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

Soke Kwan Tang, Tjoon Tow Teng, Abbas F. M. Alkarkhi, and Zhimin Li

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, at temperature 50°C, under ultrasonic frequency of 30 kHz with the presence of sonocatalyst for 60 minutes.

Index Terms—Activated carbon, rhodamine B, titanium dioxide, ultrasound.

I. 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 (RB) 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 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].

Ultrasound irradiation appears an effective method for the degradation of organic chemical pollutants in water and/or wastewater, such as pesticides, aromatic compounds, and chlorinated hydrocarbons [7-11] Sonolysis can degrade volatile organic compounds through chemical process inside the bubble [12], the surface active compounds at the interface of the bubble [7] which happen upon collapse of the cavitation. The solute molecules that cannot diffuse to the two mentioned locations are likely to undergo radical attack by hydrogen atoms and hydroxyl radicals formed from the homolysis of water [13, 14]. Sonolysis of water causes the formation of cavities and their subsequent collapse, which may generate enormous local temperature and pressure rises; consequently, water can be decomposed to hydrogen atoms and hydroxyl radicals [8]. Ultrasound also exhibits several beneficial mechanical effects in solid-liquid systems by means of the cavitation phenomenon; it causes the formation of many micro-cracks on the solid surface, thus increases the surface area between the reactants, it also cleans solid reactant or catalyst particle surfaces.

Combination of ultrasound with adsorption process was found to be more promising in the elimination of macromolecules such as phenols and dyes. Cavitational effects are dependent on the extent of deformities present in the system in order to enable the formation of cavities. Presence of sonocatalyst in the system might ease the process of cavitation and thus intensify the cavitational activity in the reactor. The sonocatalyst can simple be inert solids or can have catalytic action in terms of promoting the rates of dissociation of the oxidants, scavenging the undesired radical species. Presence of solid particles provides additional nuclei for the cavitation process and thus the numbers of cavitation events occurring in the reactor are enhanced resulting in a subsequent enhancement in the cavitation process and hence the net chemical effects [15].

In this work, ultrasound will be introduced to degrade the RB dye compounds. In an effort to find an effective way for enhancing the efficiency of the ultrasonic-based degradation of organic pollutants with lower cost, we will apply ultrasonic irradiation together with addition of titanium dioxide coated activated carbon (TiO₂/AC). The particular interest in this work is to develop the suitable catalyst to be added in order to obtain the best degradation rate of RB dye compounds from aqueous solutions. The characteristics and
process behavior of TiO$_2$/AC will be determined by various characteristics test. In addition, the priority will be investigating the effectiveness of the TiO$_2$/AC against the degradation of RB dye compounds from aqueous solutions.

II. MATERIALS AND METHODS

A. Materials

Rhodamine B dye (abbreviation: RB; C.I. number: 45170; molecular formula: $C_{28}H_{31}N_2O_3Cl$) was used as a model solute. RB dye, activated carbon, tetrabutyl-orthotitanate ($C_{16}H_{36}O_4Ti$, 97%), ethanol (C$_2$H$_5$OH, 95%), nitric acid (HNO$_3$, 65%), sulphuric acid (H$_2$SO$_4$, 97%) as well as sodium hydroxide (NaOH, 99%) were obtained from R&M Chemicals. Distilled water was used throughout the experiments.

B. 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 [16] 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°C in an oven for 4 hours. The amount of TiO$_2$ loaded on activated carbon surface was estimated from ignition loss at 800°C in an air atmosphere by using a muffle-furnace technique.

C. 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$^{-1}$.

D. Sonocatalytic Degradation of Rhodamine B Dye

All experiments were performed using a multi-frequency ultrasonic bath (Telsonic TPC 280) with frequencies 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. Another set of aqueous solution was added with 0.5 g of sonocatalyst as a comparison to determine the effectiveness of ultrasound alone without the addition of sonocatalyst. The aqueous solution was irradiated in a multi-frequency ultrasonic bath at 30°C, 40°C, and 50°C for 60 minutes.

E. 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:

$$P\, (\%) = \frac{C_0 - C}{C_0} \times 100$$  \hspace{1cm} (1)

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

III. RESULTS AND DISCUSSION

A. Characterization of TiO$_2$/AC

Fig. 1 shows the comparison of SEM images for TiO$_2$/AC before and after the degradation using 3000 magnification and 1000 magnification, respectively. It is clear that the nanoparticles of TiO$_2$ 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 TiO$_2$ nanoparticles (circled) became lesser after the degradation of RB dye. This can be observed in Fig. 1(b). The TiO$_2$/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 TiO$_2$/AC is covered with a layer of dye. The composition of the TiO$_2$/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 TiO$_2$/AC were determined by FTIR and are shown in Fig. 2. Fig. 2(a) shows the spectra of TiO$_2$/AC which is composed of the peaks at 3442.07 cm$^{-1}$ (NH stretch), 2359.99 cm$^{-1}$ ($N=N$ stretch), 1630.55 cm$^{-1}$ (NH$_2$ deformation) and 491.69 cm$^{-1}$ ($C-I$ stretch). Many new peaks appeared in the IR spectra of TiO$_2$/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 vibration and benzene ring deformation, respectively.

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. Another set of aqueous solution was added with 0.5 g of sonocatalyst as a comparison to determine the effectiveness of ultrasound alone without the addition of sonocatalyst. The aqueous solution was irradiated in a multi-frequency ultrasonic bath at 30°C, 40°C, and 50°C for 60 minutes.
B. 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 by varying different initial pH of dye solution (pH 3, pH 6 and pH 9) with the presence (0.5 g of TiO2/AC) or absence of sonocatalyst under 30 kHz ultrasonic irradiation. The figure showed that the degradation of RB dye is more favourable at pH 6 as compared to pH 3 and pH 9 in both situations. Improvement in the degradation efficiency of dye in acidic medium was associated with the protonation of Rhodamine B that enriched the hydrophobicity of the molecules. This could enhance the approachability of the molecules to the bubble–liquid interface, where the maximum concentration of •OH radicals was achieved.

The deprotonation of carboxyl group could easily occur and transformed the cationic form of Rhodamine B into zwitterionic form when the solution pH is higher than the acid dissociation constant of RB [2]. Consequently, the change of hydrophobic property of the dye molecule could inhibit them from approaching the negatively charged cavitation bubbles as well as the surface of TiO2/AC. Besides, H2O2 molecules that were formed during ultrasonic process could become highly unstable and easily self-decomposed in basic medium. The conjugate base of H2O2, −OOH anions could also react with both the •OH radical as well as H2O2 molecules in basic medium. Thus, it would decrease the concentration of •OH radicals and consequently affect degradation efficiency of Rhodamine B. The degradation rate was found to increase with oxidation potential of •OH radical in the acidic medium as reported by Wang et al. [17]. The degradation rate of RB dye with the addition of sonocatalyst is slightly higher than the degradation of RB dye using ultrasonic alone. The degradation efficiency of RB dye could reach 79.67% with the addition of TiO2/AC at pH 6. The degradation efficiency of RB dye at pH 3 and pH 9 was 47.56% and 38.67%, respectively with the addition of sonocatalyst.
Fig. 3. Effect of solution pH on the degradation efficiency of RB with and without TiO2/AC.

C. 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 TiO2/AC at different temperatures and under 30 kHz ultrasonic irradiation. The degradation rate of RB occurred at 50°C with the addition of sonocatalyst was the best degradation rate among the others which reached 88.46% as compared to 50.60% and 79.17% at 30°C and 40°C, respectively. As it is known the rate of diffusion of the sorbate molecule is increased by increasing the temperature, owing to the decrease in the viscosity of the solution. Higher temperature can increase the quantity of cavitation bubbles and results in the increase of degradation rate but less violent collapse. At higher temperatures approaching solvent boiling point a large numbers of cavitation bubbles are generated concurrently. This could act as a barrier to sound transmission and thus dampen the effective ultrasonic energy from the source which enters the liquid medium.

In addition, the operating temperature was studied until 50°C as the system might produce more water vapor when cavitation bubbles formed at higher temperature (temperature higher than 60°C). 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. [18] reported that ultrasonic cavitation is weakened because of rapid volatilization of gas from aqueous solution at high temperature.

D. Effect of Ultrasonic Frequency

Fig. 5 shows 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 TiO2/AC at different ultrasonic frequency. 30 kHz gave the best RB degradation rate with the addition of sonocatalyst which reached 82.21%. The degradation rate of RB dye was 79.17% and 73.22% at 90 kHz and 150 kHz, respectively.

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 [19]. At higher frequency, the rarefaction and compression cycles become shorter, the finite time required for the rarefaction cycle becomes too short to permit the molecules to be pulled apart sufficiently in order to generate a bubble.

E. Effect of Sonocatalyst

The increase in the degradation rate in the presence of sonocatalyst was mainly due to the presence of solid particles in a liquid which increased the nucleation sites for cavity formation. TiO2/AC could also act as a catalyst to promote water dissociation reactions when the electron shifts from the valence band to the conduction band, leaving behind a hole in the valence band. These holes are not only capable to decompose the organic dyes adsorbed on the surface of TiO2 particles directly; they could also accelerate the generation of ·OH radicals through the dissociation of H2O molecules in the bulk solution. Therefore, the use of TiO2/AC as a sonocatalyst in this work could significantly accelerate the degradation process as compared to sonolysis alone [20]. 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 azofuchsin 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 TiO2/AC particles, which result in the difference degradation ratios [18].

IV. 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. The experiments can be extended to study the degradation efficiency of Rhodamine B dye by varying the initial concentration of RB dye and also the amount of sonocatalyst (TiO₂/AC) to be added into the system. Besides, the applications of ultrasound with the addition of sonocatalyst appeared as another effective method in wastewater treatment and thus attract more attention from the researchers to discover new findings.

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REFERENCES


Soke Kwan Tang holds a Bachelor Degree in Environmental Technology in 2008 and secured a Master Degree in Environmental Engineering a year later from Universiti Sains Malaysia (USM). She is currently pursuing a doctoral degree (Ph.D) in Environmental Technology at the same university. Her research mainly emphasis on wastewater treatment and currently focus on sonolysis of dye waste from aqueous solutions.

Tjoon Teng is a Professor in School of Industrial Technology at Universiti Sains Malaysia (USM). He graduated with a first-class honours bachelor’s degree in Chemical Engineering at Nanyang University, Singapore in 1969 and secured his Master’s and doctoral (Ph.D) degrees in Chemical Engineering in 1971 and 1975, respectively at Universite de Montreal, Canada.

He has been granted a Post-doctoral fellowship in Universite de Montreal in 1975 after obtained his doctorate. He started his career as a lecturer at USM, Malaysia in 1975, and has been dynamic in research works ever since. He has research experienced in various areas of chemical engineering as well as environmental science and technology with particular emphasis on wastewater treatment, acid-gas removal and aqueous solution properties.

Prof Teng is a council member of the Malaysian Institution of Chemical Engineers, a member of the Canadian Society for Chemical Engineers, and a member of the American Chemical Society. He is also a member of the Editorial Board of the Journal of Physical Sciences. His professional activities include being council member of the IChEM, sitting in the technical committee of Conferences/Symposiums related to the profession of chemical engineering and to his field of research. His current research interests are: physical properties of aqueous multi-component solutions, acid gas removal, and industrial wastewater treatment. He has published more than 100 publications. He has acted as an external assessor for academic promotion of other universities and as a referee for papers in the Journal of Physical Sciences.

Abbas F. M. Alkarkhi is an Associate Professor of Statistics at the School of Industrial Technology, Universiti Sains Malaysia. He graduated with a bachelor’s and master degrees in statistics from Baghdad University in 1985 and 1992, respectively and secured his doctorate (Ph.D) in applied statistics at Universiti Sains Malaysia in 2002.

He has worked in Iraq and Libya before joining Universiti Sains Malaysia in 2002. He has taught a number of courses in statistics since 1992. His specialization is in statistics (optimization and experimental design, and multivariate methods) and he has done a research on the applications of optimization and multivariate analysis.

Dr. Abbas has involved in teaching short courses as well as collaborated with his colleagues in the School of Industrial Technology in publishing papers in national and international journals.

Zhimin Li is originally from Lan Zhou, Gan Su, China. She completed her Bachelor degree in Environmental Technology in 2011. She is currently pursuing a Master degree in Environmental Technology as well at the same university.

Currently, she is focusing on the adsorption of heavy metals from wastewater.