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High efficiency removal of As(III) from waters using a new and friendly adsorbent based on sugarcane bagasse and corncob husk Fe-coated biochars

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ABSTRACT

Water contamination of As is a big issue in many areas around the globe. Therefore, cheap and efficient techniques are essential facing traditional treatment methods. Then, biochars (BC) emerged recently as material that can be used for As removal. However, research about efficiency of BC produced from local feedstock is still needed. The purpose of this study is to assess the efficiency of BC produced from sugarcane bagasse (SB) together with corncob husk (CH) with and without Fe(III) (BC_{Fe}) modification to be used for removal of As(III) from waters. The BC and BC_{Fe} produced at different pyrolysis temperatures were characterised using FTIR and SEM/EDS. Adsorption capacities of BC and BC_{Fe} were evaluated *via* batch adsorption, desorption and column tests and their performance was compared with adsorption using activated carbon. The results showed that Fe modification improve substantially the As(III) adsorption in a way that both $BC_{Fe\text{-}SB}$ and $BC_{Fe\text{-}CH}$ removed from 85% to 99.9% from 1000 µg/L As(III) solutions. Both materials fitted well in Langmuir model and the maximum adsorption capacity was 20 mg/g for $BC_{Fe\text{-}SB}$ and 50 mg/g for $BC_{Fe\text{-}CH}$. The adsorption kinetics of BC_{Fe} was fast ($\leq$ 30 min) and it had a better performance than activated carbon. The column tests showed that the process is efficient even at high As(III) concentrations. The fast removal process and good removal results make the $BC_{Fe\text{-}SB}$ and $BC_{Fe\text{-}CH}$ attractive for *in situ* and commercial (filters) use, since time and efficiency are required in new technologies.

1. Introduction

Arsenic (As) contamination of aquatic systems is a worldwide problem that severely affects people and animals. The concern related to As comes from its prevalence and high toxicity, which depends on its chemical form (Jain and Ali, 2000). Generally, As(III) species are the most toxic followed by As(V) and organic species (Jain and Ali, 2000; Wang and Mulligan, 2006).

Weathering of rocks, leaching of soils and volcanic emissions are the main natural sources of As in aquatic systems (Smedley and Kinniburgh, 2002). Human activities like mining, smelting, fossil fuel combustion, waste disposal and use of some pesticides and herbicides also contribute to the input of this metalloid in the environment (Azizur Rahman and Hasegawa, 2012; Morin and Calas, 2006). The increasing amount of As released *via* anthropogenic sources boosts the world problems related to As chronic exposure, which can cause skin diseases and cancer (Sharma and Sohn, 2009). In this way, a cheap and efficient method to remove As from contaminated water and effluents is highly desirable.

Currently, the best known techniques for the removal of As and other contaminants from aquatic systems include processes such as (ad)sorption and ion-exchange using activated carbon/modified activated carbon and alumina, iron coated sand, ion-exchange resins (Asfaram et al., 2015; Bazrafshan et al., 2017; Cumbal et al., 2003; Dambies, 2005; Haron, 1997), biosorbents (chitin, chitosan, cellulose sponge (Guo and Chen, 2005; Muñoz et al., 2002), biomass (Ghimire et al., 2002; J. Kim et al., 2006; Pokhrel and Viraraghavan, 2006)) and nanoadsorbent (Asfaram et al., 2017a, 2018; Lata and Samadder, 2016; Qu et al., 2013), such as nanocrystalline magnetite (Mayo et al., 2007), graphene oxide (Chandra et al., 2010) and $Mn_{0.4}Zn_{0.6}Fe_2O_4$ nanoparticles (Asfaram et al., 2018). Some of other techniques used are coagulation, electrocoagulation (Nidheesh and Singh, 2017; Ratna Kumar et al., 2004; Thakur and Mondal, 2017), coprecipitation, phytoremediation (Leão et al., 2017; Natarajan et al., 2011), bioremediation (Gihring et al., 2001) and biofilters (Sharma and Sohn, 2009;

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Vithanage et al., 2017), solvent extraction (Budinova et al., 2006), foam flotation (Kordmostafapour et al., 2006; Pacheco and Torem, 2002) and also membrane techniques, such as nanofiltration, reverse osmosis, and electrodialysis (Ballinas et al., 2004; Choong et al., 2007; D.H. Kim et al., 2006; Ungureanu et al., 2015).

Despite the good adsorption removal efficiency, materials used in most of these techniques are expensive and require a large amount of energy. Hence, easily available (available locally), cost-effective (processing required and treatment conditions) and efficient materials are required. The use of biochar (BC) as an adsorbent to remove As from water is classified as a low-cost adsorbent technique, making BC usage particularly advantageous when compared to the techniques described previously (Asfaram et al., 2017b). Other low-cost adsorbents can be obtained from industrial by-products/wastes chars and coals (Mohan and Chander, 2006), red mud (Genç et al., 2003; Soner Altundoğan et al., 2000), blast furnace slag (Ahn et al., 2003; Zhang and Itoh, 2005), fly ash (Diamadopoulos et al., 1993; Gupta et al., 2005), zeolites (Wang and Peng, 2010), clay minerals, coconut shells, wood char, lignin, petroleum coke, bone-char, peat, sawdust, carbon black, rice hulls, sugar, peach pits (Pollard et al., 1992) and sand (Ramakrishna et al., 2006). Besides the economic factor, agricultural products and by-products are preferable because the storage and handling of these types of wastes are easy and safe and they do not need specific operation and maintenance, and provide a noble destination for the organic load produced that could lead to accumulation of nutrients in the environment.

Surface area may not be a primary factor for adsorption on BC and, thus high surface area does not necessarily mean high adsorption capacity. Therefore, the adsorption of As probably depends on the surface chemistry (Corapcioglu and Huang, 1987). Hence, it is known that ligands as As oxyanions are adsorbed on iron hydroxide and aluminium sulphate flocs as Fe complexes (Hering, 1996). This given mechanism can be transferred to the adsorbent materials by chemical modification and thus improve the removal capacity of this type of contaminants. Consequently, the chemical modification of BC transforms it into an adsorbent with positive charge, which facilitates the As removal by the means of Coulombic interactions. Additionally, the presence of Fe groups in BC may impart a magnetic feature to the adsorbent that facilitates removal of contaminated water system (Dong et al., 2018).

This study aims to evaluate the capabilities of biochar and Fe-coated biochar produced from corncob husk (CH) and sugarcane bagasse (SB) of Brazilian crops to remove As(III) from highly contaminated aquatic systems. These feedstocks can be readily available, particularly in countries like Brazil and China, which have big sugarcane and/or maize crops (Bueno et al., 2017; Moraes et al., 2012). In addition, the use of leftover biomass from maize (corncob husk) and sugarcane (bagasse) production would minimise the waste generation and impact of these crops on the environment (Manochio et al., 2017). The As removal efficiency of Fe-coated biochars were also compared with commercially activated carbon. Furthermore, the efficiency of As removal by Fe-coated biochar in a column leaching experiment was tested.

2. Experimental

2.1. Biochar and Fe-coated biochar preparation

The corncob husk (CH) and sugarcane bagasse (SB) were washed with water and dried in a drying oven with mechanical air circulation at 80 ºC for 48 h. The material was crushed (Willey mill MA048) and the biomass powder (60 g) was pyrolyzed using a bed cylindrical reactor (0.82 cm^3) in a muffle furnace (EDGCON-3P). Four different biochars (BC) were produced after setting the pyrolysis temperature at 300, 400, 500 and 600 ºC with an increase rate of 10 ºC/min. The furnace was kept in the target temperature for 180 min (retention time) and it was cooled at room temperature for 12 h (overnight).

Fe-coated biochars (BC_{Fe}) were produced by immersing the biomass in a $FeCl_3$ solution (2.5 mol/L) for 2 h. The mixture was then dried at 80 °C for 2 h in a drying oven with mechanical air circulation. The biomass modified with Fe was pyrolyzed in porcelain crucibles using the same treatments (4 different temperatures) and conditions used for unmodified BC.

All BC and BC_{Fe} were passed through a 35-mesh sieve and stored in polypropylene bottles at room temperature until analysis.

2.2. Characterisation of biochar and Fe-coated biochar

To investigate the evolution of porosity and changes in elemental composition, the surfaces of the biochars and Fe-coated biochars were analysed by a scanning electron microscope (SEM) and by energy dispersive X-ray spectroscopy (EDS) (JEOL JSM-6010LA).

A Fourier transform infrared (FTIR) spectrometer (PerkinElmer® Spectrum 65 FTIR) with attenuated total reflection (ATR) was used to study the surface functional groups of all biochars. All spectra were obtained with 4 cm^{-1} resolution over spectral range from 4000 to 650 cm^{-1} (32 scans).

2.3. pH of zero point of charge (pH_{zpc})

The pH of zero point of charge (pH_{zpc}) was determined from adding 0.5 mg of biochar in 50 mL of ultrapure water. The experiments were performed with BC and BC_{Fe} from SB and CH (4 sets of experiments). The pH was adjusted in the range 2–12 (11 samples) using NaOH 0.10 mol/L and HCl 0.10 mol/L solutions for each biomass. All samples were shaken at 3 g at 25 ºC for 24 h. Measuring the pH of each sample and analysing the data (ΔpH × initial pH) it was found that the initial pH and the final pH were the same, which corresponds to the pH_{zpc} (Mohan et al., 2014).

2.4. Adsorption kinetics and isotherms

Adsorption kinetics experiments of As(III) on BC and BC_{Fe} produced at all pyrolysis temperatures (300, 400, 500 and 600 ºC) from SB and CH biomass were carried out by mixing 0.1 g of the adsorbent with 100 mL of 1000 µg/L As(III) solution in 125 mL erlenmeyers. The same procedure was carried out for commercially activated carbon for comparison. The erlenmeyers were shaken in a shaker for 24 h at 3 g at room temperature. Experiments were also performed without adsorbents to evaluate a possible precipitation of As. Visual MINTEQ software (freeware, version 3.0) was used to evaluate possible precipitation of As in the experiments under the same conditions. Aliquots (2 mL) were taken after 0, 1, 10, 20, 30, 45, 60, 90, 180, 300, 600 and 1440 min using syringes and immediately filtered through 0.45 µm pore size PVDF filters. All experiments were performed in duplicate at three different pH (4, 5 and 6). The As in the filtered samples were determined by inductively coupled plasma-atomic emission spectrometry (ICP OES, Agilent Technologies 700 Series).

The kinetic study provides important information regarding the reaction pathways and the mechanisms of sorption. The reaction rate and the adsorption mechanisms, for instance, play an essential role in water treatment process, since they determine the contact time necessary to the complete and efficient adsorption of the adsorbate on the adsorbent (Ho and McKay, 1999). Therefore, the pseudo-first order kinetic model and the pseudo-second order model were determined in order to investigate the sorption mechanisms of As(III) onto BC and BC_{Fe}. The equation used to describe the pseudo-first order kinetic model is (Eq. (1)) (Van Vinh et al., 2015):

$$log\,(q_e - q_t) = log q_e - (k_1/2.303)t, \tag{1}$$

where k_1 (mg/g.min) is pseudo-first order adsorption rate constant (from slopes of linear plot log(q_e − q_t) × t), q_e is the amount of adsorbate at the equilibrium time, q_t is the amount of adsorbent at equilibrium time and t is the time.