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Adsorption behavior of hydrothermally treated municipal sludge & pulp and paper industry sludge

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HIGHLIGHTS

- Hydrothermally produced adsorbents were effective adsorbents for positively charged Pb(II) metal ions.
- Hydrothermal carbonization showed potential for the production of carbonaceous material and waste materials can be used as feedstock of low-cost adsorbents.
- Pb(II) had the highest adsorption efficiency from tested metals and adsorption followed Sips adsorption isotherm.
- Adsorption kinetics followed non-linear pseudo-second order kinetic model.

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ABSTRACT

Aim of the study was to investigate how hydrothermal carbonization changes adsorption efficiency toward metal ions of typical sludges. Hydrothermal carbonization is a novel and green method of treating biomasses. Reactions take place in an aqueous environment at relatively mild temperature and high pressure resulting a different end biomass structure than obtained from traditional pyrolysis. Anaerobically digested sludge (ADS) and pulp and paper industry sludge (INS) were utilized as a feedstock. Adsorption behavior of ADS and INS was examined towards Pb(II), Cr(III), Cr(VI), As(III) and As(V). Both ADS and INS were found to remove Pb(II) effectively and followed Sips adsorption isotherm. Adsorption kinetics was fast and followed pseudo-second order model. Furthermore, intraparticle diffusion was observed to be partly responsible in the adsorption process. Hydrothermal carbonization indicated high potential for the production of novel carbonaceous materials for metal removal from waters.

1. Introduction

In wastewater and drinking water treatment activated carbon has widely been used as an adsorbent because of its efficiency to remove organic compounds, metals and other inorganic pollutants. Activated carbon refers to carbon-based materials with characteristics such as highly developed porosity, large surface area, variable surface chemistry, and high degree of surface reactivity (Bhatnagar et al., 2012).

Despite of wide use of activated carbon its exploitation is sometimes restricted due to high cost, which depends on availability of the raw material, processing requirement, treatment conditions, and both recycle and lifetime issues (Gupta et al., 2009). Therefore, researchers are looking for new low-cost alternatives for activated carbon where raw materials comprise of natural materials (wood, peat, lignite, clay etc.), as industrial, agricultural or domestic wastes and byproducts. Replacement of activated carbon by low-cost adsorbent would reduce the production cost of adsorbents. In addition exploitation of waste materials as feedstock would reduce partly the cost of waste disposal. In the view of low production cost, regeneration of the material would not be necessary (Babel and Kurniawan, 2003; Bhatnagar and Sillanpää, 2010; Dias et al., 2007).

Hydrothermal carbonization (HTC) is an unconventional method for the production of carbonaceous material. Process is attractive due to its green aspect, simplicity, low-cost, and energy and CO_2 efficiency (Titirici et al., 2012). Major advantage of HTC over other methods for the production of carbonaceous material is converting wet input material into solids without the need for energy-intensive drying before and during the process. This expands the feedstock choice to high water content raw materials such as wet animal manures, human waste, sewage sludge, municipal solid waste (MSW), aqua culture and algal residues (Libra et al., 2011).

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Reaction takes place in an aqueous environment at the moderate temperature (180–250 °C) and pressure in a closed system. Pressure formation is self-generated and mostly related to water steam but also raw material and design of vessel. At process temperature around 220 °C corresponding pressure has been reported to be approximately 20 bar. Overall HTC reaction is a combination of several simultaneous reactions. Reaction mechanism includes dehydration, decarboxylation, condensation polymerization and aromatization. However, the reaction mechanism is not understood in detail (Funke and Ziegler, 2010). HTC process results higher solid yields, more water soluble organics, and fewer gases compared to dry pyrolysis, which is the most commonly used method for the production of adsorbents.

Hydrochar resembles natural coal with respect to the type of chemical bonds, their relative quantity, and chemical composition. It has also higher hydrogen/carbon and oxygen/carbon ratios than carbonaceous material from dry pyrolysis (Libra et al., 2011). Significant differences in structural studies of hydrochars produced from small pure carbohydrates and complex biomass was not noticed. These hydrochars showed similarities with respect to morphology and local structural connectivity (Titirici and Antonietti, 2010).

In this study suitability of hydrochar produced by hydrothermal carbonization for adsorption of various metals was investigated. Adsorption behaviors of these carbonaceous materials were examined towards both cationic and anionic metal ions. Furthermore equilibrium behavior and adsorption kinetics of prepared hydrochars were investigated.

2. Methods

2.1. Materials and physicochemical characterization

Anaerobically digested municipal sludge (total solids 3.5 wt.%) (Mikkeli wastewater treatment plant, Finland) and pulp and paper industrial sludge (Dry solids (total solids 38 wt.%) Ekokem) were used as a starting material. Pulp and paper industry sludge consisted of both fiber rich primary sludge and biological secondary sludge.

Heavy metals Pb(II), As(III), As(V), Cr(III) and Cr(VI) were used for the adsorption studies. All metals were of analytical grade. 1000 mg l^{-1} stock solutions were prepared from corresponding salts ($Pb(NO_3)_2$ (Merck), $CrN_3O_9 \cdot H_2O$ (Acros Organic), $K_2Cr_2O_7$ (Sigma Aldrich), As_2O_3 (Fluka) and As_2O_5 (Alfa Aesar)). Metal salts were dissolved in deionized water except As_2O_3 and As_2O_5 which were dissolved in 25% NaOH and neutralized with 37% HCl. pH adjustments were performed by 0.1 M NaOH and 0.1 M HNO_3 (As(III) and As(V) 0.1 M HCl).

Agitation of the adsorption system under investigation was performed in Rotary shaker Ika KS 4000i at ambient temperature. Changes in the metal concentrations due the adsorption were analyzed at wavelengths of 189.042 nm (As), 298.919 nm (Cr) and 220.353 nm (Pb) by inductively coupled plasma optical emission spectrometry (ICP-OES) model iCAP 6300 (Thermo Electron Corp., USA). The amount of metal ions adsorbed per unit mass of hydrochar was calculated as follows:

$$q_e = \frac{(C_i - C_e)}{m} V \tag{1}$$

where q_e (mg g^{-1}) is equilibrium adsorption capacity, C_i and C_e (mg l^{-1}) are initial and equilibrium ion concentrations, respectively, m (g) represent the weight of the adsorbent, and V (l) is the volume of the solution.

Equilibrium isotherms were calculated according to the following equations.

Langmuir isotherm equation non-linear form:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_e is the equilibrium adsorption capacity. q_m is a theoretical maximum adsorption capacity and K_L (L mg^{-1}) affinity constant.

Freundlich isotherm equation non-linear form:

$$q_e = k_F C_e^{\frac{1}{n_F}} \tag{3}$$

in which k_F (L mg^{-1}) and n_F (mg g^{-1}) are Freundlich adsorption constants.

Sips isotherm (Langmuir–Freundlich) equation:

$$q_e = q_m \frac{(K_S C_e)^{n_S}}{1 + (K_S C_e)^{n_S}} \tag{4}$$

in which K_S (L mg^{-1}) is an affinity constant and n_S (mg g^{-1}) describes surface heterogeneity. When n_S equals unity, Sips isotherms returns to the Langmuir isotherm and predicts homogeneous adsorption. On the other hand, deviation of n_S from the unity indicates heterogeneous surface. At high concentrations Sips approaches to a constant value and at low concentrations Freundlich type equation.

Modeling of adsorption kinetics was conducted by using the pseudo-first-order and pseudo-second-order models. The non-linear pseudo-first order model is expressed as:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{5}$$

The pseudo-second-order model equation is:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{6}$$

where q_t and q_e (mg g^{-1}) are the adsorption capacity at time t (min) and at equilibrium, respectively, while k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the pseudo-first-order and pseudo-second-order rate constants. Furthermore, pore diffusion as a controlling step in the adsorption was tested by intraparticle diffusion model as follows:

$$q = k_{dif} t^{\frac{1}{2}} (+C) \tag{7}$$

where k_{id} (mg g^{-1} $min^{-1/2}$) is the rate constant of intraparticle diffusion and C (mg g^{-1}) represents the thickness of the boundary layer.

Field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) was used for surface morphology examination. Surface groups of the hydrochar were observed by Fourier transform infrared spectroscopy (FTIR Vertex 70 Bruker Corp.) with integrated Diffuse Reflectance Accessory EasiDiff™ unit. Nitrogen sorption isotherms at −196 °C were determined using TriStar 3000 (Micromeritics Inc.). The specific surface area was calculated from the adsorption branch of the isotherm using Brunauer–Emmett–Teller theory, and the total pore volume was taken from the adsorbed amount at a relative pressure of $p/p_0 = 0.97$. Ash content was defined by applying SFS-standard 3008. The amount of elements C, H, N and O were analyzed by Organic Elemental Analyzer Flash 2000 (Thermo Scientific). Surface charge and isoelectric point (IEP) charge were determined by pH titration utilizing by Zetasizer Nano ZS (Malvern Instruments Ltd.). The pH where zeta potential equals to zero is called isoelectric point (IEP). Determination of pH_{IEP} is used to evaluate surface charge of the adsorbent (Li et al., 2003). FinnSonic m08 (Hersteller) was used to disperse hydrochars in the water phase.

2.2. Synthesis of carbonaceous material

Carbonaceous material was produced in stainless steel batch reactors with inner polytetrafluoroethylene (PTFE) vessel, which