Metallurgy and materials
Metalurgia e materiais

Removal of entrained organic matter in the copper electrolyte by ozonation

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Abstract

Organic matter-in-aqueous entrainment is a serious problem in the hydrometallurgical extraction of copper from ore. Current inefficiencies, changes in the morphology and orientation of cathode deposit are some of the problems when organic matter is present in the advance electrolyte. In addition, negative effects upon metabolic activity of bioleaching microorganisms are reported due to entrained organic matter in the raffinate electrolyte. In view of these problems, the objective of this study was to evaluate ozonation as an alternative method for the removal of entrained organic matter present in an advanced electrolyte. For this purpose, ozonation during 30 min of synthetic solutions using a bubble glass column reactor at different ozone concentrations, flow rates and temperatures were studied. It was found that the increase in all of these operating parameters is not necessarily associated with an increase of the removal efficiency, and their effects on the mass transfer rate, chemical reaction rate, ozone solubility and contact time play a decisive role in the ozonation process. Thus, the best operating conditions were found at 6.7 wt.%, 1 L min^{-1} and 27 °C and reached a removal efficiency of 94.5%. This result demonstrated that removal of entrained organic matter in strongly acid solution by ozonation could be an alternative technology.

Keywords: : hydrometallurgy, copper, organic removal, entrainment, ozonation.

1. Introduction

About 20% of copper-from-ore is produced by a heap leaching-solvent extraction-electrowinning process. Leaching (LX) involves dissolving Cu with a sulfuric acid solution to produce an impure pregnant leach solution (PLS). The solvent extraction (SX) purifies the PLS to produce a high-Cu electrolyte with appropriate conditions for the electrowinning (EW) stage. Finally, in the EW, cathodes of high purity are obtained (Schlesinger *et al.*, 2011a).

As is shown in Fig.1, the SX comprises two circuits. In the first one, copper is selectively loaded into an organic phase (OP) (extractant and diluent), leaving all other impurity species present in the PLS, in the aqueous phase (raffinate). In the second circuit, the copper is stripped from the loaded organic phase into the advance electrolyte (AE), while the depleted organic phase (stripped organic) is returned to the prior stage. Both stages are carried out in mixer-settler equipment, which are specially designed to favor the separation of the organic and aqueous phases. However, this separation is not perfect, and some finely divided droplets of organic phase are entrained in the aqueous phase, known as organic-in-

aqueous entrainment (Liu *et al.*, 2015; Schlesinger *et al.*, 2011c). The degree of these entrainments depends on different physicochemical conditions, such as pH of solution, phase continuity, crud formation, density, viscosity, temperature, separation times in the settler, among others. In the case of EW, the presence of the organic phase in the advance electrolyte is associated to many catastrophic effects.

These effects may include a decrease in current efficiency, changes in orientation and morphology of the copper-crystal deposited, and the formation of the so-called "organic burn", in which a mixture of copper and organic matter strongly adhere to the cathode and cannot be readily removed by an automatic stripping machine (Schlesinger *et al.*, 2011b; Sole *et al.*, 2007). For these reasons, the

content of organic matter in the AE must be kept as low as possible. Additionally, recent reports have demonstrated negative effects upon the metabolic activity of bioleaching microorganisms, owing to the presence of organic matter in the aqueous raffinate (Davis-Belmar *et al.*, 2012; Liu *et al.*, 2015; Watling *et al.*, 2009). Therefore, many problems are associated with organic-in-aqueous entrainment.
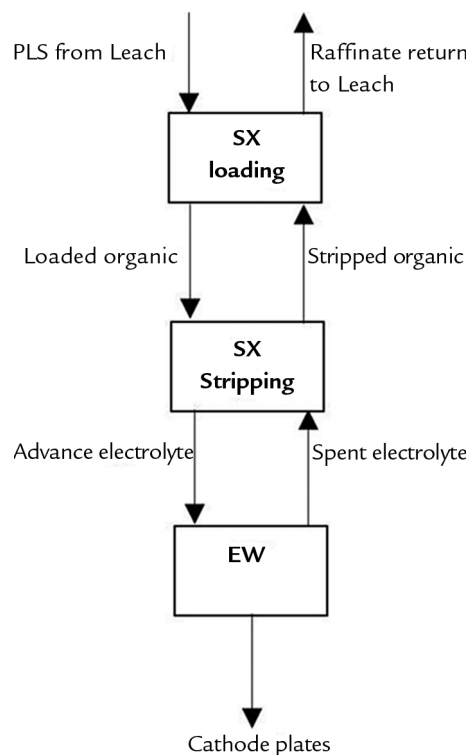

Figure1
Simplified hydrometallurgical flowsheet. The organic and aqueous streams are shown in each stage.

Different equipment and technologies are employed to reduce the organic content in the aqueous streams from the SX circuit. With regard to EW, flotation cells, coalescers, such as Picket Fence, and activated carbon column are the most typically used. The CoMatrixTM system is another equipment, which was developed for use in the copper industry, has also been used in the treatment of zinc electrolytes, among others (Spintek Filtration USA, 2006). Despite the operating difficulties of these filters, for instance, pressure loss and bed expansion during regeneration stage, they are widely used. For this reason, recent studies have focused on the determination of better regeneration methods and regenerable materials, as well as the identification of the properties that allow to improve the organic phase coalescence (Kuosa *et al.*, 2017). All these methods allow additional settling time and promote coalescence for removal of organic phase, i.e. they act in a physical way. However, a chemical

removal mechanism is possible through the ozonation, which could not only avoid the aforementioned problems, but also could result in quicker organic matter removal.

Ozone is recognized as a powerful oxidizing agent (E=2.08 V) (Rajeswari and Kanmani, 2009). Due to its minimal impact on the environment, it is increasingly used in different industrial applications that include disinfection, deodorization, color removal, wastewater treatment and some others (De Sousa *et al.*, 2016; Gao *et al.*, 2012; Miao *et al.*, 2015). Within hydrometallurgical processes, ozone has been studied as an effective oxidant in the leaching of refractory ores (Li *et al.*, 2009; Rodríguez-Rodríguez *et al.*, 2016; Tian *et al.*, 2016).

Ozone oxidizes organic matter via two different ways: direct and indirect reaction routes. In the first one, molecular ozone reacts slowly and selectively with specific functional groups, being dominant in acidic solution. On the

other hand, the indirect reaction acts through the hydroxyl radical, resulting from the decomposition of ozone catalyzed by hydroxyl ion; this pathway is fast and non-selective, i.e. it reacts with a wide range of organic and inorganic compounds and is favored with increasing pH (Hu *et al.*, 2016; Tizaoui and Grima, 2011; Zhao *et al.*, 2016, 2011a).

In general, degradation of organic matter has been studied in a wide range of pH, however its potential benefits in strong acid medium, or more specifically in copper hydrometallurgical processes, have not been widely reported as yet. Thus, the objective of this study was to evaluate the ozonation as an alternative method for removal of the entrained organic phase present in advance electrolyte. For this purpose, the effects of ozone concentration, temperature, flow rate, and the efficiency of the process were investigated on a laboratory scale in order to determine the process viability and the best operational conditions.

2. Experimental

2.1 Reagents

All experiments were accomplished with synthetic solutions, using distilled water and all chemicals were of analytical grade. The aqueous phase (AP) was prepared using copper (II) sulfate pentahydrate and sulfuric acid. On the other hand, the organic phase (OP) was prepared using LIX984N®. The reagent is a 1:1 v/v blend of LIX84® (2-hydroxy-5nonylacetophenone oxime) and LIX860N® (5-nonylsalicyl-aldoxime) at a concentration of 25% v/v in ORFOM SX12®. LIX984N® works by forming stable chelate complexes according to the general formula Cu–C_6H_3(OH)–C(Cu)=NOH (Liu *et al.*, 2015). The diluent used here was designed specifically for use in metal solvent extraction and commercialized by Chevron Phillips Chemical Company. It is comprised of about 52% paraffinic hydrocarbons, 27% alkyl aromatic hydrocarbons and 21% naphtenic hydrocarbons. The work solution (WS) was prepared by dissolving appropriate amounts of both AP and OP at a stirring speed of 250 rpm. It is worth mentioning that the WS was stable and no phase separation was observed. The composition of the synthetic solution used in all experiments is presented in Table 1

The WS was prepared as a surrogate of an electrowinning solution. Nevertheless in a real solution other ions should be present as for instance, Fe, Al, Co, Ca, Mn, Zn among others (Schlesinger *et al.*, 2011a). Although these ions can affect the treatment by ozone, the objective of this work was to study the organic phase oxidation process. The effect of other ion oxidation must be evaluated on a future study.

2.2 Equipment and procedures

The ozonation experiments were conducted for 30 minutes in a 3-L glass column reactor at different temperature, content of ozone and flow rate. The experimental setup utilized in this work is shown in Fig.2. Ozone was generated from pure oxygen gas (medicinal quality) by an ozone generator (OZO-NIA CFS-2a) which produces up to 8% O_3/O_2 and 150 g O_3/h. Gas dispersion was fed through a porous gas sparger placed at the bottom of the column to a better distribution of the gas. Another identical column with a solution of NaOH at pH 13 was used to eliminate the residual ozone. Reaction temperatures were maintained at the desired value using a circulating water bath. A total volume of 7 L was utilized and reused for all experiments. For the homogenization of the solutions, a mechanical stirrer heidolph (model RZR1) was used. A summary of the experimental conditions is presented in Table 1.

Table 1
Summary of the experimental conditions used in this study.

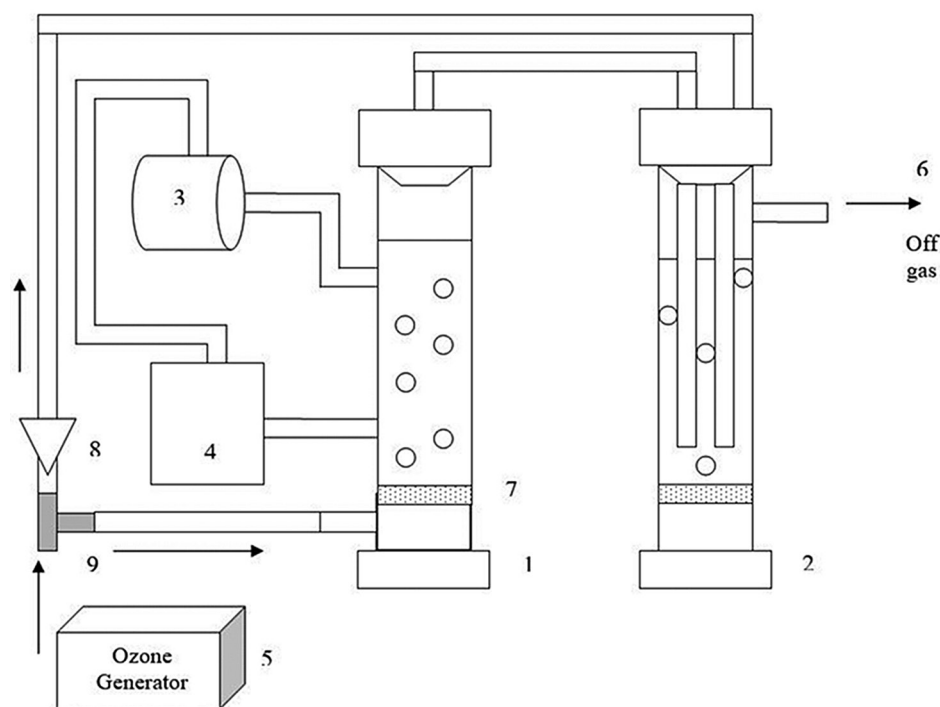| Work solution		Experimental conditions		
		Ozonation at different:		
Cu^{+2}	50 g/L	ozone dosage	ozone flow rate	temperature
H_2SO_4	150 g/L	(1.0 L/min and 27°C)	(6.7 wt. % and 27 °C)	(1.0 L/min and 6.7 wt. %)
OP	40 mg/L	3.8, 6.7, 7.3 wt. %	1.0, 2.5, 4.0 L/min	17, 27, 37 °C

Figure 2
Experimental setup: 1. Glass column reactor; 2. Column with NaOH to eliminate the residual ozone; 3. pump; 4. conditioning solution tank; 5. Ozone generator; 6. Exit of gas; 7. Porous gas sparger; 8. Flowmeter; 9. by-pass of gas flux.

2.3 Analytical methods

For each five minutes of treatment, an aliquot sample was collected and analyzed. The amount of organic residual (OR) after the ozonation treatment was measured with a Turbidity Meter model HI 93703 through a calibration curve. This instrument works by passing a beam of infrared light through a vial containing the sample being measured. The light source

is a high emission infrared LED with a wavelength peak at 890 nm, ensuring that interferences caused by colored samples are minimum. It was designed according to the ISO 7027 International Standard. Before all the measurements, the solutions were agitated at 250 rpm for 30 seconds.

A calibration curve was constructed for 6 different solutions simulating organic entrainment at 0, 10, 15, 20, 30 and 50 mg/L and for a temperature of 30°C. The solution with 10 mg/L was set to 10 NTU as the calibration point. All procedures were done according to the instruction manual HI 93703 (Microprocessor and Meter, 2005). All concentration values registered represent the average of six measurements.

2.4 TOC

In order to evaluate the organic phase mineralization, a TOC analysis was accomplished according to 5310C standard method. The experimental conditions used are shown in Table 2. Samples at the beginning and at the end of the experiment were collected for an ozonation time of 30 minutes.

Work solution		Experimental conditions		
		Ozonation at different:		
Cu^{+2}	50 g/L	ozone dosage	ozone flow rate	temperature
H_2SO_4	150 g/L	6.7 wt. %	1.0 L/min	27 °C
OP	10 mg/L			

Table 2
Experimental conditions used in the TOC analysis.

3. Results and discussion
3.1 Effect of ozone concentration

Fig. 3 shows the RO removal efficiency with different ozone dosage. It can be seen that the behavior for each concentration is quite similar. During the first 10 minutes, the organic removal takes place continuously, after which a plateau is present for the next 10 minutes, which could be ascribed to the presence of some partial oxidation products. Finally, the organic removal starts to increase again until the end of the experiment. The results show that the ozone content does not seem to be significant under the range investigated and an RO removal efficiency higher than 70% was achieved in all the conditions studied.

For a better understanding of the results, an analysis in terms of the ozone solubility was made.

In water and at 20 °C, 12.07 mgL^{-1} of ozone are dissolved (Tchobanoglous, George . Burton and Stensel, 2003). The solution of gases in water (in the absence of chemical interactions between the solute and solvent) is known to obey Henry´s law, according to which the concentration of a gas in a solution is proportional to its partial pressure over the solution (Levanov *et al.*, 2008). Henry´s constant depends on various physicochemical conditions, such as temperature and the nature of the solvent, among others. Henry´s law representation for ozone solubility is shown in equation (1):

$$H = \frac{[O_3]}{(O_3)} \qquad (1)$$

Where $[O_3]$, (O_3) represent the ozone concentration in the solution and gas respectively.

This constant is of high interest and several researches have shown the Henry´s constant for the ozone solubility under different conditions of pH, temperature and acid medium (Egorova *et al.*, 2015; Ershov and Panich, 2015; Levanov *et al.*, 2008). A Henry´s ozone constant of H= 0.19, was found by Levanov *et al.* (2008) for an sulfuric acid concentration of 1.5 M, 20°C and 1 atm. This last value indicates that only 19% of the total ozone content in the gas phase is solubilized. Thus, considering the ozone concentrations used in these experiments (3.8, 6.7 and 7.3 wt. %), only the first one is below the ozone limit solubility (7.22 mgL^{-1} < 12.07 mgL^{-1}), whereas in the other two values the ozone limit solubility is overcome (12.7 and 13.9 mgL^{-1} respectively).

According to this analysis, it was to be expected that the OR removal efficiency for both the 6.7 and 7.3 wt.% ozone concentration were similar. It is important to highlight that the ozonation is considered a complex process, which involves both kinetic reactions and transfer between phases. The concentration can alter ozone mass transfer rates and dissolved ozone concentration within the liquid phase (Konsowa *et al.*, 2010). Nevertheless, more aspects, such as gas-liquid reactors, solubility and even the number and size of the bubbles produced are of interest in the ozonation perfor-
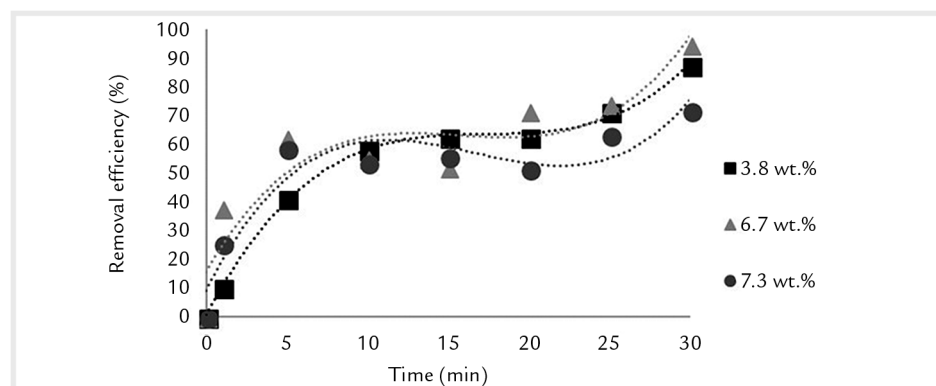

Figure 3
Effect of ozone concentration at 1.0 L/min and 27 °C.

mance (Gao *et al.*, 2012). In fact, many aspects could be ascribed to the observed efficiency difference such as, kinetics, the

gas-liquid reactor, among others (Gao *et al.*, 2012). However that discussion will not be considered at this time for being

beyond the scope of this research. Based on the results obtained, the next experiments were carried out at 6.7 wt.%.

3.2 Effect of temperature

The temperature is very important in most processes involving chemical reactions. In the ozonation treatment, several effects are present. Firstly, according to Arrhenius's law, an increase in the temperature leads to an increase in the reaction rate constant. Likewise, the temperature increases the mass transfer

coefficient of ozone in the liquid phase, favoring the process. This can be observed in Fig.4 where removal efficiency sharply enhanced from 68.1% to 94.9% when temperature was increased from 15 °C to 27 °C. However, the increase in temperature also has a negative effect, since ozonation temperature will significantly

influence the solubility and stability of ozone into aqueous solution (Miao *et al.*, 2015; Zhao *et al.*, 2009). Thus, the lowest removal efficiency (75%) at the highest temperature 37 °C can be attributed to a greater effect on the solubility and stability of ozone in the solution, over the other two favorable effects.

Figure 4
Effect of temperature
at 6.7 wt. % and 1.0 L/min.
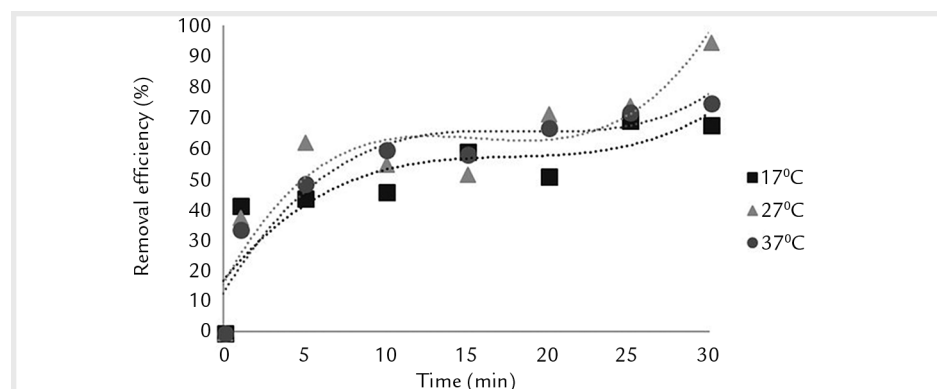
3.3 Effect of flow rate

Fig.5 depicts the effect of flow rate on OR removal efficiency. The results show that after 30 minutes of treatment, the removal efficiency decreased from 94.9% to 74.7% when flow rate was increased from 1.0 L/min to 2.5 L/min, an even greater decrease to 44.7% was obtained at 4.0 L/min. The flow rate can affect the ozonation process in different ways. On the one hand, an increase in the

flow rate improves the ozone mass transfer rate into the liquid phase. This improvement is associated to a greater number of bubbles rising through the column reactor, which are responsible for decreasing the diffusional layer thickness, as a consequence of higher agitation between the gas and liquid phases. Additionally, an increasingly flow rate, enhances the gas hold up, which favors the ozonation

reaction (Konsowa *et al.*, 2010). However, an increase on the flow rate lowers the contact time between the ozone and solution which is unfavorable to the removal efficiency (Gao *et al.*, 2012), principally at lower organic matter content. So, according to the results shown in Fig. 5, it can be seen that under the conditions investigated, the latter effect predominated over the former effects.

Figure 5
Effect of flow rate at 6.7 wt.% and 27 °C.
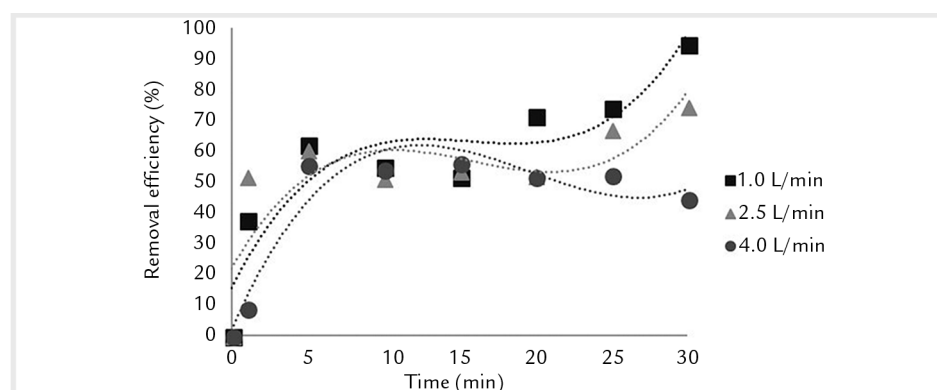
3.4 TOC

Table 3 shows the TOC analysis of the test with the best performance. Despite the initial OP concentration being four time lesser than the ones used in all experiments, it can be shown that a decrease of around 30% was obtained after 30 min of ozonation. This result indicates

that there was mineralization of the organic phase, i.e. at least 30% of the organic matter was decomposed to carbon dioxide. Considering that the mineralization was not complete, partial oxidation products such as organic acids, aldehydes and alkenes are reported as the main products

(Zhao *et al.*, 2011b). Notwithstanding, the effects of these intermediates on the process have to be studied, and this result substantiates ozonation as an interesting alternative on removal of entrained organic matter present in acid copper-containing solutions.

Work solution		Experimental conditions		
		Ozonation at different:		
Cu^{+2}	50 g/L	ozone dosage	ozone flow rate	temperature
H_2SO_4	150 g/L	6.7 wt. %	1.0 L/min	27 °C
OP	10 mg/L	$[TOC]_0$ = 15.03 mg/L	$[TOC]_{30\,min}$ = 10.41 mg/L	

Table 3
Result of TOC analysis
for an ozonation time of 30 min.

4. Conclusions

The results obtained in the present work showed the ozonation process as an alternative on the removal of entrained organic matter present in the advanced electrolyte. The system employed allowed to evaluate the different operating conditions, showing that an increase in the ozone concentration, flow rate and temperature does not necessarily signify an increase of the removal efficiency. Furthermore, the system presented a high sensibility with regard to ozone concentration at the first 10 minutes, i.e. when the concentration of the organic phase was still high. Then at 15 minutes, there was not a predominant parameter and from here (around 55 % of removal efficiency) until the end of the experiments, both the flow rate and temperature became important in the ozonation process.

The combination of these parameters have a decisive role in the ozonation process, where the effects on mass transfer rate, chemical reaction rate and ozone solubility have to be assessed in order to find the best removal efficiency. Thus, the best operating conditions were found at 6.7 wt.%, 1 L min^{-1} and 27 °C and reached a removal efficiency of 94.5% for 30 minutes of ozonation.

It is important to mention that this study was carried out on a lab scale to assess the technical feasibility of ozone treatment in a strong-acid medium. Thus, some aspects were not considered in this preliminary evaluation, such as the effect of ozonation over other important ions. For instance, ozonation could also produce the oxidation of the species Fe(II)/Fe(III), Mn(II)/Mn(III),

among others, which, due to their high oxidizing power, are detrimental for the organic phase in the SX stage. Additionally, the degradation of the OP might produce some intermediates, which could still be pernicious, for instance, for the microorganism activity, and some problems could appear in the bioleaching process. Similarly, some stable complexes could also generate problems for the stripped stage. Nevertheless, considering the significant amounts of organic phase removal in strongly acid solution, future studies will be oriented towards better understanding of ozone utilization that consider the presence of other species. Additionally, experiments on removal of the organic matter phase in raffinate aqueous solution could be analyzed as well.

Acknowledgments

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