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JOURNAL OF RARE EARTHS, Vol. 34, No. 1, Jan. 2016, P. 99
JOURNAL OF RARE EARTHS
www.re-journal.com/en/

Removal of trivalent samarium from aqueous solutions by activated biochar derived from cactus fibres

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Received 10 June 2015; revised 29 October 2015

Abstract: The efficiency of activated biochar fibres obtained from *Opuntia Ficus Indica* regarding the sorption of trivalent samarium (Sm(III)) from aqueous solutions was investigated by batch experiments. The effect of various physicochemical parameters (e.g. pH, initial metal concentration, ionic strength, temperature and contact time) on the Sm(III) adsorption was studied and the surface species were characterized by FTIR spectroscopy prior to and after the lanthanide sorption. The experimental results showed that the activated biochar fibres possessed extraordinary sorption capacity for Sm(III) in acidic solutions (q_{max}=90 g/kg, pH 3.0) and near neutral solutions (q_{max}=350 g/kg, pH 6.5). This was attributed to the formation of samarium complexes with the surface carboxylic moieties, available in high density on the lamellar structures of the bio-sorbent.

Keywords: samarium; waters; activated biochar fibres; enhanced sorption capacity; FTIR spectra; rare earths

Due to the continuously increasing global demand for green and sustainable products in energy, and manufacturing uses as well as the fact that mining and processing activities have the potential to create a number of environmental risks, efficient recovery of rare earth elements (REE) from large quantities of processing solutions and industrial wastewaters is of particular importance to protect the environment and cover the demand for green and sustainable products in energy production and manufacturing[1]. In addition, trivalent lanthanides are used as a non-radioactive analogues for trivalent actinides, such as americium and curium, because trivalent actinides and lanthanides present similar chemical behaviour in solid and aqueous phase, which is attributed to the fact that the f-elements have almost identical ionic radii[2].

Wastewaters produced by industrial activities have usual complex compositions and contain increased amounts of toxic metal ions. Toxic metal ions in wastewaters are of major environmental concern and contaminated waters, which may cause environmental and health problems and need to be treated prior to their disposal into environment. Removal of toxic metal ions from large volumes of wastewaters requires a cost effective remediation technology. Conventional technologies relying on mineral adsorbents or chemical flocculating agents are relatively expensive. Adsorption and ion exchange are among the most studied wastewater treatment technologies, which have been effectively applied using a wide range of different materials, including low-cost and highly available biomass by-products[3,4].

Activated carbons and biochars are very good adsorbents for the removal of heavy metal ions and the treatment-purification of waters, because of their large surface area and the high affinity of their surface active groups for polyvalent metal ions and other pollutants[5,6]. Therefore, activated carbons are used in a number of possible technological and analytical applications. Removal of heavy metal cations from water is influenced by various factors, such as solution concentration and pH, contact time, carbon dosage, and sorbent surface modification procedure. Although the mechanism of metal ion adsorption that has been extensively studied is not yet adequately understood[7,8] and hence investigations on the interaction of metal ions with the carbon surface active groups are of particular interest and fundamental for the development of wastewater treatment technologies based on sorption/desorption processes.

On the other hand, relatively high production costs make the use of activated carbon impractical for the treatment of large quantities of wastewater by domestic use and industry. Hence, finding cheap alternative sources and enhancing the efficiency of the existing materials could make activated carbon attractive agents for a large-scale treatment of wastewaters[3,7]. Biomass by-products could be viable sources because they are abundant in nature or are produced in large quantities as by-products or wastes from agricultural or industrial activities[9,10]. Although most organic materials are suitable for conversion into activated carbon, lignocellulosic materials with high hardness and density are far better precursors[6–10]. On the other hand, the efficiency of the materials can be enhanced by oxidizing the surface of the

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DOI: 10.1016/S1002-0721(14)60584-6

carbon in order to increase the number of surface active sites, mainly given by oxygenated active groups such as carboxylic and phenolic moieties[7,11].

The present study dealt with the adsorption of trivalent lanthanides (Ln(III)) by activated carbon/biochar prepared from a biomass by-product (Opuntia Ficus Indica cactus fibres). The fibrous structure of the precursor material, which is a biomass by-product, is expected to result in relatively low-cost product (activated biochar) with increased separation efficiency because of its large external surface available for adsorption[12,13]. The main goal of the study was besides characterisation of the material, the investigation of various parameters (e.g. pH, lanthanide concentration, ionic strength, temperature and contact time) affecting the biosorption performance and the determination of thermodynamic parameters (e.g. K_d, ΔG, ΔH and ΔS), which are of fundamental importance for the development of water treatment technologies related to toxic metal removal.

1 Materials and methods

1.1 Materials

All experiments were performed under normal atmospheric conditions in aqueous solutions. The preparation of the metal ion solutions was carried out using the nitrate salt of samarium ($Sm(NO_3)_3 \cdot 6H_2O$, Sigma-Aldrich). pH measurements were performed by a commercial glass electrode, which was calibrated using a series of buffer solutions (pH 2, 4, 7 and 10). The adsorbent used in this study was activated biochar prepared from Opuntia Ficus Indica cactus fibres, which were separated from dried leaves and prepared as described elsewhere[14]. Characterisation of the material by scanning electron microscopy (SEM, Vega TS5136LS-Tescan) and N_2-adsorption (ASAP 2000, micromeritics) for the determination of the specific surface area based on the Brunauer-Emmett-Teller-theory (BET measurements) was previously described[12–15].

The characterization of the activated after Sm(III) sorption was performed by Fourier transform infrared spectroscopy (FTIR spectrometer 8900, Shimadzu) and acid/base titrations. FTIR measurements were performed by means of translucent KBr disks including finely ground biomass, which was encapsulated at a 10:1 mass ratio. For the titrations, alkaline biosorbent suspensions (0.5 g in 15 mL of deionized water) of the product prior to and after samarium sorption were titrated by 0.1 mol/L $HClO_4$ standard solutions (BDH Laboratory Supplies) under continuous magnetic stirring. After each addition of the titrant, the pH was allowed to reach equilibrium and finally measured by means of a pH-meter (Hanna Instruments).

1.2 Adsorption measurements

The adsorption studies were performed by conducting batch-equilibrium experiments in 60 mL PE screw-cap vials. Generally, test solutions (30 mL) containing the metal ion, of known composition and concentration, were mixed with a given mass of the activated biochar (0.01 g) and the mixture was shaken in a thermostatic orbital shaker (at 100 r/min) for 24 h to assure that equilibrium had been reached. Specifically, the effect of pH was studied in the pH range between 2 and 7, at constant Sm(III) concentration ($[Sm(III)]_o=5\times10^{-4}$ mol/L) in the suspension and T=23 ºC. For studying the effect of initial Sm(III) concentration, the latter was varied between 5×10^{-6} and 9×10^{-3} mol/L in the test suspensions (0.01 g activated biochar in 30 mL solution) at pH 3 and 6.5. The effect of temperature was studied between 30 and 70 ºC using test suspensions (0.01 g biochar in 30 mL solution, $[Sm(III)]_o=5\times10^{-4}$ mol/L) at pH 3 and 6.5. For kinetic studies certain amount of the activated biochar (0.033 g) was mixed with 100 mL of Sm(III) solutions ($[Sm(III]_o$ 5×10^{-4} mol/L, T=23 ºC) at pH 3 and 6.5 and the metal concentration was determined at regular time steps. For the samarium analysis aliquots withdrawn were centrifuged and filtered with membrane filters (pore size: 450 nm) and the samarium concentration was determined spectrophotometrically (UV 2401 PC Shimadzu) by means of arsenazo-III, according to a previously described method[16]. For each test solution, a corresponding reference solution was prepared and was similar to the test solution except that it did not contain the adsorbent material.

The relative amount of Sm(III) adsorbed was determined using the following equations:

$$\text{Rel. adsorption}(\%)=100\cdot\frac{[Sm(III)]_o-[Sm(III)]_{aq}}{[Sm(III)]_o} \quad (1)$$

$$K_d=\frac{[Sm(III)]_o-[Sm(III)]_{aq}}{[Sm(III)]_{aq}}\cdot\frac{V}{m}\text{(L/kg)} \quad (2)$$

where $[Sm(III)]_o$=the total lanthanide ion concentration (mol/L) in the system or in the reference solution, $[Sm(III)]_{aq}$=lanthanide ion concentration (mol/L) in the test solution after equilibrium, V (L) is the volume of the test solution and m (kg) is the mass of the adsorbent.

Furthermore, the K_d values have been used together with the linear form of the van't Hoff equation (Eq. (3)) and the Gibbs free energy isotherm (Eq. (4)) to estimate the corresponding thermodynamic data[17]

$$\ln K_d=-\frac{\Delta H^0}{R\cdot T}+\frac{\Delta S^0}{R} \quad (3)$$

$$\Delta G^0=-R\cdot T\cdot\ln K_d \quad (4)$$

1.3 Statistical analysis

All experiments were performed in triplicate and the