



# Adsorption of copper and zinc onto carbon material in an aqueous solution oxidized by ammonium peroxydisulphate



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## ABSTRACT

The aim of the present work was to evaluate and compare of carbon materials for the ability to eliminate Cu (II) and Zn (II) ions from water. Ammonium peroxydisulphate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>)-treated carbon material (Ox-CM) was prepared from the combustion of forest branches and was compared with raw carbon material (CM). The adsorption isotherms and the influence of contact time, initial pH, and ionic strength for the adsorption of Cu (II) and Zn (II) were determined. The results of this work show that the removal ratios of Cu (II) for CM and Ox-CM after 2 h were 8.7 and 94.2%, respectively; and, those of Zn (II) for CM and Ox-CM after 2 h were 7.8 and 89.9%, respectively. The values of the parameters obtained for Cu (II) were based on the Langmuir isotherm saturated adsorption amount ( $Q_0$ ) and the adsorption equilibrium constant ( $K_L$ ): 27.47 mg/g and 0.4556 L/mg on Ox-CM; 3.66 mg/g and 0.2099 L/mg on CM, respectively. Those of  $Q_0$  and  $K_L$  for Zn (II) were as follows: 22.52 mg/g and 0.4978 L/mg on Ox-CM; 3.07 mg/g and 0.5560 L/mg on CM, respectively. In this work Ox-CM provided the optimal level of adsorption for Cu (II) and Zn (II) ions.

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## 1. Introduction

Heavy metal pollution is a serious problem worldwide [1]. Heavy metals have been widely used in various industrial activities that include smelting, battery manufacturing, metal plating, dyeing, and plastics [2]. Heavy metals are non-biodegradable and have long-lasting toxicity. Heavy metals can be accumulated in living tissues, causing various diseases and disorders [3]. Copper and zinc are among the most common heavy metals in wastewater. Copper is an essential trace element for all living things because it is an important part of the complex of respiratory enzymes and cytochrome c oxidase. In the USA, the concentration of Cu (II) in drinking water must be reported to the United States Environmental Protection Agency (USEPA) if it exceeds 1.3 mg/L [4]. Copper contributes to many diseases such as pancreas, brain and heart diseases when it accumulates in the human body. In addition, zinc is a necessary element for both humans and animals and is neces-

sary for the functioning of various enzyme systems where insufficient levels affect body development in humans and animals. Zinc may cause a bitter taste in water levels above a standard of 5.0 mg/L [5]. Zinc may cause some diseases including high blood pressure, infantilism, destruction of red blood cells, impaired wound healing, and kidney damage when it accumulates in the human body [6]. The efficient removal of heavy metal ions from wastewater makes a significant contribution to human health and eco-environmental protection. Heavy metals that are hazardous to human health and the environment, can be removed from wastewater via methods that include precipitation, coagulation, evaporation, ion exchange, membrane processing, solvent extraction, and adsorption [7]. When all the above methods are considered, adsorption of metal ions by an adsorbent is the most effective and widely used in the treatment of heavy metals wastewater [8]. Activated carbon is the adsorbent that is most widely used for the removal of many different metal ions due to a high capacity for adsorption. However, activated carbon is expensive, and effective adsorbents that are also cost-effective are needed.

Several studies have reported the use of adsorbents other than activated carbon to remove copper and zinc from water. Ho and Mcka studied the removal of Cu (II) ions using raw peat with various initial Cu (II) concentrations and masses of peat [9]. An adsorption equilibrium is described by the Langmuir isotherm model, and the adsorption mechanisms of Cu (II) have been

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analyzed using the Elovich equation and a pseudo second-order model. Saeed et al. [10] reported the removal of heavy metals (Pb, Cd, Zn, Cu and Ni) when present singly or in binary and ternary systems by milling the agrowaste of cicer arietinum (chickpea var. black gram) for use as a biosorbent. Meunier et al. [11] studied the efficiency with which cocoa shells remove Pb, Cr, Cd, Zn, Cu, Fe, Co, Al, and Ni from acidic solutions and investigated how the composition of these solutions influences the efficient removal of heavy metal ions. Veli and Alyuz [12] studied the effect of pH, initial concentration, and shaking time on the adsorption of copper and zinc ions using cankiri bentonite, which is a natural clay. The static and dynamic adsorption of Zn (II) ions onto two oxidized commercial carbon materials from water was performed by Alvarez-Merino et al. [13]. The authors reported that the oxidized carbon materials greatly increased the adsorptive capacity of Zn (II) ions, albeit with a decrease in the surface area and porosity of the two commercial carbon materials. In that application, the surface of the carbon material was oxidized by ammonium peroxydisulphate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), which conferred a large number of negative charges that strengthened the electrostatic interactions between adsorbate and adsorbent. The advantages of these materials include high adsorption efficiency, low cost, simplicity, and adsorption that is selective for heavy metals [14].

In order to introduce acidic oxygen groups on the surface of carbon materials (activated carbon or carbon nanotubes) for adsorb metals ions, oxidation is one of the most conventional modifications [15,16]. The dry and wet oxidation treatments of carbon materials as a rule were performed with dry O<sub>3</sub> and O<sub>2</sub>(air) and with wet HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> [17–19]. As a result, O<sub>3</sub> and HNO<sub>3</sub> were the most effective chemical oxidants to form carbon-oxygen surface groups (mostly carboxylic acid groups). The concentration of carboxylic acid groups with HNO<sub>3</sub>-treated was higher in the O<sub>3</sub>-treated carbon materials. Moreover, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> used as oxidants has also been constantly employed [20]. The results shown higher total oxygen content and surface acidity were obtained in the (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> oxidation of activated carbon.

Previous reports have provided the details of carbon material (CM) prepared from the combustion of forest branches. Dai et al. prepared this type of CM as well as CM treated with HNO<sub>3</sub> to remove lead ions from an aqueous solution [21]. Those results indicated that the removal ratios of Pb (II) on CM and HNO<sub>3</sub>-treated CM after 2 h were 16.6 and 97.5%, respectively, with an initial Pb (II) concentration of 25 mg/L at 25 °C and an optimal pH of 5.0. Investigations into the adsorption of Pb (II) onto CM and HNO<sub>3</sub>-treated CM have shown only scarce removal of Cu (II) and Zn (II) ions from water.

The main focus of the present study was to investigate the removal of Cu (II) and Zn (II) ions from an aqueous solution using CM treated with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> prepared from the combustion of forest branches. The influence of parameters such as contact time, initial pH, adsorbent dose, and ionic strength were investigated. The kinetics and adsorption equilibrium of Cu (II) and Zn (II) for CM treated in this manner were obtained from batch experiments. In addition, adsorption mechanisms of the metal ions were decided onto (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>-treated CM and raw CM.

## 2. Materials and methods

### 2.1. Materials

The adsorbent CM was prepared from the combustion of forest branches in a combustion power plant in Oshu City (Japan). This CM was collected from the bottom of the stove in a combustion power plant. The CM was washed repeatedly with hot water to remove the contaminants. The washed CM was then oxidized by

a 2 M solution of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in a sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, 1 M) solution with a (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>-solution/CM ratio of 50 mL/g at 25 °C for 2 days to introduce carboxylic functional groups, as described elsewhere [22]. The CM oxidized by (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was cleaned with hot deionized water until the solution pH reached a stable value. The oxidized CM was labeled Ox-CM. The adsorbents (CM and Ox-CM) were dried prior to use.

### 2.2. Chemicals

A stock solution of Cu (II) and Zn (II) ions used in the present work was prepared by dissolving an accurate quantity of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in deionized water. The oxidant ammonium peroxydisulfate was obtained from Nanjing Lipai Chem. Co., Ltd. All chemicals used in this study were of analytical grade, and solutions were prepared using deionized water. A standard solution of Cu (II) (1000 mg/L) and Zn (II) (1000 mg/L) for flame atomic adsorption spectrometry was obtained from Beijing NCS Analytical Instruments Co. Ltd. To adjust the pH, 0.1 M HCl and 0.1 M NaOH solutions were used.

### 2.3. Physical and chemical characteristics of CM and Ox-CM

The surfaces of CM and Ox-CM were observed by using a low-vacuum Scanning Electron Microscope (SEM) (5 kV, 3000X), S-3400 N (Hitachi Ltd. Tokyo, Japan). The specific surface area was calibrated using a surface analyzer, AUTOSORB 6AG (Yuasa Ionics Co., Osaka, Japan), to measure the N<sub>2</sub> adsorption via a B.E. T. method. The numbers of acidic functional groups and basic sites on the surface of the CM and Ox-CM were determined according to a method proposed by Boehm [23]. Acidity was determined by mixing 0.6 g of either CM or Ox-CM with 15 mL of NaHCO<sub>3</sub> (0.1 M), Na<sub>2</sub>CO<sub>3</sub> (0.05 M) or NaOH (0.1 M) solution in a well-sealed flask. The mixture was then shaken for 48 h at 25 °C and 165 rpm. An aliquot of the solution for each sample was back-titrated with HCl (0.1 M). NaHCO<sub>3</sub> neutralizes only carboxylic groups on the carbon surface, Na<sub>2</sub>CO<sub>3</sub> reacts with carboxylic and lactonic groups, and NaOH reacts with carboxylic, lactonic and phenolic groups. Accordingly, the difference between the groups neutralized by NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> is the lactonic groups, and the difference between those neutralized by Na<sub>2</sub>CO<sub>3</sub> and those by NaOH is the phenolic groups. Basicity was determined using a similar method, but the samples were exposed to HCl (0.1 M) and the residual base was titrated using NaOH (0.1 M). The point of zero charge (pH<sub>PZC</sub>) for the samples was determined according to a method proposed by Leon et al. [24]. Approximately 250 mg of each sample was suspended in previously degassed deionized water. Samples were shaken at 25 °C, and the pH was measured periodically. The final pH obtained in this manner was considered as the pH<sub>PZC</sub> for each sample.

### 2.4. Procedure for the adsorption experiment

The adsorption features of the adsorbents (CM and Ox-CM) were investigated as a function of contact time, initial pH, and ionic strength. The adsorption equilibrium and kinetics were obtained from batch experiments using stoppered flasks containing Cu (II) or Zn (II) ion solutions and 10 mg of the adsorbents at pH 5.0 and 25 °C. After shaking the flasks for predetermined time intervals, the Cu (II) and Zn (II) solutions were separated from the adsorbents by centrifugation at 4500 rpm for 10 min (IEC61010–2–020, Kubota, Japan). The concentrations of Cu (II) and Zn (II) ions were measured using flame atomic absorption spectrometry (Model AA6800, Shimadzu Japan) at 213.9 and 324.8 nm, respectively, for specified time courses. The amount of Cu (II) or Zn (II) adsorbed by the adsorbents in each replicate was calculated by

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