



Iron oxide dispersed over activated carbon: Support influence on the oxidation of the model molecule methylene blue

C.S. Castro^{a,*}, M.C. Guerreiro^a, L.C.A. Oliveira^a, M. Gonçalves^b, A.S. Anastácio^a, M. Nazzarro^c

^a Universidade Federal de Lavras, Depto de Química, Caixa Postal 3037, CEP 37200-000, Lavras-MG, Brazil

^b Departamento de Química Inorgánica, Universidad de Alicante, Alicante, Apartado 99, E-03080, Spain

^c Departamento de Física, Laboratorio de Cs de Superficies y Médios Porosos, Universidad Nacional de San Luis, Chacabuco 917, San Luis, Argentina

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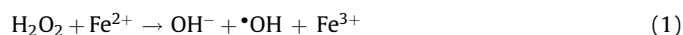
ABSTRACT

In this work materials based on iron oxide dispersed over activated carbon were prepared and tested in the H₂O₂ decomposition and removal of the methylene blue (MB) model from aqueous solution. Two different supports were evaluated: a commercial activated carbon (CAC) and an activated carbon produced by coffee used grounds (ACK). These materials, after iron impregnation (CAC/Fe and ACK/Fe), were characterized using XRD, SEM, N₂-sorption, XPS and Mössbauer spectroscopy. The main results suggest the formation of composites with high surface area and iron dispersion containing Fe³⁺ on the surface of both catalysts. Catalytic tests revealed high capacity for H₂O₂ decomposition by both composites with more activity for ACK/Fe. MB removal experiments showed intense removal of the model through combined adsorption and oxidation processes. The detection of known MB oxidation intermediates observed by ESI-MS studies confirmed the occurrence of MB oxidation processes and also showed more activity for ACK/Fe.

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1. Introduction

Several treatments must be frequently applied to wastewaters generated in industrial processes in order to reduce the organic load as well as other contaminants present, before its discharge in public effluents. The classical homogeneous Fenton system has been extensively studied for the oxidation of a great variety of organic contaminants in water [1,2]. Fenton's system consists of ferrous salts combined with hydrogen peroxide under acidic conditions, which react to form •OH:



The •OH radical reacts rapidly and non-selectively with most organic compounds by H-abstraction or addition to C–C unsaturated bonds and produces its chemical decomposition [3]. The Fenton reaction operates at the optimum pH 3 and requires stoichiometric amounts of Fe²⁺ and H₂O₂. After the process, the effluent must be neutralized generating significant amounts of sludge, and these are evident drawbacks of the process. The development of active heterogeneous Fenton systems, where soluble Fe²⁺ is replaced by Fe-containing solids without any need of low pH is of considerable interest. The heterogeneous Fenton

system could offer some advantages over the classical homogeneous reaction, such as no sludge formation, operation at near neutral pH and the possibility to recycle the iron promoter [4]. In these heterogeneous systems, the choice of the support is undoubtedly very important for the development of a good catalyst. Activated carbons are interesting materials for this purpose and due to their high surface area and porous structure they can efficiently adsorb gases and compounds dissolved in liquids [5,6].

In this context, materials based on iron oxide/activated carbon are promising in the organic removal from aqueous solution combining the oxidation properties of iron oxides and adsorption capacity of activated carbon. Considering this, the main objective of the present research was to prepare iron oxide dispersed over two different activated carbon supports in order to investigate the removal of the model molecule methylene blue from aqueous solution.

2. Experimental

2.1. Catalysts preparation

Two different activated carbon supports were investigated to produce the catalysts of iron oxide dispersed over activated carbon. A commercial activated carbon (Merck) denoted as CAC and an activated carbon produced by a food industry residue, spent coffee

* Corresponding author. Tel.: +55 35 3829 1625; fax: +55 35 3829 1271.

E-mail address: cicastro14@yahoo.com.br (C.S. Castro).

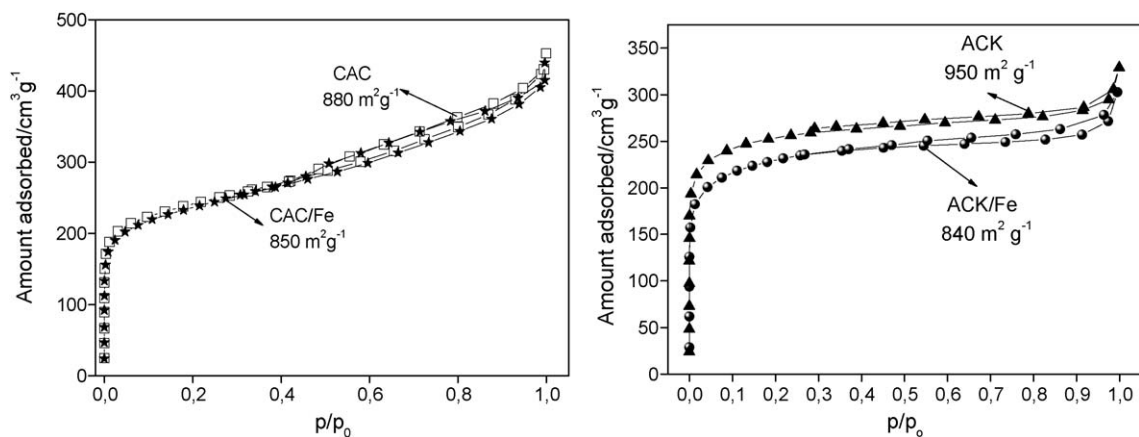


Fig. 1. Nitrogen adsorption/desorption at 77 K of CAC and CAC/Fe (a) and ACK and ACK/Fe (b).

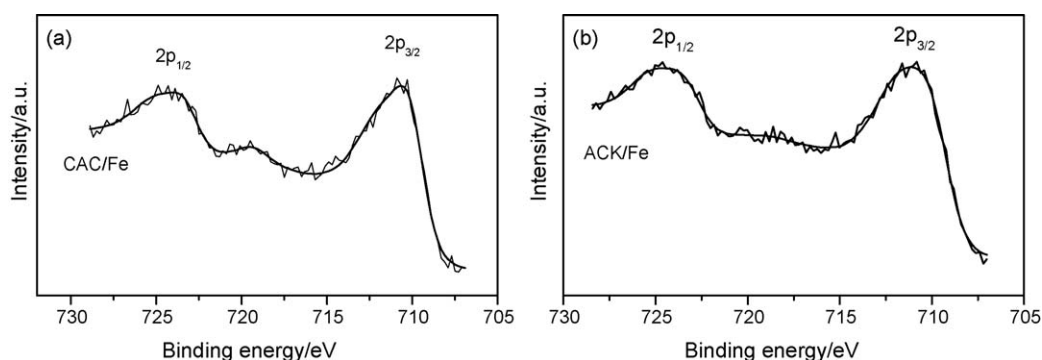


Fig. 2. XPS analysis of the CAC/Fe (a) and ACK/Fe (b).

grounds (ACK). To produce the ACK, the spent coffee grounds were impregnated (1/1, g/g) with the chemical agent K_2CO_3 . A 100 mL aqueous solution containing K_2CO_3 (8 g) and the spent coffee ground (8 g) was vigorously stirred and the mixture was heated at 80 °C until complete drying and put in an oven at 110 °C for 24 h. Then, the material was placed in a tubular furnace and heated at 10 °C min⁻¹ until 800 °C for 2 h. The resulting material was then water washed to remove the chemical remaining agent. To produce the catalysts of iron oxide dispersed over activated carbon, the iron salt ($Fe(NO_3)_3 \cdot 9H_2O$) was dissolved in 100 mL of water in contact with the activated carbons (ACK and CAC) in a proportion of 5% (g/g) (iron/activated carbon) and heated at 80 °C until complete drying. The commercial activated carbon was used without any treatment. Afterwards the samples were calcined at 300 °C for 3 h in a tubular furnace producing the catalysts denoted as CAC/Fe and ACK/Fe.

2.2. Catalysts characterization

The catalysts were characterized by powder XRD (Rigaku Geigerflex, Cu K α , $\lambda = 1.5406 \text{ \AA}$), Mössbauer spectroscopy, CMTE model MA250 and ⁵⁷Co/Rh source; nitrogen adsorption/desorption at 77 K (AUTOSORB-1, Quantachrome). The surface area of the materials was determined using the Brunauer–Emmett–Teller (BET) equation. The composites were also characterized by total iron content measured by AA (SpectrAA 110 Varian). X-ray photoelectron spectroscopy (XPS) was used to examine the chemical state of the formed oxides. The measurements were performed with a spectrometer (Kratos Analytical XSAM 800 cpi) with Mg K α radiation (1253.6 eV) as the X-ray source. In order to measure binding energies, the C (1s) signal of the carbon was used

as the reference at 284.6 eV. Morphological analysis was also performed by scanning electron microscopy (SEM Leo Evo model 40XVP).

2.3. Catalytic experiments

2.3.1. H₂O₂ decomposition

Hydrogen peroxide decomposition tests were carried out in a volumetric glass system with 30 mg of the catalysts in 7 mL

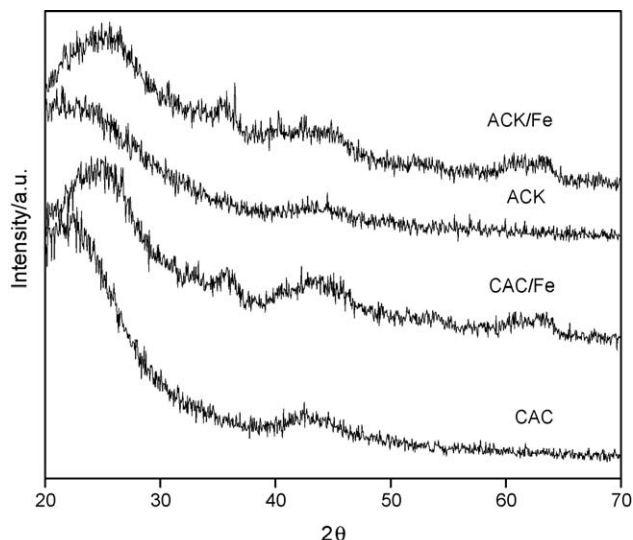


Fig. 3. XRD patterns for the materials.

solution of hydrogen peroxide 3 mol L^{-1} . In order to investigate the hydrogen peroxide decomposition mechanism, the tests were also carried out in the presence of organic compounds utilizing 7 mL solutions of 50 mg L^{-1} of the dye methylene blue, ascorbic acid or phenol.

2.3.2. Methylene blue removal

The methylene blue (MB) adsorption tests were carried out using 10 mg of the composites in contact with 10 mL of a 500 mg L^{-1} MB solution after 1, 6, 15 and 24 reaction hours. In the oxidation experiments, the oxidant agent H_2O_2 (0.1 mL , 50% , v/v) was added to the solution and the MB removal monitored by UV–vis spectroscopy at the same time as the adsorption experiments. The MB removal is expressed in % [$1 - (\text{concentration at time} = t / \text{concentration at time zero})$]. In order to study the methylene blue oxidation products, the reactions were also monitored by ESI-MS Trap mass spectroscopy (Agilent-1100 ion trap VL). Typical ESI

conditions were as follows: dry gas temperature, 600 K ; dry gas (N_2) flow rate, 5 L min^{-1} ; nebulizer pressure, 10 psi ; capillary voltage, 3.5 kV ; skimmer voltage, 35 V ; capillary exit, 125 V ; the target mass set to 300 , and ICC set to $30,000$ with a maximum accumulation time of 300 ms .

The catalyst stability was also studied through iron leaching tests using the standard oxidation conditions shown above. After the experiments the catalysts were centrifuged off ($8311 \times g$ for 20 min) and the total iron content present in the solution was monitored by AA (SpectrAA 110 Varian). The possibility of recycling the catalysts was also investigated through reuse experiments. In a typical test, 100 mg of the catalysts was placed in contact with 100 mL of methylene blue solution (500 mg L^{-1}) and 1 mL of H_2O_2 under vigorous stirring for 24 h . The catalysts were then recovered by filtration and dried at $60 \text{ }^\circ\text{C}$ overnight. The materials were subsequently used in another oxidation cycle maintaining the same standard proportions.

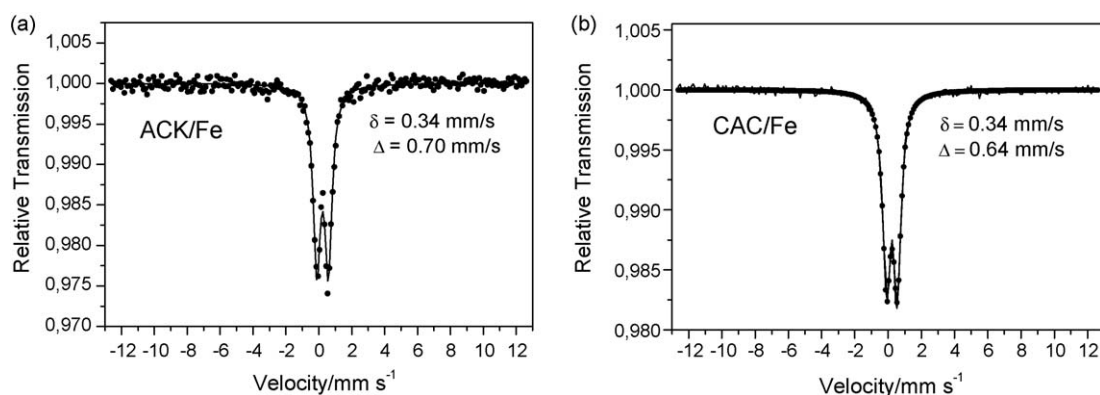


Fig. 4. Mössbauer spectra for the ACK/Fe (a) and CAC/Fe (b) composites (δ = isomer shift relative to α -Fe; Δ = quadrupole splitting).

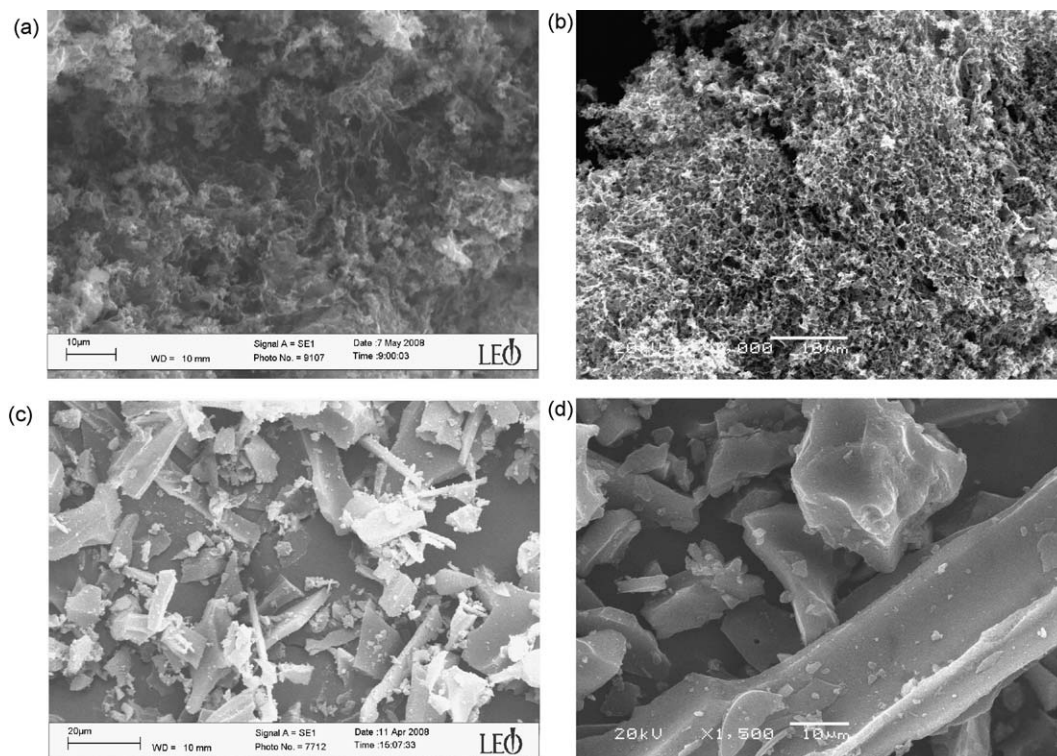


Fig. 5. SEM micrographs of ACK (a), ACK/Fe (b), CAC (c) and CAC/Fe (d).

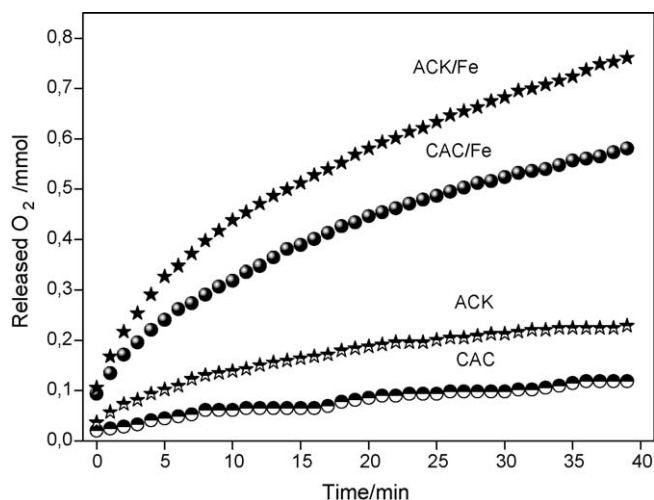


Fig. 6. Hydrogen peroxide decomposition in the presence of the activated carbons and their iron oxide composites.

3. Results and discussion

3.1. Catalysts characterization

The materials were characterized by total iron content and showed 4.8% and 6.3% for the composites CAC/Fe and ACK/Fe, respectively. The textural properties were investigated by nitrogen adsorption/desorption at 77 K (Fig. 1) and showed high surface area for all materials with a slight reduction after iron impregnation, probably due to small pore blockage [7]. This effect was more pronounced for the ACK/Fe composite. The principally microporous type feature, observed for all materials, should also be mentioned [8].

The surface iron species were investigated by XPS analysis. The XPS spectra of the 2p spectral region are shown in Fig. 2. The binding energies of Fe 2p_{3/2} and Fe 2p_{1/2} obtained from the present study are 711.0 and 724.5 eV, respectively, which corresponds to the characteristic values of Fe³⁺ [7]. The usual satellite peak obtained approximately at 720 eV is clearly distinguishable.

XRD analysis of pure activated carbons (CAC and ACK) (Fig. 3) shows broad reflections of typically amorphous materials, at $2\theta = 22.5^\circ$ and $2\theta = 44^\circ$ corresponding to the micrographitic structure characteristic of activated carbons [9]. The XRD of the composites (Fig. 3) shows new broad bands related to the formed iron phases (at around 35° and 63°) difficult to be assigned, as the composites are typically amorphous materials. The presence of these broad bands can be due to low iron concentration and/or

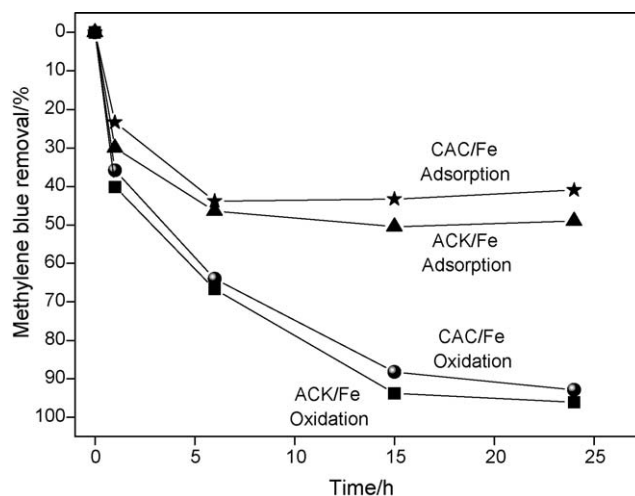


Fig. 8. Methylene blue removal in the presence of the composites CAC/Fe and ACK/Fe.

formation of small particle size iron oxide dispersed over the carbon matrix.

The ⁵⁷Fe Mössbauer spectra for the catalysts are presented in Fig. 4. The presence of only doublets can be observed for both materials, suggesting the formation of iron oxides of small particle size dispersed over carbons as also seen by XRD. The observed Mössbauer parameters are characteristic of Fe³⁺ [10] and these results are in agreement with the XPS analysis.

The morphological analyses were performed by SEM and are presented in Fig. 5. A spongy like texture can be observed for the ACK micrograph (Fig. 5a), showing small canals in its composition. After iron impregnation (Fig. 5b), a similar morphology is observed suggesting the formation of well-dispersed iron oxide particles covering the activated carbon [11]. No significant difference is observed for the micrographs of the commercial activated carbon and its composite (Fig. 5c and d, respectively) also suggesting high iron dispersion.

3.2. Catalytic experiments

3.2.1. H₂O₂ decomposition

The hydrogen peroxide decomposition (Eq. (2)) was studied in the presence of the activated carbons and their iron oxide composites and the results are displayed in Fig. 6. No significant activity in the H₂O₂ decomposition can be observed for pure activated carbons (CAC and ACK). On the other hand, after the iron impregnation on both carbons, the H₂O₂ decomposition is strongly

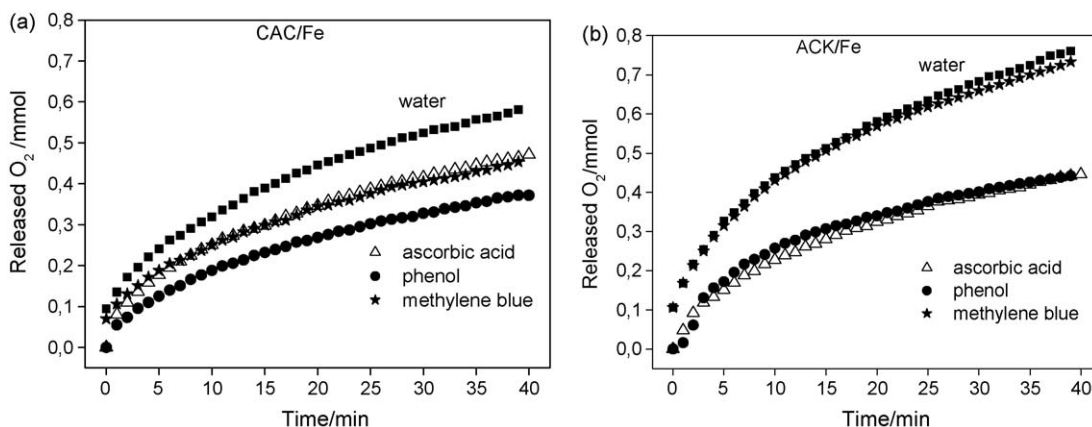


Fig. 7. Hydrogen peroxide decomposition in the presence of methylene blue, ascorbic acid and phenol and the CAC/Fe (a) and ACK/Fe (b) composites.

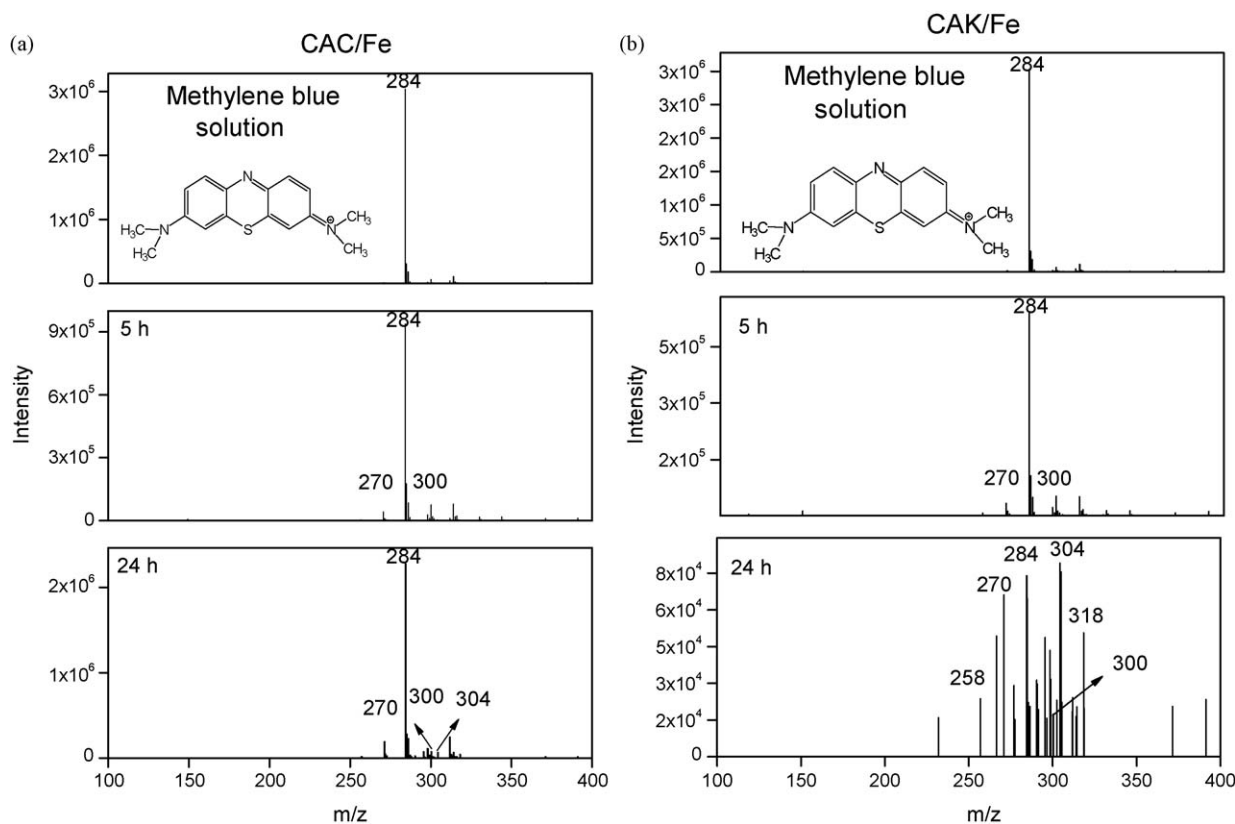


Fig. 9. ESI mass spectra in the positive mode for monitoring the oxidation of methylene blue in water at different reaction times in the presence of the CAC/Fe (a) and ACK/Fe (b) composites.

favoured with higher activity observed in the presence of ACK/Fe.



The decomposition was also studied in the presence of different radical scavenger organic compounds such as methylene blue, ascorbic acid and phenol dissolved in reaction medium (Fig. 7a and b). It can be observed that the decomposition is inhibited, especially by phenol in the case of CAC/Fe (Fig. 7a) and ascorbic acid and phenol in the case of ACK/Fe (Fig. 7b). The H_2O_2 decomposition can follow two different mechanisms: (i) radical and (ii) non-radical (vacant) mechanism [12]. The investigation can be made by the addition of an organic compound into the reaction medium. When the H_2O_2

decomposition is inhibited in the presence of the organic compounds, as observed by the prepared catalysts (Fig. 7), it strongly suggests the occurrence of the radical mechanism. In this route the organic compounds are participating in the competitive process during the H_2O_2 decomposition that may be related to reaction of the organic compounds with radical intermediates species like $\cdot\text{OH}$ and $\cdot\text{OOH}$ which have been proposed to be formed during the H_2O_2 decomposition reaction [12].

3.2.2. Methylene blue removal

These materials were also studied in the removal of the model molecule methylene blue through adsorption and oxidation

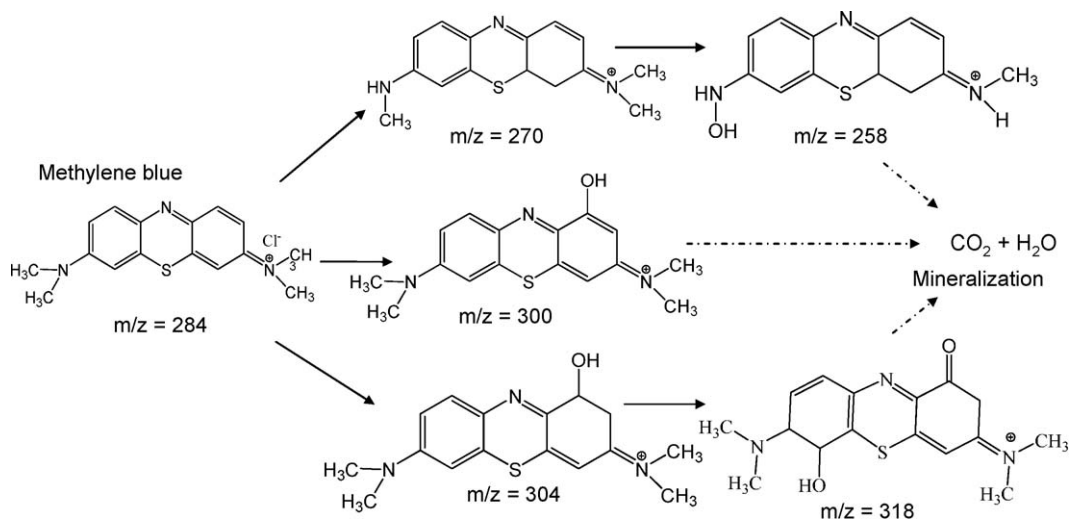


Fig. 10. Proposed scheme for intermediate structures of methylene blue oxidation using the ACK/Fe.

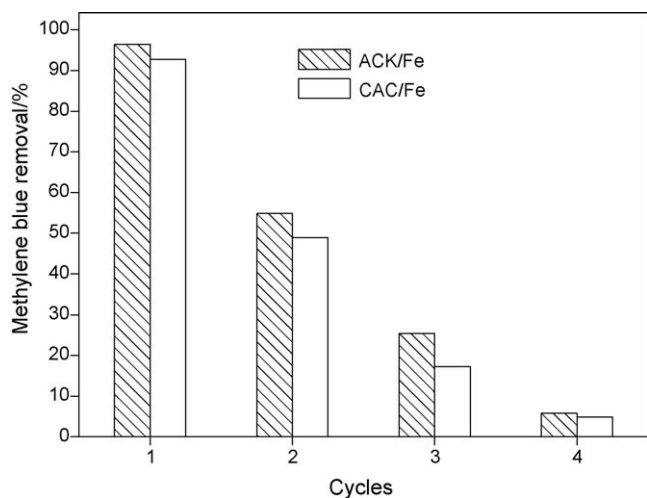


Fig. 11. The reuse of the catalysts.

processes. The results are displayed in Fig. 8 and show approximately 40% and 50% MB removal by ACK/Fe and CAC/Fe, respectively. However, a more pronounced removal is verified when H_2O_2 is added to the solution. Approximately 92% removal is observed for CAC/Fe, whereas a slightly higher removal, 97%, is verified for ACK/Fe. It is important to mention that both composites showed an expressive MB removal capacity through combined adsorption and oxidation processes removing almost 100% of MB from a high concentrate solution of the dye (500 mg L^{-1}).

In order to confirm the occurrence of methylene blue oxidation, the reactions were also monitored by ESI-MS and the results are presented in Fig. 9. For the methylene blue solution, only an intense signal at $m/z = 284$ can be observed corresponding to the dye (Fig. 9a and b). After 5 h reaction, new signals at $m/z = 270$ and $m/z = 300$, likely related to oxidation intermediates, appeared for both composites (Fig. 9a and b). However, after 24 h other new signals at $m/z = 318$ and $m/z = 258$ appeared only for the ACK/Fe (Fig. 9b) showing higher activity for this material.

Fig. 10 presents the proposed intermediate structures of the complete oxidation reaction pathway, from methylene blue to CO_2 and H_2O using the ACK/Fe [13].

The catalysts stability on the reaction medium was also investigated through iron leaching tests. Iron was not found in the solution after catalysts separation in the MB oxidation experiments. This result suggests high stability of the prepared composites in the reaction medium.

Another important characteristic of heterogeneous catalysts is the possibility of its recycling. Fig. 11 presents the cycles of reuse of both catalysts.

It can be observed that the materials lose activity only after 4 cycles of use. A deactivation of around 45% is verified for both catalysts in the second cycle of use. Moreover, it is interesting to observe that the material prepared using the activated carbon produced from spent coffee grounds presents higher activity for MB oxidation in all reuse cycles.

4. Conclusion

The iron impregnation on both activated carbons resulted in composites with high surface area and iron dispersion. The composites showed to be very active for hydrogen peroxide decomposition and higher activity was observed in the presence of the ACK/Fe. The H_2O_2 decomposition for both CAC/Fe and ACK/Fe materials takes place via a radical mechanism, probably initiated by an electron transfer from the active site, on the surface of the composite, to H_2O_2 to produce species such as $\bullet OH$ or $\bullet OOH$. These catalysts also exhibited high removal of the model molecule methylene blue (MB) through combined adsorption and oxidation processes. The ESI-MS studies confirmed the MB oxidation processes. The m/z signals account for the presence of intermediate structures in the reaction medium and the catalytic activity is shown to be higher using the catalyst prepared with the activated carbon produced by used coffee grounds (ACK/Fe).

Acknowledgements

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References

- [1] D. Kassinos, N. Varnava, C. Michael, P. Piera, *Chemosphere* 74 (2009) 866–872.
- [2] P.A. Carneiro, R.F.P. Nogueira, M.V.B. Zanoni, *Dyes Pigments* 74 (2007) 127–132.
- [3] F.J. Benitez, F.J. Real, J.L. Acero, A.I. Leal, C. Garcia, *J. Hazard. Mater.* 31 (2005) 31–39.
- [4] R.C.C. Costa, F.C.C. Moura, J.D. Ardisson, J.D. Fabris, R.M. Lago, *Appl. Catal. B* 83 (2008) 131–139.
- [5] F. Rodriguez-Reinoso, *Carbon* 36 (1998) 159–175.
- [6] T.J. Bandoz, *Activated Carbon Surfaces in Environmental Remediation*, Elsevier, New York, 2006.
- [7] A. Rey, M. Faraldos, J.A. Casas, J.A. Zazo, A. Bahamonde, J.J. Rodriguez, *Appl. Catal. B* 86 (2009) 69–77.
- [8] Y. Sudaryanto, S.B. Hartono, W. Irawaty, H. Hindarso, S. Ismadji, *Bioresour. Technol.* 97 (2006) 734–739.
- [9] M.A. Schettino, J.C.C. Freitas, A.G. Cunha, F.G. Emmerich, A.B. Soares, P.R.N. Silva, *Quim. Nova* 30 (2007) 1663–1668.
- [10] R.M. Cornel, U. Schwertmann, *The Iron Oxides*, 2nd ed., J. Wiley-VCH, New York, 2003.
- [11] Q.L. Zhang, Y.C. Lin, X. Chen, N.Y. Gao, *J. Hazard. Mater.* 148 (2007) 671–678.
- [12] L.C.A. Oliveira, C.N. Silva, M.I. Yoshida, R.M. Lago, *Carbon* 42 (2004) 2279–2284.
- [13] L.C.A. Oliveira, M. Gonçalves, M.C. Guerreiro, T.C. Ramalho, J.D. Fabris, M.C. Pereira, K. Sapaq, *Appl. Catal. A* 316 (2007) 117–124.