COMBINED TREATMENT USING OZONE FOR CYANIDE REMOVAL FROM WASTEWATER: A COMPARISON

(Tratamiento combinado con el uso de ozono para la remoción de cianuro de efluentes: una comparación)

Jefferson MORILLO ESPARZA, Nicolás CEVALLOS CUEVA, Christian SANDOVAL PAUKER,
Paul VARGAS JENTZSCH and Florinella MUÑOZ BISESTI*

Departamento de Ciencias Nucleares, Facultad de Ingeniería Química y Agroindustria, Escuela Politécnica Nacional, Ladrón de Guevara E11-253, 170525 Quito, Ecuador
*Corresponding author: florinella.munoz@epn.edu.ec

ABSTRACT

Cyanidation is widely used by several gold mining companies worldwide. Since its wastewaters contain cyanide, appropriate treatments must be applied to remove this pollutant. Combinations of ozone (O_3), hydrogen peroxide (H_2O_2) and activated carbon (AC) can be used for this purpose. In this work, synthetic cyanide solutions ($[CN^-]_o = 15.37$ mM) were treated using O_3 and the combinations O_3/H_2O_2, O_3/AC and $O_3/H_2O_2/AC$ under alkaline conditions. O_3 was produced from dry oxygen at a rate of 2.51 g O_3/h ($[O_3]$ gas-phase $= 6.9 \times 10^{-2}$ g/L). The concentration of cyanide (CN^-) and O_3 consumption were measured and the performance of the treatments evaluated. The highest cyanide removal was reached at pH 11.0 for all cases and with 10 mg H_2O_2/ mg O_3 upon adding H_2O_2. In contrast, the addition of AC did not improve the cyanide removal in comparison with O_3 alone. The best cyanide removal was achieved with the combination O_3/H_2O_2 followed by the combination $O_3/H_2O_2/AC$. Moreover, cyanidation effluents were treated using the combination O_3/H_2O_2. In this case, almost a total removal of free cyanide was achieved after 3 min of treatment.

Palabras clave: ozonificación, peróxido de hidrógeno, sistema peroxona, carbón activado, cianuración

RESUMEN

El proceso de cianuración es ampliamente utilizado en la industria minera alrededor del mundo. Las aguas residuales de este proceso contienen cianuro, lo cual obliga al uso de tratamientos apropiados para su remoción. Para ello, se pueden utilizar combinaciones de ozono (O_3), peróxido de hidrógeno (H_2O_2) y carbón activado (CA). En este trabajo se trataron, soluciones sintéticas de cianuro ($[CN^-]_o = 15.37$ mM) con el uso de O_3 y las combinaciones O_3/H_2O_2, O_3/CA y $O_3/H_2O_2/CA$ en condiciones alcalinas. Se produjo O_3 a partir de oxígeno seco con una producción de 2.51 g O_3/h ($[O_3]$ fase gaseosa $= 6.9 \times 10^{-2}$ g/L). Se evaluó el comportamiento de cada proceso y se midió la concentración de cianuro (CN^-) y el consumo de ozono durante los tratamientos. La mayor remoción de cianuro se alcanzó a pH 11.0 para todos los casos. Al añadir H_2O_2 la remoción fue mayor al usar 10 mg H_2O_2/mg O_3. Por otra parte, la adición de CA no

aumentó la remoción de cianuro en comparación al tratamiento sólo con O_3. La mejor remoción de cianuro fue alcanzada con la combinación O_3/H_2O_2 seguida de la combinación $O_3/H_2O_2/AC$. Posteriormente, se trataron efluentes del proceso de cianuración con la combinación O_3/H_2O_2. En este caso, se requirieron 3 min de tratamiento para la remoción total del cianuro libre.

INTRODUCTION

Gold has been a subject of fascination since ancient times. It is well known that this metal had also a religious and even mythical significance due to its remarkable stability. Ancients used gold to produce jewelry, sculptures, vessels, coinage as well as decoration for monuments and buildings, among others (Akcil 2002, Akcil 2003). Gold was used as commodity money during centuries and its accumulation was correlated to "social power" and even triggered wars. On this field, Schoenberger (2011) published an interesting discussion on the historical value of gold. In modern times, the importance of gold has not declined and is a well-known fact that this commodity supports the world economy. Taking into account that gold still plays a fundamental role in modern society and economy, huge projects around the world have focused on the exploitation of low-grade gold ores. To extract and concentrate gold, some processes were developed and typically been used in gold mining worldwide. The most important process currently used to separate gold from the ores is cyanidation.

Cyanidation, which was developed in Scotland in 1887 (Habashi 1987), is widely used in the USA, Canada, Turkey as well as in several developing countries (Akcil 2002, Eisler and Wiemeyer 2004, Veiga et al. 2014). It consists in the dissolution of gold from the ore in an alkaline dilute cyanide solution. Later, gold is recovered from the solution using either activated carbon, zinc or ion-exchange resins (Eisler and Wiemeyer 2004) and important amounts of cyanide remain in solution in the form of free cyanide or as complexes of other metals (Donato et al. 2007). It is difficult to establish the average consumption of water for the operation of gold mining companies since this depends on a variety of factors including the type of ores, the degree of water recycling, the technology used for the extraction and even the characteristics of the site, among others (Mudd 2007). However, there is a consensus of opinion among the scientific community and society that gold mining activities have a very strong environmental impact, and most of these impacts are due to wastewaters. Both quality and quantity are problems when it comes

to evaluating the wastewater issue of gold mining activities since huge amounts of cyanide-polluted water are generated and must be adequately treated. Considering that cyanidation has gained a bad reputation in the eyes of the public, alternative lixiviants for gold ores were explored (Hilson and Monhemius 2006). However, although these remarkable efforts, it seems that cyanidation dominance in the gold mining industry will prevail in years (or decades) to come. Therefore, treatment processes to remove cyanide from the water were (and are still) subject of intense study in the last decades.

Some well-known treatment processes to remove cyanide from gold mining wastewaters are natural cyanide degradation (in tailings ponds), biological processes, chemical processes, electrolytic oxidation and other methods such as evaporation (applied in arid regions) (Kuyucak and Akcil 2013). Probably the most applied process, due to its simplicity, is the natural cyanide degradation in tailings ponds. This process basically involves the storage of wastewaters in ponds exposed to the environment and the degradation of cyanide takes place through different natural mechanisms (volatilization, photodecomposition, chemical oxidation, microbial oxidation, hydrolysis and precipitation). The great disadvantage of this treatment is the low degradation rate, therefore enormous volumes of polluted water must be stored for long periods of time with the subsequent possibility of incidents and accidents. In fact, countless big accidents involving tailings dams happened in the past, data from some of them were compiled in earlier publications (Mudder and Botz 2004, Rico et al. 2008). However, not only incidents and accidents are responsible for negative environmental impacts; Donato et al. (2007) have extensively discussed the impact of gold cyanide-bearing tailings solutions on wildlife and their arguments suggest that wildlife deaths due to "correctly" operated and controlled tailings ponds could be underestimated.

Concerning biological processes, many researchers reported in the past the application of different microorganisms for the removal of cyanide from wastewaters (specially, from gold mining) (Evangelho et al. 2001, Akcil and Mudder 2003, Ebel et

al. 2007, Mekuto et al. 2015, Mekuto et al. 2016). Although biological systems have interesting advantages, as described by Akcil (2003), there are also limitations related to operational conditions. For instance, biological systems are often sensitive to load fluctuations in both flow rate and pollutant charge. Therefore, under certain circumstances, chemical processes are preferred, and many options were studied (Mudder and Botz 2004, Kuyucak and Akcil 2013).

The oxidation of cyanide with hydrogen peroxide is a widely used chemical method because it does not produce dangerous by-products or harmful environmental pollutants (Chergui et al. 2015). Some studies showed that higher performances in the removal of cyanide can be reached by the combined action of hydrogen peroxide and other materials such as activated carbon (plain and metal-impregnated) (Deveci et al. 2006, Yeddou et al. 2010, Yeddou et al. 2011), activated alumina (Chergui et al. 2015) and copper-impregnated pumice (Kitis et al. 2005). The combined effect of hydrogen peroxide and ozone on the oxidation of cyanide was also tested and remarkable results were reported by Monteagudo et al (2004). The results reported by these authors showed that cyanide removal was improved when hydrogen peroxide and ozone were combined for the treatment. Such improvement was attributed to the formation of hydroxyl radicals ($^\bullet$OH), a very strong oxidant agent. Processes using $^\bullet$OH radicals for the degradation of pollutants are known and grouped as advanced oxidation processes (AOPs) and have several applications in wastewater treatment (Oturan and Aaron 2014). Considering the mentioned aspects, a treatment in which an activated carbon, hydrogen peroxide and ozone are combined could improve the treatment of wastewaters containing cyanide.

In this work, the removal of cyanide was tested using activated carbon, hydrogen peroxide and ozone. The performance of treatments combining hydrogen peroxide and ozone, activated carbon and ozone, as well as ozone, hydrogen peroxide and activated carbon, was evaluated and discussed. These results can provide insights to perform improvements in existing systems and/or the development of new systems for the treatment of wastewaters containing cyanide.

EXPERIMENTAL AND METHODS

Reagents

Synthetic solutions of NaCN (400 mg/L, 15.37 mM) were prepared using NaCN (> 95 %, Sigma-Aldrich).

The pH values of the NaCN solutions were adjusted with a 0.1 N aqueous solution of NaOH (99.0 %, Merck). H_2O_2 (30 % w/w, Scharlau) and commercial activated carbon (PanReac AppliChem, ref: 121237, d80 < 38 μm) were used during the treatments in combination with O_3 (see ozonation system description below). For the measurement of O_3, 2 % w/w KI (99.0 % PanReac AppliChem), 2N $Na_2S_2O_3 \cdot 5H_2O$ (99.0 %, Baker) and 2N H_2SO_4 (97 %, Merck) aqueous solutions were prepared. All the solutions were prepared with double distilled water.

Measurement of cyanide concentration

The concentration of cyanide (CN^-) was measured using a colorimetric method (Standard Method 4500-CN-E, in a range from 0.02 to 0.2 mg/L CN^-) in a Hach DR2800 spectrophotometer. In addition, a cyanide – selective electrode method (4500-CN-F, in a range from 0.05 to 10 mg/L CN^-) with a Thermo Orion 9606BNWP electrode, was also used.

Ozonation system description

Ozone (O_3) was produced from dry oxygen (99.999 %, AGA) using a Philaqua BMT 802M generator at an approximate dose of 2.51 g O_3/h ([O_3]$_{gas-phase}$ = 6.9x10^{-2} g/L). O_3 was transferred to 90 mL samples of cyanide solutions through a porous diffuser. The concentrations of the O_3 feed (at the inlet of the reactor) and the O_3 not consumed (at the outlet of the reactor) were measured by the iodometric titration method (Standard Method 2350-E). The amount of consumed O_3 was calculated at different times by applying a mass balance into the reactor. All the tests were carried out at room temperature (~20 ºC).

Influence of activated carbon and H_2O_2 doses and pH on cyanide removal and O_3 consumption

90 mL samples of synthetic cyanide solutions (400 mg/L, 15.37 mM) were treated using O_3 alone and the combinations O_3/H_2O_2, O_3/AC and $O_3/H_2O_2/AC$ at two pH values (10 and 11). Consumed O_3 and CN^- removal were determined at different times for 7.5 min (the experiment was carried out separately for each time). All runs were carried out in triplicate. Additionally, the statistical software Statgraphics Centurion XVI (version 16.1.03) was used to compare the treatments.

The treatment using the combination H_2O_2/O_3 was performed at different ratios of H_2O_2/O_3 feed (2.0, 5.0 and 10.0 mg H_2O_2/mg O_3). When the combination AC/O_3 was employed, three different AC dosages of 0.3, 0.5 and 1.0 g/L were used. The surface area, pore

diameter and pore volume of the activated carbon were measured using a Quantachrome Instruments Nova4200e surface area and pore size analyzer by the Brunauer-Emmett-Teller (BET) method. The point of zero charge (PZC) of the activated carbon was determined using the method reported by Newcombe et al. (1993).

The conditions of the treatments with O_3, H_2O_2/O_3 and AC/O_3 that allowed the highest cyanide removal were selected for the treatment with the combination $O_3/H_2O_2/AC$. Additionally, tests with H_2O_2 and activated carbon alone were carried out for comparative purposes.

Characterization and treatment of samples from cyanidation effluents

In order to assess if the treatment (O_3, O_3/AC, O_3/H_2O_2, or $O_3/H_2O_2/AC$) that showed the highest cyanide removal for the synthetic solutions can degrade free cyanide in an industrial effluent, experiments with effluents from a cyanidation process were carried out applying the best treatment. The samples of effluents were characterized, before and after the treatment application, by measuring the following parameters: pH, cyanide concentration (Standard Methods 4500-CN-E and 4500-CN-F), chemical

oxygen demand (COD, Standard Method 5220-B), total organic carbon (TOC, Standard Method 5310-B) and turbidity.

RESULTS AND DISCUSSION

Influence of AC, H_2O_2 doses, and pH on cyanide removal and O_3 consumption

The results of cyanide removal at different times under all conditions tested are shown in **table I**. According to the results of the ANOVA test of the treatment using only O_3, the pH value had a significant effect on cyanide removal ($p < 0.05$). Moreover, the higher cyanide removal was achieved at pH 11.0. As mentioned by von Gunten (2003), the pH value plays an important role because ^-OH ions can initiate the O_3 decomposition into $^\bullet OH$ radicals. Previous studies have reported that the treatment of cyanide using O_3 is better at alkaline conditions (Andreozzi et al. 1999, Mert et al. 2014). In addition, Soto et al. (1995) found that the oxidation of the protonated form of cyanide (HCN) using O_3 is slower in comparison with the oxidation of cyanide ions (CN^-). Since at pH values higher than the pKa of HCN (pH = 9.2) the proportion of CN^- ions is higher in comparison with HCN

TABLE I. CYANIDE REMOVAL USING THE TESTED COMBINATIONS: O_3; O_3/H_2O_2; O_3/CA AND $O_3/H_2O_2/CA$ ($[CN^-]_o = 15.37$ mM)

pH	Treatment	H_2O_2* (mM)	AC** doses (g/L)	Cyanide removal (%)		
				4.5 min	6.0 min	7.5 min
pH = 10	O_3	-		79.8	90.8	100.0
	O_3/H_2O_2	0.18 (2 mg H_2O_2/mg O_3)	-	84.4	98.8	100.0
	O_3/H_2O_2	0.49 (5 mg H_2O_2/mg O_3)	-	87.0	98.2	100.0
	O_3/H_2O_2	1.02 (10 mg H_2O_2/mg O_3)	-	94.6	99.6	100.0
	O_3/CA	-	0.30	69.4	97.0	100.0
	O_3/CA	-	0.50	78.8	97.6	100.0
	O_3/CA	-	1.00	79.3	99.2	100.0
pH = 11	O_3	-	-	84.6	93.3	100.0
	O_3/H_2O_2	0.18 (2 mg H_2O_2/mg O_3)	-	88.2	98.6	100.0
	O_3/H_2O_2	0.42 (5 mg H_2O_2/mg O_3)	-	83.0	96.1	100.0
	O_3/H_2O_2	1.04 (10 mg H_2O_2/mg O_3)	-	95.9	99.8	100.0
	O_3/CA	-	0.30	72.7	89.8	100.0
	O_3/CA	-	0.50	80.6	98.0	100.0
	O_3/CA	-	1.00	79.3	92.5	100.0
	H_2O_2	1.04	-	66.7	80.8	90.0
	CA	-	0.50	12.5	29.2	20.8
	O_3/H_2O_2 /CA	1.02 (10 mg H_2O_2/mg O_3)	0.50	83.5	99.3	100.0

* The values in parenthesis are expressed in milligrams of H_2O_2 per milligram of O_3 feed
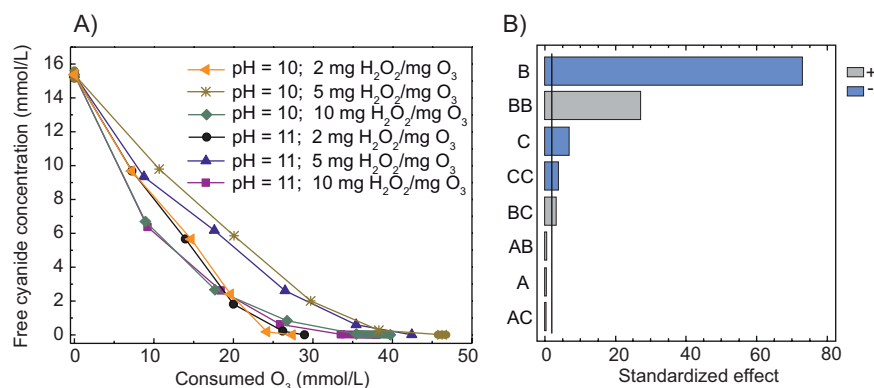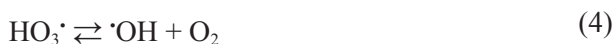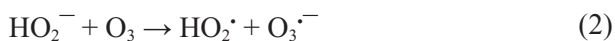**AC = activated carbon

Fig. 1. a) Cyanide removal as a function of the O_3 consumed (mM) at different H_2O_2/O_3 ratios (mg H_2O_2/mg $O_{3\ feed}$) and pH values b) Pareto chart of the main effects obtained from the cyanide removal using the treatment O_3/H_2O_2 (A = pH, B = time, C = H_2O_2/O_3 ratio)

(Stavropoulos et al. 2015), the removal of cyanide could increase at high pH values. Furthermore, working at alkaline conditions avoid the generation of the volatile species HCN which is a compound known for its high respiratory toxicity (Chan et al. 2010).

When H_2O_2 was included in the treatment, the highest free cyanide removal was achieved using 10 mg H_2O_2/mg O_3. In addition, there were not found statistically significant differences between 2 mg H_2O_2/mg O_3 and 5 mg H_2O_2/mg O_3. On the other hand, the removal of cyanide was not affected by the pH values tested (10.0 and 11.0) (**Fig. 1b**). As reported previously, the addition of H_2O_2 could increase the generation of $^{\bullet}$OH radicals because H_2O_2 anions (HO_2^-) react rapidly with O_3 which is decomposed in $^{\bullet}$OH radicals and O_2 (see eqs. (1)–(4)) (von Sonntag and von Gunten 2012). Furthermore, as shown in **figure 1**, an increment of the O_3 consumption was observed when the H_2O_2/O_3 ratio increased. This consumption may be related to a scavenging effect of O_3, since it is known that O_3 reacts rapidly with $^{\bullet}$OH radicals (von Gunten 2003). In other words, the reaction of O_3 with $^{\bullet}$OH competes with the reaction between cyanide and $^{\bullet}$OH (Gurol and Bremen 1985). Thus, more O_3 is needed in order to achieve the removal of cyanide.

$$H_2O_2 \rightleftarrows HO_2^- + H^+ \qquad (1)$$

$$HO_2^- + O_3 \rightarrow HO_2^{\bullet} + O_3^{\bullet -} \qquad (2)$$

$$O_3^{\bullet -} + H^+ \rightleftarrows HO_3^{\bullet} \qquad (3)$$

$$HO_3^{\bullet} \rightleftarrows {}^{\bullet}OH + O_2 \qquad (4)$$

The characterization of the activated carbon and the results of the cyanide removal using the combination of O_3/AC are depicted in **table II** and **figure 2**, respectively. According to the Pareto chart of the main effects obtained using this combination (**Fig. 2b**), the cyanide removal was not affected by the activated carbon dosage and the pH value (10.0 and 11.0). Furthermore, the addition of activated carbon did not increase the cyanide removal in comparison with O_3 and O_3/H_2O_2. This is in good agreement with previous results for the treatment of other compounds, for instance, Zaror (1997) reported that the addition of AC did not affect the oxidation of phenolic compounds. Moreover, Sanchez-Polo et al. (2005) mentioned that activated carbon could act as an initiator of the O_3 decomposition reaction rather than a catalyst. This behavior is explained because activated carbon loses its reactivity during the process due to a decrease of basic functional groups responsible for the promotion of O_3 decomposition. In this study, an activated carbon dose of 0.5 g/L was chosen to carry out the comparison between all the treatments (**Fig. 3**).

TABLE II. CHARACTERIZATION OF THE EMPLOYED COMMERCIAL ACTIVATED CARBON (AC)

S_{BET} (m^2/g)	V_{micro} (cm^3/g)	Φ_{micro} (Å)	pH_{PZC}
934.15	0.3843	3.68	7.40

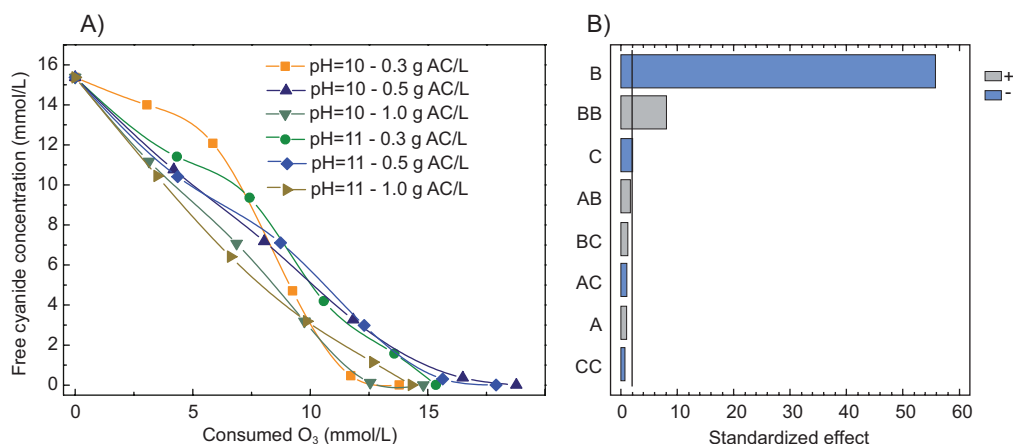(PanReac AppliChem, ref: 121237)

Fig. 2. a) Cyanide removal as a function of the O_3 consumed (mM) at different activated carbon doses (g AC/L) and pH values b) Pareto chart of the main effects obtained from the cyanide removal using activated carbon (A = pH, B = time, C = activated carbon dose)

A comparison between all treatments applied (O_3, O_3/AC, O_3/H_2O_2 and O_3/H_2O_2/AC) and the individual effect of H_2O_2 and activated carbon on the cyanide removal was carried out at the conditions which presented the best cyanide removal for each combination. As shown in **figure 3a**, the higher cyanide removal was obtained using the combination O_3/H_2O_2 (10 mg H_2O_2/mg O_3, pH = 11.0). Also, the combination O_3/H_2O_2/AC (10 mg H_2O_2/mg O_3, 0.5 g AC/L, pH = 11.0) exhibited a better cyanide removal in comparison with O_3 alone (pH = 11.0).

Regarding O_3 consumption (**Fig. 3b**), the treatment using O_3/H_2O_2 showed the highest values. In

this case, the quantity of ozone consumed increased during the process. A similar trend was obtained for the treatment using only O_3. These behaviors may be related to the scavenging effect of O_3 (von Gunten 2003). As mentioned before, the reaction of O_3 with $^\bullet$OH competes with the reaction between cyanide and $^\bullet$OH (Gurol and Bremen 1985). When the concentration of CN^- decreases the probability of O_3 to react with $^\bullet$OH radicals could increase. As a result, more O_3 needs to be consumed to degrade the residual CN^-. When activated carbon was added, the O_3 consumption decreased. For the treatment using O_3/AC (0.5 g AC/L, pH = 11.0) the O_3 consumption was
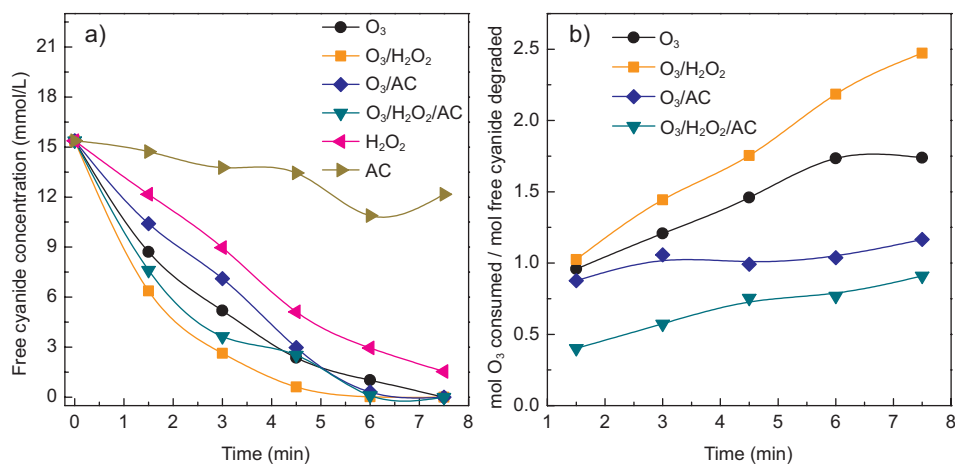

Fig. 3. a) Cyanide removal as a function of time using the tested combinations: O_3; O_3/H_2O_2 (10 mg H_2O_2 /mg O_3); O_3/CA (0.5 g AC/L) and O_3/H_2O_2/CA (10 mg H_2O_2 /mg O_3 − 0.5 g AC/L) and b) ozone consumption as function of time. ([CN^-]$_o$ = 15.37 mM, pH =11)

approximately 1 mol O_3/mol CN^-, while for the treatment using O_3/H_2O_2/AC the consumption was lower than 1 mol O_3/mol CN^-. Zaror (1997) also found that the presence of AC in the ozonation process decreased the ozone consumption. In the case of the combination O_3/AC, this reduction may be attributed to the generation of $^\bullet OH$ radicals at specific sites over the large surface of the activated carbon. It seems that these radicals produced are less available to react with the incoming O_3. Thus, the selectivity of $^\bullet OH$ radicals (i.e., the reaction of $^\bullet OH$ radicals with target components) is improved, since there is a decrease of the scavenging effect of O_3. The same principle could apply to the combination O_3/H_2O_2/AC with the difference of the increase of $^\bullet OH$ production by the addition of H_2O_2 with a subsequent decrease in the consumption of O_3. Future studies should be focused on the reaction mechanisms when O_3, H_2O_2 and activated carbon are combined in order to have a better understanding of this phenomena.

Characterization and treatment of samples from cyanidation effluents

Samples of cyanidation effluents from gold ore processing were treated using the combination O_3/H_2O_2 (10 mg H_2O_2/mg O_3, pH =11.0) which presented the highest cyanide removal. **Figure 4** shows the results of the cyanide removal from the samples of effluents ($[CN^-]_o$ = 172.5 mg/L). Moreover, the cyanide removal of synthetic solutions ($[CN^-]_o$ = 400.0 mg/L) treated

under the same conditions is reported for comparative reasons. Almost a total removal of cyanide from the effluents was achieved at 3 min. This time was lower than the time needed to achieve the same conversion in the synthetic samples because the initial free cyanide concentration was lower in the effluent.

The results of the characterization of the effluents before and after the treatment are provided in **table III**. As shown in the results, the removals of TOC and COD were 82.2 % and 76.11 %, respectively. Since TOC represents the degree of mineralization (oxidation of organic carbon content to CO_2), the removal values suggested that the treatment can trigger the formation of less toxic species. Also, the final cyanide concentration (0.08 mg/L) complies with the drinking water regulation of the Environmental Protection Agency (EPA) of the US which is 0.2 mg/L. The results suggested that the treatment could be applied for the removal of cyanide in cyanidation effluents. It should be noted that this study was only focused in the removal of free cyanide, although in these effluents cyanide can be in the form of various species such as free cyanide and cyanide complexes. Moreover, there are some reports of the capability of O_3 to oxidize also cyanide complexes (Kuyucak and Akcil 2013). Therefore, it is important to mention that future studies should also focus on the combination of the processes studied to remove this kind of compounds.
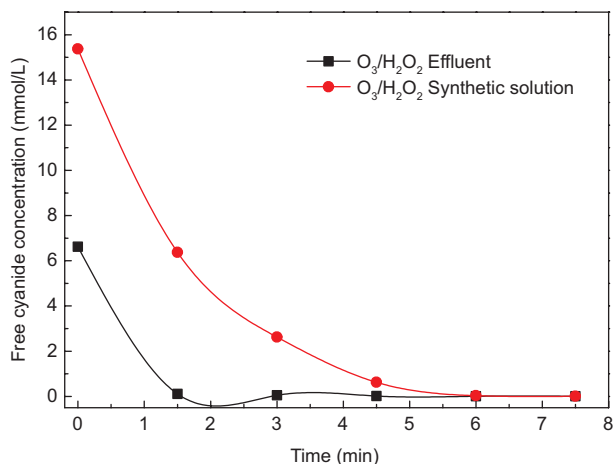

Fig. 4. Cyanide removal $[CN^-]$ as a function of time using the combination (O_3/H_2O_2) in synthetic cyanide solutions and cyanidation effluents samples (10 mg H_2O_2 /mg O_3, pH =11)

TABLE III. CHARACTERIZATION OF THE CYANIDATION EFFLUENT, BEFORE AND AFTER TREATMENT USING THE COMBINATION O_3/H_2O_2

Parameter	Initial value	Final value
$[CN^-]$ (mg/L)	172.5	0.08
pH	11	7
Turbidity (NTU)	56	68
TOC (mg/L)	137.8	24.5
COD (mg/L)	496	118.5

(pH 11; 10 mg H_2O_2/mg O_3; t = 7 min)

CONCLUSIONS

The highest cyanide removal was achieved at pH 11.0 for the ozonation process. When H_2O_2 was added, the cyanide removal was improved with the increase of the H_2O_2/O_3 ratio. This result was attributed to a possible increase in the generation of $^\bullet OH$

radicals caused by the reaction between H_2O_2 anions (HO_2^-) and O_3. The highest removal was obtained with 10 mg H_2O_2/mg O_3. Moreover, the O_3 consumption increased with the increment of H_2O_2/O_3 ratio which was attributed to a scavenging effect of O_3. For the combination O_3/AC, the statistical analysis showed that the cyanide removal was not affected by the activated carbon dosage. Also, the addition of AC did not improve the cyanide removal in comparison with O_3 alone.

According to the comparison between all the treatments applied (O_3, O_3/AC, O_3/H_2O_2 and $O_3/H_2O_2/AC$), the best cyanide removal was reached with the combination O_3/H_2O_2 followed by the combination $O_3/H_2O_2/AC$. Furthermore, the O_3 consumption increased during the process using the combinations O_3/H_2O_2 and O_3. When activated carbon was added, the O_3 consumption decreased during the process. For the combination O_3/AC the O_3 consumption was approximately 1 mol O_3/mol CN^-, while for the combination $O_3/H_2O_2/AC$ the consumption was lower than 1 mol O_3/mol CN^-.

The treatment of cyanidation effluents was carried out using the treatment with O_3/H_2O_2 (10 mg H_2O_2/mg O_3, pH = 11.0). According to the results, almost a total removal of free cyanide (CN^-) was achieved after 3 min of treatment. Moreover, the final cyanide concentration was 0.08 mg/L. This value complied with the drinking water regulation of the Environmental Protection Agency of the US which is 0.2 mg/L.

ACKNOWLEDGMENTS

REFERENCES

Akcil A. (2002). First application of cyanidation process in Turkish gold mining and its environmental impacts. Miner. Eng. 15 (9), 695-699.
DOI: 10.1016/S0892-6875(02)00165-6

Akcil A. (2003). Destruction of cyanide in gold mill effluents: Biological versus chemical treatments. Biotechnol. Adv. 21 (6), 501-511.
DOI: 10.1016/S0734-9750(03)00099-5

Akcil A. and Mudder T. (2003). Microbial destruction of cyanide wastes in gold mining: process review. Biotechnol. Lett. 25 (6), 445-450.
DOI: 10.1023/A:1022608213814

Andreozzi R., Caprio V., Insola A. and Marotta R. (1999). Advanced oxidation processes (AOP) for water purification and recovery. Catal. Today 53 (1), 51-59.
DOI: 10.1016/S0920-5861(99)00102-9

Chan A., Balasubramanian M., Blackledge W., Mohammad O.M., Alvarez L., Boss G.R. and Bigby T.D. (2010). Cobinamide is superior to other treatments in a mouse model of cyanide poisoning. Clin. Toxicol. 48 (7), 709-717.
DOI: 10.3109/15563650.2010.505197

Chergui S., Yeddou A.R., Chergui A., Halet F., Amaouche H., Nadjemi B. and Ould-Dris A. (2015). Removal of cyanide in aqueous solution by oxidation with hydrogen peroxide in presence of activated alumina. Toxicol. Environ. Chem. 97 (10), 1289-1295.
DOI: 10.1080/02772248.2015.1093129

Deveci H., Yazıcı E.Y., Alp I. and Uslu T. (2006). Removal of cyanide from aqueous solutions by plain and metal-impregnated granular activated carbons. Int. J. Miner. Process. 79 (3), 198-208.
DOI: 10.1016/j.minpro.2006.03.002

Donato D.B., Nichols O., Possingham H., Moore M., Ricci P.F. and Noller B.N. (2007). A critical review of the effects of gold cyanide-bearing tailings solutions on wildlife. Environ. Int. 33 (7), 974-984.
DOI: 10.1016/j.envint.2007.04.007

Ebel M., Evangelou M.W.H. and Schaeffer A. (2007). Cyanide phytoremediation by water hyacinths (*Eichhornia crassipes*). Chemosphere 66 (5), 816-823.
DOI: 10.1016/j.chemosphere.2006.06.041

Eisler R. and Wiemeyer S.N. (2004). Cyanide hazards to plants and animals from gold mining and related water issues. In: Reviews of environmental contamination and toxicology. Vol. 183, (G. W. Ware, Ed.). Springer, New York, USA, pp. 21-54.
DOI: 10.1007/978-1-4419-9100-3_2

Evangelho M.R., Gonçalves M.M.M., Sant'-Anna Jr. G.L. and Villas-Bôas R.C. (2001). A trickling filter application for the treatment of a gold milling effluent. Int. J. Miner. Process. 62 (1-4), 279-292.
DOI: 10.1016/S0301-7516(00)00059-4

Gurol M.D. and Bremen W.M. (1985). Kinetics and mechanism of ozonation of free cyanide species in water. Environ. Sci. Technol. 19 (9), 804-809.
DOI: 10.1021/es00139a006

Habashi F. (1987). One hundred years of cyanidation. CIM Bull. 80 (905), 108-114

Hilson G. and Monhemius A.J. (2006). Alternatives to cyanide in the gold mining industry: what prospects

for the future?. J. Clean. Prod. 14 (12-13), 1158-1167. DOI: 10.1016/j.jclepro.2004.09.005

Kitis M., Karakaya E., Yigit N.O., Civelekoglu G. and Akcil A. (2005). Heterogeneous catalytic degradation of cyanide using copper-impregnated pumice and hydrogen peroxide. Water Res. 39 (8), 1652-1662. DOI: 10.1016/j.watres.2005.01.027

Kuyucak N. and Akcil A. (2013). Cyanide and removal options from effluents in gold mining and metallurgical processes. Miner. Eng. 50-51 (1), 13-29. DOI: 10.1016/j.mineng.2013.05.027

Mekuto L., Ntwampe S.K.O. and Jackson V.A. (2015). Biodegradation of free cyanide and subsequent utilisation of biodegradation by-products by *Bacillus* consortia: optimisation using response surface methodology. Environ. Sci. Pollut. R. 22 (14), 10434-10443.
DOI: 10.1007/s11356-015-4221-4

Mekuto L., Ntwampe S.K.O. and Akcil A. (2016). An integrated biological approach for treatment of cyanidation wastewater. Sci. Total Environ. 571 (1), 711-720. DOI: 10.1016/j.scitotenv.2016.07.040

Mert B.K., Sivrioğlu Ö., Yonar T. and Özçiftçi S. (2014). Treatment of jewelry manufacturing effluent containing cyanide using ozone-based photochemical advanced oxidation processes. Ozone-Sci. Eng. 36 (2), 196-205. DOI: 10.1080/01919512.2013.860354

Monteagudo J.M., Rodriguez L. and Villaseñor J. (2004). Advanced oxidation processes for destruction of cyanide from thermoelectric power station waste waters. J. Chem. Technol. Biot. 79 (2), 117-125. DOI: 10.1002/jctb.947

Mudd G.M. (2007). Global trends in gold mining: Towards quantifying environmental and resource sustainability. Resour. Policy 32 (1-2), 42-56. DOI: 10.1016/j.resourpol.2007.05.002

Mudder T.I. and Botz M.M. (2004). Cyanide and society: a critical review. Eur. J. Miner. Process. Environ. Prot. 4 (1), 62-74

Newcombe G., Hayes R. and Drikas M. (1993). Granular activated carbon: Importance of surface properties in the adsorption of naturally occurring organics. Colloid. Surface. A. 78 (1), 65-71. DOI: 10.1016/0927-7757(93)80311-2

Oturan M.A. and Aaron J.J. (2014). Advanced oxidation processes in water/wastewater treatment: Principles and applications. A Review. Crit. Rev. Env. Sci. Tec. 44 (23), 2577-2641. DOI: 10.1080/10643389.2013.829765

Rico M., Benito G., Salgueiro A.R., Díez-Herrero A. and Pereira H.G. (2008). Reported tailings dam failures. A review of the European incidents in the worldwide context. J. Hazard. Mater. 152 (2), 846-852. DOI: 10.1016/j.jhazmat.2007.07.050

Sánchez-Polo M., von Gunten U. and Rivera-Utrilla J. (2005). Efficiency of activated carbon to transform ozone into •OH radicals: Influence of operational parameters. Water Res. 39 (14), 3189-3198. DOI: 10.1016/j.watres.2005.05.026

Schoenberger E. (2011). Why is gold valuable? Nature, social power and the value of things. Cult. Geogr. 18 (1), 3-24. DOI: 10.1177/1474474010377549

Soto H., Nava F., Leal J. and Jara J. (1995). Regeneration of cyanide by ozone oxidation of thiocyanate in cyanidation tailings. Miner. Eng. 8 (3), 273-281. DOI: 10.1016/0892-6875(94)00123-T

Stavropoulos G.G., Skodras G.S. and Papadimitriou K.G. (2015). Effect of solution chemistry on cyanide adsorption in activated carbon. Appl. Therm. Eng. 74 (1), 182-185. DOI: 10.1016/j.applthermaleng.2013.09.060

Veiga M.M., Angeloci G., Hitch M. and Velasquez-Lopez P.C. (2014). Processing centres in artisanal gold mining. J. Clean. Prod. 64 (1), 535-544. DOI: 10.1016/j.jclepro.2013.08.015

von Gunten U. (2003). Ozonation of drinking water: Part I. Oxidation kinetics and product formation. Water Res. 37 (7), 1443-1467. DOI: 10.1016/S0043-1354(02)00457-8

von Sonntag C. and von Gunten U. (2012). Chemistry of ozone in water and wastewater treatment - from basic principles to applications. IWA Publishing, London, United Kingdom, 320 pp

Yeddou A.R., Chergui S., Chergui A., Halet F., Hamza A., Nadjemi B., Ould-Dris A. and Belkouch J. (2011). Removal of cyanide in aqueous solution by oxidation with hydrogen peroxide in presence of copper-impregnated activated carbon. Miner. Eng. 24 (8), 788-793. DOI: 10.1016/j.mineng.2011.02.012

Yeddou A.R., Nadjemi B., Halet F., Ould-Dris A. and Capart R. (2010). Removal of cyanide in aqueous solution by oxidation with hydrogen peroxide in presence of activated carbon prepared from olive stones. Miner. Eng. 23 (1), 32-39. DOI: 10.1016/j.mineng.2009.09.009

Zaror C.A. (1997). Enhanced oxidation of toxic effluents using simultaneous ozonation and activated carbon treatment. J. Chem. Technol. Biotechnol. 70 (1), 21-28. DOI: 10.1002/(SICI)1097-4660(199709)70:1<21::AID-JCTB706>3.0.CO;2-3