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Methylene blue oxidation over iron oxide supported on activated carbon derived from peanut hulls

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ABSTRACT

In order to contribute to the environment preservation, catalysts based on iron oxides supported on activated carbon were prepared from peanut hulls and evaluated in Fenton reaction to remove methylene blue from model wastewaters. The activated carbons were prepared by simultaneous carbonization and activation of peanut hulls with low amounts of sodium hydroxide and then impregnated with iron nitrate solutions to get samples with 5, 7.5, 10, 12.5 and 15 wt.% Fe. All solids were microporous and made of hematite and magnetite supported on activated carbon. The amount of magnetite changed with iron content and was related to surface oxidation, producing more oxygenated groups (carboxylic acids, lactones, carboxylic anhydrides and phenols) than activated carbon. Both activated carbons and iron-based catalysts were able to remove methylene blue from aqueous streams by adsorption and oxidation, the activity of activated carbon being assigned to oxygenated groups. For iron oxide-based catalysts, the adsorption capacity was related to the increase of surface oxygenated groups while the oxidation activity was assigned to the amount and crystals size of magnetite, besides the surface oxygenated groups. The association of these properties led to catalysts with close performances, being the catalyst with 10 wt.% Fe slightly more efficient than the others in dye removal. The obtained catalysts produced low amounts of byproducts, being promising to remove dyes in industrial wastewaters. In addition, they have the advantage of being prepared with less sodium hydroxide than the traditional preparations, decreasing the amount of wash water, besides reducing the amounts of peanut hulls disposed in the environment.

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1. Introduction

In recent decades, human activities have increased the amount of waste disposed in the air, water and soil, making difficult their natural recycle and thus leading to serious damages to the environment and to the living beings [1–4]. Therefore, a lot of work has been addressed to reduce the waste accumulated in the environment by developing soft processes [5,6] and/or by transforming them into high value products [5,7,8]. Among the various alterna-

tives, a promising solution is the use of agricultural waste to obtain activated carbons, which in turn can be used to remove pollutants from wastewaters [9–11].

Especially because of the high specific surface area and porosity, activated carbons have found several applications as adsorbents for gases or liquids. They have been used in the recovery and purification of chemicals and for storing hydrogen in fuel cells [12,13], among others. They have also found catalytic applications in several reactions, such ethylbenzene dehydrogenation [14,15], biodiesel production [16] and removal of pollutants from industrial effluents [17–19]. The wide range of applications of activated carbons is related to their unique properties, such as high specific surface area, thermal resistance, electrical conductivity, hardness, resistance against acids and bases and ability for adsorbing ions,

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besides the presence of functional groups on the surface [20]. It was found [15,16,21] that these surface groups are closely related to the catalytic activity of activated carbons in several reactions. An important practical advantage of activated carbons is that most of these properties, including the kind and the amount of surface groups, can be controlled during preparation, allowing the tailoring of these solids according to their applications [16,22].

As far as the removal of pollutants is concerned, most publications on activated carbons is related to the adsorption processes of various pollutants such as dyes [9], organic compounds [23] and metals [24], among others. However, it is generally accepted that the destruction of the pollutant, instead of transfer it to an adsorbent, is a more efficient way to preserve the environment. Therefore, several studies [8,10,11,17,18,25,26] have been addressed to the abatement of organic pollutants by advanced oxidation processes (AOP), which have been recognized as more efficient to degrade organic pollutants than the conventional methods [27,28].

The advanced oxidation processes are based on the generation of hydroxyl radicals (OH^*), which are strong and non-selective oxidizing species, able to oxidize a wide range of complex organic compounds producing carbon dioxide and water [27–29]. Among the advanced oxidation processes, the Fenton reaction has emerged as a promising alternative, being catalyzed by iron-based compounds, which are highly efficient and have low cost. In spite of these advantages, the Fenton homogeneous process has some drawbacks, such as the formation of ferric hydroxide sludge in the effluent, requiring a separation step after the wastewater treatment. Another disadvantage is the limited pH range, demanding the neutralization of the effluent before its disposal in the waterways [28,30]. These difficulties can be overcome by the use of Fenton heterogeneous systems using pure or supported iron oxides. These solids have proven to be effective catalysts, with the advantage of being readily obtained in different phases by a variety of methods with tailored properties. Therefore, hematite, magnetite, maghemite and other iron compounds have been widely studied in the oxidation of organic compounds [10,25,26,28].

The heterogeneous Fenton process is especially efficient in removing colored substances such as dyes, which have a complex molecular structure and are highly recalcitrant to the conventional treatment processes [31]. Large amounts of dyes are disposed in the environment by the textile, leather, paper, rubber, cosmetics and synthetic detergents industries, causing serious environmental and health problems [25]. Among them, methylene blue (3,7-bis(dimethylamino)phenothiazin-5-ium chloride) is one of the most used in textile industries. This dye is highly toxic and can cause permanent injury to the eyes of humans and animals [1], besides other damages, including breathlessness and mental confusion [2]. In addition, color prevents light penetration and then delays photosynthetic activity, inhibiting the growth of biota, besides chelating the metal ions responsible for producing micro-toxicity to fish and other organisms [3]. Because of these problems, the restriction standards of regulatory bodies are becoming even more severe, requiring the decrease of color in effluent and watercourses. As a consequence, the presence of colored dyes in effluents become serious problems for dyestuff manufactures, dyers, finishers and water companies. Therefore, a lot of work has been carried out [10,25,26] aiming to improve the catalysts used in Fenton heterogeneous process to remove methylene blue.

In order to find alternative catalysts for heterogeneous Fenton reaction, iron oxide supported on activated carbon derived from peanut hulls was prepared and evaluated in oxidation of dyes, using methylene blue as a model molecule. Peanut is a typical plant of South America, whose fruit is largely consumed in Brazil, generating large amounts of hulls during the commercial processing of

peanuts. As far as we know, these catalysts have not been prepared and evaluated in Fenton reaction yet.

2. Experimental

2.1. Catalyst preparation

The activated carbon was prepared by simultaneous carbonization and activation of peanut hulls, using sodium hydroxide as activating agent. The peanut hulls were collected in Cruz das Almas city (Brazil), exposed to the sun and then washed in water to remove dust and inorganic impurities. After this, the material was dried in an oven at 110°C , for about 24 h, crushed, milled and sieved between 40 and 60 mesh. The solid was then impregnated with a sodium hydroxide solution, using 12 g of biomass, 6 g of sodium hydroxide and 60 mL of water, in order to obtain a biomass to activating agent weight ratio of 2, which is a value much lower than those typically used for preparing activated carbons [32]. This new procedure intends to decrease the environmental impact related to the discarding of washing water during the removal of activating agent from the active carbon, after activation. The system was then kept under stirring at room temperature, for 2 h. Subsequently, the material was dried at 120°C , for 24 h. The step of simultaneous activation and carbonization was performed in a quartz cell into a horizontal furnace which was heated ($10^\circ\text{C min}^{-1}$) up to 600°C , under nitrogen flow (100 mL min^{-1}) and kept at this temperature for 1 h. After the carbonization and activation step, the activated carbon obtained was washed with a hydrochloric acid solution (5% v/v) and then with water at 80°C . It was then dried at 120°C , for 24 h and named C sample. This activated carbon thus obtained was then impregnated with 40 mL of aqueous iron nitrate solutions (0.071, 0.109, 0.149, 0.192 and 0.237 mol L^{-1}) to get samples with 5, 7.5, 10, 12.5 and 15% (w/w) in the final solid. After this, the sample was heated under nitrogen flow (100 mL min^{-1}) up to 400°C and kept at this temperature for 2 h. The catalysts were named CF5, CF7.5, CF10, CF12.5 and CF15 samples, where the numbers indicate the nominal amount (% w/w) of iron in solids.

2.2. Samples characterization

The samples were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Mössbauer spectroscopy, specific surface area (S_g) and porosity measurements, Raman spectroscopy, temperature programmed desorption coupled to mass spectrometry (TPD/MS), X-ray photoelectron spectroscopy (XPS), chemical analysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Fourier transform infrared spectroscopy (FTIR) analyses were carried out in a Spectrum One model Perkin Elmer equipment, using samples diluted in potassium bromide discs. The spectra were recorded in the region between 4000 and 500 cm^{-1} , using 32 scans and a resolution of 4 cm^{-1} . X-ray diffraction experiments were performed at room temperature in a XRD-6000 model Shimadzu apparatus using $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{ \AA}$), generated at 40 kV and 30 mA and a nickel filter. The diffractograms were obtained with a scanning velocity of 2° min^{-1} in the range of 10 – 80° (2θ).

The Mössbauer spectra were collected in transmission geometry with a 512-channel constant acceleration spectrometer using a ^{57}Co source (nominally 50 mCi) in Rh matrix. Velocity calibration was performed versus a $12\text{ }\mu\text{m}$ -thick $\alpha\text{-Fe}$ foil. All isomer shifts (δ) were referred to this standard. The spectra were folded to minimize geometric effects and fitted using a commercial program with constraints named Recoil [33].

For specific surface area and porosity measurements, the adsorption and desorption of nitrogen were performed in an ASAP

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