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Adsorption of aqueous rare earth elements using carbon black derived from recycled tires

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HIGHLIGHTS

- Carbon black obtained from pyrolyzed tires adsorbs aqueous rare earth elements.
- Adsorption of a mixture of rare earth elements (Y, La, Ce, Nd, and Sm) was examined.
- Adsorption followed pseudo-second order kinetics and Freundlich isotherm.
- The adsorption was found to be energetically favorable and endothermic.

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ABSTRACT

The adsorption of an aqueous mixture of light rare earth elements (Y, La, Ce, Nd, and Sm) by carbon black derived from pyrolyzed end-of-life tires was investigated. The recycled tire carbon black (RTCB) was compared with other commercial carbon and functionalized carbon sorbent materials. The RTCB demonstrated improved adsorption for all the rare earth elements in this investigation over other carbon sorbent materials under a variety of conditions. The adsorption isotherms were observed to follow the Freundlich model with pseudo-second order kinetics. Analysis of thermodynamic state functions suggests the adsorption to be endothermic, energetically favorable under the conditions of study, and a dissociative adsorption mechanism. The use of RTCB as a sorbent material for extraction of aqueous REEs is attractive due to its inexpensive cost and utilization of a recycled material stream.

1. Introduction

Extraction methods of Critical Materials [1] (e.g., rare earth elements, REE) is of interest to government initiatives and industry research. In 2010, the U.S. Department of Energy released a *Critical Materials Strategy* report outlining the vital role that REE and other materials play in the clean energy economy [1]. This group of elements also plays a vital role in other current technologies such as catalysis, magnets, and display technologies. Rare earth milling and processing is a complex, ore-specific operation that has potential for environmental contamination when not controlled and managed appropriately [2].

Currently all REEs are extracted through mining and mineral processing of REE ores. Established techniques such as solvent extraction and precipitation are used for metal recovery, which are especially useful for large-scale operations with high metal ion concentrations. In contrast, adsorption can be used to recover metal ions from low-concentration sources by means of relatively simple processes. Many adsorbents for REEs have been studied [3–15]; nevertheless, there is no adsorbent material in practical use to date. The requirements for practical adsorbents include high selectivity for rare earth metal ions, adsorbability at low pH, easy desorption of the metal ions, fast adsorption and desorption rates, high adsorption capacity, durability against repeated use, low cost, and high mechanical strength. After mineral beneficiation, the most common method of separating REEs is by the use of ion-exchange resins or through solvent extraction methods using tributyl phosphate (TBP) and di-(2-ethylhexyl) phosphoric acid (D2EHPA). Ionic liquids [16,17] have also been investigated for REE separation. Nevertheless, a cost-effective and environmentally sound selective separation of individual REEs remains a challenge to date.

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This study examines using carbon black derived from whole used tires obtained by pyrolysis [18], as a sorbent material for REE. Waste tires can be recycled through several processes aiming for either material, energy, or chemical product recovery [19]. Previously, pyrolyzed tires have been examined as an inexpensive sorbent material for aqueous Cr(VI) [20] and mercury [21] removal. The use of carbon black from recycled tires has several advantages: it drastically reduces not only the cost and energy required to produce carbon black, but also environmental impacts as well. For example, the gases generated during the pyrolysis of tires can be used for supplying the heat required by the process, as it can be energetically self-sufficient [19]. Using inexpensive sorbent materials such as carbon black from recycled automobile and large mining equipment tires has the potential to make REE extraction economical while utilizing a recycled materials stream. Commercial carbon black is commonly made by partial combustion of hydrocarbons. This makes the price of carbon black dependent on the market prices of petroleum products. Using waste tires as the source for carbon black is an attractive method where the market price is not dependent on the oil industry and recycles an end-of-life material. Worldwide, large quantities of waste tires are produced annually. For example, annually 3.27×10^6 tonnes of waste tire come from the European Union, 3.87×10^6 tonnes from the U.S., and 1.01×10^6 tonnes of waste tires arising from Japan [22].

2. Experimental methods

2.1. Adsorption/desorption experiments

Various carbon particles viz., activated carbon (AC, Calgon), functionalized activated carbon (F-AC), commercial carbon black (CCB, Alfa Aesar, acetylene derived, 50% compressed, bulk density 80–120 g/L), functionalized commercial carbon black (F-CCB), and recycled tire carbon black (RTCB, ORT Wheels Engineering, LLC. [18]) were used to examine the adsorption efficiency of REE in solution. The AC, CCB and RTCB carbon particles were used as received without any treatment, whereas the F-AC and F-CCB were functionalized with phosphine groups. The phosphine functionalization of AC and CCB were carried out using the procedure described by Willocq et al. [23].

Aqueous solutions containing 100 mg per liter (or 100 ppm) of REE were used for adsorption studies, unless otherwise noted. Nitrate salts of La, Ce, Nd, Sm, and Y were used in the adsorption experiments. To mimic geothermal conditions, all the REEs were mixed together in the same solution and the various carbon sorbent materials were tested at room temperature. Adsorption studies at raised temperature were also performed on RTCB at 40, 60 and 80 °C. In each case, a sample of this mixed REE solution was taken for analysis to determine the concentration of the solution as well as the stock solution using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Spectro Genesis). The REE adsorption capacities for the different carbon particles were determined through adsorption isotherms. REE adsorption capacity gives the REEs loading on the carbon in equilibrium with residual REE concentration in solution after 24 h contact time.

Masses from 0.6 to 10 g from each of the carbon samples were weighed into 250 ml plastic reactors. Each carbon sample in the plastic reactor was contacted with 200 ml of the 100 ppm mixed REE solution and shaken in a laboratory orbital shaker for 24 h at 25 °C, while the shaker speed was maintained at 200 rpm. The adsorption experiments at elevated temperatures were performed in 300 ml round-bottom glass flasks with constant stirring. After the shaking cycle was completed, the carbon in each vessel was filtered off under vacuum using a Nalgene™ filter. From the ICP-OES solution analysis, the REE adsorbed by the carbon in each case was determined by the difference in element concentration before and after adsorption multiplied by the volume of REEs solution used. The kinetics of adsorption was examined using a concentration of 20 ppm REE mix solution, with a loading of 5 g of RTCB. The adsorption kinetics was examined by periodically withdrawing ~10 ml of solution, which was then filtered and subsequently analyzed via ICP-OES. The effect of temperature was examined over the range of 25–80 °C. The adsorption percentage was determined using the following relationship:

$$\%\ \text{Adsorption} = (C_{REE,i} - C_{REE,t})/C_{REE,i} \times 100 \qquad (1)$$

where $C_{REE,\,i}$ and $C_{REE,\,t}$ are the initial REE concentration and the REE concentration at time t (ppm), respectively.

Desorption experiments have been carried out as well. After a mixture of 100 ppm REEs were adsorbed onto the RTCB at room temperature overnight, the RTCB was filtered and then re-suspended in a stripping solution and stirred again overnight. After filtering, the solution was analyzed by ICP-OES and the percent desorbed determined. Other metals commonly found in geothermal water such as zinc and manganese [24] were also tested to see if there was an effect on the REE adsorption on RTCB.

2.2. Characterization

Scanning electron micrographs and electron dispersion spectroscopy mapping were collected using a Hitachi S-4800 SEM with an Oxford EDS detector. XRD analysis was carried out using a Rigaku Miniflex XRD (CuKα = 1.54059 Å) from 2θ = 20 to 60° with a step size of 0.01° and dwell time of 0.5°/min. The XRD data was analyzed using Rigaku PDXL2 analysis software. The Brunauer–Emmett–Teller (BET) surface area of the sorbent materials were evaluated using a Micromeritics ASAP 2020 analyzer. Prior to degassing, the carbon samples were dried at 110 °C overnight. After drying, the sample was degassed in vacuum at 200 °C for 1 h. The surface area was determined by N_2 adsorption/desorption isotherms collected at −196 °C. A Shimadzu SALD-2300 Laser Diffraction Particle Size Analyzer analyzed the particle size of RTCB. Raman Spectra was recorded using a Thermoscientific DXR Raman microscope operated with a 10 mW 532 nm laser with an estimated spot size of 2.1 μm.

3. Results

3.1. Characterization

Scanning electron micrographs of AC, CCB, and RTCB are shown in Fig. 1. The larger images are at a magnification of ×5 k, while the inset images are at a magnification of ×100 k. The images collected for AC shows a large distribution of pores (Fig. 1a) and mesopores as well. It appears as though CCB (Fig. 1b) and RTCB (Fig. 1c) particles are a collection of smaller agglomerated particles, as opposed to AC, which appears to be a continuous carbon matrix with low-volume pores. Analysis of the particle size distribution for RTCB (Fig. 1d) shows an average particle size of 19.96 ± 0.28 μm.

Multiple-point BET surface area of AC, CCB, and RTCB were analyzed under liquid nitrogen isothermal conditions. Fig. 2 shows the N_2 adsorption–desorption isotherms of the parent carbon sorbent materials. The isotherms for CCB and RTCB can be classified as type III, while the AC isotherm can be classified as type V. The isotherms for CCB and RTCB exhibit non-porous behavior, while the hysteresis observed in the AC isotherms is attributed to the mesoporosity. A relatively high BET surface area of 931.38 m^2/g was obtained for AC, while the BET surface area was much lower for CCB and RTCB at 63.79 and 57.10 m^2/g, respectively. The obtained BET surface areas for CCB and RTCB are in the range of those previously