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A composite of polyethylene terephthalate and sugarcane ash-coated $FeSO_4 \cdot 7H_2O$ (PETSCA/Fe) as a low-cost adsorbent material

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ABSTRACT

A new type of composite adsorbent material matrix was prepared containing polyethylene terephthalate and sugarcane ash-coated $FeSO_4 \cdot 7H_2O$ particles (PETSCA/Fe). The dependence of the adsorption properties of the composite on the oxidative capacity of PETSCA/Fe coating was investigated by varying the Fe doping concentration. Scanning electron microscopic analysis revealed that PETSCA/Fe particles had an irregular shape and size with roughened surface similar to melanterite. Analysis by energy dispersive spectroscopy identified Fe and Si as well as Na, S, K, Ca and Cu. *X-ray diffraction* and Fourier transform infrared spectroscopy analysis demonstrated melanterite crystals, which has been widely used for wastewater treatment.

1. Introduction

In general, the quantity of plastics of all types consumed annually all over the world has been growing in a phenomenal way. The related manufacturing processes, service industries and municipal solid waste (MSW) generate large amounts of waste plastic materials [1]; post-consumer polyethylene terephthalate (PET) is the major type of plastic found in MSW [1]. Brazil generates 92 million tons of bagasse in sugarcane processing at sugar mills. The final waste material produced by sugarcane production chain is ash (SCA). Both PET and SCA materials are considered low cost, and can be used in the treatment of effluents or added to concrete in the form of fibers [1]. Iron oxides are very abundant in the Earth's crust, and can be easily synthesized in the laboratory at a low cost [2]. Due to its redox chemical behavior and low toxicity, iron has been widely used in technological applications and in various industrial processes [3]. Thus, composite materials based on PET and SCA-coated $FeSO_4 \cdot 7H_2O$ particles (PETSCA/Fe) represent a major technological advance since they combine the activated adsorption properties of carbon with the oxidative capacity of oxides dispersed on the surface.

In this context, this work presents the preparation and use of composites based on activated PETSCA/Fe with highly dispersed iron oxides for potential use in wastewater treatment. In this study, we developed a novel type of low-cost adsorbent material prepared from waste (PET and SCA).

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2. Experimental

2.1. Sample preparation

The low-cost adsorbent material PET and SCA, which were kindly by Industry and Trade Technical Plastics, Ltd. (Itupeva-SP, Brazil) and Da Mata Sugar and Alcohol, A.S. (Valparaíso-SP, Brazil), were then sieved to give a particle size of 0.85 µm before use. The PETSCA/Fe composite was prepared by the precipitation of iron oxides formed by an NaOH drip (5.0 mol L^{-1}) in an aqueous suspension containing activated PETSCA and $FeSO_4 \cdot 7H_2O$ (14 mmol) at 70 °C [4]. The material was prepared in the PETSCA to iron oxide proportions of 1:1 and 5:1 (w/w). After precipitation of the oxides, the material was filtered and washed with deionized water until neutral pH and were dried in an oven at 60 °C for 24 h.

2.2. Characterization of the sample

The structural properties of coated PETSCA/Fe particles were investigated by X-ray diffraction (X-ray diffraction (XRD), using a Rigaku Rotaflex Diffractometer with Cu-Kα radiation ($\lambda = 1.54056$ Å). The presence of melanterite was confirmed using Fourier transform infrared spectroscopy (FTIR), recorded using a Perkin Elmer FT-IR spectrometer (Spectrum 2000 model). PETSCA particles were gold-coated and the morphology was observed using a field-emission scanning electron microscope (SEM, Zeiss EVO LS15). An elemental analysis was also performed (microanalysis) of the adsorbent materials using energy-dispersive X-ray spectroscopy (EDX) by SEM.

3. Results and discussion

3.1. Microstructures

PET is a versatile polymers that is widely used in many industrial areas because of its excellent thermal and chemical resistance and mechanical properties. Fig. 1 displays a SEM micrograph of the PETSCA/Fe were amorphous in shape and irregular in size with a roughened surface (a). Magnification of the inset (dotted square) in Fig. 1(a) shows that the PETSCA/Fe composite contained $FeSO_4 \cdot 7H_2O$ crystals, i.e. melanterite (Fig. 1(b)), which indicates that PET and SCA were likely miscible and compatible in the amorphous composite. The average diameter of particles of the PETSCA/Fe composite was about 10.0 µm, which is almost 1.5 times smaller than the diameter of activated PETSCA particles (data not shown).

Fig. 2 shows the presence of chemical elements on the surface of the PETSCA/Fe composite as investigated by EDX analysis. Melanterite was initially identified by EDX, and the SEM analysis showed that the material contained Fe^{+3} as expected in the PETSCA/Fe proportions of 5:1 > 1:1.

The electron beam for EDX analysis was focused on the composite surface as shown in Fig. 2, at a high magnification. According to these patterns, the PETSCA/Fe composite contained Na, Si, S, K, Ca and Cu in the PETSCA precursor element as well as Fe as the other precursor element. This finding is supported by previous studies, mainly on silica illustrates more efficient interactions and higher compatibility between PET chains and hydrophobic nanosilica leading to lower presence of Si and Al at this composite's surface [4]. Compounds such as Na, Si, K and Ca result from the fertilization products used for sugarcane cultivation, present in the SCA [5].

The XRD and FTIR analysis indicated the intercalation of melanterite into the amorphous PETSCA/Fe material. Melanterite was analyzed by infrared spectroscopy (Fig. 3). Iron sulfate contains loosely adsorbed water molecules and thus showed strong O-H bending at ~1630–1640 cm^{-1} (v_1) and very strong O-H stretching at ~3400 cm^{-1} (v_2). The IR spectra also exhibit features resulting from the fundamental vibrations of the SO_4^{-2} anion. Fundamental vibrational bands for melanterite were observed at ~1111–1128 cm^{-1} (v_3), ~1.02 (v_4), ~873 (v_5) and ~727 (v_6) cm^{-1}. The v_4 vibration mode at ~1.02 cm^{-1} shows that the sulfate may have been adsorbed onto a metal (i.e., Cu from SCA).

Fig. 4 shows the diffractogram for the PETSC/Fe composite, possibly indicating the presence of more than one phase. According to the diffractogram, the presence of sharp peaks at ~17.3° and ~22.6° are characteristic of melanterite and are similar with to observed for iron sulfate [8]. The sharp peaks at ~12.2° (FeS_2), ~24° (SiO_2) and ~26° are probably related to quartz present in the SCA. Therefore, exposure to the room environment influences the chemical composition of this component, which can also influence the behavior of the PETSCA/Fe composite.

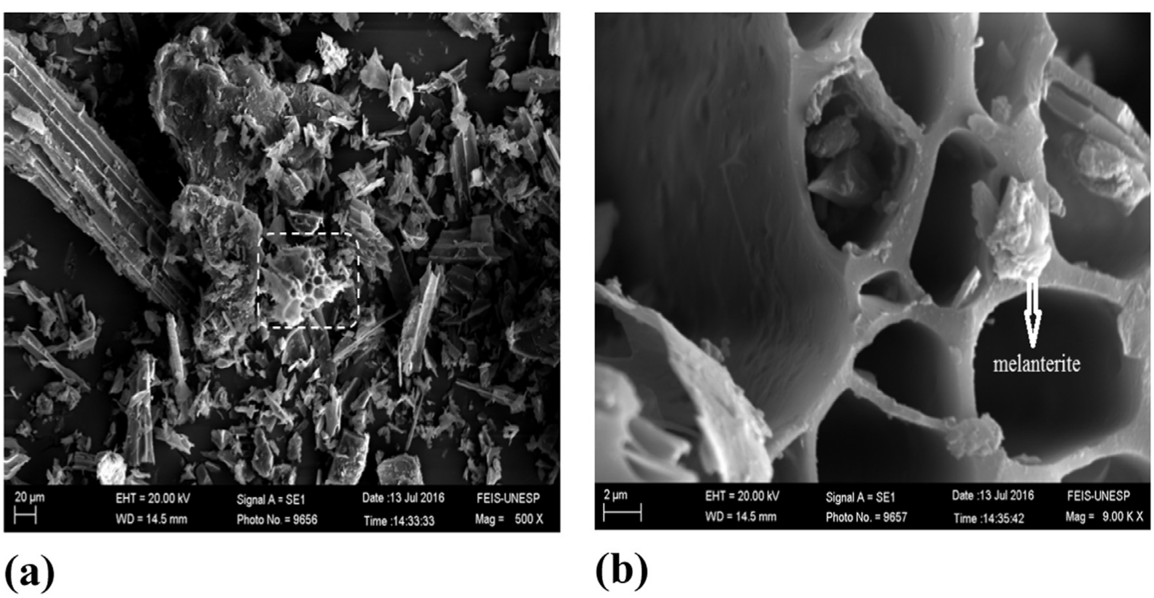

Fig. 1. (a) PETSCA/Fe; (b) highlighting melanterite in PETSCA/Fe.

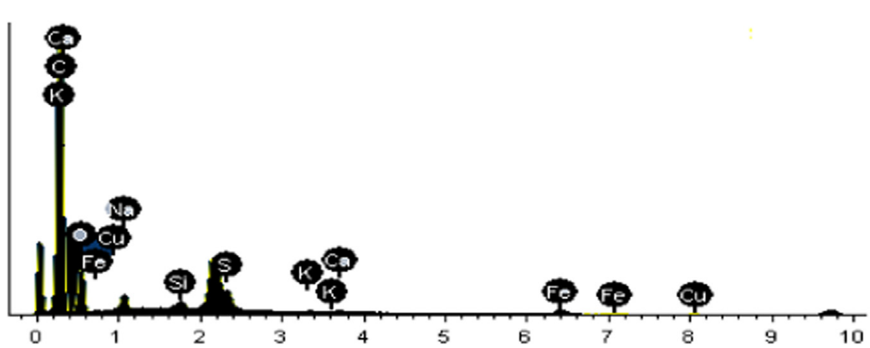

Fig. 2. Presence of chemical elements on the surface of PETSCA/Fe as investigated by EDX analysis.

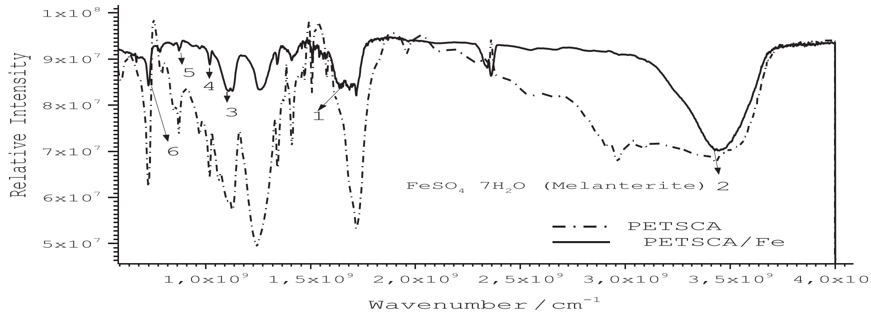

Fig. 3. Infrared spectra of PETSCA and the PETSCA/Fe composite.

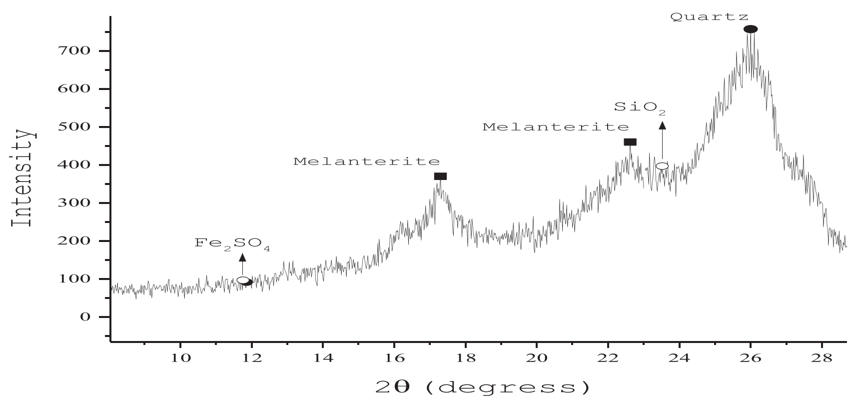

Fig. 4. XRD pattern of the PETSCA/Fe composite containing melanterite.

Some oxidation reactions result in acid generation, while others result in the dissolution and mobilization of iron and other heavy metals present in the environment [6]. The direct mechanism of conversion in melanterite crystals in the PETSCA/Fe composite was probably similar to the initial stages of the oxidation of pyrite, as shown in Eq. (1)˒[7].

$$2FeS_2(s)+7O_2+2H_2O\rightarrow 2Fe^{2+}+4H^{+}+4sO_4{}^{2-} \quad (1)$$

This reaction produces protons and thus acidity; if the oxidation potential is maintained, the oxidation of Fe^{2+} to Fe^{3+} by oxygen will take place, consuming part of the proton acidity (Eq. (2)) [8]:

$$4Fe^{2+}+O_2(aq)\ +\ 4H^{+}\rightarrow 4Fe^{3+}+2H_2O \quad (2)$$

The adsorbent properties of the PETSCA/Fe composite can be explained by advanced oxidation processes (AOPs), which rely on the generation of highly active hydroxyl free radicals, thus leading to almost universal oxidation. This occurs mainly through the Fenton reaction (Eq. (3)) [9]:

$$Fe^{2+}+H_2O_2\rightarrow Fe^{3+}+OH^{-}+HO^{\bullet} \quad (3)$$

The availability of Fe^{3+} results in a powerful oxidizing agent which can be used for the treatment of wastewater [8].

4. Conclusion

A new type of low-cost adsorbent composite material composed of PETSCA/Fe particles was developed. XRD and FTIR analysis showed melanterite resulting from an NaOH (5.0 mol L^{-1}) at 70 °C. According to the EDX analysis, the highest percentage of iron (Fe^{+3}) was found in the 5:1 PETSCA/Fe composite, which supports the possibility of using this composite for wastewater treatment.

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