

# Limitations of the removal of cyanide from coking wastewater by ozonation and by the hydrogen peroxide-ozone process

N. Pueyo, N. Miguel, J. L. Ovelleiro and M. P. Ormad

## ABSTRACT

The purpose of this study is to compare the efficiency of ozonation and the hydrogen peroxide-ozone process for the removal of cyanide from coking wastewater. The most efficient oxidation process is combined with coagulation-flocculation-decantation and lime-soda ash softening pretreatments. The oxidation in aqueous solution and industrial wastewater (at pH 9.5–12.3) by  $O_3$  was carried out using a range of concentration of consumed  $O_3$  from 10 to 290 mg/L. A molar ratio of  $H_2O_2/O_3$  from 0.1 to 5.2 with different concentrations of  $O_3$  constants was used for the  $H_2O_2-O_3$  process. The maximum cyanide removal obtained in coking wastewater was 90% using a mass ratio of  $O_3/CN^-$  of 9.5. Using lower concentrations of  $O_3$ , cyanide is not removed and can even be generated due to the presence of other cyanide precursor organic micropollutants in the industrial matrix. The concentration of  $O_3$  is reduced to half for the same cyanide removal efficiency if the pretreatments are applied to reduce the carbonate and bicarbonate ions. The cyanide removal efficiency in coking wastewater is not improved if the  $O_3$  is combined with the  $H_2O_2$ . However, the preliminary cyanide removal treatment in aqueous solution showed an increase in the cyanide removal efficiency for the  $H_2O_2-O_3$  process.

**Key words** | aqueous solution, coking effluent, cyanide, hydrogen peroxide, ozone

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## INTRODUCTION

Coking wastewater is a complex industrial waste generated from steelworks, coke processing, the iron industry, the chemical manufacturing industry, etc. (Chang *et al.* 2008; Wen-wu *et al.* 2012). The composition of coke wastewater is multiple and varies from one industry to another. In general, it contains considerable amounts of pollutants including ammonia ( $NH_3$ ), cyanide ( $CN^-$ ), thiocyanate ( $SCN^-$ ) and phenols (Zhang *et al.* 2013). Also, low concentrations of polycyclic aromatic hydrocarbons (PAHs), and nitrogen-, oxygen- and sulfur-containing heterocyclic compounds are also common in this effluent (Burmistrz & Burmistrz 2013). These compounds produce adverse effects on humans, aquatic life and terrestrial life. Cyanide in particular is considered to be a highly toxic substance in all its forms (free cyanide, cyanide salts or metal-cyanide complexes) in very low concentrations (Mudder *et al.* 2001).

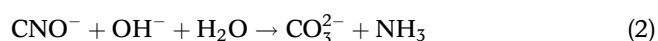
Cyanide is included in the list of priority pollutants issued by the US Environmental Protection Agency (EPA) in its

compilation of recommended water quality criteria and effluent limitations (EPA 2013). European legislation also considers cyanide as a polluting substance (Directive 2010/75/EU). Spanish legislation (Royal Decree 817/2015) classifies cyanide as a Preferential Pollutant due to its significant risk to water quality and establishes a maximum concentration of 40  $\mu g/L$  of total cyanide in continental surface waters.

Cyanide removal in wastewater can be achieved using numerous processes. Conventional oxidation processes are most commonly applied, including biological degradation, alkaline chlorination, the Degussa process (by  $H_2O_2$ ), the INCO process (by  $SO_2/air$ ) or oxidation by Caro's acid (Mudder *et al.* 2001). Biological degradation has been investigated as an effective process at pilot-plant scale but few full-scale processes have operated using this method (Dash *et al.* 2009). In the chlorination process, the pH must be controlled carefully to avoid the release of toxic by-products such as cyanogen chloride (Wedl & Fulk 1991). The Degussa

process requires an accurate measurement of the dosage of hydrogen peroxide (Yeddou *et al.* 2011), while Caro's acid is difficult to handle because it readily decomposes to oxygen and sulfuric acid (Cesar *et al.* 2013). The costs of the INCO SO<sub>2</sub>/air process can be increased if the concentration of cyanide treated is high (Robbins 1996).

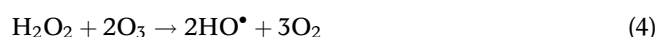
Advanced oxidation processes (AOPs) are considered an alternative method for the treatment of cyanides due to their numerous benefits. Advantages of these processes include the high ability for the removal of cyanide prior to discharge to receiving waterways in order to comply with the discharge regulation and the generation of compounds that are less toxic in comparison with the conventional oxidation processes. However, it is well known that AOPs have high economic costs because their operations often require external energy, chemicals, operators and routine maintenance (Mudder *et al.* 2001; Kim *et al.* 2003). Ozonation is a particularly promising process for treating cyanide effluents. Ozone can react with compounds in water through two mechanisms: directly or indirectly. An indirect mechanism corresponds to the decomposition of ozone at basic pH to generate reactive oxygen species such as hydroxyl, superoxide, hydroperoxide and ozonide radicals (Hoigné & Bader 1976; Glaze *et al.* 1987). The direct reaction of ozone with cyanide produces cyanate (Equation (1)). At basic pH, cyanate hydrolyzes to give ammonia and carbonate (Equation (2)). According to Equations (1) and (2), the stoichiometric mass ratio of O<sub>3</sub> to CN<sup>-</sup> is 4.3. If there is an excess of ozone, cyanate can be oxidized to nitrogen and bicarbonate (Equation (3)) (Khandelwal *et al.* 1959; Gurol & Bremen 1985).



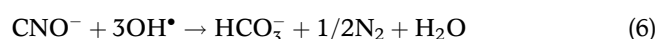
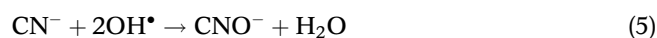
Various studies have analyzed factors that affect the decomposition of cyanide by ozonation including pH, temperature or the presence of metals such as copper and iron (Selm 1959; Gurol & Holder 1988). In the last 15 years different studies have reported the efficiency of ozonation for the removal of cyanide from aqueous solutions (Barriga-Ordóñez *et al.* 2006; Kepa *et al.* 2008) and industrial wastewaters (Van-Leeuwen *et al.* 2003; Monteagudo *et al.* 2004; Chang *et al.* 2008).

It is well known that the decomposition of ozone and the increase in the concentration of reactive oxygen species can be accelerated by the presence of hydrogen peroxide. In the peroxone process, the reaction of hydrogen peroxide

and ozone produces hydroxyl radicals and the stoichiometric molar ratio of H<sub>2</sub>O<sub>2</sub> to O<sub>3</sub> is 0.5 (Equation (4)) (Glaze *et al.* 1987; Paillard *et al.* 1988). An excess of hydrogen peroxide can have an adverse effect on the efficiency of the process applied. This is due to competing reactions that can occur and produce a scavenger effect for the oxidation of pollutants in the water (Paillard *et al.* 1988).



Cyanide reacts with hydroxyl radicals, forming cyanate which subsequently reacts with the hydroxyl radicals to produce bicarbonate, nitrite, nitrate and nitrogen (Equations (5)–(8)) (Kim *et al.* 2003; Monteagudo *et al.* 2004).



Few research studies have compared the efficiency of ozonation with that of the combined hydrogen peroxide and ozone process for the removal of cyanide in water. The results have shown a higher efficiency of cyanide removal by the hydrogen peroxide–ozone process (Kim *et al.* 2003; Monteagudo *et al.* 2004; Kepa *et al.* 2008).

Consequently, the main purpose of this study is to compare the efficiency of ozonation and the hydrogen peroxide–ozone process for the removal of cyanide from coking wastewater. AOPs were previously applied to the oxidation of cyanide from aqueous solutions in order to evaluate the oxidizing power of the agents in the absence of interfering species in the matrix. In addition, the most efficient investigated oxidation process has been combined with a chemical precipitation process in order to obtain a complete treatment not only to obtain the maximum efficiency of cyanide removal, but also to achieve a maximum quality effluent.

## MATERIALS AND METHODS

### Samples

Synthetic wastewater (SW) samples were used in this study in order to analyze the efficiency of processes in the absence

of interfering substances that are often detected in the real matrix. The SW samples were prepared with sodium cyanide (Merck) and MilliQ<sup>®</sup> water. The initial pH of the solutions was adjusted to 12.0 by the addition of sodium hydroxide solution to prevent the liberation of toxic hydrogen cyanide gas. Real wastewater (RW) samples were obtained from an inorganic chemical manufacturing facility located in northwestern Spain. The wastewater emissions resulted from the washing of gases in a scrubber. The samples were collected in glass bottles and transported to the laboratory for tests. Table 1 shows the quality characteristics of the coking wastewater used.

### Analytical methods

The total cyanide was determined following the 4500-D Standard Method using silver nitrate (Panreac) and 5-(4-dimethylaminobenzylidene)rhodanine indicator (Alfa Aesar) (Eaton *et al.* 2005). The alkalinity was determined by the 2320-B Standard Method (Eaton *et al.* 2005). The total hardness and the calcium hardness were determined by the 2340-C Standard Method and the 3500-Ca B Standard Method (Eaton *et al.* 2005), respectively. The total suspended solids (TSS) were determined by the 2540-D Standard Method (Eaton *et al.* 2005).

The pH and the conductivity were measured by a Crison GLP21 pH meter and a Crison Basic 30 conductivity meter, respectively. The ammonia was measured by a Crison GLP22 electrometer and a Hach 51927-00 ammonia-selective electrode. The turbidity was measured by a Hanna LP2000 turbidity meter. The total organic carbon (TOC) was measured by a Shimadzu TOC-VCHS analyzer following the 5310-B Standard Method (Eaton *et al.* 2005).

The identification of organic micropollutants was carried out by a gas-chromatography/mass-spectrometry (GC/MS) analysis and an extraction prior to their analysis (EPA Method 625.1984). This method is based on liquid-liquid extraction with methylene chloride, followed by a division of the extract into acid and bases plus neutral fractions. To 1 mL of both extracts were added 10 mL of anthracene D10 as an internal standard. Finally, the acid and bases plus neutral fractions were analyzed by GC/MS. A Varian 3300 gas chromatograph connected to a Finnigan MAT 800 ITD mass spectrometer was used for identifying the organic micropollutants. The chromatographic conditions were the following: column: DB-5 (J&W Scientific); injection: 2 µL in splitless mode (0.8 min.); injection and detection temperature: 250 and 300 °C; carrier gas: helium (30 cm/s) and temperature program: 60 °C (1 min) – 4 °C – 280 °C (15 min).

**Table 1** | Physicochemical characteristics of the coking wastewater

Global parameter	Range of values
pH (–)	9.5–12.3
Conductivity (mS/cm)	9,800–10,300
Total cyanide (mg CN <sup>–</sup> /L)	4.1–14.7
Alkalinity (mg CaCO <sub>3</sub> /L)	480–510
Total hardness (mg CaCO <sub>3</sub> /L)	2,940–3,070
Calcium hardness (mg CaCO <sub>3</sub> /L)	1,910–2,150
TOC (mg C/L)	50–103
Ammonia (mg NH <sub>3</sub> /L)	209–434
TSS (mg/L)	985–1,460
Turbidity (NTU)	310–380
<b>Identified organic micropollutants</b>	<b>Concentration (µg/L)</b>
<b>PAHs</b>	
Naphthalene	43.1–91.8
Acenaphthylene	17.9–45.7
Phenanthrene	12.8–31.6
Fluoranthene	3.3–13.9
9H-fluorene	3.0–19.1
Pyrene	2.6–12.8
Anthracene	1.0–6.7
1,2-dihydroacenaphthylene	0.9–6.6
Chrysene	0.1–2.4
Benzo[a]anthracene	0.1–1.5
Benzo[b]fluoranthene	<LOQ*–1.4
Benzo[k]fluoranthene	<LOQ–0.7
Benzo[a]pyrene	<LOQ–0.7
Indeno(1,2,3-cd)pyrene	<LOQ
Naphtho[1,2-b]phenanthrene	<LOQ
Benzo[ghi]perylene	<LOQ
<b>Heterocyclic nitrogenous compounds</b>	
Quinoline	47.4–454.6
9H-carbazole	12.5–190.4
1-naphthalenecarbonitrile	<LOQ–12.1
1H-indole	n.d.**–104.9
9H-fluorene-2-carbonitrile	n.d.–7.6
2-methylquinoline	n.d.–5.3
2-methylbenzonitrile	n.d.–0.2

\*Limit of quantification (LOQ): 0.001 µg/L.

\*\*n.d.: not detected.

### Applied processes

The sequence of the processes applied in the combined treatment was coagulation–flocculation–decantation (CFD),

lime–soda ash softening and oxidation. In the SW samples, the oxidation process was carried out directly without using previously the CFD and softening processes. All the tests were done at room temperature.

A CFD process was carried out for the removal of suspended solids in the wastewater. A concentration of polyaluminum chloride (PAXC18) of 4 mg/L was used as a coagulating agent and a concentration of acrylamide copolymer (AS74) of 1 mg/L was added as a flocculating agent. A jar test was carried out using an SBS six-paddle stirrer. The mixing conditions were 3 min of rapid mixing at 200 rpm to simulate the coagulation process and 15 min at 40 rpm to simulate the flocculation process, followed by 30 min of settling time.

A lime–soda ash softening process was carried out for the removal of carbonate hardness (calcium or magnesium carbonate and bicarbonate) and non-carbonate hardness (calcium or magnesium sulfate, chloride and nitrate) (Powell 1974). An optimal concentration of sodium carbonate (Panreac) of 2.4 g/L was used to remove the carbonate hardness and an optimal concentration of calcium hydroxide (Panreac) of 2.0 g/L was added to remove the non-carbonate hardness. A jar test was carried out with the same conditions as for the CFD process. This softening process was combined with the most efficient oxidation process in order to study the effect of this combined treatment on the removal of cyanides in wastewater.

The oxidation by ozone was carried out using a Fischer Model 500 ozonizer. The experimental outline of the ozonation is shown in Figure 1. The ozonizer was connected to a

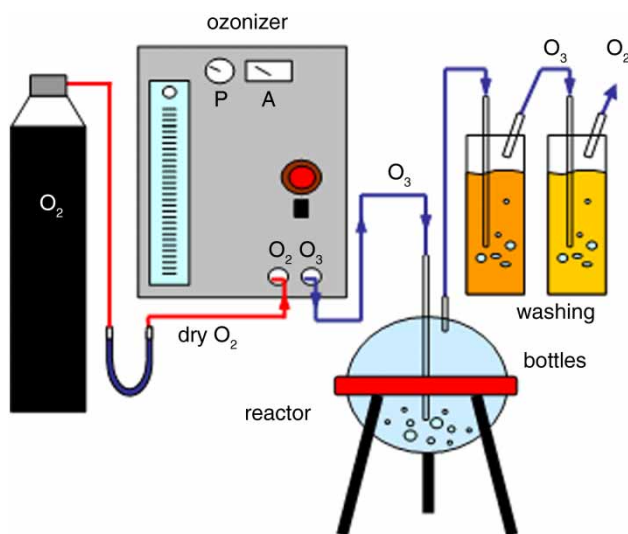


Figure 1 | Experimental outline used for ozonation.

closed glass reactor and ozone was transferred to the sample by a porous diffuser. This produced a mass flow of ozone of 13 mg/min that was passed through 500 mL of sample for different times. The range of the applied ozone ( $O_{3\text{applied}}$ ) was from 11 to 330 mg/L in the SW samples and from 60 to 900 mg/L in the RW samples. The ozone that was not consumed ( $O_{3\text{g-not consumed}}$ ) was absorbed into two washing bottles containing potassium iodide. By the titration of the solutions in the washing bottles with sodium thiosulfate and starch as indicator (Eaton *et al.* 2005), the range of the  $O_{3\text{g-not consumed}}$  was calculated to be from 1 to 180 mg/L in the SW samples and from 5 to 610 mg/L in the RW samples. The waste dissolved ozone ( $O_{3\text{waste-dissolved}}$ ) was measured by the Spectroquant<sup>®</sup> (Merck) ozone test, resulting in 0 mg/L for all the tests. Therefore, the range of the consumed ozone ( $O_{3\text{consumed}}$ ) was from 10 to 150 mg/L in the SW and from 55 to 290 mg/L in the RW according to Equation (9).

$$O_{3\text{consumed}} = O_{3\text{applied}} - O_{3\text{g-not consumed}} - O_{3\text{waste-dissolved}} \quad (9)$$

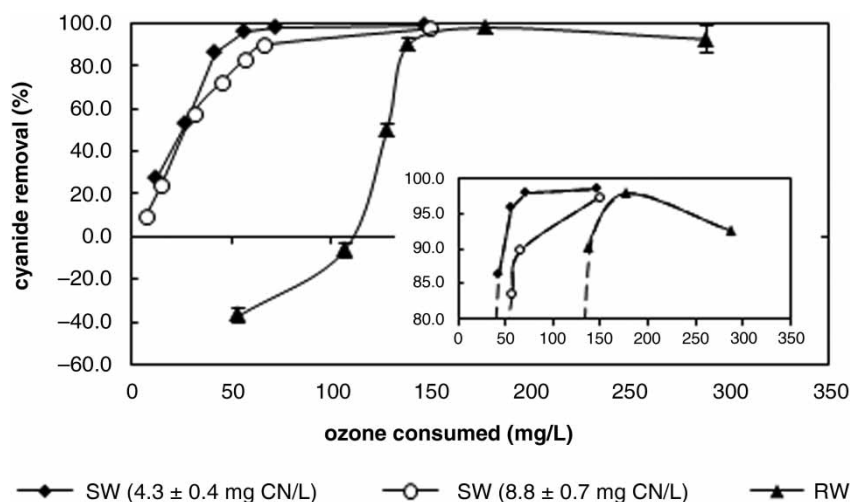
The oxidation by hydrogen peroxide–ozone was carried out with the same experimental outline as that of the ozonation. Hydrogen peroxide was added into the reactor at the beginning of the ozonation. A range of concentration of H<sub>2</sub>O<sub>2</sub> (Panreac) from 1 to 100 mg/L and a concentration of O<sub>3</sub> of 25 mg/L were used in the SW samples. A range of concentration of H<sub>2</sub>O<sub>2</sub> from 25 to 100 mg/L and concentrations of O<sub>3</sub> of 140 and 180 mg/L were used in the RW samples.

All the tests were carried out at least in duplicate. Reproducibility of the results of every duplicated test was checked with statistical analysis, where the confidence percentage was <95%. The results shown in the graphs were obtained as the average of the replicates and the error bar is the standard deviation.

## RESULTS AND DISCUSSION

### Oxidation by ozone

Figure 2 illustrates the percentage of cyanide removal in SW and RW as a function of different concentrations of ozone consumed. The results of ozonation in SW show that the cyanide removal efficiency is increased up to a maximum value if there is an increase in the ozone consumed. For an initial concentration of cyanide of 4.3 mg/L, the maximum cyanide removal efficiency of 96% is achieved with a



**Figure 2** | Ozonation of cyanide in SW and RW. RW initial conditions: pH = 12.1 ± 0.3, cyanide concentration = 14.7 ± 2.6 mg/L.

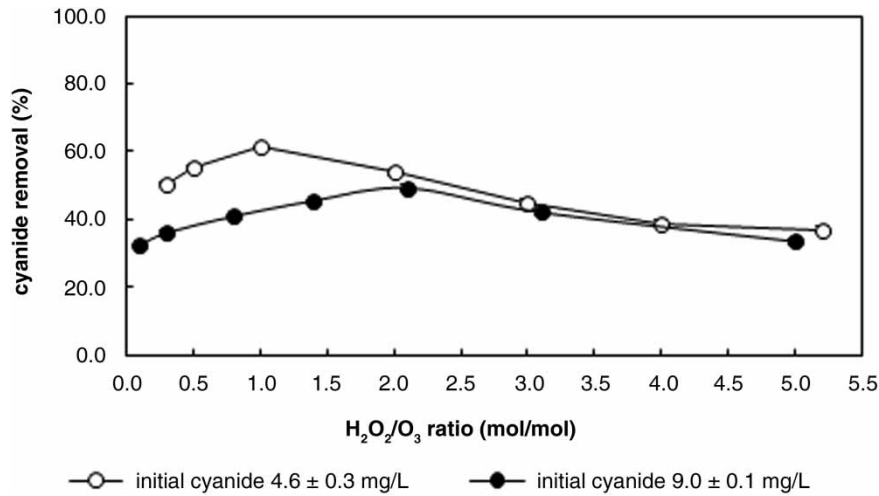
concentration of ozone of 57 mg/L, representing a mass ratio of O<sub>3</sub> to CN<sup>-</sup> of 13.3. However, for an initial concentration of cyanide of 8.8 mg/L, a mass ratio of O<sub>3</sub> to CN<sup>-</sup> of 7.5 is used to achieve a similar cyanide removal efficiency (90%). These mass ratios of ozone to cyanide used in SW are much higher than the stoichiometric mass ratio of 4.3 (Khandelwal *et al.* 1959; Gurol & Bremen 1985). These results are comparable with that obtained by Barriga-Ordoñez *et al.* (2006) in aqueous solution at initial conditions of pH of 11.0 and a concentration of cyanide of 40 mg/L. The cyanide removal efficiency was 93% with a mass ratio of O<sub>3</sub> to CN<sup>-</sup> of 2.2. Kepa *et al.* (2008) obtained a reduction of about 30% of cyanide in aqueous solution (initial pH of 7.0 and initial concentration of cyanide of 0.5 mg/L) with a mass ratio of ozone to cyanide of 14.0. Figure 2 shows that cyanide in RW (initial pH of 12.1 and initial concentration of cyanide of 14.7 mg/L) is not removed and is even generated using lower concentrations of ozone (55 or 107 mg/L). The lower the amount of ozone consumed in the removal of cyanide, the higher the formation of cyanide. This may indicate the presence of other cyanide precursor organic micropollutants in the matrix (Table 1) that react with ozone to form this compound following partial oxidation. Centi *et al.* (1989) studied the dehydration of oximes and similar compounds such as 2-methylbenzoxime by oxygen (Equation (1)) and ammonia (Equation (2)) to give nitriles. Nekrasov *et al.* (1989) showed the formation of cyanide in aqueous solution by the nitriles formed in the above reaction. Cyanide can be formed from other organic micropollutants that have the same functional group such as 1-naphthalenecarbonitrile and 9H-fluorene-2-carbonitrile. For a concentration of ozone of 128 mg/L,

the cyanide removal efficiency is increased up to a value of 50%. When using concentrations of ozone of 139 mg/L or higher (178 and 290 mg/L), the cyanide removal efficiency is increased up to a value of 90%, representing a mass ratio of O<sub>3</sub> to CN<sup>-</sup> of 9.5. Research reported by Van-Leeuwen *et al.* (2003) showed results similar to these for the removal of cyanide in coking wastewater. In particular, a mass ratio of ozone to cyanide of 8.6 was required for the total removal of cyanide from coking wastewater (initial pH of 8 and initial concentration of cyanide of 35 mg/L).

Considering that the maximum concentration of emissions of total cyanide from industrial wastewater is 2.0 mg/L, coking wastewater can be directly discharged to receiving waterways after the ozonation is applied. Also, the concentration of total cyanide after dilution of effluent along the river bed should not exceed 40 µg/L according to the environmental quality standard established in the Royal Decree 817/2015.

### Oxidation by hydrogen peroxide–ozone

The cyanide removal efficiency of the hydrogen peroxide–ozone process in SW increases up to a maximum value by increasing the concentration of hydrogen peroxide with a constant ozone concentration of 25 mg/L (Figure 3). For an initial concentration of cyanide of 4.6 mg/L, the maximum cyanide removal efficiency of 61% is achieved with a molar ratio of H<sub>2</sub>O<sub>2</sub> to O<sub>3</sub> that is double that of the stoichiometric molar ratio of 0.5 (Glaze *et al.* 1987; Paillard *et al.* 1988). For an initial concentration of cyanide of 9.0 mg/L, the molar ratio of H<sub>2</sub>O<sub>2</sub> to O<sub>3</sub> increases up to a value of



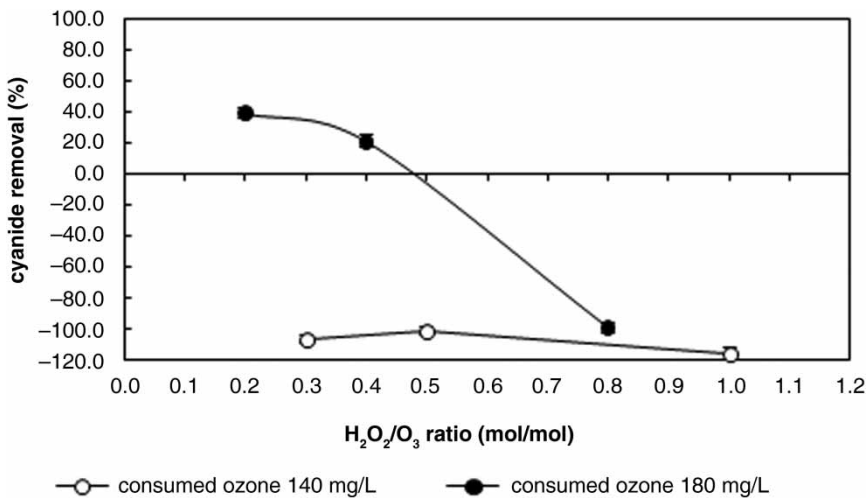
**Figure 3** | Cyanide oxidation from SW at different concentrations of H<sub>2</sub>O<sub>2</sub> (1–100 mg/L) with a constant O<sub>3</sub> concentration of 25 mg/L.

2.1 to obtain a maximum reduction of 49% cyanide in aqueous solution.

Comparing Figures 2 and 3 shows that using a concentration of ozone of 25 mg/L it is possible to remove about 50% of cyanide in SW (initial concentration of cyanide of 5 mg/L). However, the cyanide removal efficiency increases up to a value of 61% if the ozone is combined with hydrogen peroxide. For an initial concentration of cyanide of 9.0 mg/L in SW, the same improvement for the removal of cyanides is obtained by using the hydrogen peroxide–ozone process instead of single ozonation. Consequently, the addition of hydrogen peroxide slightly improves the cyanide removal efficiency in SW. Research reported by *Kepa et al. (2008)* showed an increase in the removal of cyanide in aqueous

solution from 30 to over 70% by using hydrogen peroxide and ozone.

As can be seen in Figure 4, when using a constant ozone concentration of 140 mg/L combined with any concentration of hydrogen peroxide (25, 50 or 100 mg/L), cyanide from coking wastewater is not removed and is even generated. This may indicate the presence of other cyanide precursor organic micropollutants in the matrix (Table 1) that react with hydrogen peroxide and ozone to form this compound following partial oxidation. Cyanide can be formed from similar reaction mechanisms to those described above from organic micropollutants such as 2-methylbenzoxirone, 1-naphthalenecarbonitrile or 9H-fluorene-2-carbonitrile (*Centi et al. 1989; Nekrasov et al. 1989*).



**Figure 4** | Cyanide oxidation from RW at different concentrations of H<sub>2</sub>O<sub>2</sub> (25, 50 and 100 mg/L) with a constant O<sub>3</sub> concentration (140 or 180 mg/L). Initial conditions: pH = 12.3 ± 0.4, cyanide concentration = 11.4 ± 0.5 mg/L.

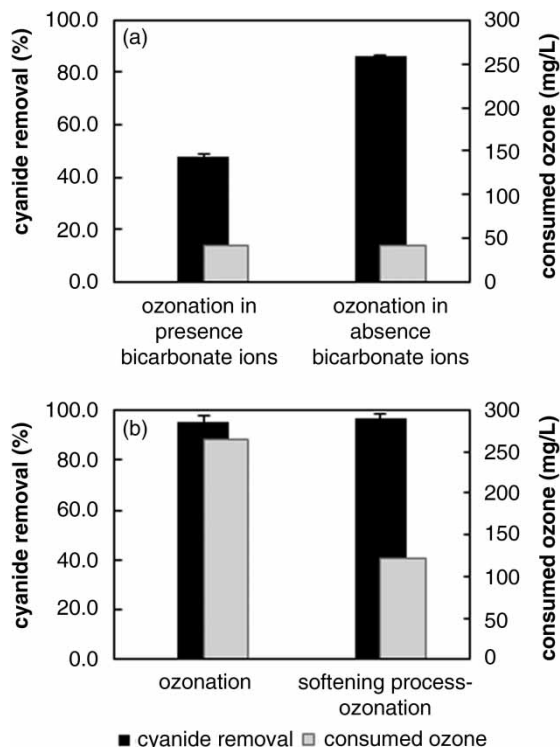
A possible reaction mechanism for the formation of cyanide from the hydrogen peroxide–ozone process of quinoline (and 2-methylquinoline) could be the following: as a first step, the radical intermediate compound (R-C<sup>•</sup>=N) is formed as a result of the reaction between reactive radicals and the organic micropollutants. The second propagation step leads directly to the formation of cyanide (C≡N) (Smith & March 2007). The effect is greater the higher the concentration of hydrogen peroxide used for the removal of cyanide. Cyanide is removed by the hydrogen peroxide–ozone process with a constant ozone concentration of 180 mg/L and a molar ratio of H<sub>2</sub>O<sub>2</sub> to O<sub>3</sub> of 0.2, obtaining a maximum reduction of cyanide of 39%. The cyanide removal efficiency decreases to a value of 21% if the molar ratio of H<sub>2</sub>O<sub>2</sub> to O<sub>3</sub> is doubled with the same concentration of ozone consumed. This result confirms the proposition of Paillard *et al.* (1988) that there is a reduction in the efficacy of the treatment if there is an excess of hydrogen peroxide. This is due to the competitive reactions that can occur and produce a scavenger effect for the oxidation of cyanide in the wastewater. This effect is also analyzed in the research reported by Monteagudo *et al.* (2004). A study by Kim *et al.* (2003) showed an insignificant increase in the cyanide removal efficiency in industrial wastewater when the concentration of hydrogen peroxide was doubled with a constant concentration of ozone.

Comparing Figures 2 and 4 shows that when using the single ozone process (140 or 180 mg/L) it is possible to obtain a higher cyanide removal efficiency (over 90%) than when the ozone is combined with hydrogen peroxide. In contrast to the results obtained for the treatment of the removal of cyanides in SW, the cyanide removal efficiency in RW is reduced by the addition of hydrogen peroxide. Monteagudo *et al.* (2004) reported a reduction of 100% of cyanide in industrial wastewater (initial pH of 9.5 and initial concentration of cyanide of 3 mg/L) by ozonation and the hydrogen peroxide–ozone process with a single optimum concentration of hydrogen peroxide (205.8 mM H<sub>2</sub>O<sub>2</sub>). The cyanide removal efficiencies obtained are lower combining ozone with any concentration of hydrogen peroxide.

### Oxidation by ozone combined with a softening process

The characterization of the coke plant wastewater (Table 1) shows that the RW has a high content of mainly calcium and magnesium ions (measured as total hardness and calcium hardness) and carbonate and bicarbonate ions (measured as alkalinity). It is well known that the presence of carbonate and bicarbonate ions in wastewater can reduce the

efficiency of AOPs due to the hydroxyl radical scavenging-effect (Hoigné & Bader 1976; Gottschalk *et al.* 2000). Accordingly, the effect of the presence or absence of carbonate and bicarbonate ions on the removal of cyanide in SW is first analyzed. Seeing that the maximum removal of cyanides in RW is obtained by ozonation, Figure 5(a) shows the percentages of cyanide removal and the concentrations of ozone consumed applying the ozonation in the presence (with a concentration of sodium bicarbonate of 1 g/L) and absence of bicarbonates in SW. The cyanide removal efficiency is doubled (86%) for the same concentration of ozone (42 mg/L) if the ozonation is applied in the absence of bicarbonate ions in aqueous solution. According to the prediction (Hoigné & Bader 1976; Gottschalk *et al.* 2000), bicarbonate ions in SW have a hydroxyl radical scavenging-effect. If the RW is pretreated by the lime–soda ash softening process, the concentration of ozone consumed is reduced to half (121 mg/L) for the same cyanide removal efficiency of 95% due to the reduction of carbonate and bicarbonate ions in the wastewater (Figure 5(b)). The reaction rate constants for carbonate and bicarbonate ions ( $k = 4.2 \cdot 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$  for carbonate ion and  $k = 1.5 \cdot 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$  for



**Figure 5** | Cyanide oxidation from (a) SW and (b) RW by ozonation combined with the softening process. SW initial condition: cyanide concentration =  $4.5 \pm 0.2$  mg/L and RW initial conditions: pH =  $9.5 \pm 0.0$ , cyanide concentration =  $4.1 \pm 0.0$  mg/L.

bicarbonate ion) are much slower than the reaction rate constant of hydroxyl radicals with cyanide ( $k = 4.5 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ ) but their concentrations are comparatively high, so that these reactions should be considered (Gottschalk *et al.* 2000). Hydroxyl radicals are generated during ozonation so that the consumption of the oxidizing agent is increased by the presence of free radical scavengers.

After the ozonation combined with the softening process, the RW was subjected to a liquid-liquid extraction and GC/MS analysis in order to measure the concentration of the organic micropollutants (Table 1). The concentration of the identified micropollutants in the RW is presented in Table 2. As can be seen, the treatment of ozone combined with the softening process is efficient for removing the

organic micropollutants, both the PAHs and the heterocyclic nitrogenous compounds.

Consequently, the combined treatment formed by the CFD, the lime-soda ash softening and the ozonation is the most efficient investigated treatment in order to obtain a complete treatment for the removal of suspended solids, carbonate hardness and non-carbonate hardness, cyanide and organics micropollutants from coking wastewater.

## CONCLUSIONS

The main conclusions that can be drawn from this study are summarized below.

- Ozonation is efficient for the removal of cyanide from coking wastewater using a mass ratio of O<sub>3</sub> to CN<sup>-</sup> of 9.5 to obtain a cyanide removal efficiency of 90%. Using lower concentrations of ozone, cyanide is not removed and can even be generated due to the presence of other cyanide precursor organic micropollutants in the matrix that react with the ozone to form cyanide following partial oxidation.
- The hydrogen peroxide-ozone process is more efficient than ozonation for the removal of cyanide from aqueous solution at high pH due to the addition of hydrogen peroxide, which accelerates the decomposition of ozone and increases the hydroxyl radical concentration. However, using the single ozonation it is possible to obtain a higher cyanide removal efficiency in coking wastewater than with ozone combined with hydrogen peroxide.
- The lime-soda ash softening pretreatment reduces the carbonate and bicarbonate ions in coking wastewater, and consequently the concentration of ozone consumed is reduced to half for the same cyanide removal efficiency of 95%. The presence of carbonate and bicarbonate ions increases the consumption of the oxidizing agent due to the hydroxyl radical scavenging-effect.
- The cyanide removal treatment in coking wastewater with ozone combined with the softening process is efficient for the removal of organic micropollutants formed mainly by PAHs and quinolines.

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**Table 2** | Organic micropollutants identified by GC/MS in RW and the concentration after ozonation combined with the softening process. Initial conditions: pH = 9.5 ± 0.0, cyanide concentration = 4.1 ± 0.0 mg/L, consumed ozone = 121 mg/L

Identified organic micropollutants	Concentration (µg/L)
<b>PAHs</b>	
Naphthalene	<LOQ*
Acenaphthylene	0.002
Phenanthrene	<LOQ
Fluoranthene	<LOQ
9H-fluorene	<LOQ
Pyrene	<LOQ
Anthracene	<LOQ
1,2-dihydroacenaphthylene	<LOQ
Chrysene	<LOQ
Benzo[a]anthracene	<LOQ
Benzo[b]fluoranthene	<LOQ
Benzo[k]fluoranthene	<LOQ
Benzo[a]pyrene	<LOQ
Indeno(1,2,3-cd)pyrene	<LOQ
Naphtho[1,2-b]phenanthrene	<LOQ
Benzo[ghi]perylene	<LOQ
<b>Heterocyclic nitrogenous compounds</b>	
Quinoline	n.d.**
9H-carbazole	n.d.
1-naphthalenecarbonitrile	n.d.
1H-indole	n.d.
9H-fluorene-2-carbonitrile	n.d.
2-methylquinoline	n.d.
2-methylbenzonitrile	n.d.

\*Limit of quantification (LOQ): 0.001 µg/L.

\*\*n.d.: not detected.



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