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Study on coupling with catalytic wet air oxidation and membrane separation in the treatment of cationic red GTL

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ABSTRACT

Coupling with the advantages of catalytic wet air oxidation (CWAO) and membrane separation under room condition, a new type of integrated fluidized-bed reactor was designed, with a PVDF hollow fiber membrane module submerged in. Its performance was investigated by the simulation of catalytic degrading cationic red GTL wastewater with initial concentration of 50 mg/L. The experimental results showed that the decolorization of cationic red GTL rose with the increase in residence time, the dosage of Mo/Zn/Al/O catalysts and aeration intensity, whereas it decreased against the increase in pH value. The optimal conditions of residence time catalyst dosage, pH value, and aeration intensity were 1.5 h, 1.5 g, 4, and 0.036 m^3/h, respectively. The decolorization efficiency was above 98%, and TOC removal efficiency was more than 67%, which were apparently superior to the performance of single CWAO process in the batch test, and moreover, the interception efficiency on catalyst was approximately 100%. It can be found from the FT-IR analysis of original influent and effluent of membrane that the bonds of C=C, C–N as well as N=N were destroyed, while new bonds of C=O, $–NO_3$, and N–H were formed. The BOD/COD ratio of the treated effluent been improved from 0.05 to 0.41.

Keywords: Catalytic wet air oxidation; Membrane separation; Cationic red GTL; Mo/Zn/Al/O catalyst

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1. Introduction

A large number of dyes are extensively utilized in many fields, overwhelming majority of which are cationic azo dyes with one or more azo bonds (N=N) and aromatics. The release of wastewater containing these dyes is a dramatic source of esthetic pollution, eutrophication, and perturbation to the environment and the living species [1].

The treatment of the wastewater with high concentration dyes has caused widespread concern in the field of industrial water treatment. As one of the most efficient methods to degrade dye wastewater, catalytic wet air oxidation (CWAO) has been proposed as an alternative to the traditional technology. The suspended dispersive nanosized catalyst is

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underutilized, because of the high specific surface area interacting with wastewater, thereby providing high degradation efficiency. However, in respect of the retention of the catalyst, recycling and isolated from the liquid, the main drawback of the catalyst powder is that the particles are too fine to be removed by gravity and easy to lost, which hinder the practical application [2–5].

A very promising method for solving this solid/liquid separation of catalysts problems is coupling the catalysis and membrane techniques. In this hybrid system, the membrane acted as a barrier for the catalyst particles remaining them in the reaction system [6]. According to literatures, the catalysis with membrane separation systems can be assembled in two distinct configuration designs. One is a submerged catalysis/separation system with the reaction and separation zone combined in a single unit of equipment [7,8], and the other is a side-stream system, where the reaction occurs in a stirred reaction vessel and the separation of the products is performed in a separated cross-flow membrane filtration unit [9–11]. The integrated submerged membrane system has advantageous features of low installation cost, low-energy consuming and easy maintenance. Although there have already been several related literatures demonstrated that the combination of membrane separation and photocatalytic technology had a high efficiency on degradation of dye wastewater [12–15], the literatures discussed coupling system of CWAO and membrane separation were uncommon, especially under room temperature and atmospheric pressure.

In this study, a novel type of fluidized-bed integrated reactor of CWAO and membrane separation was designed for the treatment of cationic red GTL under room temperature and atmospheric pressure, with the advantages: (i) confining the catalysts in the reaction environment by means of the membrane, achieving the solid–liquid separation (ii) control the residence time of molecules in the reactor and realizing a continuous process with simultaneous decomposition of products and by-products from the reaction mixture (iii) avoiding the breakage to the membrane module brought by the high temperature, high pressure, and UV irradiation, for the mild reaction condition, as well as saving energy. The effects of operating parameters, such as the residence time, the dose of catalyst, aeration intensity, and pH value on degradation efficiency, were studied in detail to establish the optimal state. The membrane effluent was analyzed as well.

2. Experimental

2.1. Experimental setup

The hybrid catalysis/separation process was conducted in a laboratory-scale installation presented in Fig. 1. The inner diameter and height of the reactor were 50 and 350 mm respectively, with a PVDF hollow fiber UF membrane module submerged in. The effective volume was 0.5 L. Mo/Zn/Al/O catalysts which had a mean particle size of 0.2 μm were preloaded in the reactor. Air was pumped through a gas diffuser placed at the bottom of reactor to ensure small bubble formation for effective purging continuously and helped to uniformly mix the catalyst slurry

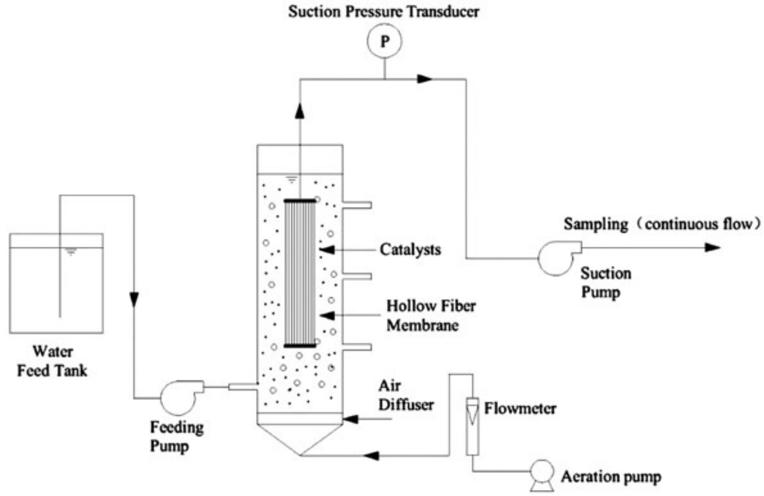

Fig. 1. Schematic diagram of experiment.

during treatment, forming three-phase fluidized-bed system. The filtration was continuously obtained by using a suction pump.

2.2. Materials

Cationic red GTL was adopted in this experiment as a model pollutant which was a typical azo dye in the textile industries and was purchased from Shanghai Dyeing Chemical Co., Ltd. (China). Mo/Zn/Al/O catalyst was prepared by coprecipitation and impregnation, which has been proved to have a very good effect on degradation of cationic red GTL in our early research [17]. The ultrafiltration membrane module made of polyvinylidene (PVDF) hollow fiber membranes with a mean pore size of 0.022 μm, inner and outer diameters being 1 and 1.8 mm, respectively, was provided by Li Sheng Co., Hainan. The effective filtration area of membrane module was 0.08 m^2.

2.3. Analytical methods

The synthesized wastewater was achieved by dissolving the cationic red GTL in de-ionized water, with the initial concentration of 50 mg/L and initial pH value of 6.9–7.2. The COD, BOD, and TOC of synthetic cationic red GTL wastewater with 50 mg/L are 82.3 mgO_2/L, 4 mgO_2/L, and 21.2 mg/L, respectively. The color removal rate (at 488 nm) of cationic red GTL was estimated on the basis of changes in 722 s VIS-Spectrophotometer (Jingmi Co., Shanghai, China). COD was measured by using a COD analyzer (CTL-12, Chengde Huatong, China) according to fast digestion-spectrophotometric method (HJ/T 399-2007). BOD_5 measurement was conducted in an Oxitop system (WTW, Germany) according to standard methods (GB 7488-87). To determine the extent of mineralization of cationic red GTL in waste solution under optimized condition, the total organic carbon (TOC) concentration was measured with Multi N/C 3100 analyzer (Analytik Jena, Germany). To figure out the rejection of particular catalyst, turbidity of permeate in the process was detected withWGZ-800 turbidimeter (Xinrui Co., Shanghai, China). We used accurate weight of membrane effluent at unit of time to describe the flux variation. The FTIR spectra were taken within the range from $4,000\,cm^{-1}$ to $400\,cm^{-1}$ on a FTIR spectrometer (PerkinElmer Spectrum 100, America) using 2 mg of the sample mixed with 200 mg dry KBr, which was pressed into a transparent disk. The liquid sample was pretreated by freeze drying at −80 ℃.

3. Results and discussion

3.1. Optimization of process parameters

3.1.1. Effect of residence time on decolorization efficiency of cationic red GTL

During the continuous process, residence time should be set at an appropriate level in order to obtain high and steady degradation efficiency. As the membrane was at the state of adsorption saturation, the membrane adsorption to the dye molecules had been excluded. The experiments of residence time on the decolorization efficiency were carried out at 0.5, 1, 1.5, 2 h, with the dye wastewater at initial pH value. The catalyst dosage and aeration intensity were kept at 1.5 g and 0.024 m^3/h.

As depicted in Fig. 2, the decolorization efficiency of reactor effluent increased with the rise of hydraulic residence time. When the residence time was long enough, the Mo/Zn/Al/O catalyst can fully interact with the dye molecules, and therefore, the whole system would maintain a steady state, avoiding an overwhelming organic loading. The color removal efficiency was only 79.93%, when the residence time was 0.5 h. When at 1.5 and 2 h residence time, the two decolorization efficiencies of cationic red GTL were stable at 91.76 and 92.03%, respectively, after 330 min running, which was only a minor difference. However, due to the relatively low effluence and large energy consumption of 2 h reaction system, 1.5 h would be the optimal residence time for this reaction based on economic and practical aspects.

3.1.2. Effect of Mo/Zn/Al/O catalyst dosage on decolorization efficiency of cationic red GTL

The dose of Mo/Zn/Al/O catalyst that was one of the most important parameters in operation can exert

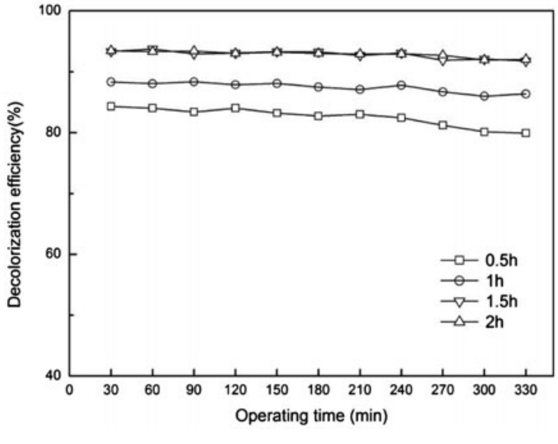

Fig. 2. Effect of residence time on decolorization efficiency of cationic red GTL.

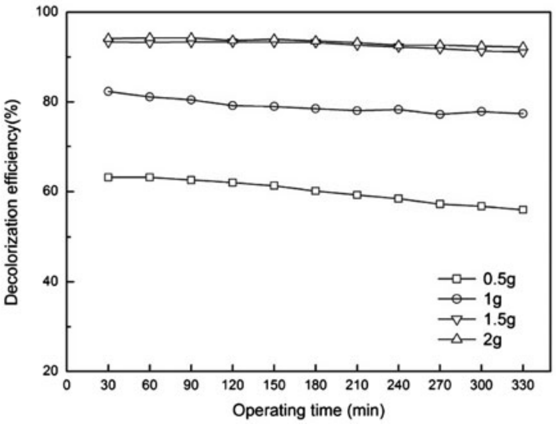

Fig. 3. Effect of Mo/Zn/Al/O catalyst dosage on decolorization efficiency of cationic red GTL.

a dramatic influence on the decolorization efficiency of cationic red GTL. The effect of catalyst dosage on color removal of dye was investigated from 0.5 to 2 g, and residence time was fixed at 1.5 h. The aeration intensity was kept at 0.024 m^3/L.

Fig. 3 shows that the decolorization efficiency increased with the rise of the catalyst dosage. Specifically, the increase in catalyst amount might enlarge the active site for adsorption, produce more $^{\cdot}$OH and $^1O_2$ and finally induce the degradation of dye molecule. When the catalyst dosage was 1.5 g, the decolorization efficiency was stable at above 91.16%. There was only a slightly increase in decolorization, when the dosage of 2.0 g was applied. In addition, it can be observed that there was a deposit of catalyst at the bottom of the reactor under this condition, which can lead to uneven mixture of wastewater and catalysts and the catalysts were not completely exploited. Due to an increase in the turbidity of the suspension, there would be a negative effect on bubble distribution. Therefore, above a certain level, additional particles are not involved in catalyst activity and decolorization efficiency would achieve at a plateau. Besides excessive catalyst dosage can aggravate membrane fouling. On the basis of the experiments discussed earlier, 1.5 g catalyst was set as the optimal catalyst dosage for this experiment.

3.1.3. Effect of aeration intensity on decolorization efficiency of cationic red GTL

A bubble column reactor with a porous plate distributor can offer best gas/liquid mass transfer efficiency. In view of this consideration, a special kind of porous plate was used as gas distributor in this study. The relationship between aeration intensity and the reaction efficiency of catalytic degradation of cationic red GTL is illustrated in Fig. 4.

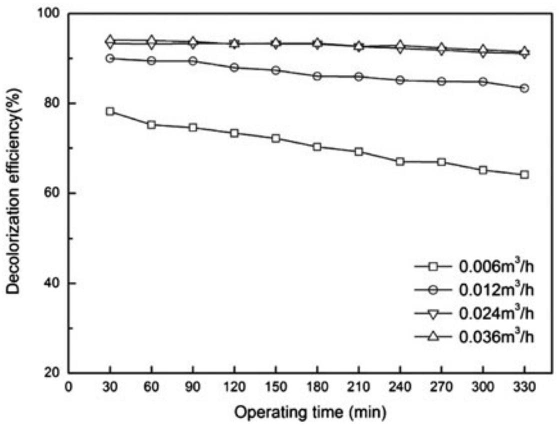

Fig. 4. Effect of aeration intensity on decolorization efficiency of cationic red GTL.

It is easy to see that the color removal efficiency constant rose up from 70.10 to 89.73% with aeration intensity considerably from 0.006 to 0.036 m^3/h after 330 min running. There was a downside trend at 0.006 m^3/h, suggesting the aeration intensity was too little to effectively degrade the dyes. Aeration played a vital role in this catalysis/membrane separation process and provided there functions. Sufficient amount of oxygen is a prerequisite for the reaction being carried out smoothly. The oxygen provided by aeration can react with catalyst and water to form intermediate and H_2O_2, and then, a free-radical chain auto oxidation process was performed. Besides higher aeration intensity can make the catalyst powder fully mix with the solution forming aqueous suspension system, which is beneficial to mass transfer and increased the contact area between catalyst and dye molecule. Additionally, a great amount of air-bubbles speeded through the hollow fiber membrane module, which can scour the membrane surface with flow. This behavior would contribute to avoid the deposit of catalyst powder on the membrane fiber surface hence reduce the membrane fouling effectively. When aeration intensity was 0.024 and 0.036 m^3/h, decolorization efficiencies were almost the same.

It can be seen from Fig. 5, when aeration intensity was 0.036 m^3/h, the declination of flux was the least 12.2%. It indicates that high aeration intensity can alleviate the membrane fouling effectively. At 0.006 m^3/h, the flux attenuated 15.5%, for the aeration intensity was too weak to make the catalysts fully mix with wastewater and the flux attenuation caused by deposit of catalyst on the membrane surface or in the membrane pore was not significant.

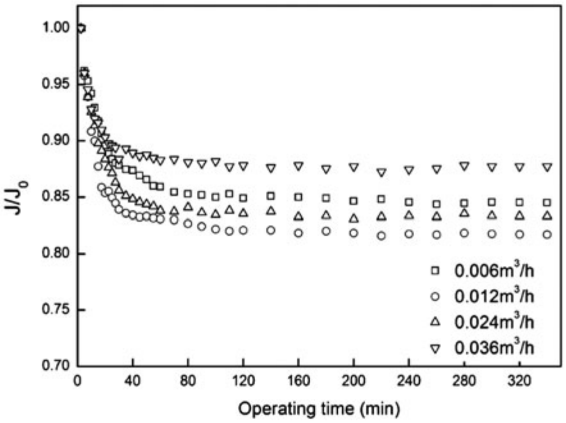

Fig. 5. The influence of aeration intensity on flux variation.

In consideration of high efficiency and the maintenance of membrane module, 0.036 m^3/h was regarded as preferential aeration intensity in the following experiments.

3.1.4. Effect of pH value on decolorization efficiency of cationic red GTL

In the CWAO system, pH value is an important parameter for determining the properties of both the solid catalyst and the solute molecules, thus affect the efficiency of the reaction. The effect of pH value on decolorization efficiency was investigated from 2 to 10. The pH value was adjusted with a pH meter using HNO_3 and NaOH. Residence time, catalyst dosage, and aeration intensity were fixed at 1.5 h, 1.5 g, and 0.036 m^3/h.

As shown in Fig. 6(a), the decolorization efficiency suffered an obvious rise with the decrease in pH value. When pH was 10, the color removal efficiency was only 75.05% during the running process, whereas it increased to 96.36% when pH was 2. Especially, when pH value of the solution was 4, the color removal was 95.92%, which had no significant differences with pH of 2. At lower pH value, degradation efficiency was quite high. The enhancement of the H^+ concentration could accelerate the reaction rate, for H^+ took part in the generation of radicals [16]. On the other hand, the pH value was the potential reason responsible for the catalyst particle size and surface charge. The surface charges of catalyst particle under different pH values were tested presenting by the zeta potential in Fig. 6(b). When the pH value was 10, the surface charge was −2.71 eV. Because of van der Waals force, relatively large Mo/Zn/Al/O aggregates grew up, and flocs could be observed which resulted in a lower decolorization efficiency. The highest surface negative charge of Mo/Zn/Al/O was −14.83 eV at pH 4. Catalyst particles were well dispersed due to the repulsion between the negative particles, which could effectively absorb and degrade the cationic dye molecules, getting a high efficiency. Moreover, a lower pH value would bring breakage to the membrane module, and the optimal pH value was set at 4.

3.2. Membrane effluent analysis

3.2.1. Experiment under optimal conditions

The experiment was carried out under optimal conditions of residence time catalyst dosage, pH value, and aeration intensity being 1.5 h, 1.5 g, 4, and 0.036 m^3/h, respectively in a long time running. The concentration of cationic red GTL was 50 mg/L.

It is observed from Fig. 7(a) that color removal and TOC decomposition efficiency stabilized at 98 and 67% during the long time running operation.

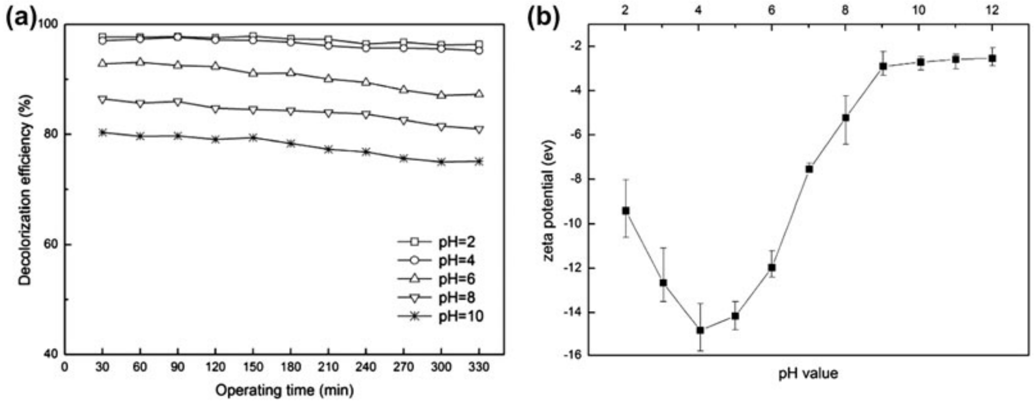

Fig. 6. (a) Effect of pH value on decolorization efficiency of cationic red GTL and (b) zeta potential variation under different pH value.

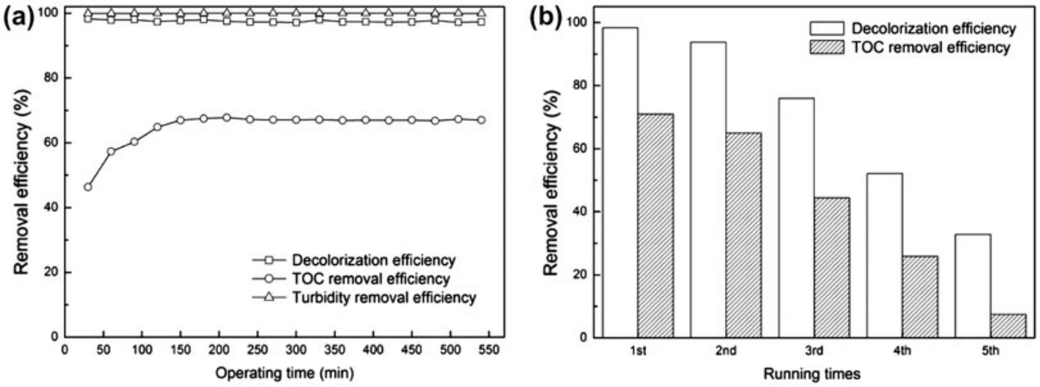

Fig. 7. (a) The color, TOC, and turbidity removal of cationic red GTL dye using hybrid system in continuous mode and (b) the color and TOC removal in the single CWAO batch test.

The observed decrease in TOC concentration was due to the benzene ring opening and further decomposition of byproducts formed resulting in CO_2, water, and other noncarbon species formation. The turbidity removal efficiency of the effluent was approximately 100%, which revealed that catalyst powders can be confined in the reaction system by ultrafiltration membrane separation. The hybrid CWAO and membrane filtration system had high degradation efficiency on cationic red GTL, simultaneously achieving the purpose of catalysts separation.

The batch test was conducted under the identical reaction conditions in order to compare the degradation efficiency with the hybrid process. After each run, catalysts were recovered as much as possible through centrifugation following with the low-temperature drying process. As depicted in Fig. 7(b), when Mo/Zn/Al/O catalysts were used for the first and second time, the color and TOC removal were 98.34, 93.77, and 70.99, 64.94%, which were similar to the continuous process. However, there was a sharp decrease in removal efficiency at the third run, and at the fifth run, the color and TOC removal efficiency declined to 32.78% and 7.52%, the catalyst only had a very weak effect on the dye degradation. The results fully explained the loss of catalysts was a very serious problem.

Furthermore, in the hybrid system, Mo/Zn/Al/O particles would deposit on the surface of the ultrafiltration membrane and form a cake layer, which was thought to be a prefiltration layer to absorb and degrade the dye molecules. This was another reason contributed to the better performance of the hybrid system, suggesting a synergistic effect between CWAO and membrane filtration [17]. All in all, the degradation efficiency in the hybrid system was apparently superior to the performance of catalyst in the batch test of single CWAO process.

3.2.2. FT-IR analysis

FT-IR was adopted in order to further investigate the degradation of cationic red GTL. Membrane effluent sample was obtained after 3 h of operation, at which the TOC removal efficiency became steady.

The FT-IR spectral comparison between the original cationic red GTL dye sample and the sample extracted from effluent of membrane after decolorization can be observed in Fig. 8, which confirmed degradation of this dye. It can be seen from the spectrum of the original dye (Fig. 8(a)), in the high wavenumber region, O–H stretch band in hydroxyl groups for the majority of condensed-phase samples was broadened and shifted to 3,500–2,500 cm^{-1} due to various types of hydrogen bond formation. The peaks at 1,600 cm^{-1} and 1,516 cm^{-1} can be assigned to characteristic of C=C aromatic skeleton vibration and C–N vibration on aromatic ring, respectively, symmetric stretching vibration of $-NO_2$ was observed at 1,147 cm^{-1}. The characteristic –N=N– of azo-dye vibration frequency was seen at 1,341 cm^{-1}. The weak adsorption peak at 1,409 cm^{-1} was a characteristic band of conjunction of

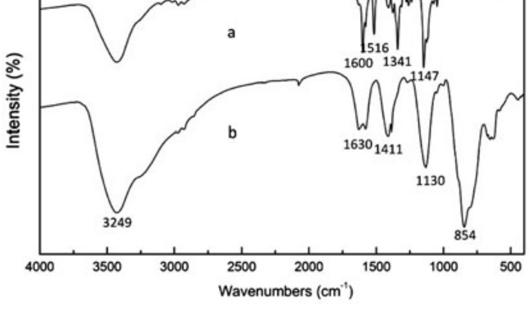

Fig. 8. FI-IR spectra of cationic red GTL (a: original wastewater b: effluent of membrane).

C–N and aromatic. Fig. 8(b) is the spectrum of membrane effluent, the intensity of O–H bond was higher than in the original dye sample. The absence of C=C and C–N vibration (1,600 cm^{-1} and 1,516 cm^{-1}) indicated that benzene rings had been broken. The disappearance of adsorption peak at 1,341 cm^{-1} shows that azo bond of cationic red GTL was attacked by heat energy and free radicals in CWAO process. The cleavage of –N=N– bonds leads to the decolorization of dyes. On the basis of the phenomenon that adsorption peak at 1,147^{-1} of –NO_2 had shifted, some part of –NO_2 was speculated transformed to –NO_3. Comparing with original dye sample, there were some new adsorption peaks appeared at the wavenumbers of 1,630 cm^{-1}, 1,411 cm^{-1}, and 854 cm^{-1}, which were consistent with C=O stretching vibration, C–N stretching vibration, and N–H vibration on olefin. It means that there were new intermediates generated during the degradation process.

3.2.3. Biodegradability

Fig. 9 reveals the variation of COD and BOD_5 during the continuous process of degradation of cationic red GTL. COD removal and BOD_5 production were visually observed. It was found that the BOD_5/COD ratio of the initial dye wastewater was only 0.05, which was difficult to be degraded by the microbes. BOD_5/COD ratio was gradually improved as the reaction proceeded. The ratio of 0.3 was achieved after 4 h running, and it stabilized at 0.4 when the whole system was at a steady state, indicating that the treated wastewater was turned to be biodegradable (BOD_5/COD > 0.3). The biodegradability of dye wastewater was obviously improved.

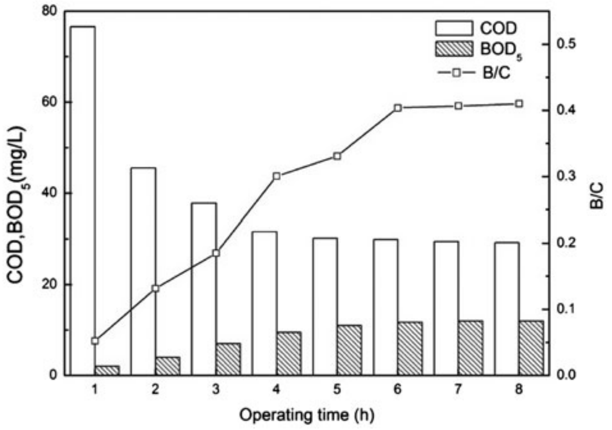

Fig. 9. Biodegradability of membrane effluent in different operating time.

4. Conclusion

The three-phased fluidized-bed system of CWAO and membrane separation has been preliminarily developed in this study, using Mo/Zn/Al/O powders as catalyst under room conditions. Experimental results indicated that in the treatment of cationic red GTL being 50 mg/L, the optimal conditions of residence time catalyst dosage, pH value, and aeration intensity were 1.5 h, 1.5 g, 4, and 0.036 m^3/h, respectively. Under such conditions, the decolorization efficiency was above 98%, and TOC removal efficiency was more than 67%, as well as catalyst interception efficiency was almost 100%. The experimental hybrid system could achieve complete catalyst separation with low-energy use.

During the degradation, the benzene rings of dye molecules were opened and further decomposition of by-products formed resulting in CO_2, water and other noncarbon species formation. The biodegradability of the treated effluent had been significantly improved.

The novel hybrid process coupling the CWAO and membrane separation is a very promising method for the removal of organic compounds, and further extensive investigations concerning the application are highly desirable.

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