Preparation a nd Characterization of Composite Goethite/Microporous Carbon from Coffee Waste

Mário César Guerreiro, _Maraísa Gonçalves, Luiz Carlos Alves Oliveira_

Dep. Química_, Universidade Federal de Lavras, Caixa Postal 37, CEP 37200-000 Lavras, MG, Brasil._
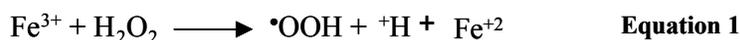
Abstract

In this work was prepared composite made with goethite and microporous activated carbon. The activated carbon was prepared from coffee waste by chemical activation with ZnCl2 under N2 atmosphere. Predetermined volumes of $FeCl_3$ solutions (1M), distilled water and carbon were mixed, right after NaOH was drop wise added as precipitating agent for the goethite preparation at 278 K. The structure properties of this composite was characterized by scanning electronic microscopy (SEM), temperature programmed reduction (TPR), X-ray diffraction (XRD), infrared (FTIR) and pulse titration with H2. The SEM analysis showed a very uniform distribution of the iron oxide over the carbon surface. FTIR spectrum and X-ray diffraction pattern of goethite was observed. The particle size of the goethite was found to be 176 nm, determined by metal pulse titration. These results, showed a material with small particle size of goethite, which is interesting to be tested as oxidation catalyst for organic compounds.

Introdution

Activated carbon has been widely used as an adsorbent and as a catalyst support in a variety of industrial and environmental applications such as removal hazardous pollutants. Almost any carbonaceous materials can be used for the preparation of activated carbon. Normally activated carbon is produced from wood, peat and waste materials from the agriculture e.g. coconut shell, sugar cane bagasse, rice husks, coffee beans and plenty of other residual materials (Boonamnuayvitaya, et al, 2004).

Pure or impregnated iron oxides, e.g. goethite, hematite, magnetite, etc, are utilized as a catalyst on the oxidation of several organic pollutants. Goethite, iron oxihidroxide (α-FeOOH), occurs as natural mineral and can be easily synthesized in the laboratory. It is one of the most thermodynamically stable iron oxide at room temperature and it has a lesser compact structure than hematite or magnetite, the later ones normally used in the catalytic reactions (Cornell & Shuwertmann, 2003).

Goethite can generate peroxyl and hydroxyl radicals, as shown in equations 1 and 2. In the first step iron(III) species is reduced to iron(II) by H_2O_2, generating peroxyl radicals. Iron(II) species produced in the first step react with another portion of H_2O_2, producing hydroxyl radical and hydroxyl anion (e.g. in Lago, et. al.;2004).

$$Fe^{3+} + H_2O_2 \longrightarrow \ ^\bullet OOH + \ ^+H + Fe^{+2} \qquad \textbf{Equation 1}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \ ^-OH + \ ^*OH \qquad \textbf{Equation 2}$$

The combination of H_2O_2/Fe^{3+} producing Fe^{2+} species and hydroperoxyl radical (Equation 1) followed by the reoxidation of Fe^{2+} species by H_2O_2 (Equation 2) is well known as a catalytic Fenton-like reaction. Therefore, pollutants can be oxidized by the combined action of hydroxyl and hydroperoxyl radicals produced in both steps (Equation 1 and 2).

Normally iron oxides present a very low surface area, and the catalytic activity of these oxides can be improved by their dispersion over an inert support. In this work we prepared activated carbon from coffee husk waste and it was used as iron oxide support. The materials were characterized and the catalytic activities were evaluated using methylene blue dye oxidation using H_2O_2 as oxidant agent, in a heterogeneous Fenton-like system.

Experimental

Preparation of the activated carbons

The raw material was a representative sample of coffee husk waste, sieved fraction from 0.15 to 0.20 mm. The two types of material were obtained: (i) activated carbon by controlled pyrolysis of husk coffee activated using zinc chloride [raw material/$ZnCl_2$ 1/1 ratio - (AC-Zn)] and (ii) the AC-Zn activation followed by activation in CO_2 (AC-Zn+CO_2). The preparation of material (i) 5 g of raw material were introduced into a tubular furnace and heated at rate of 10 K min^{-1} till 773 K and kept at this temperature for three hours, under N_2 flow (100 mL min^{-1}). The furnace was cool down to room temperature, and the pyrolysed material was washed until a neutral pH, and oven dried overnight at 380 K. For the preparation of material (ii) the same procedure described for the material (i), but one extra step was used. The material (i) was activated by heating it in a furnace at rate of 10 K min^{-1} until 1023 K and kept for at this temperature for 0.5 h, under CO_2 flow (100 mL min^{-1}). The pyrolysed material was washed till neutral pH.

Preparation of the composite AC/goethite

The composites were prepared from a suspension of 1 g of activated carbon in a 100 mL solution of $FeCl_3$ (1 mmol L^{-1}) at room temperature. About 30 mL of a 1.0 mol L^{-1} NaOH solution was added drop-wise, in order to precipitate the iron oxides (goethite) on the activated carbon surface. The materials were aged for 72 hours at 333 K and then washed with distilled water until neutral pH. The amount of goethite was calculated to be 1% in mass of the activated carbon. The obtained materials were dried at 333 K for 24 h. Two composites were prepared: (i) goethite on the activated carbon with zinc chloride (AC-Zn/Gt) and (ii) goethite on the surface activated carbon with zinc chloride and CO_2 (AC-Zn + CO_2/Gt).

Caracterization of the materials

The materials were characterized by powder XRD (Phillips PW1830) with CoKα radiation, λ=0.178897 nm; temperature programmed reduction (TPR), Quantchrome, chemebet-3000; room temperature Mössbauer spectroscopy (^{57}Co/Rh source; isomer shifts are quoted relative to the αFe) and scanning electron microscopy (SEM) (LEO EVO 40XVP, equipped with Au sputtering coated samples fixed in a carbon tape). BET area and pore volume of the samples were determined by nitrogen (77K) adsorption-desorption isotherms measured by Gas Sorption Analyzer (Quantachrome NOVA-1200). The surface areas were calculated using BET equation.

Catalytic Tests for oxidative reactions

Two reactions took place in presence of the composite, according to the substrate: (i) the H2O2 decomposition to O_2 in water, (ii) the oxidation of the methylene blue dye. The decomposition of hydrogen peroxide was carried out with 2 mL of H_2O_2 solution (50% v/v) in 5 mL of water and 10 mg of the composite. The mixture was stirred with a magnetic stirrer and the reaction was monitored by measuring the formation of O_2 in a volumetric glass system. The discoloration of the methylene blue dye was monitored by measuring the absorbance at 665nm in the UV/Vis spectrophotometer (Shimadzu UVPC 1600). The tests were carried out by 10 mL solutions 50 mg L^{-1} with 30 mg of the composite and 0.1 mL of the H_2O_2 (50%), the reaction solution absorbencies were measured at 0, 30, 60, 120, 180 and 210 min.

Leaching test

It was also studied the metal ion leaching from the composites. The tests were made using 9.9 mL distilled water, 10 mg of the composite, 0.1 mL hydrogen peroxide (50% v/v). The mixture was kept in contact for two hours. Then the precipitate was centrifuged off and the resulting material was used to prepare 19.8 mL of methylene blue solution (10 mg kg^{-1}). The homogeneous catalyst activity was tested by adding 0.2 mL of H_2O_2 (50% v/v) to the methylene blue solution, prepared in the later step, and kept reacting for 5 h. The concentration of methylene blue was measured by UV/Vis spectrophotometry.

The methylene blue dye oxidation intermediates by ESI-MS

In an attempt to identify the intermediates formed in the oxidation process, the methylene blue decomposition was monitored by mass spectrometry using a positive ion mode ESI-MS of an Agilent-1100 MS-ion trap mass spectrometer. The reaction samples were analyzed by infusing the samples into the ESI source with a syringe pump at a flow rate of $5\mu L$ min^{-1}. Spectra were obtained as an average of 5 scans of 0.2 s. Typical ESI conditions were as follows: dry gas temperature of 600 K; dry gas (N_2) flow rate of 5 L min^{-1}; nebulizer pressure of 10 psi. capillary voltage 3.5 kV; skimmer voltage of 35 V, capillary exit of 125 V, the target mass set to 300, and ICC set to 30000 with a maximum accumulation time of 300 ms.

Results and discussion

Characterization of the materials

The morphologies of the materials were analyzed by SEM. In Figure 1 is shown the SEM images obtained for the different materials.
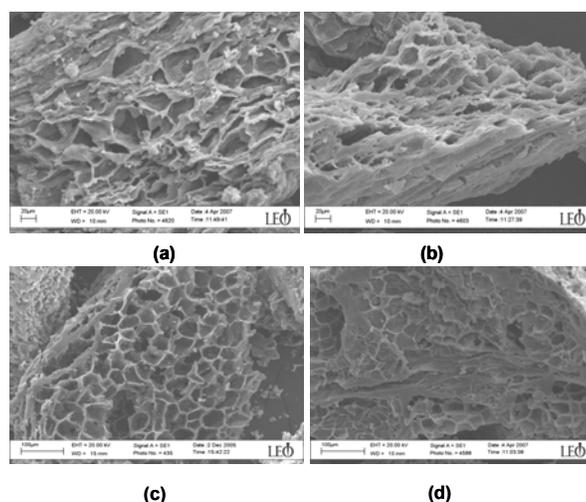

Figure 1. SEM images of the activated carbons: (a) AC-Zn and (c) AC-Zn + CO_2, and composites iron oxide and activated carbon: (b) AC-Zn/Gt and (d) AC-Zn+ CO_2/Gt.

The morphologies of the activated carbons [Figure 1 (a) and (c)] and composites AC/Gt [Figure 1 (b) and (d)] showed a honey comb like structure. The formation of large pores is probably due to the local volatiles compounds which are lost during the pyrolysis process (Boonamnuayvitaya, et al, 2005). The iron oxide crystals are not observed for any of the composites [Figure 1 (b) and (d)], indicating that the oxides is well dispersed over the AC surface with small crystallites for both materials. This hypothesis was confirmed by pulse titration technique, showing the crystallite size average of 176 and 623 nm for AC-Zn+CO2/Gt and AC-Zn/Gt, respectively.

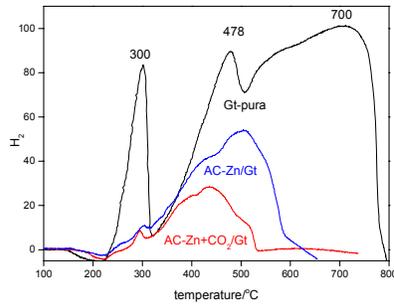In Figure 2 is show temperature programmed of reduction (TPR) analysis of composites.

Figure 2. TPR graph of the pure goethite and composites: AC-Zn/Gt and AC-Zn+ CO_2/Gt.

The TPR profiles of composite are similar of the pure goethite, showing three reduction peaks. As goethite phase is converted into hematite phase by heating, the TPR profile of hematite reduction up to Fe^0 is observed. The consumption of H_2 for the peak at 573 K is due hematite (Fe_2O_3) conversion by reduction into magnetite (Fe_3O_4). However, the followed reduction at higher temperatures does not go directly to α-Fe, which occurs *via* two steps. Temperatures above 750 K, the formation of a stable wüstite phase (FeO) becomes possible. Therefore, the intense peak at 973 K represents the direct reduction of Fe_3O_4 and FeO to Fe^0 (Zhang, 2006).

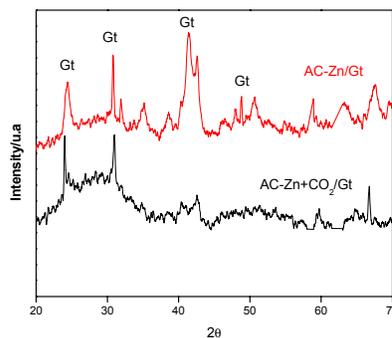The XRD of the materials are shown in Figure 3.

Figure 3. XRD graph of composites: AC-Zn/Gt and AC-Zn+ CO_2/Gt.

The XRD analysis of the composites showed only the presence of a hexagonal iron oxide phase (d_{110}=0.4202; d_{130}=0.2698; d_{111}=0.2452 and d_{221}=0.1717 nm) which can be related to the presence of goethite (Cornell & Schwertmann, 2003).

The formation of goethite phase was confirmed by Mössbauer spectroscopy with hyperfine field (B_{hf}) 37,2 T and isomeric shift (δ)0,364 mm s^{-1} (αFe^0) typical parameters for this phase (Cornel & Schuwertmann, 2003).

Decomposition of H_2O_2 in the presence of composites.

The peroxide decomposition was studied in the presence of different composites. In the Figure 4 is showed the results.
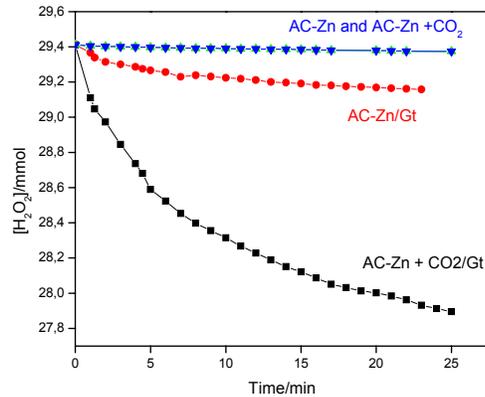
Figure 4. H_2O_2 decomposition to O_2 in water in the presence of composites.

Under the reaction conditions the decomposition of peroxide by the composites showed very low activities. The relative activity of the composites and pure activated carbon reveled that the AC-Zn+CO_2/Gt is much more active than all other materials for the H_2O_2 decomposition. Probably, it is due to the smaller particle size of goethite dispersed on the surface of the activated carbon. The decomposition the peroxide follows a pseudo first order kinetic with respect to H_2O_2 ($V_{dec} = k_{dec}[H_2O_2]$). The rate constants found for the materials were 0,00006 s^{-1} for activated carbons and 0.0003 s^{-1} and 0.0018 s^{-1} for the AC-Zn/Gt and AC-Zn + CO_2/Gt, respectively.

The oxidation of methylene blue dye with H_2O_2 in presence of the composites was spectrophotometrically monitored through the discoloration of the solution (665 nm). The results are showed in the Figure 5.
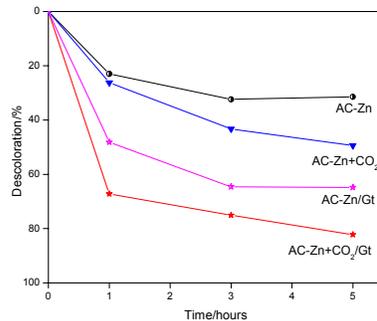

Figure 5. Oxidation of methylene blue dye with H_2O_2, in presence of the composites.

It was observed that the concentration of the methylene blue diminishes to 50% after 60 min of reaction. The pure activated carbons in presence of H_2O_2 showed the low adsorption capacity.

The adsorption process and iron leaching were controlled by measuring the discoloration of the dye solution in a batch adsorption experiment, after reaction for 5 h, with the composites and activated carbon. These results are showed in the Figure 6.
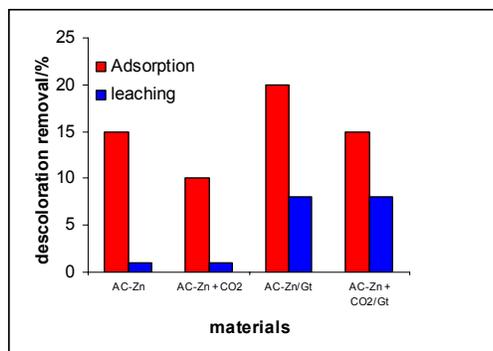
Figure 6. Percent of discoloration of the methylene blue solution. Effects of iron leached and adsorption after at 5 hours.

Adsorption contributes with up to 20% to the discoloration process of the solution discoloration. The iron content in solution, observed in the leaching test, was found to be very low, indicating that the discoloring reaction take place *via* a heterogeneous mechanism.

Identification of intermediates via ESI-MS monitoring

The identification of reaction intermediates was performed by ESI-MS during the oxidation of methylene blue dye by composite AC-Zn + CO_2/Gt and AC-Zn + CO_2 (Figure 7).
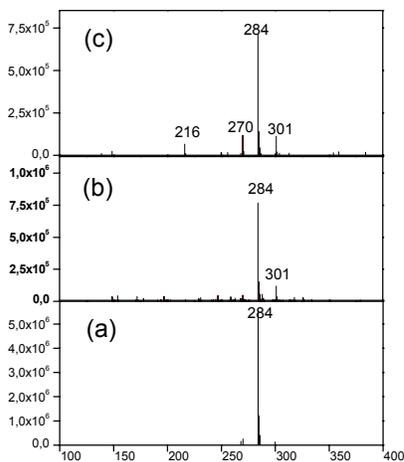

Figure 7. ESI mass spectra in the positive ion mode for monitoring the oxidation of methylene blue dye in water: (a) methylene blue standard; (b) activated carbon AC-Zn + CO_2 and (c) composite AC-Zn + CO_2/Gt; in presence of H_2O_2 at 4 hours reactions.

At beginning of the reaction the [Figure 7 (a)], ESI-MS operating in the positive ion mode, only the presence of methylene blue $m/z=284$ is observed. However, after 4 h reaction time the activated carbon [Figure 6 (b)], a new and very low intense signal with m/z 301 was detected. On the other hand, when a composite AC-Zn+CO_2/Gt, was tested, after 4 h reaction time (Figure 7 (c)) the signals with m/z= 216, 270 and 301 has appeared. The signal m/z = 301 can be due a first hydroxylation of methylene blue molecule and the signals m/z = 216 and 270, due to molecule fragmentation (Oliveira et al, 2007).

Conclusions

The composite with well dispersed goethite, showing small size of crystallites presented the best catalytic activity. The iron content is in this material very low, compared to the pure iron oxide or homogeneous catalysis normally employed, for this reason the results obtained here is very interesting, as we are looking for catalytic systems for using on degradation of organic pollutants.

Acknowledgment

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