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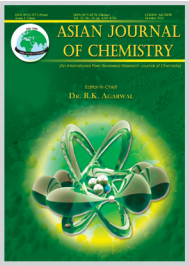

Study on Pretreatment of Saline Organic Wastewater by Ultrasound and Fenton Reagent

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The Fenton method, unmodified and combined with ultrasound, was studied to treat saline organic wastewater. The effect of pH, Fe^{2+}, H_2O_2, NaCl and Na_2SO_4 on degradation on reactive red dyestuff was explored. The pH value and Fe^{2+} concentration were key factors during the reactions. NaCl and Na_2SO_4 could decrease the degradation rate of reactive red dyestuff by the Fenton and ultrasound/Fenton method; NaCl could especially affect degradation *via* unmodified Fenton treatment. The degradation efficiency of active red dyestuff dropped to less than 4.01 % for the unmodified Fenton method in the presence of 100 ppm Na_2SO_4. The experiment proved that the ultrasound could not only improve the degradation efficiency of Fenton's reagent, but also weaken the negative effects of NaCl and Na_2SO_4. Reactive red dyestuff effluents were further treated by the US/Fenton method. A maximal degradation efficiency of reactive red dyestuff of 98.8 % was attained when the pH value was 3(± 0.2), the temperature was 20(± 2) ºC, the Fe^{2+} concentration was 13.2 mM, the H_2O_2 concentration was 264 mM, the reaction time was 4.5 h and the ultrasound frequency was 20 kHz. The effluent from chlorobutame manufacturing was degraded with US/Fenton treatment for 3 h after the coagulation process; its degradation efficiency of chemical oxygen demand achieved 94.5 %.

Key Words: Ultrasound, Fenton reagent, Saline organic wastewater, Reactive red dyestuff, Degradation.

INTRODUCTION

Biological treatment of saline wastewater usually results in poor chemical oxygen demand (COD) removal because of the adverse effects of salt on microbial flora. High salt concentrations (1 % salt) cause plasmolysis and/or loss of activity of cells[1]. Additionally, a high concentration of chlorine is toxic to microorganisms[2]. Published reports cover a variety of applications of saline wastewater (1-5 % salt) by salt-tolerant organisms[3,4]. To halophilic bacteria, the largest tolerable salt concentration[2] is approximately 10 %. The salinity changes of wastewater may negatively affect bacteria systems. Therefore, the degradation operation under high salinity is extraordinary complicated.

Over the past few years, a large number of studies have been conducted on the use of ultrasound, a new, low cost, efficient and low contaminative technology for the decomposition of harmful organic pollutants. Ultrasound combined with other oxidant methods, such as hydrogen peroxide, ozone, ultraviolet light and Fenton's reagent, will be used to further improve the degradation efficiency[5-7]. Ultrasound has long been recognized as a technology that can promote many chemical reactions with the use of inexpensive equipment. Moreover, ultrasound-based processes can often be realized in fewer steps than other processes.

This experiment researched the degradation of high-saline wastewater (20 % salt) by the application of ultrasound and Fenton's reagent.

EXPERIMENTAL

All the reagents used in the experiments are of analytical grade. The experimental setup is shown in Fig. 1. The ultrasonic horn used in the present work (Dejia Co., Ltd. Wuxi, China, maximum output voltage of 200 V, driving frequency of 20 kHz) has a tip diameter of 3 cm and was always 1 cm beneath the solution's surface. A three-necked flask equipped with an isothermal water bath (to control the temperature) and a condenser (to avoid evaporation) was used as the reactor. Ultrasound was transmitted downward and reflected when it reached the liquid-glass interface. In each experiment, 2 -mL samples were taken each hour to determine the chemical oxygen demand value.

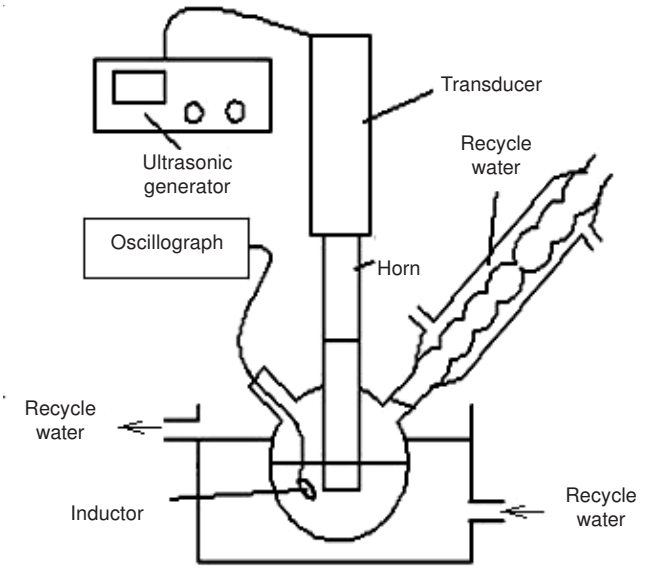

Fig. 1. Ultrasonic experimental setup

UV-VIS spectrophotometry: The concentration of reactive red dyestuff (RRD) at the maximum absorption band (516 nm) by UV-VIS spectrophotometer was detected.

The degradation efficiency of RRD = $(\rho_0 - \rho_t)/\rho_0 \times 100$ % where, ρ_0: initial concentration of reactive red dyestuff and ρ_t: concentration of reactive red dyestuff when it is degraded for t min.

Determination of chemical oxygen demand: Determination of the chemical oxygen demand involved the microwave heating method. A gravimetric technique was employed to determine the total salt (HJ/T 51-1999). Chloride content was calculated with by titration with silver nitrate (GB 11896-89).

Degradation efficiency of COD = $(COD_1\text{-}COD_2)/COD_1 \times 100$ %

where, COD_1: chemical oxygen demand of the initial wastewater; COD_2: chemical oxygen demand of the wastewater, which is degraded.

RESULTS AND DISCUSSION

Degradation of reactive red dyestuff by unmodified Fenton and US/Fenton treatment: A 20-mL solution of 1 g/L reactive red dyestuff solution, deionized water and $FeSO_4$ were added into the reactor, in that order. The reaction with or without ultrasound was carried out after adjusting the pH value (± 0.2) and temperature value (20 ± 2 ºC). A sample was taken every 5 min and scanned at 516 nm with UV-VIS.

Influence of pH on reactive red dyestuff degradation: To the reactor, 200 mL of a 100 ppm reactive red dyestuff solution was added. The pH was adjusted to 2, 3, 4 and 5 (± 0.2) and Fenton's reagent was added, resulting in Fe^{2+} and H_2O_2 concentrations of 1.1 mM and 220 mM, respectively.

After 0.5 h, the degradation rate of reactive red dyestuff at pH 2, 3, 4 and 5 was 56.13, 94.91, 65.42, 67.86 %, respectively, using the unmodified Fenton method (Fig. 2). Under the same conditions, degradation was 86.2, 97.14, 72.1, 69.51 %, respectively, using ultrasound/Fenton's reagent (Fig. 3). At pH 2, 3, 4 and 5, ultrasound increased the degradation rate 30.07, 2.23, 6.68 and 3.09 %, respectively. The optimal pH value was 3 and the degradation rate increased with time.

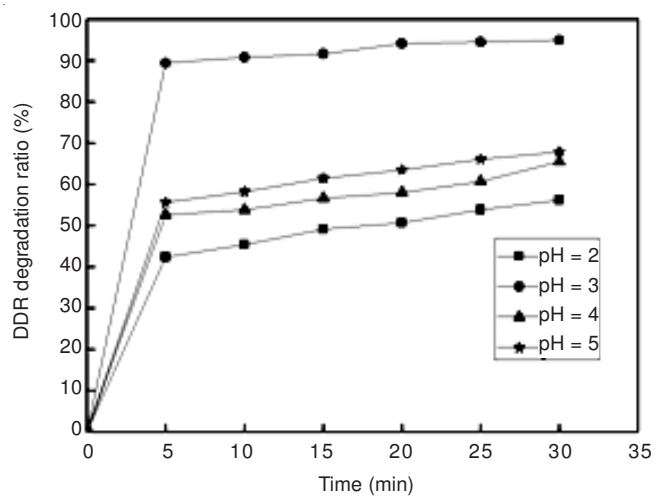

Fig. 2. Influence of pH on reactive red dyestuff degradation by Fenton's reagent

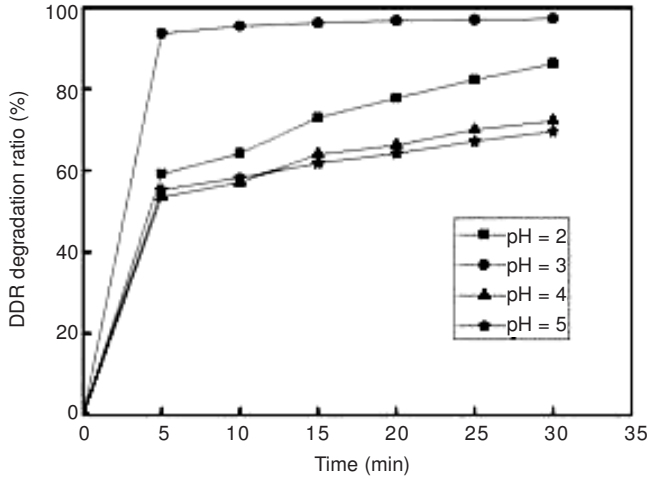

Fig. 3. Influence of pH on reactive red dyestuff degradation by ultrasound and Fenton's reagent

The theory of reaction of Fenton's reagent is given by the following equation:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot + HO^- \quad (1)$$

From reaction 1, the concentration of ·OH is inversely related to $[OH^-][Fe^{3+}]$. When the pH value is high, the formation of $^{\bullet}OH$ was inhibited and Fe^{2+} can precipitate as $Fe(OH)_2$ and lose catalytic activity. The reaction is rapid and determines the oxidation ability of Fenton's reagent.

In alkaline conditions, reaction 2 would also occur:

$$H_2O_2 \rightarrow H_2O + O_2 \quad (2)$$

H_2O_2 would, therefore, lose its oxidative ability.

At lower pH values, reaction 3 proceeded. Although this reaction is slow, it also impacts the effect of degradation. Hence, an optimal pH value for Fenton oxidation theoretically exists.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 + H^+ \quad (3)$$

For the unmodified Fenton reaction, Fe^{2+} will lose its oxidation ability through reaction 4. Ultrasound can activate Fe^{2+} according to reaction 5. Therefore, the combination of ultra-

sound/Fenton's reagent is not a simple summation of Fenton chemistry and ultrasound; synergies exist between them. Ultrasound can improve the degradation efficiency of Fenton.

$$Fe^{3+} + H_2O_2 \rightarrow Fe - O_2H^{2+} + H^+ \quad (4)$$

$$Fe - O_2H^{2+} \rightarrow Fe^{2+} + HO_2 \quad (5)$$

Influence of Fe^{2+} concentration on reactive red dyestuff degradation: The reactor was filled with 200 mL of the 100 ppm reactive red dyestuff solution. The pH value was adjusted to 3 (± 0.2). With a fixed concentration of H_2O_2 (22 mM), the concentration of Fe^{2+} was altered to make Fe^{2+}:H_2O_2 = 1:20, 1:100, 1:200 and 1:400 (mol/mol).

When Fe^{2+}:H_2O_2 is 1:400, activation cannot occur to produce enough ·OH due to the insufficient concentration of Fe^{2+} (Fig. 4). After treatment for 20 min, the degradation efficiency is 53.43 % and 74.46 % for the unmodified and ultrasound-modified Fenton procedure, respectively (Fig. 5). The reaction speed increased with increasing Fe^{2+} concentrations. After 20 min, when Fe^{2+}:H_2O_2 = 1:200, 1:100 and 1:20, the degradation rate of reactive red dyestuff was 87.31, 95.61, 97.10 %, respectively, by the unmodified Fenton's reagent and 93.22, 97.67, 98.16 %, respectively, by ultrasound/Fenton's reagent. Fe^{2+} are needed to realize the full oxidative potential. Compared with Fenton's agent alone, the inclusion of ultrasound can improve the degradation efficiency of reactive red dyestuff and improve the reaction speed. The most important result is that the higher Fe^{2+} concentrations led to a stronger oxidation ability of Fenton's reagent. The degradation efficiency of reactive red dyestuff achieved 97 % within 5 min when Fe^{2+}:H_2O_2 = 1:20 (mol).

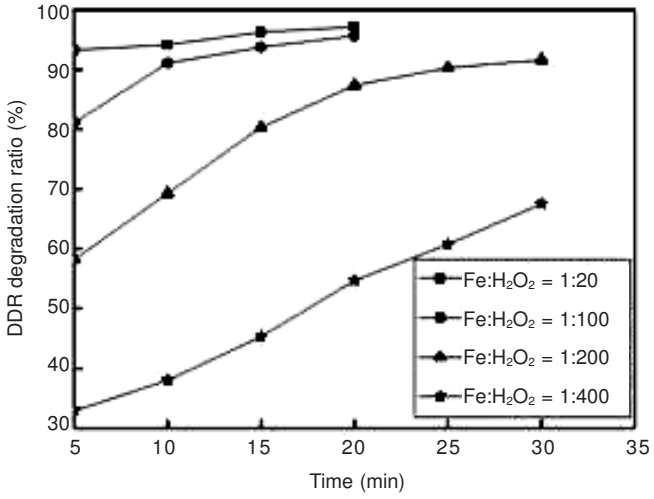

Fig. 4. Influence of Fe^{2+} concentrations on reactive red dyestuff degradation by the unmodified Fenton method

Influence of H_2O_2 concentration on reactive red dyestuff degradation: The reactor was loaded with 200 mL of the 100 ppm reactive red dyestuff solution. The pH was adjusted to 3. With a fixed concentration of Fe^{2+} (0.11 mM), the concentration of H_2O_2 was varied to make Fe^{2+}:H_2O_2 = 1:20, 1:200, 1:400, 1:800 (mol/mol). The degradation efficiency of reactive red dyestuff increased and then decreased with increasing H_2O_2 concentrations, both in the unmodified (Fig. 6) and ultrasound-modified Fenton (Fig. 7) procedures. When the H_2O_2 concentration is 44 mM, the degradation efficiency was maximized.

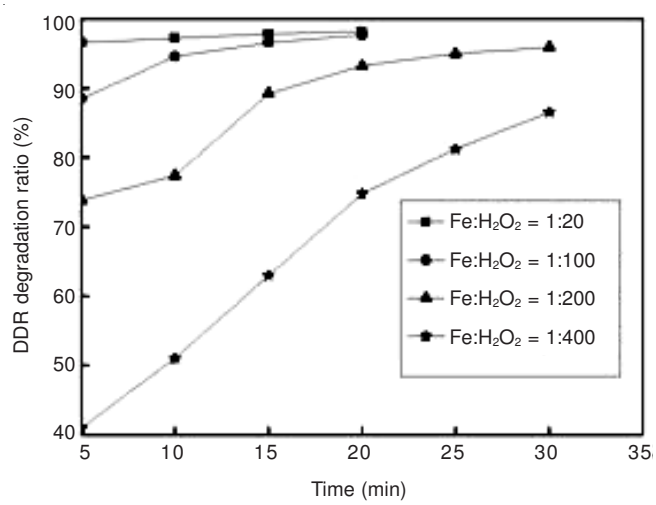

Fig. 5. Influence of Fe^{2+} concentration on reactive red dyestuff degradation by the combination of ultrasound and Fenton chemistry

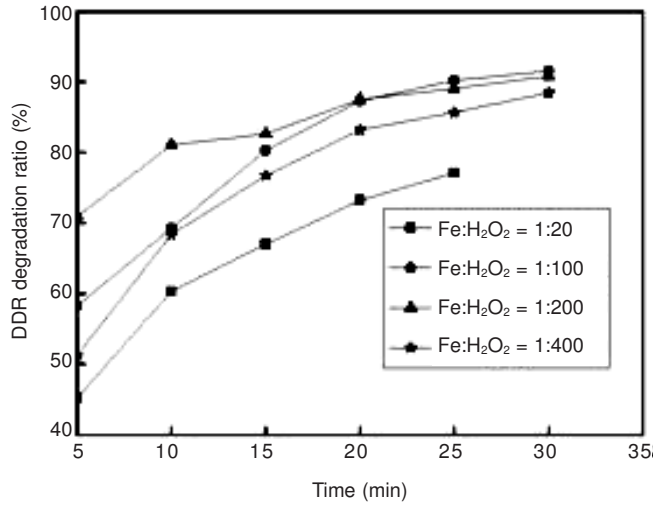

Fig. 6. Influence of H_2O_2 concentration on reactive red dyestuff degradation by Fenton's reagent

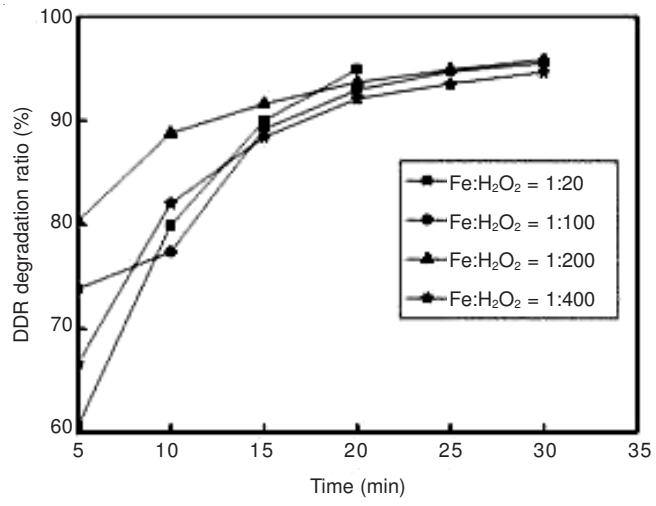

Fig. 7. Influence of H_2O_2 concentration on reactive red dyestuff degradation by ultrasound and Fenton's reagent

Influence of Fenton's reagent concentration on reactive red dyestuff degradation: The reactor was loaded with 200 mL of the 100 ppm reactive red dyestuff solution. After

adjusting the pH to 3, the ratio of Fe^{2+} : H_2O_2 of 1 : 20 (mM : mM) was varied: 0.22 : 4.4, 0.33 : 6.6, 0.44 : 8.8, 0.55 : 11.0 and 1.1 : 22.0 mM.

Fe^{2+}:H_2O_2 = 1:20 could place a premium on the fast oxidation ability of Fenton's reagent. The degradation efficiency of reactive red dyestuff increased with greater concentrations of Fenton's reagent in both systems. When the H_2O_2 concentration is 44 mmol/L, according to Figs. 8 and 9, the degradation efficiency is to the best. Ultrasound can obviously improve the degradation efficiency of Fenton's reagent.

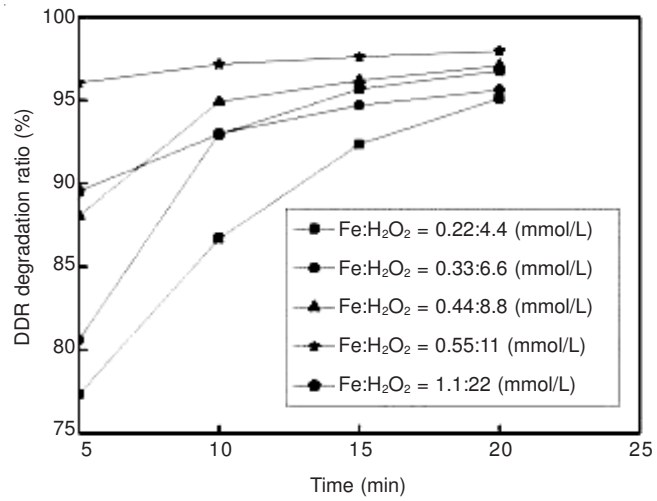

Fig. 8. Influence of Fenton's reagent concentration on reactive red dyestuff degradation

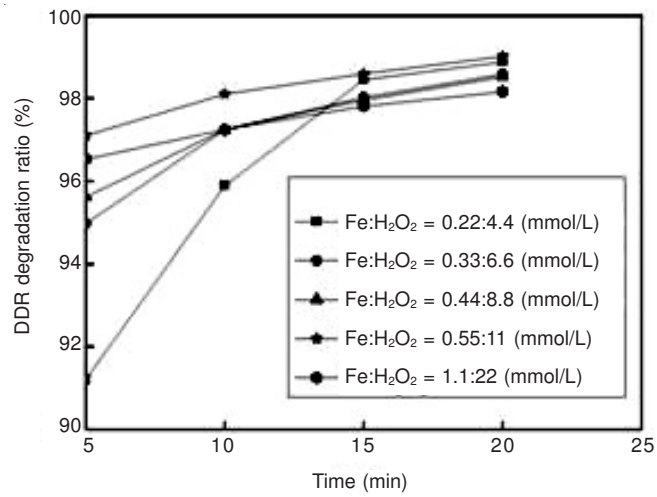

Fig. 9. Influence of Fenton's reagent concentration on reactive red dyestuff degradation when combined with ultrasound

Influence of NaCl concentration on reactive red dyestuff degradation: The reactor was loaded with 200 mL of the 100 ppm reactive red dyestuff solution. The pH was adjusted to 3, Fe^{2+} was added to a final concentration of 0.33 mM and the H_2O_2 concentration was 6.6 mmol/L. A solution of NaCl was then added so that its concentration was 0, 25, 50, or 100 ppm. After 5 min, the degradation rate was 88.02, 87.5, 81.85 and 78.59 %, respectively, with Fenton's reagent. The degradation rate of reactive red dyestuff decreased with increasing NaCl concentrations. After 20 min, the discrepancies in degradation rates lessened, with values of 96.74, 95.25, 94.89, 94.04 %, respectively. This result is due to the fact that Cl^- can act as a reductant. It can react with oxidants, competing with reactive red dyestuff and decreasing the degradation efficiency. The degradation efficiencies are 98.80, 98.38, 98.38 and 97.88 %, respectively, after 5 min (Fig. 10). After reacting for 20 min, the degradation efficiencies are 98.8, 98.38, 98.38 and 97.88 %, respectively (Fig. 11). The degradation efficiency decreases with increasing NaCl concentrations. Compared with Fenton's reagent alone, the use of ultrasound can diminish the negative effects of NaCl. This result is due to the fact that inorganic salt obstructs the translation of organic matter to the interface and obstructs the gaseity of cavitate bubbles (the degradation reacts in these two areas by ultrasound), so obstructing the efficiency of degradation.

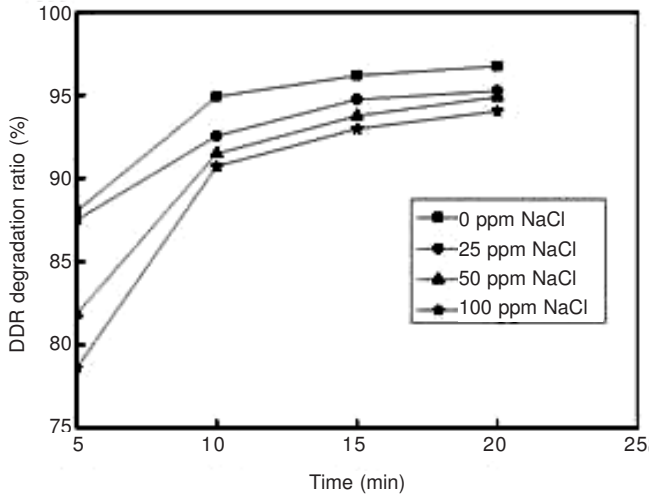

Fig. 10. Influence of NaCl concentration on reactive red dyestuff degradation by Fenton's reagent

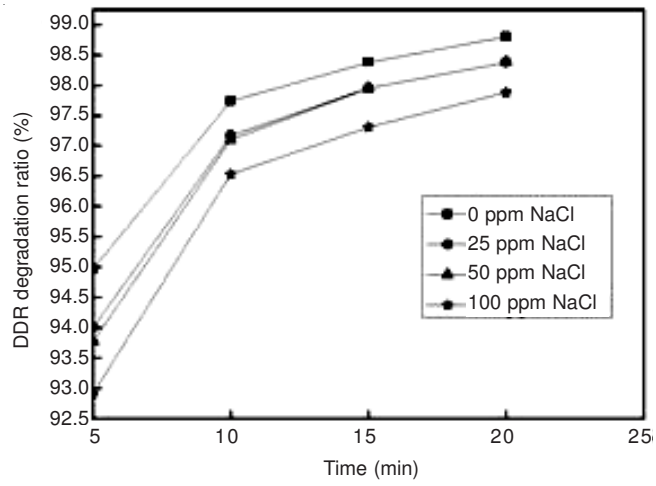

Fig. 11. Influence of NaCl concentration on reactive red dyestuff degradation by US and Fenton's reagent

Influence of Na_2SO_4 concentration on reactive red dyestuff degradation: The reactor was filled with 200 mL of the 100 ppm reactive red dyestuff solution. After adjusting the pH to 3, Fenton's reagent was added to make the Fe^{2+} and H_2O_2 concentrations 0.33 mM and 6.6 mM, respectively. A Na_2SO_4 solution was then added so that its final concentration was 0, 25, 50, or 100 ppm. After 5 min the degradation rates

were 88.02, 86.6, 86.09 and 85.8 %, respectively, for Fenton's reagent (Fig. 12). The degradation rate of reactive red dyestuff decreased with increased Na_2SO_4 concentrations; however, the differences are not noticeable. After 20 min, the reaction had almost completed and the degradation efficiencies were almost identical. After 5 min of reaction with ultrasound and Fenton's reagent, the degradation rates were 98.8, 98.02, 98.17, 98.23 %, respectively (Fig. 13). This trend occurs because the reduction reaction of SO_4^{2-} is less significant than Cl^- and, as such, the negative effect of SO_4^{2-} towards degradation of reactive red dyestuff is minimal. Additionally, when the salt concentration increased, the inorganic salt improved the translation of organic matter to the interface and improved the gaseity of cavitate bubbles (the degradation reacts in these two areas by ultrasound), so improving the efficiency of the degradation. Hence, the degradation efficiency of reactive red dyestuff decreased before increasing as a function of Na_2SO_4 concentration during the reaction with ultrasound/Fenton's reagent.

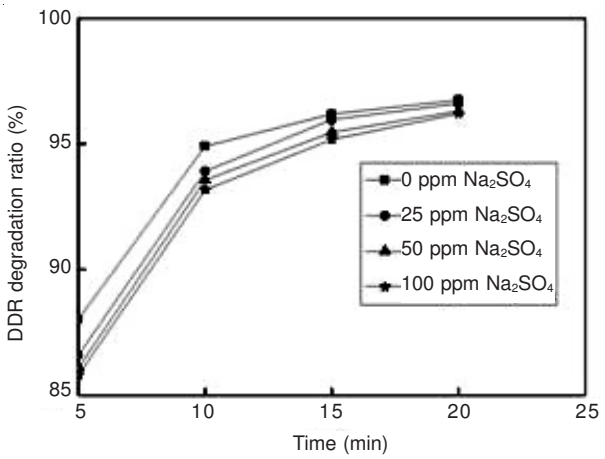

Fig. 12. Influence of Na_2SO_4 concentration on reactive red dyestuff degradation by Fenton's reagent

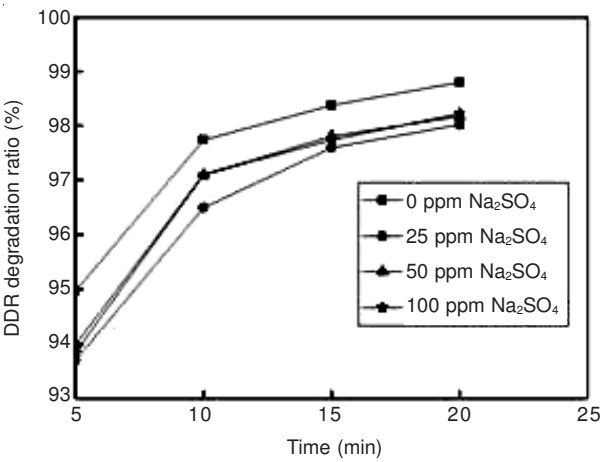

Fig. 13. Influence of Na_2SO_4 concentration on reactive red dyestuff degradation by ultrasound and Fenton's reagent

Degradation of high saline wastewater by ultrasound irradiation and Fenton's reagent

Water quality: Wastewater from a chlorobutane manufacturing plant contains large amounts of residual chlorobutane and synthetic byproducts and suspended solids are present in the wastewater. The pH of the wastewater is 5-6, the chemical oxygen demand is approximately 3×10^3 mg/L, the salt concentration is *ca.* 20 % and the chlorine concentration is approximately 1.2×10^5 mg/L.

Ultrasound irradiation alone

Effect of ultrasound intensity: Wastewater (100 mL) was degraded by ultrasound alone at 0 ºC in a water bath. Ultrasound intensity was changed by adjusting the output voltage of the ultrasonic transducer. The degradation efficiency of chemical oxygen demand under working voltages of 100 V and 200 V were plotted. The degradation efficiency of chemical oxygen demand under 200 V was greater than that at 100 V. During the 4-h degradation period, the degradation efficiency of chemical oxygen demand reached 25.2 % under 200 V (Fig. 14). Ultrasound irradiation alone has the ability to promote the degradation of wastewater, but the effect is not noticeable.

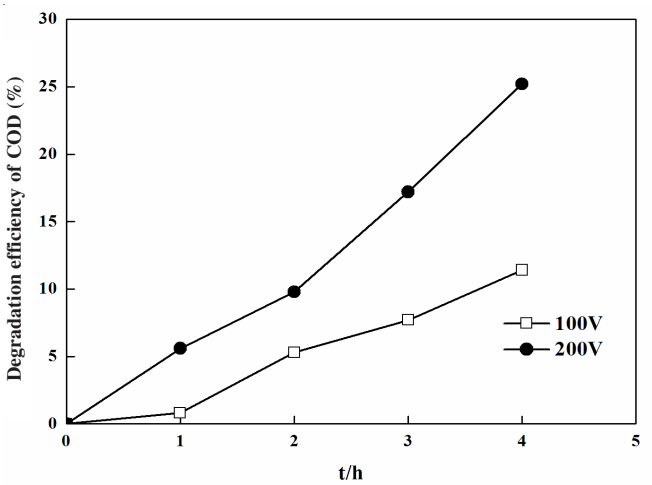

Fig. 14. Degradation efficiency of chemical oxygen demand under the influence of the ultrasound transducer voltage

Effect of temperature: Wastewater (100 mL) was degraded by 200 V ultrasound at 0, 25 and 40 ºC in a water bath and room temperature; the reaction temperature of the system was allowed to rise with reaction time (Fig. 15). On one hand, the surface tension of the liquid and cavitation threshold decreased as the temperature increased; therefore, the production of cavitation bubbles became easier. Additionally, increasing the reaction temperature can promote the process of mass transfer. On the other hand, the cavitation intensity decreases with increasing temperatures. For the above reasons, it is concluded that there is an optimal temperature; a temperature of 0 ºC is better than the other temperatures, based on Fig. 16. However, a reaction temperature of 0 ºC is difficult to realize in degrading large amounts of wastewater.

Ultrasound with oxidation

Effects of temperature: Before degrading 100 mL of wastewater by 200 V ultrasound at 25 ºC or 40 ºC, 5 mL of H_2O_2 was added. The degradation efficiency at room temperature is better than at other temperatures and it reached 60.3 % after 4 h. In addition to the reasons presented in influence of Fe^{2+} concentration on reactive red dyestuff degradation, the

reaction temperature, which promoted pyrolytic reactions, increased at room temperature with time. Considering the variation of the climate, the temperature minimally changed. To minimize experimental error, 40 ºC was selected as the reaction temperature in the next experiments.

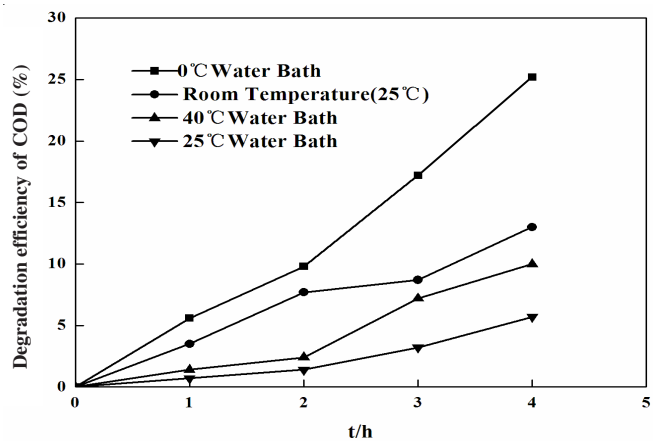

Fig. 15. Degradation efficiency of chemical oxygen demand under the influence of reaction temperature

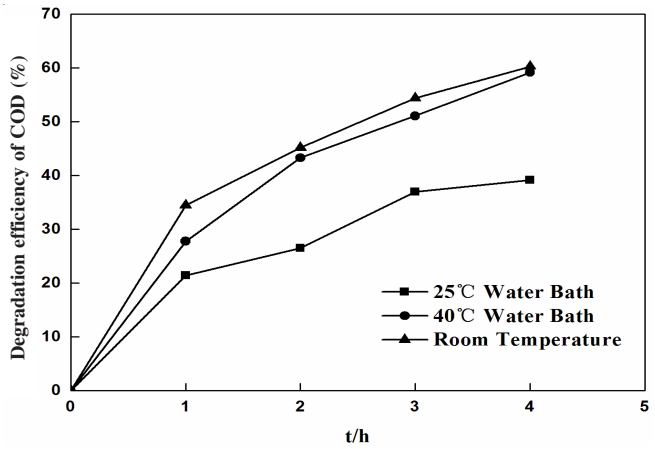

Fig. 16. Degradation efficiency of chemical oxygen demand by ultrasound/H_2O_2 under the influence of reaction temperature

Effects of H_2O_2: Before degrading the wastewater by ultrasound/H_2O_2 and H_2O_2 alone in a 40 ºC water bath, we added 3 mL, 5 mL or 7 mL of H_2O_2 into 100 mL of wastewater. The results are shown in Figs. 17 and 18. The degradation efficiency of chemical oxygen demand increased with the reaction time and increased with the concentration of H_2O_2. The optimal dosage of H_2O_2 is 5 mL per 100 mL wastewater. The $HO^{\bullet}$ concentration increased with H_2O_2 concentration. After passing the limitation, however, excessive H_2O_2 would react with $HO^{\bullet}$ as follows:

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2 \quad (6)$$

Although $HO_2^{\bullet}$ is a kind of oxidant, the oxidation-reduction potential of $HO_2^{\bullet}$ is less than $HO^{\bullet}$. Furthermore, excessive H_2O_2 can cause invalidation decomposition of $HO_2^{\bullet}$ as follows:[8]

$$2HO_2^{\bullet} + H_2O_2 \rightarrow 2H_2O_2 + O_2 \quad (7)$$

Comparing the results of ultrasound/H_2O_2 and H_2O_2 alone, it is concluded that the ultrasound can improve the degradation efficiency of H_2O_2.

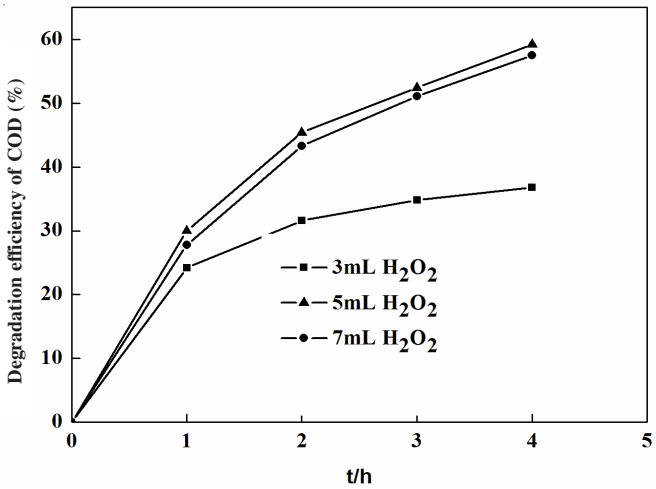

Fig. 17. Degradation efficiency of chemical oxygen demand by ultrasound/H_2O_2 under the influence of H_2O_2

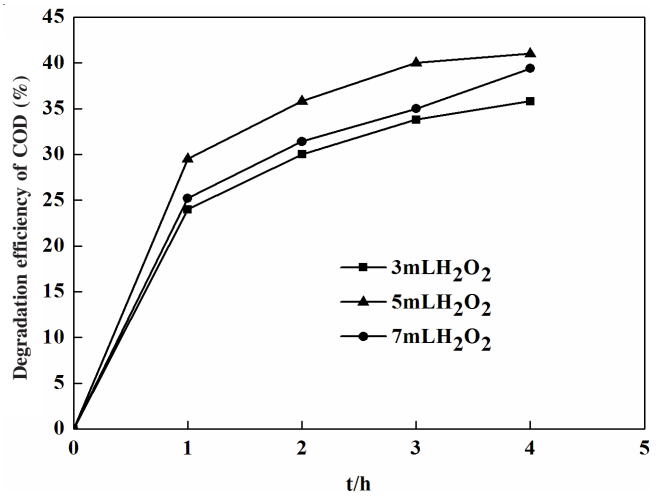

Fig. 18. Degradation efficiency of chemical oxygen demand by H_2O_2 under the influence of H_2O_2

Effects of Fe^{2+}: Before degrading the wastewater with 5 mL H_2O_2 by ultrasound/H_2O_2 or H_2O_2 alone at 40 ºC, we added 3 mL, 5 mL or 7 mL Fe^{2+} (0.01 mM) per 100 mL of wastewater. The results are shown in Figs. 19 and 20. The degradation efficiency of chemical oxygen demand increased, followed by a drop, with increasing Fe^{2+} concentrations. The main reactions of Fenton chemistry are as follows:

$$Fe^{2+}H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \quad (8)$$

When Fe^{2+} is in excess, a side reaction will take place, as shown in reaction 4 Both Fe^{2+} and H_2O_2 are able to produce and scavenge free radicals. Therefore, there is an optimal value for the concentration of reagents in the Fenton procedure.

$$Fe^{2+}HO^{\bullet} \rightarrow Fe^{3+} + HO^{-} \quad (9)$$

Fig. 19 shows that the oxidation power of iron at low concentrations was significantly enhanced by the ultrasound. This result could be explained by the possibility that there might be a synergetic effect between Fenton's reagent and ultrasound. In the Fenton process, Fe^{3+} was formed according to eqn. 4 and will react with H_2O_2 to produce a complex intermediate (Fe-O_2H^{2+}) (eqn. 5). Although Fe-O_2H^{2+} can decompose to Fe^{2+} and HOO· spontaneously, the decomposition rate is very slow. However, combined with ultrasound, the decomposition rate of Fe-O_2H^{2+} can be greatly enhanced (eqn. 6).

Once the Fe^{2+} was isolated, it reacted with H_2O_2 and produced $HO^{\bullet}$, establishing a cyclic mechanism. Hence, the degradation efficiency of ultrasound/Fenton's reagent is better than Fenton's reagent alone.

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}O_2H^{2+} + H^+ \quad (10)$$

$$Fe - O_2H^{2+} \rightarrow Fe^{2+} + HO_2\cdot \quad (11)$$

At room temperature, we repeated the experiments with optimal amounts of Fe^{2+} and H_2O_2. After 4 h of reaction, the degradation efficiency of chemical oxygen demand by ultrasound/Fenton's reagent was 69.2 %, while that of the unmodified Fenton's reagent was 39.5 %. The data also showed that there was a synergistic effect between ultrasound and Fenton reagent.

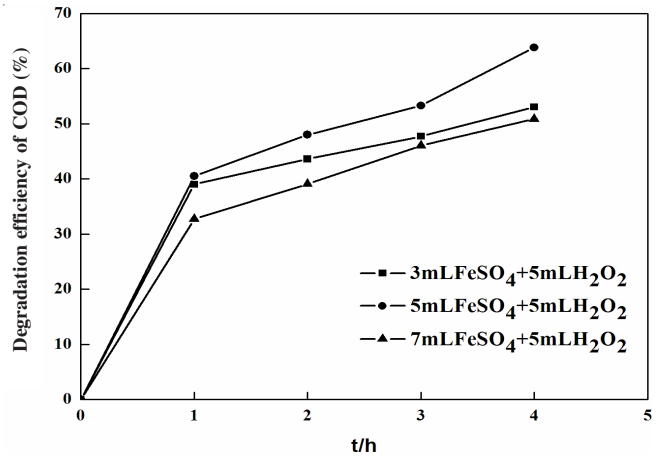

Fig. 19. Degradation efficiency of chemical oxygen demand by ultrasound/Fenton's reagent under the influence of Fe^{2+}

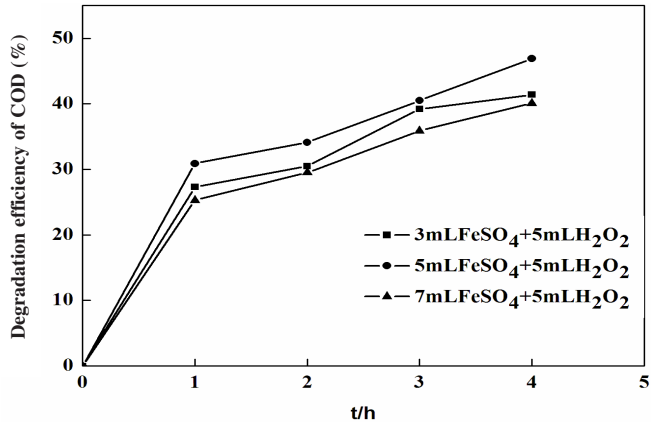

Fig. 20. Degradation efficiency of chemical oxygen demand by Fenton's reagent under the influence of Fe^{2+}

Coagulation and optimal ultrasound/Fenton process: Solid $Ca(OH)_2$ was added to the high saline wastewater (1 g/L). The wastewater solution was agitated with a magnetic stirrer. The supernatant liquid was disposed after coagulation. The degradation efficiency of chemical oxygen demand reached 25.2 % by coagulation. At room temperature, we repeated the experiments with optimal amounts of reagents: 5 mL of 0.01 mM Fe^{2+} and 5 mL of 30 % (w/w) H_2O_2. Fig. 21 displays, the degradation efficiency of chemical oxygen demand by ultrasound/Fenton's reagent and Fenton's reagent alone reached 92.6 % and 46.1 %, respectively, by the third hour. After 3 h, the degradation efficiency of chemical oxygen demand increased very slowly. Considering the economical cost, we selected 3 h as the optimal reaction time.

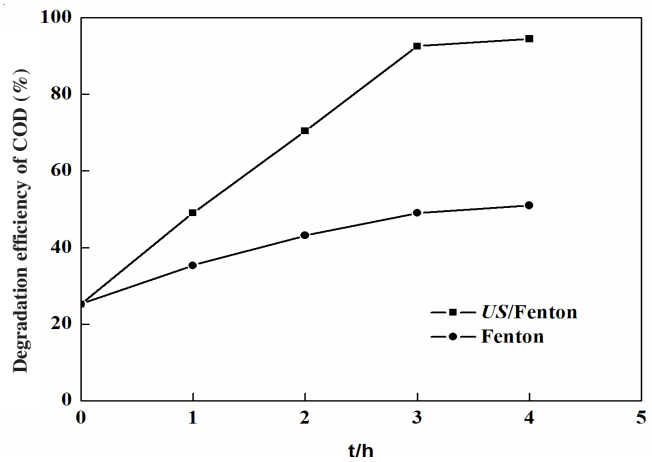

Fig. 21. Degradation efficiency of chemical oxygen demand by ultrasound/Fenton's reagent and Fenton's reagent after coagulation

Conclusion

The above results revealed that ultrasound irradiation alone has the ability to promote to the degradation of wastewater. The degradation efficiency of chemical oxygen demand under ultrasound/Fenton's reagent is larger than the summation of that of ultrasound and unmodified Fenton; there is a synergy between ultrasound and Fenton's reagent. The degradation efficiency of chemical oxygen demand reached 92.6 % by ultrasound/Fenton's reagent after 3 h of the coagulation process, reducing the chemical oxygen demand from 3×10^3 mg/L to 222 mg/L.

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