

Degradation of azo dye by Sono-Fenton method based on Fe-based amorphous alloy ribbons

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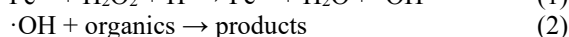
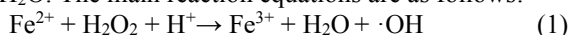
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Abstract—Azo compounds are difficult to remove from wastewater by conventional wastewater treatment methods. In this study, an Fe-based amorphous alloy was used as a catalyst for the degradation of azo dyes by Sono-Fenton method. The effects of pH, oxidant dosage and temperature on the reaction process of Sono-Fenton and its mechanism of action were investigated. The fastest degradation rate was observed at pH=2, an experimental temperature of 35°C and a H₂O₂ dosage of 100 μL, with a degradation time of 25 min.

1. Introduction

Azo dyes are a class of dyes containing -N=N- azo groups in the molecule^[1], accounting for about 50% of all dyes. They are used for dyeing and printing of natural and synthetic fibres, also for colouring paints, plastics, rubber, etc^[2]. Some azo dyes can release carcinogenic aromatic amines when they undergo reduction reactions^[3]. These aromatic amines are metabolised by the human body and cause structural and functional changes to the deoxyribonucleic acid (DNA) of cells, which can lead to cancer or allergies. Therefore, azo wastewater must be harmlessly treated before discharge.

The use of the Fenton reaction for environmental remediation is universally applicable as it can ignore the nature and functional groups of organic pollutants. Fenton's reagent is a combination of ferrous salts and H₂O₂ and the reactions using this reagent are known as Fenton's reactions. Currently, the widely accepted mechanism of the traditional Fenton reaction is a series of cyclic reactions that produce ·OH in an acidic medium, these cyclic reactions are called Haber-Weiss cycles^[4]. This mechanism considers that in the Fenton system, the catalytically generated ·OH attacks organic molecules and oxidizes them to inorganic substances such as CO₂ and H₂O. The main reaction equations are as follows:



However, the amount of ·OH produced by individual Fenton processes is limited, so in order to increase the oxidation capacity, researchers have introduced other technologies into the Fenton process. Ultrasound technology is one of them. In 1927, Richard and Loomis successfully demonstrated the degrading effect of ultrasound on organic matter^[5]. The frequency range of ultrasound is from 20 kHz to 10 MHz. The acoustic cavitation phenomenon produced by ultrasound can generate strong shock waves and microjets with

velocities above 100 m·s⁻¹. The high gradient shear of the shock waves and microjets can generate ·OH in aqueous solutions. The accompanying physicochemical effects are mainly mechanical, thermal, optical and activation effects, which can interact and promote each other to accelerate the chemical reaction process^[6]. In conclusion, the cavitation effect plays a crucial role in the ultrasonic degradation process. In recent years, a number of researchers have applied Sono-Fenton method to the treatment of pollutants. Pulicharla et al^[7] investigated the feasibility of individual ultrasonication (UIS) and Fenton oxidation (FO) and their combination (Ferro-sonication, FS) for the degradation of chlortetracycline (CTC) in wastewater sludge. The degradation of CTC by FS was improved by 15% and 8% compared to UIS and FO alone, respectively. Maroudas et al^[8] investigated ultrasound irradiation, photocatalysis with TiO₂, Fenton/Photo-Fenton reaction, and the combination of those techniques for the decolorization of industrial dyes, and found that the combination of ultrasound and photo-Fenton at pH=3 resulted in a 90% degradation of the dye.

The involvement of ultrasound effectively saves the amount of catalyst used and the budget for Fenton technology. And the high efficiency of the Fenton system oxidation also effectively reduces the energy loss of ultrasound. Therefore, the development of Sono-Fenton catalysts has become one of the most effective ways to improve the efficiency of ultrasonic reactions. For heterogeneous Fenton reaction, US can also effectively accelerate the reaction between zero-valent iron (ZVI) and water^[9], and promote the system to continuously produce more Fe²⁺.

Recent reports have shown that amorphous alloys with their good catalytic activity and unique selectivity are used in the field of wastewater treatment. Numerous research results have demonstrated their fast catalytic efficiency, good sustainability and high stability. Yang et al^[10] successfully synthesised an amorphous alloy Fe₆₃Cr₅Nb₄Y₆B₂₂ (at%) with thermally tuned magnetic

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properties and reported the combined use of magnetic and catalytic properties of FAA, which shifted from ferromagnetic to paramagnetic at elevated temperatures and was capable of auto-recovery. Ji et al^[11] compared Fe₇₈Si₁₃B₉ amorphous alloy ribbons with (FeCoNi)₇₈Si₁₃B₉ amorphous alloy ribbons of a high entropy for the degradation of orange-yellow II. It was found that Fe₇₈Si₁₃B₉ degraded orange yellow II almost completely within 70 min, whereas (FeCoNi)₇₈Si₁₃B₉ had only a physical adsorption process under the same conditions, which meant Fe₇₈Si₁₃B₉ had a faster decolourisation reaction rate. Amorphous alloys have higher Gibbs free energy^[12], and because their constituent atoms are in non-equilibrium state, their catalytic performance has been significantly improved, and their reaction activation energy is much lower than that of traditional iron powders.

Up to date, in various Sono-Fenton reactions, iron salts and crystalline iron are the main sources of Fe²⁺. The use of Fe based amorphous alloy (FAA) as the source of Fe²⁺ in Sono-Fenton has not been reported. In this paper, for the first time, FAA was used as a catalyst to degrade methyl orange (MO) in Sono-Fenton. The influence of pH, temperature and H₂O₂ concentration on the reaction was investigated. This work provides a new application for FAA material and a new promising method for the degradation of azo dyes.

Tab.1 Elemental mass composition (wt.%) of the Fe-based amorphous alloy ribbons

Element	Fe	Si	B	Nb	Cu
FAA ribbons (wt.%)	84.9	6.1	1.7	5.9	1.4

2.2. Pseudo-first-order kinetic fit

In this work, the degradation process fits well to pseudo-first-order kinetic reaction model, and the equation is shown in Eq. (3):

$$\ln \frac{C_0}{C_t} = kt \quad (3)$$

where C_0 is the initial concentration of MO dye at $t = 0$, C_t is the concentration at time t and k (min^{-1}) is the kinetic rate constant. C_t can be calculated from the absorbance of the solution at time t and the standard curve of MO.

3. Results and discussion

3.1. Characterization of catalyst

2. Experimental

2.1. Degradation experiments

FAA ribbons (the average thickness is $24 \pm 2 \mu\text{m}$) were used as raw materials in this work. The chemical composition of FAA ribbons is listed in Table 1. MO solutions were prepared with distilled water, and then the solutions were adjusted to the set pH with H₂SO₄ solution. Then 70 mL of the solution was taken in a beaker, adding FAA ribbons and H₂O₂. Finally, the dye solution was placed in an ultrasonic device which has been adjusted for the set temperature and power. During the degradation experiment, 2 mL of solution was extracted every 5 minutes using syringes, filtering the solution with a needle filter (PES, 0.45 μm). And 100 μL methanol was added to the sample bottles beforehand to terminate the reaction. In the degradation experiments, the influence of pH, H₂O₂ amount, and temperature was individually studied. When studying the effect of one of above variables, all other variables are held constant. If not otherwise specified, the experimental parameters are: $c_{\text{MO}} = 25 \text{ mg/L}$, $V_{\text{H}_2\text{O}_2} = 50 \mu\text{L}$, $m_{\text{FAA}} = 0.07 \text{ g}$, $T = 35 \text{ }^\circ\text{C}$, $\text{pH} = 2$.

Fig. 1 shows the XRD pattern of the FAA ribbons. As it can be seen, the XRD pattern only have typical diffuse scattering peaks, indicating that FAA ribbons have amorphous structure. Tab. 1 shows the elemental composition of the FAA ribbons as measured by ICP-OES. Fe is the main component at 84.9%, followed by Si and Nb at 6.1% and 5.9% respectively, and small amounts of B and Cu at 1.7% and 1.4% respectively. Fig.2a-e shows the SEM image of the FAA ribbons before degradation. The surface of FAA ribbons is smooth.

After degradation, the XRD pattern shows that the FAA ribbons still has an amorphous structure. And from Fig.2d-f, the ribbons surface cracked after the reaction and some surface layers had flaking. This is because Fe⁰ in the ribbons is turned into Fe²⁺ and transferred to the solution during the reaction.

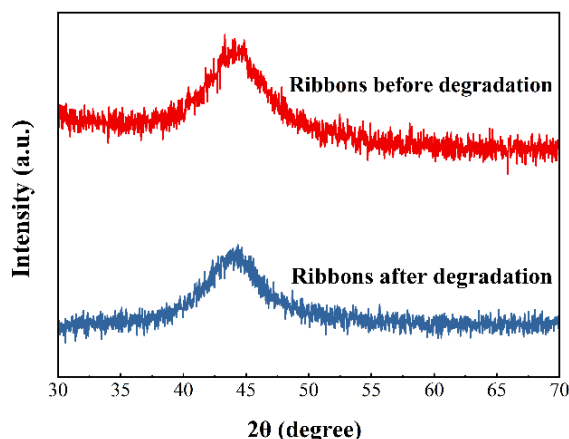


Fig.1 XRD patterns of FAA ribbons before and after degradation

3.2. Influence of pH

The effect of solution pH on the degradation process was studied. Fig. 3a shows variation curves of dye concentration at different pH and time. It can be seen that the FAA ribbons reached the fastest degradation rate at pH=2, taking only 35 minutes to completely decolourise the dye solution with a reaction rate constant k of 0.098 min^{-1} . And at pH=1, azo dyes need 55 minutes to be

completely degraded. At both pH=0 and 3, the dye failed to be completely degraded within 60 minutes with k of 0.032 min^{-1} and 0.020 min^{-1} respectively. There are varying degrees of passivation at pH=0 and pH=1. The passivation layer impedes the reaction. When pH=3, the acidity decreases, so the rate of Fe leaching slows down and the oxidation of $\cdot\text{OH}$ is reduced, resulting in a decrease in catalytic efficiency.

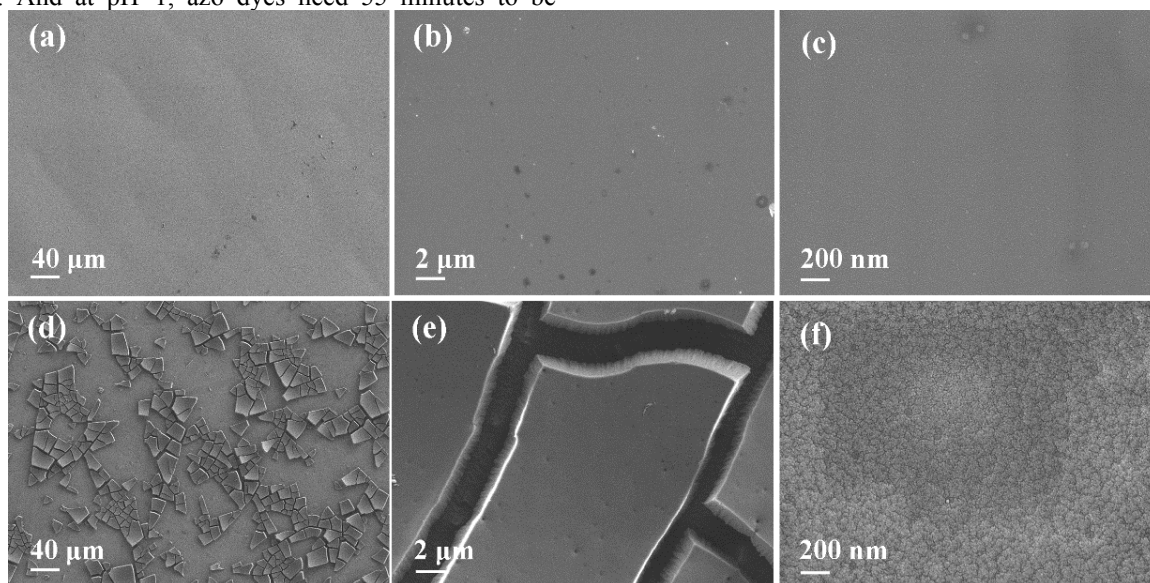


Fig.2 (a-c) SEM of FAA ribbons before degradation; (d-f) SEM of FAA ribbons after degradation

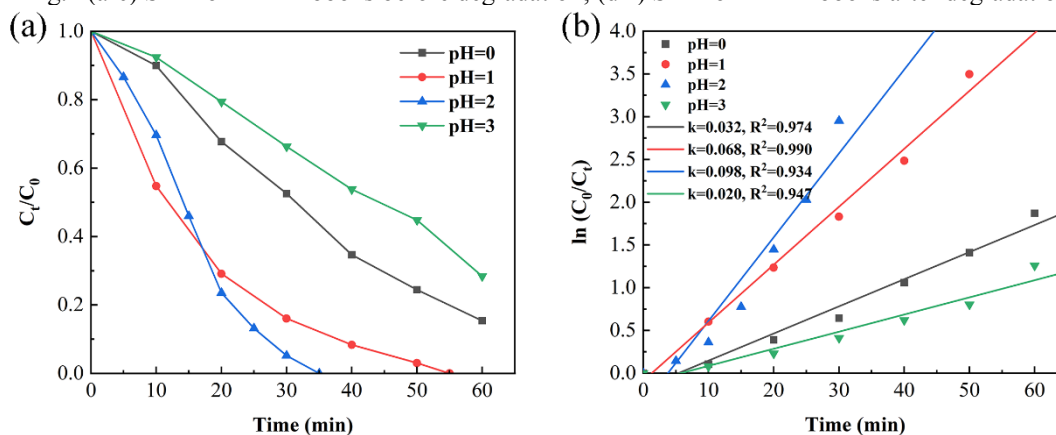


Fig.3 (a) Variation of MO concentration with time at different pH; (b) reaction rate constant k at different pH

3.3. Influence of H₂O₂

The effect of the amount of H₂O₂ on the catalytic efficiency was explored. Fig.4 shows the UV spectra of MO when different amounts of H₂O₂ were used in the degradation process. As can be seen, the optimum amount of H₂O₂ was 100 μL, where the decolourisation time was 25 min with k of 0.155 min⁻¹. At 0 μL of H₂O₂ input, the decolourisation rate of MO only reached 24% within 60 min. The decolourisation time was 35, 40 and 45 min for 50, 150 and 200 μL of H₂O₂, respectively. That is, the decolourisation time of MO first shortens with increasing H₂O₂ dosage, reaching a minimum at 100 μL, and then increases with increasing H₂O₂ dosage. When H₂O₂ dosage is too low, it will slow down the production of ·OH, while too much H₂O₂ will consume the produced ·OH and reduces the catalytic efficiency.

3.4. Influence of temperature

In order to investigate the optimum temperature, a series of degradation experiments have been carried out at

different temperatures. Fig.5 shows the UV spectra of MO decolourised at different temperatures and the reaction rate constant k . The k first increases with increasing temperature, reaching a maximum at 30 °C, and then decreases with increasing temperature. At lower temperatures, as the temperature increases: (i) the average energy of the reactants and the percentage of activated molecules per unit volume both rise, thus increasing the number of effective collisions and further increasing the rate of chemical reaction; (ii) the increase in temperature lowers the cavitation threshold, increasing the number of cavitation bubbles, thus increasing the rate of free radical generation; (iii) at lower temperatures, the gas solubility is higher and sufficient O₂ can provide more ·OH for the reaction. Above 30 °C, the temperature rises and the k decreases. The main reasons are as follows: (i) when the temperature rises, the dissolved gases decrease; (ii) the viscosity of the liquid decreases, the cavitation threshold decreases and too many cavitation bubbles are produced, which, due to scattering and attenuation, can weaken the available ultrasound energy.

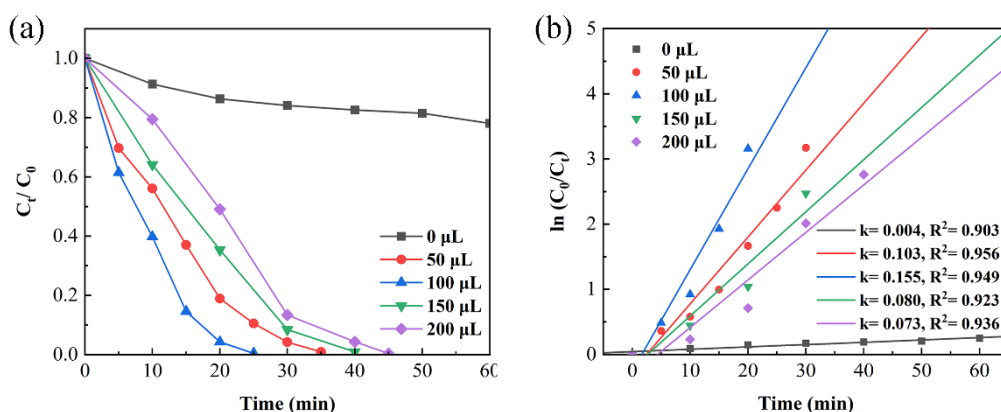


Fig.4 UV spectra of MO degraded by FAA ribbons at different oxidant dosages (a) variation of MO concentration with time; (b) reaction rate constant k

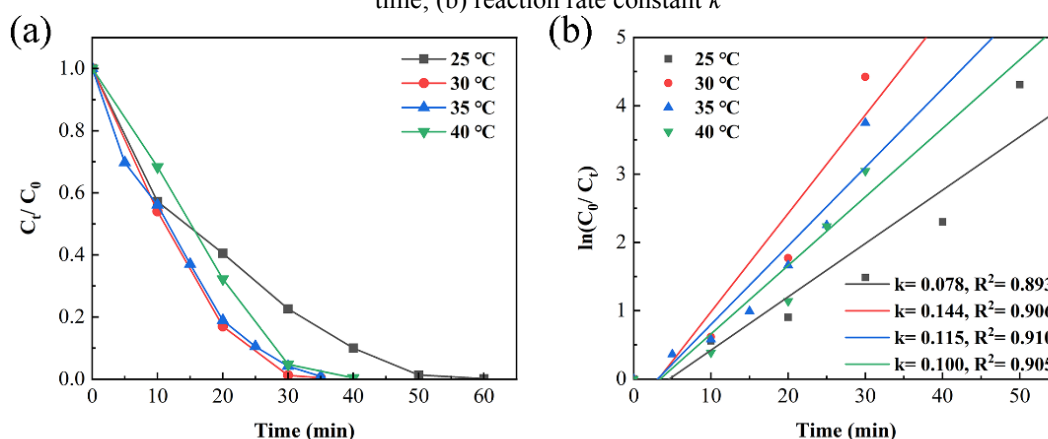


Fig.5 (a) Variation of MO concentration with time at different temperatures; (b) reaction rate constants k at different temperatures

4. Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

(1) Using FAA ribbons as catalyst in Sono-Fenton, MO can be completely degraded in 35 minutes.

(2) For this experiment, the optimum pH value is 2. When pH is 0 and 1, the passivation layer impedes the reaction. When pH is 3, the rate of Fe leaching slows down and the oxidation of $\cdot\text{OH}$ is reduced, resulting in a decrease in catalytic efficiency.

(3) The optimum amount of H_2O_2 for this experiment is 100 μL . Too little H_2O_2 slows down the production of $\cdot\text{OH}$ and reduces the catalytic efficiency. Too much H_2O_2 consumes the produced $\cdot\text{OH}$ and reduces the catalytic efficiency.

(4) The optimum temperature for this experiment is 30 $^\circ\text{C}$. In sonochemistry processes, the optimum reaction temperature is typical and depends on the medium under study and the particular reaction.

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