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Azo dye wastewater treatment in a novel process of biofilm coupled with electrolysis

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Abstract: Azo dye wastewater treatment is urgent necessary nowadays. Electrochemical technologies commonly enable more efficient degradation of recalcitrant organic contaminants than biological methods, but those rely greatly on the energy consumption. A novel process of biofilm coupled with electrolysis, i.e., bioelectrochemical system (BES), for methyl orange (MO) dye wastewater treatment was proposed and optimization of main influence factors was performed in this study. The results showed that BES had a positive effect on enhancement of color removal of MO wastewater and 81.9% of color removal efficiency was achieved at the optimum process parameters: applied voltage of 2.0 V, initial MO concentration of 20 mg/L, glucose loads of 0.5 g/L and pH of 8.0 when the hydraulic retention time (HRT) was maintained at 3 d, displaying an excellent color removal performance. Importantly, a wide range of effective pH, ranging from 6 to 9, was found, thus greatly favoring the practical application of BES described here. The absence of a peak at 463 nm showed that the azo bond of MO was almost completely cleaved after degradation in BES. From these results, the proposed method of biodegradation combined with electrochemical technique can be an effective technology for dye wastewater treatment and may hopefully be also applied for treatment of other recalcitrant compounds in water and wastewater.

Introduction

Azo dyes have been the most extensively used synthetic dyes in many industries, such as textile, leather tanning, food and paper making (Punzi et al. 2015). However, some of azo dyes discharged into environment from the effluent of the above industries can cause serious water bodies pollution and/or undesirable colors since most azo dyes are refractory to degradation in natural environment (Zou et al. 2015). Additionally, colors can decrease sunlight penetration through the water, thus disturbing the natural growth activity of aquatic organisms (Nidheesh and Gandhimathi 2012). Importantly, azo dyes or their metabolites may be toxic and carcinogenic, probably posing considerable damage to aquatic life and human beings (Hamad et al. 2018). Therefore, azo dyes wastewater should be adequately treated for meeting emission standards before being discharged into water environment.

Azo dyes are commonly characterized by containing one or more azo bonds (–N=N–) with aromatic rings. Color removal is one of the major tasks in azo dye wastewater treatment, which is conducted by attacking the conjugated double bonds (–N=N–) (Tehrani-Bagha et al. 2010). Most azo dyes are highly resistant to degradation under natural conditions due to their complex chemical structures and those are typically not removed from wastewater by using conventional biological treatment systems. Although some physical and/or physicochemical methods including precipitation, oxidation, coagulation/flocculation, electrolysis and adsorption were effective for color removal from azo dye wastewater (Castro et al. 2017, Franca et al. 2015, Shabbir et al. 2017), these methods involve high costs, generate a significant amount of sludge and even cause secondary pollution due to excessive chemical usage. To overcome the above disadvantages, in some cases physical and/or physicochemical methods were combined with traditional biological processes for treating azo dye wastewater.

Bioelectrochemical system (BES) combing biological and electrochemical technology has been developed and initially employed to remove nitrate and nitrite from water or wastewater (Chen et al. 2015, Wang et al. 2017, Zhong et al. 2016). It was first proposed by Sakakibara and Kuroda (Kuroda 1993). The BES consists of a couple of electrodes, where an electric current passes through the electrodes. In BES for nitrate reduction, denitrifying bacteria were enriched on the cathode surface and H_2 generated by water electrolysis can be used as the electron donor by microorganisms, thereby enhancing the biological degradation of nitrate. Compared with traditional electrochemical and biological techniques, the BES has been demonstrated to be far more effective in removing wastewater containing nitrate and nitrite.

Generally, wastewater decolorization can occur under the redox potential below -50 mV (Sarayu and Sandhya 2012) and BES can easily control redox potential (Sasaki et al. 2012). Thus, an attempt was made to treat Methyl orange (MO) dye

wastewater by using BES in this study. In the BES designed here, a stainless steel column was used as the cathode, where an activated carbon fiber (ACF) was attached to the surface of cathode to enrich microorganisms. The performance of BES was assessed in terms of color removal efficiency of MO. The effect of applied voltage, MO concentration, carbon source content and pH on MO denitrification rate was investigated to optimize the operation on BES. Moreover, to investigate the change of molecular and structural characteristics during the MO treatment, UV/Visible absorption spectra with reaction time was further analyzed. These results obtained from this study, BES linking biological with electrochemical process, may serve as a new suggestion for the treatment of dye wastewaters or non-biodegradable industrial wastewaters.

Material and methods

Experimental setup

The BES was made from polyvinyl chloride with a single-chamber cylinder and Figure 1 shows the schematic diagram of BES adopted in this study. The BES had a total and working volume of 4.0 L and 3.0 L respectively with an internal diameter of 16 cm and 20 cm in height. The BES consisted of an ACF (Shanghai Zhaokuo, Co., Ltd, China) wrapped around the stainless steel column (6 cm internal diameter × 12 cm height × 0.15 cm wall thickness) as the cathode electrode and a high-purity graphite rod (2 cm diameter × 13 cm length) as the anode electrode. An adjustable direct current regulated power supply (PS-305DM; Dongguan Longwei Electronic Technology, Co., Ltd, China) was connected with anode and cathode to provide voltage. Besides, an automatic stirrer (OS20; Beijing Dragon Laboratory Instruments Limited, China) was installed at the top of the BES to provide well-mixed environment.

Experimental design

After construction, the experiments were carried out for 167 days. Activated sludge (1 L, 1 g/L of MLSS), i.e., seed sludge, was collected from an oxidation ditch configuration (Fengyang Municipal Wastewater Treatment Plant, Anhui, China) and immediately washed three times using deionized water to remove soluble carbon sources. And then, it was inoculated in the BES reactor to accelerate the biofilm development onto the surface of ACF cathode, including three stages: firstly, from day 0 to day 20, a single synthetic wastewater was fed to the BES to promote the rapid growth of microorganisms; secondly, after that, a 1:1 (vol/vol) mixture of synthetic wastewater and azo dyes wastewater containing 30 mg/L MO was fed for 15 days to gradually enrich the specific microorganisms; finally, from day 36, it was intensively enriched by feeding the only MO wastewater for 30 days.

In order to investigate the effect of process parameters on MO color removal in BES, the applied voltage, MO concentration, carbon source content and pH were gradually increased respectively (see Table 1) after biofilm formation. During the experimental period, the hydraulic retention time (HRT) was maintained at 3 d according to the preliminary test. The synthetic wastewater consisted of organic carbon, nutrients and buffer solution and its composition is as follows: 40 mg/L KH_2PO_4, 40 mg/L $(NH_4)_2SO_4$, 3 mg/L $CaCl_2$, 45 mg/L $MgSO_4 \cdot 7H_2O$ and 1 mL/L of nutrient solution (1200 mg/L $FeCl_3 \cdot 6H_2O$, 130 mg/L H_3BO_3, 25 mg/L $CuSO_4 \cdot 5H_2O$, 160 mg/L KI, 100 mg/L $MnCl_2 \cdot 4H_2O$, 50 mg/L $Na_2MoO_4 \cdot 2H_2O$, 110 mg/L $ZnSO_4 \cdot 7H_2O$, 130 mg/L $CoCl_2 \cdot 6H_2O$ and 800 mg/L EDTA). In addition, glucose and MO were added into the synthetic wastewater according to the experimental arrangement, which was used as the carbon source. The other compositions acted as nutrient and buffer solution for microbial growth.

Analytical methods

Samples of effluents were filtered through a 0.22 μm-pore-size syringe filter prior to analysis. MLSS analysis was performed according to the standard methods (APHA, 2005). pH was measured by a pH meter analyzer (S20, Mettler-Toledo, Switzerland). Absorbance was analyzed by measuring the adsorption at 463 nm using an UV-3600 (Shimadzu, Japan).

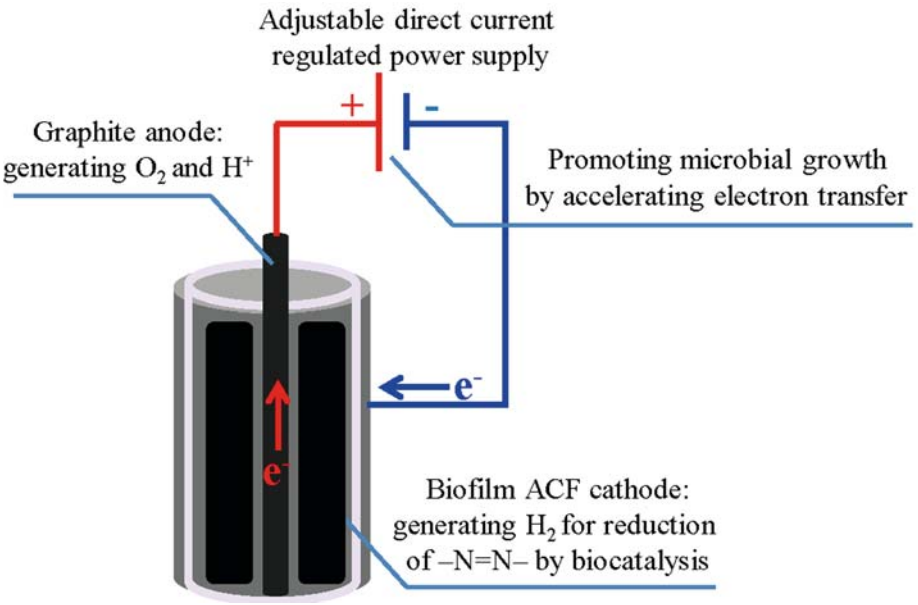

Fig. 1. Schematic diagram of BES

Results and discussion

Effect of applied voltage on color removal

The performance of color removal in BES at different applied voltages (HRT: 3 d; applied voltage: 0, 0.6, 0.8, 1.0, 1.4, 1.8, 2.2, 2.5 and 3.0) are shown in Figure 2. MO concentration of influent was maintained at 20 mg/L. It is clearly observed from Figure 2 that color removal efficiency increased with the increasing voltage applied from 0 V to 2.5 V, displaying the promoting effect of applied voltage on color removal. The BES is totally related to the current density and it was enhanced with the increasing voltage applied, providing suitable conditions for microorganism on the biofilm and electrochemical reaction (Chen et al. 2015). The highest color removal efficiency (80.5%) was observed in BES at an applied voltage of 2.5 V. The reason might be that the presence of current density was more conductive to the bacteria growth and electrochemical reaction. At 3.0 V, it was declined to 77.2%. This can be due to the fact that high concentrations of intermediate products would be formed in solution at an excessive applied voltage. There exists an inevitable comparison for electron between the further degradation of intermediate products and the rupture of –N=N– at the cathode's surface (Liu et al. 2015), leading to the decline in current efficiency.

Notably, the color removal efficiency was 68.9% at 1.8 V significantly higher than that at 1.4 V (53.5%) in BES. This may be attributed to the oxidative electrolysis of water and reduction of protons (Thrash and Coates 2008), thus producing more oxygen at anode and hydrogen at cathode, which were utilized by microorganisms as electron acceptor and electron.

Table 1. Experimental design used here

Process parameters	Set value
Applied voltage	0, 0.6, 0.8, 1.0, 1.4, 1.8, 2.2, 2.5 and 3.0 V
MO concentration	5, 10, 20, 40, 60, 80, 100 mg/L
Carbon source content	0, 0.1, 0.3, 0.5, 0.7, and 1.0 g/L
pH	3, 4, 5, 6, 7, 8, 9, 10, and 11

As the BES was controlled under no electric filed, i.e., applied voltage of 0 V, exhibiting only a typical biological reaction, the color removal efficiency was rather low (21.2%). Dye wastewater is well known to be of low biodegradability, which was hard to be treated by using only a single biological treatment method. And then, it was sharply increased up to 36.8% at 0.6 V, suggesting that micro-current flowing through the biofilm on the cathodic surface had positive effect on the microbial metabolism due to the electric field stimulation.

Effect of dye concentration on color removal

The effects of different MO concentration of influent (5, 10, 20, 40, 60, 80, 100 mg/L) on color removal performance are shown in Figure 3. During the treatment process, BES was operated at the same condition (HRT: 3 d; applied voltage: 2.0 V). Color removal efficiency gradually decreased from 90.2% to 42.8% with the increase of initial MO concentration ranging from 5 mg/L to 100 mg/L, displaying a negative effect of initial dye loading on BES, which may be most likely due to the toxicity of the dye metabolites (such as aromatic amines) produced during dye reduction at high dye concentrations (Pearce et al. 2003). Similar results were also found in a report (Sponza and Işik 2005) that increase in Direct Black 38 concentration caused a decrease in color removal efficiency in an anaerobic/aerobic sequential reactor responsible for dye wastewater treatment. These results suggested that the biomass inhibition effect could occur in BES when the dye concentration exceeded a proper range.

Effect of carbon source content on color removal

Figure 4 shows the effect of different carbon source content (0, 0.1, 0.3, 0.5, 0.7, and 1.0 g/L), glucose used here, on the color removal performance in BES. The other operation conditions were listed as follows: HRT=3 d, applied voltage=2.0 V, initial MO concentration=20 mg/L. It was observed that glucose displayed an obvious promotion on color removal efficiency in BES. The color removal efficiency was only 36.2% without addition of carbon source and it increased significantly up to 59.5% with the addition of 0.1 mg/L of glucose. This result was consistent with other studies (Al-Amrani et al. 2013, Murali et al. 2013), where co-substrate played an important role in the azo dye wastewater treatment processes. Generally, azo dyes can be

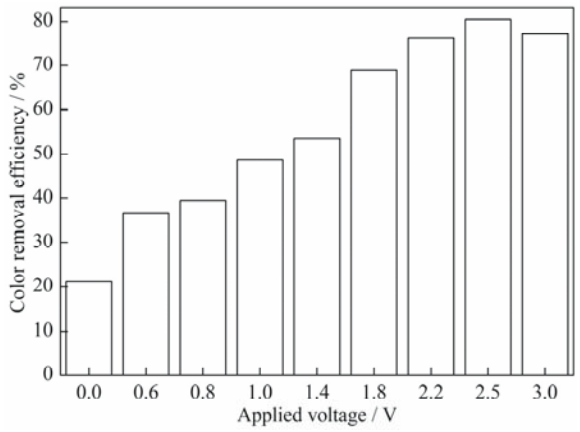

Fig. 2. Color removal efficiency at different applied voltages in BES

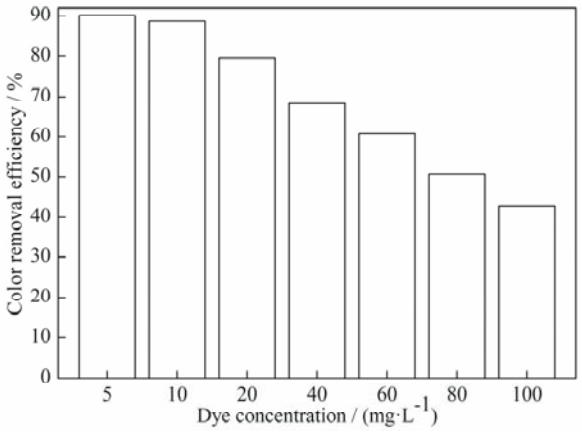

Fig. 3. Color removal efficiency with different dye concentration of influent in BES

cleaved via a four electron reduction through the linkage of azo bonds, which can be provided by an additional carbon source such as glucose or VFA (Işik and Sponza 2005). The color removal efficiency increased gradually from 59.5% to 87.9% as glucose loading increased from 0.1 to 0.7 g/L, indicating that the electrons required for the reductive cleavage of azo dyes depend to glucose content of influent. Notably, excessive glucose loading had adverse effects on color removal efficiency. When glucose concentration was continuously increased up to 1.0 g/L, the color removal efficiency was slightly decreased to 81.6%, suggesting that high glucose concentration had a spectacular inhibitory effect on decolorization of MO. This may be due to a metabolic regulation repression at high glucose concentration, mainly causing inhibition of the transcription of cyclic-AMP-dependent genes (Chang et al. 2001), which commonly occurred in biological treatment processes.

Effect of pH on color removal

The pH has a major effect on dye wastewater treatment and was regarded as the rate limiting step for the dye decolorization, which may be the transport of dye molecule across the cell membrane in a biological treatment system (Kodam et al. 2005). The above experiments were conducted without controlling the influent pH. Here, the influent pH was adjusted to different initial values (3, 4, 5, 6, 7, 8, 9, 10, and 11) to investigate the effect of pH on color removal. The other operation conditions were listed as follows: HRT=3 d, applied voltage=2.0 V, initial MO concentration=20 mg/L, glucose content=0.5 g/L. Figure 5 shows the variations of specific color removal efficiency with respect to pH. An elevation of pH in an increase ranging from 3 to 8 appeared to enhance the color removal efficiency from 28.5% to 81.9%, while a negative effect on the decolorization rate arose as the pH exceeded 8. The color removal efficiency maintained at 80±2% at pH 6–9, but dropped dramatically when pH was less than 6 or over 9, suggesting that strong acid or strong alkaline pH were unsuitable for MO wastewater color removal. The wide range of effective pH indicates that pH adjustment is not needed in most cases for BES (in contrast to other dye wastewater treatment methods commonly requiring acidic pH), thus greatly favoring the practical application of BES due to the fact that real dye wastewater usually have varying pH (Martínez-Huitle and Brillas 2009).

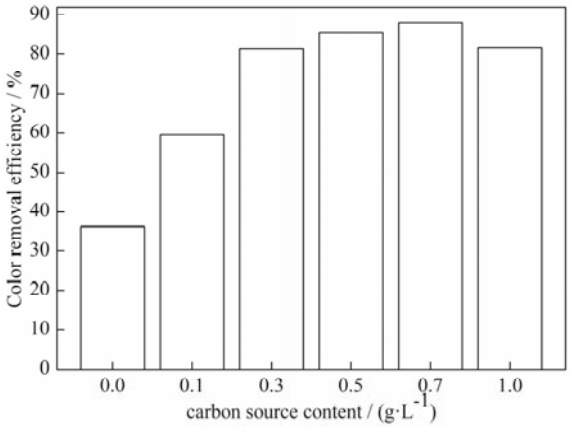

Fig. 4. Color removal rate with different carbon source content of influent in BES

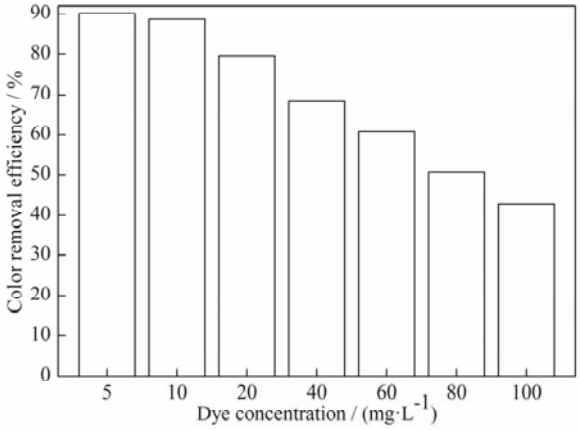

Fig. 5. Color removal rate with pH of influent in BES

Change of UV/Visible absorption spectra with reaction time in BES

As discussed above, micro-current flowing had an obvious enhanced effect on biological oxidation for treatment of dye wastewater, suggesting the combination of biological with electrochemical methods may have a competitive advantage over only biological or electrochemical process when treating non-biodegradation pollutants. To investigate the change of molecular and structural characteristics during the MO treatment by using BES, the changes in representative UV/Visible absorption spectra were recorded with a HRT of 3 d before and after oxidation, as depicted in Figure 6. There was a significant difference in main absorption bands between before and after MO degradation. Before degradation, the adsorption spectrum of MO solution was characterized by two main bands including one in UV region at 273 nm and the other in visible region at 463 nm. The peak at 273 nm is attributed to the aromatic ring of MO whereas the other peak at 463 nm is associated with the azo bond (-N=N-) (Panda et al. 2011). After degradation, the absence of a peak at 463 nm showed that the azo bond of MO was almost completely cleaved and the weakening of peak at 273 nm indicated that intermediates from MO were partly removed at the given HRT here.

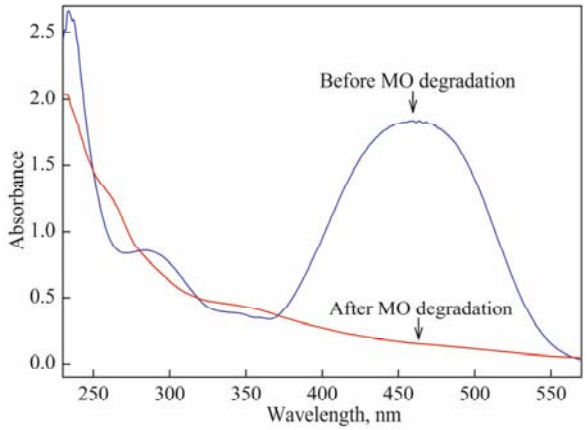

Fig. 6. Change of UV/Visible adsorption spectra with reaction time in BES

Conclusions

This study showed that color removal from MO dye wastewater in a novel biofilm coupled with electrolysis (bioelectrochemical system, BES) process was effective. Under the optimum process parameters (applied voltage = 2.0 V, initial MO concentration = 20 mg/L, glucose content = 0.5 g/L, pH = 8) color removal efficiency reached the maximum value of 81.9% when the hydraulic retention time was maintained at 3 d. A wide range of effective pH, ranging from 6 to 9, was found, thus favoring the practical application of BES described in this study. From these results, the proposed method of biodegradation combined with electrochemical technique may be an effective technology for dye wastewater treatment. Further research is needed to treat real dye wastewater collected from a different Chemical Dye Industrial Factory.

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