



Research article

Dye degradation by green heterogeneous Fenton catalysts prepared in presence of *Camellia sinensis*

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ABSTRACT

This work describes the synthesis and characterization of supported green iron catalysts, prepared with *Camellia sinensis* tea extract, and their application in heterogeneous Fenton degradation of pollutant dyes. The influence of the catalyst synthesis conditions in the iron and organic content were investigated by X-ray fluorescence and thermogravimetric analyses. Irregular, chain-like nanoparticles, in the size range of 20–100 nm, capped by polyphenolic natural compounds, were visualized by TEM micrographs. TEM-EDS revealed a high iron content in the nanoparticles as well as a high carbon content all over the catalyst surface, indicating the coverage by the polyphenolic compounds of the tea. X-ray powder diffraction revealed the amorphous nature of the nanoparticles, tentatively ascribed to iron(II)/(III) oxides and oxohydroxides composites. The Fenton degradation of different dyes was successfully accomplished, leading to complete decolorization in less than 3 h of reaction. Influence of hydrogen peroxide concentration, catalyst dosage, pH, temperature and catalyst support, were investigated. The catalysts prepared with black tea over silica furnished the higher iron contents and were the most actives for dye degradation.

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1. Introduction

Synthetic dyes are extensively used in many technological applications, as textile, paper and food industries, photo-electrochemical cells and light-harvesting arrays. Remediation of dyes wastes before disposal has been regulated by environmental protection legislations to minimize the damage to aquatic ecosystems (Forgacs et al., 2004; Raman and Kanmani, 2016). Organic dyes are difficult to decolorize under exposure to light, water, microorganisms and many chemicals, due to the complex structure and high stability. Furthermore, dyes and their degradation products present high toxicity to aquatic and human lives (Robinson et al., 2001).

Iron has been the first choice metal for groundwater treatment due to its high intrinsic reactivity, low toxicity, biodegradability, low cost, abundance, and magnetic properties, being considered a universal material for water treatment. Iron-containing nanomaterials as zerovalent nanoparticles, oxides, oxohydroxides, ferri-rites, have been widely used to remediate contaminants such as

heavy metals, azo dyes, chlorinated organic compounds, nitroaromatics (Kharisov et al., 2012; Lin and Chang, 2015). Among the variety of physical and chemical remediation processes, the heterogeneous Fenton-like system is particularly interesting because it usually leads to complete degradation and mineralization of the organic pollutant, moreover, the catalyst can be recycled avoiding the sluggish formation during traditional homogeneous Fenton process (Li et al., 2015; Fukuchi et al., 2014; Nidheesh, 2015).

There is an increase interest in environmentally friendly and sustainable methods to synthesized metal and metal oxides nanoparticles, due to its low cost, non-toxicity, operational simplicity, reproducibility and the feasibility to be scaled up. Plant extracts rich in polyphenolic compounds and caffeine, as natural reducing and capping agents, have been currently used in bio-reduction, formation and stabilization of nanoparticles (Irvani, 2011; Hoag et al., 2009; Kharissova et al., 2013; Lin et al., 2015; Gao et al., 2016). Iron catalysts produced with plant extracts of green tea (Shahwan et al., 2011; Hoag et al., 2009) and yerba mate tea (Trotte et al., 2016), mainly composed of Fe_xO_y and FeOOH, were applied in the Fenton decolorization of the dyes methylene blue, methyl orange and bromothymol blue. The source of the plant extract is known to influence the characteristics of the

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nanoparticles due to different concentrations, combinations and reduction capacity of natural reducing agents, as well as the reduction potential of the metal ions (Mittal et al., 2013; Iravani, 2011).

This work presents the preparation of iron catalysts in presence of white and black tea, two variants of different fermentation time of the plant *Camellia sinensis*, and the application in the heterogeneous Fenton-like degradation of pollutant dyes. The iron(II)/(III) nanoparticles were supported over different materials, as silica, alumina, ceria and zirconia, in order to improve the nanoparticles dispersion and stability. Iron catalysts prepared with tea extracts over solid supports for dye degradation has not been deeply investigated, similar materials supported on clay was successfully applied in the removal of arsenic(III) (Tandon et al., 2013). The influence of synthesis conditions as type of tea, proportion of tea extract to iron solution and reaction time, in the size, morphology, iron and organic contents of the nanoparticles, as well as in the decolourization activity were addressed.

2. Experimental

2.1. Materials and methods

All chemicals are of reagent grade and were used without further purification. Methyl orange (MO) from Merck was recrystallized before handling. Hydrogen peroxide (30% aqueous solution) from Vetec was titrated by the iodometric method. Silica gel (0.063–0.200 mm) was purchased from Merck, Germany, alumina (0.063–0.200 mm), zircon oxide (5 μm) and cerium oxide (<5 μm) were purchased from Sigma-Aldrich. Black and white teas were purchased from Mate Leão brand in local markets.

Solution UV-Vis spectra were recorded on a diode-array Agilent 8453 spectrophotometer in water. FT-IR analyses were acquired in a Nicolet 6700, Thermo Scientific, in KBr pellets. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM - 6510LV (Jeol technics Ltd, Tokyo, Japan) microscope, where the catalysts samples were previously covered with Au during 820 s (Denton Vacuum model DESKV), images of the samples were recorded at an operating current of 20 mA. Transmission electron microscopy (TEM) with energy-dispersive X-ray spectroscopy (EDS) was acquired in a FEI Tecnai G² F20 HRTEM equipment. The samples were dispersed in isopropanol and then treated under ultrasound for 30 min, followed by deposition on a copper grid. The X-ray powder diffraction (XRD) patterns were measured in a Rigaku Ultima IV diffractometer with Ni-filtered $\text{CuK}\beta$ radiation source ($\alpha = 0.15406$ nm, graphite monochromator, 40 kV and 20 mA) in the 2 θ angle range between 5° and 80°, at a step width of 0.1°, counting 5 s between each step. The iron contents in the catalysts were determined by X-ray fluorescence analysis using a Rigaku RIX3100 fluorescence spectrometer. Thermogravimetric (TG) analyses were carried out in Netzsch thermogravimetric system (STA449 Jupiter), equipped with a high precision balance to monitor the mass variation as a function of time. 10 mg of the samples was heated from 50 °C to 1000 °C, at 10 °C min^{-1} , under He flow (45 mL min^{-1}).

2.2. Catalyst preparation

Aqueous black and white tea extracts were prepared from 7.2 g of the dry leaves in 120 mL of water at 80 °C, under stirring, for 1 h. The tea solids were filtered off and the solution cooled down to room temperature.

The supported iron catalysts were prepared at a theoretical iron content of 25 wt%, in presence of black or white tea extract, at different reaction conditions, as shown in Table 1. A typical catalyst

was prepared as follow: 120 mL of tea extract was added drop wise to a suspension of 2.00 g of the support and 3.22 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 120 mL of water, during 40 min. The reaction was left under stirring for a given time and the catalyst was filtered off. After the solvent removal in a rotatory evaporator, a black solid was obtained. Free nanoparticles were prepared in presence of white or black tea with twice the volume of tea extract for comparison.

2.3. Decolourization tests of methyl orange (MO)

In a typical experiment, 2.0 mL of a 5.0×10^{-4} mol L^{-1} MO stock solution, a given volume of H_2O_2 and H_2O to complete a total reaction volume of 20 mL, were added to a desired mass of catalyst. The reaction was carried out under magnetic stirring, at preset time intervals, samples were taken by a glass syringe, filtered through 0.45 μm membrane filter and the MO concentration was determined spectrophotometrically. The reaction was investigated under different conditions, including, peroxide concentration, catalyst dosage, pH (adjusted with HCl or NaOH), temperature.

3. Results and discussion

3.1. Catalysts preparation and characterization

Green iron catalysts were prepared in presence of black tea (BT) or white tea (WT) as natural reducing and capping agent, supported in different oxides, as shown in Table 1. Firstly, a group of catalysts were prepared over SiO_2 , where the synthesis conditions were screened, such as type of tea, proportion of tea extract to iron solution and reaction time, and then the condition that led to the higher iron content (namely $\text{BT}^4\text{Fe/SiO}_2$) was applied to the Al_2O_3 , ZrO_2 and CeO_2 . XRD profiles (Fig. S26–30) showed only the peaks related to the support. The free nanoparticles BT^1Fe and WT^1Fe also lack well defined peaks related to crystalline iron compounds, indicating the amorphous nature of the catalysts, as reported for similar materials, since the iron oxide surface was capped and stabilized by the tea polyphenol compounds (Shahwan et al., 2011; Wang et al., 2014a, 2014b; Huang et al., 2014b; Weng et al., 2013; Trotte et al., 2016). As pointed out by Markova et al., 2014, the polyphenolic compounds found in tea extracts do not possess a reduction potential negative enough to reduce Fe^{3+} to Fe^0 , but can reduce Fe^{3+} to Fe^{2+} forming Fe(II)/Fe(III) oxides/hydroxides nanoparticles.

X-ray fluorescence spectroscopy (FRX) and thermogravimetric analyses were carried out in order to determine the amount of iron and organic compounds in the catalysts (Table 1), respectively. TG curves (Fig. 1(a)) of the black tea catalysts comprehend three main regions of weight loss: region I (40–140 °C) attributed to humidity release; region II (140–390 °C) and region III (390–900 °C) attributed to organic compounds decomposition (DTG curves are shown in Fig. S1). As the polyphenolic compounds are responsible for the nanoparticle formation and functionalization, the proportion of tea extract presented a big influence in the iron and organic contents, although the reaction time presented a little effect. Using twice the tea volume, the iron content increased from 1.81 wt% in $\text{BT}^2\text{Fe/SiO}_2$ to 4.17 wt% in $\text{BT}^4\text{Fe/SiO}_2$, therefore the content of organics increased from 13.0 to 18.0 wt%, respectively. Using five times of tea volume, however, a less pronounced increase in the iron content was observed, 2.95 wt% in $\text{BT}^5\text{Fe/SiO}_2$, in this case the resulting polyphenols content was too high, 44.3 wt%, precluding the deposition of the iron materials over the silica surface. Thus, we concluded that the proportion tea: iron ratio of 2:1 favors the iron compounds formation. The same tendency was observed for white tea (Fig. S2, S3), although lower iron and organic contents were obtained, with the catalyst $\text{WT}^5\text{Fe/SiO}_2$ presenting the higher

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