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Optimizing decolorization of Methylene Blue and Methyl Orange dye by pulsed discharged plasma in water using response surface methodology

Yanping Jin [a], Yunhai Wu [a], Julin Cao [b], Yunying Wu [c,*]

[a] Key Laboratory of Integrated Regulation and Resources Development of Shallow Lakes, Ministry of Education, Hohai University, Nanjing 210098, China
[b] College of Environment, Hohai University, Nanjing 210098, China
[c] Department of Chemistry, Hanshan Normal University, Chaozhou, China

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ABSTRACT

Dye removal using pulsed discharged plasma in water requires a proper process parametric study to determine its optimal performance characteristics. Response surface methodology was used to find out the major factors influencing Methylene Blue (MB) and Methyl Orange (MO) removal efficiency and the interactions between these factors (ultrasonic power, gas flow rate, and electrode spacing), and optimized the operating variables as well. Regression analysis showed good fit of the experimental data to the second-order polynomial model with coefficient of determination value of 0.9960 and 0.9861 for MB and MO, respectively. Under the experimental conditions: gas flow rate 0.1 m^3/h, electrode spacing 10 mm for all the dyes, and ultrasonic power 80 and 90 W for MB and MO, the highest dye removal efficiency were achieved 94.5% and 80.2% for MB and MO. The optimal results suggested that pulsed discharged plasma oxidation process was a rapid, efficient, and low energy consumption technique to remove the dyes wastewater.

1. Introduction

The increasing use of dyes in various industrial applications has resulted in the discharge of toxic dye effluents into the water streams causing serious environmental pollution [1]. Moreover, many dyes are difficult to degrade, as they are generally stable to light, oxidizing agent and are resistant to aerobic digestion [2]. Hence, the removal of dyes from process or waste effluents becomes environmentally important.

The conventional methods, such as biological oxidation, chemical coagulation and adsorption have been applied for dye removal from water and wastewaters [3,4]. Biological methods are generally cheap and simple to apply and are currently used to remove organics and color from dyeing and textile wastewater. However, this dyeing wastewater cannot be readily degraded by the conventional biological processes, *e.g.*, activated sludge process, because the structures of most commercial dye compounds are generally very complex and many dyes are non-biodegradable due to their chemical nature, molecular size and result in sludge bulking [5]. Although dyestuffs and color materials in wastewater can be effectively destroyed by wet oxidation [6], adsorption using activated carbon [7,8], and electrocoagulation using Al or Fe soluble electrodes [9], the costs of these methods are relatively high.

Therefore, novel methods, especially advanced oxidation processes (AOPs), have been applied for treating dye wastewaters that are non-biodegradable and toxic to microorganisms [10]. Researchers have tested various processes, such as photo oxidative process, electrochemical process, H_2O_2 oxidation, ultrasonic process, Fenton and Feton-like [11–14], ozone oxidation [15–17], and plasma process. More recently, among the AOPs, the pulsed discharged plasma in water has been considered to be an applicable method for the removal of organic pollutants from wastewater [18–20]. Pulsed discharged plasma in water is efficient in the formation of chemically active species such as OH, H, O, O_3, and H_2O_2. Most of these species are among the strongest oxidizing agents. The effect plays an important role in destroying harmful organic pollutants in wastewater [21]. However, in the plasma process, many factors such as pH, ultrasonic power, the electrolyte concentration, gas flow rate, electrode spacing, and the application time influence the process efficiency. The process efficiency may be increased by the optimization of these factors. In conventional multifactor experiments, optimization is usually carried out by varying a single factor while keeping all the other factors fixed at a

* Corresponding author. Tel.: +86 7682318681; fax: +86 7682318681.
E-mail address: jinyanping0408@yahoo.cn (Y. Wu).

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specific set of condition. This method is time-consuming and incapable of effective optimization. Recently, response surface methodology (RSM) has been employed to optimize and understand the performance of complex systems [22]. By application of RSM, it is possible to evaluate the interactions of possible influencing factors on treatment efficiency with a limited of planned experiments [23–25].

In the present study, RSM with Box–Behnken design (BBD), Design Expert Version 8.0.6 program (Stat-Ease Inc., Minneapolis, USA), was employed for the optimization of Methylene Blue (MB) and Methyl Orange (MO) by pulsed discharged plasma. The main objectives were to optimize the process and investigate the factors that influence the removal efficiency. Dye removal efficiency was chosen as the dependent factor (response) and the ultrasonic power, gas flow rate, and electrode spacing were selected as process variables. The optimal conditions for dyes removal were also determined from the model obtained via experimental data.

2. Materials and methods

2.1. Materials

All dyes used in this study were purchased from Nanjing RuiTai Chemical Reagents, Ltd. The structures of dyes MB and MO were shown in Fig. 1. Double distilled water was used in all the experiments, to prepare the stock solution of MB and MO. Working solutions (1.40×10^{-6} M) were prepared by suitable dilution of the stock solutions. The initial solution pH was adjusted by added a little amount of 0.1 M NaOH or 0.1 M HCl into the solution until the conductivity becomes 400 ± 50 μs/cm. Since the conductivity greatly affect the formation of plasma discharged in water, the initial conductivity should be kept constant in all experiment [21].

2.2. Experimental procedure

The schematic diagram of experimental apparatus is shown in Fig. 2. Plasma was generated from Plasma Power and pulse modulator (EcoTopia Science Institute, Nagoya University, Japan). Operation conditions: pulse repetition frequency and pulse width were set at 0.1–30 kHz and 0–2 μs, respectively. And discharge state was controlled by the value of output voltage in 80–100 V. The processing reactor, made of stainless steel, had a diameter of 480 mm and a height of 600 mm. Air was often used as bubbling gas with the purpose of improving the liquid discharge performance in some pulsed high-voltage discharge system [26]. The process gas (air) was introduced into the active volume of the plasma via a gas flow control system. The pulsed discharge reactor used in this work was done with bipolar pulse DC power supply.

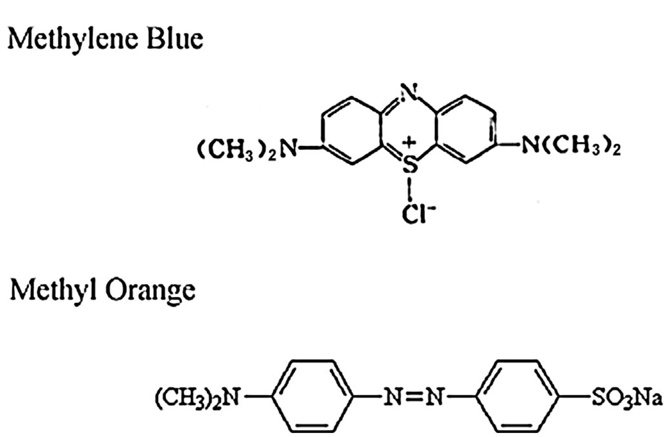

Fig. 1. Chemical structures of the two utilized dyes.

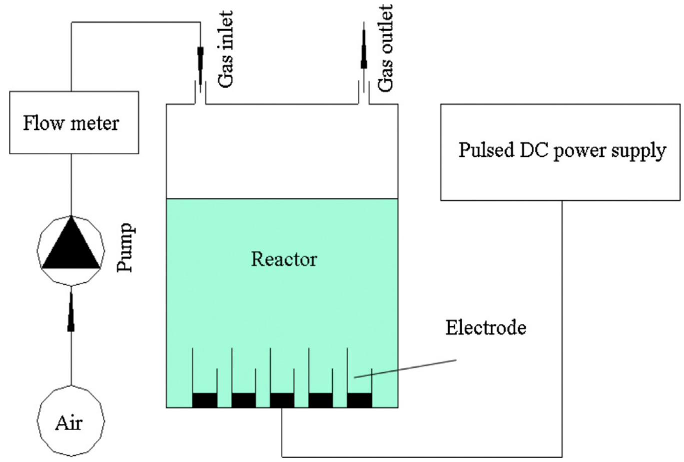

Fig. 2. Schematic diagram of the experimental apparatus.

When the plasma source was on, the press was measured by a capacitive vacuum gauge. Samples were introduced by a load lock system and placed on a grounded aluminum holder near the center of the processing reactor. The electrodes used in experiments were made of stainless (1.5 mm). The ultrasonic power was estimated by measuring the applied voltages, discharge current and the pulse repetition rate. The values of pulsed output voltage and current were measured using a digital oscilloscope (Lecroy LT264) with a high voltage probe (INC P150-GL/5 k) and a current transducer (Pearson Electronic M411). The discharge power *i.e.* $V \times I$ could be calculated from the product of the measured pulse voltage (V) and the discharge current (I).

Samples were taken periodically from the reactor and then analyzed immediately with UV-vis spectrophotometer (Shimadzu, Japan) with wavelength of 660 nm and 440 nm for MB and MO solution, respectively. The flow rate of the dye solution was 100 mL/min. Samples were taken from the reactor from the sampling traps to determine absorbance prior to the reaction. At predetermined time of 30 min, 10 mL samples were withdrawn from the reactor and analyzed to determine absorbance. The dye removal efficiency can be calculated based on the following equation:

$$\eta = \frac{\alpha_0 - \alpha_t}{\alpha_0} \times 100\% \tag{1}$$

where α_0 (mg/L) was the initial concentration and α_t (mg/L) was the concentration at discharge time t (min).

2.3. Response surface methodology

RSM is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing process. The main objective of RSM is to determine the optimum operational conditions for the systems or to determine a region that satisfies the operating specifications [27]. The main advantage of RSM is the reduced number of experimental trials needed to evaluate multiple parameters and their interactions. Its great applications particularly have been in situations where a large number of variables influencing the system feature. This feature termed as the response and normally measured on a continuous scale, which represents the most important function of the systems [28].

2.4. Experimental design

A 3-factor, 3-level factorial Box–Behnken design (BBD) was employed to investigate the effects of selected variables. BBD,