



## Activated carbon/iron oxide composites for the removal of atrazine from aqueous medium

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### ABSTRACT

The adsorption features of activated carbon and the oxidation properties of iron oxides were combined in a composite to produce new materials for atrazine removal from aqueous medium. Activated carbon/iron oxide composites were prepared at 1/1 and 5/1 mass ratios and characterized with powder X-ray diffraction (XRD), infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and nitrogen adsorption measurements. The adsorption and oxidation processes were evaluated in batch experiments, in order to monitor the atrazine removal capacity of these composites. The main iron oxide actually present in the composites was goethite ( $\alpha$ -FeOOH). Impregnation with iron oxide reduced the surface area by its deposition in the activated carbon pores. However, a higher iron concentration promoted a higher oxidation rate, indicating that the efficiency of the oxidation reaction is related with the iron content and not with the pre-concentration of the contaminant on the carbon surface through adsorption process.

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### 1. Introduction

Atrazine (2-chloro-4-ethylamine-6-isopropylamino-s-triazine) is a selective triazine herbicide used to control weeds in various crops [1,2], and in non-agricultural areas [3]. Atrazine was introduced in the market by the 1950s, becoming the most worldwide used herbicide in agricultural and forestry applications ever since, with 70,000–90,000 tons applied annually [4]. It is classified as a potential human carcinogenic by USEPA [5]; the main source of human exposure is the consumption of contaminated groundwater. The atrazine's resistance to microbial degradation, slow hydrolysis, low vapor pressure, and moderate aqueous solubility enhance its ability as groundwater contaminant [6].

Considering these facts, there is a need of developing efficient remediation treatments to clean atrazine from groundwater. The use of advanced oxidation processes (AOPs) is among the most cited in the literature for atrazine degradation [7–12]. Advanced oxidation processes are based on the activation of oxidizing agents such as  $H_2O_2$ ,  $O_3$  or  $O_2$  to generate very reactive non-selective transient oxidizing species, such as hydroxyl radicals ( $\cdot OH$ ), which can degrade organic compounds in water through Fenton mechanism.

Nevertheless, in all reported studies are based on homogeneous systems. These systems require stoichiometric amounts of  $Fe^{2+}$  and large amounts of acid, typically  $H_2SO_4$ , to adjust the pH to an opti-

imum of 3. After the chemical process is complete, the effluent must be neutralized with alkali to be safely disposed. Such disposal is a serious limitation of the homogeneous process, since significant amounts of sludge are produced. All spent chemicals and sludges formed are evident drawbacks of the homogeneous Fenton process. The development of active heterogeneous systems to promote a Fenton-like chemistry which can operate at near neutral pH is of considerable interest since they could offer some advantages, such as no need of acid or base, no sludge generation and the possibility of recycling the catalyst [13,14]. In these heterogeneous systems, the choice of the support is undoubtedly very important for the development of a good catalyst and activated carbon (AC) has been mostly used for this purpose since the 1970s [15]. Due to its high surface area and porous structure it can efficiently adsorb gases and compounds dispersed or dissolved in liquids [16–18]. Adsorption of several organic contaminants in water such as pesticides, phenols, and chlorophenol has recently been reported [19–21]. In this work, activated carbon and iron oxide composites were prepared and their adsorption and oxidation properties evaluated in the atrazine oxidation.

### 2. Experimental

#### 2.1. Materials

The atrazine solution used in this study was prepared from Gesaprim 500<sup>®</sup> (commercial herbicide) purchased from Syngenta without any previous purification.

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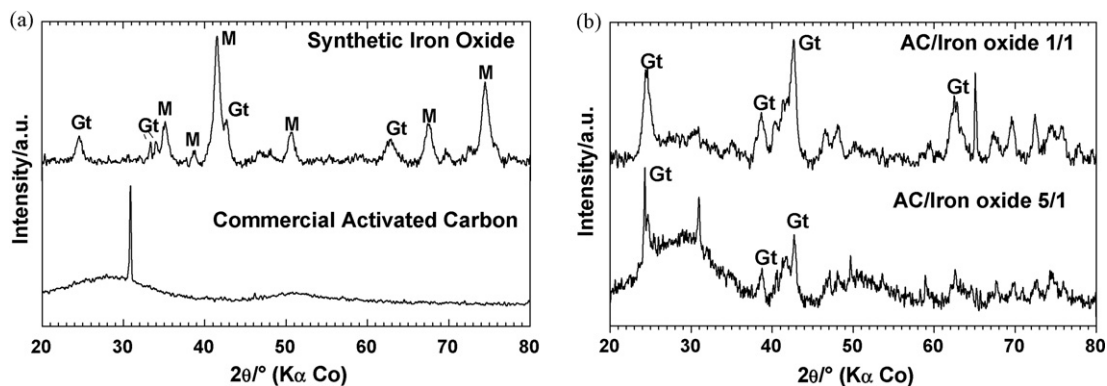


Fig. 1. Powder XRD of the activated carbon/iron oxide composites (Gt = goethite; M = maghemite or magnetite).

The activated carbon employed was purchased from Dinâmica (Brazil). Analytical grade sodium hydroxide (NaOH) and hydrogen peroxide solution (50%, v/v) were obtained from Sulfal (Brazil) and Synth (Brazil), respectively. All other chemicals used were of analytical reagent grade.

## 2.2. Preparation of the composites

Activated carbon/iron oxide composites were prepared from a suspension of commercial activated carbon in 100 mL of both  $\text{FeCl}_3$  (5.8 g, 21.6 mmol) and  $\text{FeSO}_4$  (12.0 g, 43.1 mmol) aqueous solution at 343 K. NaOH solution (20 mL, 5 mol  $\text{L}^{-1}$ ) was added dropwise to precipitate the iron oxides. The amount of activated carbon was adjusted in order to obtain activated carbon/iron oxide with weight ratios of 1/1 and 5/1. The obtained materials were dried in an oven at 333 K for 24 h. Pure iron oxide was prepared without addition of activated carbon under the same conditions described [22].

## 2.3. Characterization of the composites

The composites were characterized with powder XRD (Philips PW 1300, Co  $\text{K}\alpha$ ,  $\lambda = 0.178897$  nm), infrared spectroscopy (FTIR), using a Digilab Excalibur, series FTS 3000 spectrometer and nitrogen adsorption/desorption at 77 K (AUTOSORB-1, Quantachrome). The BET surface area of the composites was determined using the Brunauer–Emmett–Teller (BET) equation. Pore size distribu-

tion was determined using the Micromeritics density functional theory (DFT) software, with medium regularization and micropore volume obtained with the Dubinin–Radushkevich (DR) equation. Morphological analysis was also performed by scanning electron microscopy (SEM Leo Evo model 40XVP). To obtain the micrographs, the samples were prepared in stub holders with double face carbon tape and placed on an aluminum sheet and covered with gold using a Balzers SCD 050 evaporator.

## 2.4. Atrazine removal experiments

### 2.4.1. Atrazine adsorption

The adsorption of atrazine from aqueous medium by the AC/iron oxide 1/1 and 5/1 composites was investigated. Batch adsorption experiments were performed adding a known weight of 10 mg of the composite to the atrazine solution and leaving it for 24 h in a shaker at room temperature. Atrazine solutions were prepared in the following concentrations: 2, 5, 10, 15, 20 and 25 mg  $\text{kg}^{-1}$ . The mixtures were then centrifuged at  $8311 \times g$  for 20 min, the supernatant was collected and the atrazine concentration measured by UV–vis spectroscopy at 222 nm.

### 2.4.2. Atrazine oxidation

Atrazine oxidation experiments were carried out by using the prepared composites as catalyst and hydrogen peroxide as oxidizing agent in a Fenton-like process. In the tests 9.9 mL of atrazine solution (25 mg  $\text{kg}^{-1}$ ), 10 mg of catalyst and 0.1 mL of hydrogen peroxide (50%, v/v, 0.09 mol  $\text{L}^{-1}$ ) were used during 2 h of reaction. The atrazine removal process was monitored by UV–vis spectroscopy. In order to investigate the oxidation mechanism of atrazine, 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 of 600 K; dry gas ( $\text{N}_2$ ) flow rate of 5 L  $\text{min}^{-1}$ ; 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 30,000 with a maximum accumulation time of 300 ms.

Table 1

Measured surface area data for this commercial activated carbon, and corresponding activated carbon/iron oxide 1/1 and 5/1 composites

Surface analysis	Commercial AC	AC/iron oxide (5/1)	AC/iron oxide (1/1)
BET-surface area ( $\text{m}^2 \text{g}^{-1}$ )	666	568	426
Micropore volume <sup>a</sup> ( $\text{cm}^3/\text{g}$ )	0.261	0.226	0.175
Total pore volume ( $\text{cm}^3/\text{g}$ )	0.271	0.239	0.192

<sup>a</sup> Pore diameter <2 nm.

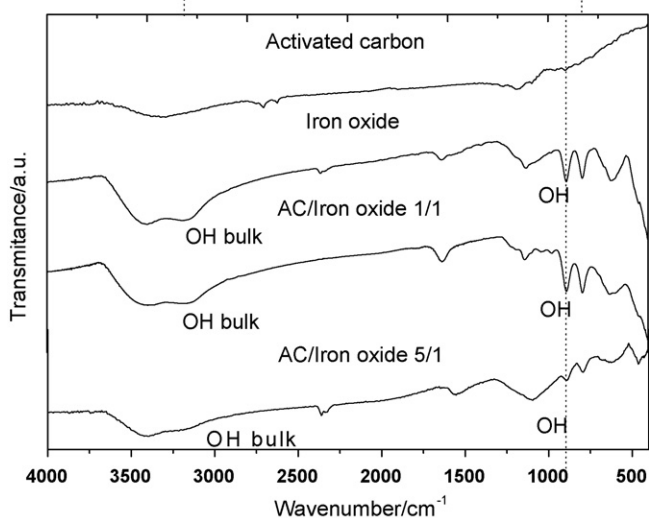


Fig. 2. FTIR spectra of iron oxide, activated carbon and corresponding composites.

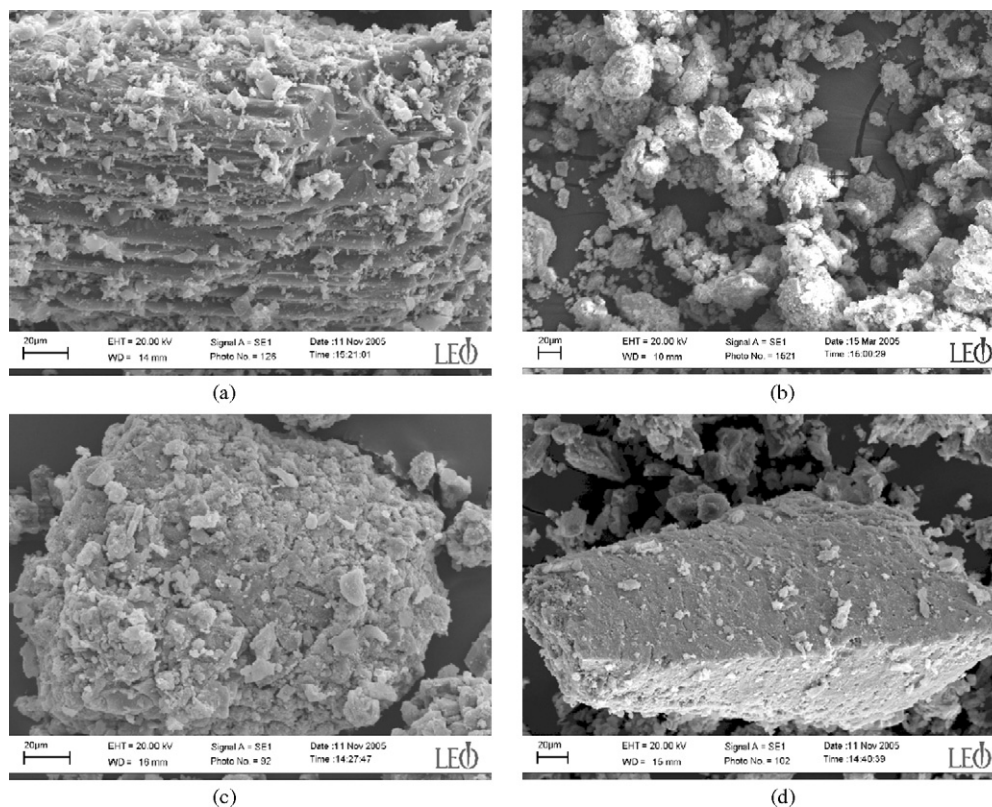


Fig. 3. SEM micrographies of commercial activated carbon (a), pure iron oxide (b) and the activated carbon/iron oxide 1/1 (c) and 5/1 (d) composites.

### 3. Results and discussion

#### 3.1. Characterization of the composites

XRD analysis of pure iron oxide (Fig. 1a) indicated the presence of a cubic iron oxide phase ( $d_{311} = 0.2515$  nm;  $d_{220} = 0.2961$  nm;  $d_{400} = 0.2089$  nm;  $d_{511} = 0.1609$  nm;  $d_{440} = 0.1479$  nm), which may be related to maghemite or magnetite. Weak reflections are also observed at  $d_{110} = 0.4202$  nm;  $d_{130} = 0.2698$  nm;  $d_{111} = 0.2452$  nm and  $d_{221} = 0.1717$  nm, which may be related to the occurrence of small amounts of goethite. Composites XRD analysis (Fig. 1b) suggest only the presence of goethite. It is interesting to observe that crystallinity increases for the composite prepared with the highest proportion of iron (AC/iron oxide 1/1) (Fig. 1b).

Fourier transform infrared (FTIR) spectra of pure iron oxide indicated an intense band due to the bulk hydroxyl stretching at  $3150\text{ cm}^{-1}$ . Moreover, the O–H bending bands at  $886$  and  $793\text{ cm}^{-1}$  correspond to vibrations in and out of the plane, respectively. Such bands are diagnostic of goethite. The same bands are observed on the spectra of the composites (Fig. 2).

The physical properties (Table 1) suggest that the BET surface area and micropore volume are affected by the presence of iron oxide in the composites. With an increase of the iron oxide content supported on the activated carbon, a reduction of the surface area and micropores volume in the composites are observed, as expected, since the iron oxides have a relatively small surface area and are covering the activated carbon surface. For example, the AC/iron oxide 5/1 showed a higher surface area ( $568\text{ m}^2\text{ g}^{-1}$ ) than

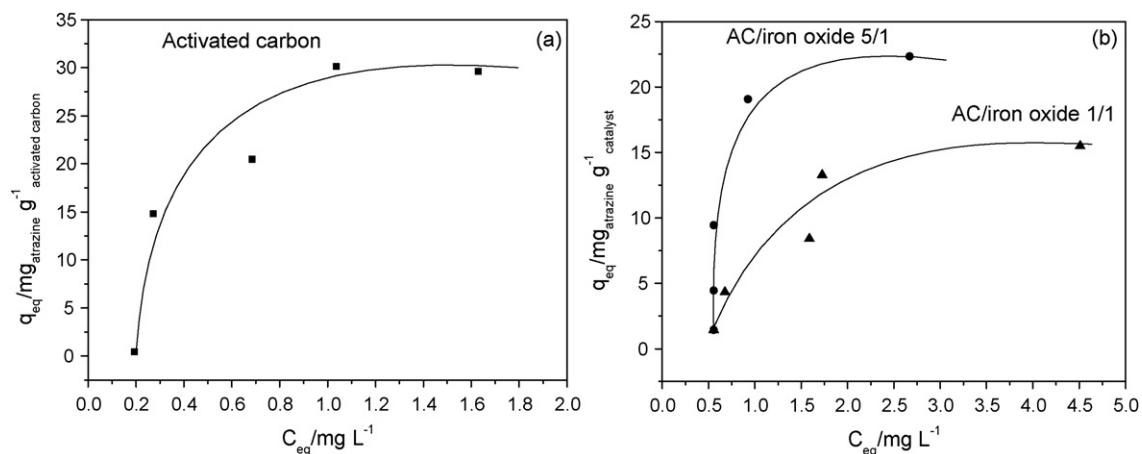


Fig. 4. Relationship between the adsorption capability ( $q_e$ ) and equilibrium concentration ( $C_e$ ): (a) activated carbon and (b) corresponding composites.

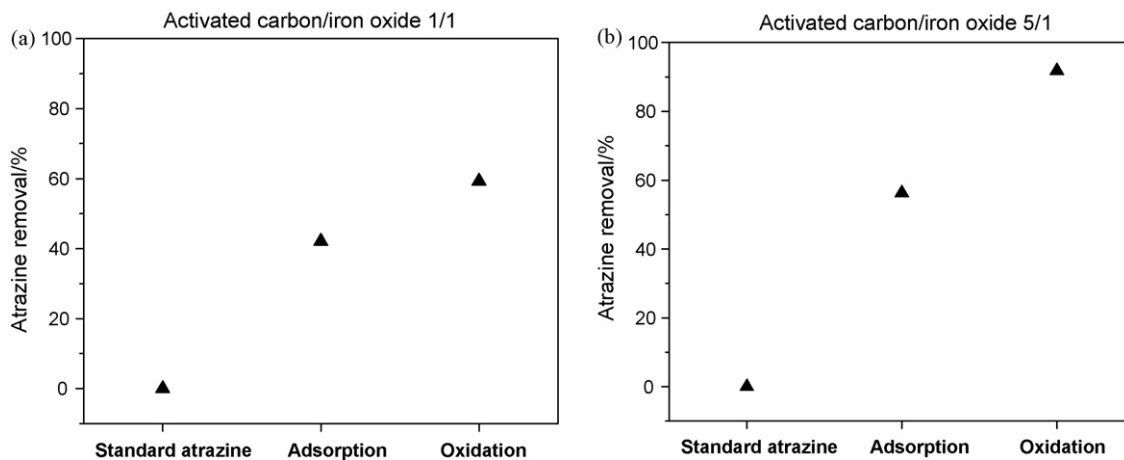


Fig. 5. Atrazine removal (%;  $\lambda_{\max} = 222 \text{ nm}$ ) by the composites 1/1 (a) and 5/1 (b) after 2 h.

the AC/iron oxide 1/1 ( $426 \text{ m}^2 \text{ g}^{-1}$ ). It should also be mentioned that the feature of both prepared composites, as well as the commercial activated carbon, is mainly of the microporous type.

SEM micrography of the commercial activated carbon (Fig. 3a) showed a porous texture of the material and the pure iron oxide (Fig. 3b) presented a spongy like texture. It can be noted by the micrographies (Fig. 3c and d) that the synthesis conditions utilized seems to lead to composites formation since changes in the texture of the composites have been observed when compared with their precursors (Fig. 3a and b). The micrography of the composite AC/iron oxide 1/1 (Fig. 3c) suggest well-dispersed iron oxide particles covering the activated carbon. In the composite with lower content of iron oxide, AC/iron oxide 5/1, exposed surface areas of activated carbon can be noted (Fig. 3d).

### 3.2. Atrazine removal experiments

#### 3.2.1. Atrazine adsorption

The adsorption capabilities can be calculated by the equation ( $q_e = x/W = (V(C_o - C_e))/W$ ), where  $x$  is the solute adsorbing capacity (mg),  $V$  is the volume of the aqueous solution (L),  $C_o$  and  $C_e$  are original and equilibrium concentrations ( $\text{mg L}^{-1}$ ), respectively,  $W$  is the mass of adsorbent used (g), and  $q_e$  is the adsorption capability (solute adsorbing capacity per adsorbent unit,  $\text{m}^2 \text{ g}^{-1}$ ).

The atrazine adsorption capability diminishes as the content of iron in the composites increases (Fig. 4a and b). The atrazine adsorption of the AC/iron oxide 5/1 composite was higher than that of AC/iron oxide 1/1 (Fig. 4b). This result is probably related to the decrease of surface area caused by the presence of a high quantity of iron oxide in the AC/iron oxide 1/1 composite (five times higher than the composite AC/iron oxide 5/1) occupying the active sites avoiding the contact of atrazine molecules to adsorption sites on the carbon surface.

#### 3.2.2. Atrazine oxidation

A high atrazine removal capability is observed for both composites, approximately 94 and 60% removal by the AC/iron oxide 5/1 and 1/1, respectively (Fig. 5).

It is also interesting to note that the addition of  $\text{H}_2\text{O}_2$  increases the atrazine removal capability for both materials. This result suggests that the iron oxides formed (essentially goethite), highly dispersed on the carbon surface is active for atrazine removal from aqueous medium. In fact, it is reported in the literature that goethite is very active on the oxidation of organic compounds [23]. It is also interesting to observe the high capacity of atrazine adsorption, approximately 45% by the 1/1 composite (Fig. 5a) versus 58% by the

AC/iron oxide 5/1 composite (Fig. 5b). The adsorption capacity of these materials is an important property since they become active adsorbents with the ability to pre-concentrate organic compounds for subsequent decomposition.

The oxidation process probably comprises of two steps: (i) adsorption of the atrazine on carbon surface and (ii) oxidation of atrazine (after  $\text{H}_2\text{O}_2$  decomposition followed by  $\cdot\text{OH}$  formation). Although the  $\text{H}_2\text{O}_2$  decomposition mechanism is not completely understood, several electron transfer processes have been suggested to take place during the reaction. According to the Fenton's mechanism, the reaction might be initiated by an active site transferring an electron to  $\text{H}_2\text{O}_2$  to produce a  $\cdot\text{OH}$  radical as suggested in previous work [24].

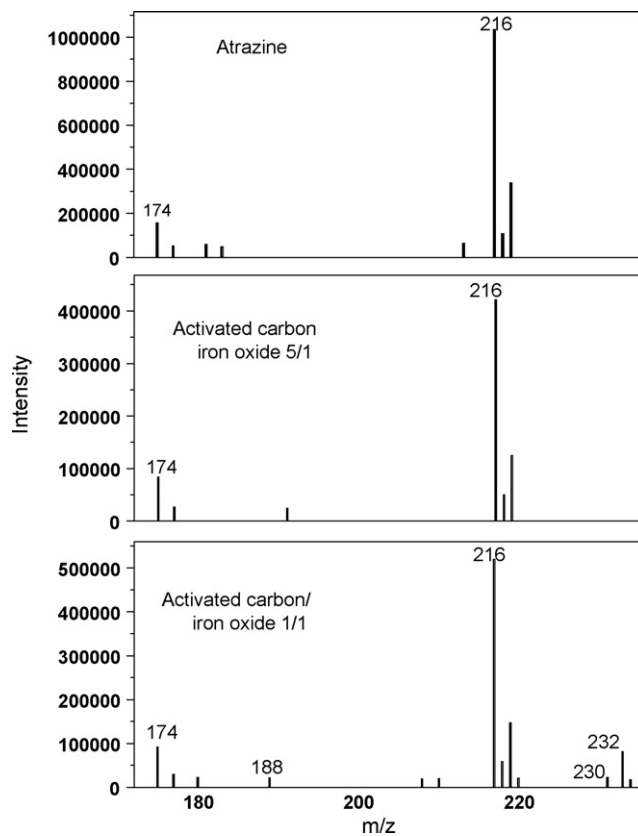


Fig. 6. ESI mass spectra of atrazine  $[\text{M}+\text{H}]^+$  and atrazine products from oxidation with  $\text{H}_2\text{O}_2$  in presence of AC/iron oxide composites at 1/1 and 5/1 mass ratios.



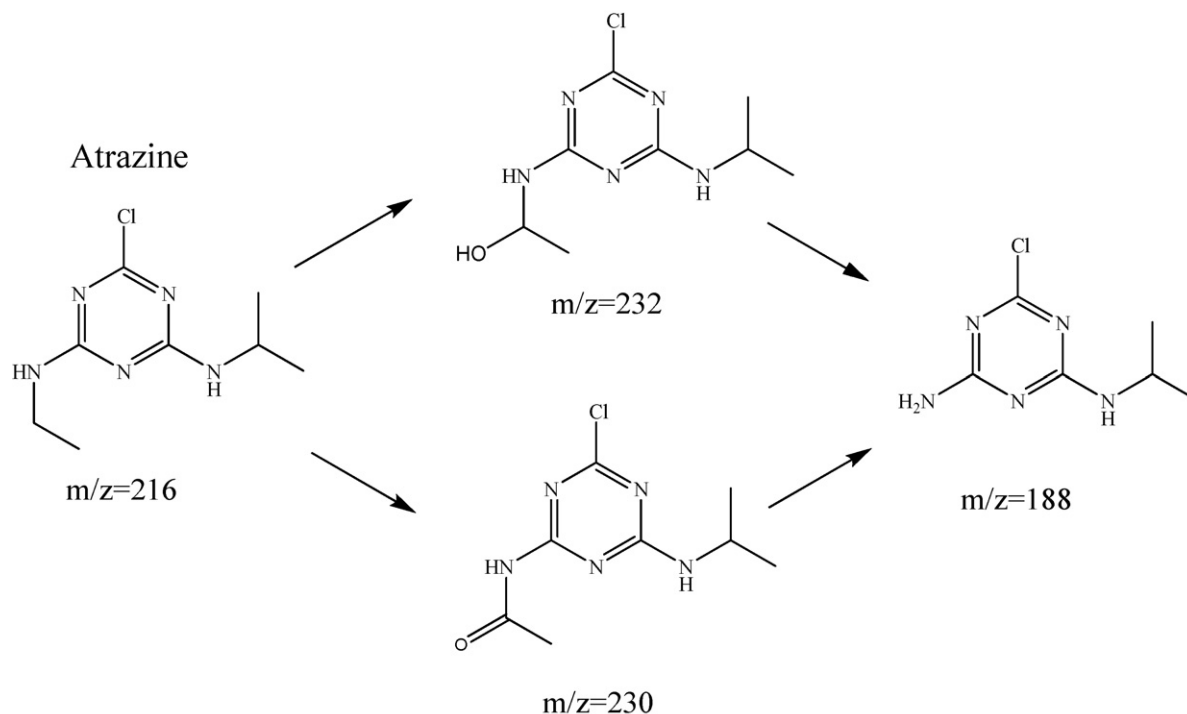


Fig. 7. Proposed scheme for atrazine oxidation by the AC/iron oxide 1/1 composite.

To investigate the oxidation mechanism of atrazine using these composites, the reactions were also monitored with ESI-MS (Fig. 6).

The signal  $m/z=216$  (Fig. 6) is related to a protonated atrazine molecule ( $M=215 \text{ g mol}^{-1}$ ). The signal  $m/z=174$  is related to deisopropil-atrazine. This product is likely formed at mass spectrometer skimmer lens, as its intensity is significantly reduced if the skimmer voltage is diminished. The AC/iron oxide 5/1 composite apparently does not oxidize atrazine as no atrazine oxidation products are observed in the mass spectra after 2 h of reaction (Fig. 6) but, the atrazine removal by this composite is remarkably increased in the presence of  $\text{H}_2\text{O}_2$  (Fig. 5) suggesting the occurrence of oxidation processes. This fact could be due to adsorption of the oxidation products by the activated carbon. On the other hand, when the AC/iron oxide 1/1 is employed, the appearance of the new signals at  $m/z=230$ , 232 and 188 is clearly observed. These products are formed by oxidation of the ethyl group of the atrazine molecule, producing the new signals at  $m/z=230$  and 232. Therefore, dealquilation of this oxidized radical may produce the signal at  $m/z=188$  (Fig. 7).

#### 4. Conclusion

Activated carbon has its chemical properties strongly modified by impregnation with iron oxides. Goethite tends to reduce the surface area and the adsorption capacity of the composite material, but increases the proportion of active sites. These active sites promote the decomposition of  $\text{H}_2\text{O}_2$  and the oxidation of atrazine in aqueous medium. Catalytic activity is shown to increase with the iron content of the composites.

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