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Kinetic and adsorptive characterization of biochar in metal ions removal

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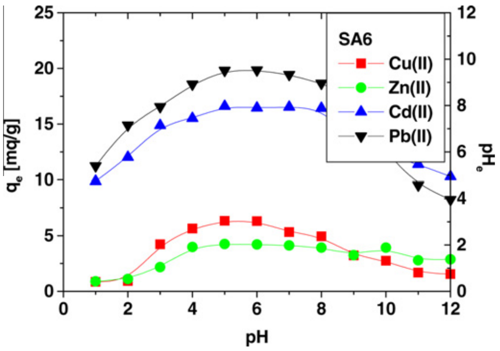
HIGHLIGHTS

- ▶ Biochars effectively removed metal ions from aqueous solutions.
- ▶ Pyrolysis at 400 °C seems optimal producing biochar as the effective metal ions sorbent.
- ▶ The maximum removal was obtained in the pH range 5–6.
- ▶ The adsorption kinetic was described well by the pseudo second order model.
- ▶ The intraparticle diffusion was not the only rate controlling step of the adsorption process.

GRAPHICAL ABSTRACT



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ABSTRACT

Kinetic and adsorption studies on the removal of metal ions such as Cu(II), Zn(II), Cd(II) and Pb(II) ions in the biochar (BC) samples have been carried out. The effects of several experimental parameters have been investigated using the batch adsorption technique at different temperature. The effectiveness of Cu(II), Zn(II), Cd(II) and Pb(II) ions removal increases with the increasing initial concentration of biochar and metal ion, pH as well as phase contact time. The maximum adsorption was found in the pH range 5.0–6.0. The kinetics of adsorption was found to be pseudo second order with intraparticle diffusion as one of the rate determining steps. Adsorption studies were also performed at different temperatures and modelled with the Langmuir and Freundlich adsorption isotherms.

1. Introduction

In the removal of hazardous contaminants from industrial waste waters from, among others, metal finishing, electroplating, plastics, pigments and mining industries, there is the distinct tendency to replace the costly activated carbons (ACs) and ion exchangers (IXs) with various low cost adsorbents, which have metal binding capacities [1–3]. BC is a porous substance, similar in appearance to charcoal that is produced by pyrolysis of feedstock under oxygen limited conditions [4]. Through pyrolysis abundant lignocellulose feedstocks, agricultural residues and biorefinery wastes, etc. can be utilized [5]. When heated to between 350 and 800 °C in a N_2 atmosphere not only BC but also bio-oil (crude oil) and non-condensable gas (‘syngas’) are obtained [6,7]. Production of biochar generally releases more energy than it consumes, depending on the moisture content of the feedstock [8]. Pyrolysis conditions and feedstock characteristics largely control the physicochemical properties of BC (e.g. composition, particle and pore size distribution) which determine the suitability for a given application as well as defininge its behavior, transport and fate in the environment.

The BC can be mainly used as large scale soil amendment for a wide range of environmental and agricultural applications

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including contaminant immobilization, soil fertilization as well as carbon sequestration. It improves soil quality by increasing soil pH (due to its neutral to basic pH), moisture holding capacity (biochar can have direct and indirect effects on soil water retention, which can be short or long lived), attracting more beneficial fungi and microbes as well as improving cation exchange capacity [9–15]. The beneficial effect of biochar application to soils on plant productivity should be also mentioned. Biochar contains stable carbon and this carbon remains sequestered for much longer periods than the original biomass [16,17]. Additionally, biochar with a high ash content can be considered a source of nutrients. In the case of low ash content it can be blended with other materials such as synthetic fertilizers, compost and manures to enhance its nutrient value. Furthermore, biochar has been shown to retain nutrients against leaching [18,19].

Generally, BC is characterized by very low homogeneity. It should also be mentioned that BC obtained at lower temperature exhibits low adsorption capacity whereas the high-temperature material is characterized by greater surface area and high microporosity [20]. The physicochemical properties determine the effects of biochar on soil functions, for example the direct effect on soil water retention is related to the large inner surface area of biochar whereas the indirect effect of biochar on water retention of soil is related to improved aggregation or structure. Biochar can affect soil aggregation due to the interactions with soil organic matter (SOM), minerals and microorganisms. The surface charge characteristics and their development over time, determine the long term effect on soil aggregation.

Biochar application is likely to improve the overall sorption capacity of soils towards common anthropogenic organic compounds (polycyclic aromatic hydrocarbons (PAHs), pesticides such as among others dichlorodiphenyltrichloroethane (DDT), herbicides as well as dyes, naphthalene nitrobenzene and 1,3-dinitrobenzene) and therefore influence toxicity, transport and fate of such contaminants and reduce their short term risk [21–25]. From an agricultural perspective it can be beneficial in terms of reducing pesticide residues in crops but detrimental in terms of reducing herbicide efficiency. Therefore compromise between the increased sorption capacities at high pyrolysis temperature activated biochar and the benefits provided by low temperature biochar in terms of reduced toxicity and absorption should be taken into account in remediation processes. The same situation occurs in the case of metal contaminated soil remediation. Biochar with high cation exchange capacities is the most suitable for use in soil remediation, but it is also likely to retain more plant nutrients by the same mechanism that it immobilizes contaminants. In the literature there is some data connected with the adsorption of Cu(II), Zn(II), Ni(II), Cd(II), Pb(II) as well as As(III,V) and Cr(III,VI) using BC derived from agricultural residues such as hardwood, corn, peanut, soybean, canola straws, oak bar, rice husk, dairy manure, and broiler litter [26,27]. For example, a dairy manure biochar made at 350 °C sorbed several times more Pb(II) than activated carbons (AC) [28].

Another aspect of the application of biochar is the reduction of the greenhouse gas emissions and its positive influence on the climate changes. It is well known that carbon dioxide is not the only gas emitted from soil. It has been demonstrated that the amount of methane produced as a part of the carbon cycle and nitrous oxide produced as a part of the nitrogen (N) cycle through the nitrification and denitrification processes can be reduced by the biochar addition to soils [29–31]. This is very important because methane is over 20 times more effective in trapping heat in the atmosphere than CO_2, while N_2O has a global warming potential that is 310 times greater than CO_2.

Biochar in a global context is very important. According to the International Biochar Initiative Organization, it is estimated that by the year 2050 (i) about 80% of all crop and forestry residues will be converted to biochar and energy, (ii) energy produced in the pyrolysis process will replace the energy that would have come from coal, (iii) significant decreases in N_2O emissions and (iv) increase in net primary production accrues from the use of biochar in soils will be observed.

As the presence of metal ions in soil and industrial waste waters can be an important source of pollution and may be a severe health hazard in the paper kinetics studies of metal ions Cu(II), Zn(II), Cd(II) and Pb(II) sorption on the BC samples were presented. They are important in evaluating adsorption operation for practical applications especially for metal ions removal from waste waters. Experiments were undertaken to understand the transport processes that take place during adsorption and to identify the rate controlling steps as well as determining external mass transfer and intraparticle diffusion rate coefficients. So far only a limited number of studies have involved the kinetic analysis of metal ions adsorption on the biochars samples.

2. Materials and methods

2.1. Materials

Biochar (BC) samples (denoted as SA4, SA6, SB4, SB6, SC4 and SC6) were obtained from pig and cow manure in a process of pyrolysis described in previous work [32]. Raw materials for the preparation of BC samples were collected, using different kind of pre-treatments (samples: SA4, SA6 – pig manure chemically pretreated slurries using Kemira separation technology; SB4, SB6, SC4 and SC6 – dairy cow manure mechanically separated slurries using Samson and Bimatech separation technology). The carbonization temperatures were 400 and 600 °C (the samples obtained at lower temperature are denoted as 4 and at higher as 6), at ambient pressure over nitrogen gas atmosphere. After the pyrolysis the BCs were ground and then sieved. In the preliminary studies it was found that the amount of Cu(II) ions adsorbed increases with the decreasing particle size of the adsorbent (these data were not presented). This is due to the increase in the available surface area with the decrease in the particle size. Therefore, the particle size fraction from 0.420 to 0.600 mm was used as optimal without further modification for all studies.

Total amount of carbon C, H and N in the BC samples was analyzed using an elemental analyzer. The average pore and surface characteristics were measured by N_2 adsorption using the BET surface area analyser. Moisture content of both the BC samples was determined according to the standard: Solid biofuels. Methods for the determination of moisture content. Oven dry method (Part 3: Moisture in general analysis sample) ICS 75.160.10, DD CEN/TS 14774-3:2004. Ash content was analyzed according to ICS 75.160.10, DD CEN/TS 14775:2004 and the volatile matter content according to ICS 75.160.10, DD CEN/TS 15148:2005. The obtained data are presented in Table 1. $CuCl_2·2H_2O$, $ZnCl_2$, $Cd(NO_3)_2·4H_2O$ and $Pb(NO_3)_2$ were used as sources of Cu(II), Zn(II), Cd(II) and Pb(II) ions. The stock solutions were further diluted to the required experimental concentrations. The other chemicals used were of analytical grade. Distilled water was used for preparing all the solutions and reagents.

2.2. Kinetic tests

A stock solution of metal ions (1 mol/dm^3) was prepared and suitably diluted accordingly to the various required initial concentrations. Adsorption experiments in the single component systems as well as in the quaternary ion systems were carried out at room temperature (20 ± 1 °C) using the batch technique. 50 cm^3 of metal