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Treatment of wastewater containing azo dye reactive brilliant red X-3B using sequential ozonation and upflow biological aerated filter process

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ABSTRACT

In this work, the treatment of wastewater containing azo dye reactive brilliant red X-3B using sequential ozonation and upflow biological aerated filter process has been studied. Decolorization was almost complete after 120 min with an ozone concentration of 34.08 mg/L, the biological oxygen demand for 5 days (BOD_5)/chemical oxygen demand (COD) ratio increased from 0.102 to 0.406, which was more effective for the subsequent upflow biological aerated filter (UBAF) to reduce COD concentration. Under the conditions of gas/liquid = 3, hydraulic load = 4.8 m^3/m^3.d, T = 20–25 °C, the mass ratio of ozone to dye = 4.5, pH 11, the COD and color of the effluent were less than 40 mg/L and 20 Pt–Co units, respectively, and the average decolorization and COD removal efficiency were 97% and 90%, respectively. The experimental results showed that the combination of ozone oxidation and upflow biological aerated filter was a promising technique to treat wastewater containing azo dye.

1. Introduction

Textile wastewater is characterized by strong color, large amount of suspended solids [SS], broadly fluctuating pH value varying from 2 to 12, high chemical oxygen demand and biotoxicity and causes coloring of the receiving water environment [1]. Azo dyes like brilliant red X-3B (contain —N=N— bonds) are the most widely used dyes in textile industry, accounting for over 50% of all commercial dyes [2]. However, large amount of azo dye remains in the effluent after the completion of the dyeing process and most azo dyes are non-biodegradable. Due to their toxicity and slow degradation, these dyes are classified as environmentally hazardous materials. Therefore, the employment of these dyes must be controlled and the effluents must be treated before being released into the aquatic and terrestrial environment [3]. Azo dyes are resistant to biodegradation under aerobic conditions whereas anaerobic treatment is applied successfully. Textile wastewater is not proper to use anaerobic process because the breakdown of azo dye leads to the formation of aromatic amines, which may be more toxic than the dye molecules themselves [4]. Although numerous physical/chemical schemes, including coagulation, flocculation, adsorption and membrane filtration, have been used to decolorize textile effluents, these techniques suffer disadvantages of sludge generation, adsorbent regeneration and membrane fouling.

In recent years, ozonation is emerging as a potential process for decolorization of dyes, since the chromophore groups with conjugated double bonds, which are responsible for color, can be broken down by ozone either directly or indirectly forming smaller molecules, which can be removed by biological treatment, thereby decreasing the color of the effluents [5,6]. It was found that refractory organic pollutants could become biodegradable after appropriate chemical oxidation. This oxidizer such as ozonation is highly efficient, decomposes quickly and causes no secondary pollution. Ozone oxidation studies have demonstrated relatively low rate of mineralization of azo dyes in wastewater treatment [7,8]. However, it was shown that ozonation required high cost in operation, though it improved biodegradability of textile wastewater to some extent [9–14].

Biological treatment of wastewater is the most economical method so that biological removal of the ozonation products following ozonation is cost-effective [15]. Upflow biological aerated filter is an alternative to the traditional activated sludge process commonly used in biological wastewater treatment. This technology is based on the principle of biofiltration through a submerged granular medium that serves two purposes: biological conversion of organic matter by the biomass attached to the large support medium surface and physical retention of suspended particles by filtration through the deep filter bed. The technology of upflow biological aerated filter (UBAF) has been developed extensively due to its lots of advantages, such as small footprint and excellent performance at much higher loading rates than that of conventional biological processes with high removal efficiencies and capacities

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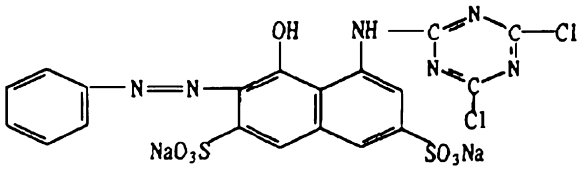

Fig. 1. Structure of reactive brilliant red X-3B.

for carbonaceous organic substances, total nitrogen (TN), ammonia and SS [16].

Over the last decade, the treatment of organic-containing wastewater by means of integrated chemical–biological processes has received a lot of attention. The potential of a previous chemical oxidation to convert initially recalcitrant compounds to more readily biodegradable intermediates, which can then be removed through subsequent biological treatment, has been reported [17]. The combination of chemical oxidation and biodegradation has a great advantage over either of the two treatments alone in the remediation of organic contaminants. To enhance biodegradability of azo dye brilliant red X-3B containing wastewater, pre-ozonation was used. With pre-ozonation, part of the refractory organic matter is usually (but not always) converted into a more biodegradable form, which can be removed by biological treatment. Integrating their advantages of ozone oxidation and upflow biological aerated filter, the coupling process was considered as a promising technique for textile dyeing wastewater treatment.

The objective of the work was to investigate the decolorization and degradation of azo dye brilliant red X-3B using sequential ozonation and UBAF process. The wastewater containing azo dye X-3B was pretreated by ozone oxidation, which increased the biodegradability of the wastewater, and most of the organic matter was removed in the next step by UBAF process.

2. Experimental

2.1. Materials

In the study, the dye of reactive brilliant red X-3B (98%) was from Jining dye manufacture of Shandong, China, and used directly without further purification. The molecular structure of reactive brilliant red X-3B was shown in Fig. 1. Other chemical reagents such as sodium hydroxide and phosphate were of an analytical grade. The water used in this work was distilled water. To investigate the effect of treatment, the simulated wastewater was confected in the laboratory based on the main pollutants found in actual wastewater. The simulated wastewater quality was shown in Table 1.

2.2. Experimental setup

The experiment was carried out using sequential ozonation and upflow biological aerated filter process. The experimental setup mainly consisted of two parts: one part was the ozone oxidation apparatus and another part was upflow biological aerated filter treatment apparatus.

Ozone was generated from dry air in a laboratory model ozone generator with a maximum capacity of 5 g/h. Ozonation experiments were conducted in a 1-L boro silicate glass reactor. Fig. 2 depicted the schematic diagram of ozone experiment system.

Table 1
The simulated wastewater quality

pH	7
Color (Pt–Co unit)	750
COD (mg/L)	400
BOD (mg/L)	45

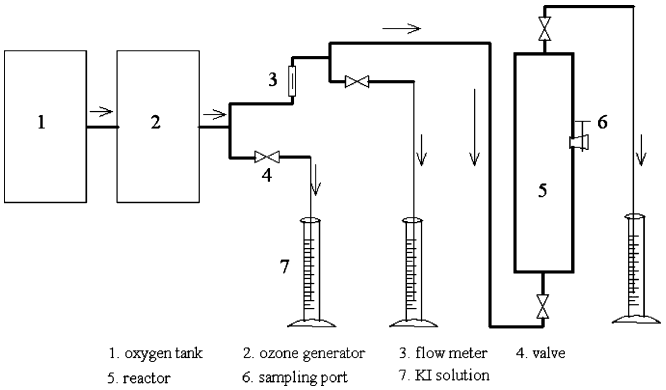

Fig. 2. Schematic diagram of ozone experiment system.

Ozone was supplied at the bottom of the reactor through glass diffuser. All connections from the ozone generator to the reaction vessel were made through Teflon tubing. The ozone concentration in the feed gas stream and outlet gas stream was measured by the iodometric method. The unreacted ozone, leaving the column, was collected in the three gas-washing bottles filled with 2% KI solution. The KI solution reacts with excess ozone liberating I_2 and the resulting I_2 was titrated against standard thiosulphated using starch as an indicator. The experiment with ozone was carried out at varying parameters such as pH, reaction time and ozone dosage. Samples were taken at regular time intervals for the determination of chemical oxygen demand (COD) and color.

Wastewater produced in textile industrial processes contains azo dyes which are not easily amenable to biological treatment. So the simulated wastewater was pretreated with ozone, which increased the biodegradability of the wastewater, and most of organic matter in wastewater was removed by subsequent UBAF. Fig. 3 showed the schematic diagram of upflow biological aerated filter process.

UBAF used for carrying out the experimental works was made of Plexiglas having 100 cm of interior diameter and 2.0-m height. Ceramics particles of 3–4 mm average diameter were filled in the filter and the media column height is 1.0 m. All equipments were shown in Table 2.

2.3. Analytical methods

Decolorization capacity of ozonation process was determined by absorbance measurements at the maximum visible absorbance

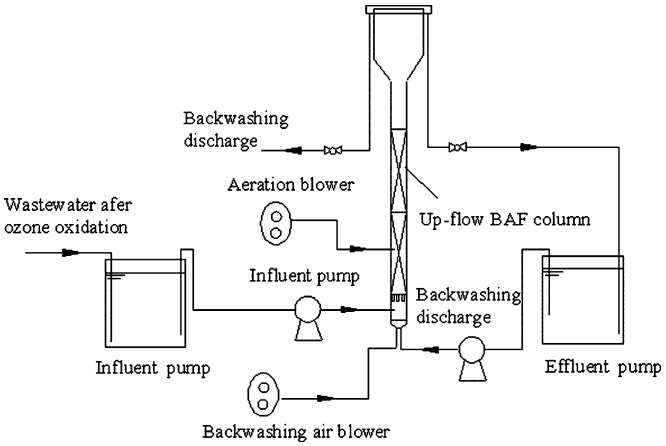

Fig. 3. Experimental setup for upflow biological aerated filter process.

Table 2
Main equipment in the experiment

Sequence number	Appellation	Specification and type
1	Ozonizer	0–5 g/h
2	Air flowmeter	0–0.2 m^3/h
3	Ozone reactor	φ115 mm × 1200 mm
4	Influent tank	40 cm × 40 cm × 50 cm
5	Influent pump	P150 Q_{max} = 18.9 L/h
6	UBAF	φ150 mm × 2000 mm
7	Aeration blower	ACO380 Q = 75 L/min
8	Blackwashing air	ACO500 Q = 470 L/min
9	Backwashing pump	WZ10-10 Q = 10 L/min
10	Effluent tank	40 cm × 40 cm × 50 cm

wavelength (536 nm). For this purpose UV–vis absorbance spectra were recorded using an UV–vis spectrophotometer (UV-752, Shanghai, China). Decolorization was determined by the following equation:

$$\text{Decolorization}\,(\%) = \frac{A_0 - A}{A_0} \times 100$$

where A_0, A are the expressed absorbency of reactive red dye simulative wastewater in the highest absorption peak place before and after ozone oxidation treatment, respectively. COD means the oxygen amount in a strong oxidizing agent, required for complete organic matter oxidation. In this work, the values of COD were obtained through oxidation with $K_2Cr_2O_7$ under acidic conditions and titrate analysis with $(NH_4)_2Fe(SO_4)_2$ aqueous solution according to national criterion of PR China [18]. The pH values of solutions were recorded by pH analyzer (Lei Ci instrument plant, Shanghai, China). The concentration of ozone was measured by iodimetry [19].

3. Results and discussion

3.1. Effect of ozone oxidation on decolorization efficiency

3.1.1. Effect of pH value

The pH value of solution plays a major role in the formation of OH radical during ozonation. Boncz et al. [20] indicated that pH value was the most important factor in the ozonation chlorophenol, since pH value determined the dissociation of organic compounds. The experiments were carried out at different pH and the data were presented in Fig. 4. It could be seen from the figure that as pH was increased, the decolorization efficiency showed increasing trend, and 100% at pH 11 when the reaction time was 60 min indicating that the rate of decomposition was initiated by the formation

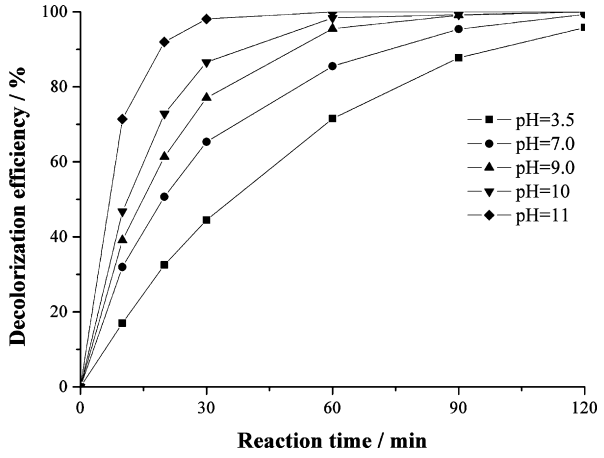

Fig. 4. Decolorization efficiency as a function of reaction time at different pH.

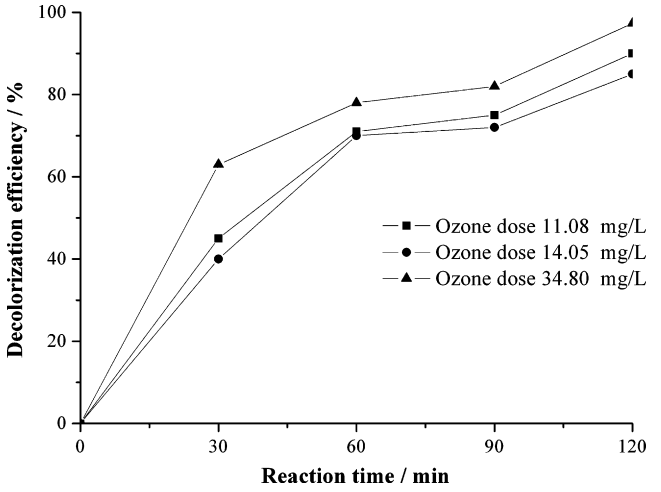

Fig. 5. Decoloration efficiency as a function of reaction time at different ozone doses (conditions: pH 11; dye concentration, 50 mg/L; T 25 °C).

of hydroxyl radicals at higher pH values. The solution also turned from brilliant red to colorless. The reactive brilliant red dye wastewater is a kind of industrial wastewater which is difficultly degraded by conventional methods. Ozone directly attacks organic matter by molecular form under acidic or neutral condition, moreover the molecular ozone response has the greatly strengthened selectivity. It only reacts with the unsaturated aromatic compounds or certain special groups. But the reason why the removal rate of color enhanced under the alkalinity condition is that ozone produces •OH, which has stronger oxidation ability. Thus those difficultly biodegraded organic matter can be effectively degraded.

3.1.2. Effect of ozone dose

Another factor affecting the decolorization efficiency is the ozone dose. The effect of ozone dose on decolorization efficiency with reaction time at three ozone doses of 11.08 mg/L, 14.05 mg/L and 34.80 mg/L was presented in Fig. 5. When the ozone dose was 11.08 mg/L decolorization efficiency observed at 120 min was 85%. At an ozone concentration of 34.80 mg/L, decolorization observed at 120 min of ozonation was 97.8% and the solution turned colorless indicating that applied ozone doses have a positive effect on decolorization efficiencies. Increase in ozone concentration enables better mass transfer of ozone and hence better performance.

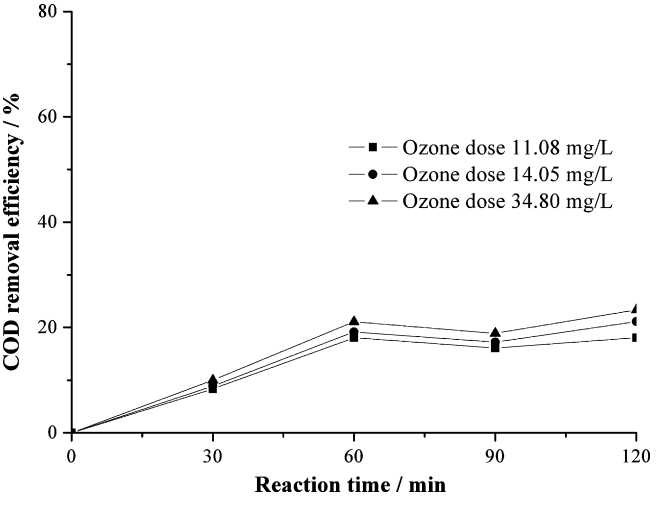

Fig. 6. COD removal efficiency as a function of time at different ozone doses (conditions: pH 11; dye concentration, 50 mg/L; T 25 °C).

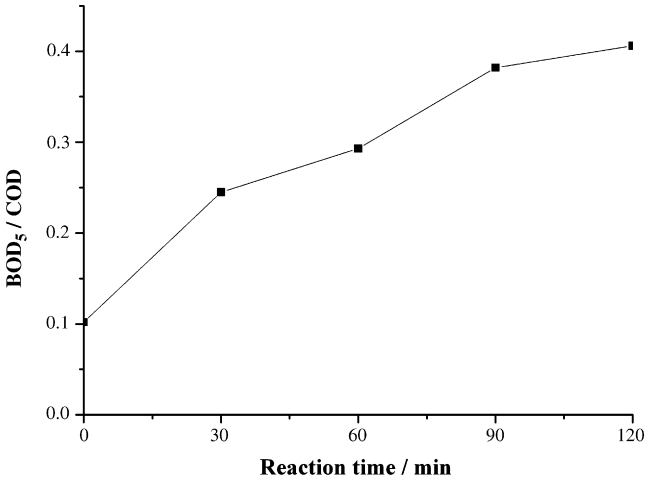

Fig. 7. Effect of ozonation time on the biodegradability of simulated wastewater (conditions: initial pH 11; initial concentration of the dye, 50 mg/L; ozone dose, 11.08 g/L).

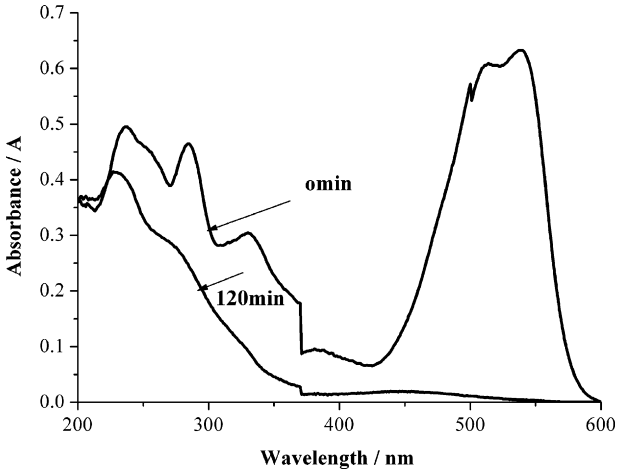

Fig. 8. The UV–vis absorption spectra of X-3B before and after ozonation (conditions: initial pH 11; initial concentration of the dye, 50 mg/L; ozone dosage, 11.08 g/L).

3.2. Effect of ozone oxidation on COD removal

Fig. 6 presented the data on COD removal efficiency with reaction time for experiments carried out with three ozone doses. For a given time, an increase in ozone concentration resulted in an increase in COD removal efficiency. In this study, the COD removal efficiency of the simulated wastewater achieved was less than 30%, and continuous increase of ozone dose had not increased the efficiency in COD removal quickly. This could be stemmed from that as the ozone oxidation continued, recalcitrant organic compounds in the wastewater that could be oxidized became less available and that the remaining inert organic compounds after ozone oxidation were difficult to break down. Singer [21] has also observed that even in the presence of excess ozone, the reaction dose not result in complete mineralization to carbon dioxide.

3.3. Effect of ozone oxidation on biodegradability

In general, chemical oxidation can change the molecular structure of compounds, which are non-biodegradable and rupture them into smaller molecules; the intermediates usually have better aerobic biodegradability than original compounds [22]. The ratio of BOD_5 to COD is often used as a measurement of biodegradability. A large BOD_5 to COD ratio indicates a higher biodegradability of the wastewater. In this study, the wastewater containing azo dye X-3B was ozonated to examine this effect. Result was shown in Fig. 7 where the increase in biodegradability was obvious with ozone oxidation. The ratio of BOD_5 to COD increased from 0.102 to 0.406. Such results indicated that the wastewater biodegradability increased with an increase in ozonation time.

Fig. 8 showed the UV–vis spectral change of X-3B at pH 11 in ozone oxidation system. As mentioned in Fig. 1, the dye X-3B has four structure units: benzene, triazine, naphthalene rings and a conjugated system linked by two azo groups. In the UV region, the absorbance bands at 234, 280 and 330 nm are attributed to the benzene ring, triazine ring and naphthalene ring, respectively, where the visible band at 536 nm is designated to the long conjugated π system linked by two azo groups. During the experiment, the intensity of absorption at 536 nm declined extremely rapidly; however, the UV bands at 234, 280 and 330 nm disappeared more slowly than the visible band. The intensity of absorption at 536 nm declined extremely rapidly, from 0.632 to 0.04 after 120 min of reaction time. The hydroxyl radicals and oxidizing agents initially attacked azo groups and open N=N bonds, destructing the long conjugated π system, and consequently causing decolorization. Since aromatic ring structures were more difficult to be destructed than the N=N bonds, the elimination of adjacent ring structures needed a long time [23].

3.4. Wastewater treatment by ozonizing-upflow biological aerated filter process

3.4.1. Start-up of UBAF and biofilm formation

The start-up of UBAF system (without ozonation) was extended for 4 weeks. Due to the low microbial population and nutrient concentration of wastewater, a previous inoculation of biological filter was necessary in order to obtain an adequate biological yield. During the operational period, the sludge from wastewater treatment plant was used as seeding sludge. When activated sludge was used as inoculum, a heterogeneous biofilm was obtained, showing several bacterial morphologies and microbial types. It is found that the biomass amount was increased after ozonation. More experiments are in progress in order to understand in detail the characteristics of bacteria on the films formed by inoculation and the influent of alteration in microbial composition over quality of treated effluent [24].

Table 3
Effect of ozone dosage in wastewater treatment using sequential ozonation and UBAF process

Ozone/dye (mass ratio)	COD(mg/L)			COD removal (%)			Color (Pt–Co unit)		
	Influent	Ozone	Effluent	Ozone	UBAF	Total	Influent	Ozone	Effluent
0	400	400	287.6	0	29.10	29.10	750	750	750
1.5	400	350	65	12.4	81.31	84.10	750	500	500
2.5	400	309	45	22.66	85.43	88.79	750	300	300
3.5	400	278	41	30.50	85.13	89.87	750	40	40
4.5	400	276	34	30.91	87.42	90.23	750	20	20

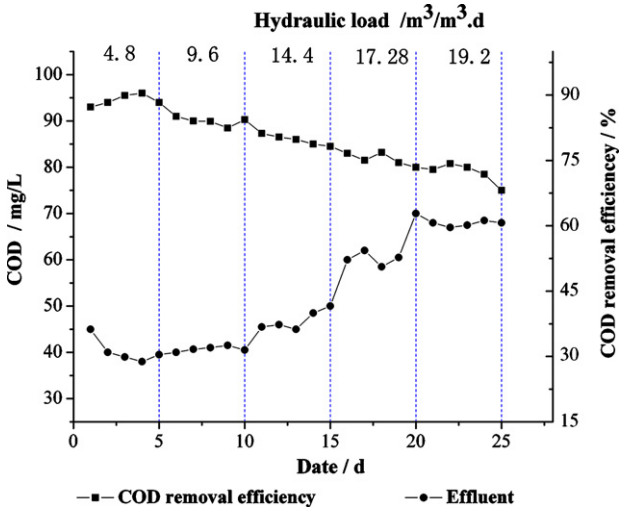

Fig. 9. Effect of hydraulic load on COD removal efficiency.

3.4.2. Effect of ozone dosage on treatment system

The simulated wastewater was treated using sequential ozonation and UBAF process in which hydraulic load of UBAF was fixed at 4.8 m^3/m^3.d, the ratio of gas to liquid at 3 and the temperature of wastewater was 20–25 °C and change in the addition of ozone dosage was carried out. The experimental results were shown in Table 3. The COD removal efficiency of the non-ozone process was about 30%, and the color degree even had slight rise. On the other hand, when the process added ozone to pre-oxidation, the removal efficiency of COD and color degree increased significantly; when the mass ratio of ozone to dye was 4.5, COD removal efficiency of the simulated wastewater was 90.23% and the color of the effluent was reduced to about 20 Pt–Co units.

3.4.3. Effect of hydraulic load on COD removal

To determine the effect of hydraulic load on COD removal efficiency, we fixed the ratio of gas to liquid at 3 and the temperature of wastewater was 20–25 °C, and changed the hydraulic load of UBAF. The treatment efficiency of this process was shown in Fig. 9. It was found if the hydraulic load was fixed at 4.8 m^3/m^3.d, the average COD of effluent was less than 40 mg/L and the COD average removal rate of the process reached 87%. With the increase in hydraulic load, the COD removal efficiency decreased. The process showed excellent treatment efficiency for the simulated wastewater.

4. Conclusions

(1) Ozonation is highly efficient in the decolorization of textile wastewater containing azo dye X-3B, but less efficient in terms of COD removal. Under the optimal conditions, the average color and COD removal efficiency were 97% and less than 30%, respectively. The subsequent UBAF process can greatly reduce COD of wastewater treated by ozone pre-oxidation. The average COD removal efficiency in the UBAF process was over 85%.

(2) Ozone pre-oxidation process can improve the biodegradability of wastewater containing azo dye reactive brilliant red X-3B significantly, which increased the value of BOD_5/COD from 0.102 to 0.406.

(3) The results obtained by the experimental study showed that the COD and color of the effluent were less than 40 mg/L and 20 Pt–Co units, respectively, which can satisfy specific criteria of water reuse. Therefore, the combination of ozonation and UBAF can be thought as an efficient option for the treatment of azo dye wastewater.

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