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# **Degradation of Phenol, Benzene and Cyanides in an Innovative Semi-industrial Ozonation Pilot Plant: The Effects of Operating Parameters**

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Running title: Ozonation of phenol, benzene and cyanides

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## **ABSTRACT**

The degradation of phenol, benzene and cyanide solutions was investigated in an innovative semi-industrial ozonation pilot plant especially designed and built to provide an effective ozone transfer under advanced oxidation process conditions.

To test the pilot, different phenol solutions (25, 50 and 100 mg/L), influent ozone contents (70, 90 and 140 g/m<sup>3</sup> TPN) and pH (4, 7, 10) were first studied. This study allowed to establish a relationship between the effluent gaseous ozone and the progression of other ozonation parameters.

Later on, mixtures of phenol, benzene and cyanides were simultaneously treated in the pilot. Phenol and benzene were quickly reduced by ozonation within 10 min and cyanides in around 30 min.

For a full assessment of the ozonation process, a simple methodology, based on actual rates of the gas vector oxygen and electricity was developed to appraise the ozonation operation costs for treating the above pollutants. Based to the results obtained, the ozonation pilot is clearly capable of treating waters containing multiple pollutants.

**KEYWORDS:** phenol; benzene; cyanides; ozone; advanced oxidation process; ozonation pilot

## **INTRODUCTION**

Benzene and phenol compounds are toxic and suspected to be carcinogenic (EPA/600/P-97/001F, 1998; EPA/635/R-02/006, 2002) and they can reach drinking water taps (Kuo et al., 1997). Major sources of these contaminating components are discharges from factories of petroleum and industrial waste overthrows. Cyanides may be found in wastewaters from mining activities or waste disposals in different forms: HCN,  $\text{CN}^-$ , or  $\text{CN}^-$  complexes, and solvents (Carrillo-Pedroza et al., 2000; Barriga-Ordonez et al., 2006), and they may come from food industries (Somboonchai et al., 2008).

These pollutants can be removed from contaminated waters by physicochemical methods, by incineration and microbial treatment, or by oxidation with ozone (Rice, 1996; Gogate and Pandit, 2004). Here we present a semi-industrial pilot plant which is likely the first of its genre as it was especially designed to provide an enhanced ozone transfer advocated elsewhere (Zhou and Smith, 2000; Gong et al., 2007; Tiwari and Bose, 2007). The aim of this study is first to show results from the degradation of phenol solutions by ozone, and then, the simultaneous oxidation of benzene, phenol and cyanides aqueous solutions to test and validate the semi-industrial pilot unit. This work is completed by a simple methodology to estimate the operation costs on ozonation treatment.

## **BRIEF BACKGROUND RELATED TO THE DEGRADATION OF BENZENE, PHENOL AND CYANIDES**

Given their low or non-biodegradable and refractory characteristics, benzene and phenol compounds may cause significant pollution of surface and ground waters, and soils (Cetin et al., 2003; Arocha et al., 1996; Badol et al., 2008; Rivett et al., 2011, Chiriac et al., 2009). ). Cyanides are extremely toxic to humans (EPA,74-90-8), and they can be oxidized by ozone (Vedula et al., 2013; Mudliara et al., 2009).

The above pollutants can be degraded by physicochemical methods like a stripping process (Ho Yeom and Je Yoo, 1999) and adsorption onto activated carbon. A disadvantage of this method is the high cost of adsorption materials (Bhatnagara and Sillanpaab, 2010). Other treatment methods for these pollutants include incineration (Matsukami, et al., 2014) and microbial treatment (Huang et al., 2011), which have drawbacks such as high energy requirements, high cost, low efficiency, incomplete removal and formation of highly hazardous intermediates (Acha et al., 2000).

Another way to treat these pollutants is by oxidation with ozone (Glaze and Wun Kan, 1989). Aromatics present a constant and high kinetic rates reacting with ozone molecules (Hoigné and Bader 1983; Langlais et al., 1991). The oxidation reaction results from cutting carbon links by opening the aromatic rings and decreasing in this way their molecular size leading to mineralization (Langlais et al., 1989). The degradation by indirect ozonation (Doré, 1988) through advanced oxidation processes (AOPs) is particularly a good solution as these reactions are developed in presence of highly reactive ephemeral hydroxyl radicals ( $\text{OH}^\circ$ ) (Glaze and Wun Kan, 1989; Einaga and Ogata 2009; Zuo et al., 2011) which are produced by a cyclic reaction combining ozone with water hydroxide ions at high pH, or by combining ozone with  $\text{H}_2\text{O}_2$ , or by UV irradiation (Wu et al. 2004), or by ultrasonic treatment (Kidak and Ince 2007), or by a catalytic ozonation (Legube and Karpel Vel Leitner 1999).

In an ozonation process, improving hydrodynamics and mass transfer capabilities are important factors to increase the removal efficiency of pollutants (Charpentier 1981). Ozone is transferred in this process from the gas to the liquid phase, thus the rate of mass transfer will depend on the interfacial area and on the ozone bubble dimensions in the liquid phase, the smaller the size of the ozone bubbles, the greater the contact surface resulting in an enhanced ozonation process (Bergman et al., 2012).

Most papers are related to single pollutant oxidation by ozone in a small laboratory set-up at different experimental conditions resulting in lower process efficiencies. Mohammadzadeh et al.

(2004) reported the treatment of synthetic phenol solutions in a bench-scale ozonation system at different pH values; they found that the removal efficiency increased with increasing pH. Another group (Pratarn et al., 2011) revealed that phenol degradation with granular activated carbon enhanced with ozone provided the best results, however they reported to get non satisfactory results treating the phenol solutions with just ozone. Also Matheswaran et al. (2009) studied the influence of phenol concentration, ozone flow rate and pH for treating phenol by ozone in a 1.5 L laboratory reactor; their results were found to be optimal at low concentrations of phenol and at high pH, however the reaction times to completely remove phenol were too long from 120 min on. Similarly Martins and Quinta-Ferreira (2011) developed a catalytic and non-catalytic ozonation to remove phenol from wastewaters. Although the catalytic system remained active after several tests, it was not useful to apply it in real effluents because the presence of radical scavengers.

## **THE OZONE PILOT PLANT DEVELOPMENT**

### ***Determination of The overall Transfer Coefficient***

The transfer resistance for a slightly soluble gas such as ozone, is localized in the film liquid side, thus the ozone mass transfer from gas into a liquid phase can be described by the two-film model (Beltran, 2004; Bergman et al., 2012) as:

$$N_A = K_L(C_L^* - C_L) \quad (1)$$

Where  $K_L$  ( $\text{m min}^{-1}$ ) is the liquid mass transfer coefficient, and  $C_L^*$  and  $C_L$  ( $\text{g m}^{-3}$ ) are the saturated and aqueous phase ozone concentration, respectively. After dissolved in water, ozone decays through both self-decomposition and oxidation of chemical compounds in the pilot.

In a gas-liquid contactor, it is difficult to determine the exchange area ( $S$ ). It is then better to express  $S$  with respect to the liquid volume  $V$ . The specific contact surface area ( $a$ ) ( $\text{m}^{-1}$ ) is thus defined by:

$$a = \frac{S}{V} \quad (2)$$

in which case the amount of mass transferred to the volume  $V$  will be equal to:

$$N_A = K_L a (C_L^* - C_L)V \quad (3)$$

To calculate  $N_A$ , the overall mass transfer coefficient  $K_L a$  ( $\text{min}^{-1}$ ) is first determined by studying in transient state the rate at which the dissolved ozone concentration diffuses in the previously deoxygenated liquid phase. Eq. 3 depicting the transfer of ozone in water is modified as follows:

$$\frac{N_A}{V} = \frac{dC_L}{dt} = K_L a (C_L^* - C_L) \quad (4)$$

The integration of Eq. 4 with the initial condition at  $t = 0$ ,  $C_L = 0$  leads to:

$$\ln \frac{C_L^* - C_L}{C_L^*} = K_L a t \quad (5)$$

Eq. 5 represents a straight line with  $K_L a$  as slope.  $K_L$  is determined from the knowledge of  $a$ . In most practical cases, the dissolution of ozone is produced by a process involving gas bubbles dispersed in the liquid phase. It is possible to characterize the ozone-water dispersion by considering the gas hold-up ( $\varepsilon$ ):

$$\varepsilon = \frac{V_G}{V_L + V_G} \quad (6)$$

Where  $V_G$  and  $V_L$  are, respectively, the volume occupied by the gas and the liquid in the contactor.

Under such condition, the specific contact surface area is defined by:

$$a = \frac{S_T}{V_L} \quad (7)$$

where  $S_T$  is the total contact surface area. Assuming spherical gas bubbles:

$$S_T = N \pi \bar{d}_B^2 \quad (8)$$

where  $N$  = number of bubbles. Thus the volume of gas bubbles is:  $V_G = N \frac{\pi}{6} \bar{d}_B^3$ . From Eq. 6,

$V_L = \frac{V_G}{\varepsilon} + V_G$  which leads to:

$$V_L = N \frac{\pi}{6} \bar{d}_B^3 \left( \frac{1-\varepsilon}{\varepsilon} \right) \quad (9)$$

Combining equations 7, 8, and 9, the specific contact surface area is obtained:

$$a = \frac{6}{\bar{d}_B} \left( \frac{\varepsilon}{1-\varepsilon} \right) \quad (10)$$

An alternative way to determine the gas hold-up is by:

$$\varepsilon = \frac{U_G}{U_L + U_S} \quad (11)$$

where:  $U_G$  = superficial gas velocity at TPN ( $\text{m s}^{-1}$ ),  $U_L$  = superficial liquid velocity ( $\text{m s}^{-1}$ ),  $U_S$  = relative velocity of bubbles with respect to the liquid ( $\text{m s}^{-1}$ ). Or by:

$$\varepsilon = \frac{h_D - h_L}{h_D} \quad (12)$$

where:  $h_D$  = height of liquid in the column with gas supply,  $h_L$  = height of liquid in the column without gas supply.

### ***Determination of the Overall Transfer Coefficient by an Empirical Formula***

$K_L a$  ( $\text{min}^{-1}$ ) can be determined by the following equation (valid for a temperature close to  $12^\circ\text{C}$ ):

$$K_L a = 0.013 U_G^{0.95} \quad (13)$$

where  $U_G$  = superficial gas velocity at TPN ( $\text{m s}^{-1}$ ), on empty contactor column with no effluent. In such condition  $U_G = \frac{G}{S}$ , with  $S$  = column cross section ( $\text{m}^2$ ), and  $G$  = gas flow rate ( $\text{m}^3 \text{TPN h}^{-1}$ ).

To dimension the ozone semi-industrial pilot, a column diameter of 0.3 m has been considered, thus  $S = 0.0706 \text{ m}^2$ . The ozone gas flow rate injected at the bottom of contactor is  $G_{max} = 2 \text{ m}^3 \text{TPN h}^{-1}$ .

Therefore  $K_L a = 0.314 \text{ min}^{-1}$ . Also taking into account  $G_{min} = 0.8 \text{ m}^3 \text{ h}^{-1}$ ,  $K_L a = 0.1303 \text{ min}^{-1}$ .

### ***Determination of the Height of a Transfer Unit (HTU)***

$$\text{HTU is defined as: } HTU = \frac{Q_L}{K_L a S} \quad (14)$$

where  $Q_L$  = liquid flow rate ( $6 \text{ m}^3 \text{ h}^{-1}$ ).  $HTU = 4.55 \text{ m}$  and  $10.87 \text{ m}$  for a maximum and minimum gas flow rate, respectively.

### ***Ozone Pilot Operation***

All ozonation experiments were conducted in the semi-industrial pilot plant (Figure 1). The 400 l solution was fed in the 5 m tall column contactor. A porous fritted diffuser located at the bottom of this column provided fairly fine ozone bubbles with diameters from 2 mm to 4 mm. Ozone gas bubbles were floated up in laminar flow condition. A counter-current closed loop recirculation system fixed at  $5 \text{ m}^3/\text{h}$  through a carrier gas flow rate of  $3 \text{ m}^3/\text{h}$  at normal temperature and pressure (TPN) (273 K and 1 atm) were set up to decrease the floating speed of the gas bubbles.

Ozone gas was generated either from dry air (with dew point of  $-75 \text{ }^\circ\text{C}$ ) or pure oxygen (99.5%, Air-liquid, France) from corona discharge using an ozone generator (OZAT<sup>®</sup> CFS-2G, Ozonia, France) able to produce ozone at 12.8% (w/w). The ozone gas levels in the influent and effluent streams were measured and recorded from their absorbance data at 254 nm (Ozone Analyzer BMT 964, Germany). Exhausted gases (effluent ozone) were destroyed at  $350^\circ\text{C}$  by a thermal destruction unit.

The pH was monitored continuously on line during the ozonation process by a sensor placed inside the column (Figure 1). The selected pH (4, 7, or 10) was kept constant throughout the oxidation experiments by adding the required alkali (NaOH) or acid ( $\text{H}_2\text{SO}_4$ ).

### ***Chemicals and Analytical Methods***

Phenol crystals (99%) were purchased from Merck (Germany). All other chemicals such as 1,2-dihydrobenzene (1,2-DHB), 1,4-dihydrobenzene (1,4-DHB), 1,4-dihydroquinone (1,4-DHQ) and maleic acid (MA) were grade reagents and supplied by Sigma-Aldrich.

Phenol solutions were measured by a colorimetric assay (Phenol Cell Test, 1.14551.0001, Merck, Spectroquant, ISO8466-1, Germany). The analytic range covered phenol from 0.1 to 2.5 mg/L. Measurements were performed in a 16 mm path rounded cell with 10 mL sample in which phenol and derivatives reacted with a thiazole derivative to form a red violet azo dye that was determined photometrically at 510 nm.

Phenol and ozonation by-products (i.e., 1,2-DHB, 1,4-DHB, 1,4-DHQ and MA) were identified and measured by high performance liquid chromatography (HPLC, Thermo Scientific, Spectra System P4000 pumps, sampling Spectra System AS 3000, detector Spectra System UV 8000, Hypersil Gold column - 100 mm x 4.6 mm, 5  $\mu$ m and Prevail Organic Acid column - 250 mm x 4.6 mm, 5 $\mu$ m). The identification was performed by comparing UV absorption spectra from HPLC peaks to the standards of phenol and assumed intermediates (i.e., 1,2-DHB, 1,4-DHB, 1,4-DHQ and MA). Mineral precipitates (i.e., calcium oxalate) produced at the end of the ozonation reaction were identified by X-ray diffraction (XRD).

Analyses, such as total organic carbon (TOC), chemical oxygen demand (COD), benzene and cyanides were carried out by Ianesco Chimie (Poitiers, France). Benzene samples were extracted by solid phase micro extraction (SPME) (ISO 11423-1) then measured by gas chromatography-mass spectrometry (GC-MS). Total cyanide was analyzed by NF EN ISO 14403 flux method. Chemical Oxygen Demand (COD) was measured in the range of 25 to 1500 mg/L by a colorimetric assay (Cell Test C4/25, 173702 COD Cat. 252071 WTW, Germany) by oxidizing 3 mL samples to potassium dichromate with a hot solution of sulfuric acid. The samples were digested with silver sulfate as catalyst for 2h at 140°C keeping chlorides masked with mercury sulfate. After cooling, green  $\text{Cr}^{3+}$  ions were determined photometrically at 585 nm. Readouts of COD data were obtained directly from a previously calibrated spectrophotometer. Total organic carbon (TOC) was analyzed by a TOC meter based on a catalytic oxidation (TOC-5000, Shimadzu).

## RESULTS AND DISCUSSION

### *Oxidation of Phenol in the Semi-industrial Ozone Pilot*

Tests of oxidation of phenol were performed in the previously described semi-industrial pilot to determine the influence of several parameters of ozonation such as ozone concentration, influent phenol concentration, byproducts, and pH. All reactions were carried out at a room temperature (20° C). Table 1 shows the set of different experimental conditions to perform phenol ozonation in the pilot plant.

### *Relationship Between the Gaseous Effluent Ozone and the Progression of Other Ozonation Parameters*

Phenol-like compounds are expected to be quickly destroyed by ozone as they are known as highly reactive and selective with compounds containing high electronic density sites (Hoigné and Bader 1983). The influent and effluent of gaseous ozone concentrations in the contactor were monitored and recorded continuously on line every second. It is worth noting that the influent gaseous ozone concentration was kept constant throughout the experiments at 90 g O<sub>3</sub>/m<sup>3</sup> (Figure 2a) to guarantee the prosecution of ozonation.

Results of treating phenol solutions by ozone show that this compound was quickly degraded (Figure 2a). According to these results a relationship was established between the effluent gaseous ozone (Figure 2a, increasing curve) and other ozonation parameters such as reaction time, progression of COD, TOC, and production and removal of byproducts (Figures 2a, and 2b, first 20 min). Thus the progress of the pilot effluent gaseous ozone concentration depicting the phenol ozonation can be explained in four stages:

First stage: this step took place at the beginning of ozonation (Figure 2a, first 10 min) showing total consumption of the influent gaseous ozone. Phenol was rapidly degraded at this period. Therefore the initial attack of ozone led to full conversion of phenol into by-products 1,2-DHB, 1,4-DHB, 1,4-

DHQ and MA (Figure 2b). The absence of ozone in the pilot gaseous effluent during the first 10 min of reaction can be explained by the high kinetic rate of phenol with ozone ( $k_{\text{phenol},\text{O}_3} = 1300$  L/mol.s) (Hoigné and Bader 1983) and the ozone demand of the by-products ( $k_{1,2\text{-DHB},\text{O}_3} = 3.1 \cdot 10^5$  L/mol s) (Gurol and Nekouinaini, 1984). The oxidation by molecular ozone in this step was less than 45% in terms of COD and 7% in terms of TOC.

Second stage: from 10 to 20 min (Figure 2a). The effluent gaseous ozone concentration increased slightly till around  $10 \text{ g/m}^3$ . Ozone was continuously consumed by MA and slightly by 1,4-DHB, and 1,2-DHB (Figure 2b). During this period, the mineralization was likely complete with conversions of 20% and 74% for TOC and COD, respectively, which was done after the opening of aromatic circles (1,4-DHB and 1,2-DHB). During this second stage, about 90% of the influent gaseous ozone was consumed, thus over this period the phenomenon of advanced oxidation process could have taken place simultaneously with the ozone molecular oxidation according to the higher consumption of ozone resulting from the formation of highly reactive hydroxyl radicals.

Third stage: from 20 to 30 min (Figure 2a). The effluent gaseous ozone concentration in the pilot continued to increase according to the almost constant levels of reaction conversions in terms of COD and TOC. At this stage all the byproducts were assumed to be removed as they were no longer detected. Incidentally, at the end of this period the refractory compound oxalic acid can still be found (Turhan and Uzman, 2008) in spite of the advanced oxidation process. This third stage corresponded to the consumption of influent gaseous ozone from about 10% to 15%, and 60% to 80% at pH 7 and pH 10, respectively. The higher consumption at high pH can be explained by the formation of hydroxyl radicals from molecular ozone and hydroxide ions (Staelin and Hoigné, 1985).

Fourth stage: the effluent gaseous ozone content approached the constant influent gaseous ozone level and attained a constant maximum level (Figure 2a). There was no more progression of COD and TOC after reaching the conversion of 80% and 60%, respectively. The gaps of both influent and

effluent gaseous ozone streams can be explained by the ozone self-decomposition in the contactor (Stahelin and Hoigné, 1985).

### ***The Effect of Influent Gaseous Ozone on Phenol Degradation***

One of the important factors to optimize ozonation processes for industrial wastewater treatment is the influent gaseous ozone concentration. The concentration of dissolved ozone in the liquid phase will vary according to the ozone concentration in the gas phase, the kinetics, the transfer efficiency, the gas bubble size, and the gas contact time with the liquid sample (Gong et al. 2007).

The effect of influent gaseous on phenol degradation (starting phenol concentration at 50 mg/L) was investigated by injecting ozone in the contactor at 70 g O<sub>3</sub> TPN/m<sup>3</sup>, 90 g O<sub>3</sub> TPN/m<sup>3</sup> and 110 g O<sub>3</sub> TPN/m<sup>3</sup> at pH 7 and pH 10. These levels of ozone were chosen according to the ozone dosages established by ITT Wastewater GmbH Wedeco (Sievers, 2011). Figures 3a and 3b show the time course of phenol at pH 10 and pH 7 for each of the applied gaseous ozone concentrations. The concentration of ozone injected into the contactor had little influence on the degradation rate of phenol. However, the removal of phenol was slower at 70 g O<sub>3</sub> TPN/m<sup>3</sup> (15 min) against 10 min at 90 O<sub>3</sub> TPN/m<sup>3</sup> or 8 min at 110 g O<sub>3</sub> TPN/m<sup>3</sup>.

Figure 4 illustrates changes in COD/COD<sup>0</sup> ratios according to each one of the influent gaseous ozone concentrations. These ratios eliminate variations in the initial phenol concentration and give more explicit estimation of COD reductions. This parameter showed a COD reduction of 78% at 70 g O<sub>3</sub> TPN/m<sup>3</sup>, and 83% at both 90 g O<sub>3</sub> TPN/m<sup>3</sup> and 110 g O<sub>3</sub> TPN/m<sup>3</sup>. COD removals were much slower at 70 g O<sub>3</sub> TPN/m<sup>3</sup> and pH 10. However, there was no difference between 90 and 110 g O<sub>3</sub> TPN/m<sup>3</sup> gaseous ozone influents. COD reductions were stabilized after about 30-45 min of ozonation.

COD removals (Figure 4) over 15 min reaction were 59%, 61% and 77% at 70 g O<sub>3</sub> TPN/m<sup>3</sup>, 90 g O<sub>3</sub> TPN/m<sup>3</sup> and 110 g O<sub>3</sub> TPN/m<sup>3</sup>, respectively, whereas phenol was no longer detected (Figure 3).

Obviously as for COD, increasing the ozone concentration from 70 g O<sub>3</sub> TPN/m<sup>3</sup> up to 90 g O<sub>3</sub> TPN/m<sup>3</sup> does not improve significantly the phenol degradation. However, some important improvements in COD removal were seen when using the higher influent gaseous ozone concentration of 110 g O<sub>3</sub> TPN/m<sup>3</sup> (Figure 4, 15 min reaction time). The effect of the influent ozone concentration on phenol removal efficiency could be explained by stoichiometric factors and rate constants managing the ozone reaction with phenol and intermediate compounds. The stoichiometric factor is calculated as follows:

$$\text{Stoichiometry (influent O}_3\text{/phenol) (mol/mol)} = [\text{ozone (g/m}^3\text{)/M}_{\text{O}_3} \text{ (g/mol)}] \times \text{gas flow rate (m}^3\text{/h)} \\ \times \text{reaction time (h)/phenol (mol)}$$

The stoichiometric factors were found to increase to some extent with high levels of ozone (Table 2). However, according to Figure 3 over 15 min no significant improvements in phenol removal were found by increasing the ozone concentration from 70 g O<sub>3</sub> TPN/m<sup>3</sup> up to 110 g O<sub>3</sub> TPN/m<sup>3</sup>. The above stoichiometric factors are reported to be sufficient for phenol removal (Hoigné and Bader, 1983; Wu and Masten, 2002).

For a given concentration of ozone, the reduction of COD was faster and slightly higher at pH 7 (Figure 4). In addition, the COD reduction was accentuated with increasing ozone concentrations. In contrast to the concentration of 90 g O<sub>3</sub>/m<sup>3</sup>, the fact of applying a concentration of 110 g O<sub>3</sub> TPN/m<sup>3</sup> provided no significant reduction in terms of COD. With regard to the study of the influence of influent gaseous ozone concentration, the level of 90 g O<sub>3</sub> TPN/m<sup>3</sup> seems to be the best compromise.

### ***The Effect of Influent Phenol Concentration***

The second parameter studied during these series of test of ozonation was the influent phenol concentration. The selected concentrations of phenol were 25 mg/L, 50 mg/L and 100 mg/L. The influent ozone concentration was set at 90 g O<sub>3</sub> TPN/m<sup>3</sup> and the pH at 7.

For 25 mg/L and 50 mg/L levels of phenol, less than 10 min reaction was enough to quickly degrade phenol by ozonation (Figure 5). While for a phenol concentration of 100 mg/L, 20 min were required. Therefore the time required for phenol degradation increases with increasing phenol concentrations.

Figure 6 shows the evolution of COD/COD<sup>0</sup> ratios for each one of the phenol concentrations applied in the column contactor. These ratios decreased more rapidly with low influent phenol concentration. In addition, the final value of COD/COD<sup>0</sup> ratio was slightly higher for low concentrations of phenol. A steady reduction in COD of 77% for phenol at 25 mg/L was observed, while the reduction in COD was 86% and 87% for phenol at 50 and 100 mg/L, respectively. This reduction could be amplified if ozonation was extended beyond 45 min because the slope of the curve for phenol at 100 mg/L is significantly different from the horizontal asymptote at the end of the experiment (Figure 6).

The study of the influence of the influent phenol concentration led to the conclusion that phenol is degraded between 10 and 20 min. The value of COD tends towards the final value of the same order of magnitude regardless of the initial phenol concentration. This could be explained by the formation during ozonation of non-oxidizable refractory byproducts (Turhan and Uzman, 2008). The byproducts of phenol degradation have not been investigated in these series of experiments by simple ozonation of phenol.

### ***Effect of pH***

The influence of pH was studied in this series of experiments of ozonation of phenol. During the experiments the pH was adjusted permanently to keep a constant value for the entire duration of phenol treatment by ozonation. The pH values tested were 4, 7 and 10. The concentration of the influent ozone and phenol were fixed at 90 g O<sub>3</sub> TPN/m<sup>3</sup> and 50 mg/L, respectively.

Figure 7 shows the changes in phenol concentration for each one of the pH values tested. These results show that the pH affects the rate of degradation of phenol. Indeed, the higher the pH, the faster will run the ozone reaction. The reaction times observed were 8, 10 and 15 min at pH 10, pH 7 and pH 4, respectively. At high pH, the advanced oxidation process takes place, which is revealed by the presence of the hydroxyl radicals (Hoigné and Bader, 1983).

Figure 8 shows the evolution of COD/COD<sup>0</sup> ratios for each one of the pH tested. These ratios decrease more rapidly at pH 10 than pH 4 or pH 7 for the first 20 min of phenol ozonation, however the pH has no influence beyond twenty min reaction (Figure 8). The final values of phenol reduction are quite similar and account for 83% at pH 4, 86% at pH 7, and 83% at pH 10.

The study of the influence of pH shows that the pH 10 prompts an improvement in efficiency and a faster COD reduction and phenol degradation during the first twenty min of the test. The maximum COD reduction obtained at pH 7 and the small gain in the cost of adding an alkali for setting the pH to 10, make the pH 7 to be optimum for phenol ozonation.

### ***Optimal Conditions for Phenol Degradation***

The above results obtained in the innovative pilot plant show that phenol solutions are degraded between 10 and 20 min regardless of the experimental conditions. The observed kinetics of the semi-industrial pilot has the same order of magnitude than those observed for smaller volumes of a few litres (Turhan and Uzman, 2008). Indeed, Turhan and Uzman (2008) obtained a constant maximum speed of 409.55 mg/L.h. Taking the example of an experiment conducted under the experimental conditions of this work (90 g O<sub>3</sub> TPN/m<sup>3</sup>, 50 mg/L phenol, pH 7), similar to those used by Turhan and Uzman (2008) namely influent phenol at 25 mg/L, 50 mg/L, 75 mg/L, and 100 mg/L, influent O<sub>3</sub> at 2 g/L.h, 4 g/L.h and 6 g/L.h equivalent to 17 g O<sub>3</sub> TPN/m<sup>3</sup>, 33 g O<sub>3</sub> TPN/m<sup>3</sup> and 50 g O<sub>3</sub>/m<sup>3</sup> at pH 9, a phenol decline by 14.2 mg/L (i.e., 50.0 - 35.8 mg/L) can be calculated

from 0 min to 2 min (Figure 7), thus  $14.2 / 2 = 7.1$  mg/L per minute, or  $7.1 \times 60 = 426$  mg/L.h, which is comparable to 409.55 mg/L.h obtained by Turhan and Uzman (2008).

For a given ozone concentration, the COD reduction is faster and slightly higher at pH 7 than pH 10, and it increases accordingly when the concentration of injected ozone increases. But the fact of applying a concentration of 110 g O<sub>3</sub> TPN/m<sup>3</sup> does not bring about significant gain in COD reduction compared to 90 g O<sub>3</sub> TPN/m<sup>3</sup>, which seems to be the best compromise.

The study of the influence of phenol concentration indicates that the value of the final COD tends towards a value of the same order of magnitude regardless of the initial phenol concentration. This can be explained by the formation, during ozonation, of a non-oxidizable byproduct under these experimental conditions (Turhan and Uzman, 2008).

### ***Simultaneous Oxidation of Phenol, Benzene and Cyanides in the Semi-industrial Ozone Pilot***

Three model compounds, phenol at 50 mg/L, benzene at 10 mg/L and cyanides at 50 mg/L were selected for simultaneous ozonation studies in the pilot. Inlet ozone levels in the range of 70 g O<sub>3</sub> TPN/m<sup>3</sup> to 140 g O<sub>3</sub> TPN/m<sup>3</sup>, a liquid recirculation of 5 m<sup>3</sup>/h and an ozone injection flow rate of 3 m<sup>3</sup>/h were applied in this work. Results of simultaneous oxidation of phenol, benzene and cyanides, and the evolution of some global parameters (TOC, COD, inlet ozone and outlet ozone levels) are represented in Figures 9a and 9b. Ozone reacted instantly with phenol and benzene during the first 10 min of ozonation. Cyanides started only to be eliminated after removal of benzene and phenol. Ozone reacted likely first with the compounds having higher ozone kinetic reaction rate. According to the literature, the higher the kinetic constant with ozone is the less the reaction time for their removal is. As the kinetic constant of phenol with ozone ( $k = 1,300 \text{ mol}^{-1} \cdot \text{s}^{-1}$ ) is higher than that of cyanides with ozone ( $k = 1,000 \text{ mol}^{-1} \cdot \text{s}^{-1}$ ) (Hoigné et al., 1985). Thus clearly phenol was removed before starting the degradation of cyanides. On the contrary, the kinetic constant of benzene with

ozone ( $k = 2 \text{ mol}^{-1} \cdot \text{s}^{-1}$ ) (Hoigné et Bader, 1983a) is smaller than the kinetic constant of cyanides with ozone. It is surprising that benzene was removed before starting the degradation of cyanides.

Figure 9b shows the evolution of influent and effluent levels of ozone during the simultaneous degradation of benzene, phenol and cyanides. The influent ozone concentration was permanently kept constant at  $90 \text{ g O}_3 \text{ TPN/m}^3$  during all ozonation experiments. With regard to the ozone levels at the effluent of the pilot (off gas), it was not detected the first 10 min of reaction (Figure 9b). Thus most of the ozone injected into the reactor was consumed during the pollutants removal. After 10 min reaction, the outlet ozone content followed a gradually rising trend, approaching a level of  $10 \text{ g O}_3/\text{m}^3$  up to 30 min reaction. Then, the ozone outlet content increased rapidly up to  $75 \text{ g O}_3/\text{m}^3$  and remained constant till the end of experiments. Beyond 60 min reaction, the ozone injected at the inlet of reactor was no longer consumed by the reaction. The gap between the inlet ozone content at  $90 \text{ g O}_3 \text{ TPN/m}^3$  and the outlet ozone content at  $75 \text{ g O}_3 \text{ TPN/m}^3$  (Figure 9b) can be explained by the self-decomposition phenomenon of ozone in solution.

### ***Effect of Influent Gaseous Ozone Onto the Simultaneous Ozonation of Benzene, Phenol and Cyanides***

Mixtures of benzene, phenol and cyanides at  $10 \text{ mg/L}$ ,  $50 \text{ mg/L}$  and  $50 \text{ mg/L}$ , respectively, were oxidized by ozone at a flow rate of  $3 \text{ m}^3 \text{ TPN/h}$  in the semi-industrial pilot plant.

Figure 10 illustrates the degradation of benzene in mixture solutions by ozonation at  $70 \text{ g O}_3 \text{ TPN/m}^3$ ,  $90 \text{ g O}_3 \text{ TPN/m}^3$  and  $140 \text{ g O}_3 \text{ TPN/m}^3$ . All benzene was oxidized within 10 min reaction. There were no significant differences treating benzene by ozone at  $90 \text{ g O}_3 \text{ TPN/m}^3$  or  $140 \text{ g O}_3 \text{ TPN/m}^3$ . However the degradation of benzene by ozone at  $70 \text{ g O}_3 \text{ TPN/m}^3$  was less extensive compared to that performed at ozone levels of 90 and  $140 \text{ g O}_3 \text{ TPN/m}^3$  (Figure 10). Similar results were observed regarding the degradation of phenol by ozone (Figure 11).

Cyanides, in contrast, started to be removed later after 10 min reaction (Figure 12). All cyanides in mixture were oxidized by ozone within 60 min ozonation (Figure 12). The ozonation of cyanides was done faster at 140 g O<sub>3</sub> TPN/m<sup>3</sup> than at 70 g O<sub>3</sub> TPN/m<sup>3</sup> or 90 g O<sub>3</sub> TPN/m<sup>3</sup> (Figure 12). COD and TOC decreased simultaneously and followed the ozonation reaction. Phenol and benzene oxidation triggered the decrease of COD from the oxidation beginning, on the contrary, TOC started to decrease after 10 min reaction, simultaneously with cyanides decrease.

As for phenol and benzene, no effect of pH on their degradation was observed, whereas cyanides were much better removed at neutral and basic pH. After 30 min reaction, 2%, 50% and 99% of cyanides were removed at respectively pH 4, pH 7 and pH 10. Indeed, the rate constant of reaction of ozone with molecular cyanide (HCN) is lower than 10<sup>-3</sup> mol<sup>-1</sup>.s<sup>-1</sup>, while the kinetic rate constant of ozone with CN<sup>-</sup> is 10<sup>3</sup> mol<sup>-1</sup>.s<sup>-1</sup> (Hoigné et al., 1985). This means that the kinetic reaction of ozone with cyanides can be 10<sup>6</sup> times faster at high pH than low pH as previously reported by Carrillo-Pedroza et al. (2000).

### ***Cost Estimation of Phenol, Benzene and Cyanide removals by Ozone in the Semi-industrial Pilot***

A simple methodology was developed to estimate the operation costs of the semi-industrial pilot plant. Data were selected based on the best results of phenol and simultaneous oxidation of mixtures of phenol, benzene and cyanides (Table 3).

Operation costs included the price for ozone generation, the cost of oxygen consumption for 400 L effluent treatment. It is worth noting that this cost estimation did not include the capital costs, labor costs, chemical costs, facilities costs and maintenance costs.

The quantity of ozone fed into the reactor was calculated based on ozone flow rate 3 m<sup>3</sup> O<sub>3</sub> TPN h<sup>-1</sup>, 90 g O<sub>3</sub> TPN/m<sup>3</sup>, 0.5 h ozonation for phenol, and 1 h ozonation for mixtures of phenol, benzene, and cyanides. The reaction time of 0.5 h for phenol reduction at 50 mg/L was taken from Figure 2a,

this time was necessary to remove 99% of phenol and their byproducts, 50% of TOC and 75% of COD. For the simultaneous oxidation of phenol, benzene and cyanides, 1 h reaction time was selected from Figure 9; at this time, most of phenol, benzene and cyanides were degraded and the reduction reached likely 75% with a COD conversion of 90%. Under this condition, the effluent gaseous ozone concentration was already constant and approached the influent gaseous ozone concentration (Figures 2b and 9b).

Table 3 presents also the relationship between operation costs and reaction time. The reaction time depended on the influent concentration of pollutants, levels of byproducts, and the influent ozone concentration. It should be noted that oxygen costs which account for 89% of the total operation expenses, remain the most important contribution to final costs. In fact, the cost of oxygen for water treatment was established to be 2.63 €/m<sup>3</sup> out of the total spending of 2.96 €/m<sup>3</sup> in case of phenol reduction.

Electricity costs were estimated based on the power consumption during a given process. It was calculated at a rate of 0.10 €/kWh. The estimated price of oxygen was 0.7 €/m<sup>3</sup>. These prices were obtained from standard industrial suppliers (Air Liquid France and EDF France). It is thus estimated that reductions of phenol alone and mixtures of phenol, benzene and cyanides cost from 3 €/m<sup>3</sup> to 6 €/m<sup>3</sup>. In a slightly different way Sievers (2011) estimated costs from 0.01 to 0.4 €/m<sup>3</sup> wastewater, taking into account a generalized energy demand of 10 kWh/ kg of O<sub>3</sub> generated (Ried et al., 2009), and assuming 0.2 €/kWh for ozone dosages up to 0.2 kg/m<sup>3</sup>. Our estimations are based on experimental data obtained in the ozone pilot, and actual prices of the gas vector oxygen and electricity.

These costs could be reduced if the ozone was generated from dry air. However, if we had used the air as a carrier gas, we would not have made savings anyway since the generation of ozone in the air is more energy consuming than the case of oxygen, and secondly we would not have reached the

ozone concentrations at which we have worked since the air concentrations are limited to a maximum of 60 g/m<sup>3</sup> TPN.

## **CONCLUSION**

The innovative semi-industrial pilot plant was successfully tested in the treatment of phenol, benzene and cyanides aqueous mixtures by ozonation. Phenol solutions were degraded between 10 and 20 min regardless of the experimental conditions; however phenol can be removed in less than 10 min at high pH. Phenol and benzene in mixtures were simultaneously oxidized within 10 min, however no significant effect of pH was observed in their degradation; whereas cyanides were removed in around 30 min at neutral and high pH. Therefore the best compromise for simultaneous ozonation of these pollutants would be to treat them at a concentration of ozone of 90 g TPN/m<sup>3</sup> and pH 7 for 30 min.

The results presented here confirm the effectiveness of the innovative ozone pilot for degrading phenol alone or in mixtures with other pollutants such as benzene and cyanides. A relationship was observed between the effluent gaseous ozone concentration and the progression of other ozonation parameters in the contactor, in a clear way, it is possible to control the ozonation process by just checking the levels of the gaseous ozone effluent.

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## FIGURES AND TABLES CAPTIONS

**Figure 1.** (a) Scheme of a 400 L semi-industrial pilot setup for ozone-based advanced oxidation process and (b) its real picture. 1-ozone gas generator, 2-reactive tank, 3-reactor, 4-recirculation column, 5-acid/base tank)

**Figure 2.** Phenol ozonation in a semi-industrial pilot ( $[\text{phenol}] = 50 \text{ mg/L}$ ;  $[\text{ozone}]_{\text{input}} = 90 \text{ g/m}^3$ ;  $\text{pH} = 7$ ). Time course of (a) TOC, COD, phenol, inlet and outlet ozone gas, and (b) byproducts.

**Figure 3.** Effect of influent gaseous ozone concentration on phenol degradation. (a) Evolution of phenol concentration over time during the ozonation of phenol at 50 mg/L and pH 10; (b) Evolution of phenol concentration over time during the ozonation of phenol at 50 mg/L and pH 7.

**Figure 4.** Effect of influent gaseous ozone concentration on phenol degradation. (a) Changes of the ratio  $\text{COD}/\text{COD}^0$  over time during the ozonation of phenol at 50 mg/L and pH 10 (b) Changes of the ratio  $\text{COD}/\text{COD}^0$  over time during the ozonation of phenol at 50 mg/L and pH 7.

**Figure 5.** Effect of influent phenol concentration. Phenol degradation over time by ozonation at  $90 \text{ g O}_3/\text{m}^3$  and pH 7.

**Figure 6.** Effect of influent phenol concentration. Evolution of  $\text{COD}/\text{COD}^0$  ratios over time during phenol degradation by ozone at  $90 \text{ g O}_3/\text{m}^3$  and pH 7.

**Figure 7.** Effect of pH on phenol degradation. Change of phenol levels over time at different pH during ozonation at  $90 \text{ g O}_3/\text{m}^3$  and phenol at 50 mg/L for each one of the pH tested.

**Figure 8.** Effect of pH on phenol degradation. Evolution of  $\text{COD}/\text{COD}^0$  ratios over time at different pH during phenol ozonation at  $90 \text{ g O}_3/\text{m}^3$  and phenol at 50 mg/L.

**Figure 9.** a) Degradation of phenol, benzene and cyanides by ozone; b) evolution of TOC, COD and influent and effluent gaseous ozone content as a function of reaction time ( $[\text{phenol}] = 50 \text{ mg/L}$ ,  $[\text{benzene}] = 10 \text{ mg/L}$ ,  $[\text{NaCN}] = 50 \text{ mg/L}$ ,  $[\text{ozone}] = 90 \text{ g/m}^3$ , flow rate of ozone gas =  $3 \text{ m}^3/\text{h}$ ,  $\text{pH} = 7$ )

**Figure 10.** Effect of ozone content on the degradation of benzene ([benzene] = 10 mg/L, [ozone] = 70, 90 and 140 g/m<sup>3</sup>, flow rate of ozone gas = 3 m<sup>3</sup>/h, pH = 7)

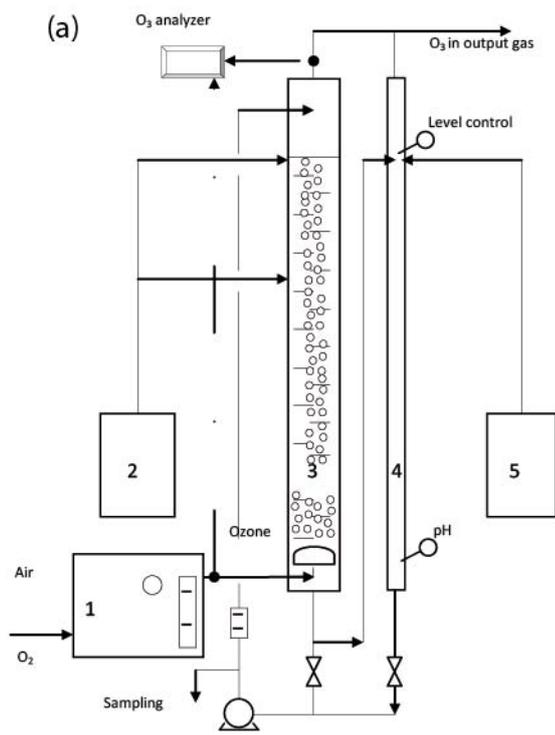
**Figure 11.** Effect of influent ozone content on the degradation of phenol by ozone ([phenol] = 50 mg/L, [ozone] = 70, 90 and 140 g/m<sup>3</sup>, flow rate of ozone gas = 3 m<sup>3</sup>/h, pH = 7)

**Figure 12.** Effect of influent ozone content on the degradation of cyanides by ozone ([CN<sup>-</sup>] = 50 mg/L, [ozone] = 70, 90 and 140 g/m<sup>3</sup>, flow rate of ozone gas = 3 m<sup>3</sup>/h, pH = 7)

**Table 1.** Experimental conditions on phenol ozonation in the semi-industrial advanced oxidation process pilot.

**Table 2.** Stoichiometric factors of phenol removal by ozonation in the semi industrial pilot. The reactor inlet parameters were ozone at 90 g O<sub>3</sub>/m<sup>3</sup>, phenol at 50 mg/L, and pH 7.

**Table 3.** Optimal conditions and operation costs for the degradation by ozonation of phenol alone and simultaneous oxidation of mixtures of phenol, benzene and cyanides.



**Figure 1**

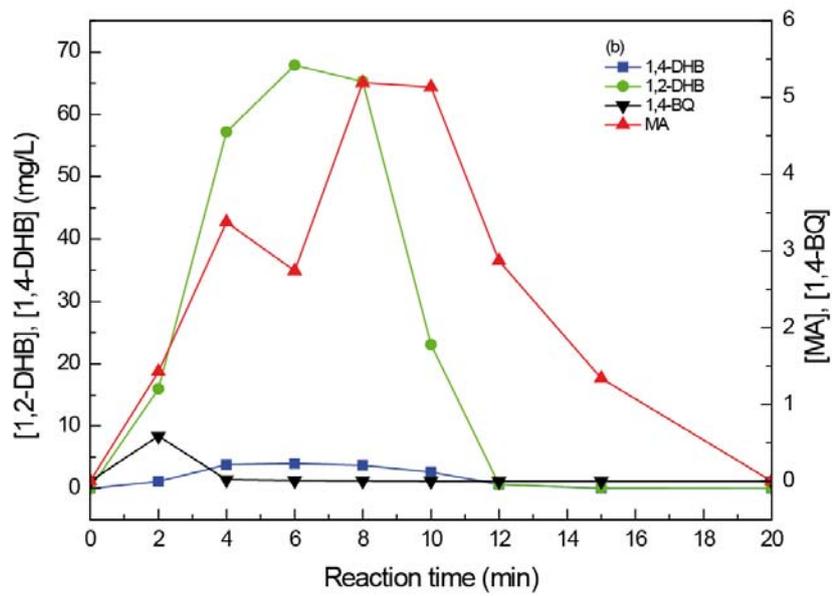
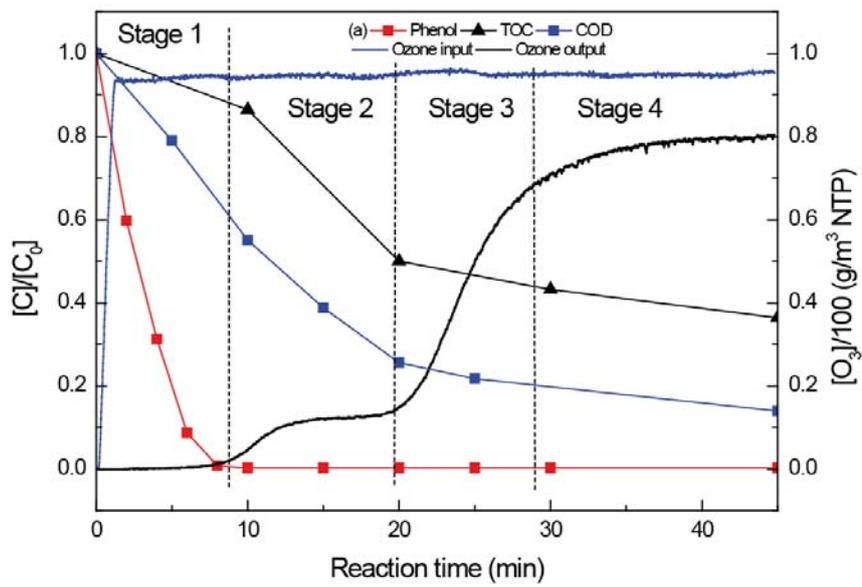


Figure 2

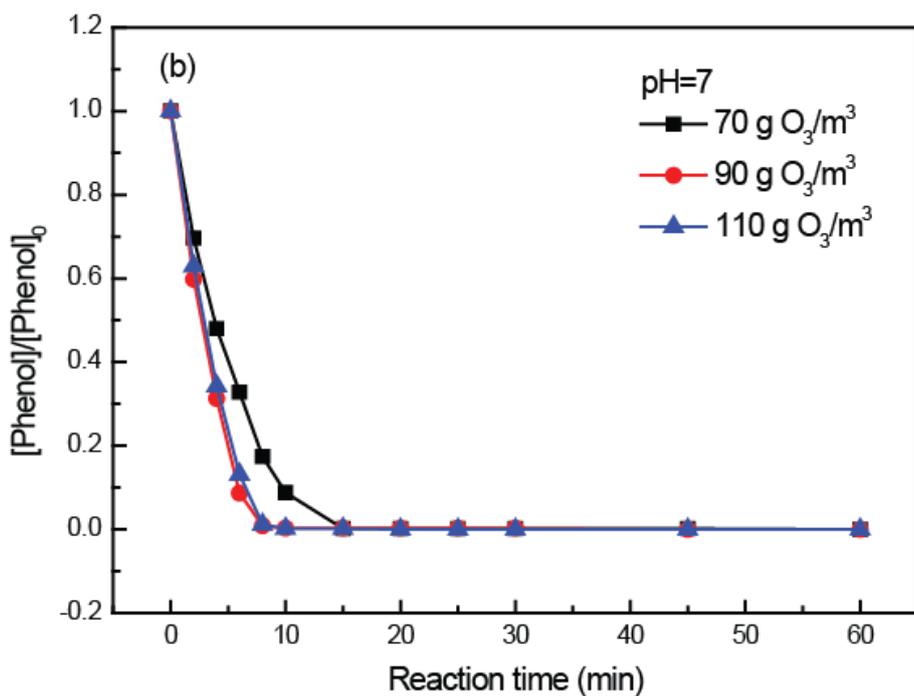
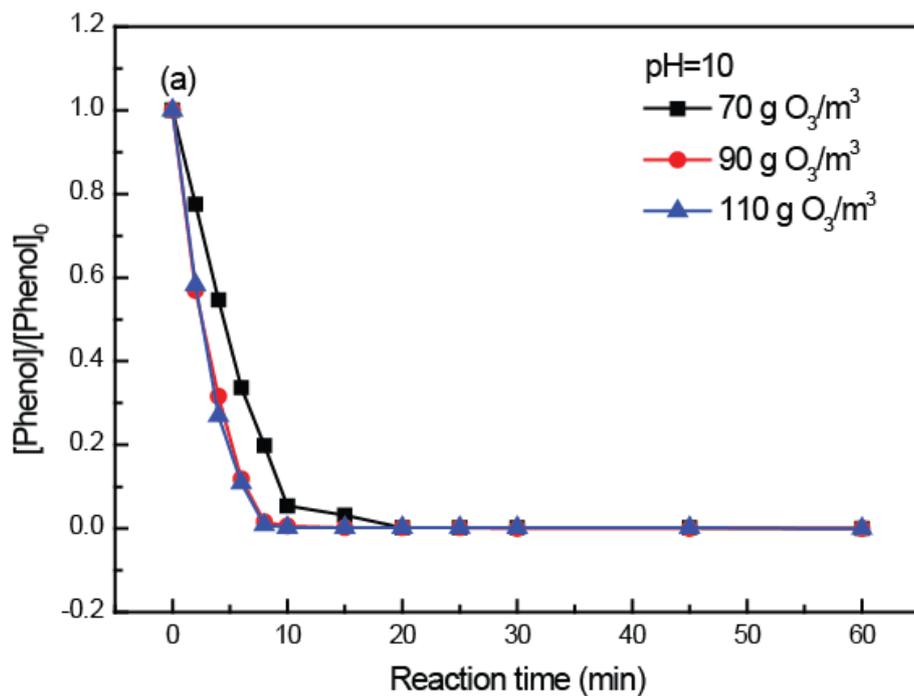


Figure 3

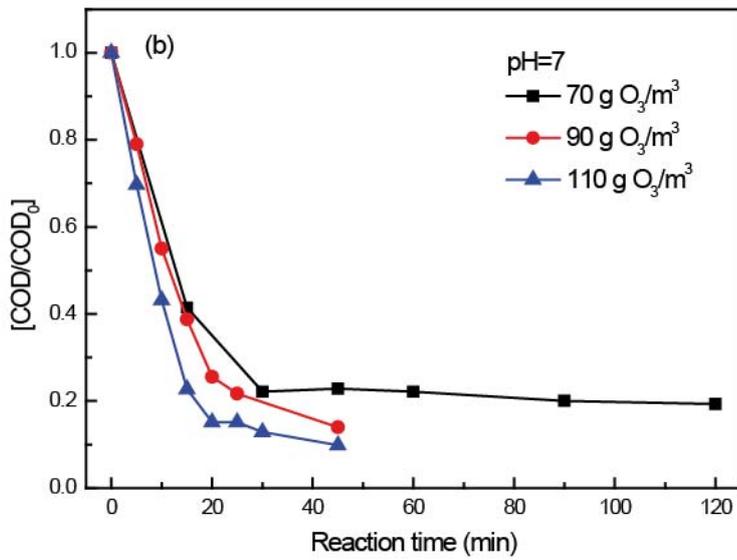
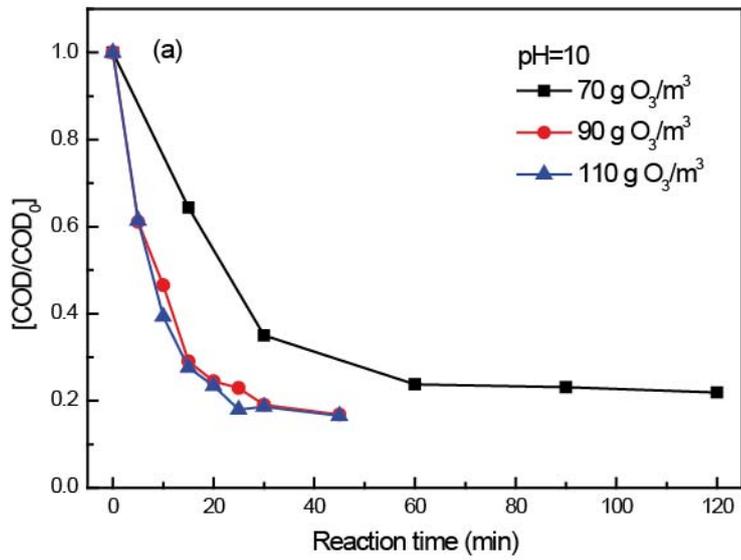


Figure 4

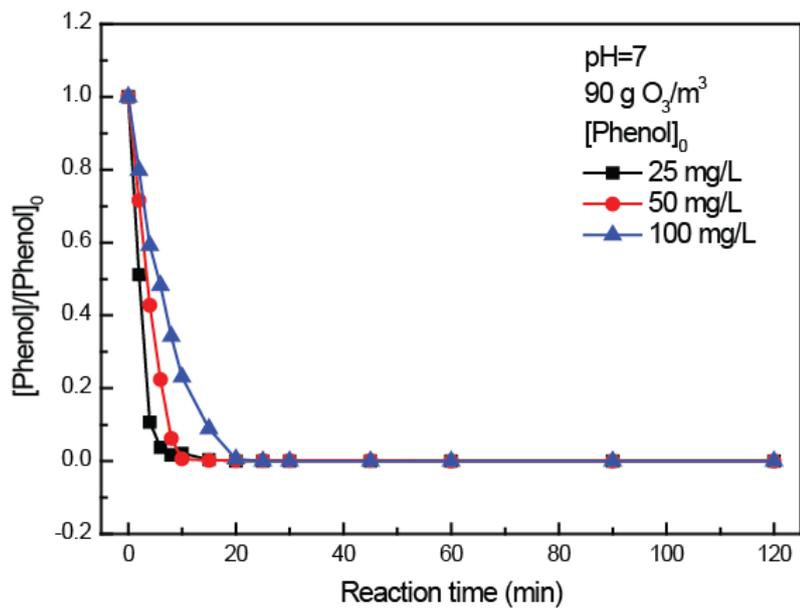
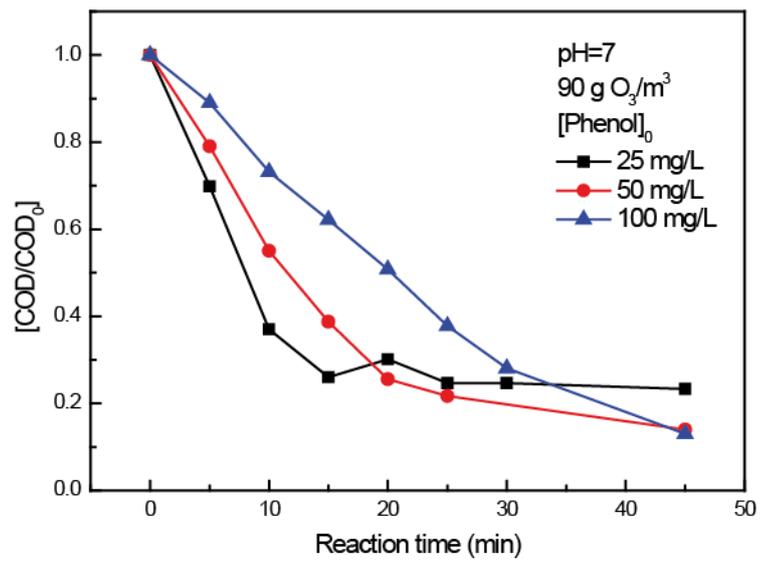


Figure 5



**Figure 6**

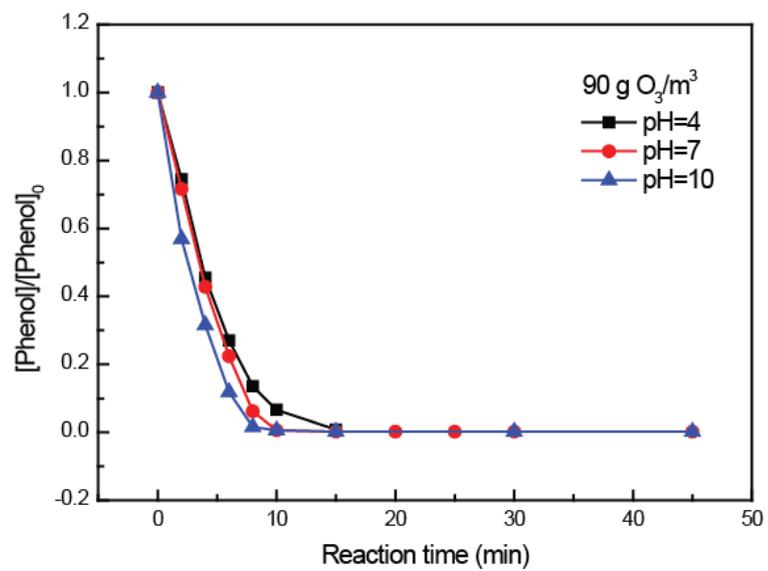


Figure 7

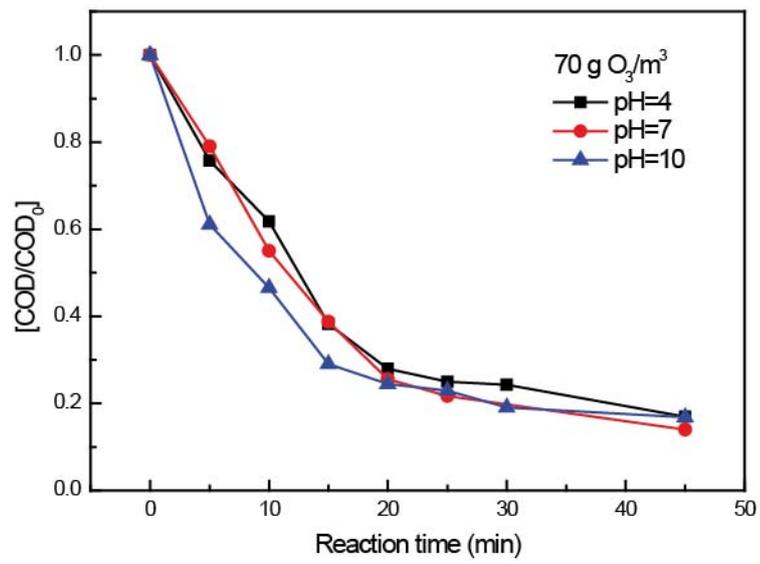


Figure 8

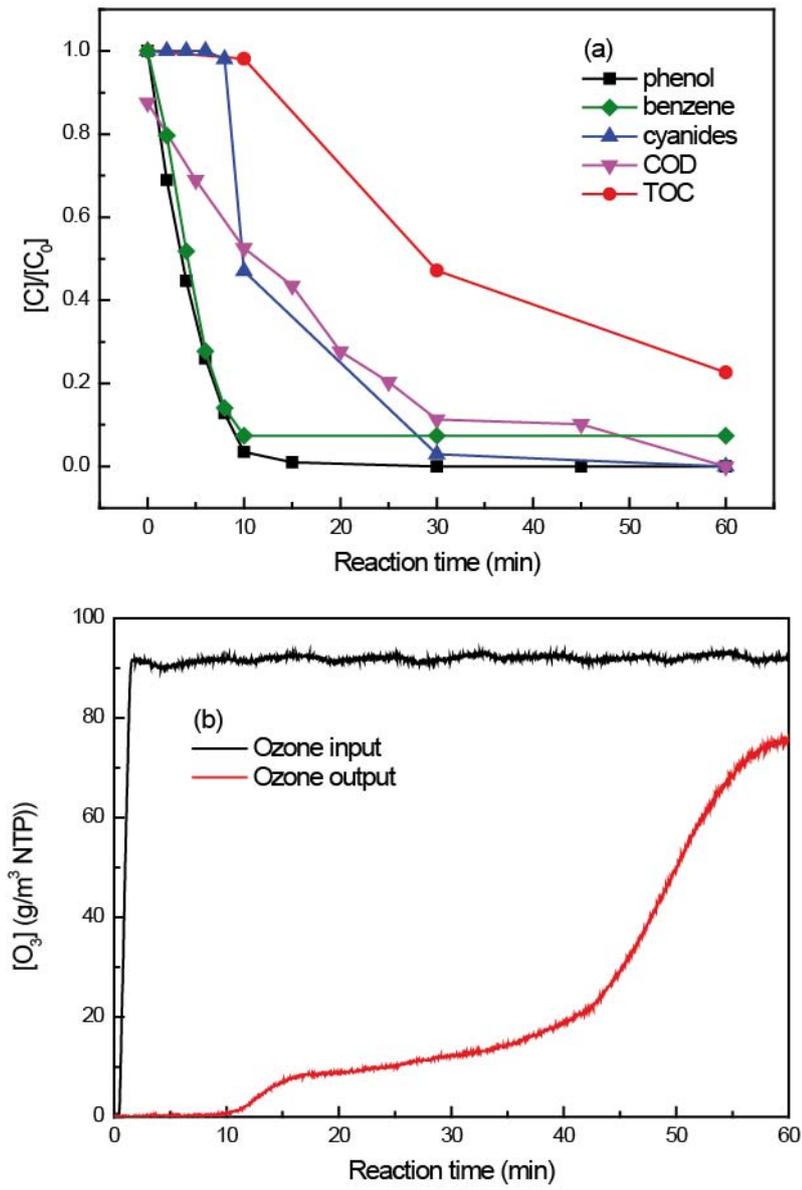
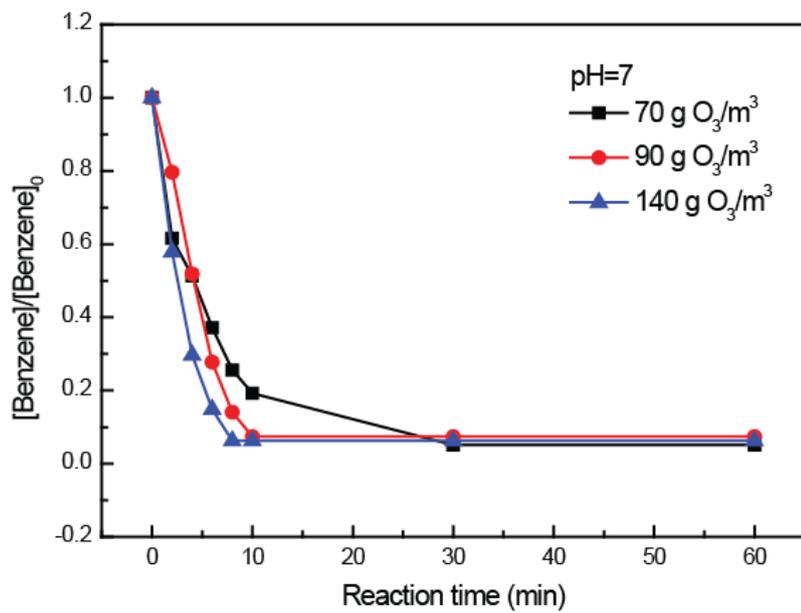
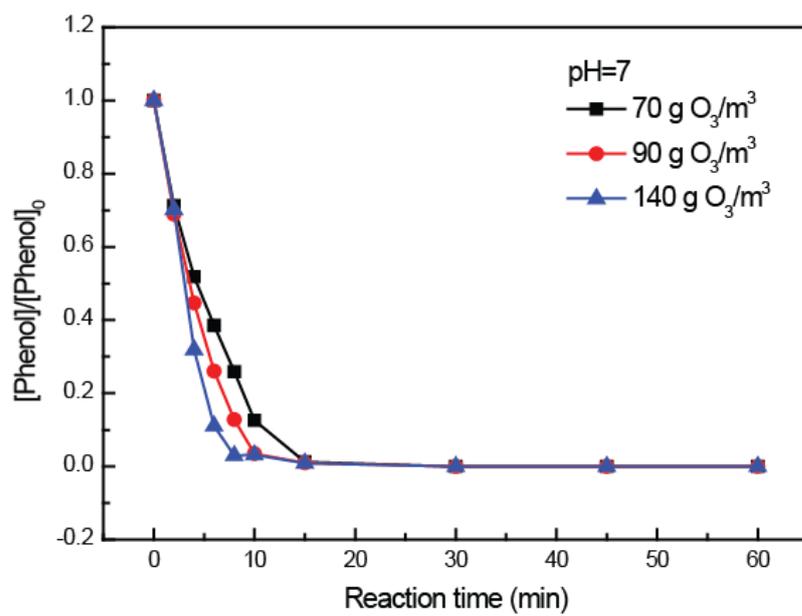


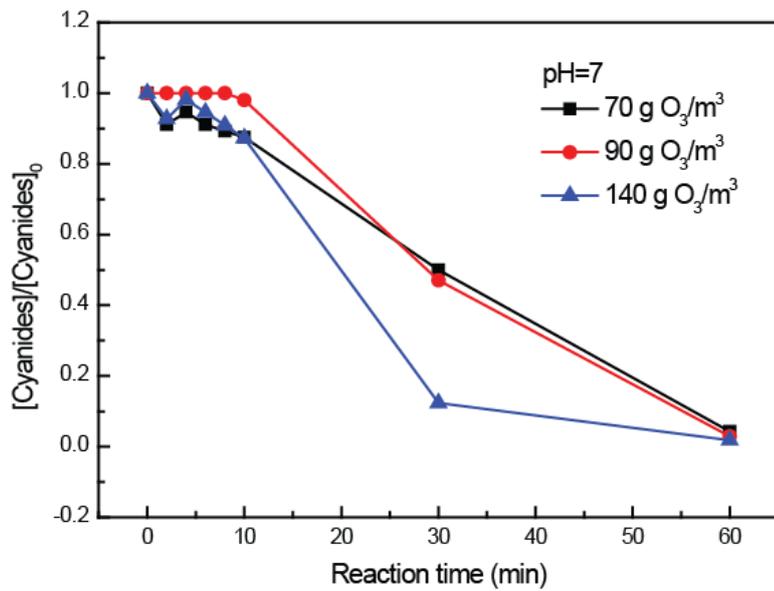
Figure 9



**Figure 10**



**Figure 11**



**Figure 12**

**Table 1**

Test series	Phenol initial concentration (mg/L)	Influent ozone concentration (g/m <sup>3</sup> )	pH
1	50	70	7
2	50	70	10
3	25	90	7
4	50	90	7
5	100	90	7
6	50	90	4
7	50	90	10
8	50	110	7
9	50	110	10

**Table 2**

[ozone] (g/m <sup>3</sup> )	70	90	110
Reaction time (min)	Stoichiometric factor O <sub>3</sub> /phenol (mol/mol)		
10	3.4	4.4	5.4
15	5.1	6.6	8.1
45	15.4	19.9	24.3

**Table 3**

Conditions	Phenol degradation	Simultaneous oxidation of phenol, benzene and cyanides
Volume of treated effluent	0.4 m <sup>3</sup>	0.4 m <sup>3</sup>
Ozone flow rate	3 m <sup>3</sup> /h	3 m <sup>3</sup> /h
Ozone content	90 g O <sub>3</sub> /m <sup>3</sup>	90 g O <sub>3</sub> /m <sup>3</sup>
Reaction time	0.5 h	1 h
pH	7	7
Pollutant content	50 mg/L phenol	50 mg/L phenol, 10 mg/L benzene, 50 mg/L cyanides
O <sub>3</sub> applied	135 g	270 O <sub>3</sub>
Energy for O <sub>3</sub> generator	1.35 kwh	2.70 kwh
Price for O <sub>3</sub> generation	0.135 €	0.270 €
Price of oxygen	1.05 €	2.10 €
Effluent treatment cost per m <sup>3</sup>	2.96 €/m <sup>3</sup>	5.93 €/m <sup>3</sup>