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Short Communication

Performance of combined process of anoxic baffled reactor-biological contact oxidation treating printing and dyeing wastewater

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Abstract

A study of the treatment of printing and dyeing wastewater was carried out using the combined process of anoxic baffled reactor-biological contact oxidation. The results showed the pH ascended continuously and the oxidation-reduction potential dropped gradually from compartment 1–6 in ABR. When hydraulic retention time was 12 h, color removal efficiency was 92% and the color of effluent of ABR could satisfy the professional emission standard (grade-1) of textile and dyeing industry of China. The total COD removal efficiency of the combined process was 86.6% and the COD of effluent could satisfy the professional emission standard (grade-2) of textile and dyeing industry of China.

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1. Introduction

A large numbers of synthetic dyes are produced world-wide every year for printing and dyeing and a portion is discharged with wastewater (Robinson et al., 2001). There are some dyestuff, slurry, dyeing aid, acid or alkali, fiber and inorganic compound in printing and dyeing wastewater. Furthermore, some dyestuff contains nitryl, amidocyanogen and heavy metals, such as copper, chrome, zinc and arsenic and so on (Yang and Huang, 2002). The components will be changed because of different dyestuff category, dyeing process, dye concentration and equipment scale (Delee et al., 1998). So the wastewater quality is unsteady. Generally speaking, the printing and dyeing wastewater is

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alkalescent, have large flow rate, high color concentration, composed of complex components, heavily polluted and difficult to be biodegraded (Huang et al., 2001). Therefore it is difficult to meet the discharge criterion only using of simple biological treatment processes, while physical chemistry treatment processes need high operation expense (Pearce et al., 2003). At present, researchers gradually discovering new treatment processes, one of which the wastewater is firstly hydrolyzed under anoxic condition, and then is treated under aerobic condition (Lourenco et al., 2000; Yu et al., 2000). Anoxic hydrolysis-aerobic treatment of the printing and dyeing wastewater has been considered to have some advantages over the conventional processes. For anoxic hydrolysis, the hydraulic retention time (HRT) is short, and non-degradable organic compounds of wastewater can be transformed into degradable matter, i.e., the degradable performance of the wastewater is improved greatly. Simultaneously, a portion of COD can be removed. Taking into consideration the slow growth rate of many

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anoxic microorganisms, the key objective of the efficient reactor design must be large quantity of anoxic sludge with very little loss of anoxic microorganisms from the bioreactor. So the residual aerobic sludge circumfluence is utilized to increase the quantity of anoxic sludge. At the same time, sludge in the whole treatment process will be in equilibrium (Chen et al., 1999).

Anoxic baffled reactor (ABR) as a hydrolysis process was adopted in this study. There were several small compartments in ABR that phase-split anoxic condition could be come into being in every compartment along the wastewater current. The flow type of the reactor was approximately piston flow. Besides these, ABR has the preferable virtues of resisting shock load and toxicity. It has some other characteristics, such as easily start-up and without short streaming, jam and back streaming (Li et al., 2001; Xu et al., 2002). Hence, the combined process, an ABR as a hydrolysis process and biological contact oxidation as an aerobic process was used in this study.

2. Methods

2.1. System configuration

Schematic diagram of experimental set-up is shown in Fig. 1. The opening ABR was made up of six compartments where the front five compartments acted as hydrolysis tank and compartment 6 acted as sedimentation tank. Every compartment had two sampling cocks at the upside and downside of its profile, and the upper was a water-sampling cock, while the lower was sludge sampling one. Setting a baffle in every compartment, hydrolysis room was separated into two portions. One was down-flow room and the other was upper-flow hydrolysis room. At the bottom of the baffle, there was a 45° guide baffle. It ensured that wastewater was mixed with the sludge adequately in the reactor room. The ABR had a size of $441 \times 156 \times 353 \,\mathrm{mm}$ $(l \times w \times h)$ and the biological contact oxidation tank had a size of $430 \times 150 \times 400 \,\mathrm{mm}$ $(l \times w \times h)$. The elasticity stuffing was filled in biological contact oxidation tank. The sludge of the sixth compartment in ABR and sedimentation

tank was pumped to the front of ABR by sludge circumfluence pump.

2.2. Characteristics of raw wastewater

Raw wastewater was printing and dyeing combined wastewater from certain printing and dyeing corporation, Nanjing city, PR China. The characteristics of wastewater were as follows: apparent color purple; color value 200 times; pH value 12.2; COD 1201.7 mg L⁻¹ and temperature 17.8 °C.

2.3. Experimental methods

The pH of raw wastewater was adjusted to 7.05. Subsequently, the wastewater was pumped into ABR by creep pump. The HRT of ABR was controlled at 12h. After being hydrolyzed, outflow of ABR entered the biological contact oxidation tank for aerobic treatment. Finally, the mixed liquid entered the sedimentation tank and sludge was deposited in this tank. At steady condition, water samples of ABR and biological contact oxidation tank were collected. Color concentration and COD in these samples were measured. Simultaneously, in order to show the stability of reactor, oxidation-reduction potential (ORP) and pH were also measured for inspecting and controlling the normal running of the combined treatment system.

3. Results and discussion

3.1. ORP and pH in ABR

Generally, in the biological treatment of printing and dyeing wastewater, dissolved oxygen, pH and ORP are usually used to inspect and control the running of biochemical reactor, and to show the stability of biochemical process. But in non-aerobic condition, only pH and ORP could be used for the same purpose. Traditionally, pH is a parameter applied to control anaerobic digestion, while ORP is a parameter applied to control wastewater biological treatment containing all oxidation reduction scope, that is to

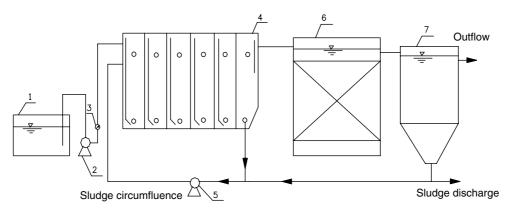


Fig. 1. Schematic diagram of experimental set-up (1. wastewater tank; 2. creep pump; 3. liquid flowmeter; 4. hydrolysis reactor; 5. sludge circumfluence pump; 6. biological contact oxidation tank; 7. sedimentation tank.).

say, ORP could be used to reflect aerobic, anoxic and anaerobic condition. In order to inspect and control the running of biochemical reactor preferably, both pH and ORP were adopted as inspecting and controlling parameters in this study.

The pH values from compartment 1-6 were 6.90, 6.91, 6.92, 7.00, 7.15 and 7.16, respectively. The pH value dropped from 7.05 of inflow to 6.90 of compartment 1, and at the latter compartment, pH value took on uptrend. At the 2nd or 3rd compartment, the variation of pH value was very small and its ascending value was only 0.01, moreover, pH values of the other compartments rose rapidly and finally exceeded 7.15. Because of these, we could see that pH dropped only at compartment 1, while rose at other compartments in hydrolysis process of this printing and dyeing wastewater. Such was different from the variational law of pH in hydrolysis process of common organic matter. Therefore, to find the reason, a ultra-violet and visible spectroscopy was used to measure the water sample of every compartment. According to the ultra-violet and visible spectra of all samples, a distinct characteristic absorption peak was found at the wavelength of 254 nm. Along the serial number of compartment in ABR, the absorbency corresponding to absorption peak reduced in turn. This showed that color matter was discomposed gradually in evidence. Diazo bond in azo dyes could be parted by azo reductive enzyme in anoxic or anaerobic condition, and then an azo dye molecule was made of two amine molecules holding '-NH₂', which could be expressed by this formula as follows (Wuhrmann et al., 1980):

$$R_1 - N = N - R_2 + 4e^- + 4H^+ \rightarrow R_1 - NH_2 + R_1 - NH_2$$

where, R_1 and R_2 were various phenyl and naphthol residues.

Afterward, amine could be decomposed to ammonia by an action of hydrogenation enzyme and hydrolysis enzyme in anoxic condition (Chen et al., 1992). So we could think that by the action of hydrolysis microbes, azo in raw wastewater produced organic amine and NH₃. And these product solutions were alkaline, so along the serial number of compartment in ABR, the quantities of organic amine and NH₃ augmented gradually. To testify it, the concentrations of NH₃-N from compartment 1-6 were measured at the temperature of 11.4 °C and the concentrations were $18.0 \,\mathrm{mg}\,\mathrm{L}^{-1}$, $18.8 \,\mathrm{mg} \,\mathrm{L}^{-1}$, $19.4 \,\mathrm{mg} \,\mathrm{L}^{-1}$, $20.7 \,\mathrm{mg} \,\mathrm{L}^{-1}$, $22.4 \,\mathrm{mg} \,\mathrm{L}^{-1}$ and 26.8 mg L⁻¹, respectively. The NH₃-N concentrations rose from compartment 1-6 in turn, so the increasing of NH₃-N concentrations counteracted the descending of pH during hydrolysis and acidification of organic carbon. As a result, the pH was ascending continuously from compartment 1–6.

The anoxic condition, a transitional condition from oxidation to reduction, was favorable to the hydrolysis and acidification of wastewater. But the reduction condition without any oxygen was not favorable to hydrolyze and acidify the wastewater. So the fitting ORP of hydrolysis was from $-100\,\mathrm{mV}$ to $+50\,\mathrm{mV}$ (Shen and Wang, 1999). In this experiment, the ORP values of compartments in ABR were

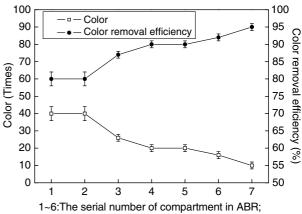
measured and the ORP values from compartment 1–6 were $-53.9 \,\mathrm{mV}$, $-58.2 \,\mathrm{mV}$, $-61.8 \,\mathrm{mV}$, $-68.0 \,\mathrm{mV}$, $-88.4 \,\mathrm{mV}$ and $-92.4 \,\mathrm{mV}$, respectively. According to these ORP values, we knew that along the serial number of compartment in ABR, ORP of water sample dropped in turn. The ORP dropped from $-53.9 \,\mathrm{mV}$ in compartment 1 to $-92.4 \,\mathrm{mV}$ in compartment 6, so anoxic degree was deeper and deeper along the serial number of compartment, but all ORP values were controlled strictly between $-100 \,\mathrm{mV}$ and $+50 \,\mathrm{mV}$.

3.2. Color removal

Color and its removal efficiency of every compartment in ABR and effluent of biological contact oxidation are shown in Fig. 2. After raw wastewater entered the ABR, the color dropped from 200 times to 40 times in compartment 1, and then dropped gradually down the reactor. In compartment 6, the color was only 16 times. Corresponding to the serial number of compartment, the color removal efficiency rose from 80% in compartment 1 to 92% in compartment 6. Linking the ultra-violet and visible spectra, it could be thought that decoloring effect of the printing and dyeing wastewater containing azo was very well. Besides these, from raw wastewater to compartment 6, the apparent colors took on purple, orange yellow, orange yellow, orange yellow, pale yellow, pale yellow and pale red brown in turn. Only pretreatment using ABR, the color of outflow could satisfy the professional emission standard (grade-1) (color ≤ 40 times) of textile and dyeing industry of PR China (GB4287-92). When the outflow of ABR entered the latter biological contact oxidation, the color of effluent dropped to 10 times, and the color removal efficiency rose up around 95%.

3.3. COD removal

COD and its removal efficiency of every compartment in ABR and effluent of biological contact oxidation are shown



7: Effluent of biological contact oxidation process

Fig. 2. Color and its removal efficiency of compartment in ABR and effluent of biological contact oxidation.

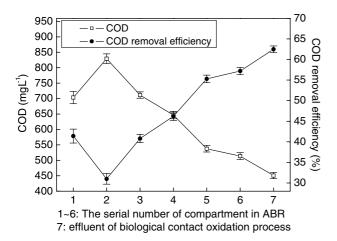


Fig. 3. COD and its removal efficiency of compartment in ABR and effluent of biological contact oxidation.

in Fig. 3. COD decreased gradually along the serial number of compartment after raw wastewater entered the ABR, concretely, the COD decreased from $829.5 \,\mathrm{mg} \,\mathrm{L}^{-1}$ in compartment 1 to $513.9 \,\mathrm{mg}\,\mathrm{L}^{-1}$ in compartment 6. Corresponding to the serial number of compartment, the COD removal efficiency rose from 31% to 57.2%. The falling values of COD of the 1st and 2nd compartment were quite larger. The reason was that the degradable matter of wastewater was decomposed firstly in the two compartments. While in the latter compartment, the chemical structure of nondegradable organic matter was shifted and they were decomposed to degradable intermediate products, so the contribution was less for COD removal in the latter compartment. Subsequently, outflow of ABR entered the biological contact oxidation tank and sedimentation tank. Finally, the COD of effluent was only $160.6 \,\mathrm{mg}\,\mathrm{L}^{-1}$, and the total COD removal efficiency was 86.6%. The COD of effluent could satisfy the professional emission standard (grade-2) $(COD_{Cr} \le 180 \text{ mg L}^{-1})$ of textile and dyeing industry of PR China (GB4287-92).

4. Conclusions

The performance of a laboratory scale combined process of anoxic baffled reactor-biological contact oxidation was investigated using printing and dyeing wastewater. The results indicated that the combined process was a better method to treat printing and dyeing wastewater.

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