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AZO DYE WASTEWATER TREATMENT IN A NOVEL THREE-DIMENSIONAL ELECTRODE REACTOR

A novel three-dimensional electrode reactor (3DER) was designed to treat the dye wastewater. The performance of 3DER was evaluated via methyl orange (MO) removal efficiency. For comparison, the performance of the two-dimensional electrode reactor (2DER) was also assessed. Furthermore, the effects of electrolyte and aeration on treatment performance were preliminarily evaluated to further optimize the operation on 3DER. A repeatable and stable MO treatment efficiency was obtained in the 3DER. The MO removal rate reached 79.5% at the applied voltage of 1.0 V, electrode spacing of 2 cm and initial MO concentration of 60 mg/dm^3, significantly higher than that in the 2DER (58.8%), suggesting the obvious improvement of particle electrodes on MO removal. Both adding electrolyte and air sparging into the 3DER contributed to the enhancement of the MO removal rate. These results obtained here suggest that the 3DER may provide an effective alternative for the treatment of azo dye wastewater and/or non-biodegradable industrial wastewaters.

1. INTRODUCTION

Synthetic azo dyes are often used widely in textile as well as in paper and leather production, which would produce large volumes of dye-containing industrial wastewaters [1]. These azo dyes are mostly responsible for the presence of color in effluents [2]. Most synthetic azo dyes, however, are refractory to degradation in the natural water environment [3], probably causing serious pollution to the receiving water bodies due to their intense color and even posing great hazards to aquatic life and human beings [4]. Consequently, decolorization of the azo dye wastewater is crucial to enhance the effluent quality.

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Compared with other techniques including adsorption [5], precipitation [6], biodegradation [7], ion exchange [8], etc., electrochemical oxidation, a significant kind of advanced oxidation process, is an effective technology for the treatment of refractory organics, owing to its obvious advantages of simple design, easy operation, and maintenance, environmentally friend and no secondary pollution [9, 10]. For an electrochemical process, the main equipment is an electrode reactor, such as electrolysis. Previous studies confirmed that a two-dimensional electrode reactor (2DER) can effectively treat azo dye wastewater [11]. However, mass transfer and current efficiency can be usually restricted by the low surface area of the cathode in the traditional 2DER [12].

Recently, a new three-dimensional electrode reactor (3DER) has been reported that can greatly overcome the disadvantages mentioned above in the 2DER [13]. Based on the 2DER, the 3DER is commonly filled with numerous particles between the anode and the cathode, thus greatly expanding the specific surface area of the electrode [14], where particle electrodes are called the third-dimensional electrode. When the 3DERis given an appropriate applied voltage, the small particles generate many charged microelectrodes [15], which contributes to the enhancement of electrocatalytic efficiency [16]. The degradation mechanisms of refractory organics in the 3DER were analyzed as follows: (1) refractory organics are directly oxidated on the surface of anode and microelectrodes, (2) those are indirectly degraded with hydrogen peroxide [13], (3) these organic compounds can be also indirectly removed with hydroxyl radicals [17]. These small particles, used as a catalyst, can accelerate the generation of hydroxyl radicals from hydrogen peroxide, which improves the removal rate of refractory organics, in the 3DER.

For this, a distinctive 3DERwas developed to investigate the decolorization performance of synthetic dye wastewater. Methyl Orange, widely used in a variety of industries, was selected as a model compound in this investigation. The influence of applied voltage, electrode spacing, and MO initial concentration on MO removal efficiency in the 3DER were measured here. Its removal performance was compared with that of the traditional 2DER. Furthermore, the effects of electrolyte and aeration on treatment performance were preliminarily evaluated in this study to further optimize the operation of 3DER. These results obtained here may serve as a new suggestion for an application of electrochemical processes in azo dye wastewater and/or non-biodegradable industrial wastewater treatment.

2. MATERIALS AND METHODS

Reactor set up. A lab-scale 3DER (Fig. 1), 42 cm high and 10 cm in inner diameter, was made of polymethyl methacrylate. A graphite rod with a diameter of 2 cm was used as the anode, according to the fact that oxygen over-potential was relatively high on graphite. A stainless steel mesh (wire diameter of 0.4 mm, mesh number of 12, Jiangsu Changzhou Metal Products Factory, Co., Ltd, China) was placed around the anode, which was used as the cathode due to its stability in the MO wastewater. A mixture of

granular activated carbon (GAC) and quartz sand (volume ratio 4:1) was packed into the space between the anode and the cathode in the 3DER, which was used as the third electrode. The electric power was provided with an adjustable direct current regulated power supply (PS-305DM). For comparison, the 2DER was also conducted without the addition of GAC and quartz sand in this study.

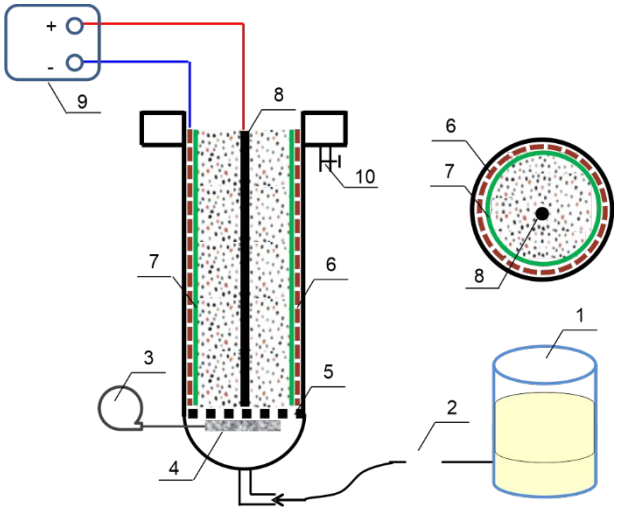

Fig. 1. Experimental set-up of a lab-scale reactor: 1 – influent, 2 – peristaltic pump, 3 – air pump, 4 – aeration stone, 5 – distribution of pore water, 6 – cathode, 7 – activated carbon fiber, 8 – anode, 9 – adjustable direct current regulated power supply, 10 – effluent

Experimental procedure. Before the experiment, the GAC and quartz sand were three times washed with deionized water, then dried at 105 °C for 24 and finally immersed in MO wastewater three times (once per 24 h). A simulated concentrated solution containing MO of 180 mg/dm^3 was prepared to provide the desired concentration of MO wastewater according to the experimental plan. Based on our preliminary experiment, the effects of applied voltage (0.6, 1.0, 1.4 V), electrode spacing (2, 3, 4 cm), and initial MO concentration (30, 60, 90 mg/dm^3) on the treatment performance of 3DER were investigated. A comparison between 3DER and 2DER was for MO removal. Furthermore, a comparison of 3DER with and without supplementary aeration (3 dm^3/min), with and without the addition of supplementary electrolyte (sodium sulfate, 2.5 g/dm^3) was used here as a supporting electrolyte) treating MO wastewater was also carried out to further optimize the operation of 3DER in this study. All experiments were conducted at a constant hydraulic detention time of 2 d at room temperature ranging from 20.2 to 29.5 °C.

Chemical analysis. All water samples were filtered through 0.22-μm Millipore filter and then placed at 4 °C before analysis. MO concentrations were analyzed by using UV-3600 (Shimadzu). The degradation of MO was monitored at 463 nm.

3. RESULTS AND DISCUSSION

3.1. EFFECTS OF APPLIED VOLTAGE ON THE MO REMOVAL EFFICIENCY

The economic efficiency of the 3DER in the treatment of MO wastewater not only depends upon the removal rate but also upon the electric energy consumption. Therefore, an appropriate applied voltage is critical to obtaining relatively high economic efficiency.

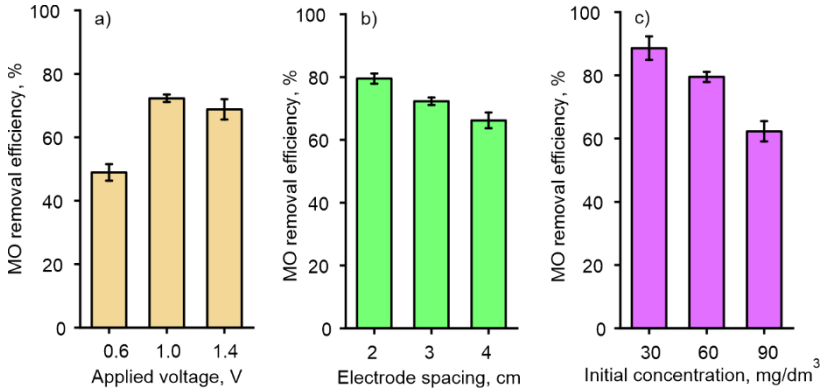

Fig. 2. Effects of applied voltage (a), electrode spacing (b) and initial MO concentration (c) on MO removal rates; a) electrode spacing 3 cm, initial MO concentration 60 mg/dm^3, b) applied voltage 1,0 V, initial MO concentration 60 mg/dm^3, c) applied voltage 1.0 V, electrode spacing 2 cm

The MO removal efficiency in the 3DER increases from 48.9% to 72.3% as the applied voltage increases from 0.6 V to 1.0 V (Fig. 2a), which may be since much more micro-electrolysis cells would be generated in the 3DER as the result of the increase of applied voltage. In the 3DER proposed here, activated carbon was firstly polarized by the external electric field and then can generate numerous microelectrodes (i.e., electric active sites) [18], thereby greatly enhancing the MO removal rate. However, higher applied voltage did not enhance the color removal rate but caused deterioration in MO removal in the 3DER. When the applied voltage continued to increase to 1.4 V, the MO removal efficiency started to decrease to 68.8%, suggesting that some side reactions may occur at relatively high applied voltage. This behavior was most likely due to the occurrence of electrolysis of water [19], leading to the decline in current efficiency in the 3DER. Moreover, at 1.4 V of applied voltage, many more intermediate products would be generated during the degradation of MO, which may cause the comparison for electrons between the azo bond (contained in MO) cleavage and the further degradation of intermediate compounds [20]. This also probably results in a decrease in current efficiency for MO removal.

3.2. EFFECTS OF ELECTRODE SPACING ON MO REMOVAL EFFICIENCY

A high MO removal rate requires high current efficiency. Cheng et al. [21] reported that the current efficiency was mostly limited by internal resistance. In the 3DER, the electrode spacing greatly affects the internal resistance. For this, the distance between the anode and the cathode in the 3DER was varied to investigate the effect of electrode spacing on MO removal rate (Fig. 2b). The MO decolorization rate gradually decreased when electrode spacing increased from 2 cm to 4 cm. This may be directly attributed to an increase in the internal resistance with the increase in electrode spacing. A similar result was also reported by Wang et al. [22] that larger electrode spacing resulted in higher internal resistances in a bio-electrochemical system. Likely substantially, the increase in internal resistance led to the decrease in electron transmission efficiency, which resulted in a decrease in MO removal rate.

3.3. EFFECTS OF INITIAL MO CONCENTRATION ON MO REMOVAL EFFICIENCY

The MO removal rate gradually decreased from 88.6% to 62.3% as the initial MO concentration increased (Fig. 2c), suggesting that the increase in MO concentration harmed the electrochemical reactions inside the 3DER proposed here. The main reason may be due to the consumption of more hydroxyl radicals ($^{\bullet}OH$) when increasing the initial MO concentration. However, a limited number of hydroxyl radicals was generated when the 3DER was provided with a fixed applied voltage. A previous report [23] demonstrated that hydroxyl radicals played an important role in electrochemical oxidation processes. Furthermore, the increases in initial MO concentration would require a higher current density and limit the mass transfer limitations [10]. All of these can result in a decrease in MO removal efficiency.

3.4. MO REMOVAL EFFICIENCIES IN TWO-DIMENSIONAL AND THREE-DIMENSIONAL ELECTROLYSES

The 3DER proposed here displayed a better MO removal performance than that of the 2DER (Fig. 3a). The removal of MO for the 3DER is 20.7% higher than the 2DER. The 3DER was designed in this study based on the 2DER, where GAC (conductive particle) was packed between anode and cathode. The GAC would be polarized to form lots of microelectrodes when the external voltage was applied, which greatly enhance current efficiency and MO removal rate. Panizza et al. [24] also found that pollutant removal rate was closely related to the applied voltage.

3.5. INFLUENCE OF ELECTROLYTE ON MO REMOVAL EFFICIENCY

The additional anhydrous sodium sulfate slightly enhanced the MO removal rate from 79.5% to 84.7% (Fig. 3b). This may attribute to the enhancement of solution conductivity

upon adding the electrolyte into MO wastewater, which contributed to the enhancement of MO degradation by improving the mass transfer rate. However, Pang et al. [25] reported that the increase in organic compounds removal efficiency was not significant when the concentration of electrolytes increased to a certain level. This was probably because excessive sulfate ions greatly reduced the number of active sites on the surface of the electrode, which badly hindered the generation of hydroxyl radicals.

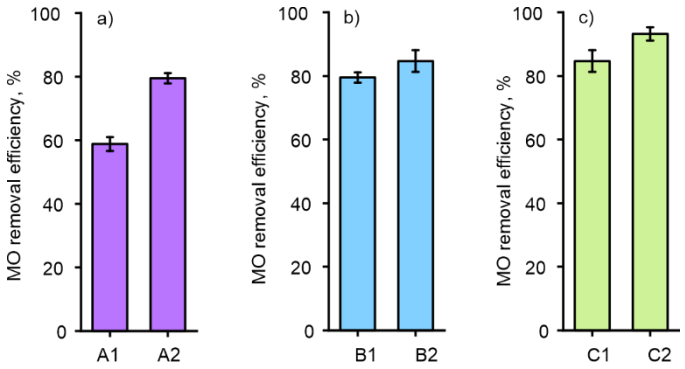

Fig. 3. MO removal efficiencies for two-dimensional electrolysis (A1), three-dimensional electrolysis (A2), without adding electrolyte (B1), after adding electrolyte (B2), without air sparging (C1) and air sparging (C2); voltage 1.0 V, electrode spacing 2 cm and initial MO concentration 60 mg/dm^3

3.6. INFLUENCE OF AIR SPARGING ON MO REMOVAL EFFICIENCY

Oxygen can be reduced at the surface of the cathode and/or GAC particles to produce hydrogen peroxide. And then, hydrogen peroxide is catalytically decomposed to generate hydroxyl radicals, which can improve the MO removal rate in the 3DER. For this, the MO degradation performance was investigated under both no aeration and aeration conditions in the 3DER. Under aeration conditions, the compressed air (3 dm^3/min) was sparged into the 3DER by a micropore pipe. The compressed air positively promoted the MO decomposition reaction (Fig. 3). Thus, the MO removal rate for air sparging into the 3DER (93.2%) was higher than that for no aeration (84.7%), due to the following two reasons: (1) the sparged air strengthens by stirring the mass transfer efficiency [26], (2) the sparged air supplies the oxygen for electrochemical reactions [27], where oxygen may be reduced to hydrogen peroxide and/or hydroxyl radicals mentioned above, two stronger oxidizing agents. However, excessive aeration may interfere with electron transfer, thus leading to a decrease in MO removal efficiency in the 3DER.

4. CONCLUSIONS

The three-dimensional electrode reactor (3DER) proposed here exhibited repeatable and stable Methyl Orange (MO) removal efficiency. The MO removal rate reached

79.5% under the following conditions: applied voltage of 1.0 V, electrode spacing of 2 cm, and initial MO concentration of 60 mg/dm^3, significantly higher than that in the 2DER (58.8%).

Both adding electrolyte and air sparging into the 3DER can effectively enhance the MO removal rate. However, further research is necessary to investigate the optimal amount of electrolyte and aeration to obtain good environmental and economic benefits.

The 3DER may provide a new suggestion for treatment of azo dye wastewater and/or non-biodegradable industrial wastewaters. Further efforts are required for overall performance improvements in the 3DER and its practical application.

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