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Polymer coated vermiculite–iron composites: Novel floatable magnetic adsorbents for water spilled contaminants

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Abstract

Magnetic adsorbents based on vermiculite-iron have been prepared and characterized by magnetic measurements, BET surface area, Mössbauer spectroscopy, powder X-ray diffraction, scanning electron microscopy, thermogravimetric and differential scanning calorimetric analyses. These magnetic materials show two important features for the remediation of contaminated sites: (i) they float on water and can be used to adsorb/absorb spilled oils and (ii) after adsorption they can be easily removed from the medium by a simple magnetic separation procedure. These magnetic materials have been coated/hydrophobized with polymers such as epoxy resin and polystyrene improving their oil remotion capacity, floatability and the chemical and mechanical resistance.

Keywords: Vermiculite; Magnetic composites; Polymer coating

1. Introduction

The development of magnetic particle technology has received considerable attention in recent years. Magnetic particles can be used to adsorb contaminants from aqueous or gaseous effluents and after the adsorption is finished the adsorbent can be separated from the medium by a simple magnetic process. Some examples of this technology is the use o magnetite particles to accelerate the coagulation of sewages (Booker et al., 1991), magnetite coated functionalized polymer such as resin to remove radionuclides from milk (Sing, 1994), poly(oxy-2,6-dimethyl-1,4-phenylene) for the adsorption of organic dyes (Safarik et al., 1995) and polymer coated magnetic particles for oil spill remediation (Orbell et al., 1997). We have developed low cost and readily prepared magnetic adsorbents based on activated carbon/iron oxide (Oliveira et al., 2002) or bentonite/iron oxide composites (Oli-

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veira et al., 2003). These magnetic composites combine the excellent adsorption features of bentonite and activated carbon to remove contaminants from aqueous effluents (Murray, 2000; Sanchez and Sanchez, 1983; Ainsworth et al., 1987; Rodriguez et al., 1988; Shu et al., 1997; Torrents and Jayasundera, 1997; Danis et al., 1998; Konstantinou et al., 2000; Cadena et al., 1990; Panday et al., 1984; Ryachi and Bencheikh, 1998; Gier and Johns, 2000; Barbier et al., 2000) with the magnetic properties of iron.

Vermiculite contains typically 5–20% water located in the interlayer space and between the particles (De la Calle and Suquet, 1988). An interesting property of vermiculite is that upon a sudden heating at temperatures higher than 700 °C the water molecules evaporate abruptly from the inside of the structure separating packets of layers. As a result, the clay volume increases 3 up to 20 times (Santos, 1975; Santos and Navajas, 1976; De la Calle and Suquet, 1988) and its density strongly decreases to ca. 0.05–0.30 g cm^{-3}. This vermiculite floats on the water surface(Santos, 1975). This expanded or exfoliated vermiculite possesses a highly developed porous structure. This exfoliated mineral has been reported in some studies as effective to remove spilled oil from the water surface due to the strong capillary action of the slit shaped pores (Martins, 1990; Leão et al., 1996; Machado, 2000).

In this work, magnetic composites based on the expanded vermiculite and iron have been prepared. These materials float on water and can be used to remove spilled oil contaminants. After adsorption, the vermiculite/oil mixture can be removed from the medium by a simple magnetic separation process. The magnetic composites were coated with hydrophobic polymers in order to increase their adsorption capacity and improve their chemical and mechanical resistance.

2. Experimental

The vermiculite was obtained from Catalão (Brazil). The granulometric fraction used was 0.2–0.5 mm, which is considered a waste by the mining industry. The approximate composition obtained by SEM/EDS microprobe is:

$$(Al_{0.30}Ti_{0.04}Fe_{0.63}Mg_{2.00})(Si_{3.21}Al_{0.79})O_{10}(OH)_2$$
$$Mg_{0.13}Na_{0.02}K_{0.10}(H_2O)_n.$$

The exfoliation was carried out by introducing the vermiculite in a quartz tube at 1000 °C for 60 s.

The composites were prepared by impregnation of exfoliated vermiculite (EV) with different volumes of a solution 0.06 M of $Fe(NO_3)_3$ to produce different Fe:EV ratios. After drying, the samples were reduced under H_2 flow in a quartz tube at 400 °C for 1 h.

Powder XRD diffractograms were obtained with a Siemens D5000 with Ni filtered Cu–K_α (λ=1.5418 Å). The TG analyses were made in a SDT simultaneous TGA-DTA model TA, under air atmosphere with heating rate of 10 °C min^{-1}. The magnetization measurements were carried out in a portable magnetometer with a fixed magnetic field of 0.3 T (Coey et al., 1992). TPR (Temperature Programmed Reduction) profiles were obtained in Chembet 3000 Quantachrome equipment. In these TPR experiments the samples are heated in the presence of H_2 and the reduction reactions monitored by the hydrogen consumption. Mössbauer spectroscopy measurements were carried out with a ^{57}Co/Rh source at liquid N_2 temperature calibrated with α-Fe. The Scanning Electron Microscopy (SEM) analyses were made in a Jeol-JKA-8900RL with Au sputtering coated samples fixed in a carbon tape.

The polymer coating was performed using a solution of the epoxy resin in ethanol or polystyrene in acetone. The coated vermiculites were prepared by immersion in the polymer solution followed by removal of the solvent at 80 °C. The adsorption experiments were carried simulating an oil spilling situation using 10 mL of contaminant, i.e., soybean oil or n-octanol, in 100 mL water. To the suspension it was added 1 g vermiculite under stirring. After 30 min the vermiculite was magnetically removed from the medium and the excess of the contaminant present on the vermiculite surface was removed by flushing water. The adsorbed soybean oil was measured by weighting. The amount of adsorbed n-octanol was obtained by extraction and analysis by gas chromatographic analyses (Shimadzu 17A, FID detector, column Carbowax 20 M, 30 m) using cyclohexanol as internal standard. All the adsorption tests were carried out in triplicate with a error of ±10%.

To study the resistance to pH 50 mg of the composite were immersed in solutions with pH varying in the range 1–13 for 78 h. After this period it was measured the iron leaching by atomic absorption (Carls Zeiss Jena AAS) and the magnetization of the composites.

The floatability tests were carried out with approximately 100 particles of vermiculite or composite in water under vigorous stirring. The number of particles going to the bottom of the flask was continuously monitored during 12 h.