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Growth of carbon structures on chrysotile surface for organic contaminants removal from wastewater

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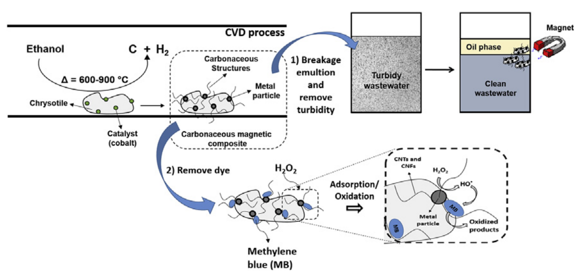
HIGHLIGHTS

- Chrysotile is used to produce amphiphilic composites by CVD at different temperatures.
- The materials can be used in adsorption and oxidation process of organic contaminants.
- The materials can remove up to 90% in turbidity of wastewater contaminated with oil.
- The composites are able to remove the methylene blue color of a solution up to 92%.

GRAPHICAL ABSTRACT



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ABSTRACT

Amphiphilic magnetic composites were produced based on chrysotile mineral and carbon structures by chemical vapor deposition at different temperatures (600–900 °C) and cobalt as catalyst. The materials were characterized by elemental analysis, X-ray diffraction, vibrating sample magnetometry, adsorption and desorption of N_2, Raman spectroscopy, scanning electronic microscopy, and thermal analysis showed an effective growth of carbon structures in all temperatures. It was observed that at 800 and 900 °C, a large amount of carbon structures are formed with fewer defects than at 600 and 700 °C, what contributes to their stability. In addition, the materials present magnetic phases that are important for their application as catalysts and adsorbents. The materials have shown to be very active to remove the oil dispersed in a real sample of emulsified wastewater from biodiesel production and to remove methylene blue by adsorption and oxidation via heterogeneous Fenton mechanism.

1. Introduction

Natural materials such as minerals are being increasingly used in environmental applications, such as in adsorption and oxidation of different contaminants (Teixeira et al., 2012a,b, 2013a; Oliveira et al., 2014). The advantages of using these materials are low cost,

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great abundance in nature, and it is easily obtained.

The literature reports the use of various natural materials such as bentonite (Rinaldi et al., 2008), forsterita (Kawasaki et al., 2009), sepiolite (Nie et al., 2011), vermiculite (Zhang et al., 2009; Purceno et al., 2011), and volcanic rock (Su and Chen, 2007) as support for metal particles to be used as catalyst or modified to improve their surface properties to be used as adsorbent of different contaminants.

Chrysotile is a low cost natural material composed of bundles of fibrils with a curly lamellar structure of phyllosilicate, rolled up to form a hollow of concentric cylinders. The crystalline structure of chrysotile is formed by the interaction between tetrahedral layers of tridymite, SiO_4, with layers of octahedral brucite, $Mg(OH)_2$, resulting in a curvature in the structure of this mineral. Chrysotile is a mineral widely available in nature, with fibrous structure, belonging to the group of serpentinites (Thompson and Mason, 2002) and in the past it was widely used in the construction field (Saada et al., 2009). However, it has been completely withdrawn from commercial use due to serious health hazards. This mineral has been frequently associated with structural and respiratory functional abnormalities, being its use restricted in many countries (Bagatin et al., 2005). On the other hand, there are still millions of tons of chrysotile waste that must be treated and disposed of safely.

Based on this scenario, in the lasts years, chrysotile has been used in several technological applications such as in catalysis, e.g. hydrolysis of soybean oil and hydrogenations of olefins (Teixeira et al., 2012a), elimination of detergents (Fachini et al., 2007), production of membranes for dry gas separation and water filtration (Burnat et al., 2015), mineral carbonation for CO_2 sequestration (Dlugogorski and Balucan, 2014; Pasquier et al., 2014), generation of free radical (Suslova et al., 1994), as adsorbent for environmental protection (Gollmann et al., 2009), also as support for metallocene (Silveira et al., 2007) and porphyrin catalysts (Nakagaki et al., 2006; Halma, 2008).

Chrysotile is a highly hydrophilic material. However, its surface properties can be modified trough functionalization or coating with materials with specific characteristics. For example, the chrysotile can be hydrophobized by growing carbon on its surface. One of the most widely used methods for carbon structures synthesis is the chemical vapor deposition (CVD). This process consists on the decomposition of a volatile carbon source in the presence of a catalyst (Fe or Co, for example), which may be supported in an inorganic matrix. There are several parameters that can affect the yield and the kind of carbon structures formed during the CVD process, *i.e.* temperature, carbon source, catalyst, inorganic matrix, the amount of precursors, etc (Joselevich et al., 2008). One of the main factors that affect the quality of the carbon structures formed is the temperature in which the CVD process is carried out. According to most of the studies in the literature, the optimum temperature of synthesis ranges from 500 up to 1100 °C (Li et al., 2008). Our research group has studied the influence of the metal catalysts and the influence of the temperature of the CVD process in the growth of carbon nanotubes and its influence on the production of amphiphilic composites using different inorganic matrixes (Purceno et al., 2011; Mambrini et al., 2012, 2013). Due to their amphiphilic behavior, these materials were used in two-phase reactions such as biphasic oxidation, to remove organic contaminants in aqueous media and in the formation/breaking of emulsions.

In this work, it was proposed a novel approach of using chrysotile. We have studied the transformation of the mining waste chrysotile in an efficient ceramic matrix for partial deposition of carbon structures by CVD process, using ethanol as a renewable carbon source. Metallic cores were used as catalysts for carbon deposition, producing low cost and safe magnetic amphiphilic materials. The resulting composites are formed by three parts with different properties: the mineral matrix, with hydrophilic characteristics, partially coating of very hydrophobic carbon structures and metal nuclei with magnetic properties. After the CVD process, the chrysotile structure is modified to another phase (forsterite), which presents no risk to human health, moreover, the carbon coating prevents the leaching of the material for the medium. Furthermore, the magnetic properties of these composites allow them to be easily removed after use by the simple approach of a magnetic field (Lemos and Teixeira, 2012; Oliveira et al., 2013; Teixeira et al., 2013c). The materials were successfully applied in the treatment of a real emulsified wastewater residue obtained from biodiesel production and in the oxidation of organic molecules in aqueous media.

2. Experimental

2.1. Composites preparation

The magnetic amphiphilic composites were synthesized from chrysotile of waste mining ($Mg_3Si_2O_5(OH)_4$) (supplied from Sama Minerações Associadas) impregnated with 20%wt Co using cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$). 5 g of chrysotile was placed in contact with 50 mL of an aqueous solution of the metal salt (100 g L^{-1}) under magnetic stirring and mild heating. After solvent evaporation, the impregnated material was kept in an oven at 100 °C for 24 h.

Carbon structures were grown on the chrysotile surface using the catalytic chemical vapor deposition (CVD) process. In the CVD process, a volatile carbon source is decomposed in the presence of the catalyst, depositing solid carbonaceous material. Typically 500 mg of the material (chrysotile with 20%wt of Co as catalyst) was placed inside of a quartz tube and heated (10 °C min^{-1}) in a tubular furnace (Lindberg Blue) at temperatures of 600, 700, 800 and 900 °C for 1 h, with ethanol (PA – Merck) as carbon source (100 mL min^{-1} in nitrogen as gas flow). The materials obtained were named as Cris/Co600, Cris/Co700, Cris/Co800, Cris/Co900 according to the temperature used in the CVD process.

2.2. Composites characterization

The materials were characterized by elemental analysis CHN (Perkin-Elmer – Séries II – CHNS/O Analyzer 2400, with a combustion chamber temperature near to 926 °C), thermogravimetric analysis – TG (in air flow, 100 mL min^{-1}, heating rate of 10 °C min^{-1} up to 900 °C in an DTG-60 Shimadzu), X-ray diffraction – XRD (Rigaku Geigerflex, with Cu Kα, with a scan rate of 4° min^{-1} from 10 to 70°), Raman spectroscopy (Bruker spectrometer SENTERRA, equipped with a CCD detector, using a laser with $\lambda = 633$ nm) and Scanning Electronic Microscopy – SEM (Quanta 200 – FEG – FEI 2006). The specific surface area values were obtained in an Autosorb IQ2 Quantachrome equipment using cycles of N_2 adsorption/desorption at −196 °C. Magnetization measurements were performed using a vibrating sample magnetometer (LakeShore 7404), with noise base of 1×10^{-6} emu, and a time constant of 300 m at room temperature and a maximum magnetic field of 2 T. Zeta potential measurements were carried out in a ZetaSiker equipment (MALVERN INSTRUMENTS) with composites dispersed in deionized water.

2.3. Wastewater treatment

Samples of emulsified wastewater were collected in an industrial biodiesel plant of soybean oil production, located in Minas Gerais/Brazil. The sample was collected after oil/water separation process and it was maintained at temperatures lower than 4 °C