Journal of Environmental Management 146 (2014) 444–450

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Ca and Fe modified biochars as adsorbents of arsenic and chromium in aqueous solutions

Evita Agrafioti [a], Dimitrios Kalderis [b], Evan Diamadopoulos [a, *]

[a] *Department of Environmental Engineering, Technical University of Crete, 73100 Chania, Greece*
[b] *Department of Natural Resources and the Environment, Technological Educational Institute of Crete, 73100 Chania, Greece*

ARTICLE INFO

Article history:
Received 7 March 2014
Received in revised form
11 July 2014
Accepted 23 July 2014
Available online 8 September 2014

Keywords:
Fe/Ca impregnation
Biochar
Arsenic
Chromium
Adsorption

ABSTRACT

This work investigated the production of Ca and Fe modified biochars in order to use them for the removal of arsenic As(V) and chromium Cr(VI) from aqueous solutions. Rice husk was impregnated with CaO at an impregnation ratio 0.114, while both rice husk and the organic fraction of municipal solid wastes were impregnated with Fe^0 and Fe^{3+} at impregnation ratios 0.114 and 0.23. The modified biochars exhibited high As(V) removal capacity (>95%), except for the case of rice husk impregnated with Fe^0, whose removal capacity reached only 58%. All modified biochars exhibited much better As(V) removal capacity compared to the non-impregnated biochars. However, the Cr(VI) removal rates were not as high as the As(V) ones. The maximum Cr(VI) removal was observed in the case of rice husk biochar impregnated with 2.3% w/w Fe^{3+}, whereas the majority of impregnation agents examined did not manage to enhance the biochars' Cr(VI) removal ability. The equilibrium study showed that the Freundlich model can adequately describe the sorption process for the majority of samples examined. Analysis of the amount of Fe present in the equilibrium solutions suggested that the main mechanisms of As(V) and Cr(VI) removal were possibly metal precipitation and electrostatic interactions between the modified biochars and the adsorbate.

1. Introduction

Biochar is the solid by-product of the pyrolytic conversion of carbonaceous biomass under oxygen-limited conditions. Applying biochar to soils is a rather novel and promising approach since this carbon rich product has the potential to remain stable against decay, mitigating global climate change (Lehmann, 2007; Woolf et al., 2010). In addition, biochar has an inherent ability to retain nutrients and thus, when used as soil amendment, it can enhance soil fertility and physical properties (i.e. water and nutrient retention) as well as crop productivity (Glaser et al., 2002; Steiner et al., 2008). From an environmental aspect, biochar porosity, surface area and negative surface charge make it a pioneer means for restoration and remediation of soils contaminated by organic and inorganic pollutants (Beesley et al., 2011; Cabrera et al., 2014; Tang et al., 2013).

Apart from soil applications, during the last years research has focused on biochar potential role in adsorbing contaminants (both heavy metals and organic pollutants) from aqueous solutions. With regard to this promising application, a great variety of biomass materials (including forestry, agricultural and waste residues) were converted to biochars, which proved to be effective adsorbents for many organic and inorganic water contaminants (Ahmad et al., 2012; Cao et al., 2009; Chen and Chen, 2009; Mohan et al., 2007, 2011; Li et al., 2013; Liu and Zhang, 2009; Lu et al., 2012; Regmi et al., 2012; Shen et al., 2012; Uchimiya et al., 2010; Zhang et al., 2011).

The ability of biochar to adsorb heavy metals from contaminated aqueous solutions may be related to electrostatic interactions between metal cations and carbon negative surface charge, to ionic exchange between biochars surface protons and metal cations and to acidic oxygen groups (e.g. carboxylic and lactonic groups), mineral impurities (e.g. ash and metal oxides) and basic nitrogen groups present in the solid matrix of the carbonaceous materials (Machida et al., 2006; Xu et al., 2013).

Lately, there is an interest regarding the modification of biochar's physical and chemical properties aiming at the enhancement of its adsorption capacity. The so called "engineered/modified biochars" are produced either by modifying the biochar production process or by impregnating the materials with chemical agents that are likely to improve biochar sorption ability. For instance, the

---

* Corresponding author. Tel.: +30 28210 37795.
E-mail address: diamad@dssl.tuc.gr (E. Diamadopoulos).

http://dx.doi.org/10.1016/j.jenvman.2014.07.029
0301-4797/© 2014 Elsevier Ltd. All rights reserved.

anaerobic digestion of biomass prior to pyrolysis has been found to positively affect biochar ability to immobilize phosphate and heavy metals (Inyang et al., 2012; Yao et al., 2011). Xue et al. (2012) reported that treatment of hydrothermally produced biochar with H_2O_2 improved its heavy metal adsorption capacity making it comparable to that of activated carbons. Zhang et al. (2013b) used $MgCl_2$ and $AlCl_3$ solutions to prepare a biochar/MgAl-LDH sample that was found to be effective for phosphate removal, while in a relative study MgO-biochar was used for phosphate and nitrate removal from aqueous solutions (Zhang et al., 2012). Engineered biochar impregnated with aluminium (Al) has also been found to effectively remove arsenic, methylene blue and phosphate from aqueous solutions (Zhang and Gao, 2013). Finally, Zhang et al. (2013a) prepared a magnetic biochar impregnated with iron (Fe) and reported that the modified biochar had strong sorption ability towards arsenic.

In our previous work (Agrafioti et al., 2014), three different biochars, derived from rice husk, sewage sludge and the organic fraction of municipal solid wastes were investigated towards their As(V), Cr(VI) and Cr(III) removal capacity from aqueous solutions. According to that study, electrostatic interactions between the adsorbents' negative surface charge and Cr(III) cations resulted to a significant Cr(III) removal. However, As(V) and Cr(VI) adsorption was not as high as the Cr(III) one, due to the anionic nature of the heavy metal species. Sewage sludge exhibited the highest adsorption capacity of metal anions due to presence of Fe in its ash, while the removal capacity of the organic fraction of the municipal solid wastes was attributed to their high ash Ca content. On the contrary, rice husk high ash content in SiO_2 (81.3% w/w of dry matter) was related to its moderate metal adsorption capacity. Thus, the objective of the present study was to prepare a series of modified biochars aiming at the enhancement of their heavy metal sorption ability. More, specifically, Ca^{2+}, Fe^0 as well as Fe^{3+} were used, separately, as impregnation agents for the production of engineered biochars derived from rice husk and the organic fraction of the municipal solid wastes. The modified biochars were subjected to batch sorption equilibrium experiments in order to investigate their ability to remove As(V) and Cr(VI) from aqueous solutions.

2. Materials and methods

2.1. Feedstocks

Rice husk and the organic fraction of municipal solid wastes were used as precursors for biochar production. Rice husk was collected from a rice mill located in northern Greece, while the organic fraction of solid wastes was obtained from the Chania municipal solid waste materials recovery facility. Both feedstocks were dried in an oven at 103 °C for 24 h, they were then milled to <0.5 mm and stored in airtight plastic containers until further use. The physical properties of both types of biomass as well as their inorganic constituents have already been reported in our previous work (Agrafioti et al., 2014). In brief, rice husk and the organic fraction of solid wastes ash content was 17.4 and 32.0% (on dry basis), respectively, while their volatile matter content was 81.6 and 65.8% (on dry basis), respectively. Their respective fixed carbon content was 1.0 and 2.2%.

2.2. Biomass pre-treatment

In the present study the two types of biomass were impregnated with calcium and iron agents. Based on our previous findings (Agrafioti et al., 2014), the high Ca^{2+} content of the organic fraction of municipal solid wastes (their ash CaO content was 49.8%) was responsible for the biochar ability to immobilize heavy metals, as compared to rice husk biochar. Thus, for the first set of experiments, in order to enhance rice husk adsorption capacity, rice husk was impregnated with Ca^{2+} at a level equivalent to that found in the organic fraction of municipal solid wastes. More specifically, calcium oxide (CaO) was dissolved in distilled water, then a specific amount of rice husk was immersed in the CaO solution and the mixture was left stirring for 2 h at room temperature. The impregnation ratio (the mass ratio of CaO to dried biomass sample) was 0.16. The mixture was then dried in an oven at 103 °C for 24 h and stored in airtight plastic containers.

Apart from Ca^{2+}, rice husk and the organic fraction of municipal solid wastes were impregnated with Fe^0 and Fe^{3+}, separately. The amount of the iron used was equal to the amount of calcium that rice husk was impregnated with (11.4% w/w). For the case of Fe^0, iron powder <150 μm was mixed with the biomass, at a ratio of 0.114, to obtain a homogeneous sample. As far as Fe^{3+} is concerned, $FeCl_3 \cdot 6H_2O$ was dissolved in distilled water and then biomass from rice husk and the organic fraction of municipal solid wastes were separately immersed in the ferric chloride solution, at an impregnation ratio of 0.55 (mass ratio of $FeCl_3 \cdot 6H_2O$ to biomass). After stirring for 2 h, the samples were dried in the oven, at 103 °C for 24 h. All samples were stored in airtight plastic containers until further use.

In our previous work (Agrafioti et al., 2014) we reported that biochar derived from sewage sludge had a significant Cr(VI) adsorption capacity, possibly related to its ferric oxide content (sludge ash contained 12.5% Fe_2O_3). Thus, for the second set of experiments, rice husk and the organic fraction of municipal solid wastes were impregnated with Fe^0 and Fe^{3+}, at impregnation ratios of 0.023 and 0.109 respectively, so that the iron content of these types of biomass was equal to that of sewage sludge (2.3% w/w). The samples were stirred, dried and stored as described above.

2.3. Biochar production

Pyrolysis was conducted in a muffle furnace (Linn High Therm) that was supplied with nitrogen in order to maintain an oxygen-free atmosphere. Pyrolysis temperature was set at 300 °C, the temperature increase rate at 17 °C/min and the nitrogen flowrate at 200 mL/min. After reaching the target temperature, the sample was kept in the operating furnace for 60 min (residence time). Afterwards, the biochars were removed from the furnace, cooled in a desiccator, weighted and stored in airtight plastic containers.

Henceforth, the biochar produced from rice husk and impregnated with Ca^{2+}, Fe^0 and Fe^{3+} would be referred to as RH-Ca^{2+}, RH-Fe^0 and RH-Fe^{3+}, respectively, whereas the corresponding biochars derived from the organic fraction of the municipal solid wastes would be referred to as SW-Fe^0 and SW-Fe^{3+}.

2.4. As(V) and Cr(VI) equilibrium experiments

Two stock solutions of 1000 mg/L As(V) and 100 mg/L Cr(VI) were prepared by dissolving $Na_2HAsO_4 \cdot 7H_2O$ and K_2CrO_4 in distilled water, respectively. These stock solutions were further diluted in distilled water in order to obtain the two working solutions.

Equilibrium experiments were conducted using 800 μg/L As(V) and 850 μg/L Cr(VI), separately. Each experiment was conducted by mixing 150 mL of the working solution with varying concentrations of adsorbents (1–16 g/L) and agitating on an orbital shaker at 200 rpm at room temperature for 24 h. The contact time had been determined by kinetic experiments in a previous study (Agrafioti et al., 2014). At the end of reaction time, samples were withdrawn and subsequently filtered through Whatman GF/C filters and syringe membrane filters (0.45 μm). The filtrates were then