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RESEARCH PAPER

Harnessing Solar Energy: Photocatalytic Degradation of Cationic Dyes via Carbon-Doped TiO_2 Nanocomposites in Advanced Oxidation Processes

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ABSTRACT

The rapid pace of urbanization and industrialization has undoubtedly advanced modern manufacturing but has simultaneously contributed to severe environmental challenges, particularly through elevated levels of airborne emissions and wastewater discharges. Among various strategies to mitigate these impacts, titanium dioxide (TiO_2) has garnered significant attention as an effective photocatalyst, owing to its low cost, chemical stability, non-toxicity, and environmentally friendly nature. TiO_2 is recognized for its exceptional photocatalytic capabilities in degrading environmental pollutants, supported by its wide bandgap energy of 3.2 eV, characteristic of an n-type semiconductor.In this study, C/TiO_2 nanocomposite photocatalyst was synthesized via a straightforward hydrothermal method to enhance photocatalytic performance. The structural and morphological properties of the synthesized nanocomposite were thoroughly characterized using techniques such as X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM). A systematic investigation was conducted to optimize the photocatalytic degradation of Brilliant Blue (BB) dye by evaluating the influence of key operational parameters, including dye concentration, catalyst loading, irradiation time, and solution pH. Mathematical modeling identified the optimal conditions for maximum photocatalytic efficiency as follows: pH 7, catalyst mass of 0.2 g, BB dye concentration of 20 $mg{\cdot}L^{-1}$, and an irradiation period of 120 minutes. Under these conditions, a degradation efficiency of 90.25% was achieved, demonstrating the potential of the C/TiO_2 nanocomposite as an effective and sustainable photocatalyst for wastewater treatment applications.

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INTRODUCTION

Dyes are highly toxic compounds that can cause permanent damage to the eyes and skin of both humans and animals. They are widely used in various industries to add color to final products. Additionally, dyes are employed in chemical laboratories for analytical purposes and in many biomedical and biological labs as biological stains. One of the most notable dyes in this category is Brilliant Blue (BB). It has been extensively utilized for dyeing silk, wool, leather, jute, and cotton. BB also has applications in biomedical fields for treating dermatological diseases, in veterinary medicine, and for producing green inks. Furthermore, it is used in controlling intestinal parasites, dyeing fungal textiles, and in the printing of paper. As a result of these applications, wastewater from dye-related industries is often highly colored, contributing to water pollution and requiring treatment before disposal. Additionally, cationic dyes, known for their brightness, are soluble in water.[1-4]. Several methods have been commonly used to treat dye wastewater, including flocculation, coagulation, and membrane separation. However, many of these methods can be expensive and often create challenges related to sludge disposal. Adsorption presents a promising alternative for treating dye wastewater. This process is simple to manage, requires minimal maintenance, and generates little sludge. Consequently, recent advancements in separation and purification technologies have focused on the preparation and identification of cost-effective, readily available, and efficient adsorbents.[5-9].

Activated carbon has demonstrated significant potential for removing dyes due to its beneficial properties, including a large surface area, a microporous structure, and high adsorption capacity. However, the high cost of activated carbon has prompted the search for more affordable alternatives, particularly those derived from biological sources. Lignocellulosic agricultural waste, often disposed of through landfilling or incineration, has emerged as a valuable resource for producing carbon materials used in adsorption processes.[10-13]. Cellulosic materials offer several unique advantages, including environmental friendliness, availability, and low cost, making them suitable raw materials for producing activated carbon. Current state-of-the-art technologies focus on utilizing low-cost, reusable, locally available, and biodegradable adsorbents derived from natural sources. Examples include rice husks, wheat bran, apricot waste, sugarcane bagasse, fly ash, and peanut shell powder. In addition to these materials, various natural and modified clays, such

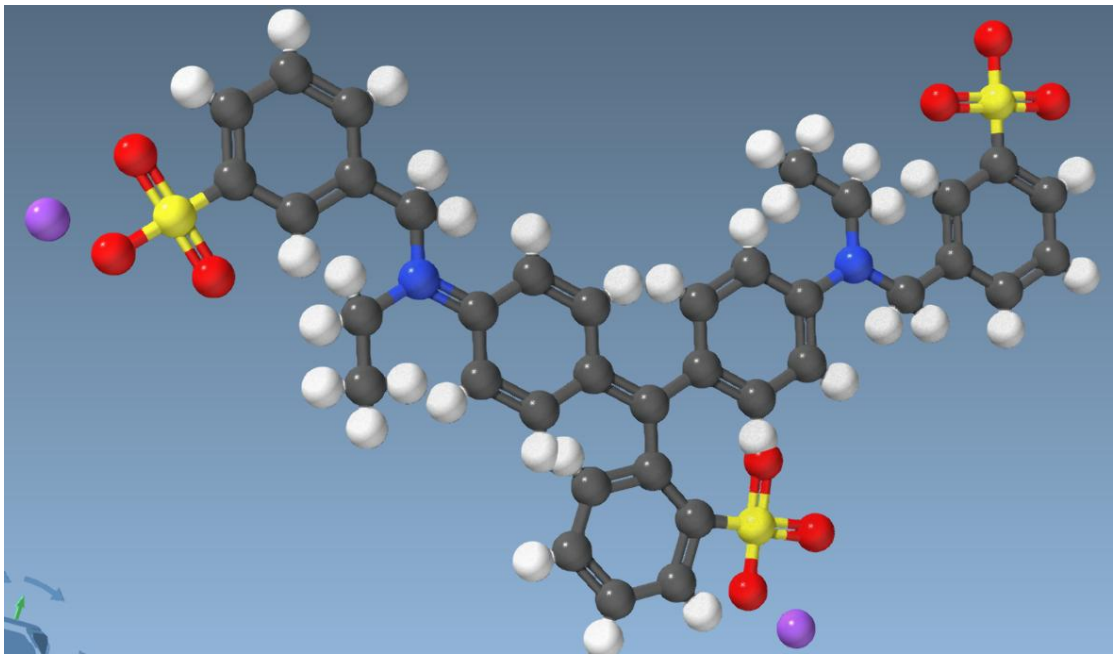

Fig. 1. Chemical structure of BB dye in 3D view

as sepiolite, zeolite, perlite, and bentonite, are also employed. Other organic materials used in the production of activated carbon include sugar industry clay, palm clusters, jackfruit peels, peat, orange peels, sugarcane dust, peat powder, neem leaves, oak seeds, olive seeds, and chemically treated guava leaf powder [14-17]. Fig. 1 shows the chemical structure of BB dye in 3D view designed by SAMSON software. This work focusing on preparation of C doped on TiO_2 and using it for applications of advanced oxidation processing for the prepared nanocomposite surface.

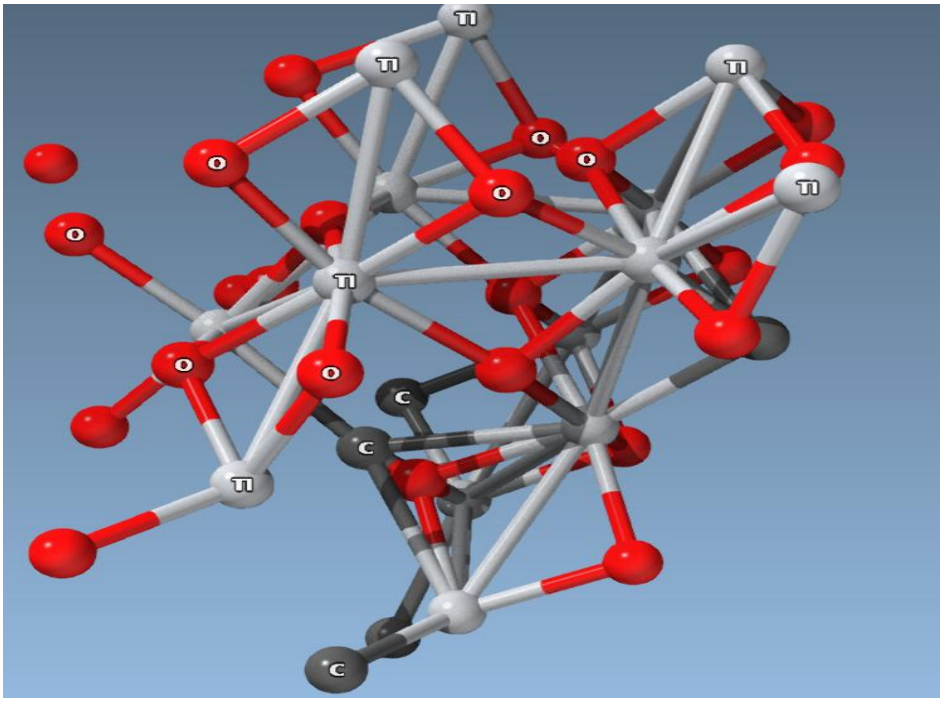

Fig. 2. CIF file generated by SAMSON software for Crystal structure of nanocomposite for carbon doped on TiO_2 surface

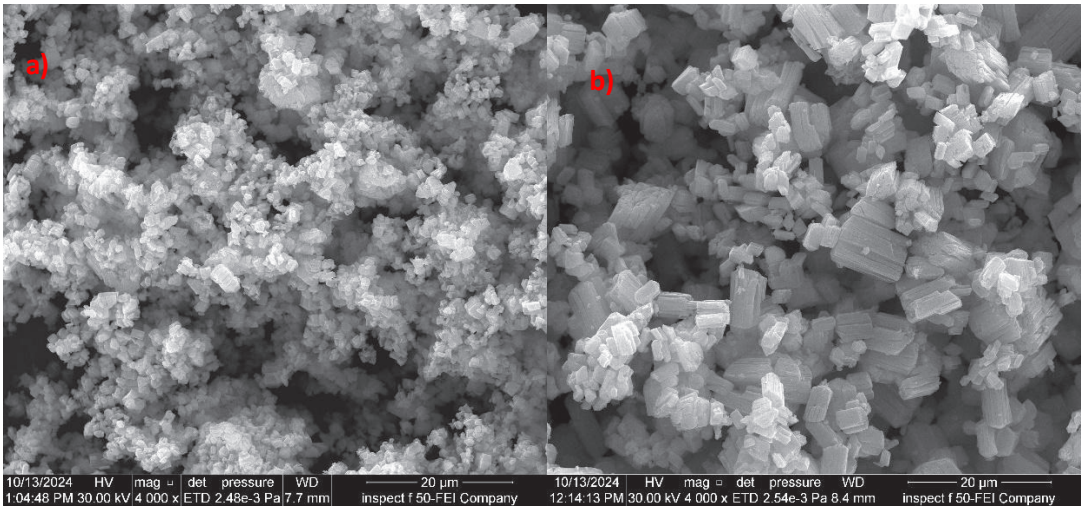

Fig. 3. FESEM image of a) activated carbon (AC) , b) carbon-doped titanium dioxide TiO_2/AC

MATERIALS AND METHODS

Preparation of activated carbon

The Hilla region of Iraq provided the palm fronds. The front was thoroughly washed to remove any debris, and then it was placed in an oven set to 80°C for the entire night to dry. It was crushed and filtered into particles ranging in size from 50 to 100 nm before being stored in an airtight container for subsequent use. Following one hour in a clean beaker of phosphoric acid to thoroughly mix the biomaterials, the mixture was thermally treated for two hours at 300 °C. Following its production, the carbon material was allowed to cool to ambient temperature, neutralized, dried in an oven set at 80 °C, and then placed in a tightly sealed container for future use.

Synthesis of TiO_2/AC nanocomposite

The hydrothermal approach was used to prepare the TiO_2-AC nanocomposite as follows: The activation-functionalized AC (0.75 g) was ultrasonically sonicated for 20 minutes in 50 mL of

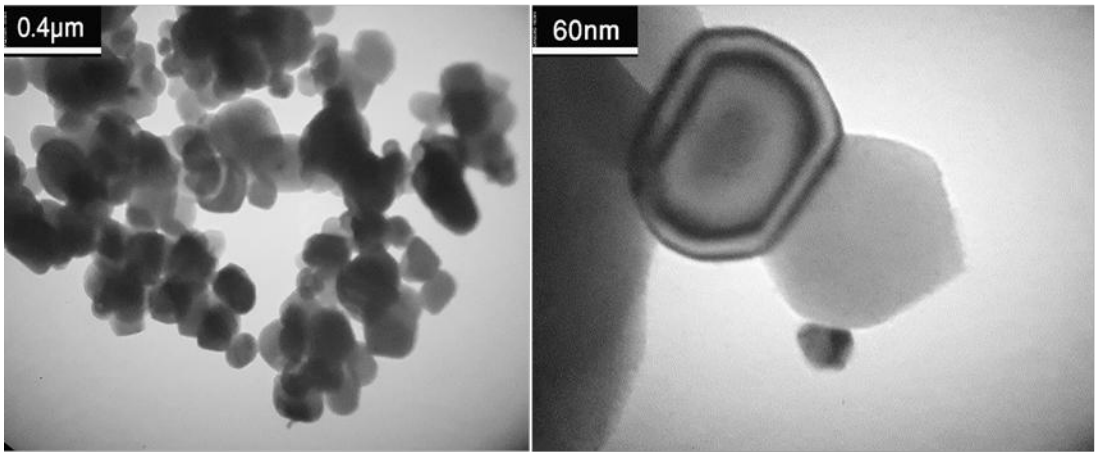

Fig. 4. TEM image of TiO_2/AC

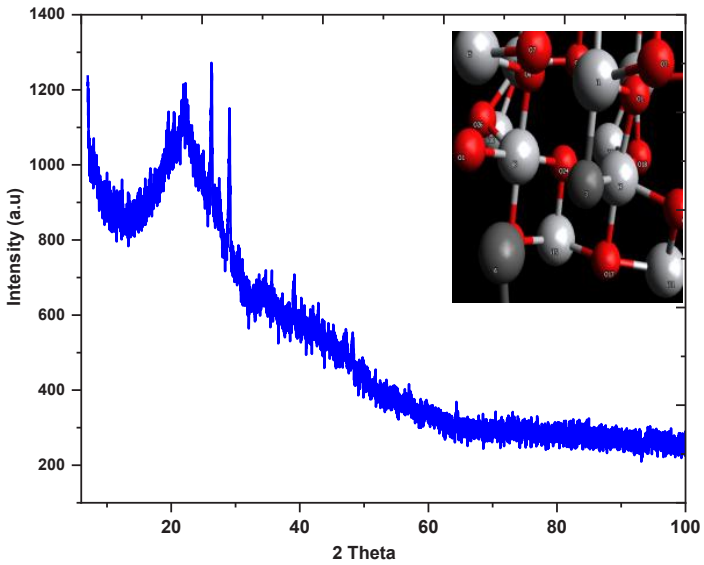

Fig. 5. X-ray diffraction (XRD) of TiO_2/AC NPs

water to produce a homogeneous dispersion of AC. A homogeneous AC solution in 50 mL of water was then mixed with 7.5 g of TiO_2 NPs and agitated for 40 minutes. After that, the 100 mL homogenous solution was heated to 150 °C for 24 hours in a stainless autoclave lined with Teflon. After that, the powder was collected and washed several times with water and ethanol. Finally, the TiO_2/AC nanocomposite was produced satisfactorily. The confirmed structure by XRD mention in Fig. 2 as CIF.file

Procedures of work

A solution with a known dye concentration was made for the photo-degradation of BB dye. It was then left to equilibrate in the dark for 10 mins. After that, 200 mL of the solution was transferred to a 300 mL beaker. After making the necessary adjustments, the dye's pH value was 7.0. The reaction was then started by turning on the lamp. The suspension was kept homogeneous during irradiation by maintaining agitation, and it was sampled following the proper illumination duration. Using a calibration curve and a UV-Vis spectrophotometer set to λ_{max} = 620 nm, the amount of dye in each deteriorated sample was measured. The conversion percentage of BB dye can be obtained at various intervals using this procedure. The following provides the photo-degradation efficiency (PDE%):

$$PDE\ \% = ((C_0\text{-}C_t)\ /\ C_0)\ x\ 100 \quad (1)$$

RESULTS AND DISCUSSION

The structures of TiO_2 NPs and AC were investigated using the FE-SEM technique, as shown in Fig. 3a–b. In contrast to the flat surface of TiO_2 NPs, when AC was introduced as a loading material, significant changes occurred in the surface morphology and texture of TiO_2/AC, resulting in the formation of multiple heterogeneous spherical shapes, confirming the reliability and robustness of our successful preparation method as shown in Fig. 3a. Importantly, Fig. 3b provides strong evidence of the successful loading of activated carbon on the surface of TiO_2 NPs, confirming the loading of activated carbon on the surface of TiO_2 NPs[18-20].

TEM morphology surface analysis (TEM) images of TiO_2/AC NPs at 0.4 and 60 nm were used in this step to investigate the surface morphology of the particles. After decorating the AC on the surface of TiO_2 NPs, Fig. 4 demonstrates that the cloud was more easily reached, and a new geometry was created; this may be related to the quantity of carbon on the TiO_2 NP surface. The TEM results provide an explanation of the geometrical structures of the as-prepared TiO_2/AC NPs Nano architectures. TEM investigations agreed well with XRD and FE-SEM examinations.[21, 22] .

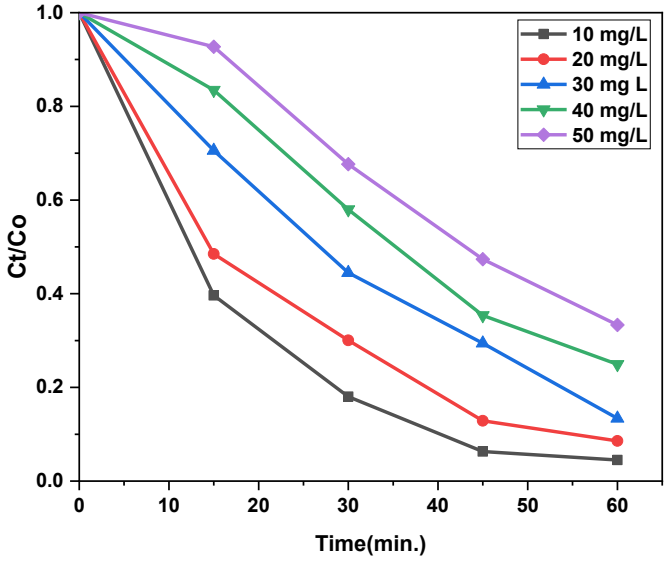

Fig. 6. Photocatalytic degradation at different concentrations of BB dye onto TiO_2/AC nanocomposite

Fig. 5 shows the TiO_2/AC NPs X-ray diffraction (XRD). The crystallinity or lack thereof of nanocomposite. was analyzed via XRD, and the recorded patterns are illustrated in Fig. 5. The TiO_2/AC NPs surface XRD pattern exhibited a crystalline structure with several peaks at 2θ° = 25.32, 26.56 °, 32.44 °, 36.28 °, and 54.12 °, all within the XRD range of TiO_2/AC NPs. [23, 24].

Effect of concentration of BB dye

The impact of various concentrations of BB dye, ranging from 10 to 50 mg/L, on its

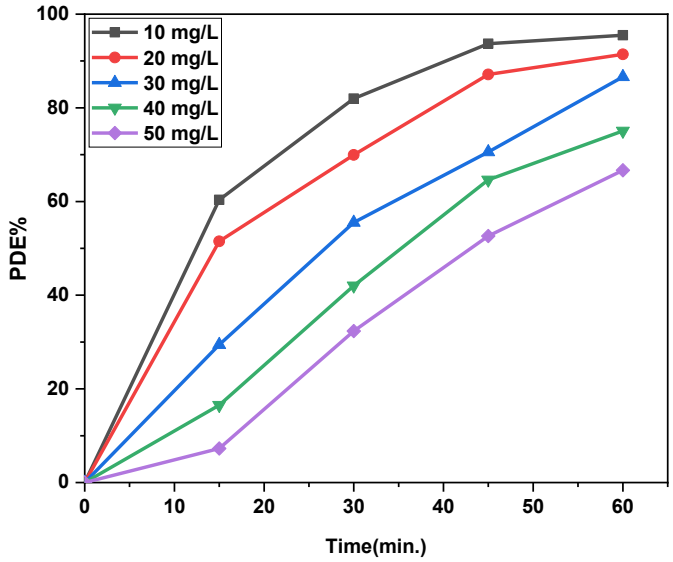

Fig. 7. Removal percentage of BB dye at different concentrations onto TiO_2/AC nanocomposite

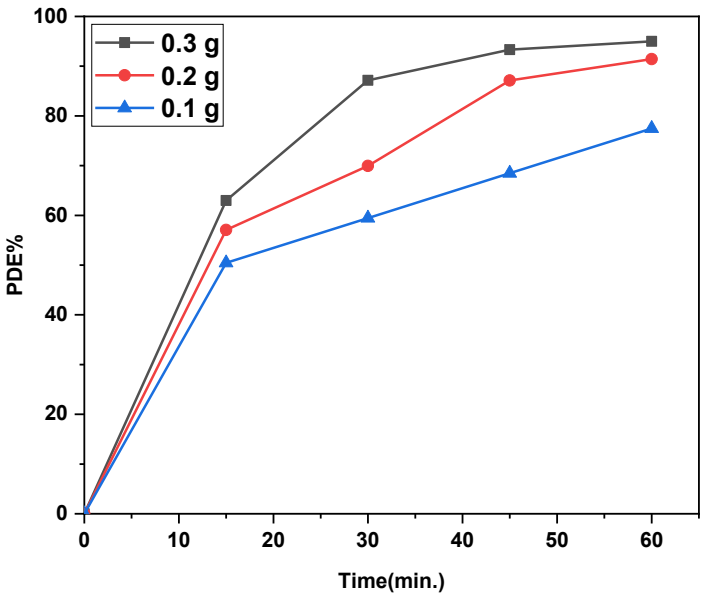

Fig. 8. Effect of the weight of TiO_2/AC nanocomposite on photocatalytic degradation BB dye

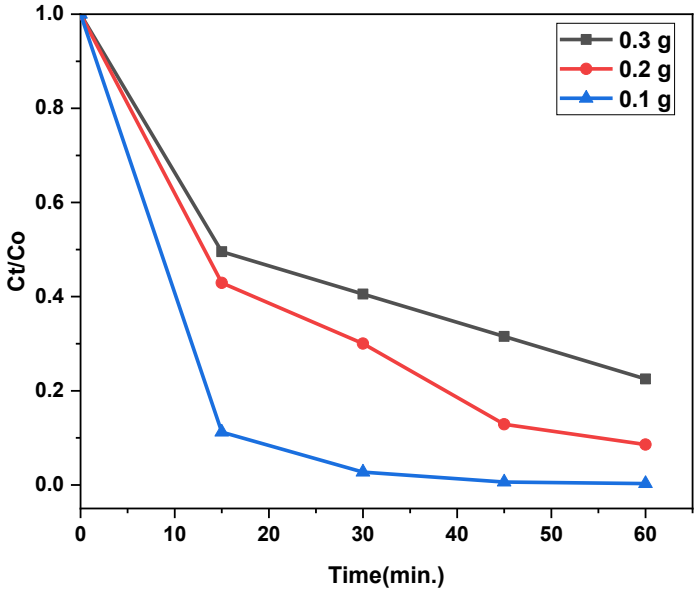

Fig. 9. Effect of mass TiO_2/AC nanocomposite on photodegradation of BB dye

photodegradation was investigated using 0.2 g of a TiO_2/AC nanocomposite in a 200 mL solution. The experiments were conducted at a light intensity of 1.3 mW/cm² and a temperature of 25 °C. It was observed that the rate of photodegradation significantly decreased as the concentration of the dye increased. The optimal concentration for maximizing the coverage area of the nanocomposite was found to be 30 mg/L. This optimal level is attributed to enhanced light absorption by the BB dye at this concentration, which improves the photocatalytic process occurring on the surface of the nanocomposite. As the concentration of dye increases, it forms multiple layers that block light penetration to the surface of the solution.[25, 26]. At the concentration of 30 mg/L, the system achieved an optimal photolysis efficiency of 90.25%, as shown in Figs. 6 and 7.

Effect of the weight of TiO_2/AC nanocomposite

The study investigated the effect of nanocomposite weight on the removal of methylene blue dye via photocatalytic degradation. The dye concentration was maintained at 20 mg/L, with an air flow rate of 10 mL/min at a temperature of 25 °C. Fig. 8, and 9 displays the range of nanocomposite weights used in the photocatalytic degradation process, which varied from 0.1 g to 0.3 g. The results indicated that as the weight of the nanocomposite increased, the rate of dye degradation also improved, reaching a peak of 0.3 g for a 200 mL solution. Initially, the photodegradation of the dye increased gradually, leading to enhanced photocatalytic efficiency. This phenomenon can be attributed to limited light absorption in the upper layers of the dye, while the deeper layers of the solution do not receive sufficient light photons. Ultimately, a nanocomposite weight of 0.2 g achieved the highest photodegradation efficiency, reaching 90.25% [25, 26].

CONCLUSION

It is expected that the combination of activated carbon AC and titanium dioxide TiO_2 nanoparticles will enhance degradation efficiency while reducing the need for costly and potentially hazardous sensitizers. In this experimental study, TiO_2 nanoparticle-based photocatalysts are synthesized and characterized. BB photocatalysis is employed to assess the effect of metal dopants on the rate and efficiency of degradation. The results will facilitate a better understanding of the fundamental concepts underlying the photocatalytic process and provide valuable insights for the development and improvement of advanced photocatalytic systems. Ultimately,

this study aims to contribute to the development of efficient and sustainable methods for removing azo dyes from various wastewater sources, thereby promoting both human welfare and environmental preservation. This phenomenon can be attributed to limited light absorption in the upper layers of the dye, while the deeper layers of the solution do not receive sufficient light photons. Ultimately, a nanocomposite weight of 0.2 g achieved the highest photodegradation efficiency, reaching 90.25%.

CONFLICT OF INTEREST

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

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