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Experimental study of the remediation of atrazine contaminated soils through soil extraction and subsequent peroxidation

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Abstract

This paper presents a feasibility study in the field of the remediation of soils contaminated with atrazine. Experimental tests were performed on an artificially contaminated synthetic soil. Atrazine was removed from the soil by flushing with an aqueous solution at 5 vol.% of ethanol. Experimental tests of evaporation and Fenton's oxidation on the extracted solution were then performed in order to transform atrazine into its oxidation products. Tests were performed in the presence of a peroxide excess the ratio between Fe^{2+} and H_2O_2 was 1:10. Peroxide was first added in order to reduce the consumption of hydroxyl radicals by their reaction with the excess of Fe^{2+}. The degradation mechanism of atrazine during oxidation with Fenton's reagent in the presence of ethanol was investigated.

Results showed that due to the non selective nature of Fenton's reagent a high consumption of reagent was needed to achieve a significant atrazine oxidation from solutions at 4.5 vol.% of ethanol. While at a Fe^{2+} concentration of 3 mM atrazine practically disappeared from pure aqueous solutions within 2 h, a degradation yield of only 28.1% was observed in the presence of ethanol even when Fe^{2+} concentration was 15 mM.
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1. Introduction

Atrazine 2-chloro-4-ethylamine-6-isopropylamino-*s*-triazine (CIFT) is a triazine selective herbicide widely used throughout the world in the production of corn and other crops.

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It is classified in the US as restricted use pesticide. Atrazine is moderately toxic to humans and other animals. It can be absorbed orally, dermally and by inhalation.

Atrazine is highly persistent in soil: the half life of atrazine in loamy soils ranges from 60 to 150 days: under dry or cold conditions it can persist for longer than 1 year [1]. Due to its low adsorption to soil particles, atrazine has a high potential for groundwater contamination, despite its moderate solubility in water, about 33 mg/l at 20 °C [2,3].

In order to protect groundwater the need exists for the remediation of the contaminated soils. Among the various technologies for the remediation of contaminated soils, the in situ soil flushing processes have been successfully proven on a wide variety of pesticides [4].

The term in situ soil flushing is used to denote the extraction of pollutants from soil by passing an extraction fluid (water or an aqueous solution) through the soil. In situ soil flushing technologies can be combined with a treatment to destroy the pollutants or remove them from the liquid used for extraction.

The main factors affecting atrazine retention in soil are the soil nature, pH and cation-exchange capacity, and the simultaneous presence of different organic pollutants. Soil permeability is the key physical parameter to determine the feasibility of a soil flushing process [5]. As soils with low permeability ($K < 1.0 \times 10^{-5}$ cm/s) naturally inhibit the permeation of fluids, soil flushing proves effective only for those classified as permeable ($K > 1.0 \times 10^{-3}$ cm/s) or, to a lesser extent, as slightly permeable (1.0×10^{-5} cm/s $< K < 1.0 \times 10^{-3}$ cm/s). The addition of flushing additives to the extracting solution has also proved highly effective in the case of organic pollutants [6,7].

This paper presents a treatability study for the remediation of soils contaminated with atrazine. Experimental tests were performed on a soil with high organic content and artificially contaminated with atrazine.

The atrazine was removed from the soil by flushing with an aqueous solution of ethanol. Ethanol was chosen as flushing additive because of its non toxicity, and because there is a lack of information about its effectiveness in the extraction of pesticides from soils. The extraction yield under addition of 1.5–5 vol.% of ethanol was determined. Other studies showed in fact that concentration of flushing additives higher than 5% can restrict the permeation of the washing solution [8].

The extracted solution was then subjected to experimental tests of evaporation and following chemical oxidation to obtain the complete removal of atrazine.

While a wide variety of papers deals with the extraction of pollutants from soils, only few studies deal with the treatment of the extracted solution. Since a large volume of flushing solution is needed to obtain a satisfactory pollutant extraction yield, a pretreatment is usually necessary to separate the pollutant from the water phase, or, at least, to concentrate it. This operation is often crucial to allow the recovery of the purified water and then to help the treatment of the concentrated phase, devoted to the pollutant degradation (in the case of organic pollutant) or precipitation (in the case of metals).

The reduction of the extracted solution volume can be realized by membrane filtration, by liquid extraction or by evaporation. As regard to the liquid extraction operation, in the case of atrazine contaminated soils, due to the high solubility of atrazine in ethanol, the use of large amount of a selective solvent is required. The most common used solvents are not useful to this aim, due to their high cost or even toxicity.

On the other side, membrane operations can be successfully used to concentrate water solutions, but, in the present case the high affinity between ethanol and atrazine does not ensure their complete separation.

Hence, in the present study an evaporation step was performed to separate ethanol from the water contaminated phase.

This last phase was the subjected to a chemical oxidation treatment. In this paper, the oxidation was carried out by hydroxyl radicals. Several studies showed that hydroxyl radicals are powerful oxidants with respect to organic compounds, such as pesticides [9–11]. In particular Fenton's reagent, a mixture of hydrogen peroxide and ferrous ions, provides a simple and economic source of hydroxyl radicals [11,12]. Under acid conditions, it can quickly oxidize a great number of organic compounds [13]. Moreover, atrazine degradation by Fenton reagent was faster compared to other hydroxyl radical generation systems, as ozone or UV treatment [9].

The degradation mechanism of atrazine during oxidation with Fenton's reagent was first investigated by Plimmer et al. [14]. They found that atrazine degradation occurs through its dealkylation into three main products: the 2-amino-4-chloro-6-(isopropylamino)-*s*-triazine (CIAT), the 2-amino-4-chloro-6-(ethylamino)-*s*-triazine (CEAT), and the chlorodiamino-*s*-triazine (CAAT).

A new degradation pathway was then proposed by Arnold et al. [9]. They indicated that the atrazine degradation by Fenton reagent occurs through simultaneous dealkylation and dechlorination: the two main terminal products are CAAT and 2-acetamido-4,6-diamino-*s*-triazine (CDAT). Further oxidation treatment is ineffective because of the low reactivity of CAAT and CDAT towards hydroxyl radicals.

However, both these and other studies [15] concluded that atrazine mineralization does not occur during Fenton oxidation treatment.

Among the main oxidation products of atrazine and other *s*-triazines, CAAT is the least resistant to biological degradation [16–21]. In order to assess a process for the remediation of atrazine contaminated soil, the chemical treatment with Fenton's reagent was investigated in the present work, as a pretreatment step for a subsequent biological treatment.

The most significant aspect in the Fenton oxidation treatment of a solution extracted from a contaminated soil is related to the simultaneous presence of more than one organic substrate: in the solution recovered after the flushing process a substantial amount of ethanol and organic acids is expected. Due to the low selectivity of hydroxyl radicals, the oxidation rate of atrazine is strongly affected by the presence of competitive substrates [22–24]. In the present paper, the effect of reaction time and of the composition of the extracted solution were investigated and the required Fenton's reagent concentration was determined to obtain the CAAT production and minimize the other less biodegradable atrazine degradation products.

2. Materials and methods

2.1. Soil preparation

The soil used in the experiment was a mixture of clay, gravel, sand and silt as shown in Table 1. A 20 vol.% of HOS was added, in order to increase the overall organic fraction.

Table 1
Composition of the soil used in the experiment

Component	Particle size	HOS (vol.%)
Gravel	9.5 mm 3/8, 6.5 mm 3/4	8
Sand	0.0625–2 mm	39
Silt	0.039–0.0625 mm	34
Clay	<0.004 mm	19

This addition had the objective to better evaluate the influence of the organic content on the extraction process. Humic substances have in fact a strong affinity for organic compounds with water solubility, such as atrazine.

Each component of the soil was passed through ASTM sieves to ensure a controlled particle size less than 2 mm. The components were mixed for 24 h in a Hobart-type mixer. After analysis to determine its chemical and physical characteristics, the soil was then placed in plastic containers prior to artificial contamination. The physical and chemical properties of the soil used are shown in Table 2.

The total porosity was determined using 100 g of air-dried soil. The sample was weighed in a moisture can and a known amount of water was added until saturation was obtained. The total porosity f was determined from:

$$f = \frac{V}{V + V_s} \tag{1}$$

where V is the volume of water added and V_s the volume of the soil particles [24].

Experimental tests were performed on samples of 300 g artificially contaminated soil. The pore volume (PV) of the soil was calculated from:

$$\mathrm{PV} = \frac{f}{100} V_c \tag{2}$$

where V_c was the Soil volume in the column. The pore volume of the samples was 108 ml.

2.2. Soil contamination

The samples were prepared by spiking atrazine (Carlo Erba Reagents) into the soil. To ensure a good distribution of atrazine, a reasonable amount of acetone was added.

Table 2
Characteristics of the soil used

pH	8.6
Organic carbon (%)	2.5
Permeability (cm/s)	3.21×10^{-3}
Porosity (%)	46
Humidity (g/kg)	24.5
Bulk density (g/ml)	1.25
Absolute density (g/ml)	2.3

The soil was kept under agitation for 30 min and then air dried. Samples were stored in plastic containers for 15 days prior to soil analysis. The concentration of atrazine in the contaminated samples was controlled at 10 $\mu g\, g^{-1}$ of soil.

2.3. Experimental procedure: soil flushing

Soil contaminated samples were washed with an aqueous solution of ethanol. In preliminary tests the solubility of atrazine in ethanol was measured as 5.88×10^3 g/l. The investigated operative parameters were extracting solution volume and the ethanol percentage.

Five sets of experiments were performed. Total extraction volumes were in the range between 3 and 15 PV. The percolation of the flushing solution was ensured by a peristaltic pump (Velp Scientifica, model SP311): the flushing solution flow rate was 0.3 l/h.

Three different ethanol concentrations were used in this solution, i.e. 1.5, 3 and 5%. The extracted solution was then filtered on a 0.45 μm Whatman filter and collected in plastic containers prior to the evaporation treatment.

2.4. Evaporation of the extracted solution

In order to reduce the ethanol concentration, the extracted solution was subjected to evaporation in a rotavapor Büchi. Evaporation tests were carried out at 95 °C and atmospheric pressure. For reference purpose evaporation tests on a solution of 4.5 vol.% of ethanol and containing 2 mg/l of atrazine were performed. The residue was collected and sent to the oxidation treatment. The total organic carbon (TOC) of the residue was determined at selected times.

2.5. Treatment of the extracted solution

After adjustment of pH, down to pH = 3, by means of hydrochloric acid, 100 ml samples of the recovered solution were subjected to oxidation treatment with Fenton's reagent by adding first hydrogen peroxide (35% solution) and after 60 s, iron(II) was added as solid heptahydrate iron sulphate ($FeSO_4{\cdot}7H_2O$) under conditions of constant agitation and at room temperature [11]. Peroxide was added first in order to reduce the consumption of hydroxyl radicals by their reaction with the excess of Fe^{2+}.

Three experimental sets were carried out at pH = 3 and ambient temperature [11]. Preliminary tests were performed on a pure aqueous solution of atrazine.

The molar ratio of Fe^{2+} to hydrogen peroxide was 1:10. Arnold et al. [9], found that using a peroxide excess causes a lower atrazine oxidation efficiency, but dealkylation may be favoured with respect to dechlorination and CAAT and CDAT are the only terminal products of the degradation pathway.

In order to assess the influence of ethanol on the oxidation of atrazine, a second series of tests were performed on a solution of 4.5 vol.% ethanol and 2 mg/l of atrazine.

A further series of chemical oxidation tests were then performed on the residue of the evaporation treatment, in order to determine the influence of both ethanol and organic acids in soil on the atrazine oxidation efficiency.

2.6. Analyses

Atrazine was analyzed by gas chromatography [25–27]. A GC 8000 supplied from Carlo Erba instrumentation equipped with a detector ECD-80 (Fisons) was used, with the following gas flows: helium (3 ml/min) as carrier gas, and nitrogen (28 ml/min) as makeup gas. Injection volumes of 1 μl were used in splitless mode in each analysis. The atrazine retention time was 20.34 min. An amount of 50 ml of filtered solution were solvent extracted with 50 ml of dichloromethane. The mixture was mixed for 5 min. To avoid foaming a small amount of sodium chloride was added.

The extracted phase was then concentrated in a rotating evaporator Büchi (temperature 42 °C; pressure 550 mm Hg) and evaporated to dryness under a gentle nitrogen stream. An amount of 10 ml of ethyl acetate was then added before the injection.

Atrazine oxidation products were identified by mass spectrometry, using a Fisons MD 800 mass spectrometer. The pH was measured with a Crison 421 pH meter. The total organic carbon was measured using a Shimadzu TOC-5000A TOC Analyzer.

3. Results and discussion

3.1. Soil flushing

The volume of extracted solution was determined in each test and the atrazine extraction efficiency was calculated as the weight percentage of atrazine extracted with respect to the amount in the contaminated sample. Fig. 1 shows the extraction efficiency as a function of the volume of flushing solution.

Data show that the atrazine extraction efficiency increases with both increasing the ethanol concentration and extraction volume.

Using an extraction volume of 15 PV and an ethanol concentration of 5 vol.% an extraction efficiency of about 95% can be attained.

In such conditions the extracted solution had a volume of about 1450 ml and the atrazine concentration was about 2 mg/l.

The ethanol concentration in that solution was about 4.5 vol.%. A large amount of ethanol was in fact fixed through the complexation by humic and fulvic acids in soils. This in accordance with other studies, which assessed the influence of organic content in soil on the effectiveness of flushing additives [23].

3.2. Evaporation of the extracted solution

Fig. 2 shows the evaporation test results. Samples were taken at selected times corresponding to different residue volumes. The TOC concentration of the residue was reported in Fig. 2 as a function of the ratio of the volume of the collected residue to the volume of the initial solution subjected to the evaporation treatment. The organic fraction of both the real and the reference solution was essentially due to ethanol since the contribution of atrazine was negligible. In addition, in the real extracted solution a contribute of about 3.5% on the

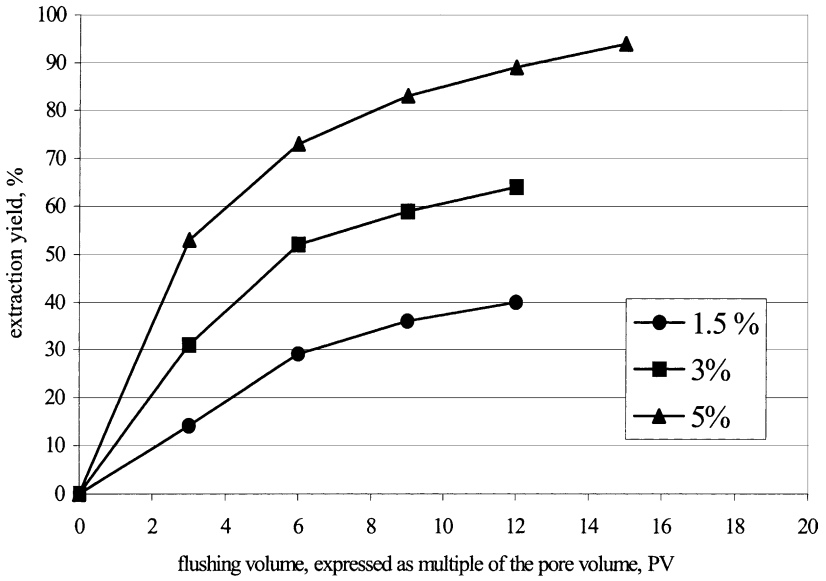

Fig. 1. Soil flushing experiments: atrazine extraction yield at selected ethanol concentration in flushing water.

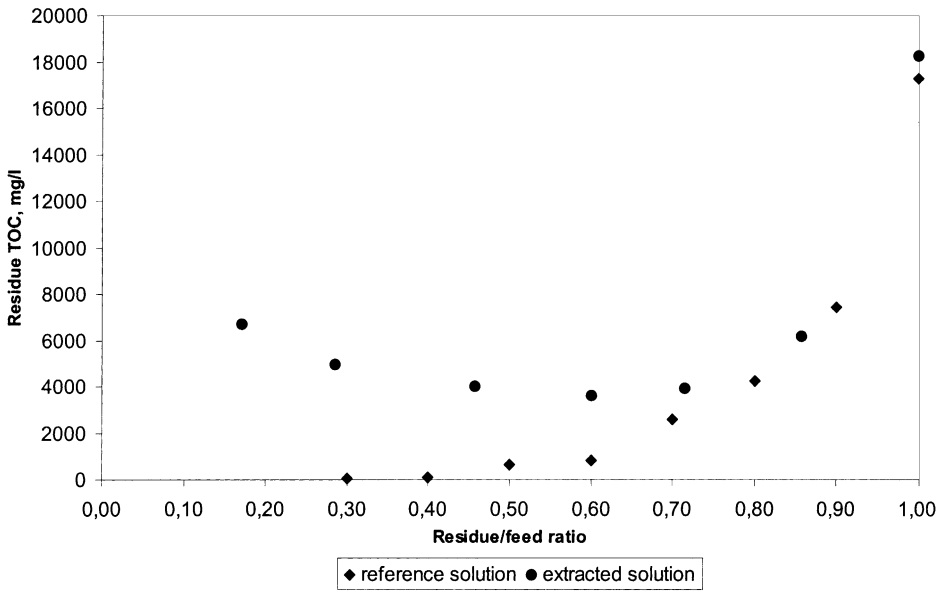

Fig. 2. Evaporation of the extracted solution ($T = 95\,^{\circ}\mathrm{C}$; $P = 1\,\mathrm{atm}$).

total TOC for the organic acids of soils was evaluated, comparing the evaporation pathway of the extracted solution to that of a solution of ethanol at 4.5 vol.%.

The evaporation pathway of the two solutions is quite different. Until a residue/extracted solution ratio of 0.8 the same trend was observed. For increasing evaporation times the organic content in the reference solution continued to drop; the total organic carbon concentration in the real solution, however, reached a minimum and then began to increase. The reason for this TOC increasing during evaporation was attributed to the low volatility of soil organic acids that began to concentrate in the residue. When the ethanol concentration decreased, they became the main organic fraction.

The minimum point was observed for a residue volume of about 60% of the initial solution volume. In correspondence of this minimum point an ethanol content of 0.15 vol.% in the reference solution was observed. The total organic content in the extracted solution at this point was higher: this was due to the interactions between the two organic substrates. The amount of ethanol in the solution was about 0.36 vol.%.

The atrazine concentration in the residue was about 3.2 mg/l. In addition the concentration of atrazine and its degradation products were negligible in the distillate.

3.3. Chemical oxidation of the extracted solution

Table 3 shows that Fenton's reagent quickly oxidized atrazine when no other organic substrate was present. At a Fe^{2+}:H_2O_2 molar ratio of 1:10, complete transformation of atrazine occurred at Fe^{2+} concentration of 2 mM/l. This confirms the results of Arnold et al. who observed that the transformation of atrazine occurs in a few hours in the presence of a peroxide excess [9].

In the extracted solution ethanol molar concentration was about 50,000 times in excess of the atrazine molar concentration. Due to the non selective nature of Fenton's reagent, the presence of ethanol greatly affects the atrazine oxidation efficiency [22]. In order to evaluate the influence of ethanol on the atrazine decay rate, a preliminary series of oxidation tests was performed on an aqueous solution of 2 mg/l of atrazine containing an ethanol concentration of 2.5 vol.%.

Table 4 shows that only a slight oxidation of atrazine occurred at the lower concentration of the reagents. In an aqueous solution of atrazine and ethanol, both compounds are oxidized simultaneously. The high reactivity of ethanol towards hydroxyl radicals lead to a higher consumption of reagents to achieve a significant atrazine oxidation.

Due to the substantial oxidation of ethanol, a strong reduction of the total organic carbon concentration in the solution was in fact observed. The reduction of the ethanol

Table 3
Experimental results: Fenton oxidation of a pure atrazine 2 mg/l solution (reaction time = 2 h)

Fe^{2+} (mM/l)	Fe^{2+}:H_2O_2 molar ratio	Atrazine removal (%)
0.5	1:10	95.0
1	1:10	98.8
2	1:10	99.9
3	1:10	>99.9

Table 4
Experimental results: Fenton oxidation of an aqueous solution of 4.5 vol.% ethanol, containing 2 mg/l of atrazine (reaction time = 2 h)

Fe^{2+} (mM/l)	Fe^{2+}:H_2O_2 molar ratio	Atrazine removal (%)	TOC removal (%)
0.5	1:10	1.0	21.7
2	1:10	6.9	28.4
4	1:10	8.1	38.0
10	1:10	20.4	60.8
15	1:10	28.1	66.6

concentration in the extracted solution was hence crucial to optimize the oxidation process.

Fig. 3 shows the results of tests performed on the residue of the evaporation treatment of the extracted solution: even at that low level of other organic substrate in the solution, the atrazine degradation was hindered: organic acids and ethanol decompose in fact simultaneously with the atrazine degradation. Only when increasing the Fenton's reagents concentration did atrazine oxidation occur with the same efficiency observed in a pure solution. Furthermore, the maximum TOC reduction in the performed tests was about 54.5%, when 18 mM/l of Fe^{2+} was added. This shows that the overall organic substrate removal was also hindered. The presence of dissolved natural organic material extracted from the contaminated soil together with the pollutant, in fact decreased the organic substrate oxidation. This can be explained by the binding of iron and the hydrophilic site of organic acids that sequestered hydroxyl radicals from the organic substrate [24].

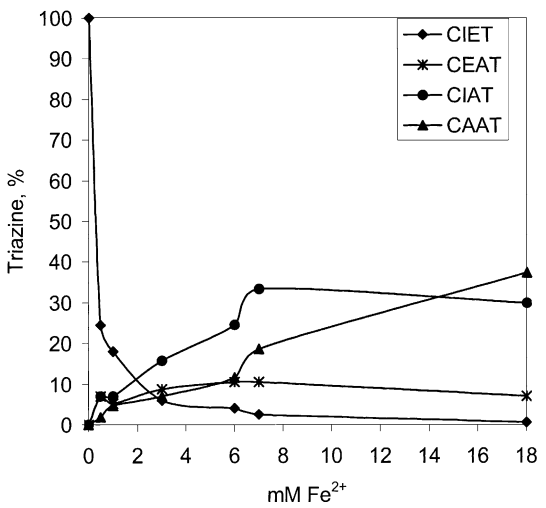

Fig. 3. Fenton's oxidation of an aqueous solution of atrazine and ethanol (0.36 vol.%): effect of reagent concentration (Fe^{2+}:H_2O_2 = 1:1).

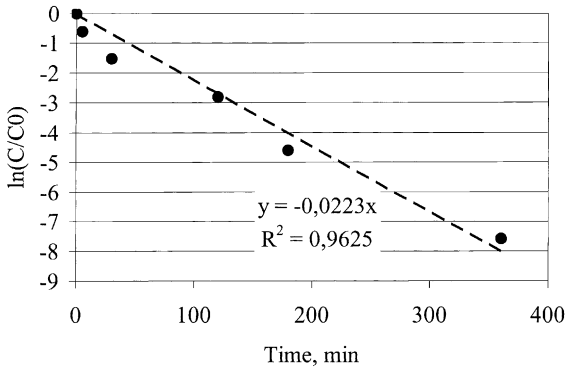

Fig. 4. Fenton's oxidation of an aqueous solution of atrazine and ethanol (0.36 vol.%): reaction progress with time (Fe^{2+}:H_2O_2 = 1:1; Fe^{2+} = 3 mM/l).

In addition, results show that Fenton's reagent caused the atrazine degradation through its dealkylation in two main byproducts: the CIAT and the CEAT. Increasing the Fe^{2+} concentration they were oxidized to the product chloro-diamino-*s*-triazine (CAAT) which represents the final compounds of the whole oxidation process [9]. This mechanism is the same as generally expected in the oxidation of a pure aqueous solution of atrazine [9]: a CAAT accumulation during Fenton'oxidation of *s*-triazines was in fact observed. Conversely, its biological degradation by pure microbial cultures was also observed [16]. The degradation of the residual amount of CAAT may be achieved in a subsequent biological treatment, possibly even in a municipal wastewater treatment plant [16].

The mass balances performed show that under the operating conditions, when reactions have been stopped, a substantial amount of initial atrazine was not transformed into the three main investigated products. This is in good agreement with the results observed in other studies [9,15], where, under the same operating conditions, only about 30–40% of the initial amount of atrazine was transformed in secondary or unidentified products.

Moreover ^{14}C mass balances performed in those studies have already shown that no loss of radioactivity occurs with the Fenton treatment of atrazine: mineralization was observed in microbial degradation studies only [15]. At the same time even the production of volatile products was excluded [9,15].

Therefore, in this paper, the mass balance can be considered reasonably closed attributing the remaining fraction of the transformed atrazine to secondary or unidentified products.

Fig. 4 shows the reaction progress: after 3 h of reaction, at a concentration of bivalent iron of 3.0 mM/l, practically all the initial CIET was oxidized. Other studies [15] showed that atrazine oxidation follows a first order kinetic reaction rate with respect to the atrazine concentration, with a rate constant in the range of 0.10–0.14 min^{-1}. The experimental results reported in Fig. 4 show that the atrazine degradation occurs more slowly. The presence of competitive substrates consumed hydroxyl radicals in the solution and therefore lowered the oxidation efficiency of atrazine.

4. Conclusions

This paper presents an experimental study about the remediation of soils contaminated with atrazine. Experimental tests were performed on an artificially contaminated synthetic soil. Atrazine was removed from the soil by flushing with an aqueous solution containing 5 vol.% of ethanol. The extraction yield is a strong function of the operating conditions, as shown in Fig. 2.

Experiments of Fenton's oxidation on the extracted solution were then performed in order to transform atrazine and its oxidation products into the CAAT product. This last product, though as toxic as atrazine, is the less resistant to biological degradation.

Results showed that:

- Fenton's reagent causes the atrazine degradation mainly through its de-alkylation in two byproducts: the 2-amino-4-chloro-6-(isopropylamino)-*s*-triazine (CIAT) and the 2-amino-4-chloro-6-(ethylamino)-*s*-triazine (CEAT);
- increasing the Fe^{2+} concentration the conversion of CIAT and CEAT into the product chloro-diamino-*s*-triazine (CAAT) was observed;
- ethanol strongly affects the atrazine oxidation through Fenton's reagent: due to the non selective nature of Fenton's reagent a higher consumption of reagent was needed to achieve a significant atrazine oxidation in the presence of ethanol;
- the same mechanisms for atrazine oxidation in presence of ethanol and soil organic acids were observed.

Due to the higher biodegradability of CAAT its complete removal from the extracted solution can be achieved through a final biological treatment: Fenton's oxidation treatment may be used in combination with biological treatments to degrade atrazine extracted from contaminated soils.

For further reading see [28].

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