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Use of Ozone to Remove Alachlor from Surface Water

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The presence of herbicides in surface and ground water constitutes a water pollution problem, which is specially important in cases where polluted water is used to prepare drinking water. Herbicides are catalogued as priority pollutants of water due to their toxicological effects. Alachlor (2-chloro, N-2,6-diethyl-N-(metoxymethyl) acetanilide), a chloroacetanilide herbicide, has a wide application in agriculture (about 37 million kg in USA) (Clay et al. 1997) and has been found in different natural water (Jury et al. 1987; Kolpin et al., 1996). Environmental agencies like EPA in USA or the European Commission for Water have established a maximum contaminant level for this herbicide of 2 and 1 µL, respectively. Thus, above these levels removal of alachlor from natural water is necessary.

Among treatment methods, ozonation has been found to be a very effective technology to eliminate this herbicide from distilled water (Somich et al. 1988) although more realistic studies are needed in surface water. Upham et al. (1997) have reported that ozonated aqueous solutions of alachlor were less toxic to rat liver epithelial cells than alachlor itself. Ozone when used as oxidant in water treatment may act directly on the organic matter or indirectly through hydroxyl radicals formed from its decomposition (Langlais et al. 1991). Preliminary studies of alachlor ozonation have shown that this herbicide is removed from distilled water by the action of hydroxyl radicals (Beltrán et al. 1996). Since the presence in water of natural substances like carbonates or humics affects the reaction rates of hydroxyl radical processes, the study of the ozonation of alachlor in surface water is recommended. In this work, ozonation of alachlor has been carried out in a surface water to gain further information of its removal rates when carbonates and/or humic substances are present.

MATERIALS AND METHODS

Alachlor (99% purity) was obtained from Chem-Service (PS-357) and used as received. The surface water was taken from Piedra Aguda reservoir located in the province of Badajoz (Spain). This type of water contained about 10^{-3} M total carbonates at pH 8.3. Other characteristics were: 26 mg/L COD, 35 mg/L total carbon (TC) and 0.250 absorbency units at 254 nm. The surface water was allowed to settle for 24 h and then filtered through 45µm Millipore membranes before use.

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Aqueous solutions of alachlor were prepared from a saturated one due to the low solubility of the herbicide in water. Thus, an excess amount of alachlor was first added to water and after agitation in the dark for 24 h, filtered through a 45μm Millipore membrane. Ozone was produced from pure oxygen in a laboratory ozonator able to generate a maximum of 4g ozone/h.

Experiments were carried out in a 200 cm long, 4.15 cm i.d. glass bubble column, equipped with a porous plate (10-16 μm porous size) situated at its bottom. The column operated continuously with countercurrent flow. Liquid flow rate was always kept constant at 15 L/h (mean residence time of the aqueous phase was 10 min). However, gas flow rate was varied between 10 and 40 L/h.

Alachlor was analysed by liquid chromatography (HPLC) using a 15 cm long, 3.9 cm i.d. C_{18} Novapack column and a 486 Water UV/visible detector. The mobile phase was an acetonitrile/water mixture (40:60 v/v) and the system was operated isocratically. Retention time was 9 min. Ozone in the gas phase was analysed with a GM19 Anseros analyser. Aqueous ozone concentration was determined by the indigo method (Bader and Hoigné, 1981). Concentration of ozone in the inlet gas was varied between 2.2×10^{-4} and 4.1×10^{-4} M. Concentration of alachlor in the aqueous solution ranged between 3.3×10^{-5} to 3.7×10^{-5} M.

RESULTS AND DISCUSSION

Variables studied in this work were gas flow rate (10 to 40 L/h), ozone concentration in the gas fed to the reactor and temperature (10 to 30 °C). Concentrations of remaining alachlor, ozone in the gas leaving the reactor, dissolved ozone and hydrogen peroxide were determined until the stationary state regime was attained.

Figure 1 shows the variation of remaining dimensionless concentration of alachlor and dissolved ozone with time for two ozonation experiments carried out at 10 and 30°C. To avoid a confusing plot results obtained at 20°C have not been included. As can be seen, the increase of temperature leads to an increase of alachlor conversion or decrease of remaining concentration. This is a logical result since rate constants of chemical reactions increase with the increase of temperature. As observed, for the conditions applied, the stationary state regime was reached after approximately 20 min. ozonation. Final conversions of alachlor were 82.9 and 91.7% at 10 and 30°C respectively. It should be noted that alachlor ozonation develops through hydroxyl radical oxidation that is affected by the presence of other substances like carbonates. The kind of surface water used had 10°M total carbonates, concentration high enough to scavenge an important fraction of hydroxyl radicals formed from the decomposition of ozone. However, as observed from experimental results, up to 92% alachlor was degraded with ozone in 20 min which suggests the ozonation is very selective towards alachlor in spite of the presence of carbonates. Another possible explanation of the high reactivity of alachlor during ozonation might be the presence of other natural substances that could act as promoters or initiators of ozone decomposition to give hydroxyl radicals. In addition to carbonates surface water absorbed radiation at 254 nm likely due to the presence of humic substances (Croué et al. 1989). These substances can accelerate the decomposition of ozone as it has

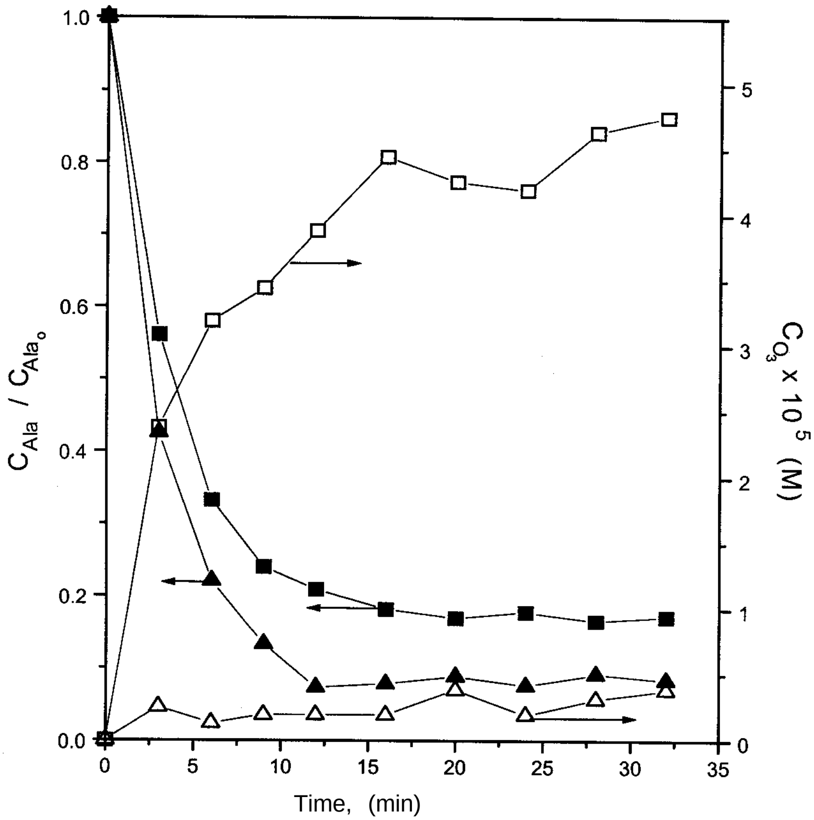

Figure 1. Variation of concentrations of alachlor (dimensionless form) and dissolved ozone during ozonation at different temperature in a surface water. Alachlor concentration: T, °C: ■ 10 ▲ 30, Ozone concentration:□ 10, Δ 30.

been demonstrated in previous works (Staehelin and Hoigné, 1985).

In Figure 1 it can also be observed that dissolved ozone accumulates in water during ozonation. Concentrations of dissolved ozone once the stationary regime was achieved varied between 4.6x10^{-5} and 3.5x10^{-6} M at 10 and 30°C respectively. The presence of dissolved ozone suggests that the rate of ozone-alachlor direct reaction is very low. Thus, at these conditions, the main route of ozone consumption is through decomposition to give hydroxyl radicals (Beltrán, 1995). The decrease of ozone concentration with the increase of temperature is the consequence of the lower solubility of ozone at higher temperatures. Thus, two opposite factors affect alachlor degradation rates during ozonation: the rate of the reaction between alachlor and hydroxyl radicals and the solubility of ozone that decreases with the increase of temperature. In any case, a high alachlor degradation can be achieved (more than 90%) at room temperature in spite of the presence of substances like carbonates that scavenge hydroxyl radicals.

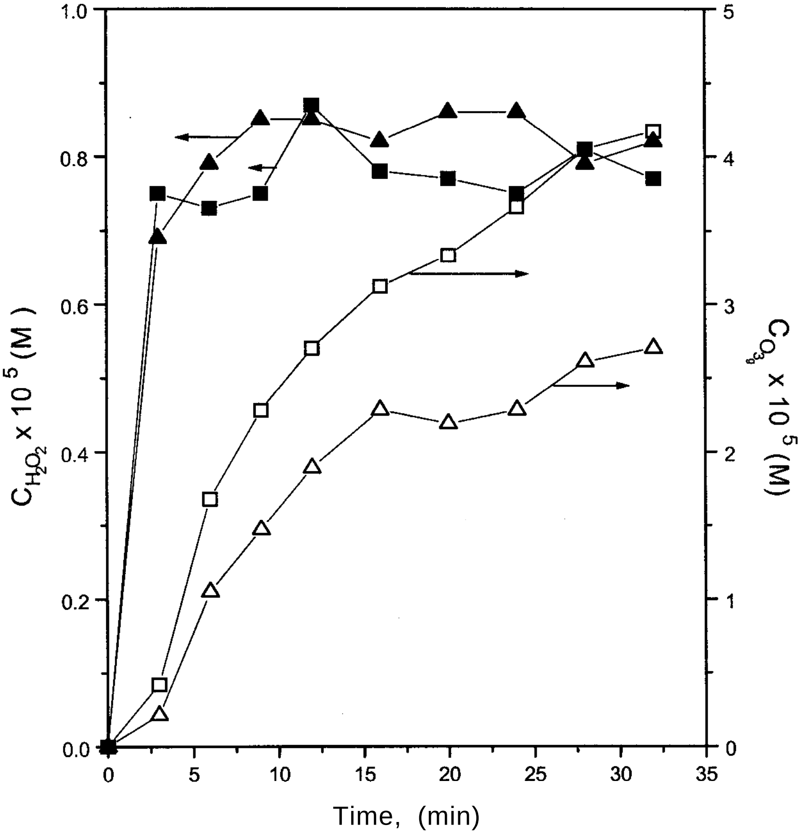

Figure 2. Variation of concentrations of hydrogen peroxide and ozone in the gas leaving the bubble column during ozonation of alachlor at different temperature in a surface water. Hydrogen peroxide concentration: T, °C: ■ 10 ▲ 30, Ozone concentration:□ 10, Δ 30.

Figure 2 presents the evolution of the concentrations of unreacted ozone (ozone in the gas leaving the column) and hydrogen peroxide formed during ozonation of alachlor for the same experiments of Figure 1. As can be seen from Figure 2 a concentration of 10^{-5} M of hydrogen peroxide was measured once the stationary regime was reached. Formation of hydrogen peroxide can be due to the action of hydroperoxyl radicals ($HO_2\cdot$) formed from the initial attack of hydroxyl radicals upon the alachlor molecule. Recombination of these radicals forms hydrogen peroxide. The presence of hydrogen peroxide can accelerate the ozone decomposition to hydroxyl radicals especially at pH higher than 7 (Staehelin and Hoigné, 1982). Thus, the high alachlor degradation rate can also be due to the presence of hydrogen peroxide that contributes to initiate the ozone decomposition. Results of synergism between ozone and hydrogen peroxide to degrade alachlor in this surface water will be presented in a following communication. Finally, from Figure 2 it can also be observed that concentration of ozone in the gas leaving the reactor column decreased with the increase of temperature. This means that the efficiency of ozonation is improved at 30°C. In this particular case, an important

Table 1. Influence of gas flow rate on alachlor ozonation in a surface water

Gas flow rate L/h	Alachlor conversion, %	Ozone efficiency, %	H_2O_2 rate x 10^6, mol/min
10	68.7	100	1.87
20	93.4	82.4	1.92
40	97.0	65.5	2.02

T=20°C, Aqueous flow rate = 0.25 L/min, Ozone concentration inlet gas = $2.2x10^{-4}$ M. Alachlor concentration in inlet water = $3.5x10^{-5}$ M.

fraction of the supplied ozone was consumed in water by chemical reactions. These results also indicate that accumulated ozone is a minor fraction of the ozone fed to the column.

The gas flow rate was another variable investigated. Table 1 presents the results obtained in the ozonation of alachlor at 10, 20 and 40 L/h gas flow rate once the stationary regime was achieved. It has to be noticed that in these experiments the ozone concentration in the gas fed to the column was kept constant at about $2.2x10^{-4}$ M. In all cases, mass flow rate of hydrogen peroxide in water at the column outlet was similar (about $2x10.^{-6}$ mol/min) but conversion of alachlor increased with the increasing gas flow rate, with the maximum value (97%) achieved at 40 L/h. However, it should be noted that efficiency of ozonation followed an opposite trend, that is, it decreased with the increase of gas flow rate. Ozone efficiency is an important parameter which gives an idea on the ozone consumption in water. In this work when 10 L/h of gas were fed to the column no ozone was detected in the gas at the column outlet (100% efficiency). It is evident that a sort of compromise should be considered while establishing the best conditions of ozonation regarding gas flow rate, ozone efficiency and conversion of alachlor.

Finally, ozonation of alachlor was carried out at different ozone partial pressure or concentration in the gas fed to the ozonation column. Final conversion of alachlor and ozone efficiency, once the stationary regime was reached, varied from 94.9% and 79% to 93.4% and 82.4% when the ozone concentration in the gas fed to the column diminished from $4.4x10^{-4}$ to $2.2x10^{-4}$ M, respectively.

Results obtained in this work show the importance of ozonation to remove alachlor from surface water. Also, they can serve as a guide to foreseen percentage removals of this herbicide from surface water. Since alachlor removal is due to the action of hydroxyl radicals, studies are now in progress to quantify the alachlor conversion and ozone efficiency of chemical ozonation processes involving ozone combined with hydrogen peroxide or *W* radiation to remove alachlor from surface water.

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