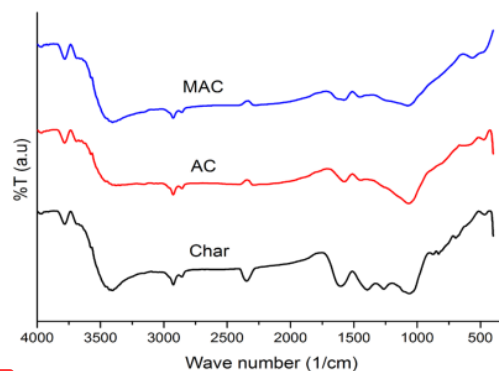

Fig. 2 FTIR spectra of (a) char, (b) activated carbon (AC),
and (c) magnetic activated carbon (MAC).

Adsorption of Zinc. The adsorption efficiency of Zn^{2+} onto char, AC, and MAC linearly increased with increases in pH until pH 4 (Fig. 3(a)). In the high acid medium, the phenolic groups on the AC surface will be protonated. Consequently, there is no ionic interaction between the phenolic groups and Zn^{2+}, resulting in the decrease of Zn^{2+} adsorbed. The highest adsorption efficiency was obtained at pH 4 due to the protonation decreased. At a high pH level (pH>4), the decreasing trend was likely caused by the formation of hydroxide complexes of Zn^{2+}, including $ZnOH^+$ and $Zn(OH)_2$. Thus, further experiments in this study were carried out at pH 4. In addition to PH, contact time is an important parameter that provides information on the equilibrium time. As seen from Fig. 3(b), the percentage removal of Zn^{2+} increased rapidly in the first 40 min and after 180 min, most of active sites have been occupied, leading to a linear curve. The effect of initial concentration for Zn^{2+} removal by char, AC, and MAC is shown in Fig. 3(c). It is evident that the higher initial concentration, the lower the percentage removal of Zn^{2+}. However, the amount of Zn^{2+} adsorbed per unit adsorbent mass

increased with increasing initial Zn^{2+} concentration and faster equilibrium was attained at a lower concentration. It may be related to the abundance of vacant sites at lower concentration.[8] In addition, the percentage removal of Zn^{2+} by MAC was higher than that of AC. It may be due to an increase in the number of active sites from magnetite.
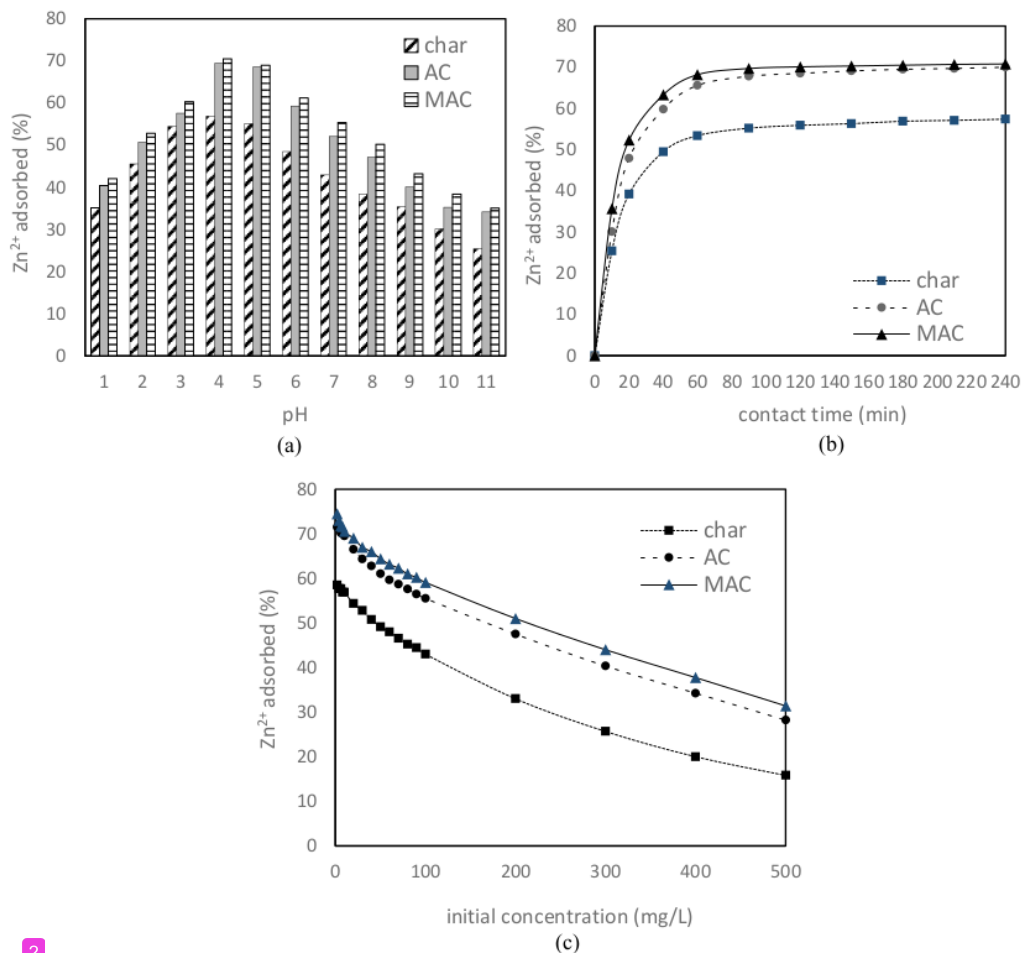
Fig. 3 Effect of (a) pH, (b) contact time, and (c) initial concentration on the removal of Zn^{2+} by char, activated carbon (AC), and magnetic activated carbon (MAC).

Summary

The magnetite (Fe_3O_4) was loaded successfully to the activated carbon (AC) prepared from pineapple crown leaf using KOH as an activator agent. Adsorption experiments showed that magnetic activated carbon (MAC) is an effective adsorbent for zinc removal from aqueous solution. The amount of zinc adsorbed by MAC was higher than AC, although the increase is meaningless.

Acknowledgment

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