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Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production

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Abstract

Bio-char by-products from fast wood/bark pyrolyses, were investigated as adsorbents for the removal of the toxic metals (As^{3+}, Cd^{2+}, Pb^{2+}) from water. Oak bark, pine bark, oak wood, and pine wood chars were obtained from fast pyrolysis at 400 and 450 °C in an auger-fed reactor and characterized. A commercial activated carbon was also investigated for comparison. Chars were sieved (>600, 600–250, 250–177, 177–149, and <149 μm) and the particle size fraction from 600 to 250 μm was used without further modification for all studies unless otherwise stated. Sorption studies were performed at different temperatures, pHs, and solid to liquid ratios in the batch mode. Maximum adsorption occurred over a pH range 3–4 for arsenic and 4–5 for lead and cadmium. Kinetic studies yielded an optimum equilibrium time of 24 h with an adsorbent dose of 10 g/L and concentration ∼100 mg/L for lead and cadmium. Sorption isotherms studies were conducted in broad concentration ranges (1–1000 ppb for arsenic, 1×10^{-5}–5×10^{-3} M for lead and cadmium). Oak bark out-performed the other chars and nearly mimicked Calgon F-400 adsorption for lead and cadmium. In an aqueous lead solution with initial concentration of 4.8×10^{-4} M, both oak bark and Calgon F-400 (10 g/L) removed nearly 100% of the heavy metal. Oak bark (10 g/L) also removed about 70% of arsenic and 50% of cadmium from aqueous solutions. Varying temperatures (e.g., 5, 25, and 40 °C) were used to determine the effect of temperatures. The equilibrium data were modeled with the help of Langmuir and Freundlich equations. Overall, the data are well fitted with both the models, with a slight advantage for Langmuir model. The oak bark char's ability to remove Pb(II) and Cd(II) is remarkable when considered in terms of the amount of metal adsorbed per unit surface area ($0.5157\ mg/m^2$ for Pb(II) and $0.213\ mg/m^2$ for Cd(II) versus that of commercial activated carbon.

Keywords: Bio-oil char; Activated carbon; Arsenic; Cadmium; Lead; Adsorption; Metals removal; Bio-oils; Bio chars; Adsorption; Water treatment

1. Introduction

Heavy metals are toxic to aquatic flora and fauna even in relatively low concentrations. Some metals can be assimilated, stored and concentrated by organisms [1,2]. Industries, including mining and electroplating, discharge aqueous effluents containing high levels of such heavy metals as uranium, cadmium, mercury, and copper. Untreated effluents may have an adverse impact on the environment [3,4]. Heavy metals including cadmium, lead, and zinc, are toxic at high concentrations and are priority pollutants observed in municipalities and specific industries throughout the United States [5,6]. Lead is

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emitted into the atmosphere by the combustion of fossil fuels and the smelting of sulfide ores, and in lakes and streams by acid mine drainage [7–10]. Pb(II) dominates in acid while $PbOH^+$ predominates in most environmental pHs. The drinking water guideline recommended by World Health Organization (WHO) and American Water Works Association (AWWA) is 0.05 mg/L [11]. The maximum allowable lead in drinking water has been set at a concentration of 15 ppb by the U.S. Environmental Protection Agency [12].

Cadmium is very toxic and causes serious damage to the kidneys and bones. It is best known for its association with itai–itai disease [13]. Cadmium ions have little tendency to hydrolyze at pH values <8 but above 11, all cadmium exists as its hydroxo-complex [7]. Cd(II) predominates in fresh water at pH 6–8. $CdOH^+$, $Cd(OH)_2$, $Cd(OH)_2$, $Cd(OH)_3^-$, $Cd(OH)_4^{2-}$ also exist depending upon the solution pH [1,7]. The chlorocomplexes $CdCl^+$, $CdCl_2$, $CdCl_3^-$ predominate in sea water and Cd(II) is present in very small amounts [7]. Cadmium accumulates in humans, causing erythrocyte destruction, nausea, salivation, diarrhea, and muscular cramps, renal degradation, chronic pulmonary problems, and skeletal deformity [2]. The major sources of cadmium release are the manufacturing of alloys, batteries, pigments and plastics. Mining and refining processes are also significant sources [14,15]. The drinking water guideline recommended by the WHO and AWWA is 0.005 mg Cd/L. In many ground waters that contain bicarbonate/carbonate anions the aqueous speciation of cadmium includes several complexes with bicarbonate/carbonate. Cadmium carbonate can be a solubility control for some elevated alkaline environments that contain high cadmium contamination.

Arsenic exists in the −3, 0, +3, and +5 oxidation states [16]. Environmental forms include arsenious acids (H_3AsO_3, H_3AsO_3, $H_3AsO_3^{2-}$), arsenic acids (H_3AsO_4, $H_3AsO_4^-$, $H_3AsO_4^{2-}$), arsenites, arsenates, methylarsenic acid, dimethylarsinic acid, arsine, etc. Arsenic(III) is a hard acid preferentially complexing with oxides and nitrogen, while arsenic(V) behaves like a soft acid, forming complexes with sulfides [7]. Inorganic forms of arsenic most often exist in water supplies [7]. Arsenic is uniquely sensitive to mobilization (pH 6.5–8.5) and under both oxidizing and reducing conditions among heavy metalloids [17]. Arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}), referred to as arsenic(III) and arsenic(V) are common in natural waters. Pentavalent species predominate and are stable in oxygen- rich aerobic environments of surface water. Trivalent arsenites predominate in moderately reducing anaerobic environments such as groundwater [18]. Redox potential (Eh) and pH control arsenic speciation. $H_2AsO_4^-$ dominates at low pH ($pH < \sim 9.2$) in oxidizing conditions. At higher pH, $HAsO_4^{2-}$ is dominant ($H_3AsO_4^0$ and AsO_4^{3-} may be present in strong acid or base conditions, respectively). Under reducing conditions at $pH < \sim 9.2$, the neutral $H_3AsO_4^0$ predominates. The WHO provisional guideline of 10 ppb (0.01 mg/L) has been adopted as the drinking water standard but many countries have retained the earlier WHO guideline of 50 ppb (0.05 mg/L) including Bangladesh and China. In 2001, U.S. EPA required public drinking water to reduce arsenic from 50 ppb (0.05 mg/L) to 10 ppb (0.01 mg/L) starting from January 2006 [19].

Numerous treatments have been developed for lead, cadmium, and arsenic contaminated water. Adsorption has evolved as one of the most used treatment techniques for removing metal ions to lowers from water which cannot be removed by other techniques. Metal adsorption removal rates by activated carbon is affected by the metal's ionic charge [1,2,20]. Many activated carbons are available commercially but few are selective for heavy metals. A search for inexpensive substitutes is underway. Wastewater treatments require vast quantities of activated carbon. Improved, tailor-made, inexpensive and readily regenerated adsorbents are needed.

Less expensive materials for lead, cadmium and arsenic removal from water include algae [21,22], carbon cloth [23], peat [3,24], agricultural byproducts [25], lignin [1,26], biomaterials [27], bagasse fly ash [28], blast furnace slag [29], red mud [30,31], iron oxide coated treated sand [32]. Low cost adsorbents for water remediation have been reviewed [33–37].

Bio-char is a pyrolytic by-product during bio-oil production [38–51]. This oxygen-rich char is different from that formed by partial combustion. Alkali and alkaline earth cations remain in the condensed phase and are concentrated in the char. Previous researchers have obtained chars by fast pyrolysis (∼500 °C in nitrogen flow) of oat hulls and corn stover in a fluidized sand bed reactor [42]. A 12% char yield was obtained in ∼1.5 s. This char was steam activated [42], characterized and used for As(V) remediation [52].

In the present study pine wood, pine bark, oak wood and oak bark were fast pyrolyzed in an auger-fed reactor (1 kg/h) at temperatures ∼400 and 450 °C. The chars obtained at the two temperatures were mixed together and used without grinding or chemical treatment. This crude by-product char is easily made at low cost. As biomass pyrolysis to liquid and gas fuels grows in importance, it is anticipated that large amounts of these chars will be available. Any use with a value in excess of its fuel value will be welcome. The basic objectives of the present investigation have been:

1. To use this low cost char generation method to produce an adsorbent during bio-oil production.
2. To demonstrate arsenic, cadmium, and lead removal by char from water/wastewater at different pHs, temperatures, and solid to liquid ratios.
3. To obtain sorption kinetics to establish the mechanism.
4. To compare these chars versus commercially available carbons/adsorbents.

2. Materials and methods

2.1. Reagents and equipment

All chemicals were AR-grade. Stock solutions of the test reagents were made by dissolving $Pb(NO_3)_2$, $Cd(NO_3)_2{\cdot}4H_2O$, $NaAsO_2$, in de-ionized water from a Millipore-Q water system. Carbons F-400 was obtained from Calgon. The pH measurements were made using an Orion pH meter. Test solutions pHs were adjusted using H_2SO_4 (0.1 N) and NaOH (0.1 N). The metal concentrations in the samples were determined using an