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Use of Ozone and Hydrogen Peroxide to Remove Alachlor from Surface Water

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In a previous work (Beltrán et al., 1998) the ozonation of the herbicide alachlor (2-chloro, N-2,6-diethyl-N-(metoxymethyl) acetanilide) present in a surface water was shown to be a suitable technology to remove this pollutant. The process is mainly carried out by hydroxyl radicals formed on ozone decomposition. However, ozonation produces a rather small concentration of hydroxyl radicals compared to that measured from other processes. Hydroxyl radical oxidation of pollutants in surface waters presents the disadvantage of the competitive effect of some natural substances like carbonates and/or humic compounds. In fact, the presence of these substances can inhibit the oxidation since hydroxyl radicals react unselectively with most of the organic and inorganic (carbonates) matter present in surface waters (Hoigné, 1982). Thus, oxidation processes able to increase the concentration of hydroxyl radicals are preferred.

Combination of ozone and hydrogen peroxide is nowdays known as a recommended technology to treat recalcitrant pollutants of water (Langlais et al., 1991). This is because the reaction between ozone and the ionic form of hydrogen peroxide leads to hydroxyl radicals (Staehelin and Hoigné, 1982). For the same experimental conditions (ozone dose and pH), concentration of hydroxyl radicals formed from the ozone-hydrogen peroxide reaction is much higher than that from the ozone selfdecomposition reaction (Beltrán, 1997). As a consequence, in this work, the combination ozone-hydrogen peroxide was studied to observe the rates of alachlor removal in a surface water.

MATERIALS AND METHODS

Alachlor and ozone were obtained as in the previous work (Beltrán et al., 1998). Hydrogen peroxide was obtained from Merck. The surface water was taken from Cordobilla reservoir situated in the provice of Badajoz (Spain). The water had pH 8 and contained 8×10^{-4} M carbonate concentration. Preparation of aqueous solutions of alachlor in this water, experimental procedure and quantitative analysis of alachlor, hydrogen peroxide and ozone (in gas and water phases) were as indicated in the previous work (Beltrán et al., 1998).

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RESULTS AND DISCUSSION

Variables studied in this work were the mass ratio of hydrogen peroxide to ozone in the influent water, the 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.

For the same hydrogen peroxide to ozone feeding mass ratio, temperature exerted a slight positive effect on the alachlor removal rate as expected. This is because, on one hand, the increase of temperature leads to an increase of rate constants of chemical reactions and, on the other hand, the ozone solubility in water is reduced. For a practical case, ambient temperature is recommended. The increase of ozone concentration while keeping constant temperature and inlet hydrogen peroxide mass flow yielded, at the conditions investigated (2 to10 mg/L), a positive increase of alachlor removal rate.

Figure 1 presents the variation of remaining dimensionless concentration of alachlor and dissolved ozone with time for two ozonation experiments carried out in the absence and presence of hydrogen peroxide in the inlet alachlor aqueous solution. As can be seen, the presence of hydrogen peroxide leads to a significant increase of the alachlor conversion or decrease of remaining concentration. Thus, once the steady state was achieved, alachlor conversion varied from 73% to 90% in the absence and presence of hydrogen peroxide, respectively. This increase was undoubtedly due to the action of hydroxyl radicals whose concentration when ozone and hydrogen peroxide are simultaneously present is much higher than that generated from ozone alone. Notice that blank experiments carried out with hydrogen peroxide as oxidant (in the absence of ozone) showed no variation in alachlor concentration. Also notice that the surface water had a significant carbonate concentration and possibly humic substances that usually act as hydroxyl radical consumers.

Figure 1 also shows the evolution of ozone concentration accumulated in water at the reactor outlet. It is seen that, at steady state (from 20 min reaction), accumulated ozone in the presence of hydrogen peroxide is approximately 4 times lower than that observed when only ozone was applied. This supports the fact that the increase of alachlor conversion in the presence of hydrogen peroxide is due to hydroxyl radicals generated from the reaction between ozone and hydrogen peroxide.

Figure 2, on the other hand, presents the variation of hydrogen peroxide and ozone concentrations in the water and gas phases, respectively, at the reactor outlet. As expected, it is seen that hydrogen peroxide concentration in the absence of ozone is much lower than that observed when hydrogen peroxide is also fed to the reactor column in spite of the ozone-hydrogen peroxide reaction. When ozone alone is added hydrogen peroxide is likely formed from hydroxyl radical substitution reactions that can release the hydroperoxide radical which eventually forms hydrogen peroxide (Hoigné, 1998). On the contrary, concentration of ozone in the gas at the reactor outlet when hydrogen peroxide was fed to the reactor was much lower than that measured when ozone alone was used as oxidant. This confirmed the consumption

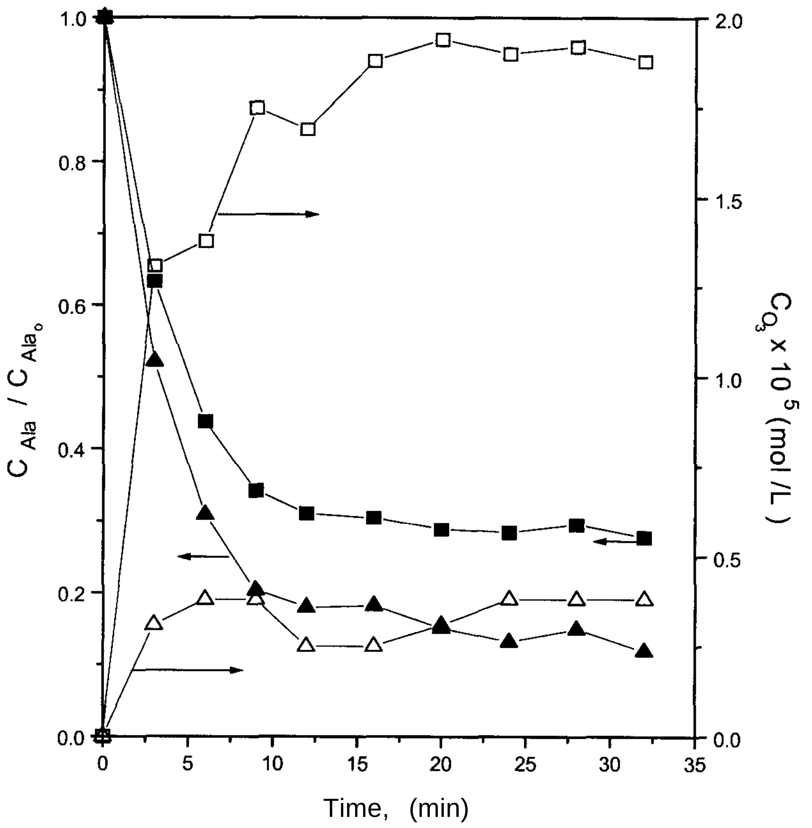

Figure 1. Variation of concentrations of alachlor (dimensionless form) and dissolved ozone during ozonation in a surface water in the absence and presence of hydrogen peroxide. Alachlor concentration: 4.5x10^{-5} M, Ozone mass feeding rate : 3.36 mg/min; Hydrogen peroxide-ozone mass feeding ratio: 0.58 g/g; Alachlor dimensionless remaining concentration: ■ No hydrogen peroxide fed ▲ With hydrogen peroxide fed. Dissolved ozone concentration: □ No hydrogen peroxide fed Δ With hydrogen peroxide fed.

of ozone by reaction with hydrogen peroxide.

The most important variable, however, in this system is the ratio of hydrogen peroxide and ozone concentrations at the reactor inlet. Table 1 shows the results obtained from ozone-hydrogen peroxide experiments carried out at different mass ratio of these oxidants. The results shown are the alachlor conversion, ozone efficiency and hydrogen peroxide mol flow at the reactor outlet once the oxidation system worked at stationary regime. It is observed that there exists an optimum mass ratio of oxidants above and below which alachlor conversion diminishes. At the experimental conditions applied in this study this optimum oxidant ratio resulted

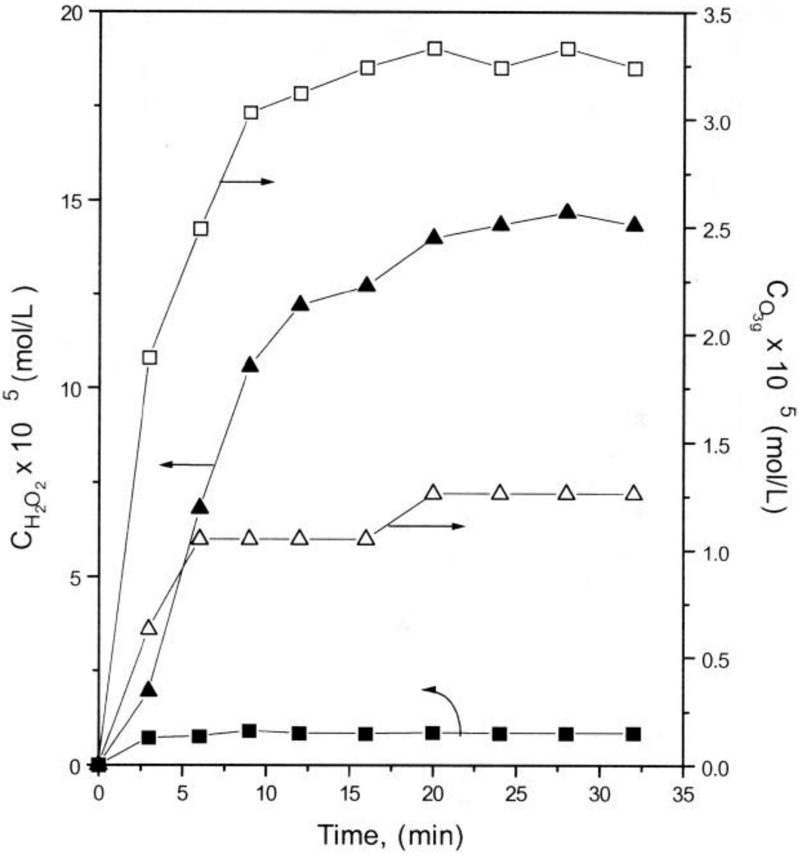

Figure 2. Variation of concentrations of hydrogen peroxide and ozone in the water and gas leaving the reactor column, respectively, during the ozonation of alachlor in a surface water in the absence and presence of hydrogen peroxide. Alachlor concentration: $4.5x10^{-5}$ M, ozone mass feeding rate : 3.36 mg/min; Hydrogen peroxide-ozone mass feeding ratio: 0.58 g/g; Hydrogen peroxide concentration: ■ No hydrogen peroxide fed ▲ With hydrogen peroxide fed, Ozone concentration in the gas:□ No hydrogen peroxide fed Δ With hydrogen peroxide fed.

to be 0.58 g/g of hydrogen peroxide/ozone which is close to 0.7 determined by Paillard et al. (1989) as the optimum ratio between both oxidants to remove pollutants in ultrapure water. The difference is likely due to the presence of carbonate and/or humic substances in the surface water treated. Specially, humic substances are known to react fast with ozone (Croué et al., 1989) so that it is likely that in the presence of these substances more ozone is required as observed in this work. Since the ozone mass rate was always fed constant (3.36 mg/min), the results confirmed the double role hydrogen peroxide plays in these oxidation systems.

Table 1. Influence of hydrogen peroxide to ozone mass feeding ratio on alachlor ozonation in a surface water

H_2O_2/O_3 mass ratio g/g	Alachlor conversion, %	Ozone efficiency, %	H_2O_2 rate x 10^6, mol/min
0	72.3	84.5	2.12
0.31	83.4	90.2	18.32
0.58	88.2	94.1	35.82
1.16	84.9	93.1	60.57
1.85	77.5	93.7	51.40

T=20°C, Aqueous flow rate = 0.25 L/min, Ozone concentration in inlet gas = 2.2×10^{-4} M. Alachlor concentration in inlet water = 4.5×10^{-5} M.

Thus, on one hand, hydrogen peroxide acts as initiator of hydroxyl radicals through its reaction with ozone, and, on the other hand, as inhibitor of the process because it also reacts with hydroxyl radicals (Christensen et al., 1982). The inhibiting role of hydrogen peroxide is noticed at high concentration as deduced from Table 1. Thus, at these conditions it is also likely that ozone mass transfer controls the absorption rate and hence the chemical reaction rate of alachlor. This would explain that alachlor conversion slightly diminishes when hydrogen peroxide to ozone mass ratio is increased above the optimum value. Similar results were found for the ozone efficiency. Maximum ozone efficiency was also achieved when the hydrogen peroxide to ozone mass ratio was 0.58 g/g. As far as the mol rate of hydrogen peroxide at the reactor outlet is concerned the results show that this mol rate increased with the increasing hydrogen peroxide to ozone mass ratio at the reactor inlet up to a value of 605 mol/min corresponding to 1.16 g hydrogen peroxide per g of ozone fed. Above this value a slight decrease of hydrogen peroxide mol rate at the reactor outlet was observed.

Combination of ozone and hydrogen peroxide resulted in a significant increase of alachlor removal in the surface water investigated. It should also be noted that similar results, not shown here, were observed in the surface water described in the previous work (Beltrán et al., 1998). Determination of the optimum ratio between oxidants (hydrogen peroxide and ozone) is the most important point of these systems because of the double nature of hydrogen peroxide as initiator and consumer of hydroxyl radicals and the problems associated with ozone mass transfer at high hydrogen peroxide concentrations. Once these problems are overcome the combination of ozone and hydrogen peroxide seems to be an attractive technology to remove alachlor from contaminated surface waters.

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