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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.
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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:

$$(Al_{0.30}Ti_{0.04}Fe_{0.63}Mg_{2.00})(Si_{3.21}Al_{0.79})O_{10}(OH)_2$$
$$Mg_{0.13}Na_{0.02}K_{0.10}(H_2O)_n.$$
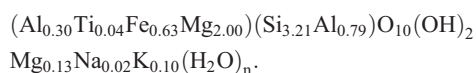
The exfoliation was carried out by introducing the vermiculite in a quartz tube at 1000 °C for 60 s.

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$_\alpha$ (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.

3. Results and discussion

3.1. Preparation of the magnetic composites and characterization of the magnetic phases
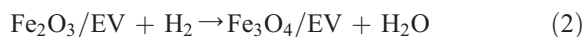
The magnetic composites were prepared in three steps: (i) wet impregnation of the iron nitrate on the vermiculite surface, (ii) thermal decomposition precursor to form Fe_2O_3/EV and (iii) controlled reduction of Fe_2O_3 with H_2 to form the magnetic phases Fe^o and Fe_3O_4.

In the first step, the $Fe(NO_3)_3$ is impregnated on the vermiculite surface from an aqueous solution and after calcination at 500 °C the phase Fe_2O_3 is formed according to the process:

$$Fe(NO_3)_3/EV \rightarrow Fe_2O_3/EV + NO_x. \quad (1)$$

In the third step, the hematite phase Fe_2O_3 is reduced with H_2 to form the magnetic phases Fe^o and Fe_3O_4.

TPR (Temperature Programmed Reduction) experiments coupled with Mössbauer and DRX studies showed that Fe_2O_3 is reduced near 325 °C to produce Fe_3O_4 (Eq. 2). The reduction of Fe_3O_4 to Fe^o takes place as a broad peak between ca. 400 up to 600 °C Eq. ((3)).

$$Fe_2O_3/EV + H_2 \rightarrow Fe_3O_4/EV + H_2O \quad (2)$$

$$Fe_3O_4/EV + H_2 \rightarrow Fe^o/EV + H_2O. \quad (3)$$

By controlling the reduction conditions, i.e., temperature and time, it is possible to produce selectively

the phases Fe_3O_4 or Fe^o. The composites were prepared by reduction at 500 °C in order to produce the phase Fe^o that shows the highest magnetization.

The preparation of the magnetic composites were also attempted by the direct formation of the phase magnetite Fe_3O_4 on the EV surface by precipitation from a $Fe^{2+}_{(aq)}/Fe^{3+}_{(aq)}$ with NaOH solution, as described earlier for composites carbon/Fe_3O_4 and bentonite/Fe_3O_4 (Oliveira et al., 2002, 2003). However, no composite was produced resulting in the formation of the oxide Fe_3O_4 completely separated from the EV.

The composites were prepared with different Fe:EV weight ratios, i.e., 0.1:1, 0.5:1, 1.5:1, 3.0:1 (iron as Fe_2O_3). The magnetization of the obtained materials, before and after reduction with H_2, is displayed in Fig. 1.

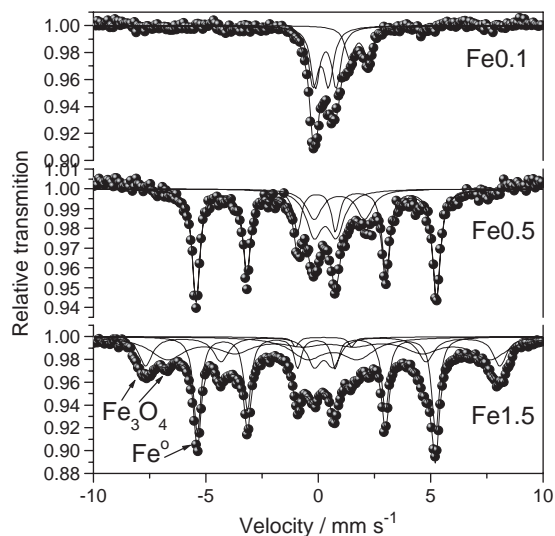Non-reduced composites did not show any significant magnetization (Fig. 1). On the other hand, the

Table 1
Mössbauer parameters for the composite Fe1.5/EV

Phase	δ/mm s^{-1} ± (0.05 mm s^{-1})	ε/mm s^{-1} ± (0.05 mm s^{-1})	B_{HF}/T ± (0.5 T)	Área/%
Fe^o	0.00	0.00	33.0	59
Fe_3O_4 [A]	0.65	0.04	46.6	33
Fe_3O_4 [B]	0.32	0.07	49.8	
Fe^{3+}	0.33	−0.01	49.5	8

δ (isomer shift relative to α-Fe^o), ε (quadrupole shift).

Fig. 1. Magnetization of the magnetic composites with different Fe:EV ratios.

Fig. 2. Mössbauer spectra of the composites reduced at 400 °C under H_2 flow for 1 h.
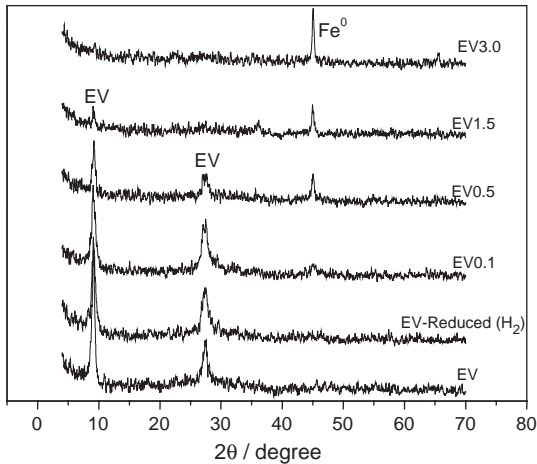
Fig. 3. Powder XRD of the composites reduced at 400 °C under H_2 flow for.

reduction with H_2 produced a bulky magnetization which increased from 1 to 4, 21, 26 and 42 J kg^{-1} T^{-1} as the Fe:EV ratios increased from 1:0 up to 1:3.0.

To identify the iron phases formed upon reduction, the obtained composites were analyzed by room temperature Mössbauer spectroscopy and by powder X-ray diffraction.

Mössbauer spectrum of the composite Fe1.5/EV reduced at 400 °C with H_2 showed the formation of two phases: Fe^o with 59% and Fe_3O_4 with 33% relative intensity (Table 1 and Fig. 2). It was also observed a central doublet likely related to Fe^{3+} species. These oxidized species can be related to: (i) Fe_{clay}^{3+} in the clay structure which was not reduced by H_2 under the reaction conditions and (ii) Fe^{3+} formed when the reduced sample was oxidized by air at room tempera-

ture. For the composite Fe0.5/EV reduced at 400 °C no magnetite signal was observed by the Mössbauer spectrum but a strong signal for Fe^o with approximately 80% relative area and two doublets probably related to Fe^{2+} and Fe^{3+} species dispersed on the material. The significant baseline deviation in the Mössbauer spectrum suggests the occurrence of superparamagnetism, likely related to the presence of magnetic iron phases at nanometric particle size. It is interesting to observe that the Mössbauer spectrum of the composite Fe0.1/EV with the lowest Fe/EV ratio showed only a series of doublet likely related to the high dispersion of the magnetic iron phases.

Powder XRD patterns confirmed the formation of iron metal with a diffraction peak at 2θ ca. 45° (Fig. 3). The intensity of this peak increases as the mass ratios of the composites Fe/EV increases. The small and broad peak at ca. 36° suggests the presence of small amounts of the spinel magnetite. The vermiculite diffraction peaks at ca. 9° and 25° gradually decrease in intensity as the Fe content increases in the composite. As the reduction with H_2 did not change the XRD profile of the EV (Fig. 3), this effect is likely related to the formation of an increasingly thick iron oxide/iron metal layer completely covering the clay surface and disturbing the diffraction process by the underlying EV structure. This can be noticed in the SEM (Scanning Electron Microscopy) images obtained for the different composites (Fig. 4).

The vermiculite particles are gradually covered with increasingly amounts of iron phases which tend to crystallize in the edges of the clay mineral layers.

To study the thermal stability of the magnetic composites thermogravimetric analyses in air were carried out (Fig. 5).
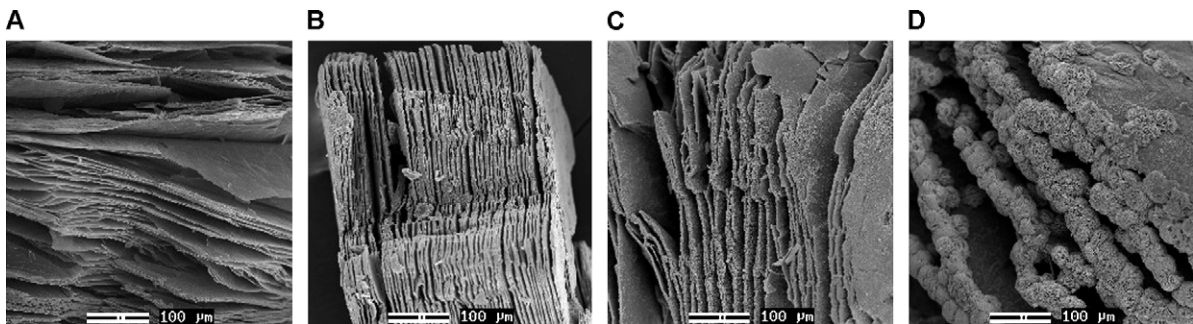

Fig. 4. SEM of the composites with different iron content: (A) Fe0.0/EV, (B) Fe0.1/EV, (C) Fe1.5/EV and (D) Fe3.0/EV.
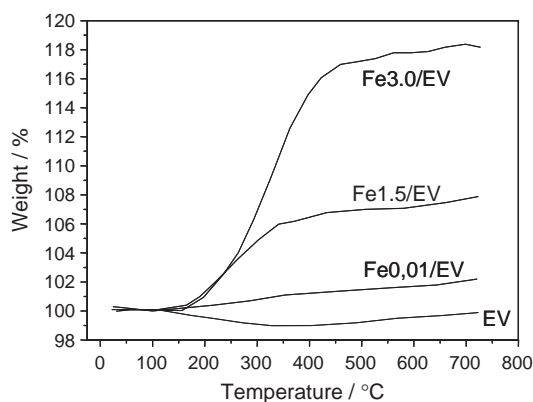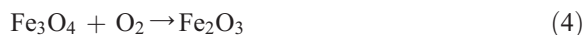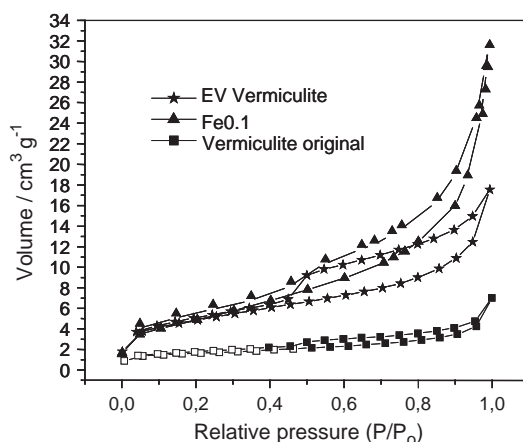
Fig. 5. Thermogravimetric analyses of the Fe/EV composites in air.

Fig. 6. Nitrogen adsorption isotherms for the samples natural vermiculite, exfoliated vermiculite (EV) and composite Fe0.1/EV.

The pure exfoliated vermiculite shows a small mass loss of approximately 1.5%. The mass of the reduced composites increases up at 150–200 °C related to the oxidation of the reduced phases according to the processes:

$$Fe_3O_4 + O_2 \rightarrow Fe_2O_3 \qquad (4)$$

$$Fe^o + O_2 \rightarrow Fe_2O_3. \qquad (5)$$

The mass increases from 1 to 7 and 18% for the composites with Fe/EV ratios of 0.01, 1.5 and 3.0%, respectively.

These oxidation reactions are also observed in the DSC (Differential Scanning Calorimetry) profiles as a broad exothermic peak in the temperature range of 200–400 °C (not shown).

The magnetization, BET surface area and microporosity of the composites with different Fe/EV weight ratios are displayed in Table 2.

The exfoliation increases the surface area from 4 to 17 m^2 g^{-1} with an increase in the microporous volume. The exfoliation process creates mainly meso and macroporous (Santos and Navajas,

1976), composed by the slits within the separated layers. These slit shaped pores are also suggested by the H3 hysteresis type observed in the nitrogen adsorption isotherms shown in Fig. 6 (Gregg and Sing, 1982; Hidrobo et al., 2003; Temujina et al., 2004).

The iron phases in the composite contribute to a significant increase in the surface area and the microporous volume.

3.2. Composite polymer coating

To provide the Fe/EV adsorbents a more hydrophobic character, the composites were coated with two different polymers, i.e., polystyrene and epoxy resin. This coating should produce an increase on the oil absorption/adsorption capacity and also improve the chemical and mechanical resistance of the com-

Table 2
BET surface area and microporosity of the vermiculite magnetic composites

Composite	Surf. area BET/m^2 g^{-1}	Micropores/cm^3 g^{-1}
Vermiculite	4	0.01
EV	17	0.02
Fe 0.1/EV	17	0.05
Fe 0.5/EV	22	0.12
Fe 1.5/EV	25	0.13
Fe 3.0/EV	30	0.15

Table 3
BET surface areas of the different polymer coated Fe0.1/EV composites

Composite	Hydrophobic agent/wt.%	BET surf. Area /m^2 g^{-1}
Fe0.1/EV	–	17
Fe0.1/EV/Epox0.01	Epoxy resin 1%	8
Fe0.1/EV/Epox0.1	Epoxy resin 9%	5
Fe0.1/EV/Epox0.5	Epoxy resin 33%	4
Fe0.1/EV/PS0.10	PS 9%	11
Fe0.1/EV/PS0.25	PS 20%	5
Fe0.1/EV/PS1	PS 50%	5

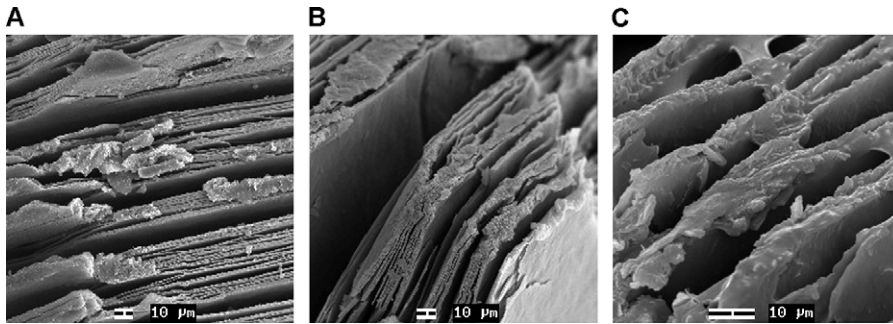Epox = epoxy resin and PS = polystyrene.

Fig. 7. SEM of the hydrophobized composite with polystyrene coated Fe0.1/EV: (A) Fe0.1/EV/PS0.10, (B) Fe0.1/EV/0.25, (C) Fe0.1/EV/PS1.0.

posite. The polymer polystyrene (PS) was selected due to its strong hydrophobic character which should increase the oil removal capacity. On the other hand, the epoxy resin (EPOX), though less hydrophobic in nature, should present a better adherence to the EV surface.

The composite Fe0.1/EV was coated by impregnation with different amounts of polymers in solutions, i.e., epoxy resin in ethanol and polystyrene in acetone. Table 3 presents the characterization of the coated composites obtained.

It can be observed that the surface area decreases as the polymer content in the composite increases. These results suggest that the coating with higher concentrations of the epoxy resin or polystyrene seems to be filling and blocking the composite porous structure leading to a decrease in the surface area. This can be clearly seem in the scanning electron micrographs

(Fig. 7). Similar results have been observed for the epoxy coated composites.

3.3. Oil removal studies

The hydrophobized composites were used for the removal of water-spilled oil contaminants. As contaminants, a very hydrophobic oil, i.e., soybean cooking oil, and a more polar viscous organic compound, i.e., n-octanol, were studied. The results can be seen in Figs. 8 and 9.

Fig. 8 shows that the composites Fe0.1/EV/epox0.1 and Fe0.1/EV/epox0.01 showed the best results removing ca. 2.3 and 2.1 $g_{oil}/g_{composite}$, respectively. For these samples the polymer coating resulted in an increase of approximately 50 and 20% in the adsorption capacity, compared to 1.5 $g_{oil}/g_{composite}$, shown by the uncoated composite. On the other
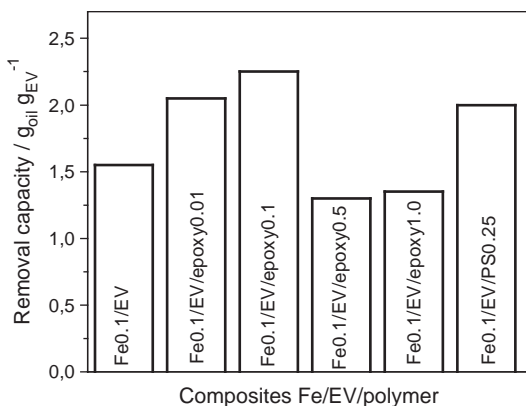

Fig. 8. Adsorption of water spilled soybean cooking oil by the polymer coated hydrophobized composites.
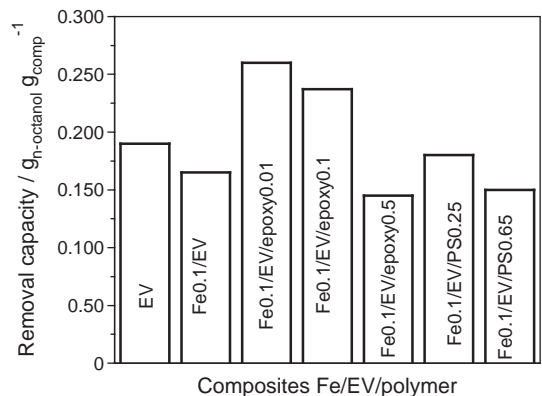

Fig. 9. Adsorption of water spilled n-octanol by the polymer coated hydrophobized composites.

hand, the hydrophobized composites EV0.1/epox0.5 and EV0.1/epox1 presented a decrease on the adsorption capacity with values of 1.2 and 1.3 $g_{oil}/g_{composite}$, respectively. These results suggest that with high polymer concentration the porous structure of the composite seems to be blocked and the removal capacity strongly reduced. The polystyrene coated composite Fe0.1/EV/PS0.25 also showed a much higher adsorption capacity of 1.9 $g_{oil}/g_{composite}$ compared to the original composite.

For the adsorption of n-octanol (Fig. 9) much lower adsorption capacities have been obtained compared to soybean oil. This is probably related to the more hydrophilic character of the alcohol. For these samples also, hydrophobization with epoxy resin improved the adsorption capacity. The composites Fe0.1/EV/epox0.1 and Fe0.1/EV/epox0.01 showed higher adsorption of n-octanol, 0.24 and 0.27 $g_{octanol}/g_{composite}$, respectively, compared to 0.15 $g_{octanol}/g_{composite}$ for the original composite. The composite Fe0.1/EV/epox0.5 again showed significantly reduced adsorption capacity. For the polystyrene hydrophobized composites Fe0.1/EV/PS0.10, Fe0.1/EV/PS0.25 and EV0.1/PS1.0 were not significantly different from original composite.

3.4. pH resistance

The chemical resistance of the magnetic composite Fe0.1/EV was studied by exposing the adsorbent to different pHs varying from 1 to 13 for 78 h at room temperature. After 78 h the iron leaching and
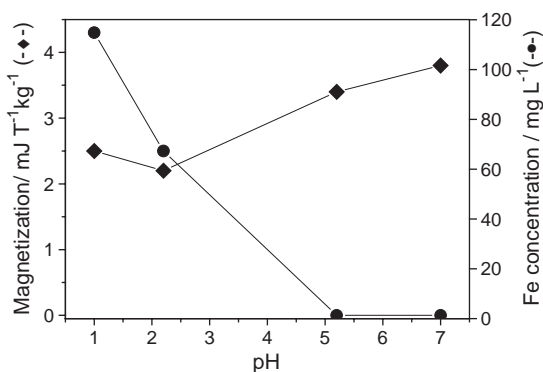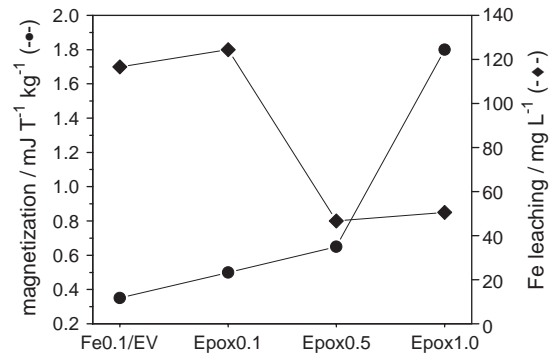

Fig. 11. Iron leaching and magnetization of the composites coated exposed to solution with pH 1 for 78 h.

the magnetization of the composites were measured (Fig. 10).

No significant iron leaching took place at pH higher than 4. On the other hand, at pH lower than 3 a strong Fe solubilization occurred leading to a strong decrease in the magnetization.

In order to investigate the effect of the polymer coating on the protection of the adsorbent, the different polymer coated composites were exposed to the most aggressive medium, i.e., pH 1, for 78 h. The magnetization and iron leaching after this treatment are shown in Fig. 11.

As the polymer content increases in the composite an improved resistance to the low pH is obtained, with higher magnetization and lower iron leaching. These results clearly indicate that the polymer layer can protect the magnetic iron phases from the aqueous medium.
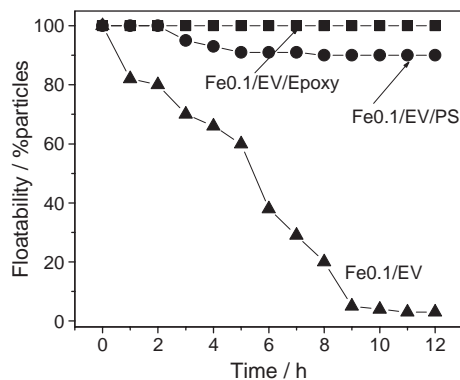

Fig. 10. Iron leaching and magnetization of Fe0.1/EV exposed to solutions with different pHs.

Fig. 12. Floatability study for the different composites.

3.5. Floatability test

Floatability is an important property of these composites for environmental application. The exfoliated vermiculite used to prepare the composites is very fragile and can easily delaminate and sink. This delamination process is especially important in small particle size exfoliated vermiculites, as the one used in this work. The composite Fe0.1/EV under stirring immediately starts to sink in water. After 9 h the composite is severely damaged and is completely sunk in water. On the other hand, it was clearly observed that the polystyrene and epoxy coated composites are much more mechanically resistant and no apparent delamination takes place even under vigorous stirring. These polymer coated composites remain floating even after 12 h in water (Fig. 12).

4. Conclusion

The magnetic composites reported in this work can be prepared by a very simple procedure using available and low cost chemicals. Magnetization measurements, XRD and Mössbauer data suggest that the main magnetic phase formed in the composites is Fe^o and small amounts of Fe_3O_4, magnetite. The presence of the Fe^o and oxides in the composite increases the surface area. These composites show several advantages over the simply exfoliated vermiculite, such as: (i) they are magnetic and can be removed from the application medium by a simple magnetic separation procedure, (ii) the hydrophobization produces a strong increase in the oil adsorption/absorption capacity, (iii) the hydrophobization strongly increases the chemical resistance of the composites towards very acidic medium, (iv) the hydrophobization strongly improves the mechanical resistance of the vermiculite, avoiding the delamination process and resulting in a completely floatable composite for long periods of time.

Acknowledgements

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