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Sonocatalytic Degradation of Rhodamine B in Aqueous Solution in the Presence of TiO₂ Coated Activated Carbon

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Abstract

Synthesis of titanium dioxide coated activated carbon (TiO₂/AC) has been undertaken using sol-gel method and its application in Rhodamine B (RB) dye removal has been investigated. The synthesized sonocatalyst (TiO₂/AC) was characterized by using SEM and FTIR techniques. The effects of the TiO₂/AC on the sonocatalytic degradation of RB dye and the operational parameters such as pH, temperature, ultrasonic frequency with the presence/absence of sonocatalyst of the sonocatalytic degradation of RB were concerned in this study. The degradation efficiency of RB in aqueous solution could be achieved 82.21% with the addition of TiO₂/AC at the best conditions. The best conditions for sonocatalytic degradation of RB were found to be pH 6, temperature 50°C, ultrasonic frequency of 30 kHz with the presence of sonocatalyst for 60 minutes.

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1. Introduction

The wastewaters discharged from textile and dyestuff industries cause serious environmental problems by destroying various life forms and consume dissolved oxygen due to its strong color, a large amount of suspended solids, highly fluctuating pH as well as high temperature. Synthetic dyes are commonly used in several manufacturing industries such as textile dyeing, paper printing, cosmetics and pharmaceuticals, and it is estimated that 10 – 15% of the dyestuff lost in the effluent during the dyeing processes [1].

Rhodamine B is widely used in industrial purposes and capable to cause irritation to the skin, eyes, gastrointestinal tract as well as respiratory tract [2]. In California, Rhodamine B is suspected to be carcinogenic. However, despite the large amount of data on its toxic effects, RB is still used in biology as a staining fluorescent dye, sometimes in combination with auramine O, as the auramine-rhodamine stain

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to demonstrate acid-fast organisms, notably *Mycobacterium*. Therefore, treatment of dye-containing effluents, i.e. Rhodamine B is a topic of significant interest among researchers.

Color is one of the vital characteristics of these effluent streams and seems to be the most undesired, as it affects the nature of water by inhibiting sunlight penetration hence reducing photosynthetic action. Thus, color removal from industrial effluents has become a major concern in wastewater treatment, and treatment is needed before discharging to receiving water. Various conventional methods have been used to remove color from textile dyeing wastewater such as coagulation-flocculation process [3], adsorption [4], liquid membrane [5] and advanced oxidation process (AOP) [6]. A great number of researches have been done on the application of ultrasound in the degradation of dyes, phenol and other organic pollutants in wastewater [7]. Combination of ultrasound with adsorption process was found to be more promising in the elimination of macromolecules such as phenols and dyes. The aim of the present work was to investigate sonocatalytic degradation of RB from aqueous solution with the presence or absence of TiO_2/AC .

2. Experimental

2.1. Materials

Rhodamine B (RB) dye (abbreviation: RB; C.I. number: 45170; molecular formula: $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$) was used as a model solute. RB dye [Xanthylum, 9-(2-carboxyphenyl)-3, 6-bis(diethylamino)-, chloride (1:1)] (molecular weight: 479.02 g/mol) was used as received. RB dye, activated carbon, tetrabutyl-orthotitanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$, 97%), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 95%), nitric acid (HNO_3 , 65%), sulphuric acid (H_2SO_4 , 97%) as well as sodium hydroxide (NaOH , 99%) were obtained from R&M Chemicals. Distilled water was used throughout the experiments.

2.2. Preparation of Titanium Dioxide Coated Activated Carbon (TiO_2/AC)

The TiO_2/AC was prepared based on the procedure mentioned by Zhu and Zou [8] with a slight modification. The activated carbons were ground and sieved to the size within the range of 45 μm to 125 μm . The activated carbons were impregnated with the fine TiO_2 nanoparticles. The TiO_2 nanoparticles were synthesized by hydrolysis of precursor chemicals to form a uniform sol according to the described method. 50 mL of tetrabutyl-orthotitanate were dissolved in 200 mL of ethanol and the solution was stirred for 30 minutes at room temperature followed by the addition of a mixture of deionised water and 0.1 M nitric acid under vigorous stirring. The addition of a mixture of deionised water and 0.1 M nitric acid was stopped after the mixture became sol. Once the TiO_2 sol was prepared, 50 grams of activated carbon were introduced into the solution. After gelation of the sol, the impregnated activated carbons were heat treated at 200 $^\circ\text{C}$ in an oven for 4 hours. The amount of TiO_2 loaded on activated carbon surface was estimated from ignition loss at 800 $^\circ\text{C}$ in an air atmosphere by using a muffle-furnace technique.

2.3. Sonocatalyst Characterization

The structure and morphology of the prepared TiO_2/AC were analyzed by a scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDX) (Zeiss Supra 35VP). The chemical compositions of the sonocatalyst were determined using Thermo Scientific, Nicolet iS10 fourier transform infrared spectroscopy (FTIR). The sample was tested after the completion of the blank spectrum scanning. The scanning range was set from 400 to 4000 cm^{-1} .

2.4. Sonocatalytic Degradation of Rhodamine B Dye

All experiments were performed using a multi-frequency ultrasonic bath (Telsonic TPC 280) with frequency of 30 kHz, 90 kHz, and 150 kHz. A 250 mL screw cap conical flask was used as the reactor. It was located in the bath (the position of flask was fixed in which maximum surface disturbance occurs to ensure uniformity of ultrasonic waves). In each experimental run, 100 mL aqueous solution of RB dye (200 mg/L) was added to the conical flask, and the pH value of the solution was adjusted using pH meter (Metrohm 827 pH lab) to a desired level using 0.1 M sulphuric acid or 0.1 M sodium hydroxide. The aqueous solution was irradiated in a multi-frequency ultrasonic bath at 30°C, 40°C, and 50°C for 60 minutes.

2.5. Analysis of Liquid Sample

After desired reaction time, all samples were filtered and the filtrates were sent for the measurement of RB concentration. The final concentration of RB by using a UV-Vis spectrophotometer (Model: Shimadzu UV-160PC) set at a wavelength of 554.3 nm. The degradation efficiency of RB dye is defined by:

$$P(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where P is the percentage (%) of degradation, C_0 and C_t are the initial dye concentration and dye concentration at measurable time t , respectively (mg/L).

3. Results and Discussion

3.1. Characterization of TiO₂/AC

Fig. 1 shows the comparison of SEM images for TiO₂/AC before and after the degradation using 3000 magnification and 1000 magnification, respectively. It is clear that the nanoparticles of TiO₂ aggregated into clusters and were successfully impregnated on the activated carbon as shown in Fig. 1(a). The structure of the sonocatalyst was modified and the number of TiO₂ nanoparticles (circled) became less after the degradation of RB dye. This can be observed in Fig. 1(b). The TiO₂/AC exhibits uneven and rough surface morphology [Fig. 1(a)] while the surface of RB dye-loaded adsorbent [Fig. 1(b)], however, clearly shows that the surface of TiO₂/AC is covered with a layer of dye. The composition of the TiO₂/AC was determined by energy dispersive X-ray spectroscopy (EDX). The atomic percentages (%) for spots were titanium (21.45%), carbon (44.63%) and oxygen (33.92%).

The IR spectra of TiO₂/AC were determined by FTIR and are shown in Fig. 2. Fig. 2(a) shows the spectra of TiO₂/AC which is composed of the peaks at 3442.07 cm⁻¹ (NH stretch), 2359.99 cm⁻¹ (N≡N stretch), 1630.55 cm⁻¹ (NH₂ deformation) and 491.69 cm⁻¹ (C-I stretch). Many new peaks appeared in the IR spectra of TiO₂/AC after degradation, it was clearly shown in Fig. 2(b). The new peaks can be assigned as follows: the peak at 1546.43 cm⁻¹ and 1534.89 cm⁻¹ were due to N-H stretching vibration. The band at 1461.25 cm⁻¹ was due to CH₂ deformation while the peak at 1384.03 cm⁻¹ was based by NH₂ deformation. The peak at 1048.27 cm⁻¹ can be assigned to C-O stretching vibration and the band at 534.19 cm⁻¹ was due to S-S stretch. In addition, the peaks around 585.08 cm⁻¹ and 575.45 cm⁻¹ were due to NO₂ bending vibration and benzene ring deformation, respectively.

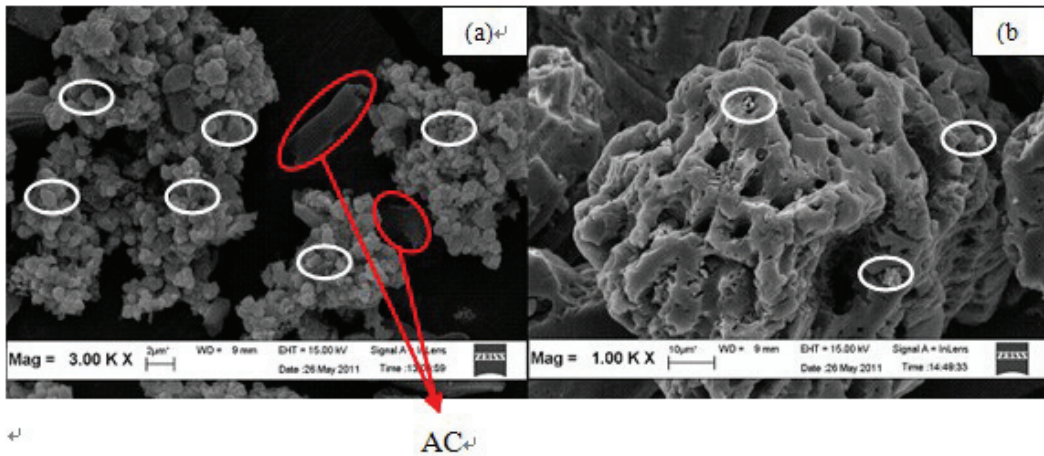


Fig. 1. SEM images of the particles of (a) TiO₂/AC before degradation, (b) TiO₂/AC after degradation.

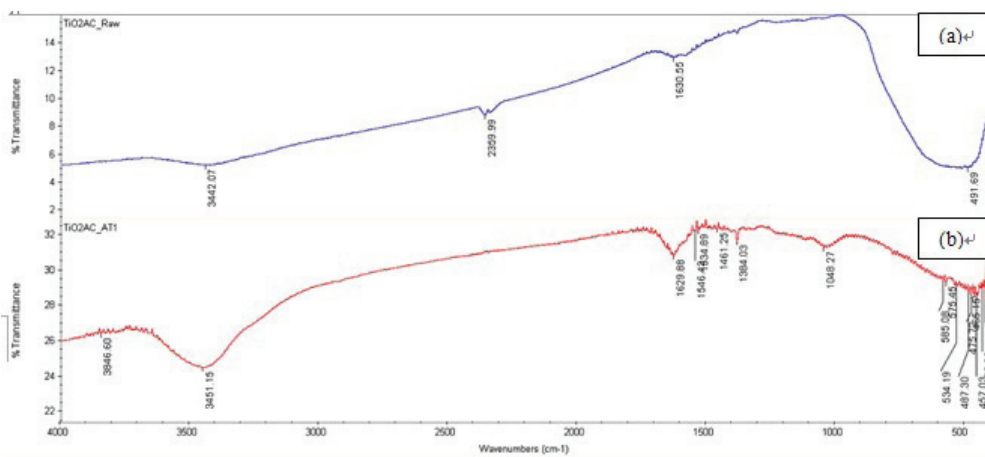


Fig. 2. IR spectra of (a) Raw TiO₂/AC, (b) Raw TiO₂/AC and TiO₂/AC after degradation.

3.2. Effect of Solution pH

The pH of the solution is an important parameter which affects the sonolysis process. The effect of solution pH on the degradation of RB dye was studied by varying the initial pH of the RB dye. The result was as shown in Fig. 3. The experiments were carried out at 50°C for 60 minutes at different initial pH of dye solution (pH 3, pH 6 and pH 9) with the presence (50 g of TiO₂/AC) or absence of sonocatalyst. The figure showed that the degradation of RB dye is more favourable at pH 6 as compared to pH 3 and pH 9. The degradation rate of RB dye with the addition of sonocatalyst is slightly higher than the degradation of RB dye using ultrasonic alone. RB molecule has an amine group that can be protonated at low pH. This protonated RB is easier to be degraded under acidic condition. The degradation rate was found to increase with oxidation potential of ·OH radical in the acidic medium as reported by Wang et al. [9].

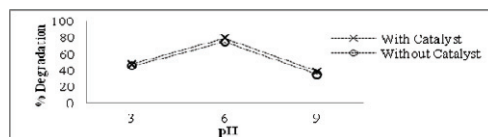


Fig. 3. Effect of solution pH on the degradation efficiency of RB with and without TiO_2/AC .

3.3. Effect of Temperature

The effect of temperature on the degradation of RB dye is illustrated in Fig. 4. The experiments were done at pH 6 for 60 minutes with the presence or absence of TiO_2/AC at different temperatures. The degradation rate of RB occurred at 50°C was the best degradation rate among the others. Higher temperature can increase the quantity of cavitation bubbles and results in the increase of degradation rate. However, cavitation bubbles formed at higher temperature (higher than 60°C) will produce more water vapor. This water vapor reduces the temperature and pressure generated when cavitation bubbles collapse and hence reduces the degradation efficiency on organic compounds. Wang et al. [10] reported that ultrasonic cavitation is weakened because of rapid volatilization of gas from aqueous solution at high temperature.

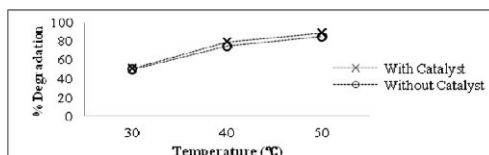


Fig. 4: Effect of temperature on the degradation efficiency of RB with and without TiO_2/AC .

3.4. Effect of Ultrasonic Frequency

Fig. 5 showed the effect of ultrasonic frequency on the degradation rate of RB dye at pH 6 and 50°C for 60 minutes with the presence or absence of TiO_2/AC at different ultrasonic frequency. 30 kHz gave the best RB degradation rate with the addition of sonocatalyst. A higher degradation rate was obtained at the lower ultrasonic frequency. This phenomenon is caused by the production of cavitation in the liquid that increases when the ultrasonic frequency decreases [11].

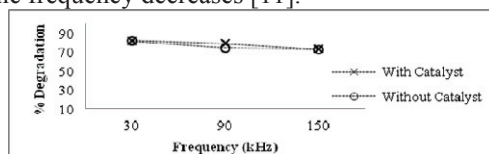


Fig. 5. Effect of ultrasonic frequency on the degradation efficiency of RB with and without TiO_2/AC .

3.5. Effect of Sonocatalyst

Obviously, the sonocatalyst can degrade some anionic dyes completely, but the cationic dyes cannot be degraded efficiently. The reason can be explained that anionic dyes such as acid red and azofuchsine molecules and cationic dyes such as Rhodamine B and ethyl violet molecules have different charges after ionization. Thus, the electrostatic attraction or repulsion has occurred between organic dye ions and TiO_2/AC particles, which result in the difference degradation ratios [10].

4. Conclusion

TiO₂/AC appeared to be an effective sonocatalyst for sonocatalytic degradation of RB dye in aqueous solution. Sonocatalytic degradation of RB dye could be achieved up to 82.21% degradation efficiency with the addition of sonocatalyst (TiO₂/AC). The best conditions of the sonocatalytic degradation of RB are: pH 6, temperature of 50°C, ultrasonic frequency of 30 kHz in the presence of sonocatalyst for 60 minutes.

Acknowledgements

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