

Controlling two-phase foam through the Fenton oxidation process

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ABSTRACT

Direct discharge of wastewater from flotation processes can pose a significant threat to environmental protection due to the presence of residual organic surfactants. These surfactants can decrease the surface tension of aqueous solutions and generate stable foam, which can interfere with further purification treatments. To address this issue, sodium oleate (NaOL), one of the most commonly used surfactants, was studied, and the Fenton oxidation process was utilized to degrade NaOL and mitigate foam generation. In this work, the foamability of NaOL before and after Fenton oxidation pretreatment, the optimal conditions for NaOL degradation, and the effect of temperature on the oxidative process were examined. The findings demonstrate that the foamability of NaOL solution is directly proportional to its concentration, and the Fenton oxidation process can significantly reduce the maximum foam volume and half-life period of the foam. Moreover, the activation energy was determined to be 37.60 kJ/mol, indicating that the oxidative reaction proceeds with a low energy barrier.

Keywords: Residual flotation reagents; Two-phase foam; Fenton oxidation process; Sodium oleate; Degradation

1. Introduction

Flotation separation is a common method for recovering valuable minerals from gangue [1–4]. The most important factor that affects the separation efficiency is the choice of reagents. Surfactants with different chemical structures and functional groups are always employed in different mineral

systems to modify the surface properties of the targeted minerals [5].

Sodium oleate, an anionic surfactant, has been extensively used in the flotation of minerals such as ilmenite, rutile, and apatite. The elongated carbon chain, which is coupled with specific functional groups, facilitates targeted mineral binding and enhances mineral attachment onto air bubbles [6–8]. Even though the use of surfactants

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could largely improve the flotation separation efficiency, excessive foaming might create serious problems in many industrial processes [9]. The uncontrolled discharge of flotation wastewater containing residual surfactants could pose a significant threat to the environment, as these compounds contribute to the formation of foam in rivers and wastewater treatment plants, resulting in reduced water quality and potential adverse effects on human health and the ecosystem [10,11].

The excessive formation of foam in aqueous solutions resulting from the presence of residual organic surfactants has been addressed by utilizing a typical antifoam or defoamer consisting of oil [9,12], hydrophobic solid particles [13], or a mixture of both [14]. Researchers worldwide have also devoted tremendous efforts to synthesizing different types of defoamers, including organic siloxane [15], polyether, silicon, ether graft, amines, imines, and amide siloxane [16]. Defoamers have been demonstrated to be effective in reducing foam formation in aqueous solutions by altering their surface tension through interactions with residual organic substrates. However, caution must be exercised when adding another organic substrate, as it may introduce further organic matter to the solution and potentially exacerbate the issue at hand. Previous research demonstrated that the Fenton oxidation process is a highly effective and environmentally friendly approach for the degradation of organic matter; however, there is limited research focused on the correlation between residual organic matter and the resultant foaming performance following Fenton oxidation treatment [17–19].

The primary objectives of this study are to establish the feasibility and practicality of utilizing the Fenton oxidation process to control two-phase foam. Sodium oleate (NaOL) was selected as the common residual surfactant in flotation wastewater in this work. The relationship between the half-life period and maximum foam volume and NaOL concentration before and after the Fenton oxidation treatment was revealed. Furthermore, the effect of pH value, reaction time, H_2O_2 and $FeSO_4$ concentration was investigated to find the optimal conditions for degradation.

Therefore, the aim of the study is to present a novel perspective on utilizing advanced oxidation processes to mitigate foam generation. Furthermore, the study serves as a guide for researchers to explore more eco-friendly alternatives and promote the purification of flotation wastewater.

2. Materials and methods

2.1. Materials

NaOL and $FeSO_4 \cdot 7H_2O$ with analytical purity were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Industrial grade (50%) H_2O_2 was obtained from Hubei Sanning Chemical Co., Ltd., China. Diluted HCl and NaOH were used to regulate the pH to the desired value. Deionized water (18.25 M Ω) obtained from a Milli-Q Direct 16 (Millipore Q, USA) was employed throughout the experiments.

2.2. Methods

2.2.1. Degradation of sodium oleate using the Fenton oxidation process

50 mL of sodium oleate solution with a concentration of 50 mg/L was placed into a 100 mL beaker, and the solution was then magnetically stirred at 200 rpm for 2 min. Next, the pH of the solution was adjusted to an appropriate value by adding phosphoric acid. $FeSO_4 \cdot 7H_2O$ and H_2O_2 were successively added into the solution to start the Fenton oxidation reaction. Finally, after a given reaction time, NaOH was added to adjust the pH to 10 and stop the process.

2.2.2. Measurement of the concentration of sodium oleate

The relationship between the concentration of sodium oleate and surface tension was established in Fig. 1 and subsequently utilized to calculate the residual concentration of the solution. The solute concentration in the solution was deduced through determining the sensitivity of the surface tension to the concentration within a particular range. The experimental procedure involved preparing an initial solution with a concentration of 50 mg/L, which was then diluted to 5, 4, 3, 2 and 1 mg/L. The surface tension of each solution was measured and used to establish the relationship between the surface tension and concentration.

As demonstrated in Fig. 1a, concentration caused a notable effect on surface tension, and the surface tension significantly dropped as the concentration increased. However, when the concentration surpassed 10 mg/L, the surface tension slightly declined. Therefore, to establish a functional

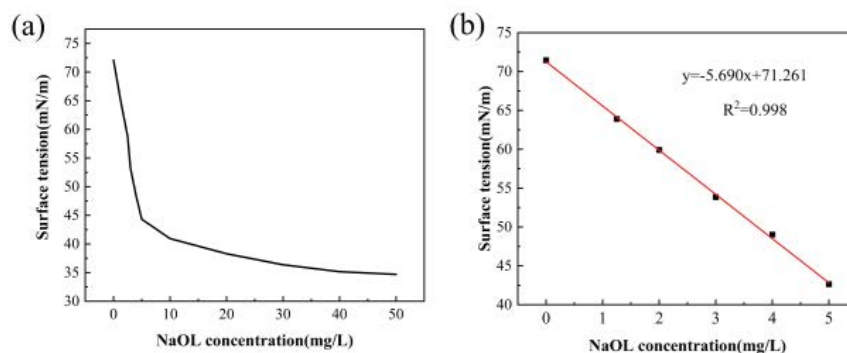


Fig. 1. (a) Effect of sodium oleate concentration as a function of surface tension and (b) fitting curve for sodium oleate concentration as a function of surface tension at low concentration.

relationship between surface tension and concentration, a concentration range of 0–5 mg/L was selected for curve fitting, and the resulting relationship is depicted in Fig. 1b. The linear formula is calculated through Eq. (1).

$$y = -5.690x + 71.261 \quad (1)$$

where y is the surface tension diagram of the sodium oleate solution; x is the concentration diagram of the sodium oleate solution.

The correlation coefficient (R^2) is 0.998, which is sufficiently high for further calculation of concentration.

2.2.3. Measuring the foamability of the sodium oleate solution

The foamability testing apparatus for gas–liquid two-phase systems comprises three essential components, namely, an air pump, a gas flow meter, and a foam volume measurement column/cylinder. One critical aspect of the setup involves connecting the graduated cylinder of the foam height column, which is commonly used in the Bikerman technique, to two foam testers with opposing scales to help obtain accurate and straightforward measurements.

To test the foam characteristics, 50 mL of the target solution was introduced into the Teflon sand core column. Subsequently, the air pump was opened and adjusted to a flow rate of 200 mL/min, resulting in the formation of foam upon the introduction of air. At this point, the liquid level initially decreases from the zero scale to a specific height H_2 , while the foam rises to a particular height H_1 , in which the maximum foam volume (MFV) corresponds to the sum of foam column H_1 and foam column H_2 . Fig. 2 illustrates the schematic diagram of the foam characteristic testing apparatus. The MFV and half-life period (HLP) were measured immediately after 20 s.

3. Results and discussion

3.1. Effect of NaOL concentration on MFV and HLP

The effect of NaOL concentration on MFV and HLP was evaluated, and the results are provided in Fig. 3. As shown in Fig. 3, with increasing NaOL concentration from 0 to 50 mg/L, the MFV showed an upward trend, rising from 0 to 67.7 mL. A further increase in NaOL concentration caused a negligible effect on MFV, as the value was rather steady. Regarding the HLP, a proportional relationship with the NaOL concentration was observed, wherein the foam was unstable and unable to persist for extended periods when the concentration was less than 30 mg/L. After the concentration was increased beyond this threshold, the HLP exhibited a sharp rise and eventually surpassed 1,800 s at a concentration of 50 mg/L, implying that the foam could remain stable in the solution for a relatively long duration. The results indicate that the foam stability was directly proportional to the NaOL concentration. The increase in concentration significantly reduced the surface tension of the aqueous solution and the pressure difference between the liquid films, thereby impeding the diffusion of gas from the liquid film. Furthermore, as the concentration increased, NaOL was enriched on the surface of the liquid film, forming a thick surface coating that inhibited

the drainage of the neighboring liquid film and enhanced foam stability. However, it has been reported that at NaOL concentrations above 1×10^{-3} mol/L, further increases in concentration diminish foam stability, as increasing oleate ions reduce the fluid content and enhance the rigidity [20].

3.2. Optimizing the parameters of the Fenton oxidation process

Operational parameters, such as pH value, reaction time, H_2O_2 and Fe^{2+} , concentration are the most important factors that affect the degradation efficiency during the Fenton oxidation process. Hence, all the parameters mentioned above were selected to determine the optimal conditions and achieve the effective degradation of sodium oleate [21].

As demonstrated in Fig. 4a, the degradation of NaOL is largely dependent on the pH value. When the pH was between 2 and 3, the degradation of NaOL accelerated substantially, reaching a peak of more than 75% at pH 3. When the pH was increased further, the degradation experienced a decline and reached its lowest point (less than 15%); thus, the oxidation effect would be heavily eliminated in an alkaline environment. According to Fenton oxidation theory, when

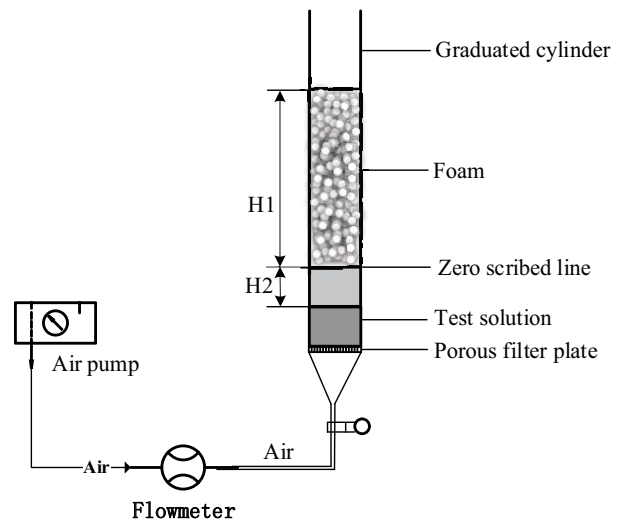


Fig. 2. Schematic diagram of the foam characteristic testing device.

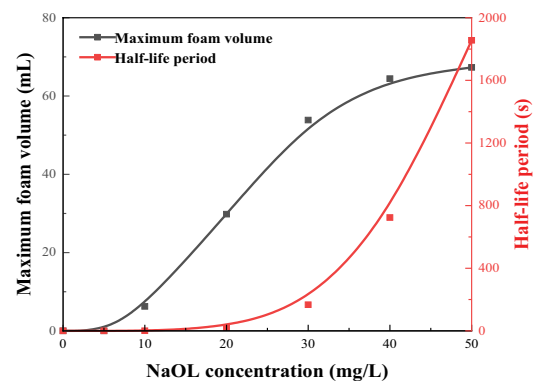
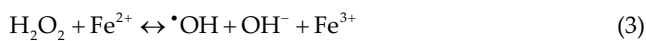
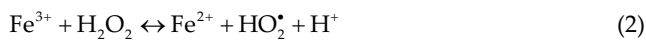


Fig. 3. Effect of sodium oleate concentration on the maximum foam volume and half-life period.

the pH is extremely low, the reaction in Eq. (2) is severely constrained due to the excessive H^+ concentration, which prevents Fe^{3+} from being reduced to Fe^{2+} and thereby eradicates the catalytic process. That is, a change in pH directly influences the complexation equilibrium system of Fe^{3+} and Fe^{2+} , hence influencing the oxidation effect. When the pH is too high, Eq. (3) becomes limited since the generation of active OH^{\bullet} is restricted. Moreover, the Fe^{2+} in the solution reacts with the additional OH^- to generate precipitates, losing its catalytic activity [22–24]. In this regard, pH 3 was selected for further experiments.



Under the optimal pH value, the effects of the $FeSO_4$ concentration and H_2O_2 concentration were demonstrated, and the results are presented in Fig. 4b and c. From Fig. 4b it can be seen that the degradation of NaOL experienced an upward trend, increasing from 60% to 80% when the $FeSO_4$ concentration was increased to 0.15 mmol/L. Further increases in $FeSO_4$ concentration would detrimentally impact its capacity to degrade; hence, 0.15 mmol/L was chosen as the best $FeSO_4$ concentration for future tests. For the H_2O_2 concentration, it can be observed that the degradation of NaOL marginally increased and reached equilibrium when the concentration was increased to 1.4 mmol/L, reaching 98.99%. A further increase in H_2O_2 concentration exhibits no effect on degradation because extra H_2O_2 does not produce more active OH^{\bullet} sites along the chain reaction but rather oxidizes Fe^{2+} to Fe^{3+} at the start of the process. On the other hand, when the H_2O_2 concentration reaches

a greater level, additional increases in the H_2O_2 concentration may produce various side reactions throughout the experiment, such as those in Eqs. (4) and (5), resulting in a significant self-loss in radical OH free radicals [25].



Fig. 4d provides information about the effect of reaction time on degradation. The speed was relatively fast, as almost 80% of the NaOL decomposed in the first 10 min, and the NaOL could be fully decomposed within 1 h. The results demonstrate that the Fenton oxidation process exhibits several characteristics, including fast speed, ideal efficiency, and environmental friendliness in terms of decomposing organic matter; thus, the process could provide a good alternative for reducing foam generation.

3.3. Degradation kinetics

In this work, the degradation kinetics of NaOL by the Fenton oxidation process were evaluated at different contact times ranging from 0 to 5 min and at different temperatures, including 293, 298, 303, 313, and 323 K. The apparent kinetics rate constants (k) under different conditions were determined using the following first-order kinetics model:

$$\ln\left(\frac{C_0}{C_t}\right) = k \times t \quad (6)$$

where C_0 is the initial concentration of NaOL and C_t is the concentration of NaOL at reaction time t . Fig. 5a provides

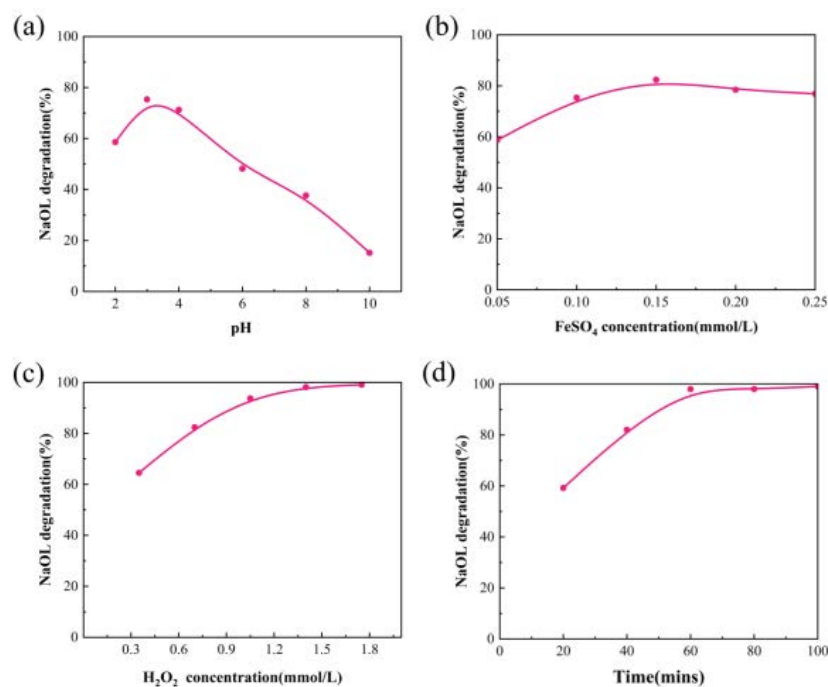


Fig. 4. Effect of (a) pH, (b) $FeSO_4$ concentration, (c) H_2O_2 concentration and (d) reaction time on sodium oleate degradation.

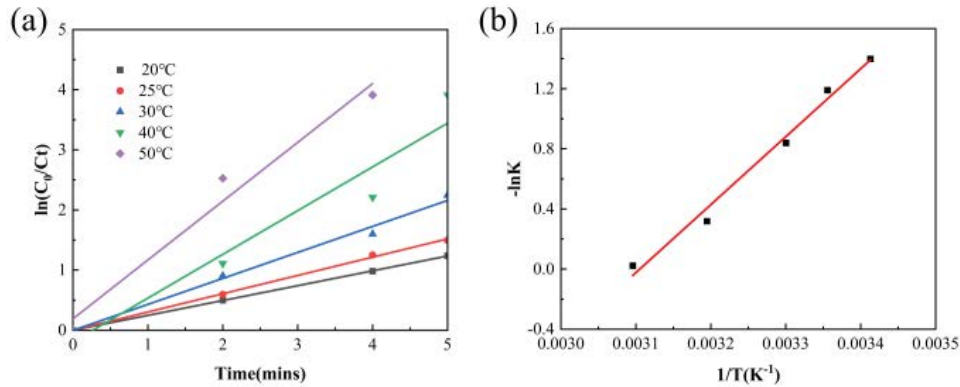


Fig. 5. (a) Plots of the pseudo-first-order kinetic model and (b) plots of link vs. 1/T for the degradation of sodium oleate.

information about the plot of $\ln(C_0/C_t)$ over reaction time t with the fitted values of k , which is summarized in Table 1. From Fig. 5a and Table 1, it can be seen that the experimental results matched well with the pseudo-first-order model, as the correlation coefficient (R^2) was high and temperature showed a significant effect on the pseudo-first-order rate constants. When the temperature was increased from 293 to 323 K, the rate constant significantly grew from 0.246 to 0.978. This result implied that increasing temperature had a positive effect on the degradation of sodium oleate since the high temperature could increase the reaction rate between H_2O_2 and Fe^{2+} , thus increasing the rate of HO^\bullet formation [25]. Based on Fig. 5b and Eq. (7), the activation energy (E_a) of the Fenton process was computed from the slope of the Arrhenius plot and was 37.60 kJ/mol, demonstrating that the oxidative reaction proceeded with a low energy barrier [26,27].

$$\ln K = -\left(\frac{E_a}{R}\right) \times \left(\frac{1}{T}\right) + \ln A \quad (7)$$

3.4. Controlling two-phase foam through the Fenton oxidation process

The concentration of NaOL plays a significant role in the stability of two-phase foam, and reducing the concentration of NaOL has been shown to effectively lower the MFV and HLP. To further explore this relationship, the effects of reaction time on MFV and HLP after Fenton oxidation treatment were investigated and are presented in Fig. 6. The results demonstrate that increasing the reaction time leads to a gradual reduction in MFV and HLP. In the first 30 min of treatment, MFV and HLP decreased from 67.7 to 37.7 mL and 1,852 to 295 s, respectively. The Fenton oxidation process has been demonstrated to effectively control two-phase foam by degrading residual organic surfactants present in aqueous solutions. Organic surfactants are known to adsorb onto the gas–liquid interface, thereby reducing surface tension and facilitating the formation of stable foam. The Fenton oxidation process generates highly reactive hydroxyl radicals that can efficiently breakdown the chemical bonds of the residual organic surfactants, thereby reducing their concentration in the solution. As a result, the

Table 1
Rate parameters for the degradation of sodium oleate by the Fenton oxidation process

T (K)	293	298	303	313	323
k	0.246	0.304	0.432	0.727	0.978
R ²	0.99993	0.99851	0.991	0.93539	0.9725

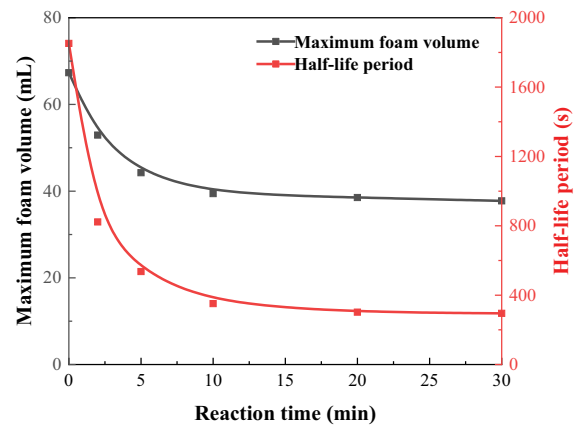


Fig. 6. Effect of the Fenton oxidation process on maximum foam volume and half-life period.

amount of surfactants adsorbed on the gas–liquid interface is reduced, leading to decreased foam stability. Thus, the Fenton oxidation process presents a promising approach to control two-phase foam through the degradation of residual organic surfactants in aqueous solutions.

4. Conclusions

The primary findings of this study can be summarized as follows: The MFV and HLP of the two-phase foam were positively correlated with the NaOL concentration. Fenton oxidation was capable of rapidly decomposing NaOL within a short time frame (60 min) with high efficiency (nearly 100%). The experimental data were in good agreement with the pseudo-first-order kinetic model, and the activation energy was determined to be 37.60 kJ/mol,

indicating that the oxidative reaction has a low energy barrier. Fenton oxidation exhibited significant potential in mitigating foam generation, as demonstrated by the considerable reduction in MFV and HLP following treatment. Moreover, in contrast to conventional chemical defoamers, Fenton oxidation presents an ecological advantage by degrading organic matter without introducing any additional organic compounds, making it a sustainable approach for foam management.

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