



Removal of organic dyes using Cr-containing activated carbon prepared from leather waste

Luiz C.A. Oliveira^{a,*}, Camila Van Zanten Coura^a, Iara R. Guimarães^b, Maraisa Gonçalves^b

^a Department of Chemistry, Federal University of Minas Gerais, Belo Horizonte, 31270-901, Minas Gerais State, Brazil

^b Department of Chemistry, Federal University of Lavras, P.O. Box 3037, Lavras, MG, 37200-000, Brazil

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ABSTRACT

In this work, hydrogen peroxide decomposition and oxidation of organics in aqueous medium were studied in the presence of activated carbon prepared from wet blue leather waste. The wet blue leather waste, after controlled pyrolysis under CO₂ flow, was transformed into chromium-containing activated carbons. The carbon with Cr showed high microporous surface area (up to 889 m² g⁻¹). Moreover, the obtained carbon was impregnated with nanoparticles of chromium oxide from the wet blue leather. The chromium oxide was nanodispersed on the activated carbon, and the particle size increased with the activation time. It is proposed that these chromium species on the carbon can activate H₂O₂ to generate HO• radicals, which can lead to two competitive reactions, i.e. the hydrogen peroxide decomposition or the oxidation of organics in water. In fact, in this work we observed that activated carbon obtained from leather waste presented high removal of methylene blue dye combining the adsorption and oxidation processes.

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1. Introduction

The tanning industry generates a large amount of solid and liquid residues from the tanning process, which uses chromium (III) to obtain the wet blue leather. The solid residues (leather shavings and scraps) contain around 3% in mass of Cr³⁺. The leather tanning process uses, among other tanning agents, Cr³⁺ leading to a product called wet blue leather, which is stable and inert due to a polynuclear chromium–collagen complex, which is formed in the tanning process. The wet blue leather is one of the most used processed leathers, and therefore the tanning industries produce a large amount of solid waste containing chromium [1–5]. The chromium present in this waste is chromium (III) and it is considered harmless to the environment. However, under uncontrollable conditions in the environment it can be oxidized to the mutagenic chromium (VI) form [6]. The production of chromium-containing solid waste in Brazil is approximately 100,000 tons year⁻¹, which has turned out to be a serious environmental problem. Several technologies are utilized for removing this waste from the tanning industry mainly as adsorbent to remove metallic and organic contaminants from aqueous medium [2].

The surface chemistry of activated carbons has been extensively studied due to their importance for many applications [7–11].

Moreover, carbon impregnation with different active phases has been widely investigated. Some examples of catalytic properties of impregnated carbons are: dehydration and dehydrogenation of alcohols [12], oxidation of Fe(II) by oxygen [13,14], activation of O₃ [15] and the decomposition of H₂O₂ to O₂ [16].

In this work it is reported that an activated carbon with high surface area can be obtained from a serious solid waste to produce a material with strongly modified redox properties, resulting in a remarkable effect on the catalytic properties towards the decomposition of H₂O₂ and the oxidation of organics in water. Moreover, the impregnation step with active phase was avoided because the chromium came directly from the wet blue leather waste. Chromium shows interesting features for this system such as: different oxidation states which can co-exist under the reaction conditions and the high reactivity towards H₂O₂ activation [17]. An interesting feature of activated carbons is that they can act as an adsorbent for the organic compound and also as catalyst/promoter for its oxidation. The presence of the active oxidizing species on the carbon surface near the pre-concentrated contaminant can potentially increase the process efficiency. The understanding of the reaction mechanism, the nature of the active site and the improvement of the carbon activity for this type of reaction are of considerable interest. In the present paper methylene blue dye was used as a model compound present in water, aiming at a possible elucidation of the chemical mechanisms involved in the oxidative reaction. The effect of the chromium on the surface of the activated carbon was evaluated as to the oxidation reaction.

* Corresponding author. Tel.: +55 31 3409 6384; fax: +55 31 3409 5700.
E-mail address: luizoliveira@qui.ufmg.br (L.C.A. Oliveira).

Table 1
Chemical characterization of the wet blue leather waste used in the activated carbon preparation.

Parameter	Unit ^a	
Volatile solids	% (w/w)	98.7
Organic carbon (C)	g kg ⁻¹	481
Kjeldahl nitrogen (N)	g kg ⁻¹	140
Calcium (Ca)	g kg ⁻¹	0.80
Lead (Pb)	mg kg ⁻¹	17.6
Copper (Cu)	mg kg ⁻¹	2.7
Chromium (Cr)	mg kg ⁻¹	22,250
Sulfur (S)	g kg ⁻¹	2.3
Iron (Fe)	mg kg ⁻¹	1183
Phosphorus (P)	g kg ⁻¹	0.1
Magnesium (Mg)	g kg ⁻¹	0.2
Manganese (Mn)	mg kg ⁻¹	13.2
Mercury (Hg)	mg kg ⁻¹	<0.5 ^b
Molybdenum (Mo)	mg kg ⁻¹	<0.5 ^b
Nickel (Ni)	mg kg ⁻¹	13.2
Potassium (K)	mg kg ⁻¹	670
Selenium (Se)	mg kg ⁻¹	<0.5 ^b
Sodium (Na)	mg kg ⁻¹	1065
Zinc (Zn)	mg kg ⁻¹	13.3
pH	–	7.0
Electrical conductivity	dS/m	495

^a Results expressed from the dry base sample.

^b Not determined, lower concentrations than the quantification limit.

2. Experimental

2.1. Preparation of the carbons

The material used in the activated carbon preparation was the wet blue leather waste from the Vanzella industry located in Rolândia-PR, Brazil. The complete chemical characterization of the leather waste is presented in Table 1. It is interesting to observe the high content of chromium, which makes this solid waste one of the most dangerous and harmful residues if discarded into the environment without any further treatment. The material was ground and sieved and the fraction from 0.30 to 0.40 mm was used. Two types of material were obtained: (i) black carbon by controlled pyrolysis of wet blue leather waste (carbon-N₂). This material was heated to 850 °C in a tubular furnace, under N₂ flow (100 cm³ min⁻¹) at rate of 10 °C min⁻¹ and kept at this temperature for 0.5 h. The other materials (ii) activated carbon by activation with CO₂ stream for 0.5 h (carbon-0.5) and 2 h (carbon-2). For (ii), the sieved material was heated to 850 °C at 10 °C min⁻¹ under CO₂ stream (100 cm³ min⁻¹) the material was kept at this temperature for 0.5 or 2 h.

2.2. Characterization of the materials

The materials and activated carbon were characterized by Nitrogen adsorption at 77 K (–196 °C) and CO₂ adsorption at 273 K (0 °C), in a Coulter Omnisorb 610 system and in an AUTOSORB 1-Quantachrome, respectively. The surface area was calculated using the BET model; the total pore volume was estimated from the amount of nitrogen adsorbed at $P/P_0 = 0.95$ and the micropore volume was derived from DR plot; the pore size distribution (PSD) was calculated based on the density functional theory (DFT). The samples were degassed overnight at 300 °C before each adsorption measurement. H₂ chemisorption analysis was performed using the Quantachrome ChemBET 3000 equipment. Before reduction, the sample was pre-treated with a N₂ flow (50 cm³ min⁻¹) at 150 °C for 0.5 h, followed by pure H₂ flux at 50 cm³ min⁻¹, raising the temperature up to 300 °C at 10 °C min⁻¹, and kept for 2 h at this temperature. Then, after evacuation and cooling to 30 °C the sample underwent H₂ uptake and isotherms were obtained at 70 °C and pressures between 60 and 400 mbar. Then, in sequence after evacuation for 1 h at 300 °C and cooling, the sample was reduced

at 500 °C. H₂ uptakes at 30 °C were obtained, pressures varying between 60 and 400 mbar. The chromium dispersions were calculated assuming on top adsorption of hydrogen atom on chromium atoms.

The powder X-ray diffraction (XRD) data were obtained in a RIGAKU model GEIGERFLEX using Cu K α radiation. X-ray photoelectron spectroscopy (XPS) data were obtained by KRATOS Analytical XSAM 800 cpi ESCA equipped with a Mg anode (Mg K α radiation, 1253.6 eV) and spherical analyzer operating at 15 kV and 15 mA.

2.3. Catalytic tests

2.3.1. Oxidative reactions

Two types of reactions were carried out in the activated carbon presence, according to the substrate: (i) the H₂O₂ decomposition to O₂ in water and (ii) the methylene blue dye oxidation. All reactions were done at pH 6.0.

The former, is typical hydrogen peroxide decomposition, and was carried out in the following proportion, 2 mL of H₂O₂ solution (30%, v/v), 5 mL of water and 30 mg of the commercial carbon, carbon-0.5 or carbon-2. The mixture was stirred with a magnetic rod stirrer and the reaction was monitored by measuring the O₂ formation in a volumetric glass system.

The catalytic properties of the material were tested via oxidation of methylene blue dye. The oxidation tests were carried out using 9.9 mL of a dye solution (10 mg L⁻¹) in water. 10 mg of the catalyst were used and also 0.1 mL of H₂O₂ (VETEC, 30%) as oxidant. The reaction progress of methylene blue dye oxidation was monitored with UV–vis spectroscopy (UV–vis Spectrometer (Spectrovision), with scanning between 400 and 480 nm) and electrospray ESI–MS (Agilent-1100), allowing to identify intermediates formed during this reaction. The reactions took place at 25 ± 1 °C and pH 6.0.

Total Organic Carbon (TOC) measurements were carried out in TOC 500A Shimadzu.

2.3.2. ESI–MS study

In an attempt to identify the intermediates formed, the methylene blue dye decomposition was monitored using an electrospray ion source in an Agilent ion trap mass spectrometer (ESI–MS). The reaction samples were analyzed by introducing aliquots into the ESI source with a syringe pump at a flow rate of 5 μ L min⁻¹. The spectrum obtained were an average of 50 scans of 0.2 s. Typical ESI–MS conditions were as follows: heated capillary temperature, 150 °C; dry gas (N₂) at a flow rate of 5 L min⁻¹; spray voltage 4 kV; capillary voltage 25 V; tube lens offset voltage, 25 V. For ESI–MS/MS, the parent ion of interest was first isolated by applying an appropriate waveform across the end cap electrodes of the ion trap to resonantly eject all trapped ions, except those ions with m/z ratio of interest. The isolated ions were then subjected to a supplementary AC signal, to resonantly excite them to cause collision-induced dissociation (CID) using helium as a reagent gas. The collision energy was set to a value at which ions were produced in measurable abundance.

The chromium on the activated carbon and content leaching during all reactions was evaluated by atomic absorption analysis, using a Varian AA 110 equipment. We found 0.045 and 0.058 mg L⁻¹ of chromium leaching from carbon-0.5 and carbon-2, respectively. We observed that this concentration of chromium does not lead to a homogeneous reaction.

3. Results and discussion

3.1. Characterization of the activated carbon

X-ray diffraction (XRD) analyses were used to investigate the chromium phase on the activated carbon surface. Fig. 1 shows the

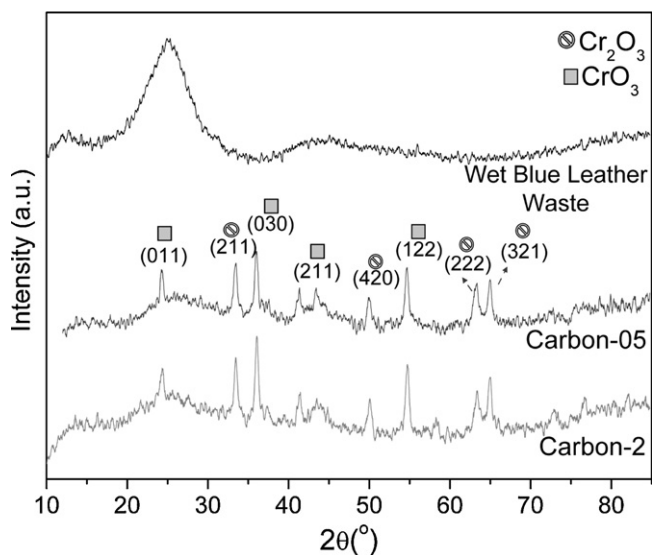


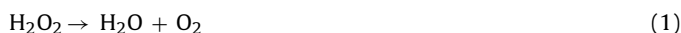
Fig. 1. XRD of the activated carbons and also of raw material, wet blue leather waste (○ = Cr₂O₃ and □ = CrO₃).

XRD of the wet blue carbon, carbon-0.5 and carbon-2 materials. Wet blue leather presented a typical XRD pattern of an amorphous sample. The carbon-0.5 and carbon-2 samples presented signals at $2\theta = 24.5^\circ$, 33.6° , 36.1° , 41.6° , 50.2° and 54.9° related to Cr₂O₃ and CrO₃. These results suggest that the pyrolysis process under CO₂ atmosphere produce carbonaceous materials with chromium oxide dispersed on the carbon. As reported by other authors [17,18] small particles of chromium oxide disperse over a catalytic support can oxidize pollutants in aqueous and gas phase.

We observed that the activation of the carbons, using different times, produces materials with substantial differences in specific area and porosity [3]. Moreover, the carbon-0.5 and carbon-2 samples present approximately the same total pore volume, 0.47 and 0.48 cm³ g⁻¹, respectively. However, carbon-0.5 presents basically microporosity with the type I (microporous) isotherm. The carbon-2 yields a type II isotherm with an important adsorption at low P/Po ratio, this is indicative of simultaneous presence of micro and mesopores [19]. Carbon-0.5 and carbon-2, due to the chromium within the structure, can be a potential catalyst for oxidation processes. Several works can be found in the literature showing catalytic application of chromium-impregnated activated carbon for the oxidation of organic contaminants [20,21].

3.2. Catalytic tests

The catalytic activity of the activated carbons was studied using two reactions: (i) the H₂O₂ decomposition (Eq. (1)):



and (ii) the oxidation of methylene blue dye with H₂O₂ in aqueous medium.

3.2.1. H₂O₂ decomposition

The H₂O₂ decompositions in the presence of carbons are presented in Fig. 2a. It is observed that the materials strongly favored the H₂O₂ decomposition, possibly due to the chromium presence on the surface. Fig. 2b shows the H₂O₂ decomposition utilizing the carbon-0.5 sample in the presence of organic compounds (ascorbic acid and methanol). It can also be observed that the H₂O₂ decomposition is strongly inhibited by the presence of another organic compound. The reaction inhibition might be due to a competitive process involving the organic substrate and the active surface that

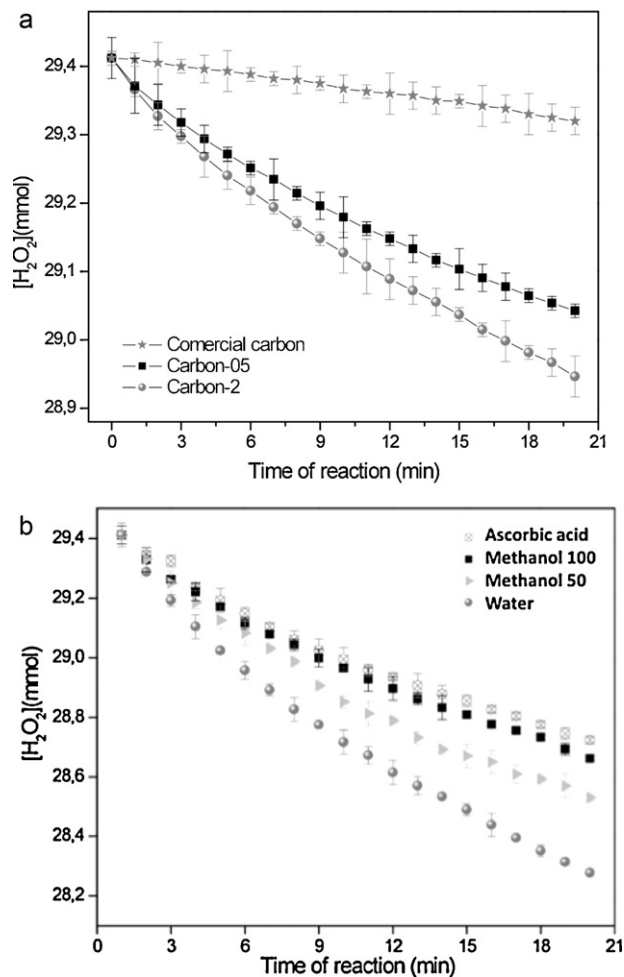


Fig. 2. Decomposition of H₂O₂ in the presence of activated carbon.

could be related to the adsorption of the organic compounds on the active sites of the composite and their reactions with intermediate species in the H₂O₂ decomposition reaction. Ascorbic acid is a radical scavenger and may be reacting with radical intermediates, such as HO• or HOO•, species that are presumably formed during the H₂O₂ decomposition cycle [22]. Also in Fig. 2b the H₂O₂ decomposition utilizing the carbon-2 in the presence of methanol (50 and 100 mg L⁻¹) is shown. It also can be observed that the H₂O₂ decomposition is strongly inhibited by the presence of the two methanol concentrations. The reaction inhibition might be due to a competitive process involving the organic substrate and the active surface that could be related to the adsorption of the organic compounds on the active sites of the composite and their reactions with intermediate species in the H₂O₂ decomposition reaction.

3.2.2. Methylene blue dye oxidation monitored by UV–vis spectroscopy

It has been observed that there was no significant removal of the methylene blue solution in contact with the H₂O₂ solution in the absence of carbon or in the presence of carbon without activation. In the presence of the activated carbons a significant discoloration is observed (Fig. 3a) after 10 min of reaction. Total discoloration took place after 150 min for the all materials. Moreover, a significant removal of methylene blue dye by adsorption takes place, i.e. in the absence of hydrogen peroxide. The materials presented a removal capacity of approximately 40%, 59% and 63% for commercial carbon, carbon-0.5 and carbon-2, respectively. The sample activated for 2 h (carbon-2) showed a better discoloration capacity

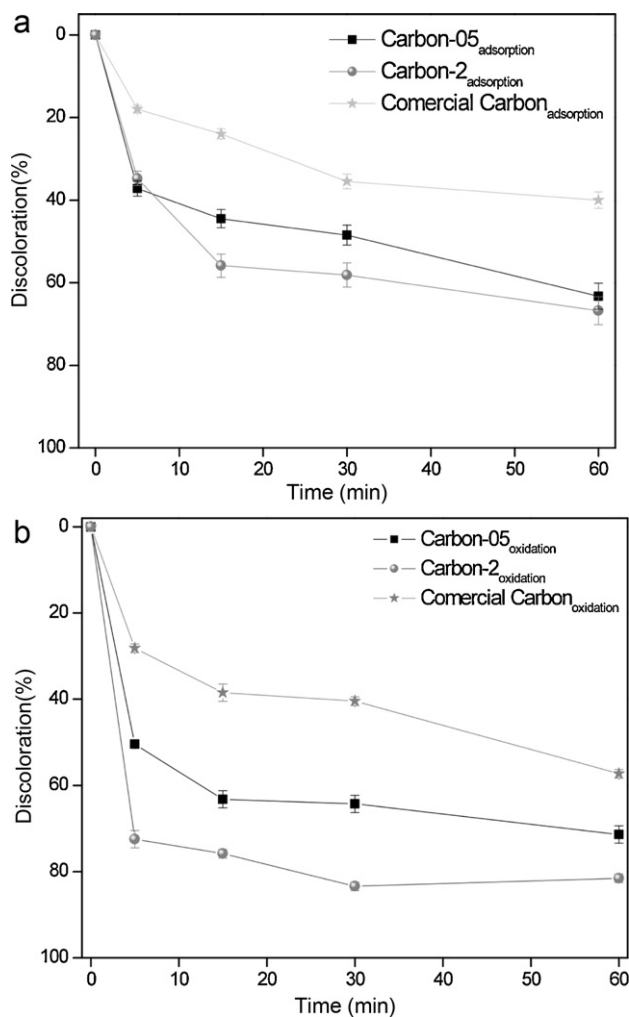


Fig. 3. Removal of methylene blue in the adsorption process (a) and in the presence of H_2O_2 and activated carbons (b).

of the aqueous medium in the presence of H_2O_2 than the carbon-0.5 sample probably due to mesoporosity in the carbon-2 sample that permits the substrate to access part of the active phase in the pores as suggested in the illustration in Fig. 3b. In this case, the materials presented a removal capacity of approximately 55%, 70% and 83% for commercial carbon, carbon-0.5 and carbon-2, respectively.

The chromium present on the surface of activated carbon does not suffer leaching in water. The carbon-0.5 and carbon-2 samples were treated with HNO_3 , H_2SO_4 and HCl (1 mol L^{-1}) for 3 h at 100°C and these treatments caused complete Cr-extraction from activated carbon. On the other hand, to investigate the possibility of homogeneous reactions produced by Cr species leached from the carbon-0.5 or carbon-2 samples into the aqueous medium, atomic absorption analyses were carried out in the aqueous phases after all the reactions. The obtained concentrations of Cr were all below the detection limit of the atomic absorption equipment indicating that the reaction is not caused by homogeneous species in the solution. Moreover, the chromium leaching was monitored by measuring the oxidation of quinoline solution in a batch experiment. The Cr content in solution, observed in the leaching test, presented a removal capacity of only 2%, confirming that this reaction takes place mainly via a heterogeneous mechanism.

3.2.3. Methylene blue dye oxidation monitored by ESI-MS

The identification of reaction intermediates was performed by on-line ESI-MS during the oxidation of methylene blue dye by

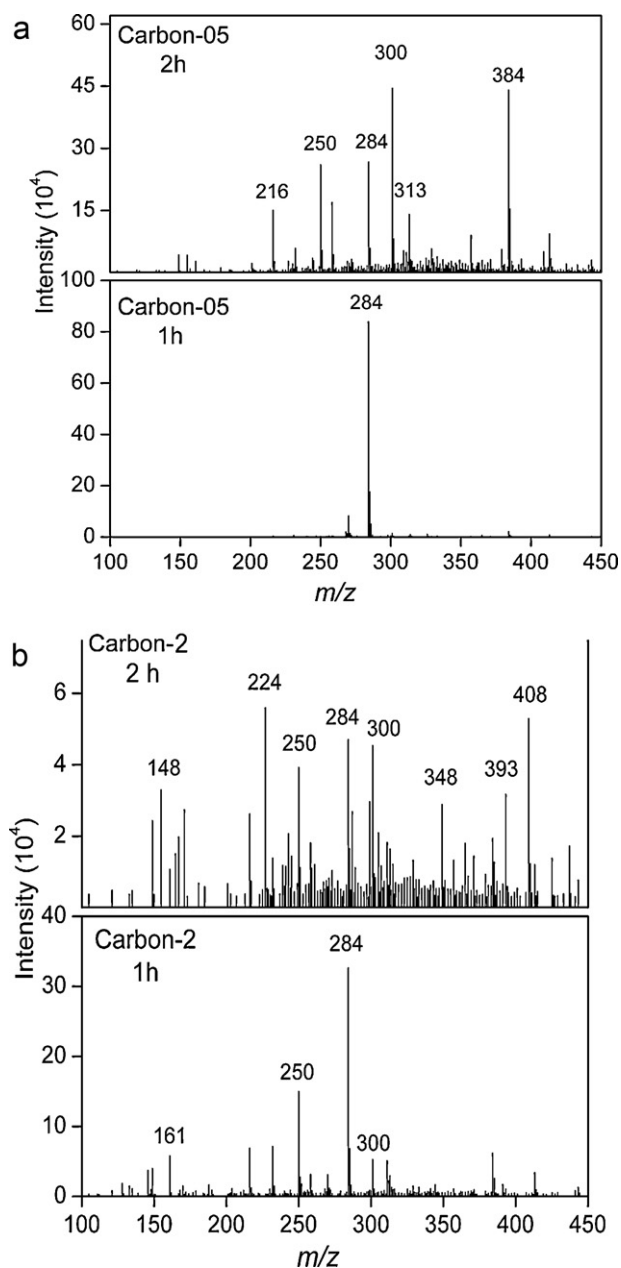


Fig. 4. ESI mass spectrum in the positive ion mode for monitoring the oxidation by the Cr activated carbon in the presence of H_2O_2 .

the Cr-impregnated activated carbon from the leather industry. ESI mass spectrum was obtained for the standard dye solution. As expected the ESI-MS operating in the positive ion mode detects the presence of a single cation in the aqueous solution due to the methylene blue dye (m/z 284). On the other hand, after different reaction times with the carbon-0.5 and carbon-2 (Fig. 4), new and relatively intense ions are also clearly detected. After 1 h of reaction with the Cr-containing activated carbon and hydrogen peroxide, some new m/z signals appear, for example, at 300, 316, 332 and 384 indicating that the hydroxylation is occurring in the process. At this reaction time, other m/z signals appear (m/z = 148, 216 and 250), likely related to methylene blue oxidation intermediates, also suggesting that the structural ring was somehow fragmented [23,24]. It is interesting to observe that the catalyst carbon-2 present a great capacity of intermediate formation suggesting that this material is more active, probably due to different porosity and chromium species on the surface.

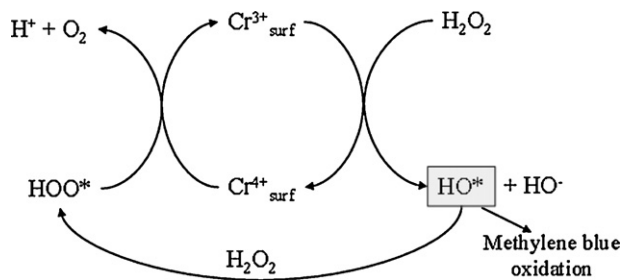


Fig. 5. Mechanism proposal for the activation of H_2O_2 by Cr^{3+} of the carbon.

Previous work has clearly indicated that Cr^{3+} could participate in a Haber–Weiss mechanism to generate HO^\bullet free radicals, as shown in Eq. (2) [17].



The proposed mechanism was based on the activation of H_2O_2 via a Haber Weiss mechanism to form a radical HO^\bullet (Fig. 5). This hydroxyl radical can then react by two competitive pathways: (i) the oxidation of an organic molecule or (ii) the formation of O_2 via the radical HOO^\bullet . The results obtained in this work suggest that the Cr in the carbon structure strongly favors the oxidation of the methylene blue dye, acting as an electron donor in a Haber–Weiss mechanism. However, it was observed by Bokare and Choi [25] that the $\text{Cr(VI)/H}_2\text{O}_2$ redox system presents a higher capacity for the degradation of aquatic organic pollutants. The authors suggest that the oxidation mechanism involves the formation of a tetraperoxochromate(V) complex and its subsequent reaction leads to the generation of hydroxyl radicals.

The possible intermediate structures are reported in Fig. 6. In order to get deeper insight about the $m/z = 300$ signal, the Gibbs free energy for the stability of some possible isomers with $m/z = 300$ at DFT level was calculated in our previous work [26]. From our data, one may note that the most stable fragment of the hydroxyl group is at the C2 position. This could strongly suggest that the reaction with the catalysts is initiated by the activation of H_2O_2 to produce an HO^\bullet radical [20,24].

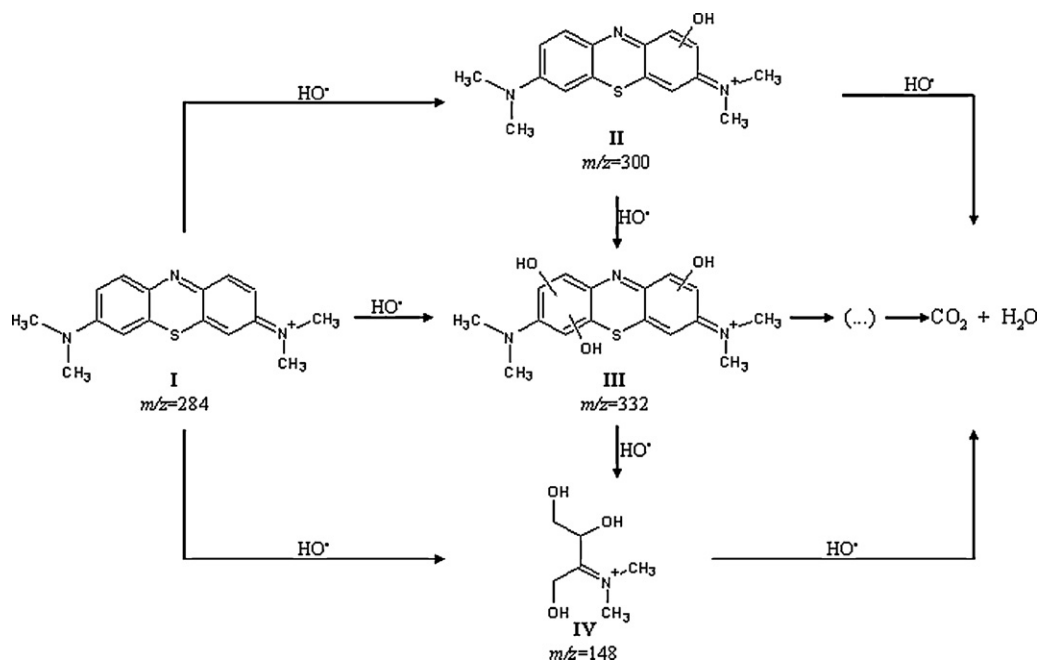


Fig. 6. Scheme with intermediates proposed for the oxidation of methylene blue dye.

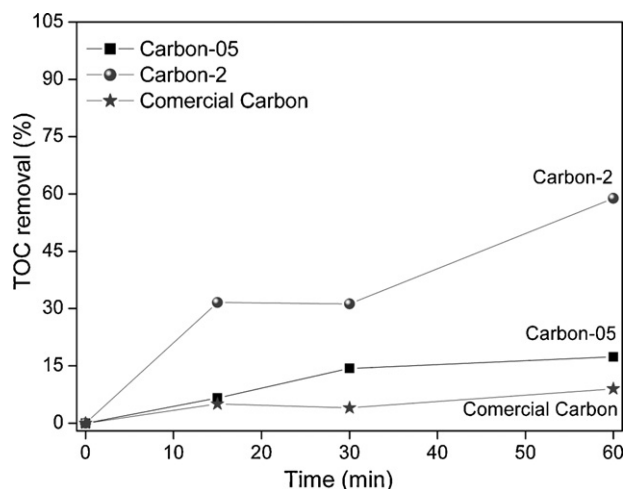


Fig. 7. Total organic carbon analyses for the carbon-0.5 and carbon-2 samples.

Fig. 7 shows the TOC removal for the samples carbon-0.5 and also carbon-2 at different reaction times. It can be observed that the thermal treatment for 2 h (carbon-2 sample) produced a higher TOC removal (approximately 60% removal in 60 min of contact time) than the material after 30 min of pyrolysis (carbon-0.5), suggesting that the presence of chromium phases might play a role in the removal process. It is interesting to comment that the TOC removal obtained with these materials was much better than many reaction processes studied by other authors [9] attesting that the activated carbon with chromium obtained from leather waste is a good catalyst in the oxidation of an important organic pollutant such as methylene blue dye.

A strong increase of hydrogen peroxide decomposition was found, but, unfortunately, it was due to the leaching of chromium from the carbonaceous matrix to the solution. This fact, characterizes a homogeneous catalysis and not a heterogeneous process as proposed by this work. For example, for pH 4 and 2, levels of chromium solution of 22 and 46 mg L^{-1} were observed measured

by atomic absorption. For this reason, we suggested that the system should be used until approximately pH 5.

4. Conclusions

Kinetic studies and on-line ESI-MS reaction monitoring with intermediate interception suggest that nascent HO• radicals promote two competitive processes, i.e. hydroxylation/oxidation of the organic compounds and hydrogen peroxide decomposition. These results indicated that the Cr-containing activated carbon acts by a Fenton-like mechanism through which Cr³⁺_{surf} species reacts with H₂O₂ to form hydroxyl radicals. Another advantage of this work is that the impregnation step can be dispensed with because the chromium is originally present in the leather waste precursor and it remains on the surface of the activated carbon obtained. The results presented in this work also showed that the activated carbon, with high surface area and impregnated chromium, can be obtained by a very simple means. Moreover, the ash analyses showed that all the initial chromium is in activated carbon, therefore no chromium is lost during thermal decomposition and that mainly trivalent chromium is produced. Furthermore, to avoid the chromium leaching the AC//H₂O₂ system should be used in a minimal pH of approximately 5.

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References

- [1] K. Kanagaraj, N.K. Chandra Babu, A.B. Mandal, Recovery and reuse of chromium from chrome tanning waste water aiming towards zero discharge of pollution, *J. Clean. Prod.* 16 (2008) 1807–1813.
- [2] L.C.A. Oliveira, M. Gonçalves, D.Q.L. Oliveira, M.C. Guerreiro, L.R.G. Guilherme, R.M. Dallago, Solid waste from leather industry as adsorbent of organic dyes in aqueous-medium, *J. Hazard. Mater.* 141 (2007) 344–347.
- [3] L.C.A. Oliveira, M.C. Guerreiro, M. Gonçalves, D.Q.L. Oliveira, L.C.M. Costa, Preparation of activated carbon from leather waste: a new material containing small particle of chromium oxide, *Mater. Lett.* 62 (2008) 3710–3712.
- [4] M.M. Taylor, J. Lee, L.P. Bumanlag, E.H. Balada, E.M. Brown, Treatments to enhance properties of chrome-free (wet white) leather, *J. Am. Leather Chem. Assoc.* 106 (2011) 35–43.
- [5] S. Tahiri, M. de la Guardia, Treatment and valorisation of leather industry solid wastes: a review, *J. Am. Leather Chem. Assoc.* 104 (2009) 52–67.
- [6] R.J. Bartlett, *Environ. Health Perspect.* 92 (1991) 17–24.
- [7] A. Cassano, J. Adzet, R. Molinari, M.G. Buonomenna, J. Roig, E. Drioli, Membrane treatment by nanofiltration of exhausted vegetable tannin liquors from the leather industry, *Water Res.* 37 (2003) 2426–2434.
- [8] S.B.C. Pergher, L.C.A. Oliveira, A. Smaniotto, D.I. Petkowicz, Magnetic zeolites for removal of metals in water, *Quim. Nova* 28 (2005) 751–755.
- [9] P.A. Throver, *Chemistry and physics of carbon: a series of advances*, vol. 21, first ed., Marcel Dekker, New York, 1989.
- [10] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, Modification of the surface chemistry of activated carbons, *Carbon* 37 (1999) 1379–1389.
- [11] M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marim, On the characterization of acidic and basic surface sites on carbons by various techniques, *Carbon* 37 (1999) 1215–1221.
- [12] G.S. Szymanski, G. Rychlicki, Importance of oxygen surface groups in catalytic dehydration and dehydrogenation of butan-2-ol promoted by carbon catalysts, *Carbon* 29 (1991) 489–498.
- [13] E. Ahumada, H. Lizama, F. Orellana, C. Suarez, A. Huidobro, A.S. Escibano, F.R. Reinoso, Catalytic oxidation of Fe(II) by activated carbon in the presence of oxygen: effect of the surface oxidation degree on the catalytic activity, *Carbon* 40 (2002) 2827–2834.
- [14] V.A. Likholobov, N.I. Kuznetsova, M. Gurrath, H.P. Boehm, Promotion effect of carbon on the oxidation of ferrous ions by oxygen in the presence of sodium nitrite, *Appl. Catal. A: Gen.* 128 (1995) 41–52.
- [15] U. Jans, J. Hoigne, Atmospheric water: transformation of ozone into OH-radicals by sensitized photoreactions or black carbon, *Atmos. Environ.* 34 (2000) 1069–1085.
- [16] H. Falcon, R.E. Carbonio, Study of the heterogeneous decomposition of hydrogen peroxide: its application to the development of catalysts for carbon-based oxygen cathodes, *J. Electroanal. Chem.* 339 (1992) 69–83.
- [17] F. Magalhaes, M.C. Pereira, S.E.C. Botrel, J.D. Fabris, W.A. Macedo, R. Mendonça, R.M. Lago, L.C.A. Oliveira, Cr-containing magnetites Fe_{3-x}Cr_xO₄: the role of Cr³⁺ and Fe²⁺ on the stability and reactivity towards H₂O₂ reactions, *Appl. Catal. A* 332 (2007) 115–123.
- [18] L.C.A. Oliveira, R.M. Lago, J.D. Fabris, K. Sapag, Catalytic oxidation of aromatic VOCs with Cr or Pd-impregnated Al-pillared bentonite: byproduct formation and deactivation studies, *Appl. Clay Sci.* 39 (2008) 218–222.
- [19] S.J. Gregg, K.S.W. Sing, *Adsorption Surface Area and Porosity*, second ed., Academic Press, New York, 1982.
- [20] L.C.A. Oliveira, T.C. Ramalho, E.F. Souza, M. Gonçalves, D.Q.L. Oliveira, M.C. Pereira, J.D. Fabris, Catalytic properties of goethite prepared in the presence of Nb on oxidation reactions in water: computational and experimental studies, *Appl. Catal. B* 83 (2008) 169–176.
- [21] G.K. Prasad, M.V.S. Suryanarayana, S. Banerjee, The reaction of thiodiglycol on metal-impregnated carbon, *Carbon* 39 (2001) 2131–2142.
- [22] I.R. Guimarães, L.C.A. Oliveira, P.F. Queiroz, T.C. Ramalho, M. Pereira, J.D. Fabris, F.D. Ardisson, Modified goethites as catalyst for oxidation of quinoline: evidence of heterogeneous Fenton process, *Appl. Catal. A: Gen.* 347 (2008) 89–93.
- [23] A. Esteves, L.C.A. Oliveira, T.C. Ramalho, M. Gonçalves, A.S. Anastácio, H.W.P. Carvalho, New materials based on modified synthetic Nb₂O₅ as photocatalyst for oxidation of organic contaminants, *Catal. Commun.* 10 (2008) 330–332.
- [24] L.C.A. Oliveira, M. Gonçalves, M.C. Guerreiro, T.C. Ramalho, J.D. Fabris, M.C. Pereira, K. Sapag, A new catalyst material based on niobia/iron oxide composite on the oxidation of organic contaminants in water via heterogeneous Fenton mechanisms, *Appl. Catal. A: Gen.* 316 (2007) 117–124.
- [25] A.D. Bokare, W. Choi, Chromate-induced activation of hydrogen peroxide for oxidative degradation of aqueous organic pollutants, *Environ. Sci. Technol.* 44 (2010) 7232–7237.
- [26] A.C. Silva, D.Q.L. Oliveira, L.C.A. Oliveira, A.S. Anastácio, T.C. Ramalho, J.H. Lopes, H.W.P. Carvalho, C.E.R. Torres, Nb-containing hematites Fe_{2-x}Nb_xO₃: the role of Nb⁵⁺ on the reactivity in presence of the H₂O₂ or ultraviolet light, *Appl. Catal. A: Gen.* 357 (2009) 79–84.