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Ultrasound-Assisted Copper Foam/H2O2 System for Treatment of Printing and Dyeing Wastewater

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Ultrasound-assisted copper foam/H_2O_2 system was used to pretreat printing and dyeing wastewater (hereinafter as the wastewater). Before and after the treatment, the chromaticity and the change of B/C of the wastewater were investigated respectively. The results showed that the system can quickly remove the chromaticity of the wastewater in a short period of time. The B/C of the wastewater was significantly increased, improving the biodegradability of the wastewater. In addition, the UV-vis scanning and GC-MS analysis of the wastewater before and after the treatment were carried out to further analyze the treatment effect of the system on the wastewater.

1. Introduction

Ultrasound, as an advanced oxidation technology which is newly emerged, is often used to treat various high-concentration hard-to-degrade wastewater due to its mild degradation conditions, wide application range, and high reaction speed (Hao et al., 2003). However, it is usually less efficient to use ultrasound alone. In order to change its characteristics of “high energy-consumption and low efficiency”, ultrasound has been used in recent years in conjunction with other advanced oxidation technologies and has achieved good results in actual wastewater treatment. The processing of dyes has many procedures, the production process is complicated, which makes the components of the printing and dyeing wastewater become very complex and there are many types of toxic and harmful substances in the wastewater. Therefore, compared with general industrial wastewater, printing and dyeing wastewater has higher chromaticity, and its biodegradability is very poor, making it more difficult to be handled (Hua et al., 1996). Basing on Fenton-like technology, this study uses the ultrasound-assisted copper foam method to pretreat printing and dyeing wastewater, performs efficient treatment of difficult-to-degrade wastewater by free radical reaction. In this paper, ultrasound-assisted copper foam/H_2O_2 system was used to pretreat the wastewater. The effects of this treatment system on the chromaticity, and COD, BOD and removal of the wastewater were investigated respectively. UV-vis scanning and GC-MS analysis were performed on the wastewater before and after the treatment to analyze the treatment effect.

2. Raw water quality analysis

The printing and dyeing wastewater used in this experiment was from a wastewater treatment project of a printing and dyeing company in Beijing. After the experimental determination, the conventional water quality parameters of the wastewater are shown in Table 1.

Table 1: Design of influent water quality *(Unit: mg/l)*

Project Description	COD_{cr}	BOD_5	TOC	Chromaticity (times)	PH
Raw water quality	2700	440	932	2000	2.89

It can be seen from the table that the chromaticity and TOC of the raw water are very high, the water quality is acidic and the pH is 2.89. Both COD and BOD are quite high, and the B/C of the wastewater is low, about 0.16, which belongs to the category of difficult-to-degrade wastewater.

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3. Experimental results and discussion

Before performing the experiment of ultrasound-assisted copper foam/H_2O_2 treatment of printing and dyeing wastewater, the wastewater has been formulated to optimize the experimental conditions of the system. In this paper, the experiment takes the optimal experimental conditions to process the actual wastewater. Take 500 ml of actual wastewater and put it into the reactor, there is no need to adjust its pH value, then add 5.0 mmol/L H_2O_2 solution, add copper foam into it, turn on the ultrasound equipment, adjust the ultrasonic power to 300W for reaction, because the actual wastewater has a high organic concentration, the reaction time has been extended to 2 hours in the experiment. During the experiment, the ultrasonic probe is at about 1.5 cm below the surface of the water, and a magnetic stirrer is turned on to keep the reaction fluid homogenous. Before use, the copper foam was soaked in deionized water for preparation.

The actual printing and dyeing wastewater has a high chromaticity and its components are complex. In this experiment, COD, TOC, BOD, and chromaticity are used as evaluation indicators to evaluate the degradation effect of the actual wastewater.

3.1 Changes in COD and TOC

In the evaluation of organic wastewater, COD are important organic contamination parameters that can be quickly determined. The COD of the actual wastewater used in this experiment is 2700 mg/L, it's of high concentration and the biodegradability of the wastewater is not good, uneasy to process.

In the experiment, the rapid degradation method is used to detect the COD value in the wastewater degradation process, observe the changes, detect the COD change during the wastewater degradation process, and calculate its removal rate.The experimental results are shown in Figure 1, respectively.

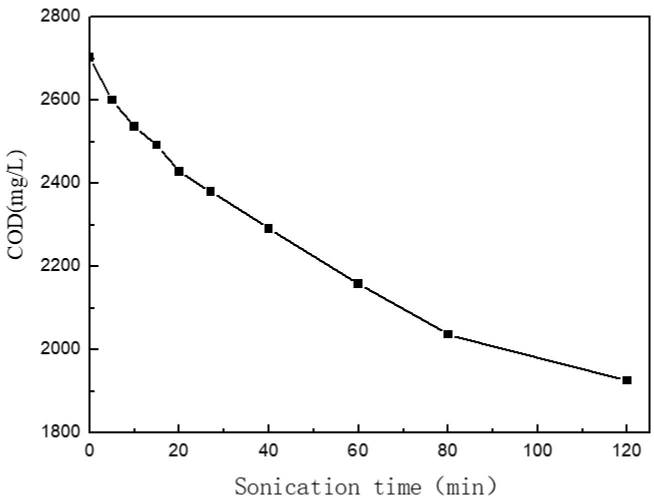


Figure 1: The change of COD concentration and its removal rate with time

From Figure 1, it can be seen that with the progress of the reaction, the COD in the actual wastewater continuously decrease as the processing time increases, and the removal effect is significant. When the ultrasonic time reaches 2h, the COD concentration in wastewater decreases from 2700 mg/L to 1926 mg/L with a degradation rate of 28.7%. The degradation rates of COD are faster 30 min before the reaction, with progress of the reaction, the degradation rate gradually decreases.

It is speculated that the possible reason is that, on the one hand, H_2O_2 added at the initial stage of the reaction will be decomposed largely to high-level oxidizing agent •OH, which will oxidize and degrade the organic pollutants; on the other hand, when the concentration of organic matters is higher, it also has a higher probability of collision with the high-level oxidizing agent •OH, therefore, the removal rate of pollutants at the beginning of the reaction is larger.

3.2 Changes in BOD and BOD/COD

BOD and B/C are important parameters to evaluate the biodegradability of wastewater. It is of great significance to analyze BOD and B/C for the degradation of organic wastewater. One of the focuses of this paper is the change of BOD in the pretreatment process of the actual printing and dyeing wastewater by ultrasound-assisted copper foam/H_2O_2 system, and whether it can improve the biodegradability of the wastewater to facilitate follow-up biological treatment process.

The BOD value of wastewater raw water is 440 mg/L, B/C is 0.16, and the wastewater has poor biodegradability. The change of BOD during the degradation process of wastewater is tested and combined with the COD value obtained in the previous section to calculate the change of B/C with time. The experimental results are shown in Figure 2 and Figure 3.

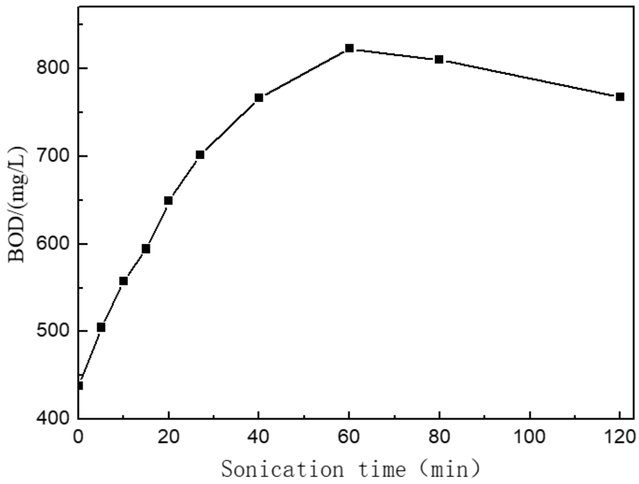


Figure 2: Changes of BOD concentration with time

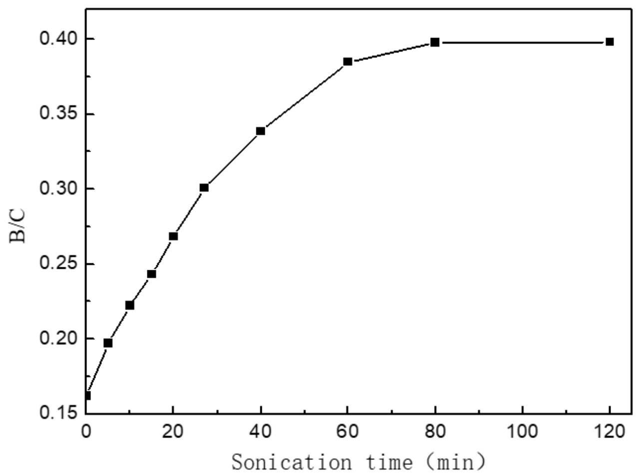


Figure 3: Changes of B/C with time

It can be seen from the figure that, during actual wastewater treatment by the ultrasound-assisted copper foam/H_2O_2 system, within 30 minutes before the reaction, the BOD rises continuously; while within 30 minutes after the reaction, the BOD starts to decrease. At the end of the reaction for 2h, the BOD value of the wastewater is 767 mg/L, which is higher than the initial BOD value in the raw water. At the same time, during the entire reaction process, B/C increases continuously, at the end of the reaction for 2h, the final B/C increases from the initial 0.16 to 0.40, at this time, the biodegradability of the wastewater is acceptable, and the follow-up biochemical wastewater treatment can be performed, indicating that the ultrasound-assisted copper foam/H_2O_2 system has improved the biodegradability of the actual printing and dyeing wastewater.

3.3 Chromaticity changes

Printing and dyeing wastewater usually has the characteristics of high chromaticity, in the treatment process, the removal of chromaticity has always been a difficult and hot topic. The chromaticity of the selected wastewater is measured by the dilution times method, and its chromaticity value reaches 2000. In this study, ultrasound-assisted copper foam/H_2O_2 system is used to pretreat the wastewater, which can quickly decrease its chromaticity and reduce the follow-up processing load. The measurement of the chromaticity is performed using the dilution times method. The experimental results are shown in Figure 4

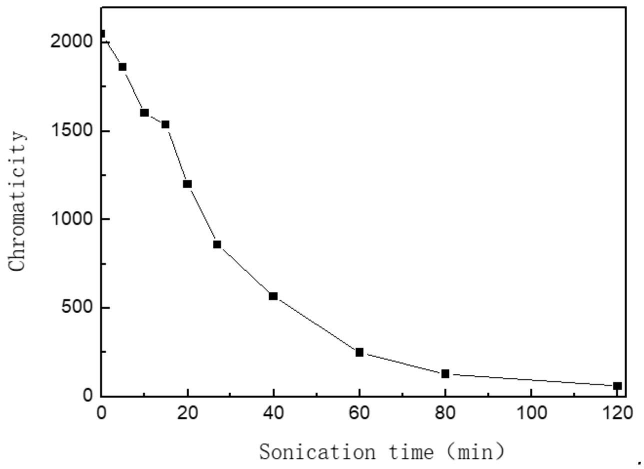


Figure 4: Changes of chromaticity with time

From Figures 4 we can see that in the course of the reaction, the effect of the chromaticity removal of the wastewater is obvious, especially 1h before reaction, the wastewater decolorization speed is very fast. At 2h after reaction, the chromaticity of the wastewater at this time is reduced to 60 by the dilution times method, which meets the requirement of direct discharge.

The high-level oxidizing agent •OH produced by the ultrasound-assisted copper foam/H_2O_2 system used in this study, usually achieves the decolorization of wastewater by two means (Kim et al., 2007): First, •OH has a lone electron that can combine with the non-steady state electrons present in the dye molecule to complete the dye decolorization; second, •OH has a high redox potential, which can oxidize the dye molecules and decolorize them (Neppolian et al., 2004). This oxidation is non-selective and efficient and can change the type of bonding of the dye molecules, resulting in discoloration. Therefore, the ultrasound-assisted copper foam/H_2O_2 system used in the experiment has a good decolorization effect and can achieve direct discharge requirements.

3.4 UV-vis analysis

This study uses ultrasound-assisted copper foam/H_2O_2 system to treat printing and dyeing wastewater under optimized experimental conditions. 2h after reaction, perform UV-vis scanning to analyze the changes in water quality before and after the reaction by comparing the scanning results of the raw water of the actual printing and dyeing wastewater. The experimental results are shown in Figure 5.

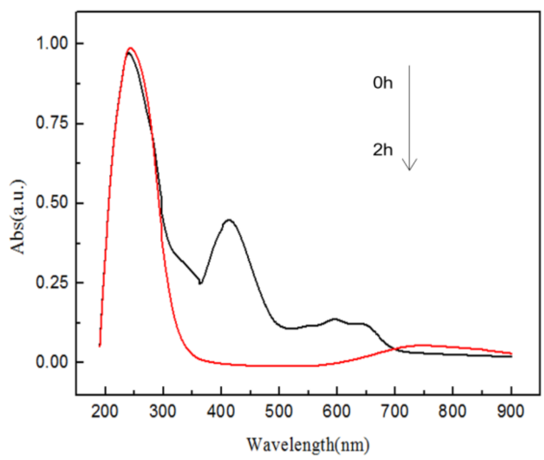


Figure 5: UV-vis scan of actual wastewater before and after the treatment

As can be seen from Figure 5, after 2 hours of reaction, the absorption peak of the raw wastewater almost disappears in the visible wavelength range, that is, the system has a good effect on the removal of chromaticity of the actual wastewater; in the UV region, the absorption peak of the raw wastewater increases slightly. It is speculated that after the reaction, there are UV-absorbing substances generated, and the organic matters in the wastewater are not completely degraded.

3.5 GC-MS analysis

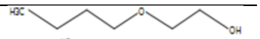
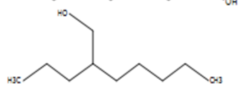
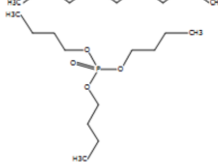
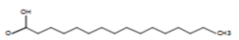
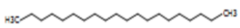
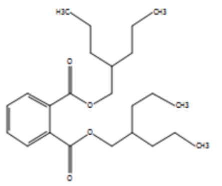
In order to analyze the water quality of the raw water of printing and dyeing wastewater, its main pollutants and types of dyes, and to analyze the wastewater quality after ultrasound-assisted copper foam/H2O2 system pretreatment, the GC-MS method is used to test the wastewater before and after the reaction.

The actual printing and dyeing wastewater usually contains dyes molecules, surfactants, plasticizers and other types of additives (Zhang et al., 2009), the types and content of pollutants are related to the technological process of the printing and dyeing textile factories, different production processes lead to changes in the type and content of pollutants in the wastewater. Comparing the results of the GC-MS test with the standard NIST library, the main pollutants in the wastewater are obtained.

The raw water of the printing and dyeing wastewater contains a large amount of dyes, dye intermediates, and various additives used in the production and processing processes, mainly are substances with macromolecules. The dyes are mainly anthraquinone dyes, with good fastness to light and washing, making the wastewater present a color of yellow-green, which can only be removed by specific decolorizing microorganisms (El-Gohary et al., 2009), affecting the biodegradability of the wastewater; wastewater contains a large amount of tributyl phosphate, which is used as defoamer in industry and applied in the textile printing and dyeing industry. Phthalates are the most commonly used PVC plasticizers, which increase the softness of textiles, and are also a class of macromolecules organic matter that are difficult to be decomposed and utilized by microorganisms; n-hexadecenoic acid is a high-grade saturated fatty acid that can be used as surfactant and is commonly used in synthetic detergents.

The main purpose of using ultrasound-assisted copper foam/H2O2 system for the pretreatment of printing and dyeing wastewater is to quickly decrease the chromaticity of the wastewater, while improving its biodegradability (Pestryakov et al., 1996). In the actual wastewater, it’s mainly the degradation of anthraquinone dyes. From GC-MS analysis of the treated wastewater we can know that the main pollutants are shown as Table 2.

Table 2: Major pollutants in wastewater after reaction

No.	Retention time	Compound name	Molecular Formula	Molecular weight	Molecular Structure
1	5.811	Ethanol, 2-butoxy	$C_6H_{14}O_2$	118.	
2	10.995	1-Heptanol, 2-propyl	$C_{10}H_{22}O$	158	
3	15.189	Tributyl phosphate	$C_{12}H_{27}O_4P$	266	
4	20.015	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	256	
5	20.318	Eicosane	$C_{20}H_{42}$	282	
6	25.079	Di-2-pentyl phthalate	$C_{24}H_{38}O_4$	390	

As shown in Table 2, large amounts of macromolecule organics still exist in the wastewater after the reaction, but the original anthraquinone dyes and dibutyl phthalate are not detected, and a large number of small molecular substances are generated, which is consistent with the increased biodegradability of wastewater. At the same time, the removal of anthraquinone dyes also leads to decolorization of wastewater; di-2-pentyl phthalate still exists, which may be product of the oxidation of the aromatic ring of anthraquinone dyes by •OH (Pestryakov et al., 2002); there are still a large number of alkanes, tributyl phosphate and palmitic acid in the wastewater, so the COD value of the wastewater is still high, and further biological treatment is required to reach the standard removal rate (Nakajima et al., 2007).

4. Conclusion

In this study, ultrasound-assisted copper foam/H_2O_2 system was used to pretreat the printing and dyeing wastewater. The changes of chromaticity, COD and B/C before and after the treatment of actual wastewater were investigated respectively (Sponza et al., 2002).

(1) The ultrasound-assisted copper foam/H_2O_2 system can effectively remove the chromaticity of the printing and dyeing wastewater. After 2 hours of reaction, the chromaticity value of the wastewater was reduced to 60, which met the direct discharge standards.

(2) Ultrasound-assisted copper foam/H_2O_2 system can significantly improve the biodegradability of printing and dyeing wastewater. After 2 hours of reaction, the COD value of wastewater significantly decreased from 2700 mg/L to 1926.3 mg/L, the degradation rate reached 28.7%; BOD increased to 767mg/L. The calculations showed that the B/C of the wastewater increased from 0.16 to 0.40 and the biodegradability was significantly improved.

(3) Changes in the substances. GC-MS analysis of the printing and dyeing wastewater before and after the treatment showed that the macromolecule substances in the wastewater were reduced and large amounts of small molecules were generated. At the same time, the content of substances containing chromogenic groups in the wastewater was greatly reduced.

The results showed that the ultrasound-assisted copper foam/H_2O_2 system had a significant effect on the pre-treatment of printing and dyeing wastewater, which also provided a new idea for the treatment of difficult-to-degrade printing and dyeing wastewater (Zhang et al., 2009).

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