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Research Article

Exploring hexagonal boron nitride (BN) as an efficient visible light-induced catalyst for the remediation of recalcitrant antibiotics from aqueous media

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ABSTRACT

Hexagonal boron nitride (h-BN) is a novel non-metallic material which is newly discovered in the field of photocatalysis due to its high surface area, excellent optical features and high electrical conductivity. Herein, hexagonal boron nitride whiskers were fabricated by using the polymeric precursor method and, the photocatalytic degradation performance was measured towards tetracycline antibiotic under visible-light-illumination. The morphological, physical, and optical features of the catalyst were identified by several characterization analyses. The characteristic peaks associated with the hexagonal phase of boron nitride were determined and high crystallinity of h-BN was confirmed by X-ray diffraction analysis. The characteristic B–N absorption peaks were detected in the Fourier transfer infrared spectrum. Brunauer–Emmet–Teller specific surface area of the boron nitride catalyst was calculated as 1019 m^2/g which was relatively high, supplying abundant active regions to interact with the target pollutant. In photocatalytic degradation experiments, 91.9% of tetracycline decomposition was achieved within 180 min with a catalyst dosage of 0.2 g/L and initial concentration of 10 mg/L. The outstanding catalytic activity of the h-BN catalyst was attributed to the high surface area and negatively charged groups on the surface which captured the photo-induced holes and inhibited the recombination rate of charge carriers. These findings highlight the potential application of h-BN in the field of photocatalytic processes.

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INTRODUCTION

Until now, environmental pollution has been considered a crisis that threatened human health and the ecosystem. Particularly, organic pollutants from the pharmaceutical industry and hospital effluents can be persistent in the aquatic environment [1]. Tetracycline (TC) is a member of polyketide antibiotics and commonly used in veterinary, animal farm, aquaculture and human medicines to prevent bacterial infections [2]. TC is detected in the

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aquatic medium because of the wide utilization and inefficient treatment by biological techniques. Tetracycline contamination is a serious problem due to harmful impacts on microorganism structure and wildlife. Additionally, exposure high levels of TC cause an increase in diseases in human life. Therefore, the removal of TC from water environment is significantly matter in recent years. Unfortunately, elimination of the pharmaceutical molecules is generally complicated and high cost by physical, chemical, or other traditional methods. So, various green technologies have been suggested by researchers. In this regard, photocatalytic remediation is sustainable, cost-effective and environmentally friendly technique and thus, attracted extensive attention due to its solar energy utilization [1]. In a typical photocatalytic process, photons are first absorbed with energy higher than the band gap energy of semiconductor material. Then, the photo-excited electrons (e^-) are transported from the valence band (VB) to the conduction band (CB) of the semiconductor, while positively charged holes (h^+) in the VB induce the formation of electron/hole pairs. This pair generates highly reactive superoxide and hydroxyl radicals which react with contaminants to convert them to non-toxic small molecules [3]. Inspired from this perspective, discovering and application of an effective and eco-friendly photocatalyst play a strategic role in the remediation of the persistent molecules from contaminated water. As an example, Luo and co-workers used photocatalysis process to efficiently remove tetracycline by $LaMnO_3$/g-C_3N_4 hybrid catalyst and they achieved 61.4% TC degradation after 120 min visible light irradiation [4]. Recently, Jiang et al. [5] constructed sulphur-doped g-C_3N_4 and evaluated its catalytic activity towards TC antibiotic. They reported that 34.7% TC removal was obtained in 60 min with bulk g-C_3N_4 while it increased to 78% with sulphur-doped g-C_3N_4. Yan et al. [6] reported that Bi_2WO_6/boron nitride heterojunction demonstrated 99.1% photodegradation degree of TC within 120 min. They mentioned that the boron nitride supplied more active sites and boosted the separation rate of electron/hole.

Hexagonal boron nitride (h-BN) is a non-oxide and non-metallic substance including equal boron and nitrogen atoms. In the structure, these atoms are covalently bonded via sp^2 bonds and the two-dimensional layers are linked together via van der Waals forces [7]. h-BN is also named as "white graphene" due to their similar structures. In recent years, h-BN is widely used in several fields such as photocatalysis, adsorption, biomedical applications and hydrogen storage according to its high surface area, high electrical insulation, good temperature resistance, biocompatibility and thermal conductivity [8, 9]. Due to the hydrophobicity and π conjugation in its structure, h-BN could easily connect with the aromatic rings of organic pollutants via π-π and hydrophobic interactions [10]. Therefore, h-BN has gained the attention of researchers in recent years to remove contaminants from water media. Li et al. [8] explored the adsorption ability of h-BN and observed that the color of methylene blue almost disappeared and 98% methylene blue was removed within 5 min. Fu et al. [11] prepared h-BN/TiO_2 samples for the photocatalytic removal of dye molecules and they observed that with the increasing of h-BN amount, degradation efficiencies were remarkably enhanced. Shenoy et al. [12] prepared α-Fe_2O_3/h-BN composites and they reported that the photodegradation efficiencies towards Methylene Blue increased from 51% to 91% after the introduction of h-BN into the structure. The enhancement was ascribed to the electrostatic interaction between boron nitride and photo-generated holes and thus inhibited the recombination rate of charge pairs.

Based on this background, herein, novel whisker-type h-BN was synthesized via polymeric precursor technique to clarify their photocatalytic degradation performance towards tetracycline which is one of the most commonly used antibiotics in the pharmaceutical industry. Characterization techniques such as Scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Fourier transfer infrared (FTIR), Photoluminescence (PL), UV-vis diffuse reflectance spectra (DRS) were used to identify the catalyst structure. The influence of the pH value of the solution on the photocatalytic process was examined. The photocatalytic removal mechanism was explored with radical scavenging experiments. This study provides a novel and applicable usage of a hexagonal phase of boron nitride as a highly active photocatalyst.

MATERIALS AND METHOD

Chemicals

All chemicals were supplied commercially and used as received. Boric acid and melamine were obtained from Isolab. Benzoquinone (BQ), isopropanol (IPA), and Ethylene diamine tetra acetic acid disodium salt (EDTA) were obtained from the company of Sigma-Aldrich.

Fabrication of h-BN

Hexagonal boron nitride (h-BN) particles were fabricated by using H_3BO_3 (boric acid) and polymeric precursor namely melamine ($C_3N_6H_6$) [8]. Firstly, H_3BO_3 and $C_3N_6H_6$ with a molar ratio of 1:1 were magnetically stirred in 400 mL distilled water for 30 min at 90 °C and then the suspension was stirred at ~25 °C for 18 h. After that, a white precipitate was collected and dried at 60 °C for 5–6 h. Then, the product was moved in a tube furnace under an H_2 (5%)/N2 atmosphere and heated at 900 °C for 3 h. Finally, the white powders were obtained.

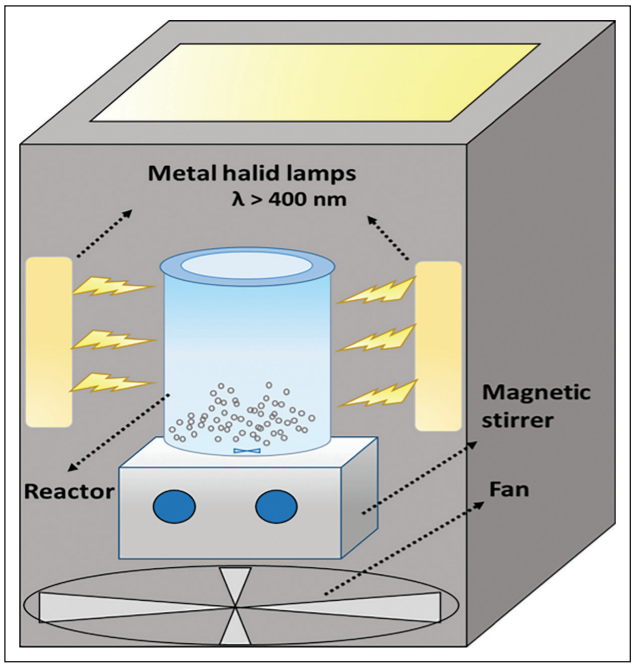

Figure 1. Schematic illustration of photochemical reactor.

Characterization

The morphological structure of boron nitride was examined by using the scanning electron microscopy (SEM) technique with Philips XL30 ESEM-FEG/EDAX equipment. Fourier transfer infrared (FTIR, Perkin Elmer Spectrum One-ATR) spectra were applied to investigate the structural groups of hexagonal boron nitride. The crystallinity phase structure was determined by X-ray powder diffraction (XRD, Panalytical X'Pert PRO). The specific surface area was obtained with Brunauer-Emmett-Teller (BET) technique by using a Quadrasorb SI-MP analyzer at 77 K. Photoluminescence (PL) data was obtained by Perkin Elmer FL6500 spectrophotometer with an excitation wavelength of 325 nm for h-BN. Perkin-Elmer Lambda 750 spectrophotometer was used to perform UV-vis diffuse reflectance spectra (DRS) analysis. The band gap energy of hexagonal boron nitride was calculated by using the Kubelka-Munk equation and Tauc plot technique.

Photocatalytic Degradation Tests

In this study, photocatalytic decomposition of tetracycline antibiotic (TC) was investigated under solar light irradiation in a square-shaped reactor (Fig. 1) equipped with metal halide lamps (Osram 150 W, 100 mW cm^{-2}) with a wavelength of λ: 400–800 nm. A fan was used to keep the temperature of the system constant during the photochemical process. In each experiment, the h-BN catalyst with the dosage of 0.2 g/L was first dispersed in a TC solution ($C_{initial}$: 10 mg/L; pH: 6.7) and the suspension was kept stirred magnetically with 500 rpm at room temperature (25 °C). In pH experiments, the initial solution pH of the TC solution was changed by using 0.1 M HCl and 0.1 M NaOH. To perform scavenger tests, EDTA, IPA and BQ agents were spiked into the initial TC solution. After the lights were opened and 4 mL of aliquots were collected and filtered with a syringe filter (0.20 μm). Finally, the residual antibiotic concentration was analyzed by using UV–vis spectrophotometer at the wavelength of 360 nm. Adsorption tests were also performed in dark to clarify the adsorption role in the removal mechanism.

RESULTS AND DISCUSSION

Characterization

The morphological feature of h-BN was examined by using the SEM technique. As shown in Figure 2, hexagonal boron nitride presented a short fibre and whiskers-like shape which was located randomly. Also, some defects were observed as graben on the h-BN surface which can act as interaction sites for the target pollutants. The obtained SEM images are in good agreement with previous reports in which h-BN whiskers were observed as nonuniform morphology [8, 13].

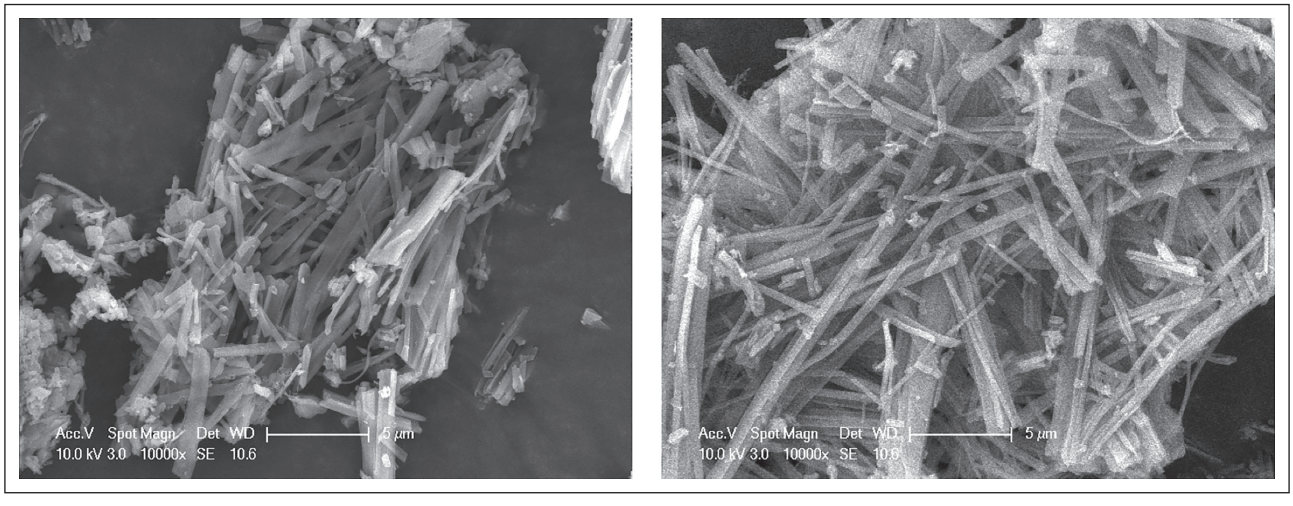

Figure 2. SEM images of h-BN.

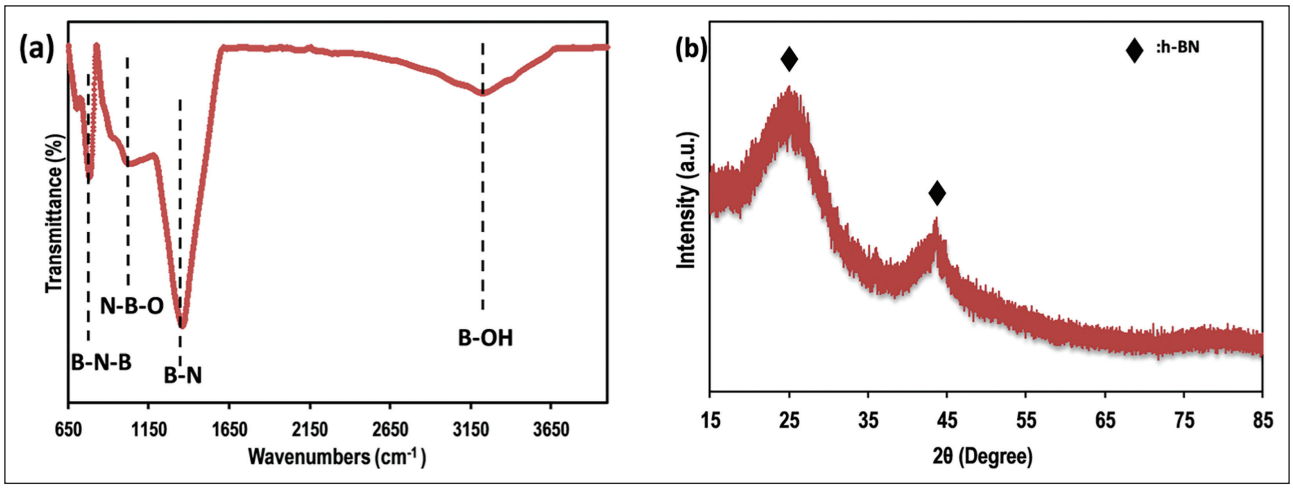

Figure 3. FTIR spectrum **(a)** and XRD pattern **(b)** of h-BN.

To identify surface functional groups in the structure, FTIR analysis was performed. In Figure 3a two peaks examined at 783 cm^{-1} and 1363 cm^{-1} were associated with δ(B–N–B) and ν(B–N) stretching vibrations, respectively [14]. The peak observed at 3400 cm^{-1} was assigned to the hydroxyl groups and adsorbed water [15]. Moreover, the peak located at 3261 cm^{-1} corresponded to the hydroxyl groups on the surface of h-BN with the bonds of B–OH [16]. Meanwhile, the boron oxynitride (N–B–O) bond was detected at around 900–1100 cm^{-1} [17]. The characteristic IR absorption peaks of the hexagonal phase of boron nitride indicated successful preparation of the h-BN with the polymeric precursor technique [8]. Moreover, no other peaks were found revealing that the precursors transformed to the h-BN sample. The obtained characteristic FTIR peaks were in agreement with previous studies in the literature [18, 19]. İkram et al. [16] observed boron oxynitride bond in h-BN structure. Moreover, Shenoy et al. [12] proved pure h-BN structure with an observation of B–N–B and B–N bonds in the h-BN structure via FTIR analysis. Similarly, Li and co-workers observed absorption peaks of the δ(B–N–B) and ν(B–N) bonds in the h-BN whisker [8]. The hydroxyl groups on the h-BN surface were also detected by Liu et al. [9] at around of 3200 cm^{-1}. According to all these results, the successful preparation of the hexagonal phase of boron nitride was proved by the FTIR analysis.

The phase composition and crystallographic structure of hexagonal boron nitride were examined by XRD analysis, and the result was represented in Figure 3b. The characteristic peaks of h-BN were fitted to the hexagonal phase of BN using the Joint Committee on Powder Diffraction Standards (JCPDS 73-2095) [8]. Also, the graphitic phase of boron nitride was demonstrated by the detection of 41.6° peak which corresponds to the (100) plane (JCPDS card No. 34-0421) [20]. Other peaks were not observed in the XRD spectrum, which confirmed that high purity of crystal h-BN was achieved via the polymeric precursor method.

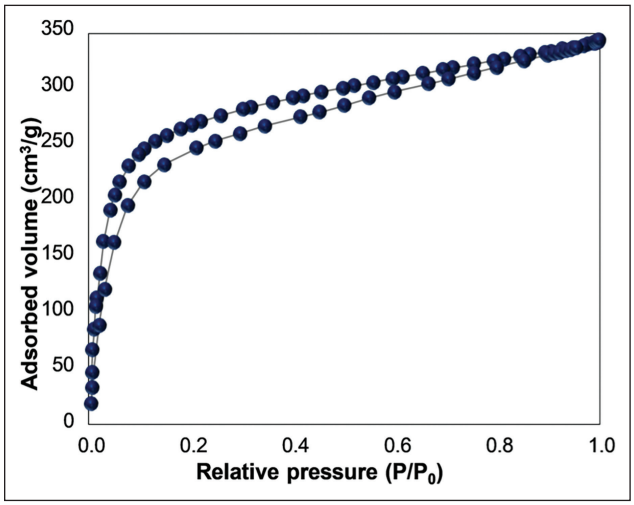

Figure 4. Nitrogen adsorption-desorption isotherm of h-BN.

The Brunauer–Emmett–Teller (BET) surface area of the material was calculated as 1050.1 m^2/g, which was found much greater than commercial boron nitride powder (25 m^2/g) [8]. The high surface area supplies many regions to contact with pollutants, leading to enhanced photocatalytic degradation performance. Similarly, Li et. al. also prepared whisker-shaped boron nitride and calculated the surface area as 964.4 m^2/g [8]. Similarly, Luo et al. [13] fabricated the hexagonal phase of boron nitride by polymeric precursor technique and they found the surface area as 964.3 m^2/g. Figure 4 shows the nitrogen adsorption-desorption isotherms of hexagonal boron nitride. According to result, the isotherms are closely be classified as the combination of characteristic type I, type II and H4 loops based on the International Union of Pure and Applied Chemistry (IUPAC) classification. This indicates that microporous and macroporous coexist in as-obtained h-BN. Additionally; H4 hysteresis indicated that the narrow slit pores [21].

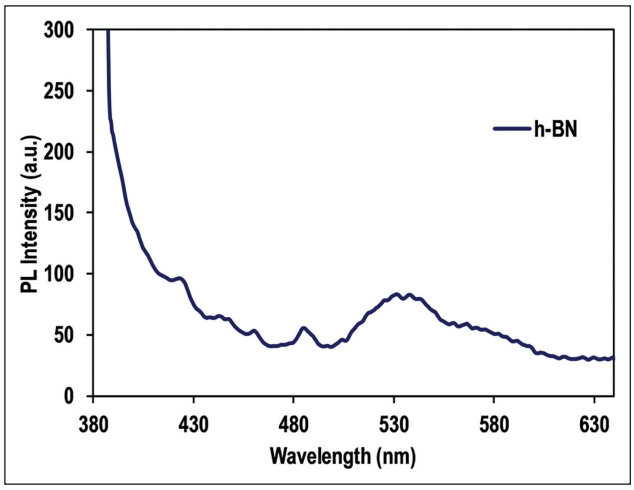

Figure 5. PL spectrum of h-BN.

The optical properties of h-BN were explored by PL and UV-vis DRS techniques and the results were shown in Figures 5, 6. PL spectra were obtained to explore the recombination issue and migration feature of the catalyst (Fig. 5) and it was shown that h-BN presented an excitation wavelength of 530 nm. It is known the PL intensity indicates the electron/hole recombination rate in which the peak intensity of h-BN was found relatively lower revealing enhanced separation of charge carriers and hindered recombination rate. Besides, the band gap feature of h-BN was investigated by DRS analysis. UV-Vis absorption spectrum and Kubelka-Munk function plot ($(aE)^2$) vs. photon energy (hv) were shown in Figure 6. The absorption edge of h-BN was determined as approximately 310 nm and the band gap energy of h-BN was determined as 4.5 eV which were in accordance with the literature [22]. Similarly, Gu et al. [1] reported the band gap energy of BN as 4.41 eV while He et al. [23] reported it as 3.98 eV.

Photocatalytic Activity Measurements

Tetracycline hydrochloride (TC) is the commonly used antibiotics to inhibit gram-positive and gram-negative bacteria [24, 25]. The occurrence of TC in the environment through contaminative wastewater is a serious threat to human health and the ecological system. Therefore, removal of TC from wastewater is a global concern and requires to be arranged immediately. In the present work, the photocatalytic efficiency of h-BN sample was tested for the elimination of tetracycline antibiotic. Both adsorption and photocatalytic tests were conducted. As shown in Figure 7a, the adsorptive removal of tetracycline was calculated as 20% within 180 min. In the tetracycline structure, NH_2 and OH groups are some of the functional states while boron nitride structure consists of abundant hydroxyl groups. The adsorption of tetracycline on the boron nitride surface could be via interactions between antibiotic molecules and hydroxyl groups of h-BN [26]. Under visible light illumination, 85.7% and 91.9% photocatalytic removal of TC were observed within 60 min and 180 min, respectively (Fig. 7b). Since the similar efficiencies of 60 min and 180 min, parameter experiments were performed for 60 min. Considering the insignificant adsorption performance of h-BN, the TC removal could be accomplished by the photocatalytic degradation reaction. Despite the wide band gap energy of boron nitride, the high degradation performance could be related to its positively charged hole capturing effect owing to negatively charged groups on the surface of h-BN. The great photocatalytic activity of h-BN towards TC elimination indicated that it could be a good alternative to remove organic contaminants from wastewater. On the other hand, h-BN by itself could be also used to boost catalytic activities of other semiconductors in the field of photocatalysis. For instance, Fu et al. [27] prepared h-BN/ZnO composite for the photocatalytic degradation of Rhodamine B and Methylene Blue dyes and reported that the introduction of boron nitride

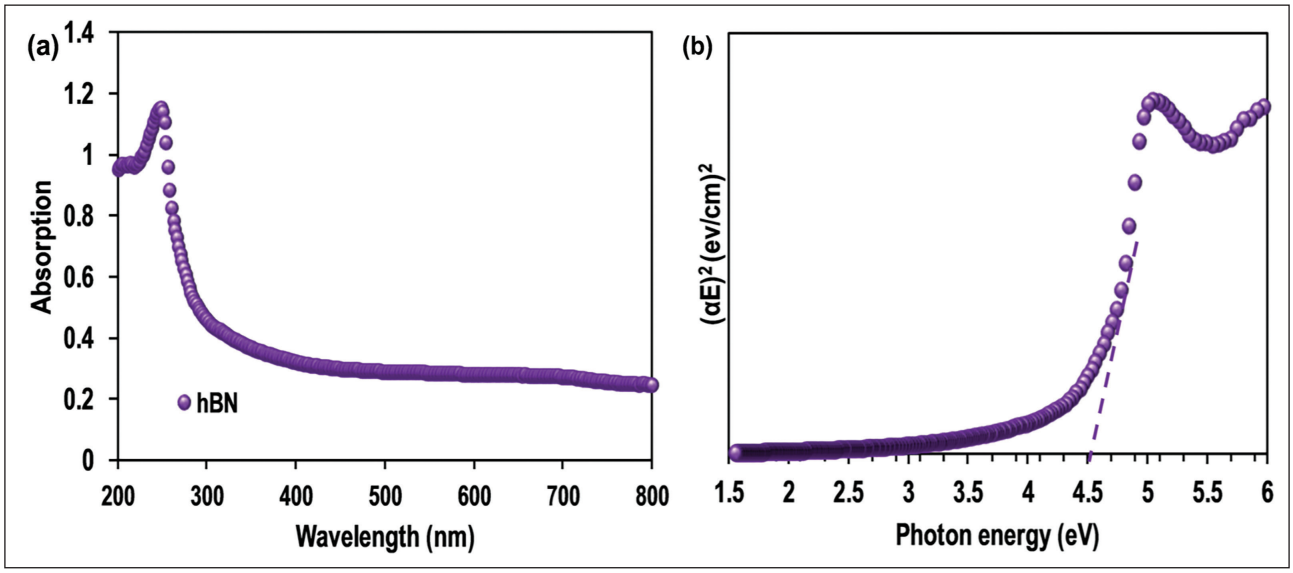

Figure 6. UV-Vis diffuse reflectance spectra **(a)** and Kubelka-Munk spectrum **(b)** of h-BN.

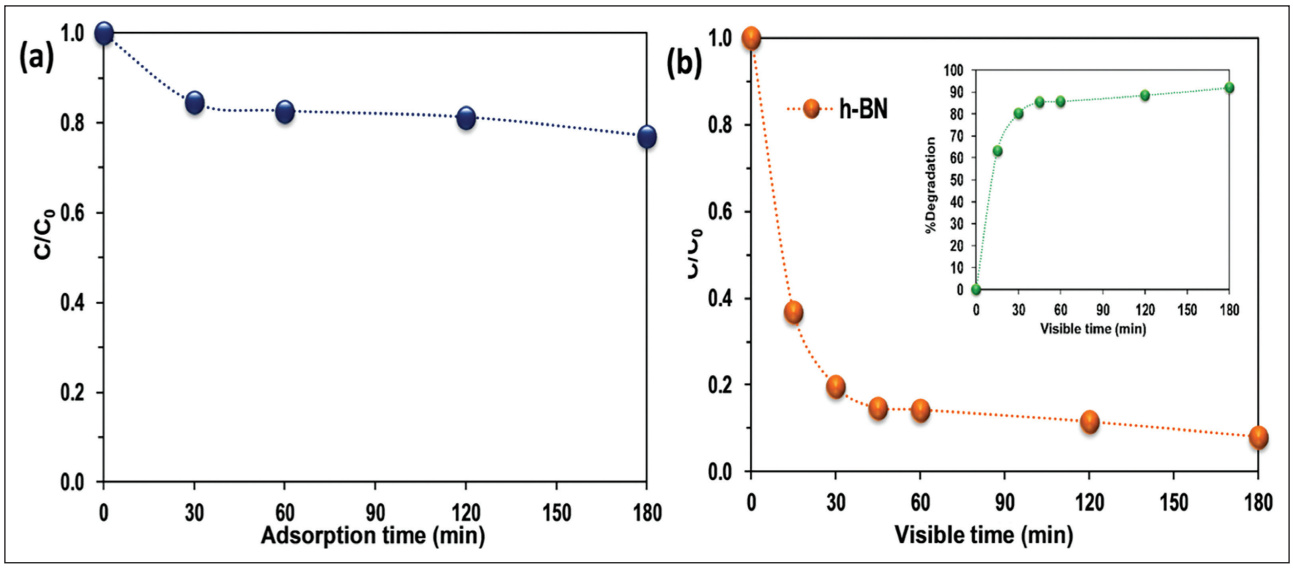

Figure 7. Adsorption **(a)** and photocatalytic **(b)** performance of h-BN.

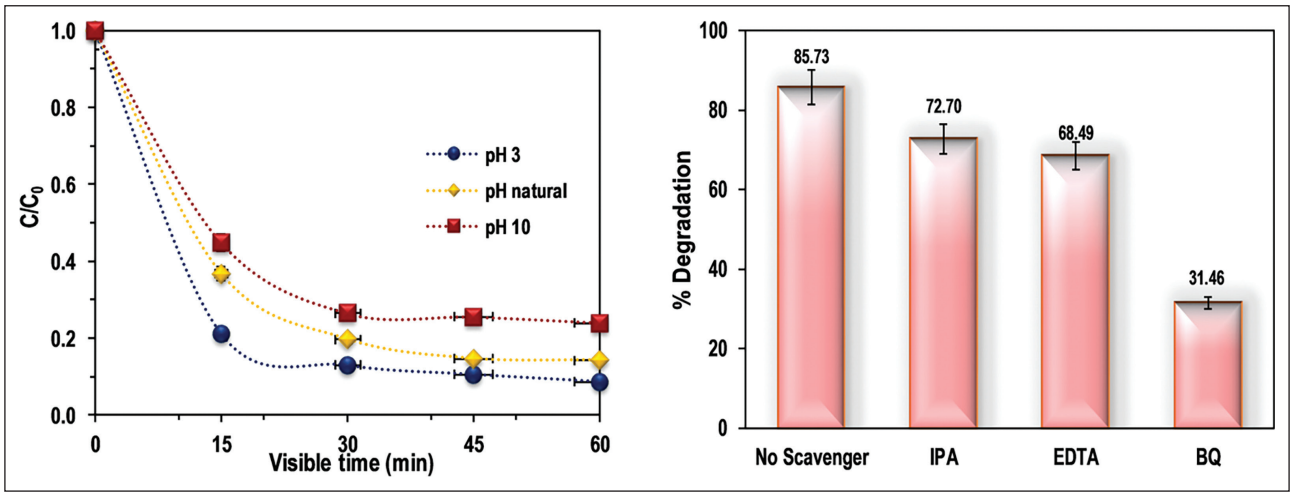

Figure 8. The effect of solution pH on TC removal **(a)** and radical trapping experiments **(b)**.

greatly increased the catalytic performance of raw ZnO. They attributed the enhancement to the hole transfer of h-BN and extra regions for the adsorption of pollutants via electrostatic forces. Lv et al. [28] mentioned that the photocatalytic activity of Ag_3VO_4 was considerably promoted after addition of the h-BN and the rate constant of the composite was detected six times higher than pure Ag_3VO_4. According to a study in 2017, the photocatalytic efficiency of $Bi_4O_5Br_2$ was increased from 55% to 97% with the loading of h-BN (1 wt %), which was assigned to the enhanced conductivity of heterojunction for electron-hole separation [29].

Influence of Solution pH on TC degradation

Initial solution pH is a significant parameter in photocatalytic processes, so the TC degradation over h-BN whiskers was investigated at three pH conditions (3, natural 6.7, 10). As shown in Figure 8a, 85.7% of the degradation rate was achieved at the initial pH 6.7 while the removal efficiencies increased to 91.3% (pH 3) and decreased to 76.0% (pH 10). It was observed that the degradation was inhibited in an alkaline medium while it favored acidic conditions. The TC molecule has three different pK_a values namely 3.30, 7.68 and 9.69 and it is significantly influenced by the initial solution pH value [30]. At pH values lower than 3.3, the cationic form TCH^{3+}, TCH_2° forms at pH values of between 3.4–9.7, and anionic TCH^- and TC^{2-} species were dominant at pH values higher than 9.7 [31, 32]. As reported in previous studies, the isoelectric point of h-BN is 2.7 [33]. So, the enhancement of TC degradation in acidic conditions could be ascribed to the electrostatic attraction between the negatively charged h-BN surface and protonated form of TC. By the way in alkaline conditions, the TC molecule exists in anionic form and electrostatic repulsion occurred between negatively charged h-BN surface and TC molecule resulting in low

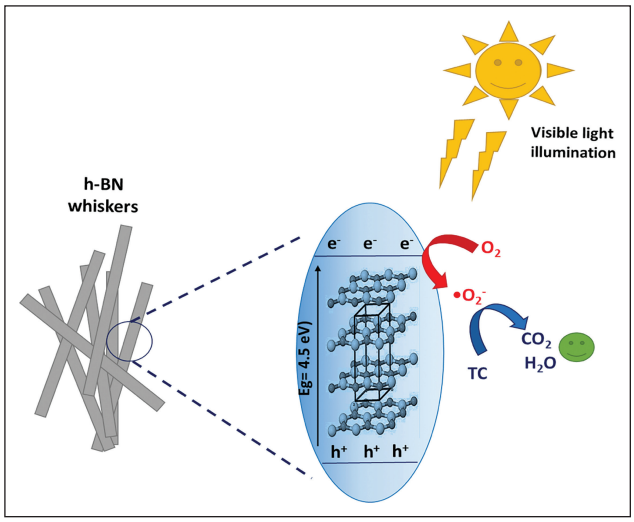

Figure 9. The possible photocatalytic degradation mechanism of TC on h-BN.

degradation efficiency. As a result, due to the surface charge of h-BN and TC chemical states, the initial solution pH was defined as a significant parameter and acidic media was determined as optimum condition to remove TC on h-BN.

Investigation of Active Radical Species

During photocatalytic reaction, various active substances were produced such as hydroxyl radicals (•OH), photoinduced holes (h^+) and superoxide anions ($\bullet O_2^-$). In order to understand the main active species in the TC degradation over h-BN whiskers, different reagents namely IPA, EDTA and BQ were added to the solution which acted as scavengers of •OH, h^+ and $\bullet O_2^-$, respectively. As depicted in Figure 8b, IPA and EDTA restricted removal rate from 85.7% to 72.7% and 68.4%, respectively. The degradation was significantly inhibited with the addition of BQ, and the removal efficiency was decreased to 31.4%, referring that superoxide anions were the key radicals in the TC degradation system. These results indicate that the possible mechanism of TC degradation onto h-BN dominantly triggered by superoxide anions and this process was schematized in Figure 9. When the catalyst is exposed to the light which has a higher wavelength than the band gap (E_g) of catalyst, the photoexcited electrons are occurred and transfer to the conduction band of the catalyst. Due to the transfer of the electrons, positively charged holes occur at the valence band (Eq. 1). Photo-induced electrons and holes take part in the reduction and oxidation reactions, respectively. In general, electron-hole pairs tend to recombine. But in this process, positively charged holes are captured by negatively charged hydroxyl groups on the surface of h-BN which was detected by FTIR analysis. Owing to the occupation of holes, recombination of pairs is inhibited, and electrons could be free and generate reactive radicals. Photo–induced electron in the conduction band of h-BN reduce the adsorbed oxygen molecules to generate superoxide radicals (Eq. 2). After that, the as-produced $\bullet O_2^-$ can oxidize the adsorbed TC molecules into CO_2 and H_2O (Eq. 3) [34].

$$\text{h-BN}+h\nu \rightarrow e^- + h^+ \quad \text{(Eq. 1)}$$

$$(O_2)_{ads} + e^- \rightarrow \bullet O_2^- \quad \text{(Eq. 2)}$$

$$\text{Pollutant molecules} + \bullet O_2^- \rightarrow CO_2 + H_2O \quad \text{(Eq. 3)}$$

CONCLUSIONS

Herein, the hexagonal phase of boron nitride was synthesized to investigate the photocatalytic ability for the degradation of TC antibiotics. The randomly located whisker shape of h-BN was observed by SEM technique. 20% adsorptive removal of TC was obtained via interactions between hydroxyl groups of boron nitride and functional groups of antibiotic molecule. Photocatalytic degradation efficiency reached 91% with visible light irradiation within 180 min (catalyst dosage: 0.2 g/L; initial pollutant concentration: 10 mg/L). The considerably high photocatalytic efficiency of h-BN was assigned to the excellent surface area and low recombination rate of h-BN. According to pH studies, it was observed that the optimum performance was obtained in acidic conditions. Tetracycline degradation was inhibited at higher pH while it favored lower pH values owing to the electrostatic repulsion and attraction circumstances, respectively. In the radical trapping experiments, superoxide radicals were detected as the vital active species for tetracycline degradation on the h-BN catalyst. According to the possible mechanisms, the photo-induced electrons generated $\bullet O_2^-$ anions which subsequently converted TC molecules to non-toxic products. This study provides a guide for the production of h-BN with outstanding photocatalytic performance to urgently solve water pollution globally.

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DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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