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Comparison of Different Treatments for Alachlor Removal from Water

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The presence of herbicides in surface and ground water constitutes an important focus of water pollution. Thus, most of herbicides are catalogued as priority pollutants of water due to their toxicological effects. Alachlor (2 Chloro, N-2,6-diethyl–N–methoxymethyl acetanilide) is an herbicide of the family of chloroacetanilides with a wide application in agriculture, about 37 x 10^6 kg in USA (Clay et al., 1997). Due to the increasing use of this type of substances, herbicide concentration in surface and ground water has been reported to present values well above the recommended levels (2 μg L^{-1} according to the EPA or 1 μg L^{-1} for the European Commission for Water, AWWA, 1990) for this sort of compounds (Jury et al., 1987; Kolpin et al., 1996; Galassi et al., 1996).

Ozone has been successfully used to remove alachlor from distilled and surface water (Somich et al., 1988; Beltrán et al., 1996, 1999a). Also, it has been reported that ozonated solutions of alachlor showed a lower toxicity than the original solution of the herbicide (Upham et al., 1997).

In this work, several oxidation processes for alachlor removal have been compared. Experiments have been carried out by using both ultrapure and surface water from a river located in Badajoz (South West of Spain). In addition, the presence of typical ionic species found in natural water, for instance iron and manganese, has also been investigated.

MATERIALS AND METHODS

Alachlor (99%) was obtained from Chem–Service, mono hydrated manganese sulfate, dihydrated ferrous sulfate and hydrogen peroxide (33% w/v) were purchased from Panreac and used as received. Aqueous solutions of alachlor were prepared by saturation as described elsewhere (Beltrán et al., 1999b). Organic free water was obtained from a Milli-Q system. Surface water taken from Gevora river (Badajoz, Spain) was allowed to settle down for 24 h and filtered through 45 μm Millipore membranes before use. Main characteristics of surface water are summarized in Table 1.

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Table 1. Characterisation of surface water from Gevora river after filtration.

pH	$Ab_{254\ nm}$	COD, mg L^{-1}	TC, mg L^{-1}	IC, mg L^{-1}
8.0	0.096	7.2	12	1.44

Table 2. Operating conditions used in oxidation experiments of alachlor (Ala).

Run [a]	pH initial/final	$[Ala]_0$, $Mx10^5$	O_3 dose, mg min^{-1}	UV on/off	$[Mn(II)]_0$ mg L^{-1}	$[Fe(II)]_0$ mg L^{-1}
DA1	5.9/5.4	4.28	0.266	Off	--	--
DA2	8.1/7.0	4.80	0.293	Off	--	--
DA3	8.1/5.9	4.70	0.253	On	--	--
DA4	8.0/7.1	4.74	0.276	Off	--	5.0
DA5	8.1/7.1	4.56	0.283	Off	--	0.5
DA6	7.9/6.0	4.47	0.260	On	--	5.0
DA7	8.0/6.1	4.71	0.249	On	--	2.0
DA8	8.0/6.0	4.39	0.243	On	--	0.5
NA1	7	4.05	0.248	Off	--	--
NA2	7	4.00	0.310	On	--	--
NA3	7	4.62	--	On	--	--
NA4[b]	7	4.47	0.228	Off	--	--
NA5	7	4.57	0.265	Off	0.2	--
NA6	7	4.34	0.259	Off	1.0	--
NA7	7	4.48	0.290	On	1.0	--

T = 20 °C, v_o (aqueous flow rate) = 0.195 L·min^{-1}, Gas flow rate = 20 L·h^{-1},
V (volume of reactor) = 1.95 L, I_o (intensity of incident radiation) = $1.91x10^{-6}$ Einstein·$(L·s)^{-1}$,
L (effective path of radiation through reactor) = 6.6 cm. [a] DA = Distilled water (non-buffered)
NA = Natural water (phosphoric acid/phosphate buffer). [b] Dose H_2O_2 = 0.137 mg·min^{-1}.

Ozone was generated from pure oxygen from a laboratory ozonator able to produce a maximum of 4 g ozone h^{-1}. Experiments were carried out in a 200 cm length, 4.15 cm ID glass bubble column equipped with a porous plate (10-16 μm porous size) situated at its bottom. The column operated in continuous regime for both the liquid and gas phases. Liquid flow rate was set at 11.7 L h^{-1} in all experiments (mean residence time of the liquid phase = 10 min). The ozone – oxygen mixture was countercurrently fed to the reactor with a flow rate of 20 L h^{-1}. Temperature was kept constant (293 K) with the aid of a thermostatic system.

Alachlor concentration was determined by HPLC analysis. For this purpose, a C18 Novapack column (15 cm length, 3.4 mm ID) was used. The mobile phase was an acetonitrile – water mixture (40:60 v/v) with a flowrate of 1 mL min^{-1}. Detection of the parent compound was accomplished by absorption at 254 nm by means of a 486 Water UV/Visible detector. Ozone in the gas phase was monitored with a GM19 Anseros analyser. Dissolved ozone and peroxides were determined by the Indigo and fluorescence methods, respectively (Bader and Hoigné, 1981; Lazrus, 1985).

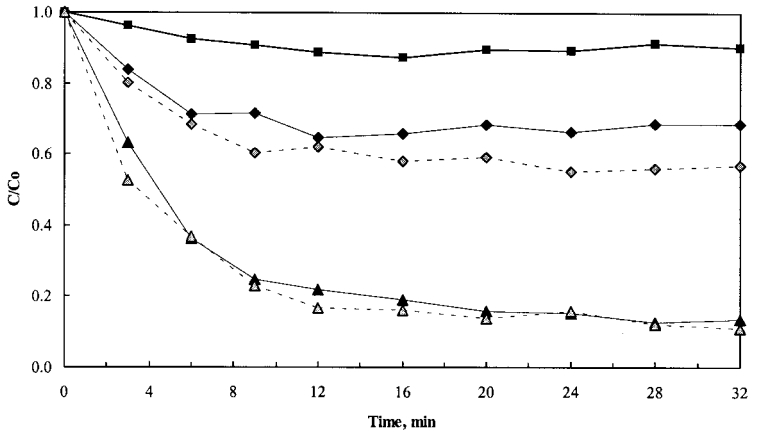

Figure 1. Variation of alachlor concentration (dimensionless form) with different treatments in distilled water. T= 20 °C, v_o= 0.195 L·min^{-1}, Q_G= 20 L·h^{-1}, V= 1.95 L, I_o= 1.91x10^{-6} Einstein·(L·s)$^{-1}$, L= 6.6 cm: ■ Ozone (pH 6); ◆ ◇ Ozone (pH 8) + Fe^{2+} (dotted line); ▲ △ Ozone + UV (pH 8) + Fe^{2+} (dotted line).

RESULTS AND DISCUSSION

In order to investigate the efficacy of different treatments used in pollution water remediation a series of alachlor oxidation experiments was carried out in ultrapure water by using several combinations of ozone and UV radiation in the presence and absence of ferrous iron (see Table 2). Figure 1 shows the evolution of the normalized alachlor concentration with time for this experimental series. As it can be observed from this figure, single ozonation of alachlor at initial pH = 6.0 resulted in a poor conversion of the parent compound after steady-state conditions were achieved (10% alachlor removal). However, an increase of the starting pH up to a value of 8.0 led to a significant enhancement of the process (31% alachlor conversion).

Therefore, experimental results suggested that the main route of alachlor degradation was through reaction with hydroxyl radicals generated in the ozone decomposition catalysed at high pH (Beltrán et al., 1996). Addition of ferrous iron to the reaction media resulted in slight improvement of the final efficacy of the ozonation (45% conversion), probably due to the presence of an additional mechanism of hydroxyl radical generation (eq. [1]) or formation of a new oxidising agent (eq. [2]), namely the ferryl ion (Legube and Karpel Vel Leitner, 1999):

$$Fe^{2+} + O_3 \rightarrow Fe^{3+} + \bullet O_3^- \; ; \quad \bullet O_3^- \rightarrow HO_3 \bullet \rightarrow O_2 + HO \bullet \qquad [1]$$

$$Fe^{2+} + O_3 \rightarrow (FeO)^{2+} + O_2 \qquad [2]$$

The presence of UV radiation in the ozonation process led to a remarkable increase of alachlor depletion at steady-state conditions. The enhancement of the treatment could undoubtedly be attributed to both the contribution of the direct photolysis of

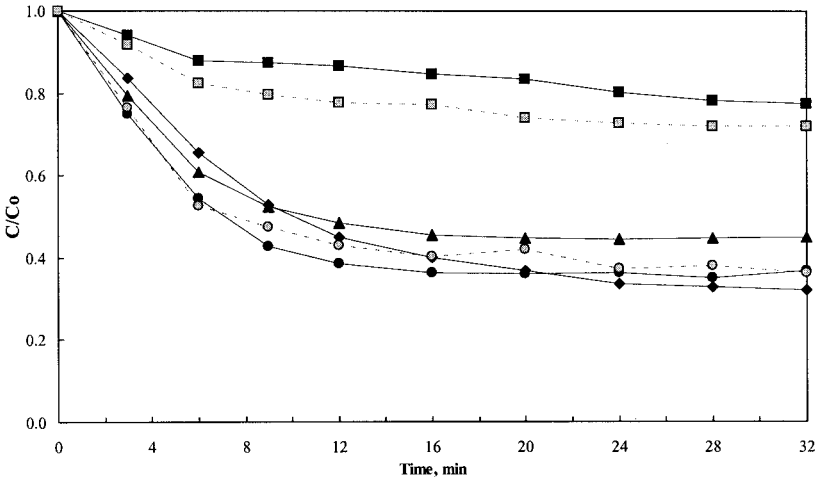

Figure 2. Variation of alachlor concentration (dimensionless form) with different treatments in natural water. T= 20 °C, pH buffered 7, v_o= 0.195 L·min^{-1}, Q_G= 20 L·h^{-1}, V= 1.95 L, I_o= 1.91x10^{-6} Einstein·(L·s)$^{-1}$, L= 6.6 cm: ■ □ Ozone + Mn^{2+} (dotted line); ▲ UV; ● ○ Ozone + UV + Mn^{2+} (dotted line); ◆ Ozone + H_2O_2

alachlor (eq. [3]) and the generation of hydroxyl radicals from the photolysis of ozone (eq. [4]):

$$Alachlor + h\nu \rightarrow Byproduts \quad [3]$$

$$O_3 + H_2O + h\nu \longrightarrow H_2O_2 + O_2 \quad [4]$$

$$H_2O_2 + h\nu \rightarrow 2HO\bullet \quad [5]$$

In this system (UV/O_3) the presence of ferrous iron had no influence on the final conversion achieved, suggesting that the reaction between ozone and ferrous iron could be neglected if compared to parallel reactions of ozone occurring in the mechanism (i.e. photolysis of ozone). The decrease in the pH value of the reaction media (almost 2 units for the UV/O_3 experiments) indicated the formation of acidic species throughout the experiments.

To check for the potential influence of the presence of additional substances found in natural water, some experiments were completed by utilising this type of water. Thus, broadly speaking it can be said that results obtained showed a trend similar to experiments conducted with ultrapure water (see Fig. 2). In terms of alachlor conversion, single ozonation of the solution was slightly improved in the presence of Mn (II). Similarly to formation of the ferryl ion, the activation of ozone by Mn (II) has been claimed to occur without generation of the hydroxyl radical (Andreozzi et al., 1992). These authors proposed the formation of a complex between Mn (III) and the organic compound leading to an intermediate product easily oxidized by ozone.

Again the presence of UV radiation in combination with ozone resulted in a notorious enhancement of the process. However, the final conversion achieved (64 %) was lower than the conversion obtained in ultrapure water (88 %). These results could be explained by considering both the presence of substances other than alachlor competing for the oxidising agents and the lower pH used to complete these experiments. The high contribution of the direct photolysis to alachlor removal is shown in Fig 2 by means of an experiment in the absence of ozone. Thus, a conversion value of 55 % was obtained by the simple application of UV radiation in comparison with the 65 % conversion when ozone was simultaneously used. Similarly to the system UV/O_3, the addition of hydrogen peroxide to the ozonation treatment led to the generation of hydroxyl radicals which readily reacted with alachlor:

$$O_3 + HO_2^- \rightarrow OH\bullet + \bullet O_2^- + O_2 \qquad [6]$$

Contrarily to the single ozonation, addition of Mn (II) to the system O_3/H_2O_2 or UV/O_3 did show no effect on alachlor removal.

The contributions of the different routes of alachlor elimination were calculated by taking into consideration the direct reaction of the ozone molecule with alachlor ($r_{D,A}$):

$$r_{D,A} = k_D C_A C_{O3} \qquad [7]$$

the direct photolysis of alachlor ($r_{UV,A}$):

$$r_{UV,A} = I_0 F_A \phi_A (1 - \exp(-2.303 L \Sigma(\varepsilon_i C_i))) \qquad [8]$$

and the reaction with the hydroxyl radical ($r_{HO,A}$):

$$r_{HO,A} = k_{HO} C_A C_{HO} \qquad [9]$$

where k_D and k_{OH} are the kinetic constants of the reaction of alachlor with ozone or the hydroxyl radical, respectively, C_i, is the concentration of species i, I_o the intensity of incident radiation, F_A the fraction of radiation absorbed by alachlor, Φ_A the quantum yield of alachlor (0.177 mol·Einstein^{-1}), L, the effective path of radiation through the reactor and ε_i, the extinction coefficient of species i (539.4 mol·(L·s)$^{-1}$). The term $r_{HO,A}$ was calculated by means of the mol balance in eq. [10] applied at steady-state conditions:

$$V \cdot (r_{UV,A} + r_{D,A} + r_{HO,A}) = v_O \cdot (C_{A0} - C_{Af}) \qquad [10]$$

where V and υ_o are the reactor volume and liquid flow rate, respectively.

Table 3 shows the results obtained for the experiments presented in Table 2. It is noticed the high contribution of the radical route of alachlor removal no matter the oxidation system used. Direct oxidation of alachlor with ozone was increased as the pH was lowered, however, in the presence of UV radiation this contribution could be neglected. Table 3 also presents the concentration of dissolved ozone and peroxides determined when steady-state conditions were reached.

Table 3. Final concentrations and rates for oxidation of Alachlor.

	% Conv.	$[Perox]_f$ Mx10^5	$[O_3]_f$, Mx10^5	pH_f	$r_{UV,A}$ $M^{-1}\cdot s^{-1}$ x10^8	$r_{D,A}$ $M^{-1}\cdot s^{-1}$ x10^8	$r_{HO,A}$ $M^{-1}\cdot s^{-1}$ x10^8	$\%_{UV.A}$ [a]	$\%_{D,A}$ [b]	$\%_{HO.A}$ [c]
DA1	10.0	0.27	3.50	5.5		0.38	0.34		52.6	47.4
DA2	31.3	0.30	2.40	7		0.22	2.28		8.9	91.1
DA3	87.2	2.75	0.40	6	0.66	<0.01	6.17	9.6	0.1	90.3
DA4	45.0	0.29	3.38	7		0.25	3.31		6.9	93.1
DA5	46.0	0.30	3.45	7		0.24	3.26		6.8	93.2
DA6	88.0	2.60	0.37	6	0.57	<0.01	5.98	8.6	0.1	91.3
DA7	88.4	0.28	0.43	6	0.52	<0.01	6.42	7.5	0.1	92.5
DA8	87.4	0.27	0.40	6	0.56	<0.01	5.83	8.7	0.1	91.2
NA1	22.5	0.61	3.30	7		0.29	1.23		19.1	80.9
NA2	63.7	5.00	0.25	7	2.71	0.01	1.51	64.1	0.2	35.7
NA3	54.5	0.67	--	7	4.13		0.07	98.4		1.6
NA4	67.6	13.5	0.25	7		0.01	5.02		0.2	99.8
NA5	25.0	0.66	3.50	7		0.34	1.57		17.6	82.4
NA6	28.0	0.76	3.50	7		0.31	1.72		15.1	84.9
NA7	63.0	5.12	3.50	7	3.09	0.16	1.45	65.7	3.5	30.8

T = 20 °C, v_o (aqueous flow rate) = 0.195 L·min^{-1}, Gas flow rate = 20 L·h^{-1},
V (volume of reactor) = 1.95 L, I_o (intensity of incident radiation) = 1.91x10^{-6} Einstein·(L·s)$^{-1}$,
L (effective path) = 6.6 cm, Φ_A (quantum yield of alachlor) = 0.177 mol·Einstein^{-1}, ε_I (extinction coefficient) mol·(L·s)$^{-1}$; 539.4 alachlor; 19 peroxides; 130 by-products of alachlor.
[a] Percentage of removal via UV direct radiation. [b] Percentage of removal via Ozone reaction.
[c] Percentage of removal via radical reactions.

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