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# Role of minerals in carbonaceous adsorbents for removal of Pb(II) ions from aqueous solution

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## Abstract

Adsorptive removal of Pb(II) ions from aqueous solution onto a non-activated charcoal (CC) of oak wood origin was studied in comparison with an activated carbon of coal origin. The adsorption capacity for Pb(II) of the non-activated charcoal increased significantly with deceasing particle diameter, whereas the activated carbon (AC) exhibited approximately constant capacity for Pb(II) adsorption as a function of particle size. Adsorption to the ashes prepared from the non-activated charcoal and the activated carbon was also investigated to examine the role of mineral ash. Although the ash from the activated carbon did not show any Pb(II) adsorption, the ash from the charcoal was very effective for Pb(II) adsorption. Furthermore, Pb(II) was hardly adsorbed when the ash was removed from the non-activated charcoal by acid treatment. Based on the results, the adsorption sites for Pb(II) are considered to be acidic surface functional groups on the external and internal surfaces for the activated carbon, mineral ash containing oxides of manganese and magnesium exposed on the external surface are dominantly responsible for the Pb(II) adsorption for the non-activated charcoal.

*Keywords:* Heavy metal ions; Charcoal; Activated carbon; Ash; Adsorption

## 1. Introduction

Adsorption is one of the attractive techniques for removing noxious substances and for water purification. Silica gels, activated alumina, oxides and hydroxides of metals, zeolites, clay minerals, synthetic polymers and carbonaceous materials, such as activated carbon and molecular carbon sieves are used as adsorbents [1,2]. Activated charcoal is widely used for treatment of industrial waste water [3] and drinking water in waterworks and the end of the line in tap water in the home [4]. It is also applied to prehospital use for childhood poisoning [5,6]. It can accommodate both organic [7–10] and inorganic compounds, such as heavy metal ions [11–13]. In practice, the activated charcoal is employed more frequently for adsorption of organic compounds rather than heavy metal ions. The surface of activated charcoal thanks to its developed porous structure and high specific surface area consisting largely of graphene layers. This is advantageous for adsorption of organic compounds but not necessarily for heavy metal ions, because organic materials, especially non-dissociating organic compounds, in aqueous solution preferentially adsorb on the graphene layers of the activated charcoal [7,8] whereas heavy metal ions are adsorbed at specific surface sites, such as acidic surface functional groups [14,15] and metal oxides [16,17]. According to these considerations, there is a room for non-activated charcoal, which does not have a sufficiently developed porous structure but is abundant and inexpensive, to be utilized for the adsorption of heavy metal ions when there are some effective components inside the charcoal, although it cannot be used for the adsorption of organic compounds.

In this study, adsorption of a heavy metal ion in aqueous solution onto non-activated charcoal was studied comparing

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with activated carbon. Pb(II) ions were employed as a heavy metal because it is one of the most hazardous heavy metals found in the environment as well as mercury, cadmium, chromium. The removal of Pb(II) ions by adsorption onto activated carbon [18–22] or charcoal [13] is widely investigated. In spite of these efforts, the adsorption sites for Pb(II) ions are not made clear sufficiently. The objectives of the study are to clarify the effect of pulverization on the Pb(II) ions adsorption onto the non-activated charcoal comparing it with activated carbon.

Adsorption isotherms and influence of particle diameter on the adsorption of Pb(II) were studied in a batch system. Adsorption sites were also characterized examining surface functional groups, composition of minerals in the ash and adsorption isotherms of the Pb(II) ions. Furthermore, adsorption of the Pb(II) ions onto the ashes of the charcoal and the activated carbon, and the non-activated charcoal from which the ash was removed were investigated to specify the adsorption sites.

## 2. Experimental

A non-activated charcoal (CC) was employed for the comparison with an activated carbon (AC), both of them commercially available materials. The CC and the AC (Cargon Mitsubishi S60) were of oak wood and coal origin, respectively. They were pulverized and then sieved into nine groups from less than 45 to 1000 μm in average particle diameter. The particles ranging 125–250 μm were used as a standard size for measuring physical properties, such as BET surface area, pore volume, methylene blue and iodine adsorption capacities and acidic surface functional groups. The BET surface area was determined by a surface analyzer (Beckman Coulter Model SA3100). The pore volume was calculated from the $N_2$ adsorption isotherm using the Barrett–Joyner–Halenda (BJH) method [23]. The surface functional groups on the carbonaceous adsorbents were estimated by Boehm titration [24–26], in which it was assumed that $NaOC_2H_5$ neutralized carboxylic, lactonic, phenolic and carbonyl groups, NaOH neutralized carboxylic, lactonic and phenolic groups, $Na_2CO_3$ neutralized carboxylic and lactonic groups and $NaHCO_3$ neutralized only carboxylic groups [27–32]. The CC and the AC were calcined at 850 °C in air for 5 h with a furnace to obtain mineral ashes. These ashes were also used as adsorbents in the experiments. Composition of minerals were determined by ICP-AES (RIGAKU CIROS-120EOP) in which the ash samples were decomposed in a mixture of nitric acid, hydrochloric acid and/or hydrofluoric acid by use of microwave heating (RIGAKU Multiwave 3000). For the CC less than 45 μm, acid washing was carried out to remove minerals using 1 M nitric acid, 1 M hydrochloric acid and hydrofluoric acid. The acid washed CCs were rinsed with de-ionized water repeatedly until solution pH reached a constant value. All adsorbents were dried overnight at 110 °C in an oven and then allowed to cool in a desiccator prior to use. The Pb(II) aqueous solution was prepared from reagent grade Pb(II) chloride dissolving it in de-ionized water.

All adsorption experiments were carried out at 25 °C with agitation speed of 100 rpm for a week using 50 mL Pb(II) solution in 100 mL conical flasks. The Pb(II) concentrations for the experiments ranged from 0.025 to 5.0 mmol/L. One week was found to be sufficient to attain adsorption equilibrium state in the preliminary study. The adsorbent dosage was 100 mg for the CC and the AC, and 5 mg for the CC ash and the AC ash because the ash content in the adsorbents was less than 5%. Adsorption isotherms of Pb(II) were obtained by changing the initial Pb(II) concentration. The equilibrium solution pH was measured by a portable pH meter (HORIBA Model D-21). The Pb(II) amounts on the adsorbents were calculated by difference between the initial and the equilibrium Pb(II) concentrations in the solution. The Pb(II) concentration was measured by an atomic absorption spectrometer (AAS, HITACHI Model 180-30) after the solution was separated form the adsorbent with a centrifuge.

## 3. Results and discussion

### 3.1. Properties of adsorbents and Pb(II) species in solution

Table 1 shows the properties of the non-activated charcoal made from oak wood and the activated carbon of coal origin ranging 125–250 μm in particle diameter. Physical adsorption properties of BET surface area, pore volume, methylene blue and iodine adsorption capacities for the AC are always

Table 1
Properties of charcoal (CC) and activated carbon (AC)

| | Charcoal (oak wood based) 125–250 μm | Activated carbon (coal based) 125–250 μm |
|---|---|---|
| Surface area (BET) ($m^2$/g) | 21 | 1200 |
| Pore volume (ml/g) | 0.023 | 0.921 |
| Methylene blue adsorption (mg/g) | 6.4 | 110 |
| Idodine adsorption (mg/g) | 150 | 1100 |
| Acidic surface functional groups (Boehm titration) (mequiv $g^{-1}$) | | |
| Carboxylic | n.d. | 0.008 |
| Lactonic | n.d. | 0.078 |
| Phenolic | n.d. | 0.017 |
| Carbonylic | n.d. | 0.007 |
| Ash content (wt.%) | 1.4 | 1.9 |
| Mineral compositon in ash (%) | | |
| Na | 0.8 | 2.8 |
| Mg | 3.9 | 0.1 |
| Al | 0.1 | 21.1 |
| Si | 0.4 | 20.3 |
| K | 1.2 | 5.6 |
| Ca | 40.6 | 0.8 |
| Mn | 3.2 | n.d. |
| Fe | 0.87 | 3.4 |