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Advancing TiO_2 for Environmental Sustainability: A Comparative Study for Tackling Antibiotic Pollution

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KEYWORDS

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ABSTRACT

The present work investigates TiO_2-based photocatalyst, including non-doped (AT), mono-doped (NAT and CAT), and co-doped (NCAT) variants, for the removal of tetracycline under UV light irradiation. The photocatalyst were synthesized using the sol-gel method assisted by microwave irradiation. Among these, the co-doped, NCAT photocatalyst demonstrated the highest photocatalytic activity, achieving 93% TC removal at pH 7 at 30 ℃ in 100 min. This superior performance can be attributed to the synergistic effect of N and Ce co-doping in the AC-TiO_2 lattice, which enhances photocatalytic activity by narrowing the band gap and improving the trapping and transfers of excited electron-holes pairs. These enhancements significantly improve the degradation efficiency of TC.

1. INTRODUCTION

Tetracycline is an antibiotic used to treat bacterial infections in humans, such as *Helicobacter pylori* [1], *Salmonella enterica*, and *Listeria monocytogenes* [2]. It is also utilized to promote animal growth in animal husbandry [3]. TC exhibits limited metabolism due to its chemical stability, leading to excretion from the human body, 90% in its parent form through urine and feces. TC is typically detected in concentrations ranging from ng L^{-1} to to μg L^{-1}, respectively, [4]. The prolonged release of TC into the environment raises significant concerns since it can affect our ecology, and human being.

Over the years, adsorption [5-7] and photocatalysis [8-9] have been widely utilized for the treatment of TC pollutants due to their high efficiency in adsorption and contaminant degradation. However, adsorbents often become saturated with pollutants over time, leading to a decline in achieving complete pollutant elimination. In order to overcome this limitation, activated carbon (AC) is frequently used as a support material for TiO_2, a well-established photocatalyst. The combination of AC and TiO_2 enhances adsorption capacity and improves photocatalytic efficiency. However, the application of TiO_2 is still constrained by certain drawbacks, including the rapid recombination of electron-hole pairs and its high bandgap energy, which restrict its photocatalytic activity to the UV wavelength range [10-11].

Various strategies have been explored to enhance the photoactivity of TiO_2-based composites, such as designing heterojunctions, morphologies modification, dual cocatalyst, and doping with metals, non-metals, or rare-earth metals. Doping with non-metals such as carbon such as carbon [12], nitrogen (N) [13], sulphur [14] narrow the bandgap and extend the light-response region substituting oxygen atoms in the TiO_2 lattice [13]. In addition, introducing rare-earth metals such as yttrium [15], lanthanum [16], and cerium (Ce) [17] has also proven effective in addressing the challenge of rapid electron-hole recombination.

The present study focuses on investigating TiO_2-based catalysts designed to enhance the degradation of TC and AMX antibiotics under UV light irradiation. The primary objective was to evaluate the influence of doped elements on the catalyst's performance. The catalyst was synthesized using sol-gel-assisted microwave irradiation method, incorporating two types of dopants: non-metals and rare-earth metals. To the best of our knowledge, no detailed study has yet compared the efficiency of mono-doped and co-doped N- and Ce-based catalysts in the degradation of TC and AMX. The catalytic performance of these catalysts was therefore evaluated under UV light irradiation.

2. EXPERIMENTAL PROCEDURE

2.1 Synthesis of TiO_2–Based Composite

The synthesis procedure of TiO_2-based composite including mono-doped and co-doped, was described in our previous work [18]. Briefly, N-dopant (0.02 g) and Ce-dopant (0.20 g) were added to a solution containing acetic acid (5 mL), mixed with distilled water (10 mL), and stirred continuously for 10 min using a magnetic stirrer. This solution was designated as Solution A. For Solution B, titanium (IV) isopropoxide (5 mL) was added to isopropanol (15 mL) and stirred for 10 min.

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Then, Solution B was slowly added dropwise to Solution A and stirred for 1 h. Afterward, AC (0.50 g) was added to form NCAT composite. The composite was left to dry for 12 h in a drying oven at 100 ℃ before being subjected to microwave irradiation at 600 W for 15 min. For the preparation of mono-doped CAT and NAT, 0.20 g cerium (III) nitrate hexahydrate, and 0.02 g urea were used, respectively. No dopants were added to solution A to obtain the ACTiO_2 photocatalyst, denoted as AT. The resulting composites were then evaluated for their photocatalytic capabilities.

2.2 Degradation Experiments

The experiments were conducted in a self-assembled black box, wrapped with black paperboard, with dimensions of 70 x 50 x 40 cm. A 0.20 g sample of the NCAT composite was introduced into 100 mL of a 10 mg/L antibiotic solution, with a solution pH of 7. The temperature of the system was maintained at 30 ℃. The mixture was allowed to react in the dark for 30 min to attained adsorption-desorption equilibrium. Subsequently, UV light was switched on, and the system was irradiated for 100 min. After reaching the final equilibrium state, 5 mL of aliquots were taken from the sample and filtered through a 0.45 µm syringe nylon filter, and analyzed using a UV-Vis spectrophotometer at wavelengths of 360 nm for TC [17]. For comparison, photocatalytic experiments were conducted under the same reaction conditions using AC, AT, mono doped NAT, CAT, and co-doped NCAT.

3. RESULTS AND DISCUSSION

3.1 Degradation of Tetracycline Using the Photocatalyst.

The percentage performance of antibiotic degradation was calculated using various photocatalysts. When AC was used without the addition of TiO_2 or other dopants, a low degradation of 18.6% for TC was observed after 100 min of UV light irradiation. This is likely due to AC only being able to adsorb the molecules but not participate in the photocatalytic process, as TiO_2, the photocatalyst, was absent to facilitate the breakdown of TC. When TiO_2 was doped onto the AC surface (AT composite), the degradation of TC increased to 63.5%, indicating that TiO_2 enhanced the degradation process under UV light exposure. The catalytic activity of the system further improved when AT was doped with nitrogen to produced NAT, achieving a degradation of 80.2%. However, when comparing AT doped with cerium only (CAT), the degradation performance of the NAT was lower, with CAT achieving a degradation of 85.6%. The improved degradation with cerium is probably due to its ability to act as a redox couple, reducing the recombination rate of electron-hole pairs during the catalytic process, thereby increasing the degradation rate [19].

When combining the two materials into a single catalyst, the degradation percentage significantly increased, reducing TC by up to 93%. This improvement is due to the synergistic effect of both elements, which enhanced degradation by narrowing the band gap [20] and improving the ability to prevent electron-hole recombination [19]. This allows for a continuous supply of electrons and holes, facilitating the release of radicals that further interact with TC molecules, breaking them down into simpler compounds and desorbing them from the composite's active site. Figure 1 illustrates the degradation of TC on various photocatalysts, including AC, AT, NAT, CAT, and NCAT, under UV light irradiation.

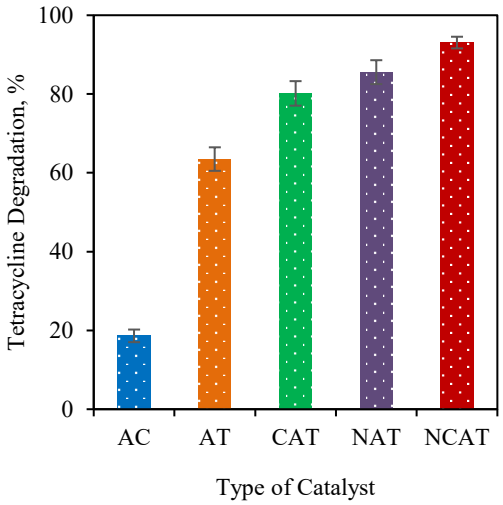

Figure 1. Degradation percentage of tetracycline by AC, AT, CAT, NAT and NCAT under 100 min.

4. CONCLUSION

The nitrogen and cerium is successfully doped with AC-TiO by sol-gel assisted microwave irradiation approach. The NCAT composite provide a better photocatalytic activity by degrading TC up to 93% in 100 min under UV light irradiation at an initial concentration of 10 mg L^{-1} and a catalyst loading at 2.0 g L^{-1}. The investigation reveal that co-doping material with non-metal and rare-earth metal can create a synergistic effect by narrowing the band gap and electron-holes trapping in composite lattice to actively form radicals that involve in the degradation process.

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