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Combined effect of US/PFS on the black liquor of making paper

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Abstract: The reed pulping black liquor is used as a sample. Researches of (1) combined effect of ultrasound(US)/polyferric sulphate (PFS)/hydrogen peroxide(H_2O_2); (2) effects of the horn tip areas; (3) effect of dose of PFS were carried. Extrapolation of these experiments indicated treatment results are possibly related to complex chemical compositions in the reed pulping black liquor.

Keywords: sonochemistry; reed pulping black liquor; horn tip irradiation area; coagulant

Introduction

The chemical effects of ultrasound have been studied for many years. The sonochemical degradation of a variety of chemical contaminates in the aqueous solution has been previously reported (Hua, 1995). Substrates such as chlorinated hydrocarbons, pesticides, phenols, and esters are transformed into short-chain organic acids, CO_2 and inorganic ions as the final products. Time scales of treatment in simple batch reactors are reported to range from minutes to hours for complete degradation. The principle of ultrasonic degradation is due to the phenomenon of cavitations, which are the nucleation, growth and collapse of bubbles in a liquid. The collapse of the bubble leads to local extremes of temperature and pressure as well as energetic mechanical action in the vicinity of the collapsing cavitations on bubble. Each of these effects can influence chemical reactivity(Hua, 1992).

Peeter Kruus and co-workers(Peeter, 1997) studied the decomposition of chlorobenzene in dilute aqueous solution by ultrasonic irradiation at two different tip sizes at 20 kHz. The results showed that treatment effects of large horn area are more efficient than small horn at a low intensity. In that paper, pollutant was single chemical composition. The aim of this work is to study treatment effects of ultrasound irradiation at two different horn areas at 24 kHz and 16 kHz on real reed pulping black liquor.

1 Experimental materials

Reed pulping black liquor (COD_{Cr}: 3768 mg/L, pH: 10—11) was obtained from Chenming Paper Mill, Wuhan. The ultrasonic equipment used for 24 kHz and 16 kHz frequencies was a 606H Model ultrasonic processor (max output power 250 W), and power meter (model 2100L, USA). We make the transducer. The diameter of ultrasonic horns of 24 kHz is 9.5 mm(small), and that of 16 kHz is 38 mm(large). Polyferric sulphate (PFS/A.R), from Wuhan Institute of Environmental Science, was 3.5% aqueous solution by distilled water. H_2O_2 (30%) diluted by distilled water is 3 mg/ml of aqueous solution. Colourity of wastewater is analysed on a UV-visible spectrophotometer (UV-912 model, Beijing) at a wavelength of 450 nm(Su, 1990). COD_{Cr} determination of wastewater is analysed by $K_2Cr_2O_7$ method(Liu, 1988). Reactor is organic glass, diameter 51 mm, height 80 mm and wall 2 mm.

2 Results and discussion

2.1 Effect of US/PFS

The schematic representation of the experimental set-up for ultrasound is shown in Fig.1.

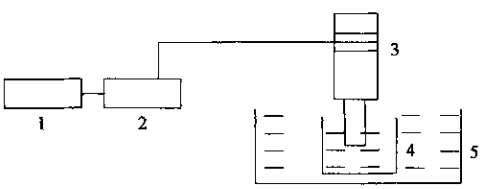

Fig.1 The experimental set-up diagram

1. ultrasonic processor; 2. power meter; 3. horn; 4. reactor; 5. water bath

The temperature of the solution in reactor is maintained at temperature of 30 ± 2℃. In the absence of ultrasound irradiation, 50 ml of a 3768 mg/L concentration of reed pulping black liquor was taken in a test tube(100 ml), and 3 ml of PFS(3.5%) is added to the solution which was shaken violently by hand. After 20 min, the supernatant solution(pH 3—5) was carefully removed and analysed. The result of analysis showed the removal rate of colourity and COD_{Cr} was 81.92% and 63.70%, respectively.

In the presence of ultrasound irradiation, 50 ml black liquor(3768 mg/L) was poured into reactor of organic glass for sonication at 24 kHz and 16 kHz. Two ultrasonic horns of

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24 kHz and 16 kHz were the same with respect to the above reactor. The runs were done under a normal atmosphere. 3 ml of PFS(3.5%) was taken into solution, treatment times of ultrasound was 5 min. After analysis, the variation of the degradation ratio of colourity and COD_{Cr} with electric power (W) at 24 kHz and 16 kHz is shown in Fig.2 and 3 for two tip sizes.

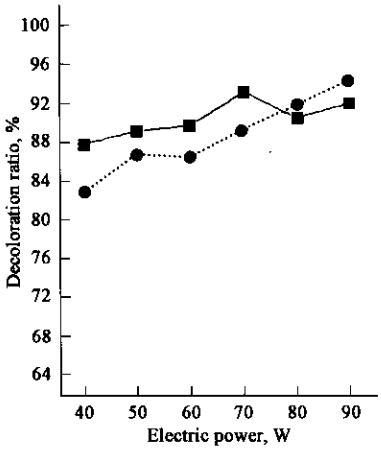

Fig.2 The decoloration ratio vs the electric power
■: 24 kHz with small horn; ●: 16 kHz with large horn

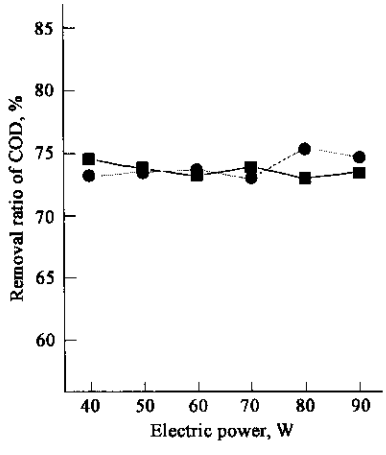

Fig.3 The removal ratio of COD vs the electric power
■: 24 kHz with small horn; ●: 16 kHz with large horn

Fig. 2 and 3 show the removal ratio of the colourity and COD_{Cr} is greater with ultrasound than without ultrasound (81.92% and 63.7%, respectively). In Fig. 2, the removal ratio of the color increases with electric power(W) increasing. The degradation effect is higher with small horn than with large horn, under the same irradiation. From Fig. 3, it can be seen that removal ratio of COD_{Cr} is obviously enhanced by US, and also be seen not to differ markedly with two different tip sizes (since the frequency of 24 kHz and 16 kHz is vicinal, the influence of frequency is neglected) like previous paper(Peeter, 1997). From above figures, so far as two differ tip areas go, the influence of irradiation areas is not obvious. The reason may be explained that chemical compositions are too much complex.

2.2 Effect of US/ PFS/H_2O_2

0.3 ml of H_2O_2(3 mg/ml) and 3 ml of PFS(3.5%) are taken into the test tube with 50 ml of reed pulping black liquor (3768 mg/L), and then shaken violently. The supernatant solution is analysed after 20 min. The result is that removal ratio of colourity and COD_{Cr} are 82.6% and 64.10%, respectively. It indicated the effect of H_2O_2 oxidation at lower dose has no display compares to with PFS (3 ml) alone(81.92%, 63.70%). In order to illustrate H_2O_2 oxidation, keeping dose of PFS(3 ml) and the varying dose of H_2O_2(3 mg/ml). The results are shown in Table 1.

Table 1 The results of the effect of US/PFS/ H_2O_2

H_2O_2, ml	0.3	0.5	0.7	1.0	1.5	2.0	3.0	4.0
Decolored ratio, %	82.67	84.23	86.15	90.76	91.76	93.38	93.30	87.92
Removal ratio of COD_{Cr}, %	64.10	66.50	74.36	76.92	77.15	75.56	75.00	69.23

Table 1 shows the effects of H_2O_2 oxidation increase with addition to H_2O_2 (range from 0.3 ml—2.0 ml), but treatment effects reduce with further addition to H_2O_2. Further experiments are studied, namely, the combined effects of US(with two different tip sizes)/PFS (3 ml)/H_2O_2 (0.3 ml). Sonication time is 5 min. The results are shown in Fig.4 and 5 respectively.

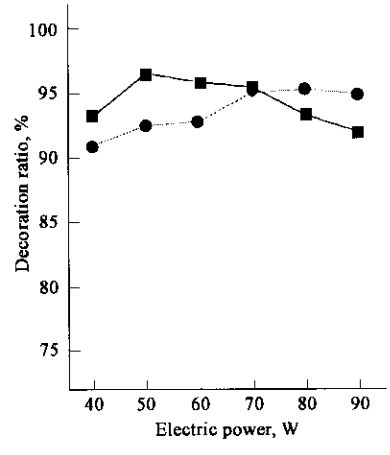

Fig.4 The decolouration ratio vs the electric power
■: 24 kHz with small horn; ●: 16 kHz with large horn

In the experiment, because of adding small amounts of H_2O_2 (0.3 ml), the optimal removal ratio of COD_{Cr} is 77.41%, the enhancement amount of removal ratio of COD_{Cr} is 13.31%. About 50%—80% H_2O_2 is saved at the same treatment effects. Namely, the combined effect of US/PFS/ H_2O_2 is better than that of PFS/H_2O_2 (64.10%). The maximum enhancement amount of removal ratio of colourity and COD_{Cr} is about 13.85% and 13.31% respectively,

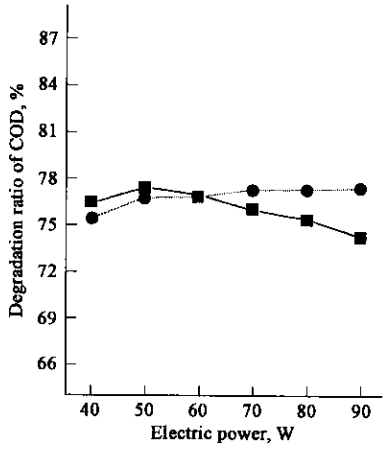

Fig.5 The removal ratio of COD_{Cr} vs the electric power
■: 24 kHz with small horn; ●: 16 kHz with large horn

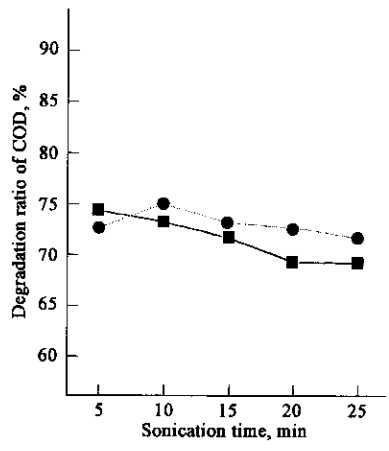

Fig.6 The removal ratio of COD_{Cr} vs the time(US/PFS)
■: 24 kHz with small horn; ●: 16 kHz with large horn

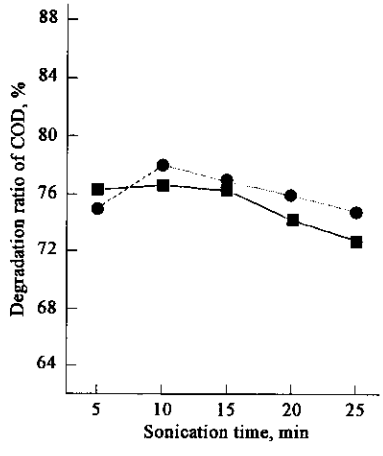

Fig.7 The removal ratio of COD_{Cr} vs the time(US/PFS/H_2O_2)
■: 24 kHz with small horn; ●: 16 kHz with large horn

compared to that method without ultrasound.

The possible explanation is due to small amount of H_2O_2 added to solution and irradiated by US, which is helpful to formation of Fenton reactant and it lead to enhancement of degradation rate of organism(Fang, 1996; Qi, 1996).

At lower electric power(< 70 W), the influence of the tip sizes on COD_{Cr} is still not apparent, whereas at higher electric power(> 70 W), treatment effects depend on horn area. The reason is explained(Peeter, 1997).

2.3 Effect of sonication time

In this experiment, under the condition of the same electric power(40 W) and the varying sonication time, the results(US/PFS and US/PFS/H_2O_2) are shown in Fig.6 and 7 respectively(only given removal ratio of COD_{Cr}). From Fig 6 and 7, it can be seen that within the limit time, organic compounds in waste water collide with coagulants that make common settling rate increase, and lead to enhance removal rate of COD_{Cr} by ultrasound. But removal rates of COD_{Cr} decrease with increasing time of sonication time, this is because shatter effect of ultrasound makes large molecule organic compounds into small molecule compounds, leads to increase steady of colloid particles, and makes flocci into micro particles which suspend in solution. All of these are not beneficial to flocculation settling. So it is important to control sonication time at the spectific electric power. From Fig.6 and 7, it can be seen that sonication time ranges from 5 to 10 min.

3 Conclusions

The ultrasound and the PFS has the synergistic effect on the treatment of black liquor of making paper.

At low electric power, about 50%—80% of H_2O_2 is saved under the same treatment effect.

Treatment effects do not apparently depend on the horn tip irradiation areas for the real wastewater.

Treatment effects are apparent by combined effect of US/PFS/H_2O_2 at the short time.

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