

AQUEOUS ATRAZINE REMOVAL BY ACTIVATED CARBON / METAL OXIDES COMPOSITES

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Abstract

In this work the removal of atrazine herbicide from aqueous medium was investigated using different catalysts based on activated carbon impregnated iron or chromium oxides. The materials were characterized by powder XRD, scanning electron microscopy (SEM) and infrared spectroscopy (FTIR). The characterization showed the formation of small particle size goethite (α -FeOOH) phase on activated carbon surface. For the catalyst with chromium it can be observed by XPS analyses the Cr_2O_3 phase. The atrazine oxidation intermediates were monitored by ESI-MS ion trap and the oxidation products distribution is shown to be dependent on the catalytic system employed.

Introduction

Atrazine (2-chloro-4-ethylamine-6-isopropylamino-s-triazine) is a triazine selective herbicide widely used throughout the world in the control of weeds in various crop cultures (Royal Society of Chemistry; The British Crop Protection Council) and also in nonagricultural areas (Commission of the European Communities). Atrazine was introduced in the 1950s, and since then it has become the most used herbicide in agricultural and forestry applications, with 70,000–90,000 tonnes applied annually worldwide (Ta N., et al.). It is classified as a possible human carcinogen by the U.S.EPA (Belluck, D. A., et al.) and main source of human exposures is from the consumption of contaminated groundwater. Atrazine's resistance to microbial degradation, slow hydrolysis, low vapor pressure, and moderate aqueous solubility enhance its potential for contaminating groundwater (U.S. EPA Office of Pesticide Programs).

Considering these facts, there is a need of developing efficient treatments for contaminating groundwater. The use of advanced oxidation processes (AOPs) is among of the most cited in literature for atrazine oxidation (Nélieu, S. et al.; Pratap, K. et al.; Acero, J. L. et al.; Hiskia, A. et al.). Advanced oxidation processes (AOPs) are based on the activation of oxidizing agents like H_2O_2 , O_3 or O_2 for generation of very reactive non-selective transient oxidizing species such as the hydroxyl radicals (OH^*), which can degrade the organic compounds in water.

Nevertheless, for all the works mentioned above, the authors utilize homogeneous systems. This homogeneous system requires stoichiometric amounts of Fe^{2+} and large quantities of acid, usually H_2SO_4 , to adjust the optimum pH to 3. After the process the effluent must be neutralized with a base to be safely discharged. Upon neutralization significant amounts of sludge are formed, which is serious limitation of the process due to its disposal problems. The spent acid, base and the formed sludge, are evident drawbacks of the Fenton process. The development of active heterogeneous systems to promote a Fenton-like chemistry which can operate at near neutral pH has a considerable interest since it could offer some advantages, such as no need of acid or base, no sludge generation and the possibility of recycling the catalyst (Cuzzola A. et al.; Ferraz W. et al.). Herein heterogeneous systems, the support choice is undoubtedly very important on developing of a good catalyst and activated carbon has been mostly used for this aim since the 70 decade (Reinoso F.R. et al.). Due to its high surface area and porous structure it can efficiently adsorb gases and compounds dispersed or dissolved in liquids (Oliveira L.C.A. et al.; Culp GL et al.; Ruthven DM. et al.). The adsorption of several organic contaminants in water, such as pesticides, phenols and chlorophenol, has recently been also reported (Oliveira, L.C.A.; Baup S. et al.; Garner I.A. et al.; Martýn-Gullon I. et al.).

Methods

Preparation of the composites

The composites of activated carbon (AC)/iron oxide were prepared from a suspension of activated carbon in a 100 mL solution of FeCl_3 (5.8 g, 21.55 mmol) and FeSO_4 (12 g, 43.1 mmol) at 343 K. NaOH solution (20 mL, 5 mol L^{-1}) was added drop wise to precipitate iron oxides. The amount of activated carbon was adjusted in order to obtain AC/iron oxide weight ratios of 5/1 and 1/1. The obtained materials were dried in an oven at 333 K for 24 h. The composite of AC/chromium oxide was prepared from a aqueous suspension of 7.7 g $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 10 mg activated carbon at 343 K for one hour and dried in an oven at 333 K for 24 h.

Characterization of the composites

The prepared composites were characterized by powder XRD (Co $\text{K}\alpha$, $\lambda = 1.78897 \text{ \AA}$), infrared spectroscopy (FTIR), using an Excalibur FTS 3000 series (Digilab), scanning electron microscopy (SEM) (Leo-Evo 40XVP) with Au sputtering coated samples fixed on a carbon tape and XPS analysis. XPS data were obtained using a XSAM 800 cpi ESCA (KRATOS Analytical) equipped with a Mg anode (Mg K radiation, 1256.6 eV) and spherical analyzer at 15 KV and 15 mA.

The performance of the catalysts was investigated by monitoring the oxidation kinetics of the methylene blue dye (a model molecule). The influence of organic acids (dipicolinic acid and formic acid), in a Fenton-like system was also studied. A typical test was made using 10 mg of the catalyst, 9.9 mL methylene blue (10 mg Kg^{-1}), 0.1 mL H_2O_2 (50% v/v) and dipicolinic acid (5 mg, 1/2 proportion, dipicolinic acid/catalyst, w/w ratio) or formic acid solution (44 μL , 1/1 proportion, mol H_2O_2 /mol formic acid) with a reaction time of 4 h. These conditions were studied previously by the authors in another work [12]. The dye decomposition was monitored by measuring absorbance at 665 nm with a UVPC 1600 - UV/Vis spectrophotometer (Shimadzu), all reactions were carried out at 278 K.

It was also studied the metal ion leaching from the composites in the presence of the organic acids. The tests were made using 9.9 mL distilled water, 10 mg of the composite, 0.1 mL hydrogen peroxide (50% v/v) and 5 mg of dipicolinic acid or 44 μL of formic acid solution. 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 one hour. The concentration of methylene blue was measured by UV/Vis spectrophotometry. The catalyst has been recovered by filtration and a second leaching test was carried out, repeating procedure described above.

Atrazine oxidation tests

The atrazine oxidation tests were carried out in aqueous medium using the prepared composites as a catalyst and hydrogen peroxide as oxidizing agent. In a typical experiment were used 9.9 mL atrazine solution (20 mg kg^{-1}), 10 mg of the catalyst and 0.1 mL of hydrogen peroxide (50% v/v). The atrazine stock solution used herein was prepared from Gesaprin 500[®] commercial herbicide. The mixture was stirred with a magnetic stirrer and the atrazine intermediates products were monitored by mass spectroscopy ESI/MS Trap (Agilent-1100 ion trap VL). The reaction time was 2 h and 5 h for the composite AC/iron oxide 1/1 and 5/1 and 2.5 h and 5 h for the composite AC/chromium oxide. 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 composites

The XRD analysis of the AC/iron oxide 1/1 and AC/iron oxide 5/1 and AC/chromium oxide composites are shown in Figure 1.

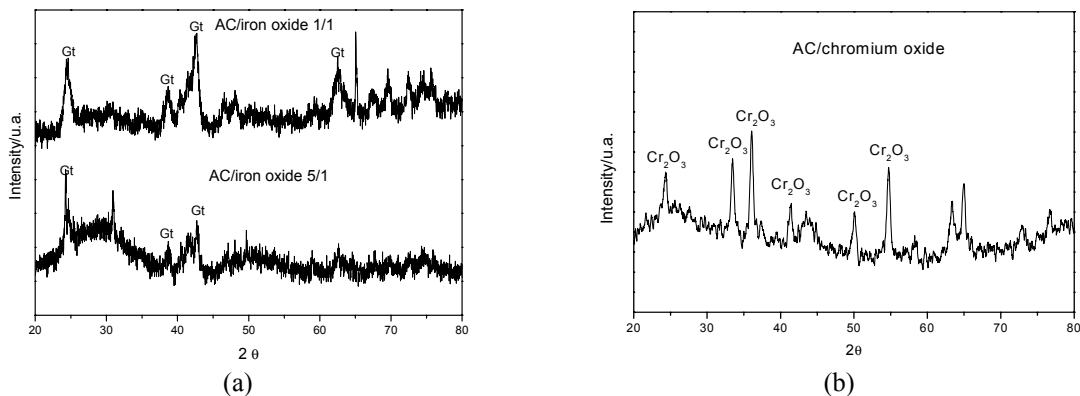


Figure 1. Powder XRD of the AC/iron oxide composites (Fig. 1-a) and AC/chromium oxide composite (Fig. 1-b) (gt=goethite).

XRD analyses of the AC/iron oxide composites (Fig. 1-a) suggest the presence of a hexagonal iron oxide phase ($d=0.4202$; $d=0.2698$; $d=0.2452$ and $d=0.1717$ nm) which may be related to the presence of goethite. For the composite with chromium (Fig 1-b) it can be observed the presence of Cr_2O_3 phase ($d= 0.362$; 0.266 and 0.167 nm).

Fourier transform infrared (FTIR) spectra of the composites AC/iron oxide 1/1 AC/iron oxide 5/1 are shown in Figure 2.

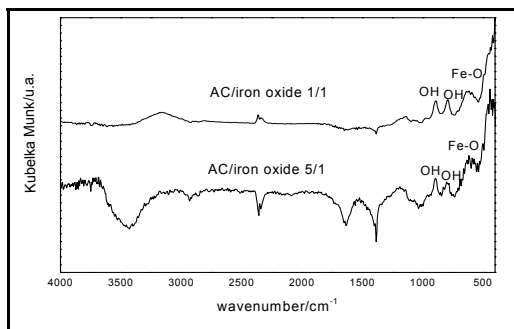


Figure 2. FTIR of the composites AC/iron oxide 1/1 and AC/iron oxide 5/1.

It is possible to observe in the infrared spectra of the composites the bands related to the goethite phase: the O-H bending bands at ca. 886 (α -OH) and 793 (γ -OH) cm^{-1} , which bend in and out of the plane, respectively. This result is consonant with the X-ray diffratogram presented previously.

The AC/chromium oxide composite was characterized by XPS analysis and the spectrum is presented in Figure 3.

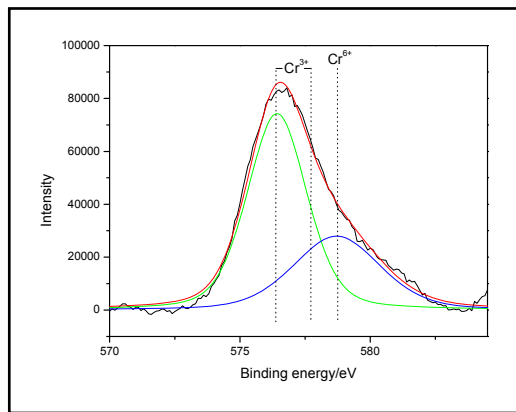


Figure 3. XPS analysis of the composite AC/chromium oxide.

XPS analyses of the composite AC/chromium oxide shows two signals at 576 and 577 due to the presence of Cr^{3+} and 579 due to Cr^{6+} . As this material has chromium species in two different oxidation state, it can show catalytic activity for oxidation reactions.

It is important to detach that Cr^{6+} species were not detected by X-ray diffraction probably because of the small particle size of chromium oxides.

The material morphologies were investigated by SEM and the micrographies are shown in Figure 4.

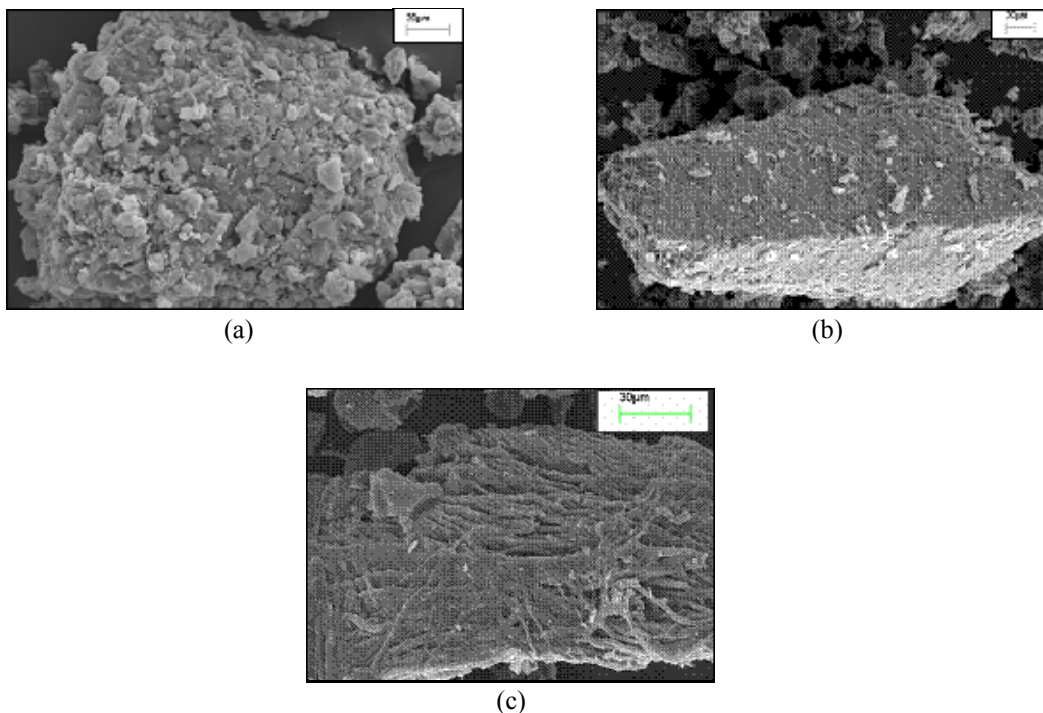
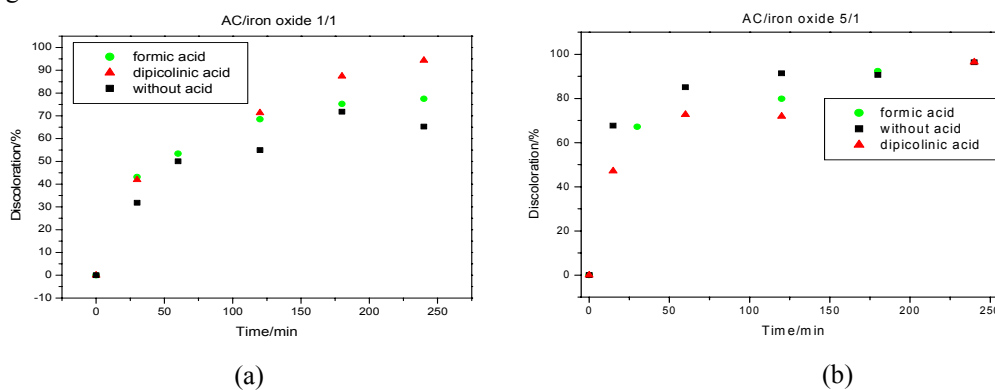
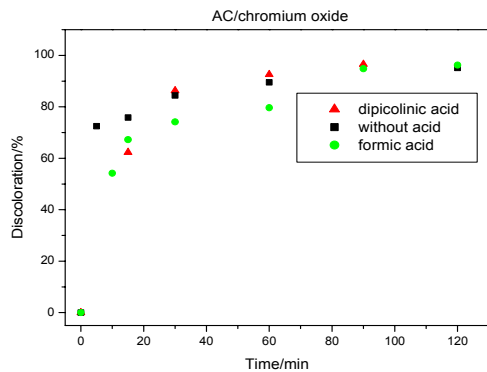


Figure 4. SEM micrographies of the composites AC/iron oxide 1/1 (Fig. 4-a), AC/iron oxide 5/1 (Fig. 4-b) and AC/chromium oxide (Fig. 4-c).

The SEM micrographies of the materials containing iron (Fig. 4-a and 4-b) suggest a well dispersed iron oxide over the AC surface, and in both materials we can find iron oxide crystals covering all the AC surface. For the composite with chromium (Fig. 4-c), a fibrous like material is observed, and no chromium oxide crystals are observed. The fibrous like AC is due to the structure of the AC used.

The catalytic activity of the composites was investigated using methylene blue dye as a molecule model, and the kinetics of the reactions were followed using a Fenton-like oxidation system. The results are presented in Figure 5.





(c)

Figure 5. Oxidation kinetics of the dye methylene blue using the composites AC/iron oxide 1/1 (Fig. 5-a), AC/iron oxide 5/1 (Fig. 5-b) and AC/chromium oxide (Fig. 5-c) in the presence of organic acids, formic acid and dipicolinic acid.

The reaction kinetics shows that the materials have different behavior depending on the oxide content, oxide type and the organic acid present. For the composite AC/iron oxide 1/1 (Fig. 5-a) the maximum discoloration is about 95% after 4 h reaction using dipicolinic acid. Moreover, the presence of organic acid speeds up the reaction after 1 h reaction time. However, for the composite AC/iron oxide 5/1 (Fig. 5-b) no significant difference is observed after 4 h reaction, and the maximum discoloration is around 90%. Using the composite AC/chromium oxide (Fig. 5-c), over 70% of discoloration is observed after 30 minutes, reaching up 95% and the presence of organic acids has no significant difference on the reaction kinetics.

The heterogeneous catalyst leaching stability was evaluated in the presence of the organic acids. The results are shown in Figure 6.

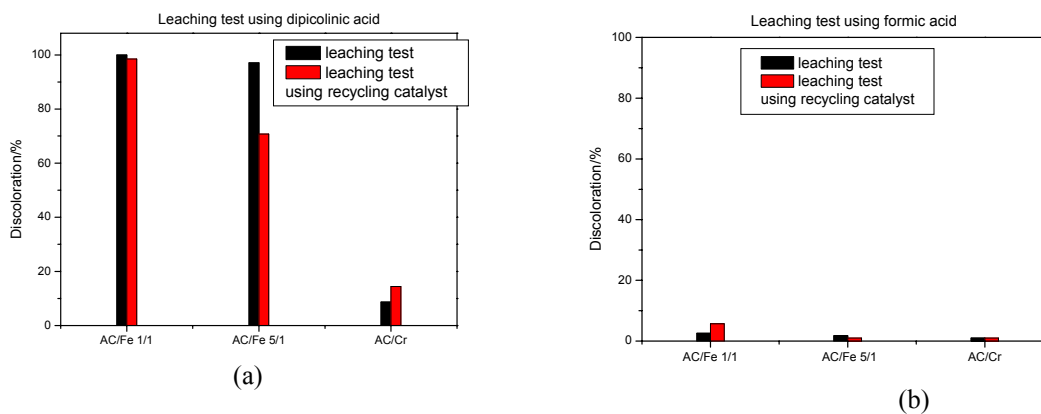


Figure 6. Metal ion leaching tests from the prepared composites (AC/Fe 1/1 = activated carbon/iron oxide 1/1, AC/Fe 5/1 = activated carbon/iron oxide 5/1 and AC/Cr = activated carbon/chromium oxide). Reaction time of 1 hour.

Leaching tests in the presence of formic acid (Fig. 6-b) has shown that the catalytic activity of the homogeneous system shows to be very small for all the presented materials.

However, when we used dipicolinic acid very active species were formed in solution in the presence of iron oxide composites. The amount of iron in solution was determined by atomic absorption technique (Spectra AA110, Varian Inc.). The average amount of iron found in solution were 9 and 10 mg kg⁻¹ for the composites 5/1 and 1/1, respectively. Almost a total discoloration occurs in the leaching test for the iron containing composites. For verifying if the iron leached was those only weak bounded to the carbon surface, a consecutive leaching test was carried out using a recycled catalyst from the first reaction. Even for the second leaching test the homogenous active species were present, showing that the dipicolinic acid is effective to extract iron from the composite surface.

Only a small amount of iron is present in the solution which indicate a very active specie is formed and the homogeneous system is still interesting for the catalytic removal of water pollutants.

The chromium composite shows no leaching effect, even when dipicolinic acid was employed.

Atrazine oxidation

To investigate the oxidation mechanism of atrazine using the prepared composites the reactions were monitored by ESI-MS. The Figure 7 shows the atrazine oxidation by AC/iron oxide system and the ESI mass spectra of standard atrazine $[M+H]^+$.

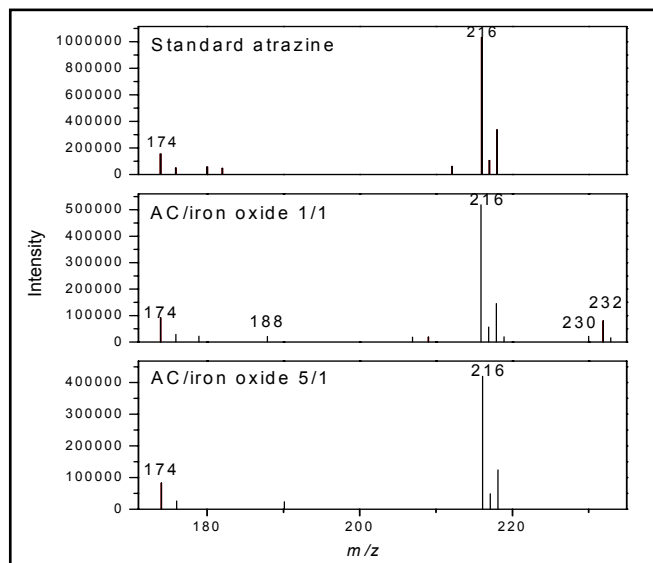


Figure 7. ESI mass spectra of standard atrazine $[M+H]^+$ and atrazine oxidation with H_2O_2 in the presence of AC/iron oxide composites 1/1 and 5/1 after 2 h reaction.

The experiments of atrazine oxidation were carried out without addition of organic acid, as no significant effect in the catalytic activity on the oxidation of methylene blue was observed.

The signal $m/z=216$ (Fig. 7) is related to a protonated atrazine molecule ($MM=215\text{ g mol}^{-1}$). The signal $m/z=174$ is related to deisopropil-atrazine. This product could be formed at skimmer of the mass spectrometer, as we can find this ion using a gas chromatograph standard. If the skimmer voltage is diminished, the 174 ion intensity is significantly reduced.

When the composite AC/iron oxide 5/1 is used we do not observe atrazine oxidation products after 2 h reaction time. This fact could be due to slower reaction rate and adsorption of the reaction products by the AC (Fig. 7). Nevertheless, when the AC/iron oxide 1/1 is employed, it is clearly observed the appearance of the new signals $m/z=230$, 232 and 188. It must be also mentioned that after 5 h reaction time, the less intense signals of the same oxidation products are detected.

Figure 8 displays the proposed scheme for atrazine oxidation with AC/iron oxide 1/1.

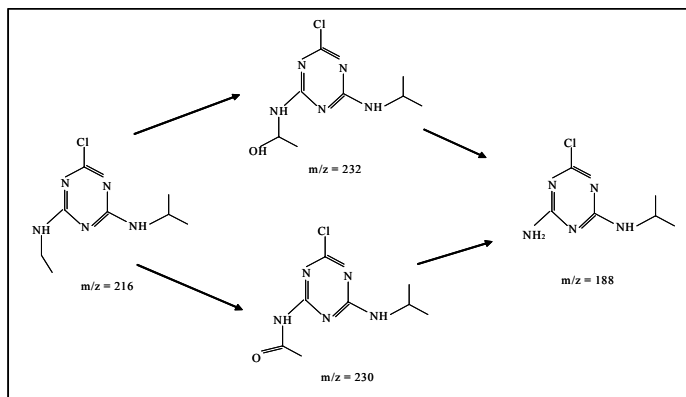


Figure 8. Proposed scheme for atrazine oxidation in the presence of AC/iron oxide 1/1.

The observed products is formed by oxidation of the ethyl radical of atrazine molecule producing the new signals $m/z=230$ and 232. Therefore dealquilation of this oxidated radical may produce the signal $m/z=188$.

The Figure 9 shows the atrazine oxidation by AC/chromium oxide system.

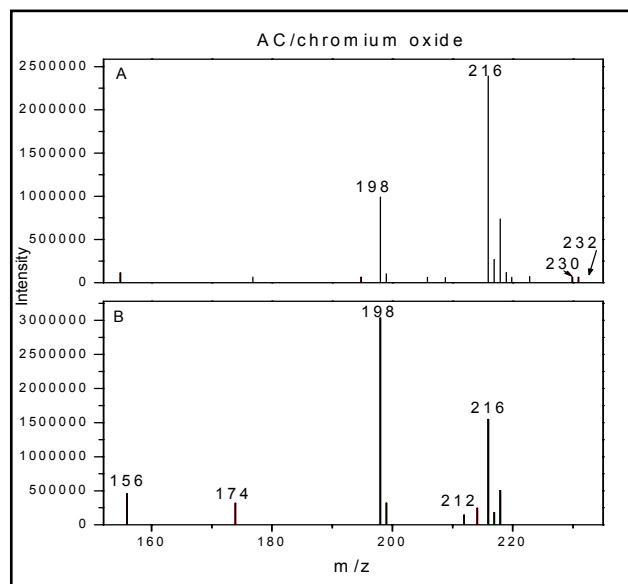


Figure 9. Atrazine oxidation with H_2O_2 in the presence of AC/chromium oxide after 2.5 h (A) and 5 h (B) reaction.

After 2.5 h reaction (Fig. 9-A), it can be observed the formation of the signals $m/z=230$, $m/z=232$ and a high intense signal $m/z=198$. After 5 h reaction (Fig. 9-B) it can be observed the appearance of new signals $m/z=156$ and $m/z=212$.

Figure 10 displays the proposed scheme for atrazine oxidation with AC/chromium oxide.

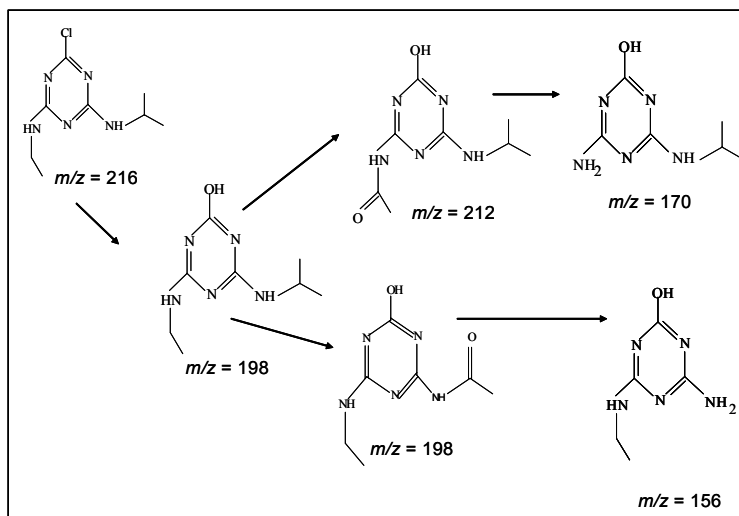


Figure 10. Proposed scheme for atrazine oxidation in the presence of AC/chromium oxide 1/1.

The main product observed (Fig. 10) for atrazine oxidation in the presence of the catalyst AC/chromium oxide is the -Cl substitution by the -OH forming hydroxy-atrazine ($m/z=198$).

This result suggests that the chromium containing catalyst might follow a different mechanism compared to that proposed to the iron containing catalysts, as the substitution products are not observed for the iron oxide composites.

Conclusion

The characterization of the iron containing composites showed that the main iron phase present is goethite and for the chromium containing composite the phase is Cr_2O_3 . XPS analyses of chromium composite showed that both Cr^{3+} and Cr^{6+} species are present. The catalytic activity tests showed that the materials are effective on the atrazine oxidation. The mechanism of atrazine degradation in the presence of the chromium composite showed to be different from that proposed for the iron oxide composites.

Acknowledgment

Authors are grateful to the Chemistry Department, CAPQ and LME laboratories and financial support from CAPES, FAPEMIG and CNPq.

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