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Ozonation of pentylacetate contaminated waters from textile care industry

Ozonización de aguas contaminadas con pentilacetato de la industria de limpieza en seco de textiles

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In this article the use of ozone for the treatment of pentylacetate contaminated waters is evaluated. Pentylacetate has started to be used in the drycleaning process as a new solvent due to its economic benefits. However, in the technical literature experimental data involving pentylacetate ozonation has not yet been reported. This article presents experimental results on the effect of pH on the rate of pentyalcetate removal by ozonation of contaminated waters. At acid pH, pentylacetate is removed by a combination of single sparging and direct ozone reaction. As pH increases, the rate of pentylacetate removal also increases, showing the importance of free radical mechanism. The constant of indirect reaction rate for pentylacetate removal due to radicals is 2.6 x 10^9 $M^{-1}s^{-1}$.

Keywords: ozone, pentylacetate, reaction kinetics, wastewater treatment

En este artículo, se evalúa el uso del ozono para el tratamiento de aguas contaminadas con pentilacetato. El pentilacetato es un nuevo solvente que se ha comenzado a utilizar en el proceso de limpieza en seco de textiles, debido a sus beneficios económicos. Sin embargo, en la literatura técnica no existen datos experimentales registrados sobre ozonización de aguas contaminadas con pentilacetato. Este artículo presenta resultados experimentales del efecto del pH en la velocidad de eliminación de pentilacetato de aguas contaminadas a través de un proceso de ozonización. A pH ácido, el pentilacetato se elimina mediante una combinación de simple volatilización y reacción directa con el ozono molecular. Cuando el pH se incrementa, aumenta la velocidad de eliminación de pentilacetato, mostrando la importancia del mecanismo por radicales libres. La constante de velocidad de reacción para la eliminación indirecta del pentilacetato por acción de radicales es de 2,6 x 10^9 $M^{-1}s^{-1}$.

Palabras clave: ozono, pentilacetato, cinética de reacciones, tratamiento de aguas residuals

Introduction

Textile care industry can generally be categorised into dry and wet cleaning. Such processes produce environmental concern. Wetcleaning is characterised by a high water consumption in combination with specialised detergents and additives; while drycleaning uses predominantly non-aqueous solvents mainly perchloroethylene and hydrocarbon solvents (EPA, 1998; Kurz *et al.,* 2001). In this respect, new technologies are necessary for solvent recycling and wastewater reuse as water process in order to reduce environmental impact.

This paper approaches this topic and suggests the use of ozone in textile care industry for wastewater reclamation and reuse. Ozone is known by its capacity to oxidise complex organic compounds that are frequently present in effluents from textile industries and domestic laundries (Seo *et al.*, 2001; Arslan *et al.*, 2002). The reaction mechanism is a combination of direct oxidation where a selective attack of molecular ozone on double bonds takes place, and an indirect reaction involving non-selective free-radicals generated as a result of hydroxyl-induced ozone decomposition (Hoigné, 1998). In the case of complex effluents, such as wastewater generated during wetcleaning step after the drycleaning, there are compounds that can inhibit the action of free radicals reducing the intensity of the propagation reactions (*e.g.* sodium carbonate, scavengers, humectants, etc.).

Within this context, in this article the use of ozone for the treatment of pentylacetate contaminated waters is evaluated. Pentylacetate has started to be used in the drycleaning process as a new solvent due to its economic benefits. However, in the technical literature experimental data involving pentylacetate ozonation has not yet been reported. This paper addresses this issue, in particular, the effect of pH on pentylacetate removal rate and reaction mechanism, and reports the corresponding reaction rate constants with view to reactor design. This work was part of a wider innovative project that focused on technology development for water and solvent reclamation and reuse in the textile care industry (DBU, 2003).

Experimental

Materials

Pentylacetate (96% purity) and all the chemicals used in this study were analytical reagent grade supplied by Merck. *Tert*-butyl alcohol (*t*-BuOH) (> 99% purity) was used as a radical scavenger since it reacts very rapidly with hydroxyl radicals ($k_{\bullet OH,t\text{-BuOH}} = 5 \times 10^8\ M^{-1}s^{-1}$), but very slowly with ozone, $k_{O3,t\text{-BuOH}} = 0.03\ M^{-1}s^{-1}$ (Hoigné, 1998). Sodium 4-chlorobenzoate CBA (> 98% purity) was used as a reference compound. All solutions were prepared with ultrapure water obtained from a Millipore MilliQ system. Ozone was produced from pure O_2 supplied by Linde using an ozone generator (WEDECO Katadyn GmbH, Germany) rated at 25 $gO_3\ h^{-1}$ production.

Experimental system

Experiments were performed at laboratory scale, using a temperature-controlled reactor system based on a 2 dm^3 stirred reactor and operated in a semi-batch mode (see Figure 1). pH values were adjusted to 2, 7, 9 using phosphoric acid or potassium phosphate buffer. The reactor temperature was set at 20 ± 0.5 °C. Typically, 5 dm^3min^{-1} O_3/O_2 gas mixture was continuously fed to the reactor through a sparger. Initially, ozone gas was dissolved into pentylacetate-free buffered solution until ozone saturation was achieved. Then, a concentrated pentylacetate solution was injected into the mixture so that an initial concentration in the range $15x10^{-6}$ - $230x10^{-6}$ M was attained. Samples were taken periodically for further analysis; and $NaNO_2$ was used to eliminate residual dissolved ozone.

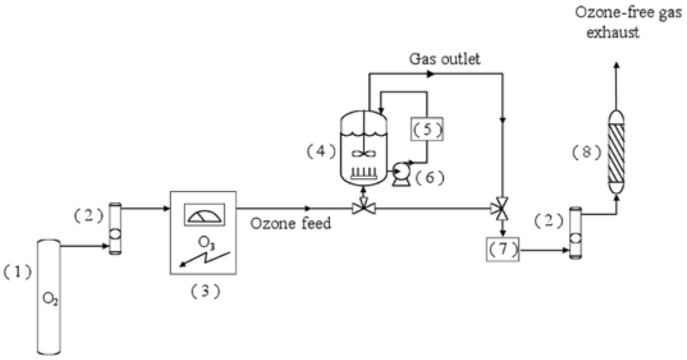

Figure 1: Experimental system: (1) Oxygen tank, (2) flowmeter, (3) ozone generator, (4) stirred tank reactor, (5) ozone liquid analyser, (6) liquid recirculation pump, (7) ozone gas analyser, (8) activated carbon trap.

Analytical methods

Inlet and outlet ozone gas concentrations were monitored using an ozone gas analyser (PCI-WEDECO, HC-500). Ozone concentration in aqueous solution was recorded on-line, using an ATI ozone analyser.

Pentylacetate was determined by gas chromatography using a GC-17A Shimadzu gas chromatograph, equipped with a capillary column (J&W Scientific DB-WAX, 30 m length x 0.25 mm i.d., 0.5 µm film thickness), a split injector and FID detector. A 23 cm^3min^{-1} flow of helium gas was used as carrier gas at 600 kPa. Split injections were conducted at 10:1 ratio and 18 cm^3min^{-1} flow. Prior to the injection, pentylacetate was extracted from ozonated samples using hexane at 1:1 ratio, during 60 min. Separation started at

40°C and then the temperature was increased at 10°Cmin^{-1} to attain 240°C after 5 min, using a constant flow rate of 1.7 cm^{3}min^{-1}. After each separation, elution proceeded for further 2 min before the oven cold down and stabilises the column before next run. Data were stored and processed using a Shimadzu Class-up^{TM} V 4.3 automated software system.

Sodium 4-chlorobenzoate was determined by liquid chromatography. A Hewlett Packard 1050 model chromatograph was used, fitted with a Lichrospher® 100 RP-18 (5 μm) separating column. 10 μL samples were injected and detection was carried out using a Shimadzu SPD-6A UV spectrophotometric detector at 234 nm. Separation was performed with an acetonitrile-NaH_2PO_4 solution gradient, at 40ºC. A mixture of 5% acetonitrile and 95% 3 mM NaH_2PO_4 solution was used as solvent A. Solvent B was prepared using a mixture of 70% acetonitrile and 30% 3 mM NaH_2PO_4 solution. Elution started with 2% B and then increased linearly to attain 100% B after 15 min, using a constant flow rate of 0.6 cm^{3}min^{-1}. After 5 min at 100% B, elution proceeded using 2% B for further 10 min, to stabilise the column before next injection.

Results and discussion

Effect of pH on pentylacetate removal rate

Figure 2 shows the pentylacetate PA dimensionless concentration as a function of ozonation time (20 °C, 230 x 10^{-6} M initial PA concentration) under different pH conditions (pH 2-9) and in absence of radical scavengers. Dimensionless concentrations were calculated as a fraction of initial PA concentration.

As seen in Figure 2, the PA removal rate increased with pH. Indeed, the PA removal rate increased around 80% as pH raised from 2 to 9. All PA was removed after 20 min ozonation at pH 9, as compared with more than 60 min required at pH 2. At acid pH, PA is eliminated by a combination of stripping and direct ozone reaction with a pseudo-first order kinetic rate constant of 0.7 x 10^{-3} s^{-1}; while at pH 9 PA the pseudo-first order kinetic rate constant is increased to 3.5 x10^{-3} s^{-1}. At basic pH, the increase in the PA removal rate was due to PA reaction with hydroxyl radicals coming from ozone aqueous decomposition.

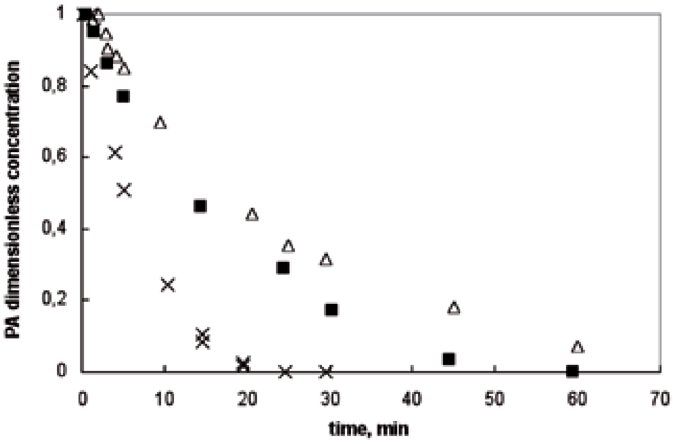

Figure 2: Ozonation of PA. Influence of pH: Δ pH = 2, ■ pH = 7, x pH = 9.

Kinetic modelling

PA removal rate by ozonation in water could be described by a simplified and unbalanced reaction mechanism as follows:

Sparging:

$$PA_{(aq)} \rightarrow PA_{(g)} \qquad -\frac{dC_{PA}}{dt} = r_S = k_S C_{PA} \qquad (1)$$

Direct reaction:

$$O_{3(aq)} + PA_{(aq)} \rightarrow \text{products} \qquad -\frac{dC_{PA}}{dt} = r_D = k_D C_{PA} C_{O3} \qquad (2)$$

Indirect reaction:

$$^{\bullet}OH_{(aq)} + PA_{(aq)} \rightarrow \text{products} \qquad -\frac{dC_{PA}}{dt} = r_I = k_I C_{PA} C_{\bullet OH} \qquad (3)$$

The total rate of PA removal could then be represented as a linear combination of terms representing sparging and ozonation:

$$-\frac{dC_{PA}}{dt} = r_S + r_D + r_I = k_S C_{PA} + k_D C_{PA} C_{O3} + k_I C_{PA} C_{\bullet OH} \qquad (4)$$

where, r_S, r_D and r_I represent the removal rate due to sparging, direct and indirect ozone reactions, respectively. C_{PA}, C_{O3}, and $C_{\bullet OH}$ are the species concentrations; k_S is the sparging removal rate constant; k_D and k_I represent the second-order rate constants for PA reaction with O_3 and ·OH radicals, respectively.

Direct reaction kinetics

Figure 3 presents the corresponding linearised plot for data obtained at pH 2, in presence of *t*-BuOH (0.01 M); conditions where the direct reaction mechanism prevailed.

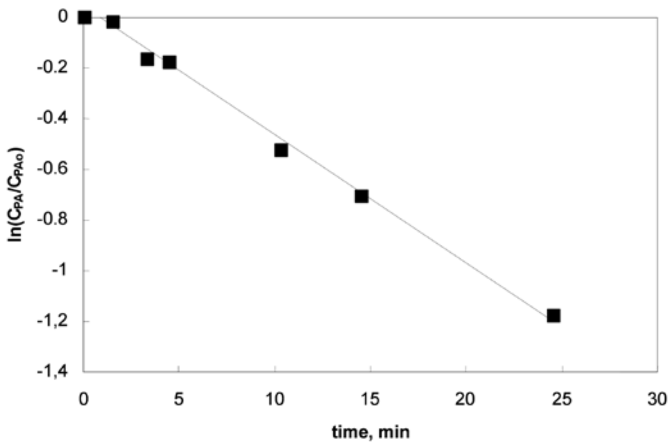

Figure 3: Determination of direct reaction constant between O_3 and PA in aqueous phase. pH 2, 20°C, 0.01M *t*-BuOH.

Experimental points fitted well a linear pseudo-first order model, with correlation coefficients above 0.99. The second-order direct reaction rate constant, k_D, at 20 °C was 2.7 $M^{-1}s^{-1}$.

Indirect reaction kinetics

Indirect rate constant of the reaction between PA and hydroxyl radicals, was determined at pH 9, in absence of free radicals scavengers and without sparging, at 20ºC. Sodium 4-chlorobenzoate CBA was used as a probe compound, whose constant rate with hydroxyl radicals is known, $k_{I,CBA}$= 4.4 x10^9 $M^{-1}s^{-1}$ (Hoigné, 1997). Both, PA as well as CBA reactions with hydroxyl radicals are described by means of second order kinetics:

$$-\frac{dC_{PA}}{dt} = k_{I,PA}C_{\bullet OH}C_{PA} \qquad (5)$$

$$-\frac{dC_{CBA}}{dt} = k_{I,CBA}C_{\bullet OH}C_{CBA} \qquad (6)$$

where, $k_{I,PA}$ and $k_{I,CBA}$ represent intrinsic rate constants of hydroxyl radical reactions of PA and CBA, respectively. By dividing the equations (5) and (6) and by integrating the expression that relates rate constants to solute concentration variations during reaction yields:

$$\ln\frac{C_{CBA}}{C_{CBA_0}} = \frac{k_{I,CBA}}{k_{I,PA}}\ln\frac{C_{PA}}{C_{PA_0}} \qquad (7)$$

Experiments were carried out with different initial concentrations ratio C_{CBAo}:C_{PAo} (1:1, 1:3, 3:1). Figure 4 shows experimental results, according to equation (7).

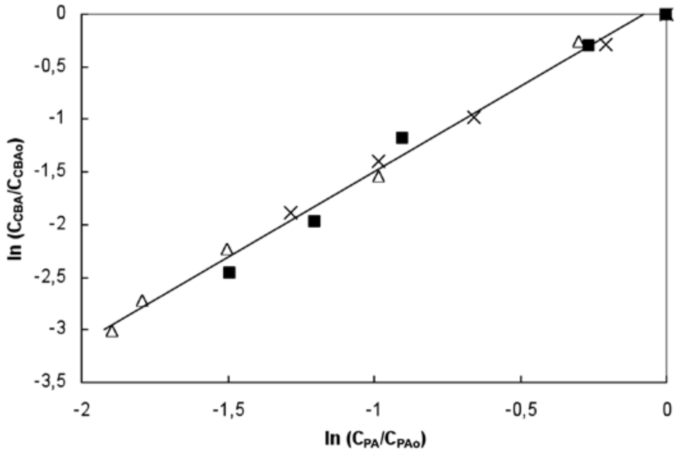

Figure 4: Determination of indirect reaction constant. C_{CBAo}:C_{PAo} initial concentrations ratio: x 1:1, Δ 1:3, ■ 3:1.

Data fitted quite well the linealised model with a correlation coefficient above 0.99. The rate constant of second order indirect reaction between hydroxyl radicals and pentylacetate, $k_{I,PA}$, at 20 °C was 2.6 x10^9 $M^{-1}s^{-1}$, which is smaller than indirect reaction rate constants reported for other researchers using different organic model compounds (Sánchez-Polo *et al.*, 2002; Valdés *et al.*, 2003).

Conclusions

This study shows that PA could be effectively removed using ozone at basic pH. Experimental results show that ozone treatment removes PA from contaminated waters by a combined mechanism. At acid pH, pentylacetate is eliminated by a combination of stripping and direct ozone reaction with a pseudofirst order kinetic rate constant of 0.7 x10^{-3} s^{-1}; while at pH 9 pseudofirst order kinetic rate constant of PA is increased to 3.5 x10^{-3} s^{-1}. At basic pH, PA is oxidised by hydroxyl radicals coming from ozone aqueous decomposition. The overall rate of the indirect reaction between ozone and pentylacetate could be approximated to a second order kinetic model with a rate constant at 20°C of $2.6\text{x}10^9$ $M^{-1}s^{-1}$. The radical reaction contribution at pH 9 accounts for 80% PA removal rate. This is a key issue regarding process design, since free radical scavengers, such as carbonates, may be present in water and affect the PA removal efficiency.

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