



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



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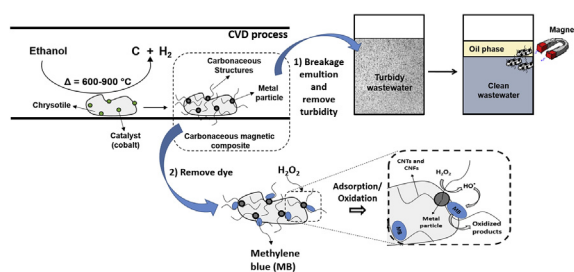
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HIGHLIGHTS

- 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 N₂, 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.

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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), forsterite (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, $\text{Mg}(\text{OH})_2$, 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 last 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 (Długogorski 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 through 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 (Josevich 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 ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) (supplied from Sama Minerações Associadas) impregnated with 20%wt Co using cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). 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 $\text{Cu K}\alpha$, 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 $\lambda = 633 \text{ nm}$) 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 $1 \times 10^{-6} \text{ emu}$, 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

before the experiments. Tests of emulsion breaking and turbidity removal were performed using 100 mg of amphiphilic carbonaceous materials. The compounds were placed in contact with 6 mL of the emulsified wastewater in a glass tube and mechanical stirring for 1 min. Then, the breaking of the emulsion was made by approaching of a magnet on the bottom of the glass tube and after that, the samples were analyzed by optical microscopy (Cole Parmer Instrument – 41500–50), UV–Vis spectrophotometry (Shimadzu UV 2550) and turbidity (HACH 2100 AN). Blank tests were performed in the same conditions without composites. The reuse of magnetic carbonaceous materials was investigated up to five times or until reached less than 20% of the wastewater turbidity removal efficiency.

The removal of methylene blue (MB) (50 mg L^{-1}) in aqueous solution by heterogeneous Fenton-Like reactions was also evaluated in the presence of the composites (30 mg). Preliminary tests were made in dark conditions, without H_2O_2 , during 24 h to evaluate only the adsorption process promoted by each material. After this step, 300 μL of H_2O_2 (32%) was added and the color removals were evaluated using the absorbance of the MB solution, which was monitored over time by UV–Vis spectrometry at 612 nm wavelength, after magnetic separation of the composites.

3. Results and discussion

3.1. Composites characterization

Waste of the chrysotile mineral extraction was used as support for carbon structures synthesis by CVD process, at different temperatures (600–900 °C) using cobalt as catalyst and ethanol as

carbon source, which is responsible for the reduction of cobalt species and for the formation of carbon structures (Teixeira et al., 2012b). Chrysotile waste, used in this work, is a hydrated magnesium silicate, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ and it has an elemental composition of 21.4%wt Mg, 3.8% Fe, and less than 0.4% of heavy metals. Iron has been usually found in Chrysotile structures replacing the magnesium ions (Sarvaramini and Larachi, 2011).

Elemental analysis (CHN) of the materials obtained after CVD process confirmed that all temperatures were effective for growing carbon structures with yields of 23, 28, 31, and 27% of carbon for the materials Cris/Co obtained at 600, 700, 800, and 900 °C, respectively. In general, higher temperatures of CVD process increase the carbon content deposited on the material. However, it was observed a decrease of carbon content at 900 °C, probably due to the fast pyrolysis reaction of the carbon source at this temperature, promoting a fast catalyst particles encapsulation by amorphous carbon, preventing thus, the growth of organized carbon structures (Cui et al., 2008).

TG curves of the cobalt based materials (Fig. 1a) show a weight loss between 300 and 600 °C, related to the oxidation of carbonaceous materials deposited on the chrysotile surface. However, the amount of carbon was not evaluated directly from the weight loss of the composites, because pure chrysotile showed also a gradual weight loss from 25 to 800 °C of 20% due to the dehydroxylation of the mineral. This event is overlapped to the carbon oxidation event.

DTG curves (Fig. 1b) show an increase on the decomposition temperature for the materials Cris/Co600; Cris/Co700; Cris/Co800 and Cris/Co900, respectively. Higher decomposition temperatures of carbon materials indicate the presence of more stable/organized structures (Trigueiro et al., 2007). These results suggest that higher

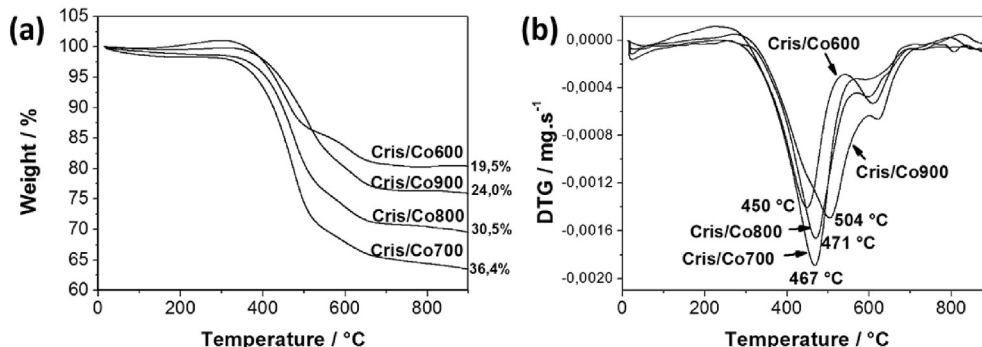


Fig. 1. TG (a) and DTG (b) analysis, in synthetic air, of chrysotile samples impregnated with Co after CVD process at different temperatures.

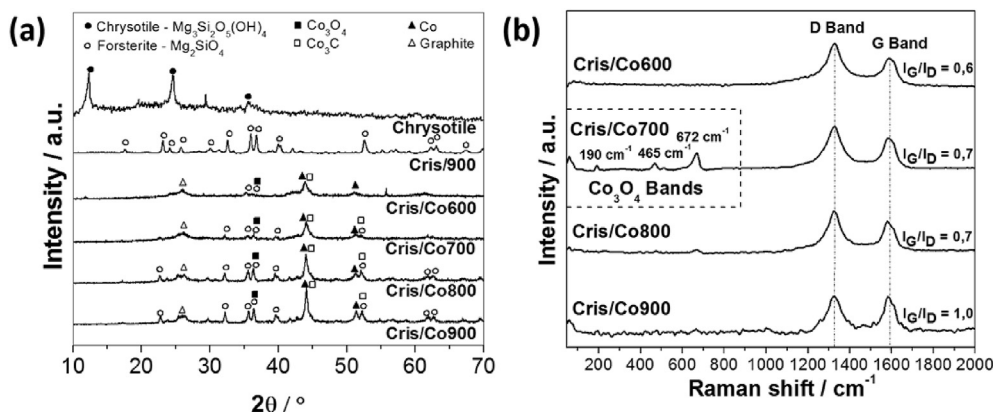


Fig. 2. (a) XRD patterns, and (b) Raman spectra for pure chrysotile and the materials obtained after CVD process at different temperatures with ethanol and chrysotile impregnated with cobalt 15 wt%.

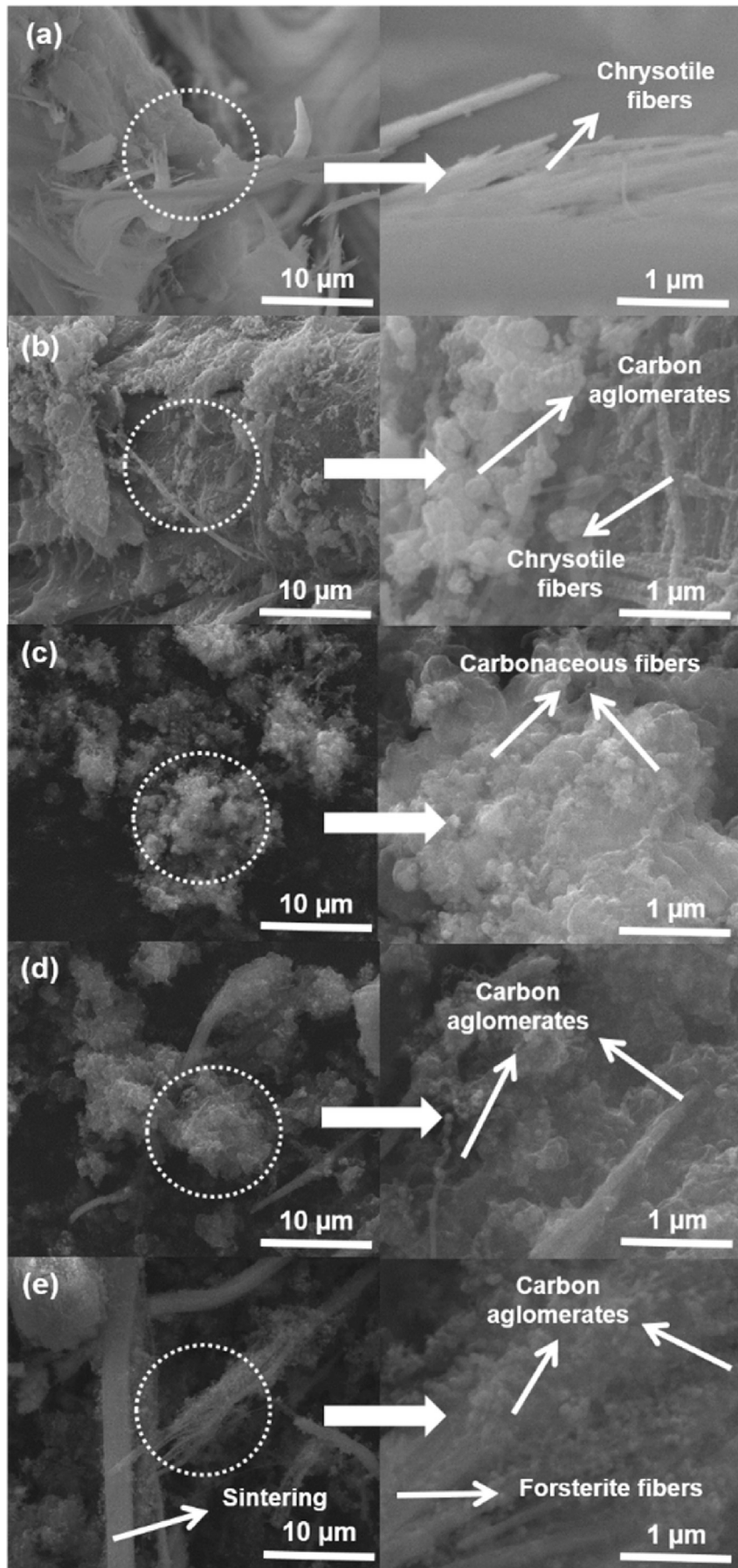


Fig. 3. SEM images of: (a) pure chrysotile, (b) Cris/Co600, (c) Cris/Co700, (d) Cris/Co800 and (e) Cris/Co900.

temperatures of the CVD process provide more stable carbon structures on the surface of the support (Yue et al., 2011).

XRD pattern for sample obtained at 600 °C, Cris/Co600, shows typical reflections of chrysotile, $Mg_3Si_2O_5(OH)_4$, and the phase Mg_2SiO_4 (forsterite) (Fig. 2a). The forsterite phase is formed by dehydroxylation of chrysotile at high temperatures and it can be assigned by the reflections peaks observed for the pure chrysotile thermally treated at 900 °C (Bush and Schumacher, 1982). For samples obtained at temperatures higher than 600 °C, it is possible to observe only the Mg_2SiO_4 phase, indicating that the chrysotile structure was completely destroyed to form forsterite. The graphitic phase, with characteristic reflection at 26.5°, appears in all samples impregnated with cobalt. The magnetic phases of cobalt oxide (Co_3O_4), metallic cobalt (Co^0), and cobalt carbide (Co_3C) were identified in the XRD patterns. These phases are formed from the gradual reduction of Co species due the reaction with ethanol and concomitant deposition of carbon to further produce cobalt carbide.

Raman spectra of the materials, after CVD process (Fig. 2b), showed bands at about 1350 cm^{-1} (D band), related to the presence of defective carbonaceous structures, and at 1600 cm^{-1} (G band), associated with C–C tangential bond vibration of organized graphitic materials (Jorio et al., 2003). The ratio of G and D bands intensity (I_G/I_D) may be a parameter to indicate the predominance of amorphous or more organized and crystalline carbon structures (Dresselhaus et al., 2005). The decomposition of ethanol can form different carbon structures such as carbon nanotubes, nanofibers, amorphous carbon and graphitic layers around the catalyst nanoparticles (Zhu et al., 2012). No significant difference was observed between the intensities of D and G bands for the materials, thus the ratios I_G/I_D remain close to 1. However, I_G/I_D ratio increases with the temperature of the CVD process, indicating that higher temperatures lead to the production of more crystalline and stable carbon structures (Yue et al., 2011). This result is in agreement to the thermal analysis results (see Fig. 1). In some Raman spectra is also possible to observe bands at lower frequencies (below 700 cm^{-1}) that are consistent with values presented in literature for cobalt oxide species, Co_3O_4 (Tripathy et al., 2008).

SEM images for pure chrysotile show a microfibrillar structure typical of this mineral (Fig. 3). It is observed a set of long fibers extending throughout the sample. After the CVD process, all materials are coated by a high amount of carbonaceous structures. However, it is still possible to observe the silicate fibers, though more agglomerated and larger compared to the chrysotile before the CVD process due to sintering and phase changes.

Chrysotile and the materials after CVD process were characterized by N_2 adsorption/desorption experiments (Fig. S2 and Table S1, Supplementary Material). The composites show similar specific surface area values, but higher than the chrysotile. Specific surface areas of 52, 69, 39, 26 and $12\text{ m}^2\text{ g}^{-1}$ were obtained for Cris/Co600, Cris/Co700, Cris/Co800, Cris/Co900 and pure chrysotile, respectively. The slight difference observed may be explained by the carbon deposition over the chrysotile. The composites obtained at 600 and 700 °C, even with similar carbon content, show higher specific surface areas than Cris/Co800 and Cris/Co900, what is likely related to the modifications on the chrysotile structure by heating. At temperatures below 800 °C, chrysotile loses water and forms a non-hydrated magnesium silicate (Teixeira et al., 2013b). Due the heating of chrysotile above 800 °C, the mineral structure suffers a nucleation process becoming a material with lower specific surface area. Indeed, the specific surface area of chrysotile after heat at 900 °C is $7\text{ m}^2\text{ g}^{-1}$.

An important characteristic of these amphiphilic composites is their magnetic behavior. The presence of magnetic phases coated by carbon, such as metallic cores of Co_3O_4 , Co^0 and carbides allows

the materials to be removed by a magnetic separation process (Teixeira et al., 2012a). Fig. 4 shows the magnetization curves obtained for chrysotile and for the composites.

The saturation magnetization measurements for Cris/Co600, Cris/Co700, Cris/Co800 and Cris/Co900 were 15, 17, 15 and 27 emu g^{-1} , respectively. The highest value of 27 emu g^{-1} for the Cris/Co900 sample is likely related to the presence Co^0 – with high value of saturation magnetization of 166.1 emu g^{-1} (Coey, 2009). The formation of this phase was favored by the high temperature (900 °C) in which the CVD process was carried out.

3.2. Wastewater treatment

The amphiphilic characteristic of the magnetic composites is very interesting to promote the turbidity removal of wastewater. These materials can be well dispersed into a polar phase, such as an aqueous medium, besides the good interaction with the organic and insoluble molecules dispersed in the water, which are responsible for the turbidity. Cloudy water is an emulsified system, where two phases are dispersed one into the other. The synthesized materials were used to remove the turbidity of the biodiesel wastewater, and for adsorption/oxidation of the methylene blue in aqueous medium. Fig. 5 shows the removal of turbidity using the materials obtained after the CVD process.

The sample Cris/Co700 showed almost 90% of efficiency for turbidity removal. Carbon structures on the materials surface have a very hydrophobic character and are fundamental to ensure good interaction between the organic contaminant and the composite. The differences observed in the materials should be related to the type of carbon nanostructure grown on the surface of the mineral. The temperature of CVD process influences the kind, e.g. graphite, nanotubes and quantity of carbon structures formed. Carbon structures with low amounts of defects present high hydrophobicity and may interact better with hydrophobic media like oil phase (Sun et al., 2014). In addition, the sample Cris/Co700 reached the higher carbon yield after the CVD process. Thus, the surface of chrysotile is more coated by carbon structures in this material, what contributes to the higher hydrophobicity of this sample. The turbidity removal efficiency decreases with the use of the material, suggesting the surface saturation after five reuse cycles, what reduces its activity.

Cris/Co800 showed the best removal efficiency turbidity for all reuse tests. The material dispersed in the emulsion after the

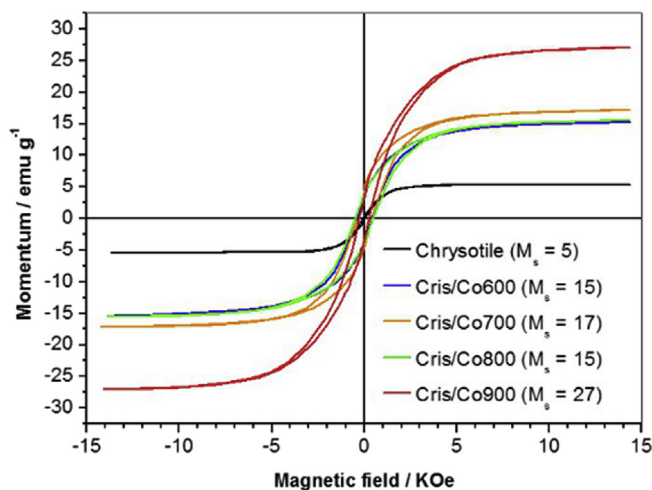


Fig. 4. Magnetization curves obtained for pure chrysotile and chrysotile with cobalt 15 wt% after the CVD process performed at different temperatures with ethanol.

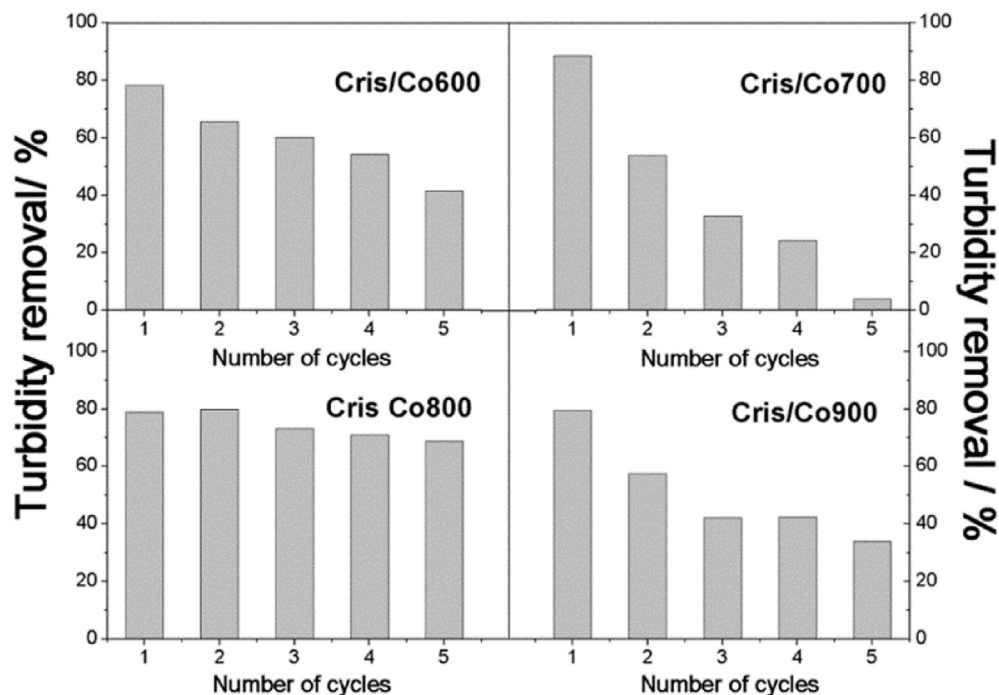


Fig. 5. Turbidity removal of a real effluent sample from biodiesel production promoted by the composites Cris/Co600, Cris/Co700, Cris/Co800 and Cris/Co900.

adsorption process was magnetically removed and the turbidity removal of the system is clearly observed (Oliveira et al., 2010).

The magnetic materials were also tested in the removal of organic contaminants in aqueous solutions by adsorption followed by oxidation via heterogeneous Fenton process using the cationic dye methylene blue (MB) as substrate (Fig. 6). To evaluate the isolated contribution of these processes, the composites were held in contact with MB solutions for 24 h in order to reach the adsorption equilibrium. Afterwards, H_2O_2 was added to the system.

The composites showed a color removal higher than 50% during the adsorption stage. Although the composites present similar specific surface areas, the MB adsorption capacities are different and increase with the carbon content of the materials. The highest color removal efficiency was obtained for Cris/Co800 (87%). According to CHN elemental analysis, this material presents the highest carbon content. For the material obtained at 900 °C, the

color removal promoted by adsorption decreases, likely due to the lower carbon content and lower specific surface area (Fig. S2, Supplementary Material). Furthermore, the surface charge on solid materials in a suspension may influence the adsorption process. Surface charges determined by Zeta potential experiments are -15.01 , -15.70 , -17.87 , and -15.37 mV for Cris/Co600, Cris/Co700, Cris/Co800 and Cris/Co900, respectively. The negative charges suggest that the surface of composites presents affinity and should have a good interaction with positively charged molecules, such as MB molecules. The Zeta potential measurements are in agreement with color removals obtained, especially for the Cris/Co800, which showed a higher adsorption capacity. On the other hand, the Zeta potential of pure chrysotile shows a positive surface charge, i.e. $+7.36$ mV, which explains the low MB adsorption observed in aqueous media. However, when the chrysotile is heated at 900 °C, its structure changes to forsterite and the surface charge becomes

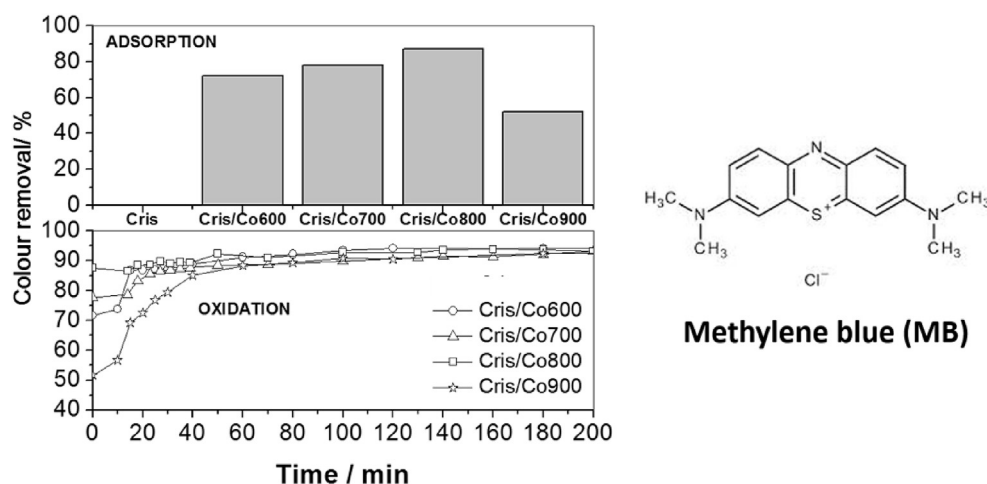


Fig. 6. Discoloration of MB by adsorption after 24 h contact (above), followed by oxidation with H_2O_2 (below).

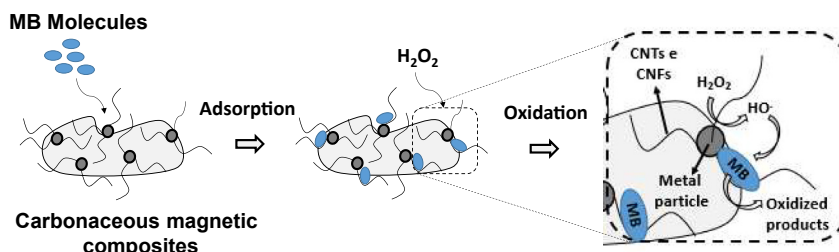


Fig. 7. Scheme of adsorption/oxidation combined processes of methylene blue promoted by the materials.

negative, i.e. -14.67 mV, obtained for the pure chrysotile after heating to 900 °C.

After addition of hydrogen peroxide, H₂O₂, there is a great color removal of the MB solution, which is related to oxidative degradation of the dye molecules. After 180 min, all systems show a color removal greater than 92%. These results are probably related to the active cobalt phases, presented in the composites, which promote the heterogeneous Fenton-Like process oxidizing the MB (Makhlouf et al., 2013). On the other hand, experiments performed with only chrysotile led to a color removal lower than 2%, after adsorption and oxidation process under the same conditions.

In our system, reduced Co species, such as Co₃O₄, Co⁰ or Co₃C are able to activate the hydrogen peroxide on the surface of the composites in a heterogeneous Fenton-like mechanism (Bokare and Choi, 2014), forming hydroxyl groups ($\cdot\text{OH}$) (Eq. (1)). Then, the $\cdot\text{OH}$ radicals may react with other H₂O₂ molecules to form hydroperoxyl radicals, HOO \cdot (Eq. (2)). Both $\cdot\text{OOH}$ and specially $\cdot\text{OH}$ radicals are highly oxidizing agents that can oxidize the methylene blue molecules.



Finally, hydroperoxyl radicals may also transfer one electron to Co³⁺ regenerating the Co²⁺ species (Eq. (3)) and the H⁺ species formed reacts with OH⁻ previously formed in the Eq. (1), keeping the pH near to neutral.



In addition, the presence of metallic species, like Co⁰, could reduce the Co³⁺ ions species by an electron transfer from Co⁰ to Co³⁺. These electrons would be transferred to the metal oxide through the semiconductor structures on the surface. This reduction has also been observed for the iron species (Fe⁰ and Fe₃O₄) commonly used in heterogeneous Fenton reactions, where the Fe⁰ is able to transfer electrons to Fe₃O₄ through the semiconductor structure of the iron oxide (Costa et al., 2008; Dias et al., 2016).

Based on this mechanism and others seen in the literature (Amorim et al., 2013) we propose a reaction pathway for adsorption/oxidation of methylene blue in aqueous medium on the surface of the Cris/Co materials as shown in Fig. 7.

According to the mechanism proposed above, the methylene blue is initially pre-concentrated on the surface of the composites from the adsorption process promoted by the carbonaceous material. Subsequently, the addition of hydrogen peroxide promotes the oxidation of the dye adsorbed on the surface of the material via the heterogeneous Fenton-Like process.

4. Conclusions

New magnetic amphiphilic composites based on chrysotile mineral and carbon were successfully obtained by CVD process using ethanol as carbon source. Indeed, the temperature of the CVD process has shown to be an important parameter that influences the kind of the carbon structures grown and their yield on the chrysotile surface. The material obtained at 800 °C resulted in the highest yield of carbon structures. The composites showed great performances in the removal of the turbidity from biodiesel wastewater and in the discoloration of MB solutions via the heterogeneous Fenton-Like process.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2016.06.022>.

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