



Decomposition of sodium butyl xanthate (SBX) in aqueous solution by means of OCF: Ozonator combined with flotator



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ABSTRACT

In this study, ozonator combined with flotator (OCF) have been applied to treat the mineral processing wastewater. The process efficiency has been evaluated in the bench scale. Removing xanthate from aqueous solution was conducted by OCF. In all cases, the butyl xanthate concentration in the treated water was found to be negligible ($<0.42 \text{ mg L}^{-1}$). The experiments were preceded under different reaction conditions to study the ozonation time and pH on the oxidation of butyl xanthate. The concentration of butyl xanthate and sulfide are analyzed at special time intervals to elucidate the decomposition of butyl xanthate. In addition, oxidation reduction potential and pH are continuously measured in the course of experiments. Chemical oxygen demand is chosen as a mineralization index of the ozonation of butyl xanthate. The degradation mechanism between butyl xanthate and ozone has been discussed. The OCF technology showed to be an efficient process, which requires ozone and flotator, and the treated water ended up with a very low residual concentration of xanthate and COD. It can be inferred from ultraviolet spectrum, HPLC-MS and COD measurement that SO_4^{2-} is produced. The COD of butyl xanthate solution declined dramatically, the removal rate of COD reached 72.21% when ozonation time is 60 min. And the biodegradability (BOD/COD) of butyl xanthate solution increased markedly and shifted from 0.251 to 0.361. It is believed that this ozonation–flotation technique, here named OCF, using ozonator and flotator has a high potential as a alternative method for pollutants removal (flotation reagents, such as butyl xanthate) from waste mining effluents.

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1. Introduction

The rapid development of the industry is continuously creating huge demand of water in various fields including dyeing and printing, chemical, textile, petrochemical, mining. Mining is the basic industries of national economy, and it plays a indispensable and increasingly important role in economic and social development. But it also brings a large amount of wastewater (Dai, 2005). For example, the total discharge amount of all concentration plants wastewater in China account for 10% of the total industrial wastewater discharge (The National Environment Statistical Bulletin, 2004). In the wastewater of mineral processing, there are a lot of flotation reagents which used to concentrate the valuable minerals from the ore, then remained in the wastewater and discharged (Dai, 2005), which often poses a risk to the ecology environment and challenged the increasingly strict environmental demand in China.

Flotation reagents usually are some toxic, for instance, butyl xanthate. The main hazards of xanthate to human and animal are to harm the nervous system and liver, and it also has adverse effects on the hematopoietic system (Zhao et al., 2006). Xanthate is most widely used as a collector in flotation of sulfide mineral. Wastewater containing xanthate even if a small amount of residual volume is toxic to the aquatic fauna (Li, 1990). So wastewater of mineral processing contained xanthate should be treated properly before disposal.

In the situation of increasing water resources shortage, to recycle wastewater of mineral processing as much as possible is vital to each mining enterprise. Residual flotation reagents in mineral processing wastewater not only result in environment problem but also affect the reuse of wastewater (Zhang, 2007). Therefore, it is necessary to develop effective methods to remove the residual reagents.

Conventional treatment such as neutralization, coagulation, precipitation, cannot effectively eliminate the pollution of mining wastewater brought by a large amount of flotation reagents and

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Nomenclature

t	ozonation time (min)	η_{COD}	removal efficiency of COD defined by Eq. (1) (%)
$C_{\text{SBX}0}$	initial concentration of SBX in bulk liquid (mg/L)	$\eta_{\text{COD}} = (C_{\text{COD}0} - C_{\text{COD}}) / C_{\text{COD}0}$	
C_{SBX}	concentration of SBX in bulk liquid (mg/L)	C_{BOD}	concentration of biochemical oxygen demand (BOD) (mg/L)
η_{SBX}	removal efficiency of SBX defined by Eq. (2) (%)	ORP	oxidation–reduction potential (mV)
	$\eta_{\text{SBX}} = (C_{\text{SBX}0} - C_{\text{SBX}}) / C_{\text{SBX}0}$	C_{S}^{2-}	concentration of $\text{S}^{2-}/\text{HS}^-$ in bulk liquid (mg/L)
$C_{\text{COD}0}$	initial concentration of chemical oxygen demand (COD) (mg/L)		
C_{COD}	concentration of chemical oxygen demand (COD) (mg/L)		

also does not meet the criteria of water quality for safe disposal to the environment (Yan and Zhong, 1999; Xie et al., 2002, 2003; Huang and Wang, 2004). Advanced treatment technology is, therefore, urgently needed for further decreasing the residual constituents in the mining wastewater. Basically, the main treatment technologies are activated carbon adsorption, membrane filtration and chemical oxidation using chlorine and ozone. However, activated carbon adsorption can efficiently remove the residual dissolved organics matters, but the regeneration of used carbon and regenerant wastes create further problems (Lin, 1989; Gao and Yang, 2001). Membrane filtration technology has proved to be efficient with regard to disinfection, but it is considered unsuitable owing to high running cost and the continual backwashing to avoid system clogging (Wang and Ding, 2006; Liu et al., 2002). Chemical oxidation using chlorine also generates the by-products such as trihalomethanes and other halogenated organics compounds which are cancerogenic, and therefore gaining the universal vigilance (Tang et al., 2002; Tian et al., 2003). In this context, the use of ozone as an oxidant for the treatment of wastewater is gaining popularity. In recent years, ozonation as a treatment method have been more extensively applied and studied in the field of wastewater (Lee et al., 2008; Wang et al., 2004). Ozone is a powerful oxidant yet it offers the advantage that little or no secondary products are formed upon treatment of the wastewater. However, to treat flotation wastewater contained flotation reagents with ozonation-based methods were not reported as yet.

In this work, ozone combined with flotator (OCF) has been applied to remove the most commonly used flotation reagent (SBX) from water, and the degradation mechanism between SBX and ozone have been discussed in detail in the bench scale.

2. Experimental

2.1. Ozone

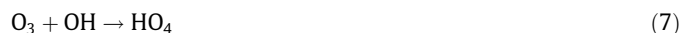
The generation of ozone is accomplished by corona-discharge systems in which pure oxygen (97.5%) is subjected to an electric discharge. Power is supplied in the form of high alternating current voltage, creating ionized gas in the space between two electrodes. Ozone generation is controlled by adjusting the input oxygen flow rate and output flowmeter on the ozonator. Oxygen flow is fixed at 4.0 L/min during experiment, and ozone concentration in ozone-containing gas is 48.53 g/m³.

2.2. Chemistry of ozone in water

The ORP of ozone is 2.07, just lower than F_2 , which can oxidize most organic matter to small molecule that is relatively easy biodegradable.

Several phenomena occur in an ozonation reaction with water containing organics. These phenomenon include (i) direct chemical reaction of ozone with organics in water as an electron acceptor;

(ii) indirect pathway through the generation of a very strong non-selective hydroxyl radical oxidant ($\cdot\text{OH}$) by the hydroxyl ion catalyzed decomposition of ozone in the solution. Once ozone enters water, it becomes highly unstable and rapidly decomposes through a series of reactions including ignition (1), propagation (2)–(6) and termination (7), (8) as follows (Zhang, 2003; Lee et al., 2008):



However, it has been demonstrated that the chemical composition of water can greatly influence these reactions. The chain of reaction is initiated by the hydroxyl ions presented in water with the generation of HO_2 (1) which can initiate further reactions. The decomposition of ozone to its secondary oxidants, particularly hydroxyl radical, is very rapid in high pH level in water (5). It is reported that oxidation of ozone is highly selective whereas oxidation by hydroxyl is nonselective and hence more effective oxidant than ozone (Rice, 1996).

2.3. Model pollutants

The sodium butyl xanthate (SBX) with chemical formular as $\text{C}_4\text{H}_9\text{OCS}_2\text{Na}$, has molecular weight of 172, which is provided by Jinchuan mining plant (≥ 82 wt%) and used without any further purification. The molecular structure of SBX is shown as Fig. 1. The concentration of SBX as the sole organic target is 100 mg/L in removal tests. Besides, the concentration of SBX is 1000 mg/L in other tests. The initial values of pH and COD of experimental solution (1000 mg/L) are 10.25 and 6823.10 mg/L, respectively.

All experimental solutions are prepared with deionized water without other buffers.

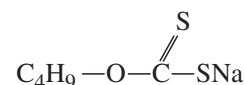


Fig. 1. The molecular structure of SBX.

2.4. Detection

Samples were taken for analysis at regular intervals during experiment. The input and off gas ozone concentrations were measured by KI method (Sun, 2008). COD was estimated by the standard dichromate method. For BOD measurement, samples were incubated for 5 days at 20 °C. A UV/Vis spectrometer was used to detect the concentration of SBX and calculate the removal efficiency of SBX, all measurements were made with a 1 cm quartz cell and deionized water as reference solution. And the spectra of samples were recorded at 301 nm.

The ORP meter composed of platinum electrode as the indicator electrode and saturated calomel electrode as the reference electrode was used to continually monitor the ORP of the SBX solution, and the ORP mentioned in this paper was the real testing value.

BOD₅ was detection by the classic dilution and inoculation method, Specific operational approach according to GB 7488-7488 (HJ505-2009).

2.5. Experimental apparatus of OCF

The lab bench scale ozonation system consists of an ozone generator, a self-feeding agitation impeller flotator, a raw water tank. The flotator is a self-feeding flotator with the rotational speed 2280 rpm (model XFD-63, Changchun Exploration Machinery Factory, China). Wastewater is injected in up flow direction into the reactor and ozone is supplied through negative pressure due to high-speed rotating of flotator. In the OCF system, the reactor is an ordinary flotation cell with 1.0 L volume. All experiments were performed by the *semi-batch* method using home-made SBX solution at 20 °C. The original pH of solution was recorded and

not adjusted in the course of experiments. The operating conditions and schematic diagram of the plant are represented in Table 1 and Fig. 2, respectively.

2.6. The rationality of this technics

- (i) To reinforce the efficiency of gas–liquid mixture, this technique utilized violent stirring and high-speed rotating churn-dasher of the flotator to break bubbles to microvesicle.
- (ii) Its rationale is slightly similar to dissolved air flotation (DAF) which is extensively used in industrial water treatment. As one of the most comprehensive flotation machine, using flotator as gas–liquid mixer will be widely accepted by mine enterprises.

3. Results and discussion

3.1. Removal tests

3.1.1. pH effect

The OCF has been applied to treat SBX solution (100 mg/L). The effect of pH, ozonation time on removal efficiency of SBX has been investigated respectively, as shown in Figs. 3 and 4.

It can be inferred from Fig. 3 that the removal efficiency of SBX is approximately reached 100% at pH 2–12. And at pH 2–12, the maximum of η_{SBX} appears. It also shows that the effect of original pH on η_{SBX} is un conspicuous. In other words, degradation of SBX in the OCF system has a great adaptability to original pH of SBX solution.

3.1.2. Ozonation time effect

As represented in Fig. 4, the η_{SBX} reached 87.55% at $t = 1$, and almost 100% reduction appears at $t = 6$, noting that the OCF system can effectively and rapidly remove SBX from aqueous solution, but it cannot demonstrate whether SBX have been mineralized or not.

3.2. Variation of η_{SBX} , pH, η_{COD} , and ORP in ozonation of SBX

The results (Fig. 5) were analyzed on the basis of removal of some water quality parameters, including η_{SBX} , pH, η_{COD} , and ORP. The pH value of SBX solution decreases with increasing

Table 1
Operating conditions of OCF pilot plant.

Flotator	Rotational speed of flotator, rpm	2280
	Cubage of flotation cell, L	1.0
Ozonator	Raw materials	O ₂ (97.5 Wt%)
	Input oxygen flow, L/min	4.0
	Output gas flow	0.18 m ³ /h
	Ozone concentration in ozone-containing gas	48.53 g/m ³
	Cooling-down method	Water-cooling

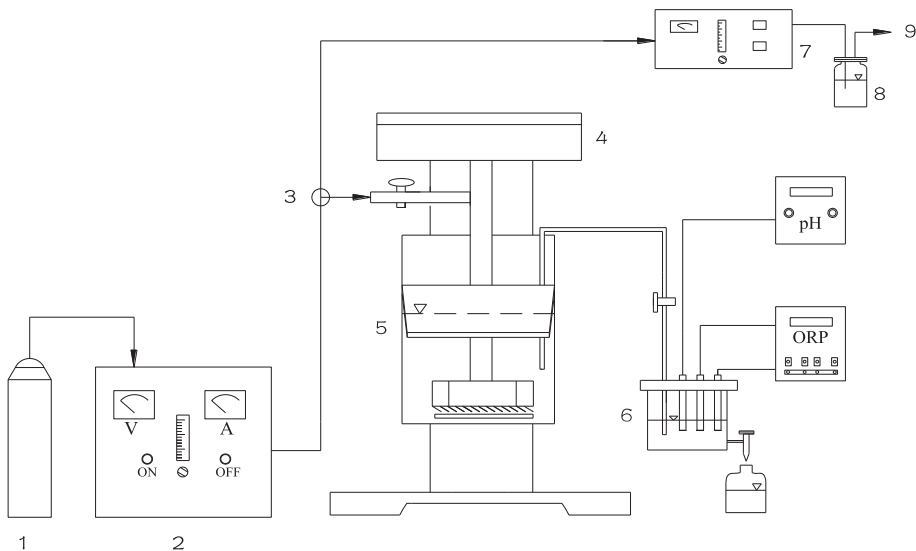


Fig. 2. The schematic diagram of the OCF system. Components: (1) oxygen cylinder, (2) ozonator, (3) two-way valves, (4) flotator, (5) flotation cell, (6) sample cell, (7) gas ozone detector, (8) KI solution, (9) vent to hood.

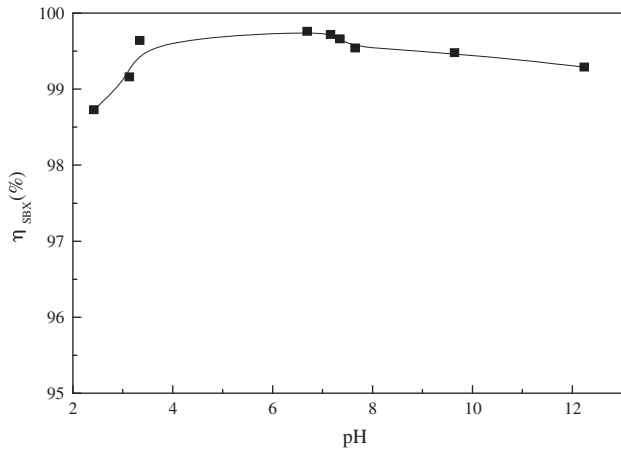


Fig. 3. The relationship between η_{SBX} and pH. $t = 6$ min.

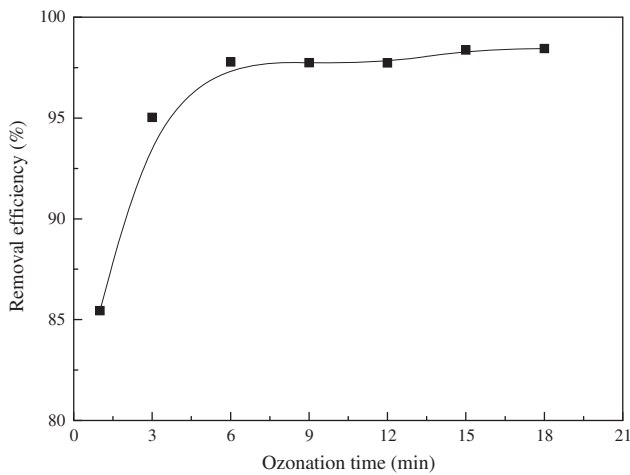


Fig. 4. The relationship between η_{SBX} and ozonation time. Initial pH = 7.32.

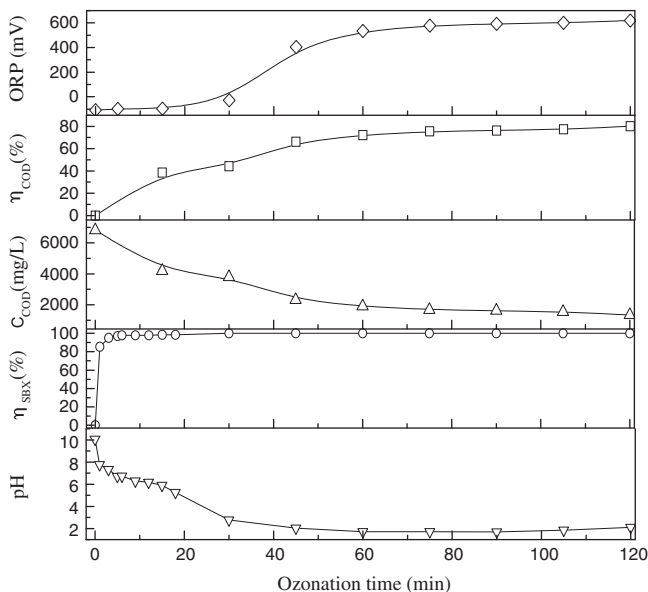


Fig. 5. Concentrations profile of η_{SBX} , pH, η_{COD} , ORP when ozonation of SBX occurred in semibatch system.

ozonation time. After ozonation for 1 min the pH drops from 10.25 to 7.76, then pH decreases rapidly in the early 30 min and then decreases slightly to 1.69 at $t = 90$ min with increasing ozonation time. These phenomena demonstrates that no dioxanthogen (ROCS_2)₂ was produced (Beltran, 2007). Because (i) if the initial attack of ozone on SBX is mainly toward the formation of dioxanthogen (ROCS_2)₂, the solution pH will increase instead of descending, according to the reaction (9):



(ii) Oxidation of xanthate to dioxanthogen refers to electron transfer, but the reaction between ozone and most organics does not, which is different from other common oxidants, such as KI_3 , KMnO_4 .

The acid solution pH, after ozonation for 4 min, may be contribute to the cause of generation of CS_2 , H_2S , SO_4^{2-} .

As depicted in Fig. 5, the η_{SBX} reached 87.55% at $t = 1$ min., and reached almost 100% after ozonation for 6 min. It demonstrated that the degradation of xanthate by ozone is efficient and rapid. OCF has proven to be an effective way for the removal of SBX in the aqueous solution.

COD is a common reference index of water quality, reflected the concentration of organic matters. The relationship between removal efficiency of COD and ozonation time, by the OCF process, is also represented in the Fig. 5.

It can also be seen from Fig. 5 that the decomposition of SBX accompanies with moderate diminution of C_{COD} , and η_{COD} increases with ozonation time. The 72.21% C_{COD} reduction is observed when ozonation time is close to 60 min, and constantly extended ozonation time the comparatively less C_{COD} reduction is observed. This phenomenon might due to the conversion of SBX molecule to soluble fragments by ozonation, and generation of negative sulfide ion or sulfate. It is apparent from the results that OCF is an efficient treatment option to diminish C_{COD} of mineral processing wastewater containing SBX.

Although a majority of COD have been removed using OCF system at $t = 60$, the residual C_{COD} is still high, noting that the OCF system did not further oxidate the residual contents which still contribute to residual C_{COD} within 120 min.

It can be improved by two aspects: (i) to adjust and control the pH of SBX solution (the solution pH of SBX did not adjust in the process of ozonation in this paper) in the course of oxidation, and (ii) to further combine OCF with other process, such as UV light, H_2O_2 , TiO₂, zeolite, etc. Its aim is to form strong non-selective hydroxyl radical oxidant to mineralize the SBX solution completely.

The ORP of SBX solution exhibits climbing tendency with increasing ozonation time. The ORP increased remarkably in the ozonation time range of 15–45 min, which noting the intense ozonation reaction between ozone and SBX is occurred in this period. To continually prolong ozonation time at the first 15 min, the comparatively less ORP rise is observed.

3.3. Decomposition of SBX and formation of S^{2-} , SO_4^{2-}

To provide further information to dedicate whether SBX has been oxidized to S^{2-} , SO_4^{2-} or not, sulfide content (C_S^{2-}) was also tested in this experiment at desired intervals, as represented in Table 2.

The results (Table 2) confirmed the possibility of formation of S^{2-} in the course of decomposition of SBX, the C_S^{2-} increases with

Table 2

The relationship between C_S^{2-} and ozonation time (initial pH = 10.25).

t (min)	0	15	60	120
C_S^{2-} (mg/L)	0	134.7	171.21	193.47

increasing ozonation time. However, S^{2-} cannot be eliminated completely by OCF system within 120 min (it can be improved by addition of microdosage $MnCl_2$ or treated by ion-exchange resins) (Sun, 2003; Wang et al., 2006).

It is apparent that C_5^{2-} increases in the range of $t = 15$ –120. This may be attributed to two causes: one is that S^{2-} has been oxidized to higher valence state such as SO_4^{2-} , SO_3^{2-} , etc; the other is the volatilization of H_2S (formed under acidic pH) during oxidation (Wang and hu, 1988).

From Fig. 5, the pH of the SBX solution is 2.76 at $t = 30$. If all of the S^{2-} in solution are not be oxidized to higher valence state in the process of ozonation, the saturated concentration of H_2S in aqueous solution is 0.1 mol/L, under the condition of 0.1 Mpa, 25 °C (Tang and Dai, 2000).



ionization constant:

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]} = 9.1 \times 10^{-8} \quad (12)$$

$$K_2 = \frac{[H^+][S^{2-}]}{[HS^-]} = 1.2 \times 10^{-15} \quad (13)$$

$$\frac{[H^+]^2[S^{2-}]}{[H_2S]} = 1.1 \times 10^{-22} \quad (14)$$

It can be inferred by calculation that, even if the H_2S is saturation in solution, the pH of the SBX solution cannot be lower than 2.76. In addition, the solubility of H_2S is much greater than that of ozone and oxygen (at 10 °C, the gas volume of H_2S dissolved in 1.0 L water can reach 5.112 g, while oxygen is only 0.05 g) (Gokel et al., 2006), so the decrease of H_2S in solution due to aerated stripping by continuously feeding ozone-containing oxygen is quite limited. Based on the above discussion, it can be concluded that the slightly increase of H_2S during ozonation is due to that S^{2-} has been oxidized to higher valence state, which is consistent with opinion (Gottschalk et al., 2002) that H_2S/S^{2-} can be oxidized by ozone to SO_4^{2-} readily.

The reaction is given by:



The experimental tests are also confirmed this conjecture. When $Ba(OH)_2$ solution was added to water sample, a large amount of white precipitate are generated immediately (especially in the water sample oxidized for 120 min). It can be, therefore, concluded that a considerable stack of SO_4^{2-} is generated during ozonation of SBX solution, corresponding to the phenomena of rather low pH of oxidized SBX solution and reached high η_{COD} .

From Fig. 5, the initial pH of the SBX solution is 10.25, therefore, $\cdot OH$ could be induced due to the initiation of OH^- , as shown in Eqs. 1, 16, 17 (Beltran et al., 2007).



The non-selective $\cdot OH$ greatly accelerate the course of degradation of SBX and breaking of bonds. Because of electrophilicity, $\cdot OH$ might attack on the site of highest electron density of the SBX during this course. The C–O may be broke by $\cdot OH$ and nucleophilic reaction may be occurred in C=S bond by $\cdot OH$, as a result, CS_2 , H_2S , SO_2 , CO_2 , n-butanol, intermediate, are generated and the decrease of pH is observed as seen in Fig. 6. A simplified scheme of the decomposition pathways of the ozonation of SBX using OCF process.

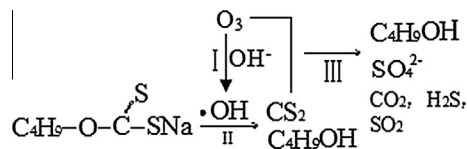


Fig. 6. Simplified scheme of the decomposition pathways of the ozonation of butyl xanthate.

With the generation of n-butanol and the increase of acidity, the radical chain reaction is terminated, the decomposition of ozone is inhibited as the n-butanol is a depressant of ozone decomposition, which could put an end to radical chain reaction. Therefore, under the condition of unadjusted the paper, the duration of reaction II is transitory (Beltran et al., 2007).

As pH below 4, reaction III is predominant, so pH descending tendency should become comparatively slow, corresponding to the results (Fig. 5). Further oxidation, ozone is mainly react with CS_2 , and then CS_2 has been oxidized to H_2S , SO_2 , SO_4^{2-} , etc. But n-butanol could not be oxidized by OCF process, thus the intermediates produced from the decomposition of SBX, n-butanol, sulfide of low valence state, etc, jointly contribute approximately 20% COD relative to the initial value.

3.4. Removal of COD associated with variation of ORP

The application of ORP as a supplementary index of industrial wastewater treatment system has often been reported (Hou et al., 2006; Yang et al., 2006). Fig. 7 presents the variation of ORP of SBX solution with η_{COD} . As shown in Fig. 7, the value of ORP reveals slight variation in the initial period while increases significantly in the later period with higher η_{COD} . For $\eta_{COD} < 40\%$, the values of ORP are between -110 and 0 mV. In this stage, the organics of COD in the SBX solution are predominant for controlling the ORP of solution with slight variation. While the ORP > 535 mV, the η_{COD} becomes $> 72.21\%$.

It could be noted that the distinct variation of ORP is keeping synchronous with the variation of η_{COD} . The oxidation–reduction state of SBX solution is changed remarkably during the ozonation time (15–45 min), and in this period the SBX solution became clear. Thus, indeed, correlation exists between the ORP of SBX solution and the η_{COD} . ORP is a useful parameter associated with the oxidation date of the ozonation of SBX in terms of η_{COD} . The removal efficiency of COD can be reflected by real-time monitoring the variation of ORP in aqueous solution.

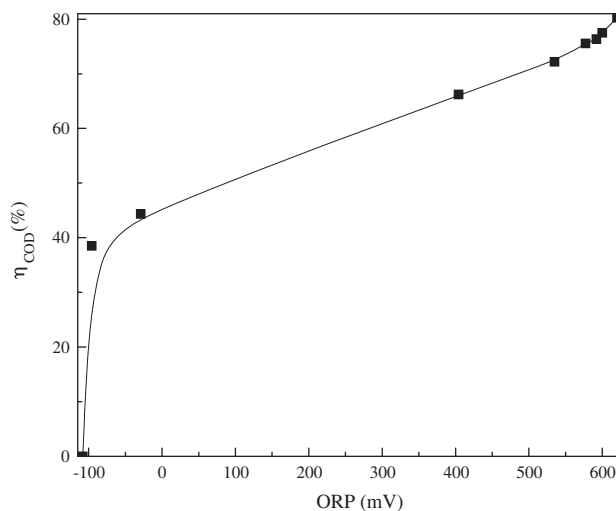


Fig. 7. The relationship between ORP and η_{COD} .

Table 3The C_{BOD5}/C_{COD} ratio of the collectors.

Collectors	SBX	Butyl amine aerofloat	Diethyl-amino-xanthate
C_{BOD5} (mg/L)	39	44	102
C_{COD} (mg/L)	229	210	232
C_{BOD5}/C_{COD}	0.17	0.21	0.44

Table 4

The relationship between ozonation time and BOD of butyl xanthate solution.

t (min)	0	15	60	120
C_{BOD5} (mg/L)	1715	1291.5	684	602.5
C_{COD}	6823.1	4195.2	1896.4	1347.6
C_{BOD5}/C_{COD}	0.251	0.308	0.361	0.447

3.5. Variation of biodegradability in ozonation of SBX

The advantage of microbe to degrade organic pollutants is usually worth considering. In general, the biodegradability of organism can be denoted as C_{BOD5}/C_{COD} . And it is ordinarily believed that the organic pollutants with ratio in the range of 0.3–0.35 is readily biodegradable.

Table 3 lists the C_{BOD5}/C_{COD} of three kinds of common collector (4.1×10^{-5} mol/L). It can be seen that the C_{BOD5}/C_{COD} of SBX is 0.17, much lower than butyl diethyl-amino-xanthate. It is a kind of refractory organics.

The C_{BOD5}/C_{COD} of SBX (5000 mg/L) sampled from solution during ozonation at special intervals is also investigated in this experiment, as shown in Table 4.

It can be inferred from Table 4 that the C_{BOD5}/C_{COD} of SBX solution increases with increasing ozonation time. At $t = 15$ min, the C_{BOD5}/C_{COD} reached 0.308, greatly improved the biodegradability of SBX solution. It was found that the biodegradability (C_{BOD5}/C_{COD}) of SBX solution can be improved by OCF system. Therefore, it could make full use of the environmental microbe to biodegrade the refractory SBX in aqueous solution, so as to improve total economic benefit. In addition, it is also confirmed the opinion that ozonation can improve the biodegradability of the organic wastewater.

4. Conclusions

OCF has proven to be an effective way for the removal of SBX in the aqueous solution. The decomposition of butyl xanthate accompanies with the diminishing of COD and the generation of SO_4^{2-} . It can be concluded that.

The degradation of SBX in OCF system has a great adaptability to initial pH of SBX solution. The OCF system can effectively and rapidly remove SBX from aqueous solution, the η_{SBX} reached 87.55% at $t = 1$, and almost 100% reduction appears at $t = 6$.

The decomposition of SBX accompanies with moderate diminution of C_{COD} , η_{COD} increases with ozonation time, the 72.21% C_{COD} reduction is observed when ozonation time is close to 60 min.

A considerable stack of SO_4^{2-} is generated during ozonation of SBX solution, corresponding to the phenomena of rather low pH of oxidized SBX solution and reached high η_{COD} . Sulfide of low valence state, n-butanol, intermediates jointly contribute approximately 20% COD relative to the initial value.

Correlation exists between the ORP of SBX solution and the η_{COD} . The removal efficiency of COD can be reflected by real-time monitoring the variation of ORP in aqueous solution.

The biodegradability (C_{BOD5}/C_{COD}) of SBX solution can be improved by OCF system. At $t = 15$, the C_{BOD5}/C_{COD} reached 0.308, greatly improving the biodegradability of SBX solution.

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