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Ozone and Ozone/UV Decolorization of Bleaching Waters of the Paper Industry

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This study examines the use of ozone and ozone/ultraviolet radiation treatments of a kraft bleach plant effluent proceeding from the bleaching stages for kraft pulp decolorization. An outline for the reaction is proposed in which the oxidizable compounds of the effluent are grouped into three classes: easily degradable colored compounds, colored compounds of difficult degradation, and uncolored compounds. The constants for the second-order reaction rate at 20 °C and the stoichiometric coefficient were determined.

Ozonization is a widely investigated method to eliminate or reduce pollution caused by the effluents of the pulp and paper industry. This method can be economically competitive with other processes in the treatment of diluted effluents. Some research work in this topic can be found in the bibliography (Huriet and Gelly, 1970; Furgason et al., 1973; Nebel et al., 1974; Ng et al., 1978) mainly in the decolorization of the kraft black liquors, but only one (Melnik and Netzer, 1975) made a simple kinetic study. In developing the kinetic model, effluent color was attributed to two unidentified species which differed in their reactivity to ozone. It was supposed that each one of them reacted with free ozone independently, and following first-order kinetics, it was found that the most reactive species is that which is responsible for most of the initial color.

The use of ozone/UV in the treatment of refractory pollutants in wastewaters has been recently developed (Garrison et al., 1975; Kuo et al., 1977; Peyton et al., 1982a,b). The treatment of kraft bleach plant effluent proceeding from the bleaching stages using oxidant and oxidant/UV processes has been studied by Coburn et al. (1984). In their study, they modify the radiation intensity, the oxidant dosification, and the reaction time. They found that the best treatment was obtained using ozone without UV radiation. They observed a significant increase in the biodegradability.

Materials and Experimental Techniques

The effluent utilized was prepared from wastewaters from the chlorination stage and from alkaline extraction (in a ratio of 2:1 by volume), proceeding from kraft bleach plant pulp. The characteristics of this effluent were 2.18

for pH, 3288 mg of Pt/L for color, and 1721 mg of O₂/L for COD.

The analyses done were for the pH and color of the effluent and the ozone concentration in the outlet gas. Color determination of the effluent was done by the chloroplatinic method as described in the standard of the Canadian Pulp and Paper Association (1974). Ozone concentration in the gas phase was determined by measuring absorbency at 253.7 nm (Rice, 1981). Oxalate actinometry (Leighton and Forbes, 1930; De Bernardez and Cassano, 1985) was performed in order to measure the photon flux entering the reactor.

The experiments were carried out in a tubular reactor capable of providing a good contact between the liquid and gas reactants and which offered the possibility of irradiating the reactant mixture with ultraviolet radiation of 253.7 nm. Figure 1 illustrates the experimental installation.

The reactor is a simple bubble reactor with a cocurrent circulation of gas and liquid. A diffuser valve at the entrance produces the mix between the liquid and gas reactants. The exit zone was designed to maintain a constant level, while at the same time permitting all the gas to exit. It consists of a spherical vessel with a 4540-cm³ capacity with exits for the gas and for recirculation of the liquid. Distilled water as thermostatic fluid circulates in a jacket. One cylindrical reflector of the circular section surrounds each lamp, giving the overall system a clover leaf shape. Table I shows the characteristics of this reacting system.

The ozone used in the reaction is produced before it enters the reactor. Bottled gas (air or oxygen) passes through an SLO CONSTREMA ozonizer. The production

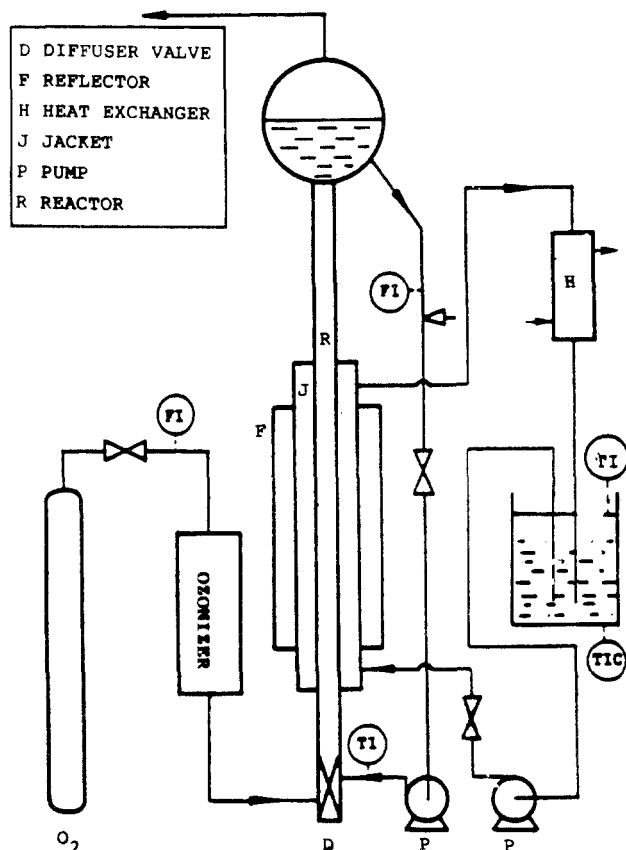


Figure 1. Experimental installation.

Table I. Characteristics of the Reacting System

reactor	characteristics	quartz cylinder
	length	100 cm
	outer radius	1.1 cm
	inner radius	0.925 cm
jacket	characteristics	quartz cylinder
	length	48 cm
	outer radius	2.70 cm
	inner radius	2.50 cm
lamps	characteristics	4 Hg lamps (low pressure)
	power	15 W/lamp
	intensity	0.33 A
	wavelength	253.7 nm
	emission power (253.7 nm)	23.70 μ einstein/s
	radius	0.80 cm
	length	34.0 cm
	distance lamp center to reactor center	3.65 cm
	distance lamp basis to reactor basis	33.0 cm
reflectors	characteristics	4 cylindrical reflectors (circular sect.)
	reflection coeff	0.60
	radius	2.17 cm
	length	34.0 cm
	distance reflector center to reactor center	2.94 cm

of ozone is 4–6 g of O_3 /h, when oxygen is used.

Mathematical Model of the Reactor

The hypotheses used in the elaboration of the mathematical model of the reactor are constant density of the liquid phase; perfect mixture in the liquid phase due to high recirculation flow; plug flow for the gas phase; negligible accumulation of ozone in the gas phase; slow reaction, which should be confirmed once the kinetic constants are determined; and isothermal conditions.

Taking into account that the liquid phase is perfectly stirred, the mass balance for the ozone in the liquid phase integrated for the entire volume of the reactor leads to

$$\frac{dC_{O_3(l)}}{dt} = \frac{1}{V_l} \left(\int_{V_t} N_{O_3(l)} a dV_t \right) + r_{O_3} \quad (1)$$

In a differential volume of the reactor, $dV_t = S dz$, located at height z from the entrance of the reactor, the ozone balance for the gas phase within a given time t with the previous hypothesis is

$$N_{O_3(l)} a S dz = q_g dC_{O_3(g)} = -K_a a S dz (C_{O_3(g)}/A - C_{O_3(l)}) \quad (2)$$

$$A = H/(RT\delta) \quad (3)$$

where H is Henry's constant for ozone.

Integrating this last differential equation between the entrance, 0, and the exit, 1, of the reactor, we obtain the concentration of ozone in the outlet gas, $C^1_{O_3(g)}$, for a given time:

$$C^1_{O_3(g)} = A(1 - K_a)((C^0_{O_3(g)}/A - C_{O_3(l)}) + C_{O_3(l)}) \quad (4)$$

where K_a is given by

$$K_a = 1 - \exp\left(-\frac{K_1 a V_t}{A q_g}\right) \quad (5)$$

Given that the flux densities, $N_{O_3(g)}$ and $N_{O_3(l)}$, are equal and of opposite sign, the term of the integral that appears in the mass balance for the ozone in the liquid phase can be stated as

$$\int_{V_t} N_{O_3(l)} a dV_t = -\left(\int_{z^0}^{z^1} N_{O_3(g)} a S dz \right) = -\left(\int_{C^0_{O_3(g)}}^{C^1_{O_3(g)}} q_g dC_{O_3(g)} \right) \quad (6)$$

$$\int_{V_t} N_{O_3(l)} a dV_t = q_g (C^0_{O_3(g)} - C^1_{O_3(g)}) = q_g K_a (C^0_{O_3(g)} - A C_{O_3(l)}) \quad (7)$$

Replacing the integral that appears in eq 1 with its value gives

$$\frac{dC_{O_3(l)}}{dt} = \frac{q_g}{V_l} (K_a (C^0_{O_3(g)} - A C_{O_3(l)})) + r_{O_3} \quad (8)$$

A value of 0.06 cm/s can be adopted for the transfer constant of the gas-phase reactant in the liquid phase for this type of reactor (Doraiswamy and Sharma, 1984). Given that the interfacial area can be calculated by means of the following equation:

$$a = 6h/d_b \quad (9)$$

where h is the fraction of the gas phase in the reactor and d_b is the bubble diameter, the value of K_a can be estimated by eq 5. For the flow rates used, $K_a \approx 0.986$.

From the value of this constant, it can be assumed that the gas that exits from the reactor will be very close to equilibrium with the liquid content.

At the exit of the reactor, there is a spherical vessel for separation of gas and liquid phases. A pipe leads from this to a spectrophotometer, which measures the concentration of ozone in the outlet gas. It was considered that the contents of the sphere were perfectly stirred and that the assumption of plug flow in the pipe to the spectrophotometer is valid. This was taken into consideration when

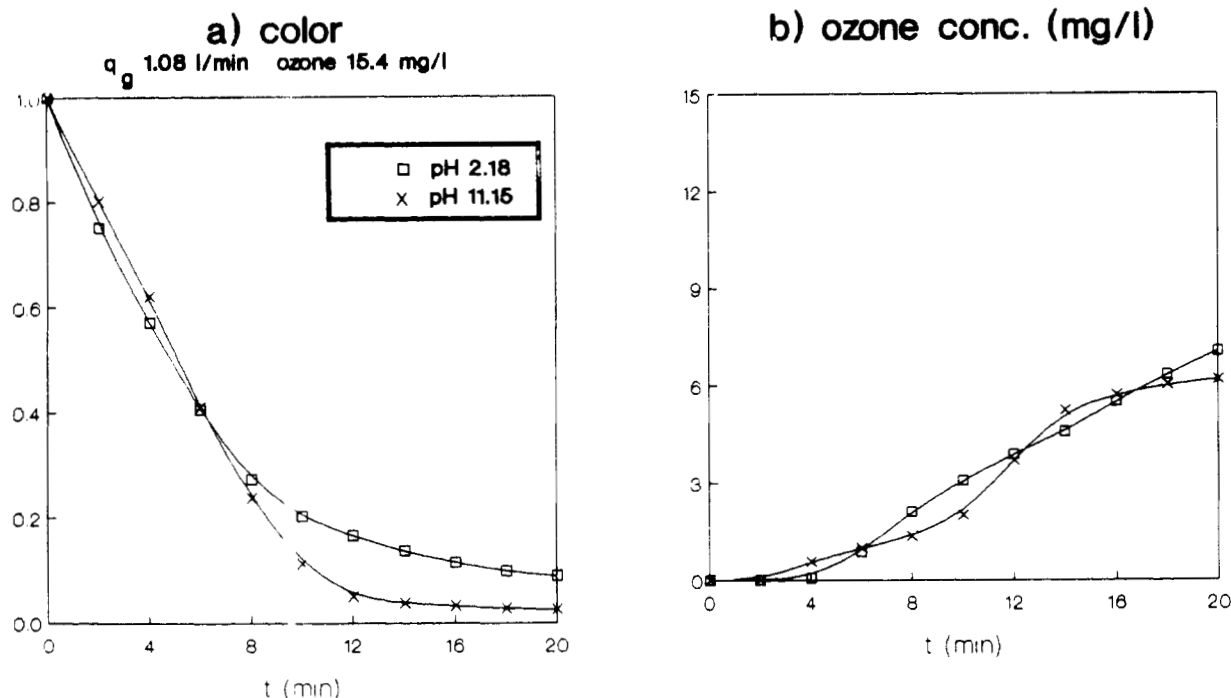


Figure 2. Experiments carried out with ozone. Influence of the pH on (a) color degradation and (b) variation of the ozone concentration in the outlet gas.

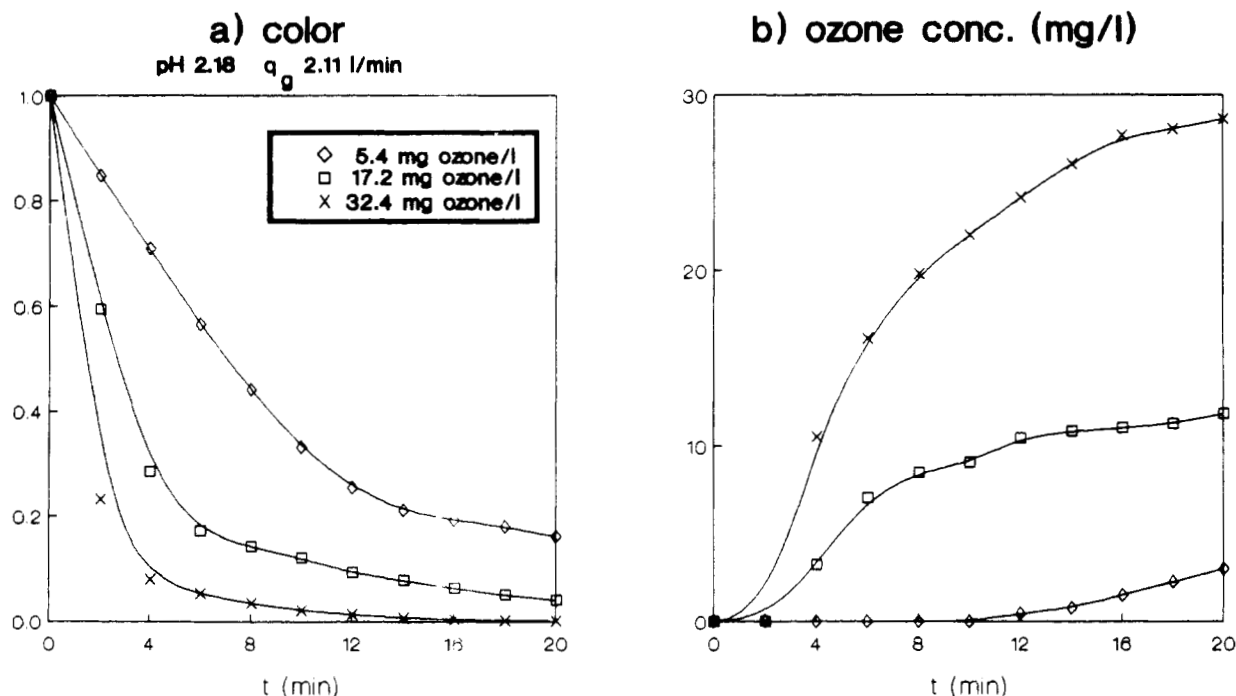


Figure 3. Experiments carried out at pH 2.18 with ozone. Influence of ozone concentration on (a) color degradation and (b) variation of ozone concentration in the outlet gas.

preparing the tables of results. Consequently, the concentration of ozone in the sphere, $C_{O_3(gm)}$, will be given as

$$\frac{dC_{O_3(gm)}}{dt} = \frac{q_g}{V_s} ((1 - K_a)C_{O_3(g)}^0 - AC_{O_3(l)} - C_{O_3(gm)}) \quad (10)$$

in which V_s is the volume of the sphere.

Experimental Results

Figures 2–6 show the variation with time of the color of the effluent and of the ozone concentration in the outlet gas. It can be seen that in all cases there are two zones, an initial one in which the reaction rate is high and an-

other, at longer reaction times, in which the reaction takes place much more slowly. This suggests that the colored compounds of the effluent may be grouped according to greater or lesser ease of degradation with reference to ozone. The influence of the ozone concentration and the ozone flow rate on the decolorization is significant (Figures 3 and 4), and the influence of the pH is negligible (Figure 2).

In addition, the outlet concentration of ozone increases as the reaction continues. However, when an almost total decolorization of the effluent has been achieved, the value of the concentration of ozone in the outlet gas is lower than at the entrance. This means that there was an additional

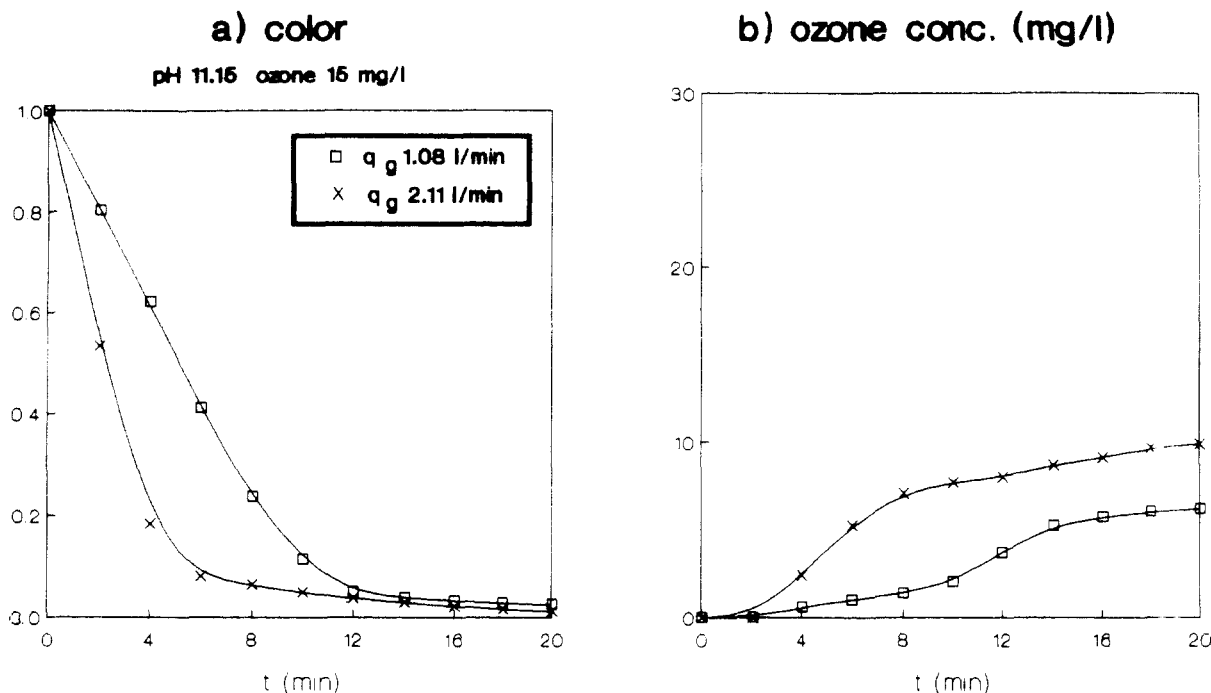
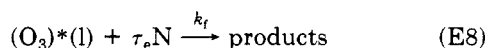
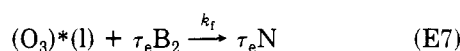
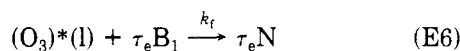
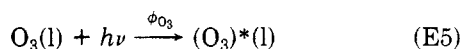
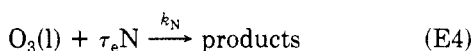
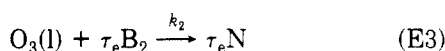
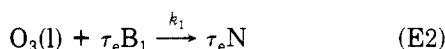


Figure 4. Experiments carried out at pH 11.15 with ozone. Influence of the ozone flow rate on (a) color degradation and (b) variation of ozone concentration in the outlet gas.

consumption of ozone due to the reactions that take place between this oxidizing agent and the uncolored compounds in the effluent.

According to the results obtained, a possible explanatory sequence for the ozonization must include the mass-transfer step, the reactions of ozone with two types of colored compounds present in the effluent, B_1 (easily degradable substance) and B_2 (substances of more difficult degradation), and the possible photochemical reactions when UV radiation was used. Furthermore, the reaction between uncolored compounds, N , and the ozone must also be taken into account. So



where τ_e is a stoichiometric coefficient.

Step E5 is the photochemical activation of the ozone in the liquid phase. Steps E6–E8 are the deactivation of the activated ozone and are similar to the dark steps E2–E4.

From the kinetic point of view and according to Irazoqui et al. (1973), the reaction rate of the activation step (step E5) will be proportional to the local volumetric rate of energy absorption by the ozone, $e^a_{O_3}$:

$$r_{f,O_3^*} = \phi_{O_3} e^a_{O_3} \quad (11)$$

In the experimental conditions, the quantum yield of the formation of the activated species $(O_3)^*(l)$ will be ap-

proximately one, because this value corresponds to ozone activation in water and the probability that the activated ozone reacts with compounds B_1 , B_2 , or N (steps E6, E7, and E8, respectively) is greater than the deactivation with other activated species. In order to simplify the mathematical model, it can be assumed that the activated ozone will react with the compounds present in the effluent in a similar way. Then the kinetic constant for steps E6–E8 will be the same.

In this case, both effluent compounds and the ozone in the liquid phase absorb the radiant energy, but only the radiant energy absorbed by the ozone will produce color degradation. The local volumetric rate of energy absorption by the ozone will be proportional to the global local volumetric rate of energy absorption. The proportionality coefficient is a relation between the absorbance coefficients of the ozone (0.063 cm^{-1}) and the effluents (6.5 cm^{-1}):

$$e^a_{O_3} = \frac{0.063 C_{O_3(l)}}{0.063 C_{O_3(l)} + 6.5(Y_{B_1} + Y_{B_2} + Y_N)} e^a \quad (12)$$

where the ozone concentration is expressed in milligrams of O_3 /liter.

In accordance with the mechanism of the ozonization, the expression of the mass balance for the ozone in the liquid phase is as follows:

$$\frac{dC_{O_3(l)}}{dt} = \frac{q_g}{V_l} K_a (C^0_{O_3(g)} - AC_{O_3(l)}) - k_1 Y_{B_1} C_{O_3(l)} - k_2 Y_{B_2} C_{O_3(l)} - k_N Y_N C_{O_3(l)} - r_p \quad (13)$$

where r_p corresponds to the photochemical steps

$$r_p = \frac{0.063 C_{O_3(l)} \phi_{O_3}}{0.063 C_{O_3(l)} + 6.5(Y_{B_1} + Y_{B_2} + Y_N)} W_{abs} \quad (14)$$

W_{abs} is the flux of photons absorbed by the reaction medium. This value equals

$$W_{abs} = \int_{V_l} e^a dV_l \quad (15)$$

The evaluation of W_{abs} has been determined by volume integration of e^a to the tubular reactor using the ESVE

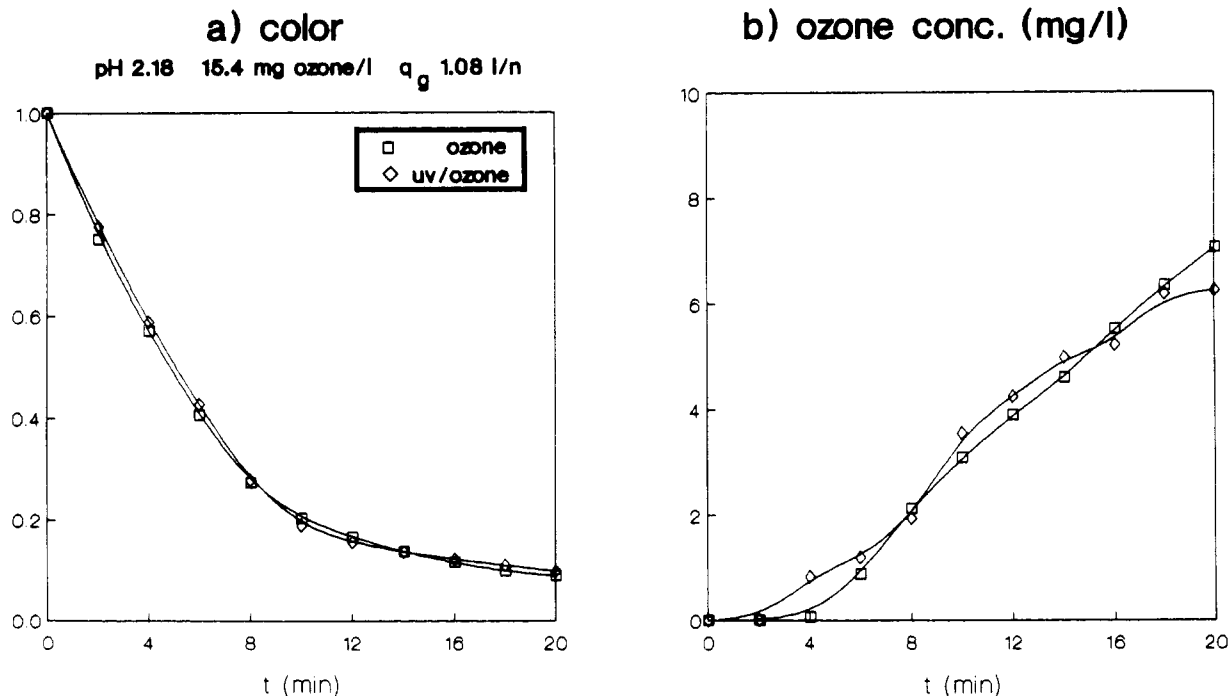


Figure 5. Influence of UV radiation on (a) color degradation and (b) ozone concentration in the outlet gas.

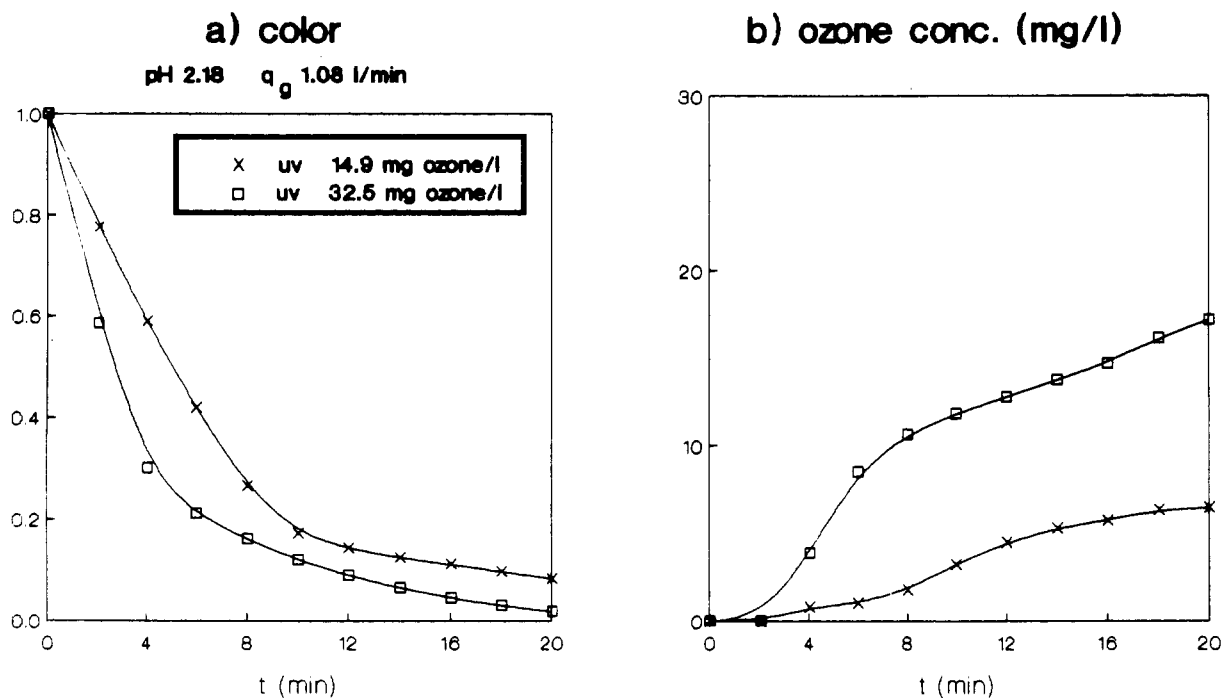


Figure 6. Influence of ozone concentration in the experiments performed with UV radiation on (a) color degradation and (b) variation of ozone concentration in the outlet gas.

model (Irazaqui et al., 1973). The result was $W_{\text{abs}} = 2.14 \times 10^{-3}$ einstein/min.

The corresponding mass balances for the compounds present in the effluents are

$$\frac{dY_{B_1}}{dt} = -\tau_e k_1 Y_{B_1} C_{O_3(l)} - \frac{\tau_e r_p Y_{B_1}}{Y_{B_1} + Y_{B_2} + Y_N} \quad (16)$$

$$\frac{dY_{B_2}}{dt} = -\tau_e k_2 Y_{B_2} C_{O_3(l)} - \frac{\tau_e r_p Y_{B_2}}{Y_{B_1} + Y_{B_2} + Y_N} \quad (17)$$

$$\frac{dY_N}{dt} = -\tau_e k_N Y_N C_{O_3(l)} - \frac{\tau_e r_p Y_N}{Y_{B_1} + Y_{B_2} + Y_N} \quad (18)$$

The modified Simplex method combined with the Runge-Kutta method (Himmelblau, 1968) was used to determine the parameters of the model. The objective function was a weighted sum of the squared errors of the total color and of the ozone concentration in the outlet gas. The values determined for the constants in each of the experiments were used in the plots of the figures. The constants do not vary significantly with the experimental conditions. This means that their variations are within the experimental error. In order to appreciate the influence of UV radiation, it is interesting to study first the experiments performed with ozone and then the experiments performed with ozone/UV. For the experiments carried out with ozone, the average of all the values ob-

tained was $k_1 = 80 \pm 7$ L/(mg min), $k_2 = 3.1 \pm 0.4$ L/(mg min), $k_N = 2.3 \pm 0.2$ L/(mg min), $\tau_e = 0.013 \pm 0.001$ 1/mg, and $Y_{B_1}^0 = 0.83 \pm 0.07$. Both the adjustment and the estimation of the parameters were significant with a confidence coefficient of 95%.

It can be observed, with respect to the evolution of the color of the effluent, that the presence of ultraviolet radiation practically does not modify the color degradation rate (Figure 5). As a result of the high value of the absorbance of the effluent, the photochemical reaction will only take place near the wall reactor (e.g., at 0.5 cm from the reactor wall, the radiation intensity and the photochemical reaction will be approximately $\exp(-6.5 \times 0.5) = 0.038$ of the values at the wall). The influence of the ozone concentration on the color degradation rate is very strong, but operating at high ozone concentration, not all the ozone reacts to produce color degradation as can be seen in Figure 6.

As in the experiments performed with ozone, the average value of the constants obtained was $k_1 = 79 \pm 8$ L/(mg min), $k_2 = 3.0 \pm 0.2$ L/(mg min), $k_N = 2.3 \pm 0.1$ L/(mg min), $\tau_e = 0.012 \pm 0.001$ 1/mg of O_3 , and $Y_{B_1}^0 = 0.78 \pm 0.08$.

It can be noted that the values of these constants are placed between the confidence intervals of the same parameters in the case of ozonization without ultraviolet radiation.

Conclusions

From the point of view of industrial application of this treatment, the range of reaction times of interest is for degradation of B_1 compounds, as they form the majority of the effluent. Given that their rate of degradation is high, such treatment can be economical. Furthermore, in this range of reaction times, the proportion of ozone consumed in eliminating colored compounds is greater than at longer reaction times. That is to say that at initial times the same quantity of ozone consumed produces a higher reduction of color in the effluent than at longer times.

The colored compounds in the B_1 group, which by definition will have feasible reaction times in an industrial process, make up about 90% of the total color. Also, the rate of decolorization of these compounds is much faster than that of B_2 compounds in hydrogen peroxide treatments, both with and without the presence of ultraviolet radiation (Prat et al., 1988).

The elimination of color due to B_2 compounds is much slower, given that the value of the rate constant of this process, k_2 , is approximately 26 times less than k_1 and therefore would be much more costly. However, prolonging the treatment could result in other benefits, not exclusively that of decolorization, which, in certain cases, could prove of interest.

From the results obtained by using the ozone with ultraviolet radiation, it can be deduced that the action of the radiation is not important. The introduction of ultraviolet radiation does not increase substantially the color degradation rate.

Acknowledgment

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Nomenclature

A = see eq 2

a = interfacial area per unit of volume of the apparatus, m^{-1}

C = concentration, $kmol \cdot m^{-3}$

d = diameter, m

e^a = local volumetric rate of energy adsorption, $einstein \cdot m^{-3} \cdot s^{-1}$
 H = Henry's constant, $atm \cdot (mole \text{ fraction of solute in solution})^{-1}$

h = volumetric fraction of the gas phase in the reactor

K = transfer constant, $m \cdot s^{-1}$

k = kinetic constant, s^{-1}

N = flux density, $kmol \cdot m^{-2} \cdot s^{-1}$

q = volumetric flow rate, $m^3 \cdot s^{-1}$

r = reaction rate, $kmol \cdot m^{-3} \cdot s^{-1}$

R = universal gas constant, $atm \cdot m^3 \cdot K^{-1} \cdot kmol^{-1}$

S = surface, m^2

T = absolute temperature, K

t = time, s

V = volume, m^3

Y = fraction of the initial color

z = axial coordinate, m

Greek Letters

ϕ = quantum yield, $mol/einstein$

δ = molar density of the effluent, $kmol/m^3$

τ = coefficient of reaction

Subscripts

a = mass transfer

B_1 = easily degradable colored compounds

B_2 = colored compounds of difficult degradation

b = bubble

e = stoichiometric

f = formation

g = gas

l = liquid

m = average value

N = uncolored compounds

O_3 = ozone

p = photochemical

s = sphere

t = total

Superscripts

0 = inlet

1 = outlet

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Toluene Disproportionation Reaction over HZSM-5 Zeolites: Kinetics and Mechanism

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Six samples of ZSM-5 catalyst with silica-to-alumina ratios ranging from 30 to 167 were used to investigate the kinetics, product distribution, and mechanism in the toluene disproportionation reaction. The reaction was carried out under the conditions of atmospheric pressure and a temperature range of 470-570 °C. Both nitrogen and hydrogen carrier gases were used during the experiment. The toluene disproportionation reaction showed a first-order dependence on the toluene partial pressure with an activation energy of 28.4 kcal/mol. Based on the results obtained, a generalized equation for the pseudo-first-order rate constant is proposed.

The preliminary findings of toluene disproportionation over ZSM-5 catalysts were first patented by Kaeding (1977). Later in 1981, Kaeding et al. published the results of the toluene disproportionation reaction over HZSM-5 zeolites. At atmospheric pressure and a temperature range of 450-600 °C, the authors reported that the main products in the reaction were benzene and xylenes. The percentage conversion of toluene and the ratio of benzene to xylene were found to increase with increasing temperature, and *p*-xylene present in the xylene mixture was always in equilibrium with its isomers. However, when the authors studied this reaction on ZSM-5 zeolites modified with boron or magnesium or phosphorus, they found that the percentage of *p*-xylene in the xylene mixture was higher than its equilibrium value. Similar results with modified ZSM-5 zeolites were reported by Young et al. (1982).

Meshram et al. (1983) systematically investigated the effect of catalytic parameters like the silica/alumina ratio, calcination temperature, and surface acidity on the disproportionation reaction. The authors observed that the catalytic activity of HZSM-5 increases with the temperature but decreases with an increase of SiO₂/Al₂O₃. The benzene/xylene ratio was found to be independent of pressure, while the percentage of toluene converted was dependent on the pressure. The authors explained the relationship between the surface acidity and the catalytic activity based on two types of active sites of medium acidity and strong acidity. They proposed that the strong sites promote the dealkylation of toluene, while the medium sites promote the disproportionation reaction.

Kulkarni et al. (1983) have investigated the toluene disproportionation reaction over HZSM-5 samples synthesized from gels of different pH values. In the temperature range 500-650 °C, the authors found that a HZSM-5 sample prepared from a gel of pH 9.5 showed

higher activity than the HZSM-5 prepared from a gel of pH 6.5.

Mavrodinova et al. (1985) studied the toluene conversion over HZSM-5 zeolite and reported that the coke forms only on the external surface of the zeolite. The amount of coke formed on HZSM-5 was found to be one-third less than that formed over hydrogen forms of omega and offretite. At 457 °C, the percentage of *p*-xylene in the total xylene product was of the order of 40% in HZSM-5 and 50% in H-offretite. However, the authors reported that the activity for toluene conversion over H-offretite and H-omega reduced drastically at 457 °C relative to the activity of HZSM-5.

The kinetics of toluene disproportionation over HZSM-5 in the presence of H₂ was investigated by Beltrame et al. (1985). In the temperature range 240-300 °C, the authors tested various kinetic models and reported that the bimolecular surface reaction mechanism was the only probable one. Nayak and Riekert (1986), on the other hand, analyzed the toluene disproportionation reaction by a pseudo-first-order kinetic model.

The catalytic activity and product distribution in the toluene disproportionation reaction over HZSM-5 samples of disparate preparations were investigated by Nayak and Riekert (1986). On seven samples of HZSM-5 of various crystal sizes, the authors found the ratio of benzene/xylenes to be dependent on only the percentage conversion of toluene but independent of the mode of synthesis of the ZSM-5 and the reaction temperature. The amount of *p*-xylene in the xylene isomer product mixture was reported to be higher than the equilibrium amount only if the catalyst contained large crystals.

Meshram (1987) had recently extended the disproportionation reaction to modified and poisoned ZSM-5 zeolites. From the studies conducted on NiHZSM-5,