



Efficient Degradation of Methyl Violet 10B Dye by Different Light Sources using Boron-doped TiO₂-ZnO Photocatalyst

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Received: 13 August 2024;

Accepted: 11 October 2024;

Published online: 30 October 2024;

AJC-21789

Boron-doped TiO₂-ZnO nanocomposite was prepared by sonochemically using boron trichloride, tetra *n*-butyl orthotitanate and zinc acetate in appropriate proportion. The as-prepared nanocomposite was successfully characterized by XRD, EDX, SEM and BET techniques. The operational factors that affect the rate of photocatalytic degradation of methyl violet 10B present in wastewater were optimized, which include initial dye concentration, catalyst amount, pH level and different light intensities such as incandescent light bulb, UV lamp and sunlight. During sonication under sunlight, it was found that the most effective removal rate achieved was 95% when using 0.02 g of B doped TiO₂-ZnO per 100 mL of methyl violet 10B solution. The impact of different dye concentrations on the photocatalytic degradation demonstrated the threshold at which concentrations may be readily eliminated. The most effective pollutant degradation was achieved at 5 ppm. The introduction of oxygen using sonophotocatalysis process into the polluted stream enhanced the photocatalytic breakdown of the pollutants. The photocatalyst can be recycled for four cycles without loss the catalyst stability and the degradation rate obeys first-order kinetics.

Keywords: Boron, Methyl violet 10B dye, Sonophotocatalysis, Photocatalytic degradation, Wastewater.

INTRODUCTION

The growing issues around energy and the environment have led to a major emphasis on clean energy source advocacy in recent years [1,2]. The conversion of solar energy into useful resources is the primary focus of comprehensive study efforts [3] and now utilized in applications such as photochemical cells, solar cells and photocatalysis [4]. Photocatalytic breakdown of organic dye pollution is of significant interest because of its practical uses and economic advantages. Various methods, such as adsorption, reduction, oxidation, electrochemical processes and membrane filtering, have been used to eliminate these contaminants from industrial wastewaters [5]. In recent years, research in photocatalysis has substantially accelerated, as this technology is regarded as clean, eco-friendly and energy efficient for wastewater treatment, achieving the complete mineralization of dangerous pollutants.

The photocatalytic degradation method is highly effective in eliminating organic contaminants from wastewater and is

considered one of the most effective advanced oxidation processes (AOPs). It has been widely employed in the treatment of wastewater ever since powdered photocatalysts were developed. However, the powdered catalysts face challenges due to their limited reusability in suspension systems and lower absorption in the visible light spectrum. To address these issues, a more efficient technique is needed to decrease the catalyst dose or alternative chemical based oxidant. The unique qualities of nanobubbles influence the surrounding medium resulting in the improvement of the AOPs efficiency to eliminate the secondary pollutants, which in turn makes the process more efficient and less harmful to the environment [6].

Titanium dioxide (TiO₂) has garnered significant interest among semiconductor materials because of its exceptional photocatalytic efficiency, durability against photo-corrosion, photostability, affordability and non-toxic nature [7,8]. It has been proven possible to purify and remediate polluted waters with even low quantities of contaminants by using TiO₂ as a photocatalyst. The broad band gap of 3.2 eV allows activation

only by UV radiation and prevents indoor use. The high integration rate of photogenerated electron-hole pairs reduces the photocatalytic efficiency of TiO₂. Extensive doping techniques are used to alter the electrical properties of TiO₂ in order to enhance catalytic performance [9,10]. Metal doping may modify the phase change of TiO₂, affecting its photocatalytic activity. Boron is a doping agent of interest for photocatalysis [11-15].

This work focuses on the synthesis of boron-doped TiO₂-ZnO nanoparticles by sonochemically and characterized by XRD, EDX, SEM and BET techniques. Moreover, as-prepared material was used as photocatalyst in degrading methyl violet 10-B dye under different light intensities such as incandescent light bulb, UV lamp and sunlight and compared their efficiencies too.

EXPERIMENTAL

Tetra *n*-butyl orthotitanate ([Ti(O-Bu)₄]), zinc acetate (ZnAc), boron trichloride (BCl₃), ethanol and hydrochloric acid were used. Sigma Aldrich supplies all of the chemicals, which are 99% pure and used as such.

Characterization: The XRD analysis of the as-synthesized nanocomposite was carried out using CuK α radiation of D2 phaser Bruker at room temperature, ranging 2 θ value from 10° to 80° with a scanning rate of 0.02° per second. The UV-Vis spectra of boron-doped TiO₂-ZnO nanocomposite were taken between 200 and 1100 nm by SYSTRONICS 2203 double beam spectrophotometer.

Catalyst preparation: Three separate solutions *viz.* 2% boron trichloride as dopant with 50 mL of ethanol in 100 mL beaker; 50 mL of tetra *n*-butyl orthotitanate in 50 mL of ethanol and 40 g of zinc acetate in 40 mL of ethanol and 40 mL of distilled water were mixed in a separate beakers and stirred continuously for 30 min. Finally, 36 mL of 4.4 M HCl was added slowly to zinc acetate solution and stirred for 30 min. All the solutions were mixed together with continuous stirring for another 30 min. After that the solution was sonicated when exposed ultrasonic waves using ultrasonic probe (TransO-

Sonic, Model: D-120/P) for 45 s using 25 \pm 3 kHz frequency, dried in a vacuum at 100 °C and finally calcined at 600 °C.

Photocatalytic degradation studies: The synthesized material were tested for their photocatalytic activity by decomposing methyl violet 10B dye in an aqueous solution. Using a sonicator, the experiment was carried out in the open air and in sunlight. Comparison studies were conducted to determine whether dark adsorption impacts the photocatalytic effect. Light irradiation was selected because of the minimal degradation in darkness. For the photocatalytic breakdown test, a 100 mL solution of methyl violet 10B was mixed with 0.02 g of catalyst at a concentration of 5 mg/L. A 5 mL of sample was taken periodically, centrifuged and examined employing a UV-visible spectrophotometer at a wavelength of 580 nm. The degradation efficiency % of the solution was determined using a following formula:

$$\text{Degradation efficiency (\%)} = \frac{C_o - C_t}{C_t} \times 100$$

where C_o and C_t are the concentrations before and after degradation at the specific interval of time.

RESULTS AND DISCUSSION

SEM and EDAX studies: Fig. 1a displays the SEM image of B doped TiO₂-ZnO nanocomposite. The porous nature of TiO₂ is crucial for achieving a high roughness factor and facilitating the entry of redox couples into the mixture. The majority of B doped TiO₂-ZnO powders exhibit uniformity with distinct grain boundaries. The B doped TiO₂-ZnO consists of linked polygonal, sporadic shaped particles. Fig. 1b depicts the results of energy-dispersive X-ray spectroscopy (EDX) performed on boron-doped TiO₂-ZnO. The prominent peak provides evidence of the existence of oxygen, titanium, zinc and boron in the nanocomposite.

XRD studies: The 2 θ values of B doped TiO₂-ZnO show peaks at 15°, 25°, 33°, 35°, 56°, 62° and 75° correspond to the crystallographic planes (001), (101), (100), (002), (110), (103) and (110) as seen in Fig. 2. The peaks were compared to the

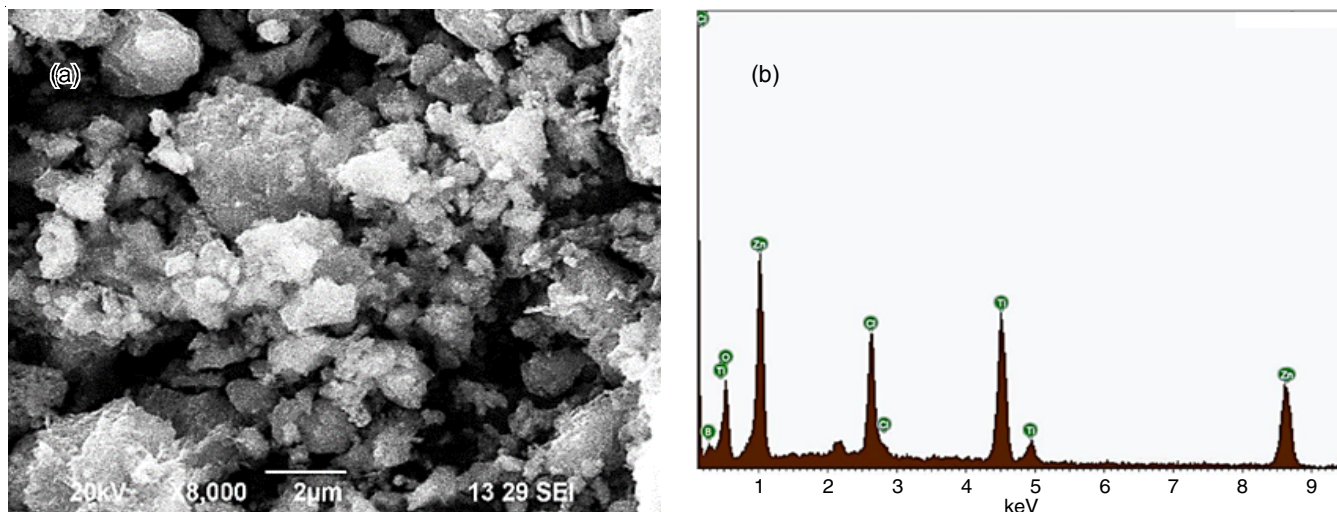


Fig. 1. (a) SEM and (b) EDX analysis of boron doped TiO₂-ZnO photocatalyst

baseline value on the JCPDS card nos. 21-1272, 36-1451 and 85-1068. The presence of these diffraction peaks indicates that TiO₂ has a tetragonal (anatase) crystal structure, whereas ZnO and boron have a hexagonal crystal structure.

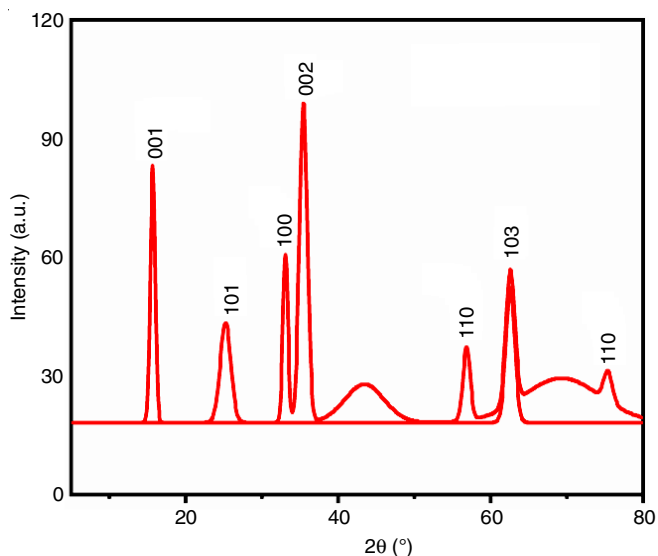


Fig. 2. XRD spectrum of boron doped TiO₂-ZnO photocatalyst

BET studies: Fig. 3a displays the nitrogen adsorption-desorption isotherm, representing the surface region of the BET analysis performed on boron doped TiO₂-ZnO photocatalyst. The loop observed in Fig. 3b shows hysteresis in the initially formed loop due to mono-multilayer adsorption, which is followed by desorption in the subsequent loop. The pore volume was determined at 6.7137 nm and its dimension at 0.911 cm³/g. The specific surface area, as determined by Brunauer-Emmett-Teller, was found to be 439.07 m²/g.

Degradation under various light sources: The stability of pollutants in wastewater is frequently evaluated under accelerated testing conditions using typical light sources. The intensity and wavelength of radiation may have different results

based on the light source employed [16]. An experiment was conducted using methyl violet 10B dye with a B doped TiO₂-ZnO catalyst under different light sources.

UV light lamp: The photocatalytic degradation studies were conducted in a custom-made double-walled reaction glass UV chamber equipped with 18 W UV tubes emitting energy at 365 nm wavelength. Water was circulated through the jacketed wall reactor to provide a consistent temperature. The dye underwent degradation under these conditions and samples were taken at 30 min intervals over a period of 3 h. Ultimately, the degradation rate of dye was determined to be 55%.

Incandescent light bulb: An enclosed box was used to hide a 200-watt incandescent light bulb, which was then put within the box and covered with a black cloth. It was determined that the samples should be stirred after being put at a distance of 20 cm from the incandescent light bulb. An interval of 30 min was followed by the collection and measurement of the aliquots. The breakdown rate of dye molecules under incandescent light bulb was 57%.

Sunlight: The experiment was carried out on a bright and sunny day. A magnetic stirrer was set up and the solution beaker was allowed to swirl. The beaker was then positioned in such a way that the sunlight rays directly hit the solution beaker. Aliquots were removed at regular intervals of 30 min. The photodegradation rate of methyl violet 10B dye under sunlight was determined to be 78%. Introducing more photons with greater intensity enhances photodegradation efficiency and accelerates reaction rates in the system [17-22].

Sonophotocatalysis: Sonophotocatalysis is more efficient in degradation due to the catalyst being bombarded by ultrasonic vibrations. Using sunlight instead of a UV lamp and an incandescent light bulb resulted in a greater colour eradication rate in the photocatalytic process. The natural sunlight had a light intensity of around 950 to 1000 W m⁻² lux, which was greater than that of the UV lamp (18 W) and the incandescent light bulb (200 W). However, further study is needed to investigate the impact of different ranges of UV-light intensity on the

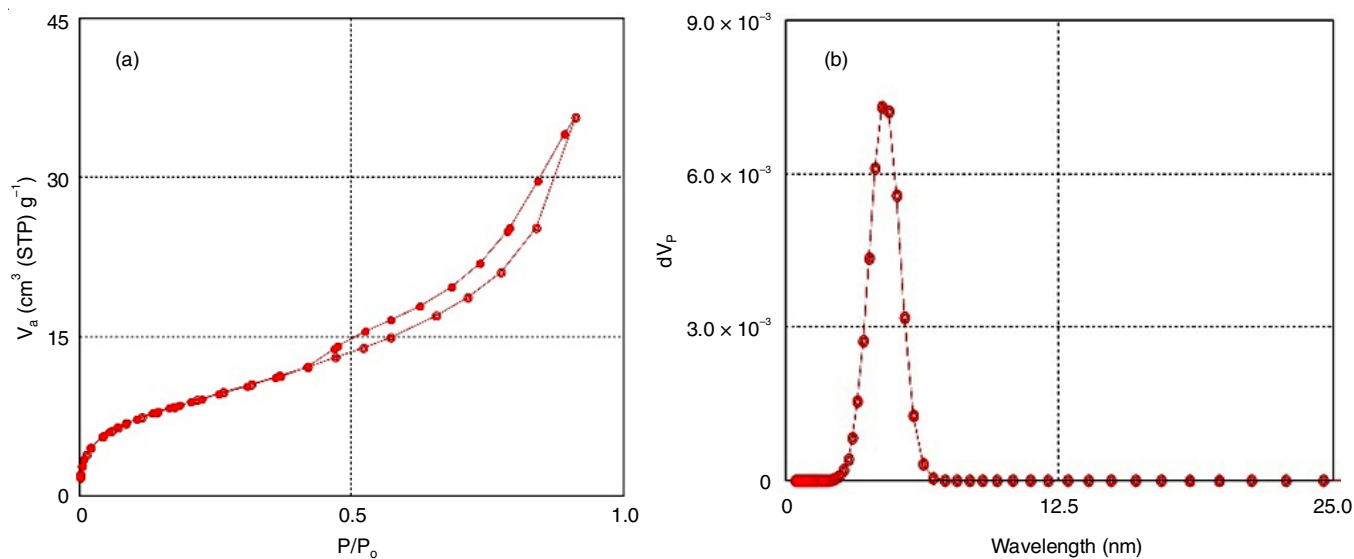


Fig. 3. (a) N₂ adsorption-desorption isotherm (b) pore size analysis of boron doped TiO₂-ZnO

colour removal. The actual temperature of the resulting solution was greater than when the UV lamps were used. This is due to the presence of several forms of radiant energy in sunlight, which also release invisible heat. The comparative trials employing various light sources demonstrated varying colour removal efficiencies: 57% degradation under an incandescent light bulb, 55% under an UV lamp, 78% under sunlight and 95% degradation with sonication in the presence of sunlight as shown in Fig. 4.

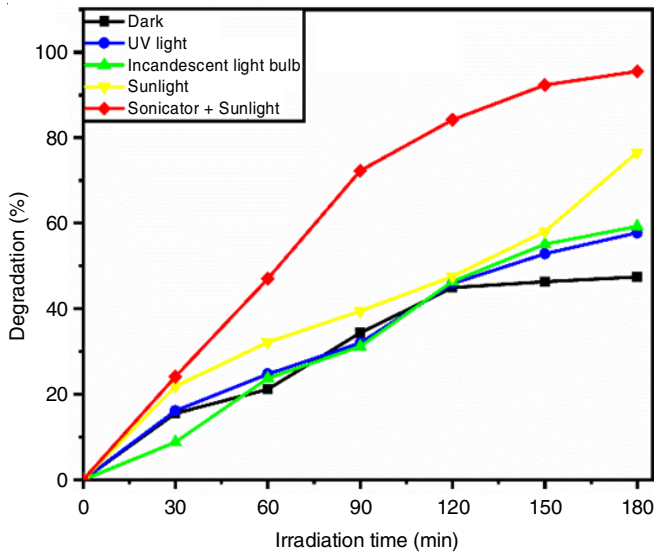


Fig. 4. Photodegradation of methyl violet 10-B under various light source by boron doped TiO₂-ZnO photocatalyst

Degradation in presence of oxygen: Oxygen in solution acts as a charged particle receptor in photocatalysis reactions. It acts as an electron absorber by capturing the excited band of conduction electron to prevent fusion. The degradation experiments were carried out under sunlight using methyl violet-10B (5 ppm) with B doped TiO₂-ZnO (0.02 g) in the presence of ambient oxygen at pH 12. Fig. 5 shows that 97% of MV 10B dye breakdown occurred within 180 min.

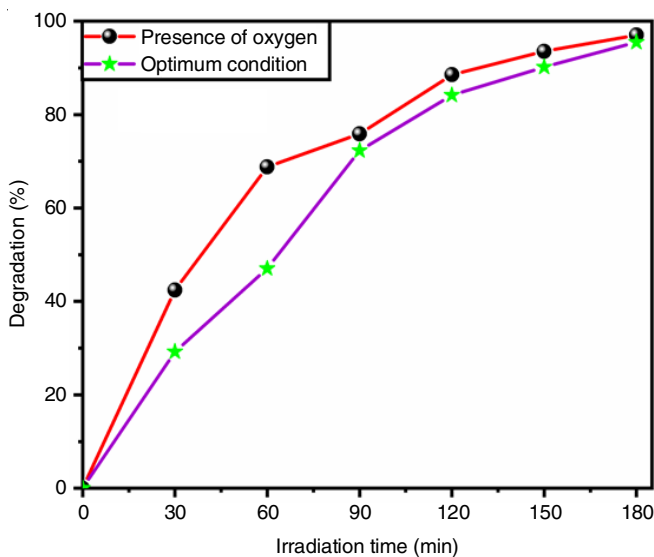
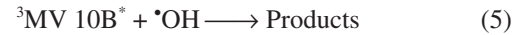
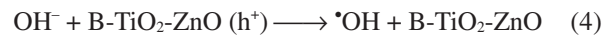
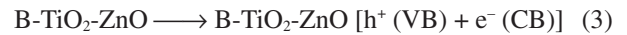


Fig. 5. Degradation in presence of oxygen

Mechanism: Experimental evidence suggests that the following is a possible process for the photocatalytic breakdown of methyl violet 10B (MV 10B):



Under the influence of B-doped TiO₂-ZnO nanocomposite as photocatalyst, methyl violet 10B dye molecules were stimulated to the transition to the first excited singlet state (¹MV 10B^{*}) when exposed to sunlight. Intersystem crossover (ISC) subsequently moves these molecules in an excited state to the triplet state (³MV 10B^{*}). Conversely, the semiconductor boron doped TiO₂-ZnO absorbs photons and generates an electron-hole pair, resulting in boron doped TiO₂-ZnO [h⁺ (VB) + e⁻ (CB)]. The hydroxide ion (OH⁻) will undergo a reaction with the hole in the semiconductor, resulting in the formation of hydroxyl radicals (^{*}OH). These radicals would subsequently convert the dye molecules in the triplet state (³MV 10B^{*}) into the products [23,24].

Kinetic study: Fig. 6 demonstrates the kinetics of methyl violet-10B disappearance at the optimal conditions and in the presence of oxygen. The findings indicate that the photocatalytic breakdown of methyl violet-10B dye follows a first-order kinetic model, represented by the equation:

$$\ln \frac{C_0}{C} = kt \quad (1)$$

where C₀ is the concentration prior irradiation and C is the concentration that exists after irradiation at time interval. The R² value was found to be 0.9875 in the presence of oxygen and 0.9797 under perfect conditions. The rate constants were determined to be 0.0189 min⁻¹, with a corresponding half-life of 36.57 min.

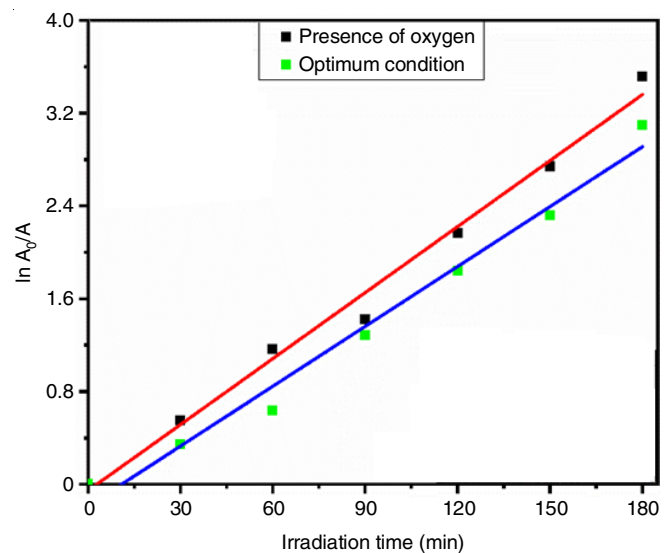


Fig. 6. Kinetic plot after degradation of methyl violet 10-B

Recycling of photocatalyst: A recycling experiment was conducted using methyl violet 10B dye for up to four cycles to assess the reusability of boron doped TiO₂-ZnO nanocomposite as photocatalyst. After each run, the catalyst was separated, rinsed to remove the colourant and then drained for use in photo-degradation. In the following cycles, the proportion of catalyst to dye concentration used in the first cycle varied. However, as the cycle number increases, the degradation efficiency falls to 54% (Fig. 7). This might be because some catalyst is lost during the washing and drying process.

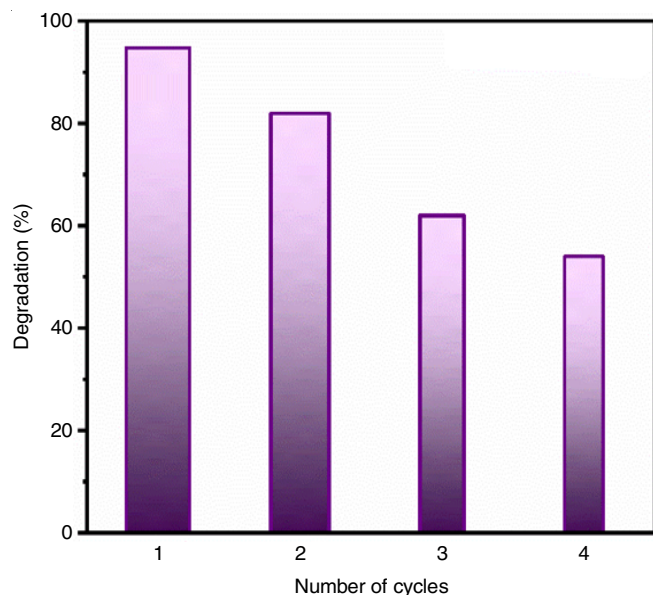


Fig. 7. Recycling of boron doped TiO₂-ZnO photocatalyst

Conclusion

This work revealed the photocatalytic activity of a boron-TiO₂-ZnO photocatalyst, which was synthesized sonochemically. The morphology of boron doped TiO₂-ZnO was polygonal, with particles size measuring 11.9 nm. Using 0.02 g of B doped TiO₂-ZnO per 100 mL of methyl violet 10B solution resulted in the highest effective removal rate of 95% during sonication under sunlight. The degradation experiments were performed using several light sources, among which the dye methyl violet 10B dye exhibited a high degradation rate when exposed to sunlight and subjected to sonophotocatalysis. This can be attributed to the bombardment of the dye molecules by ultrasonic waves. The injection of oxygen into the contaminated stream increased the photocatalytic degradation of the contaminant to 97%. The deteriorating rate follows first-order kinetics. The photocatalyst was recycled for four cycles to determine its stability and the deterioration decreased with succeeding runs owing to catalyst loss during washing.

ACKNOWLEDGEMENTS

The authors express their gratitude to Karunya Institute of Technology and Sciences, Coimbatore, Vel's Institute of Technology, Chennai and Scott Christian College, Nagercoil, India for providing the instrumentations facilities.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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