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Degradation of ethylthionocarbamate by activated sludge coupled with interior microelectrolysis

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ABSTRACT

Degradation behavior of ethylthionocarbamate by activated sludge coupled with interior microelectrolysis (ASCIE) was investigated. Degradation kinetics and removal efficiency of ethylthionocarbamate were also discussed in comparison with traditional activated sludge (AS) and interior microelectrolysis (IE), respectively. The results showed that the degradation rate decreased sharply when most ethylthionocarbamate was removed from the solution of these three different processes, the degradation rate of ethylthionocarbamate was ranked from high to low as ASCIE > IE > AS, and the corresponding maximum degradation rate was 5.705, 4.185, and 1.90 mg/(L d), respectively. The degradation of ethylthionocarbamate under these three different processes can be accurately described by first-order exponential decay kinetics.

Keywords: Ethylthionocarbamate; Activated sludge; Interior microelectrolysis; Galvanic cell reaction; Degradation kinetics

1. Introduction

Ethylthionocarbamate has been widely used as flotation reagent in sulfide mineral processing for many decades [1], which is high toxic and difficult to biodegrade. Normally, they are discharged directly into the environment without any treatment. It is known that even small concentration of these reagents in water streams is toxic to water life, besides their deleterious influence on the end stream processes during recycling [2]. The serious environmental problems associated with flotation reagents in mineral processing plant wastewater have been well documented [3,4].

The flotation wastewater pollution is controlled mainly by physical and chemical methods. However, these methods are obviously deficient, such as high energy consumption, high operating costs, and may cause secondary pollution [5], inhibiting their widespread application and limiting their availability. The biological treatment is most commonly used in practice worldwide and regarded as efficient options to deal with flotation wastewater due to its simplicity, stability, low cost, and environmental benignity. An ideal scheme for the treatment of ethylthionocarbamate flotation wastewater is to pretreat the wastewater by

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physiochemical processes to improve biodegradability and reduce toxicity before biological treatment.

The IE method has been paid increasing attention recently, which is thought to have little or no harmful effects on environment for the use of harmless reagents and need no extra energy [6,7]. More importantly, IE could be extensively adaptable to wide variations of compositions of wastewater, especially in the treatment of refractory and toxic wastewater [8,9], such as textile wastewater [10], pesticide wastewater [11], and anthraquinone dye wastewater [12]. And the half-cell reactions can be represented as [13]:

Iron anode (oxidation):

$$\begin{aligned}&\mathrm{Fe(s)} - 2\mathrm{e}^- \rightarrow \mathrm{Fe}^{2+} + \mathrm{(aq)},\\ &\quad E^\theta\ (\mathrm{Fe}^{2+}/\mathrm{Fe}) = -0.44\ \mathrm{V}\end{aligned} \tag{1}$$

$$\begin{aligned}&\mathrm{Fe}^{2+}\mathrm{(aq)} - \mathrm{e}^- \rightarrow \mathrm{Fe}^{3+} + \mathrm{(aq)},\\ &\quad E^\theta\ (\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}) = +0.77\ \mathrm{V}\end{aligned} \tag{2}$$

Carbon cathode (reduction):

$$\begin{aligned}&2\mathrm{H}^+\mathrm{(aq)} + 2\mathrm{e}^- \rightarrow 2[\mathrm{H}] \rightarrow \mathrm{H_2(g)},\\ &\quad E^\theta\ (\mathrm{H}^+/\mathrm{H}_2) = 0\ \mathrm{V}\end{aligned} \tag{3}$$

In the presence of oxygen:

$$\begin{aligned}&\mathrm{O_2(g)} + 4\mathrm{H}^+\mathrm{(aq)} + 4\mathrm{e}^- \rightarrow 2\mathrm{H_2O},\\ &\quad E^\theta\ (\mathrm{O_2/H_2O_2}) = +1.23\ \mathrm{V}\end{aligned} \tag{4}$$

$$\begin{aligned}&\mathrm{O_2(g)} + 2\mathrm{H}^+\mathrm{(aq)} + 2\mathrm{e}^- \rightarrow \mathrm{H_2O_2},\\ &\quad E^\theta\ (\mathrm{O_2/H_2O_2}) = +0.68\ \mathrm{V}\end{aligned} \tag{5}$$

$$\begin{aligned}&\mathrm{O_2(g)} + 2\mathrm{H_2O} + 4\mathrm{e}^- \rightarrow 4\mathrm{OH}^-\mathrm{(aq)},\\ &\quad E^\theta\ (\mathrm{O_2/OH^-}) = +0.40\ \mathrm{V}\end{aligned} \tag{6}$$

From a chemical point of view, numerous microscopic galvanic cells are formed between the particles of iron and activated carbon in wastewater, which results in the galvanic cell reaction. Products released from the galvanic cell reaction include hydroxyl, atomic hydrogen, and Fe(II), which have high activities to decompose contaminants [14,15]. From a biological point of view, iron is an important and indispensable component of biomolecule which undergoes redox in cells, and Fe(II) is often used in activated sludge (AS) treatment plants as a coagulant [13,16]. Thus, it would be more advisable to combine IE with AS processes together, which has many merits, such as low-cost iron scraps, low operating costs, high process efficiency, and the enhancement of the biodegradability of wastewater. Therefore, in the present investigation, the degradation behavior of ethylthionocarbamate by ASCIE was studied, and the removal efficiency and kinetics process of ethylthionocarbamate were also discussed.

2. Materials and methods

2.1. Materials

The analytical grade reagents were purchased from Tianjin Chemical Co., Ltd (Tianjin, P.R. China). Ethylthionocarbamate was obtained from Zhuzhou Mineral Processing Reagent Plant (Zhuzhou, P.R. China). The granular activated carbon (GAC) had a mean particle diameter of 2–3 mm, which was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, P.R. China). Waste iron chips were obtained from a metal machining mill in Wuhan, P.R. China, and they were 1–3 mm in length and 0.5–1.0 mm in width. Waste iron chips were firstly degreased in a 10% NaOH solution, and then soaked in a diluted (2%) hydrochloride acid solution for 40 min. Finally, the chips were cleaned with distilled water and dried in a drying oven at 80˚C for 12 h, and then placed in a drying chamber for later use.

Activated sludge used was collected from a sewage treatment plant (Wuhan, P.R. China).

2.2. Culture medium and enrichment

Enrichment was conducted aerobically in 1 L shaking flasks containing 200 mL culture medium and 200 mL AS sample. The medium contained the following constituents: $\mathrm{NH_4Cl}$ (1.5 g/L), $\mathrm{KH_2PO_4}$ (0.6 g/L), $\mathrm{MgCl_2{\cdot}6H_2O}$ (0.1 g/L), $\mathrm{CaCl_2}$ (0.1 g/L), yeast extract (1.0 g/L), and trace solutions (1%, v/v). The composition of the trace element solution: $\mathrm{(NH_4)_6Mo_7O_{24}{\cdot}4H_2O}$ 300 mg/L, $\mathrm{H_3BO_3}$ 10 mg/L, $\mathrm{FeSO_4{\cdot}7H_2O}$ 2000 mg/L, $\mathrm{MnSO_4{\cdot}H_2O}$ 500 mg/L, $\mathrm{CoCl_2}$ 2000 mg/L, $\mathrm{ZnSO_4{\cdot}7H_2O}$ 90 mg/L, $\mathrm{CuSO_4{\cdot}5H_2O}$ 150 mg/L, and $\mathrm{AlCl_3{\cdot}6H_2O}$ 90 mg/L. During enrichment, ethylthionocarbamate concentration was gradually increased from 10 to 50 mg/L at 12-d intervals under incubation at 28˚C and 180 rpm. After two months, the mixed bacterial consortia capable of biodegrading ethylthionocarbamate were obtained.

2.3. Experimental procedure

In ASCIE experiment, the enriched bacteria was transferred into 1 L shaking flasks filled with 200 mL medium and yeast extract was omitted from the medium. And the enriched bacteria were added to get the initial concentration of 2.0 g MLSS/L. The waste iron chips, GAC, and ethylthionocarbamate (30 mg/L) were added to medium. Iron chips were thoroughly mixed with GAC in the desired proportion before being added to the flasks. Then, the final volume of mixture should be adjusted to 500 mL with culture medium. Also, the initial pH of solution was adjusted to 6.5 with 0.5 M HCl in order to account for the degradation of ethylthionocarbamate by AS or IE process alone. In AS experiment containing no iron chips and GAC, IE experiment containing no AS was run in parallel. The flasks were immediately placed into a thermostatic oscillator with 180 rpm for 16 d at 28℃. Thereafter, samples were withdrawn periodically collected from the flasks to measure the concentration of ethylthionocarbamate and pH. All the experiments were conducted in triplicate.

To study the effect of dissolved oxygen concentration on ethylthionocarbamate degradation efficiency in ASCIE experiment, three parallel controlled trials experiments in serum bottle were carried out as follows. The mixture in serum bottle A was flushed with high-purity nitrogen gas for 20 min, the mixture in serum bottle B was flushed without any pretreatment, and C was flushed with compressed air for 20 min. Finally, the serum bottles A and C were immediately sealed with butyl rubber stoppers and aluminum caps. And three experiments were performed under the same conditions described above. The initial dissolved oxygen concentration in flasks A, B, and C was about 0.2 mg/L, 2.5 mg/L, and 7.05 mg/L, respectively.

2.4. Analytical methods

A pH meter (ORZ0N818, USA) was employed for measuring pH values. Ethylthionocarbamate concentration was analyzed using a UV–vis spectrophotometer (Shimadzu, Japan). Dissolved oxygen concentration was measured by a dissolved oxygen analyzer (HQ10, HACH).

3. Results and discussion

3.1. Effect of iron chips dosage

The effect of iron chips dosage was investigated, and the results are shown in Fig. 1.

The results indicate that the degradation of ethylthionocarbamate is significantly influenced by the dosage of iron chips. The reason is that iron chips dosage determines the amount of galvanic cells in an IE process; a higher iron chips dosage results in the formation of more galvanic cells. A large enhancement in ethylthionocarbamate removal is observed by increasing the iron chips dosage from 20 to 30 g/L, but when the iron chips dosage exceeds 30 g/L, the degradation rate of ethylthionocarbamate increased slowly. Furthermore, considerable colority was visible in the mix solution. This may have been caused by high concentrations of residual Fe^{3+} [17]. Therefore, the optimum dosage of iron chips was 30 g/L.

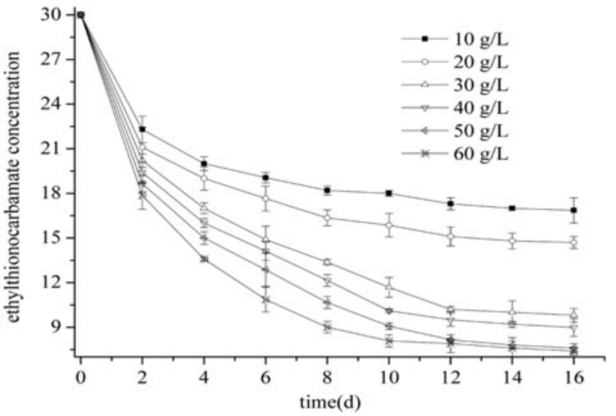

Fig. 1. Effect of iron chips dosage on the degradation of ethylthionocarbamate (Fe/C mass ratio is 3:1).

Fig. 1 also indicates the degradation rate of ethylthionocarbamate is faster in beginning and then becomes slower under different iron chips dosage. The reason for this is that IE plays a major role in the the degradation of ethylthionocarbamate in the first eight days. After that, IE effect decreased, ethylthionocarbamate removal was mainly due to biodegradation, and thus, the degradation rate was relatively slow. With - iron chips dosage of 10, 20, 30, 40, 50, and 60 g/L, most ethylthionocarbamate was degraded during the period of the first 12 d, accounting for 96.65, 97.38, 98.02, 97.53, 97.54, and 97.79% of the total degradation, respectively.

3.2. Effect of Fe/C mass ratio

Fig. 2 shows the effect of Fe/C mass ratio on the degradation of ethylthionocarbamate. As we know, optimizing the Fe/C mass ratio can enhance the effective contact area between iron chip and GAC and thus enlarge the number of galvanic cells formed. Ethylthionocarbamate removal efficiency increased rapidly with increasing Fe/C mass ratio in the range of 1:2−4:1, but later decreased when the Fe/C mass ratio was increased from 4:1 to 6:1. The reason for this opposite correlation is that the effect of IE is weak at a Fe/C mass ratio of 1:2 due to surplus GAC and

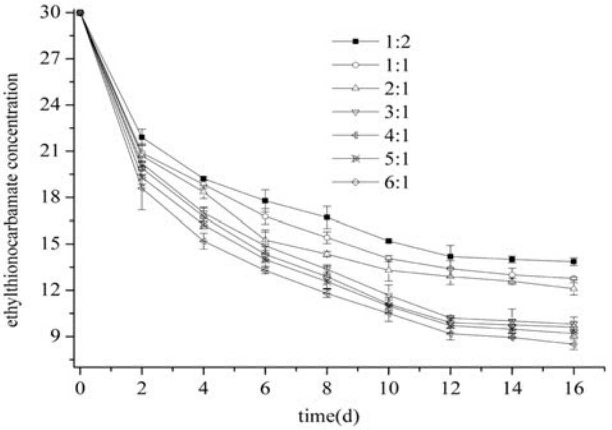

Fig. 2. Effect of Fe/C mass ratio on the degradation of ethylthionocarbamate (total mass of Fe and C equal to 20 g).

inadequate iron chips, which was disadvantageous for ethylthionocarbamate removal. As the Fe/C mass ratio increased, the microelectrolytic effect strengthened owing to increased iron chips, resulting in the rapid increase in the degradation of ethylthionocarbamate. However, when the Fe/C mass ratio exceeded 4:1, the dosage of iron chips exceeded that of GAC, and the effective contact area between iron chips and GAC was reduced as the Fe/C mass ratio increased [17], leading to the abatement of ethylthionocarbamate removal efficiency. The results indicate that lower or higher Fe/C mass ratio is no benefit in improving removal efficiency of ethylthionocarbamate. Therefore, the optimal Fe/C mass ratio is 4:1.

3.3. Effect of initial dissolved oxygen concentration

First, dissolved oxygen concentration affects the activity of aerobic bacteria. What's more, solution's dissolved oxygen concentration affects electrochemical reduction and coagulation in an IE process [17]. For those reasons, dissolved oxygen concentration is the important factor that affects the degradation efficiency of ethylthionocarbamate.

Fig. 3 shows that ethylthionocarbamate removal efficiency was accelerated with an increase in dissolved oxygen concentration range from 0.2 to 7.05 mg/L. The reason is that relatively high dissolved oxygen concentration is beneficial to promote the growth and metabolic processes of aerobic bacteria. Additionally, the electrode voltage was much higher in Eqs. (4)–(6) (+1.23, +0.68, and +0.40 V) than in Eq. (3) (0 V), and more energy was provided when oxygen participated in the cathodic reaction [13]. Thus, the electrode reactions were strengthened and production rate of Fe^{2+} was increased, and Fe^{2+} released into the solution can be easily oxidized to Fe^{3+} in the presence of oxygen. Moreover, Fe^{2+} could be oxidized to Fe^{3+} by aerobic bacteria. As a result, active ferrous and iron hydroxides are generated (Eqs. (7)–(10)). Simultaneously, processes such as adsorption, enmeshment, and coprecipitation with newly generated ferrous and ferric hydroxide floc occur [7], contributing to the overall removal of ethylthionocarbamate.

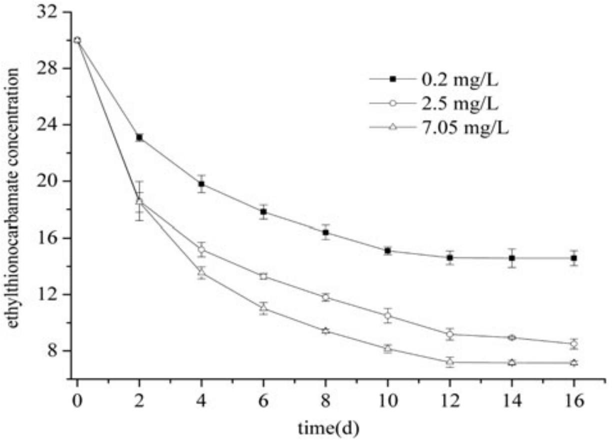

Fig. 3. Effect of initial dissolved oxygen concentration on the degradation of ethylthionocarbamate.

$$Fe^{2+} - e^- + 3OH^- \rightarrow Fe(OH)_3 \downarrow \quad (7)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \downarrow \quad (8)$$

$$Fe(OH)_2 - e^- + OH^- \rightarrow Fe(OH)_3 \downarrow \quad (9)$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \downarrow \quad (10)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^{\cdot} + OH^- \quad (11)$$

Additionally, based on Eq. (5), H_2O_2 is generated and subsequently combined with Fe^{2+} to form Fenton's reagents to generate hydroxyl radicals (Eq. (11)) [18], which shows high oxidizability, with the assistance of AS and IE process; theoretically, it can promote the decomposition of ethylthionocarbamate into small molecule substances and effectively improve the biodegradability of ethylthionocarbamate flotation wastewater, which was beneficial to the subsequent biodegradation of ethylthionocarbamate by enriched bacteria. Thus, it can significantly improve the degradation efficiency of ethylthionocarbamate.

3.4. Degradation of ethylthionocarbamate under different processes

From Fig. 4, under three different processes, the degradation rate decreased sharply when most ethylthionocarbamate was removed from the solution. The degradation rate of ethylthionocarbamate was ranked from high to low as ASCIE > IE > AS, and the corresponding maximum degradation rate was 5.705, 4.185, and 1.90 mg/(L d), respectively.

In AS process, the enriched mixed bacteria could rapidly degrade ethylthionocarbamate without lag period, the removal efficiency reached 36.53% in 8 d, compared with 40.37% in 16 d, only increased by 3.84%.

In IE process, adsorption, flocculation, coprecipitation, enmeshment, electrophoresis, and redox contribute to the removal of ethylthionocarbamate. There was no significant change in the removal efficiency of ethylthionocarbamate after 8 d, which further illustrates IE plays a dominant role in the degradation of ethylthionocarbamate in the first eight days, and then gradually reduced. The IE reduced ethylthionocarbamate from 30 to 13.05 mg/L in 16 d, which corresponds to ethylthionocarbamate removal efficiency of 56.50%.

In ASCIE process, both AS and IE could remove synergetic ethylthionocarbamate, meanwhile, iron ion formed during the IE process could promote metabolism of aerobic microorganisms [12]. Ethylthionocarbamate removal efficiency was 71.67% in 16 d, which showed the highest ethylthionocarbamate removal efficiency in these three processes. It is demonstrated that the ASCIE process can be an efficient method for improving the removal efficiency of ethylthionocarbamate flotation wastewater.

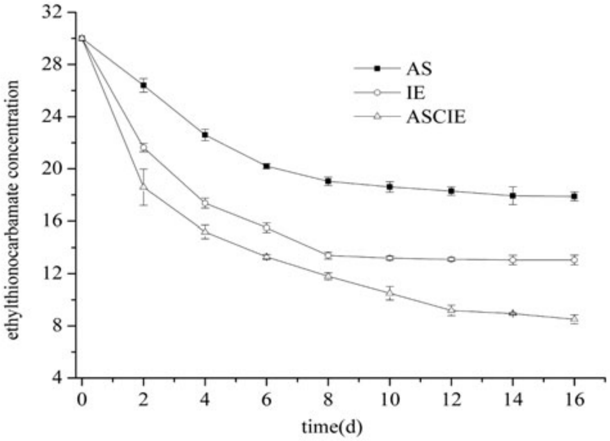

Fig. 4. Degradation of ethylthionocarbamate under different processes.

The variations of pH in different processes are shown in Fig. 5.

pH is one of the key factors that not only affects the microbial activity in AS process, but also influences the chemical states of the substances and redox potential. Moreover, it can modify the surface charge of the GAC and affect its electrostatic interaction [8]. Therefore, it could be considered as an important impact factor in AS, IE, and ASCIE processes.

In AS process, pH is slowly increased during the whole process, and pH increased from 6.50 to 7.06 after 16 d.

In IE process, it showed that pH value increased slowly at the beginning of the experiment. However, after 8 d, pH value was almost constant. This illustrates IE plays a major role in the degradation of ethylthionocarbamate in the first eight days, and these conclusions are in accordance with that obtained from Fig. 1.

In ASCIE process, pH values increased from initial 6.50 to 7.05 after 6 d, which were changed from acidity to near neutral. According to Eqs. (1)–(5) [19], a certain amount of H^+ would be consumed is the important reason resulting in the increase in pH in ASCIE process.

It was also observed that the final pH values under three different processes were almost constant and near neutral, and 7.06 in AS, 6.89 in IE, and 7.18 in ASCIE, respectively. This indicates that IE as a pretreatment process for ethylthionocarbamate flotation wastewater, and its effluent could have entered subsequent biological processes without pH adjustment.

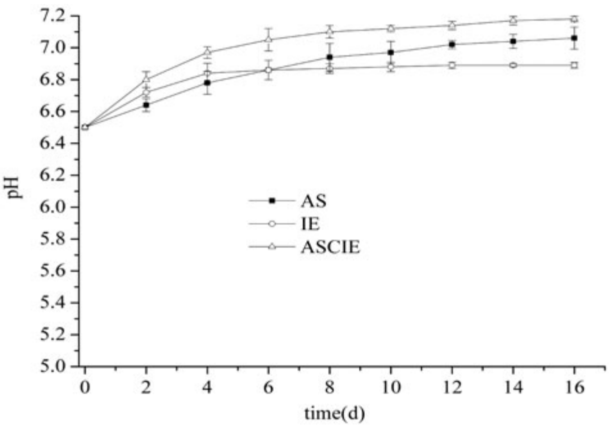

Fig. 5. The variations of pH in different processes.

Table 1
Kinetic parameters of degradation ethylthionocarbamate under different processes

Conditions	A	D	B_0	R^2
AS	13.0431	4.4252	17.3004	0.9892
IE	17.2544	3.0110	12.7598	0.9971
ASCIE	20.3714	3.2719	9.0698	0.9800

3.5. Degradation kinetics

The first-order exponential decay equations were employed to compare the degradation effect of ethylthionocarbamate under different processes. And the first-order exponential decay equations can be expressed as follows:

$$C = A\ \exp\left(-\frac{t}{D}\right) + B_0 \tag{12}$$

where C is the concentration of ethylthionocarbamate, A is the decay intensity constant, D is decay index, and t is the reaction time and B_0 is a constant.

Table 1 shows that first-order exponential decay equations can accurately describe the degradation of ethylthionocarbamate under different processes.

In AS process, the disappearance of ethylthionocarbamate was due to biodegradation, and A value was the lowest. In IE process, A value higher than that of AS but lower than that of ASCIE is lack of the actions of AS compared with ASCIE. In ASCIE, multiple processes such as AS, flocculation, coprecipitation, enmeshment, electrophoresis, and redox are contributed to ethylthionocarbamate removal; therefore, A value was the highest. Namely, A value of ethylthionocarbamate was ranked from high to low as $A_{\mathrm{ASCIE}} > A_{\mathrm{IE}} > A_{\mathrm{AS}}$, these results are consistent with the discussion in the previous section.

4. Conclusions

The ASCIE process can be an efficient method for improving the removal efficiency of ethylthionocarbamate flotation wastewater. In ASCIE, physical, chemical, and biological actions all have effects on the removal of ethylthionocarbamate. And removal efficiency was significantly accelerated with an increase in dissolved oxygen concentration. Under three different processes, the degradation rate decreased sharply when most ethylthionocarbamate was removed from the solution, the degradation rate of ethylthionocarbamate was ranked from high to low as ASCIE > IE > AS, and the corresponding maximum degradation rate was 5.705, 4.185, and 1.90 mg/(L d), respectively. Their degradation processes fitted well with the first-order exponential decay kinetics equation.

Acknowledgments

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