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Process behavior of TiO_2 nanotube-enhanced sonocatalytic degradation of Rhodamine B in aqueous solution

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ABSTRACT

Sonocatalytic degradation of Rhodamine B was investigated using titanium dioxide (TiO_2) powder and titanium dioxide nanotubes (TiO_2 NTs) which were synthesized using sol–gel and hydrothermal method, respectively. Structural and crystalline information for both types of catalyst were characterized using transmission electron microscope (TEM), X-ray diffractometer (XRD) and surface analyzer. Remarkable improvement in the sonocatalytic activity of TiO_2 NTs was achieved due to their high specific surface area and unique pore system. Effects of reaction parameters such as pH (2–10), ultrasonic power (20–100 W), ultrasonic frequency (35 kHz and 130 kHz) and the presence of air flow (1 L/min) were also investigated. Under optimum conditions, i.e., with 8 millimolar (mM) of hydrogen peroxide (H_2O_2) and 1 L/min of air flow at neutral pH, 85% degradation of 50 mg/L Rhodamine B could be achieved in 120 min by the system with 2 g/L of TiO_2 NTs. The sonocatalytic process was observed to behave according to a pseudo-first-order kinetics under different experimental conditions. In conclusion, sonocatalytic degradation in the presence of TiO_2 NTs shows a great potential for the efficient treatment of organic dyes in wastewater.

1. Introduction

The release of persistent and complex dyes with toxic, carcinogenic and mutagenic properties may cause negative impacts to human health and ecosystem. In 1974, Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) found that basic and diazo direct dyes have the highest toxicity among 4000 dyes tested [1]. Rhodamine B is a member of basic dyes. It is capable of causing irritation to the skin, eyes and respiratory tract if swallowed [2]. It is estimated that 10–15% of this dyes is lost in the effluent during dyeing process [3]. Therefore, there is a need to study the removal of Rhodamine B from polluted streams to avoid any hazardous and harmful effects towards environment and human health.

As the presence of dyes in industrial effluent is highly undesirable, many methods have been investigated for their removal. Methods such as coagulation, filtration and adsorption by activated carbon are only able to transfer the organic pollutants from one phase to another to consequently cause the release of secondary pollutants into the environment [3,4]. As such, degradation methods such as oxidation are preferred as no secondary pollutant is created. Many advanced oxidation processes (AOPs) that are able to generate highly reactive hydroxyl ($^{\bullet}OH$) radicals emerge as promising alternatives for the effective removal of recalcitrant organic pollutants from effluents. One plausible method is photocatalytic process using UV light. However, low penetrability of UV light in water medium (limited to several millimeters) leads to poor degradation efficiency and limits the success in actual wastewater treatment system [4,5]. In this respect, sonocatalytic degradation of organic pollutants appears to be a better destructive technology. Generally, it has a strong penetration ability which can usually reach 20–30 cm from the energy source [6]. Reactive radicals such as $^{\bullet}OH$, $^{\bullet}H$ and $^{\bullet}OOH$ generated during ultrasonic irradiation are used to oxidize and degrade the organic compounds [7].

The selection of TiO_2 is based on its biological and chemical properties such as high catalytic activity, high chemical stability, low cost and low toxicity [4,8]. Many researchers have shown that the presence of TiO_2 could increase the sonocatalytic degradation of organic pollutants [4,6,7]. However, report on sonocatalytic degradation using titanium dioxide nanotubes (TiO_2 NTs) is hardly found in the literature. In this work, TiO_2 NTs catalyst was prepared by the combination of sol–gel process with hydrothermal treatment to be used for the degradation of organic dye in aqueous solution under ultrasonic irradiation. TiO_2 in the form of nanotube has improved properties compared to TiO_2 powder such as high aspect ratio and high surface to volume ratio to result in higher specific surface area [9,10]. These special features provide more channels for enhanced electrons and holes transfer to increase the degradation efficiency. Furthermore, higher sedimentation rate of TiO_2 NTs makes the process more technically viable as the catalyst recovery and reusability will be relatively easy [8,11]. In the present study, sonocatalytic degradation of Rhodamine B (as the

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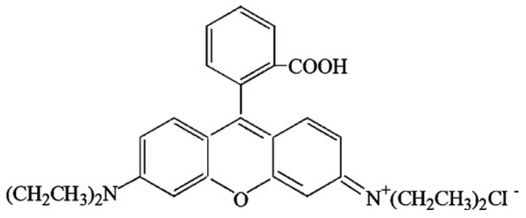

Fig. 1. Chemical structure of Rhodamine B.

model dye compound) is used to demonstrate the performance and behaviors of TiO_2 NTs under various conditions. Particular focus is given to differences in the characteristics and performance of the two types of TiO_2 catalysts as well as the elucidation of process behaviors.

2. Experimental

2.1. Chemicals and materials

Rhodamine B was obtained from Sigma–Aldrich as a commercially available dye. It is also known as Rhodamine 610, C.I. Pigment Violet 1, Basic Violet 10 or C.I. 45170 with a molecular formula of $C_{28}H_{31}N_2O_3Cl$ and a molecular weight of 479.01 g/mol. The chemical structure of Rhodamine B is shown in Fig. 1. It is made up of xanthenes structure and is highly soluble in water. Hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH, 99%), tetra-n-butyl-orthotitanate ($C_{16}H_{36}O_4Ti$ or $Ti(OBu)_4$ for synthesis, ≥98%), ethanol (CH_3CH_2OH, 96%) and hydrogen peroxide solution (H_2O_2, 30%, w/w) were obtained from Merck. Meanwhile, potassium hydroxide (KOH, ≥98%) was purchased from System Chemical Company. All the chemicals were used as received and distilled water was used throughout the study.

2.2. Preparation of powder and TiO_2 NTs

TiO_2 powder was prepared using a sol–gel method and subsequently subjected to heat-treatment. First, $Ti(OBu)_4$ was dissolved in ethanol at a volume ratio of 4:1 and left for 1 h under continuous stirring. Then, a known quantity of 0.1 M HCl was added to control the pH of the solution to prevent the precipitation of TiO_2. The mixture was then hydrolyzed at room temperature under stirring for 2 h to obtain a transparent sol. Next, the sol was aged for 2 days at room temperature to obtain a dry gel. The resulting gel was then washed with distilled water and dried overnight at 100 °C in an oven. After that, the dried gel was calcined at 500 °C for 3 h.

TiO_2 NTs were synthesized using a hydrothermal method which was initially developed by Kasuga et al. [12] and later modified by Bavykin et al. [13]. 3.0 g of synthesized TiO_2 powder was first mixed with 98 mL of 10 M NaOH and 2 mL of 10 M KOH solution in a Teflon vessel. The mixture was then refluxed at 100 °C under continuous stirring for 48 h. The resulting white powder was thoroughly washed with distilled water to remove excess Na^+ ions. Then, the powder was repeatedly treated with 0.1 M of HCl until the washing solution reached a pH of 3 to promote complete exchange of Na^+ by H^+ to form hydrogen titanate. Then, it was washed with distilled water and dried in an oven for several hours at 100 °C. Finally, the dried samples were calcined at a temperature of 300 °C for 2 h. The TiO_2 NTs could lose their tubular morphology and experience a decrease in specific area if calcined at 500 °C and above as reported in our recent study [14]. Hence, only TiO_2 NTs that was calcined at 300 °C was used in this study.

2.3. Catalysts characterization

The TEM images of the prepared catalyst samples were analyzed using a Phillips CM 12 transmission electron microscope equipped with an image analyzer and operated at 120 kV. Small amount of sample in powder form was first dispersed in ethanol and the suspension was dropped onto a perforated carbon film supported by a copper grid. After drying, the dried droplet was observed under TEM. Powder X-ray diffraction (XRD) method was used for crystal phase identification and the estimation of crystallite size. The XRD test was performed using a Philips PW 3040/60 X'Pert PRO powder diffractometer system using monochromatized Cu K_α radiation ($\lambda = 1.5418$ a) at 40 kV and 30 mA. The specific surface area, pore size and pore volume measurements based on nitrogen adsorption–desorption data at 77.35 K were made using a Micromeritics surface analyzer (model ASAP-2020). Meanwhile, no thermal analysis was conducted in this study as the main scopes were dedicated to the study on the structural morphology and X-ray diffraction characteristics, particularly with respect to the transformation from TiO_2 powder to nanotubes. However, the thermal properties of TiO_2 dry gel powder and nanotubes had been

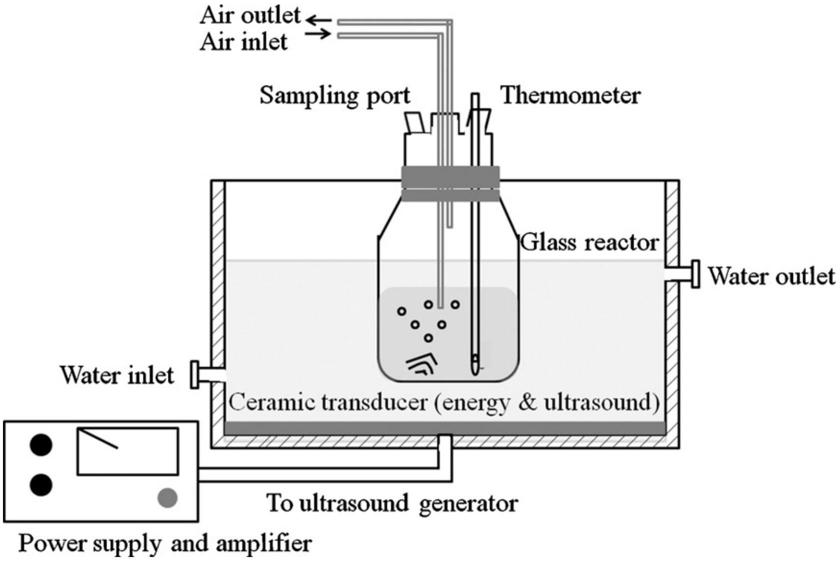

Fig. 2. Schematic diagram of the sonocatalytic experimental set up.