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A combined process of anaerobic baffled reactor (ABR) and anaerobic/aerobic (A/O) for treatment of dyeing wastewater

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Abstract. A combined process of anaerobic baffled reactor (ABR) and anaerobic/aerobic (A/O) was utilized for the treatment of dyeing wastewater. The pre-treatment characteristics of the ABR at different hydraulic retention time (HRT) and the treatment efficiency of the ABR-A/O combined process were investigated. The results showed that the color, chemical oxygen demand (COD) can be effectively removed and the biodegradation ability was rapid improved in the ABR unit, the effluent concentration of COD, five day chemical oxygen demand (BOD_5), ammonia nitrogen (NH_4^+-N) and color of the ABR-A/O combined process were 95-172mg/L, 28.2-64.6mg/L, 3.21-5.56 mg/L and 20-50 times, the COD, NH_4^+-N and color concentration can meet with the discharge standards of water pollutants for dyeing and finishing of textile industry of China (GB 4287-2012). The concentration and number of different complex organic matters in the effluent were found to be significantly lower than in the raw water by chromatography–mass spectrometry (GC–MS).

Key words. Anaerobic baffled reactor, dyeing wastewater, A/O process, GC–MS analysis.

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1. Introduction

Dyeing wastewater is complex in composition and has poor biodegradability [1]. Up to 60%–70% components in the dyeing wastewater are azo dyes and aromatic amines, which were difficult to be bio-degraded [2, 3]. It was necessary to develop a kind of efficient, cost-effective and no secondary pollution method to treatment of dyeing wastewater.A typical biochemical process for treating dyeing wastewater was an anaerobic and aerobic (A/O) process [4, 5], because the bio-degradation of the dyeing wastewater was efficient and cost-effective. During the anaerobic process, microbial hydrolytic acidification is used to facilitate the decomposition of recalcitrant organics and their chromophoric groups [6]. During the aerobic process, the effluent of the anaerobic process is further treated so that the organics and nutritional elements (e.g. nitrogen and phosphorus) can be removed [7, 8].

The anaerobic baffled reactor (ABR) is a classical anaerobic reactor. In this reactor, vertical baffle plates are used to separate the inner space of the reactor into several compartments. Each compartment is further divided into upflow and downflow chambers. Because each compartment works almost independently, gradient microbial phases can be cultured successively within these compartments. This leads to the temporal and spatial separation of different stages of the anaerobic reaction [9, 10]. In conclusion, the ABR has many favorable features, such as high efficiency, separation of the microbial phases, and operational stability. Currently, the ABR is widely used for the treatment of industrial wastewater [11, 12].

The combined process of ABR and A/O for dyeing wastewater treatment was relatively rare, the effect on the ABR removal efficiency of HRT and organic substances change has no reported. In the study, we developed a combined process that integrated the ABR reactor and A/O process for the treatment of the dyeing wastewater. To investigate the overall performance of this combined process, a comprehensive study of the operational mechanism and the factors influencing the whole process was conducted. The aims of the experiment were as follows: (1) The effect on the ABR removal efficiency of HRT was studied. (2) The organic substances change profiles was investigated in the ABR-A/O combined process. (3) The ecological system of the O unit of the A/O process was observed, especially the indicated microorganisms.

2. Experimental apparatus and methods

2.1. Experimental apparatus

The ABR unit used in this experiment was made of plexiglass, with an effective height of 300mm and an effective volume of 45L. The inner space of the ABR unit was divided into five compartments, and the width ratio between the up-flow and down-flow chambers in each compartment was 4:1. A guide plate with a dip angle of 45 ° was placed at the lower end of each baffle plate. There was a sampling port at the top of each compartment and a sludge-discharging port at the bottom of each compartment. An A/O unit and a secondary sedimentation tank were serially connected to the ABR. The effective height of the A/O reactor was 300 mm and its effective volume was 45 L. The volume ratio between the A zone and the O zone was 1:4.

2.2. Seed sludge

The seed sludge of the ABR unit was obtained from an industrial wastewater treatment plant in an industrial park (Xuzhou, China). The concentration of mixture liquor suspended solids (MLSS) was 36.5 g/L, and the ratio between the volatile suspended solids (MLVSS) and MLSS was 0.76, the seed sludge was added into the five compartments of the ABR at a ratio of 2:1:1:1:1. The seed sludge of the A/O process was taken from the A/O unit of a municipal wastewater treatment plant (Xuzhou, China). The concentration of MLSS was 2.75 g/L, the sludge volume (SV_{30}) was 34%, and the sludge volume index (SVI) was 103. The seed sludge was evenly added into the A/O reactor.

2.3. Raw wastewater

Raw wastewater was taken from a WWTP (Xuzhou, China). About 90% was the dyeing wastewater and 10% was sewage from the neighborhood. The quality of the raw wastewater is summarized in Table 1.

Table 1. Quality parameters of the raw wastewater

Quality parameters	range	mean value	Quality parameters	range	mean value
COD/mg·L^{-1}	418–766	517	color/times	250-512	380
BOD_5/mg·L^{-1}	57.4–123.6	95	pH	7.86-8.96	8.37
B/C	0.15-0.23	0.2	NH_4^+-N/mg·L^{-1}	35.4-45.2	38.5

2.4. Operational procedure

The operational procedure consisted of two phases. (1) The load-raising phase after the start-up phase (lasted 45 days). The ABR was operated under HRT of 32, 24, 18, 14 and 10 h, the temperature was maintained at 20 °C – 22 °C, and the influent of the ABR was raw wastewater. (2) The experimental phase. The ABR was operated at HRT of 24 h. The HRT and dissolved oxygen (DO) of the A unit was maintained at 6 h and 0.1-0.5 mg/L, and the HRT and DO of the O unit were maintained at 18 h and 2-5 mg/L. The inner and outer loop rates were respectively 50%-100% and 100%-150%, and the water temperature was 20 °C – 22 °C.

2.5. Analytical methods

The Chinese National Standards were adopted for the determination of chemical oxygen demand (COD), five day biological oxygen demand ($BOD_{5)}$, pH, MLSS, MLVSS, ammonia nitrogen (NH_4^+-N), total nitrogen (TN) and color. A gas chromatography–mass spectrometry (GC–MS) method was used for the analysis of organic substances in the wastewater. A B-5 type low-polarity capillary column was used with a helium carrier gas flow rate of 0.8 mL/min and consecutive column temperatures of 60 °C (2 min), 10 °C (2 min) and 300 °C (30 min). Electron ionization (EI) was used as a detector in the mass spectrometry, with the electron energy set to 70 eV, source temperature to 200 °C, amplifier voltage to 1050 V, and full scan mode used at a speed of 500 u/s and range of 35 $\sim$ 400 u.

3. Results and discussion

3.1. Effect on the ABR removal efficiency of HRT during load-raising phase

The change of the COD, BOD$_5$, B/C, color removal efficiency under the different HRT conditions was shown in Tab.2.

Table 2. The change of COD, BOD$_5$, BOD/COD (B/C) and color at different HRT

HRT		32 h	24 h	18 h	14 h	10 h
COD	influent	528–713	488–766	655–721	438–628	418–598
	effluent	280–401	312–482	432–508	352–478	354–467
	removal rate	38.2–53.7	24.8–43.5	26.5–35.1	21.6–30.8	16.9–26.1
color	influent	300–510	300–400	300–400	250–400	250–400
	effluent	100–250	100–180	100–200	100–200	120–200
	removal rate	50–70	55–70	50–68	55–60	44–55
BOD$_5$	Influent (*)	130.5	102.6	149	122	96.5
	effluent (*)	124	140	144	130	120
B/C	Influent (*)	0.21	0.16	0.23	0.22	0.19
	effluent (*)	0.39	0.37	0.35	0.33	0.30

Note: 1. operation time was 35d, 35d, 25d, 25d and 25d, respectively.
2. The COD and BOD$_5$ unit was mg/L, and the removal rate unit was %.
3. (*) was averaged value.

As shown in Tab.2, the influent COD was 418-766 mg/L and the HRT was 32, 24, 18, 14 and 10 h, the corresponding average COD removal rates were 46.1%, 36.3%, 29.4%, 25.5% and 22.5%. The COD removal rate reached its peak when the HRT was 32 h, because the long HRT ensured a prolonged contact time between organics and microorganisms, which provided a favorable environment for anaerobic bacteria and enhanced the efficiency of organic degradation in the wastewater [13, 14]. In addition, the prolonged HRT also contributed to remove part of the insoluble COD (suspended or colloidal COD).

BOD$_5$ and B/C ratio profiles were shown in Tab.2. When the influent BOD$_5$ concentration was 96.5-149 mg/L, the concentration of effluent BOD$_5$ was 120–

144 mg/L. With a shortening of the HRT, the effluent B/C ratio displayed a decreasing trend and reached 0.3 (lowest point) when the HRT was 10 h. In contrast, the effluent B/C ratio was 0.39 (highest point) when the HRT was 32 h, a shortened HRT will lead to incomplete degradation of large-molecular substances (aromatic hydrocarbons) by hydrolytic and acidogenic bacteria.

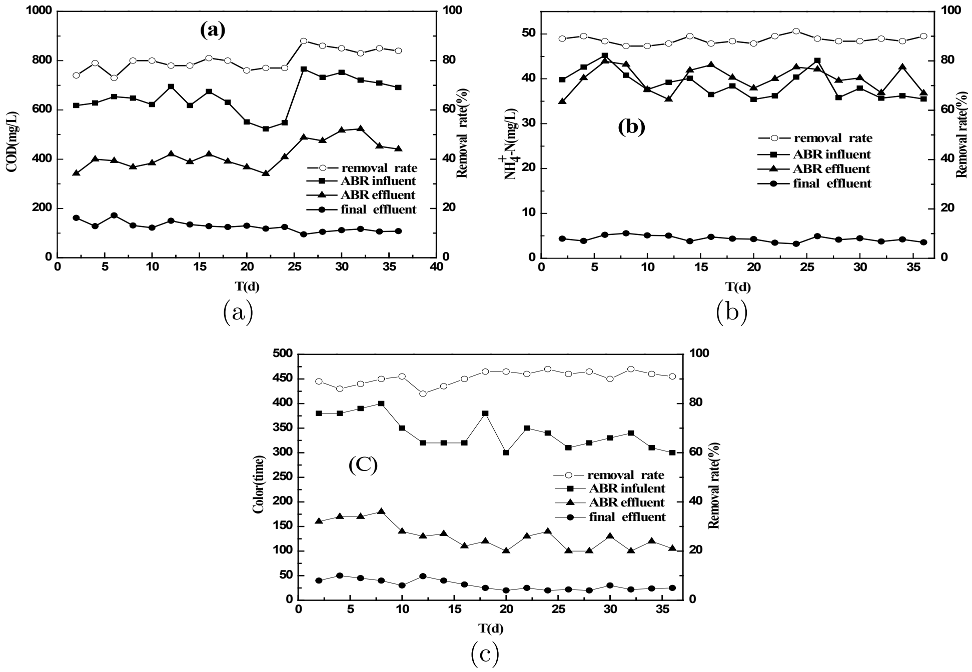
During the load-raising phase, the sludge yield rate of ABR was 0.16–0.24 kg VSS/kg BOD, which was lower than the start-up period.As is shown in Tab.2, when the influent color was 250-510 times and the HRT was 32, 24, 18, 14 and 10 h, the effluent color was 100-250 times, the color removal rate was 50–70%, 55–70%, 50–68%, 55–60% and 44–55%, which indicated that the ABR had a desirable decolorization ability, because dye molecules are heterocyclic compounds (e.g. polycyclic aromatic hydrocarbons), while anaerobic microbes involved hydrolytic and acidogenic bacteria contain a range of ring-opening enzymes. The hydrolytic and acidogenic bacteria facilitates the anaerobic fermentation of polycyclic aromatic hydrocarbons and heterocyclic compounds [15]. The ring-opening reaction destroys the molecular structure of dye compounds and the chromophoric groups, resulting in decolorization of the wastewater. With the shortening of the HRT, the color removal rate in the reactor decreased, because some of dye molecules were flushed out of the reactor before they were degraded effectively. It was also found that when the influent color turned dark (i.e. red, reddish brown, purple red or purple brown), the effluent from the reactor was generally light red or pink, which indicates that the ABR had the effect of decolorization the wastewater.

3.2. Main pollutants removal by the ABR-A/O combined process

Based on the operational cost, removal efficiency of the ABR unit, the ABR unit kept the HRT of 24 h was selected and further investigate the overall efficiency of the ABR-A/O process.

Fig. 1 showed that the performance of the ABR-A/O combined process for removal of COD, NH_4^+-N, color. As shown in Fig. 1 (a), the effluent COD concentration was 95-172 mg/L with mean value of 124 mg/L and the removal rate was more 80%. It should be noted that the B/C in the raw water was only 0.21, the raw water was recalcitrant wastewater. However, the effluent B/C was 0.39 after the hydrolytic process in the ABR. Therefore, the ABR can effectively remove large-molecular organics in the raw water. In addition, the the effluent BOD_5 concentration was 28.2-64.6 mg/L with mean value of 48.4 mg/L and the removal rate was more 88.5%.

As shown in Fig. 1 (b), the influent and effluent NH_4^+-N concentration were 35.4-45.2 mg/L and 3.21-5.56 mg/L, the NH_4^+-N removal rate was more than 90%, which indicated that the ABR-A/O process was excellent for removing NH_4^+-N. The ABR effluent average concentration was 30.9 mg/L, the ABR unit did not significantly remove NH_4^+-N. Under anaerobic (ABR unit) and anoxic (the A unit of the A/O process) conditions, azo reductase can break down the azo bond of the azo molecules and convert them into amine molecules with two amino groups ($-NH_2$). but the O unit of the A/O process provides a favorable environment for the growth of nitrifying bacteria, which can degrade the NH_4^+-N. Therefore, the concentration of NH_4^+-N in



(a) (b)

(c)

Fig. 1. COD, NH_4^+-N, color profiles in ABR-A/O combined process

the final effluent was substantially reduced. In conclusion, the combined process of ABR-A/O can effective treatment of the dyeing wastewater. In addition, the total nitrogen (TN) removal rate was more 60% and the effluent TN concentration was 6.52-9.87 mg/L with mean value of 8.43 mg/L, because for the A unit and organic carbon source, the NH_4^+-N was oxidized into the NO_3^--N in the O unit of the A/O process, and the NO_3^--N was converted into N_2 in the A unit of the A/O process. The organic matters was as elector donor of the de-nitrification process, the NO_3^--N and NO_2^--N concentration of the effluent were 3.33–6.21 mg/L and 0.01–1.32 mg/L.

As shown in Fig. 1 (c), the A/O process also had color removal ability. The color of the final effluent was 20-50 times, which meets the "discharge standards of water pollutants for dyeing and finishing of textile industry of China" (GB 4287-2012).

3.3. GC–MS Analysis

The raw water, ABR effluent and A/O effluent respectively contained 46, 32 and 23 types of major pollutants, the result was showed in Tab.3.

In the effluent of the A/O, 13.0% were methyl alkanes, no anilines and organic acids were detected. Compared to the effluent of the ABR and the raw water, the types and concentration of the A/O effluent was much less. The testimonies were as follows: (1)2, 5-dichloro-p-phenylenediamin was detected in the ABR effluent, but was not found in the A/O effluent. (2) Phthalates were detected in the raw water and the ABR effluent, but they were not detected in the A/O effluent. (3)Compared with the effluent of the ABR and the raw water, the 2, 6-di-tert-butyl-p-cresol content in the A/O effluent decreased to some extent. There are two reasons involved: (1) The aerobic microbes in the A/O process had a strong effect on the removal of recalcitrant matters in the ABR effluent. (2) The internal circulation of the A/O process extended the HRT of recalcitrant matters in the reactor, which consequently enhanced their microbial degradation.

Table 3. Organic substances detected by GC-MS analysis

major organic substances	ABR influent	ABR effluent	A/O effluent
straight-chain alkanes	10	15	15
methyl alkanes	5	4	3
cyclanes	1	1	1
benzenes	1	1	1
phenols	1	1	1
aminobenzenes	1	1	—
organic acids	1	—	—
esters	4	2	—
miscellanies	4	2	1
unidentified components	8	5	1
total (types)	36	32	23

According to the ion current analysis, the $C_{20} \sim C_{33}$ straight-chain alkanes were detected in the ABR effluent and the A/O effluent. Because for the ring-opening decomposition of cyclic compounds. The existence of these straight-chain alkanes confirms the desirable efficiency of the microbial degradation of recalcitrant organic matters in the ABR unit and A/O process.

3.4. Analysis of biological phases (indicated microorganisms)

Rich biological phases (indicated microorganisms) in the O unit of the A/O process were observed, which was showed in Fig. 2.

The significance of biological phases was discussed in the following two aspects: (1) Rich biological phases observed in the O unit of the A/O process indicated that many species of microorganisms capable of reproducing quickly in the O unit of the A/O process, the environment of the O unit of the A/O process was suitable for proliferation of the indicated microorganisms, because the ABR process and the A unit of the A/O process can effective reduced the toxic and concentration of recalcitrant organic matters. (2)The concentration of pollutants of the O unit of the A/O process was suitable for the growth of the indicated microorganisms, which

(a) Rotifer (b) Vorticella (c) Floc-forming bacteria

Fig. 2. Typical biological forms observed by microscopy in the O unit of the A/O process

suggested that the environment of the O unit was good and helpful for forming the protozoan (*Vorticella*) and micro-metazoa (*Rotifers*).

4. Conclusion

The ABR unit and the A/O process has different biochemical process during the treatment of dyeing wastewater, the ABR-A/O combined process was feasible for effective purification of the dyeing wastewater. The conclusions of the experiment were as follows: (1) The ABR unit can provide an important treatment process for decomposing recalcitrant organic matters. In the unit, the bio-gradable ability (B/C) of the dyeing wastewater was rapid improved, the COD and color were significantly removed. In addition, the ABR unit has good shock load ability. (2) When HRT was 24h, the COD removal rate of the ABR-A/O combined process was more than 80%. The TN, NO_3^--N, NH_4^+-N and color concentration in the A/O effluent were 6.52–9.87 mg/L, 3.33–6.21 mg/L, 3.21–5.56 mg/L and 20–50 times, respectively. (3) The GC–MS analysis provided proof that the concentration and number of recalcitrant organic matters in the effluent treated by the ABR-A/O combined process decreased substantially compared to the levels in the raw water. (4) The observed results indicated that some indicated microorganisms can exist in the A/O process, which illustrated that the ecosystem of the ABR-A/O combined process was stable.

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