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# A magnetic nanocomposite produced from camel bones for an efficient adsorption of toxic metals from water

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A new, simple, clean, and green procedure for the production of a magnetic nanocomposite (MBBC) from waste camel bone biochar was here described. MBBC particles were in the nano-size range (~12 nm), having characteristics of both hydroxyapatite and magnetite. The produced nanocomposite was characterized by FT-IR, XRD, TG, SEM, TEM, BET, XRD, Zeta potential and XPS analyses. MBBC exhibited a paramagnetic behavior, having a saturation magnetization of 50.20 emu/g and a mesoporous structure with a BET surface area of 162 $m^2/g$. The FT-IR spectrum of MBBC displayed doublet peaks at 573 −601 $cm^{-1}$ (corresponding to Fe—O vibrations) and a peak at 1046 $cm^{-1}$ (associated with $HPO_4$), which support the successful formation of MBBC. The maximum adsorption capacities of MBBC, as for the Langmuir isotherm model fittings, were 344.8, 322.6 and 294.1 mg/g for Pb(II), Cd(II) and Co(II), respectively. MBBC showed rapid heavy metals adsorption rates, accomplishing ~75% adsorption within 5 min. After adsorption accomplishment, MBBC particles were magnetically separated from treated water and heavy metals from saturated MBBC were efficiently desorbed by elution with 0.01 M HCl. Under such elution, the MBBC stability against acid leaching of Fe was proved. Hence, it could be inferred that the production of MBBC from waste camel bones and its utilization for the removal of heavy metals from water is a novel approach within the cleaner production concept.



## 1. Introduction

Heavy metals, which are non-biodegradable and persistent, have a deleterious impact on both ecosystems and human health. The presence of heavy metals in the aquatic environment may limit the availability of water for its intended usage. Thus, for environmental sustainability and natural water resources conservation, stringent environmental regulations have been imposed worldwide to limit heavy metals concentration in waste effluents before their discharge into natural water reservoirs. However, in developing countries, fast industrialization together with the lack of control on heavy metals discharges is actually a relevant environmental problem.

Various physical, chemical, biological, and electrochemical treatment technologies with their respective pros and cons may be used for the removal of heavy metals from water. Among them, adsorption based treatments have been widely used to remove metal ions from water due to their low operational cost, high efficiency, handling ease, and minimal sludge generation (Yin et al., 2016). Although activated carbon is the most commonly used material for the adsorption of heavy metals from wastewater, the utilization of non-conventional adsorbents obtained from different precursors has also been reported (Khan et al., 2008).

After adsorption completion, an easy, fast, and cost effective separation of the saturated absorbent is essential for the accomplishment of an efficient removal of toxic heavy metal ions form water. Magnetic separation processes (MSPs) were introduced in the early 90's to overcome this phase separation issue (Booker et al., 1991). Since then, the MSPs have gained considerable attention for an effective adsorptive removal of contaminants from aqueous and gaseous phases (Booker et al., 1991). Prior to use, adsorbent particles to be used in MSPs must be embedded, encapsulated, or coated

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with metal oxides in order to introduce magnetic properties. Then, after the adsorptive removal of pollutants, magnetic adsorbents can be rapidly and easily separated from the aqueous and/or gaseous phase by applying an external magnetic field.

The removal of heavy metal ions from water by magnetic adsorbents is well reported in the literature. However, the adsorption capacities of such adsorbents are relatively low. For example, shellac coated iron oxide, with 39.1 emu/g saturation magnetization, was utilized for the removal of Cd(II) and showed to have an adsorption capacity of 18.8 mg/g (Gong et al., 2012). Amine functionalized silica magnetite, with a saturation magnetization of 57.2 emu/g, was used for the adsorptive removal of Cu(II) with 10.41 mg/g adsorption capacity (Lin et al., 2011). Pb(II) and Cu(II) maximum adsorption capacities of 81.78 and 69.67 mg/g were recently determined for magnetic hydrogel beads with a maximum saturation magnetization of 14.63 emu/g (Sahraei et al., 2017). Then, an efficient magnetic nanocomposite ($Fe_3O_4$@TAS) with a saturation magnetization of 41.4 emu/g, was produced and used for the adsorption of Cd(II), Cr(III) and Co(II) from water, with the respective capacities being 286, 370 and 270 mg/g (Alqadami et al., 2017).

Biochar (BC), a multifunctional solid carbon-rich residue generated by the pyrolysis of biomass, which has been traditionally used for carbon sequestration, bioenergy production and soil fertility enhancement, has recently emerged as an alternative, ecofriendly, economical, and sustainable adsorbent for water treatment (Mohan et al., 2014a). The adsorptive potential of BC for the removal of toxic metals from water is well reported (Cibati et al., 2017; Ding et al., 2016; Park et al., 2016; Qian et al., 2016; Xu et al., 2017), BC having been considered as a low-cost adsorbent (Inyang et al., 2015). In their recent review on BC utilization for aqueous heavy metal removal, Inyang et al. (2015) classified feedstock for the production of BC into three groups: i) agricultural and forest residues; ii) industrial by-products; and iii) non-conventional materials, which include bones. As for the latter, Choi et al. (Choy et al., 2004) produced a cattle bones based BC with maximum adsorption capacities of 0.477, 0.709, and 0.505 mmol/g of Cd(II), Cu(II) and Zn(II), respectively. A swine bones BC was prepared and utilized by Pan et al. (2009) for the adsorptive removal of Co(II) through ion-exchange mechanism with 108 mg/g adsorption capacity. Park et al. (2015) produced BC from chicken bones, the obtained material having Cu(II), Cd(II) and Zn(II) maximum adsorption capacities of 130, 109 and 93 mg/g, respectively. On the other hand, commercially supplied bone BC was used by Choy and McKay (2005) for the removal of Cd(II), Cu(II), and Zn(II) with maximum adsorption capacities of 0.477, 0.709, and 0.505 mmol/g, respectively. Also, González Vázquez et al. (González Vázquez et al., 2016) studied the adsorption of Zn(II) and Cd(II) onto a commercially available bone char, with capacities around 60 and 90 mg/g, respectively, which remained mostly the same under the application of a static magnetic field. However, these authors (González Vázquez et al., 2016) used a commercial bone char as received, i.e., no magnetization or additional modification was employed to alter or improve its magnetic properties. In fact, to the best of our knowledge no results have been published on the adsorptive use of magnetically modified BC intending to ease the BC separation after the adsorption process.

*Camelus dromedarius*, comprises a major livestock of Arabian Peninsula, generating 26% of waste bones (Wabaidur et al., 2017). Actually, no use is given to this stuff, which means a loss of potential revenues and also large disposal costs to avoid major aesthetic, environmental, and health problems. Therefore, Hassan et al. (2008) aimed the utilization of camel bone BC for the removal of Hg(II) from water with a maximum adsorption capacity of 28.24 mg/g. These authors (Hassan et al., 2008) highlighted the advantages of camel bone BC over many other adsorbents, due to its low cost, availability of the raw material and good efficiency. In this context, and trying to give a step forward in the cleaner production of adsorbents, the challenge of the present work was to produce, for the very first time, a magnetic nanocomposite (MBBC) from camel bone biochar and to assess its applicability for the adsorptive removal of bivalent heavy metals viz. Pb(II), Cd(II), and Co(II) from water. Finally, in view of a practical and sustainable application, it was also aimed to study: i) the recovery of adsorbed metals by acid elution; and ii) the stability of MBBC against acid leaching of Fe throughout the metal elution.

## 2. Experimental

### *2.1. Chemicals and reagents*

All chemicals and reagents used were of analytical reagent (A.R) grade or as specified. Ferrous chloride tetra hydrate ($FeCl_2.4H_2O$), and Ferric chloride hexa hydrate ($FeCl_3.6H_2O$) were purchased from Sigma-Aldrich, USA. Hydrochloric acid (HCl), ammonia solution (25% $NH_4OH$) and hydrogen peroxide (30% $H_2O_2$) were procured from Merck, Germany. Heavy metals stock solutions were prepared by using cobalt nitrate hexa hydrate $Co(NO_3)_2 \cdot 6H_2O$ (99.99%), cadmium nitrate tetra hydrate $Cd(NO_3)_2 \cdot 4H_2O$, and lead nitrate $Pb(NO_3)_2$ (99%) salts, which were purchased from BDH, England. Sodium hydroxide (NaOH) was purchased from BDH, England. All solutions were prepared in ultrapure water.

### *2.2. Production and optimization of MBBC*

Camel bones were collected from a local meat shop and then washed with deionized (D.I.) water to remove dirt. After washing, bones were cut into small pieces and then treated with a 30% $H_2O_2$ solution to remove traces of flesh, fat, and blood. The bones were again washed with D.I. water, dried overnight in an oven at 100 °C and then mechanically grounded. The grounded bones were placed in a boat shaped crucible and then pyrolysed in a tubular furnace. For this purpose, the furnace was heated at 10 °C/min rate until 500 °C, kept for 2 h at this temperature and then allowed to cool to room temperature. During bones heating, residence time and cooling, an inert atmosphere inside the furnace was ensured by a 100 mL/min $N_2$ flow rate. The resulting biochar was mechanically grounded and named as bone biochar (BBC). Then, a co-precipitation method was used to magnetize BBC. Typically, 2.7 g $FeCl_3.H_2O$ and 0.0994 g $FeCl_2.4H_2O$ were added to 200 mL of 0.1 M HCl solution in three necks round bottom flask and the mixture was continuously stirred for 30 min under $N_2$ atmosphere (to avoid oxidation). BBC was then added to this mixture, which was further stirred for 60 min at 80 °C. Different masses of BCC were tested at this point, namely 0.00, 0.05, 0.10, 0.15 and 0.20 g. The aim was to maximize product output within a cleaner production scheme and, with this purpose, to find out the optimum mass of BCC to be used for the production of a magnetic bone biochar (MBBC) with maximum metals adsorption capacity. Then, 20 mL of $NH_4OH$ solution were added drop wise to the mixture under high-speed mechanical stirring at 80 °C. A black color hybrid product was collected by sedimentation with the help of an external magnetic field. This product was then washed several times with D.I. water until obtaining a stable ferrofluid. Finally, the obtained hybrid product (MBBC) was dried overnight in a vacuum oven at 50 °C.

### *2.3. Characterization of MBBC*

A Fourier transform infrared spectrometer (FT-IR: Nicolet 6700, Thermo Scientific, USA) was used to record infrared spectra of MBBC before and after utilization for metal adsorption. FT-IR