

Article

Combined Biological and Photocatalytic Degradation of Dibutyl Phthalate in a Simulated Wastewater Treatment Plant

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Abstract: The removal of organic pollutant in wastewater has become a major priority in water treatment. In this study, organic pollutant dibutyl phthalate (DBP) has been biologically and photocatalytically degraded in wastewater using modified transition metal dichalcogenides. The as-synthesized nanoparticles were characterized using various characterization techniques, which includes XRD, Raman, FT-IR, SEM, TEM, UV-Vis, XPS, PL, EIS, and photocurrent responses. The nanoparticles synthesized by slightly modified hydrothermal method depicted a hexagonal phase, as evidenced by XRD and Raman analyses. The biological degradation of 69% dibutyl phthalate was achieved. Moreover, the total organic carbon removal efficiency of 70% was further achieved. Incorporating biological and photocatalytic systems significantly improved dibutyl phthalate removal in secondary effluent by three folds when compared to the unilateral operating setup. The optimized parameters such as pH = 7, 5 ppm and DBP concentration with the addition of 10 mg catalysts loading were employed for the photocatalytic degradation of dibutyl phthalate in water. Pristine WS₂ exhibited photocatalytic efficiencies of 46% after 60 min illumination. The use of dual system 3% Ce/Gd-WS₂ exhibited the highest photodegradation of 85%, with a chemical oxygen demand of 80% and total organic carbon of 77%. The enhanced activity by the composite is attested to the formation of heterojunction exhibiting excellent charge separation and low rate of recombination. The 3% Ce/Gd-WS₂ can be used up to seven times and still achieve a degradation of 56%.

Keywords: biological activity; dibutyl phthalate; heterojunction; photocatalytic; total organic carbon



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1. Introduction

Industrial contaminants have been considered as emerging pollutants threatening the life of human beings and environmental safety since the commencement of the 21st century [1]. Industrial contaminants such as phthalates esters (PAEs) are utilized in industrial productions such as plastics and they are considered as main hazardous contaminant because of their excessive demand and ecological toxicities [2]. Moreover, PAEs have been blacklisted by the United State Environmental Protection Agency (SUEPA) and Chinese Environmental Monitoring Center as an industrial pollutant of priority [3]. Typically, Dibutyl phthalate (DBP) is used globally as plasticizer in cosmetics and additives in paints [4]. The global consumption of DBP increases rapidly due to high demand. The global production of DBP was at 1.8 million tons in 1975; since then, it has rapidly increased to more than 6–8 million tons annually [5].

Dibutyl phthalate is considered an endocrine disrupting chemical (EDC) due to its negative effect on the endocrine system of human beings and wildlife [6]. The exposure of DBP is associated with decreased sperm quality in males while in female it results in breast cancer [7]. Due to weak covalent interaction of DBP and conventional plastics such as polyvinyl chloride (PVC), DBP can easily detach from plastics to the environment [8]. Various conventional technologies have been employed for DBP removal. Wastewater

treatment plant (WWTP), as one of the conventional technologies, can be used to biologically degrade organic pollutants such as DBP in water using vast number of microorganisms [9].

The use of conventional WWTP to biologically degrade the recalcitrant emerging pollutants such as phthalates proves to be inefficient. This is due to fact that phthalates are stable and tends to be partially removed when fragmented in the biological section of WWTP [9]. Photocatalysis is one of the advanced oxidation processes serving as an ideal technology toward the photodegradation of organic pollutants in water. This technique utilizes renewable solar energy to mineralize organic pollutants into carbon dioxide and water. The photocatalytic degradation of organic pollutants by using semiconductors has gained enormous attention as it proved to be ideal process for environmental remediation. The inability of conventional WWTP to remove emerging pollutants in water necessitated developing a robust system that uses combined biological and photocatalytic processes toward the degradation of dibutyl phthalate.

2. Results

2.1. Characterization of Pristine, Metal Doped, and Co-Doped Nanoparticles

Extensive characterizations of the as-prepared materials were explored in our previous publication [10]. Briefly, the as-synthesized material synthesized by slightly modified hydrothermal process displayed a hexagonal phase (2H) confirmed with JCPDS card no. (04-001-9286) as depicted by XRD spectrum (Figure S1(AI)) on the supplementary information. The phases of the nanoparticles were further evidenced by a Raman spectrum and FT-IR spectrum in Figure S1(AII) and Figure S1(AIII), respectively. The morphological analyses revealed that pristine WS₂ (Figure S1(AIVa)) and metal doped shown by Figure S1(AIVb,c) displays agglomeration with particle sizes of 20 nm. A change of morphology was observed with co-doping to nanorods with lattice fringes having a d-spacing of 0.62 nm and 0.31 nm corresponding to the (002) and (100) planes of WS₂ and CeO₂, respectively, as depicted by Figure S1(AIVd) and this further confirms the formation of heterojunction. Figure S1(AV(a–d)) further evaluates particle morphologies. SEM technique displayed that particles exhibited oval shapes and multiple forms of morphological orientation. The particles' elemental composition, surface chemical states, and valence band edge potential were evaluated by XPS. The survey spectrum depicted the presence of all elements (W, S, O, Ce, and Gd) for pristine WS₂, metal doped, and co-doped WS₂, and it is illustrated in Figure S1(BIa). The XPS deconvoluted peaks of tungsten Figure S1(BIb)) and sulfur (Figure S1(BIc)) attested to the oxidation states of W⁴⁺ and S²⁻, respectively, in WS₂. The presence of dopands Ce and Gd on the surface of pristine WS₂ was observed with dopands existing as Ce³⁺ (Figure S1(BIc)) and Gd³⁺ (Figure S1(BId)), respectively. The valence band shown in Figure S1(BIg) was found to be 2.75 eV for pristine WS₂, 2.75 eV, and 3.06 eV for metal dopands and 2.50 eV for 3% Ce/Gd-WS₂. The band gap (Figure S1(CIa)) value of pristine WS₂ was found to be 2.49 eV, and metal-doped cerium and gadolinium (Ce-WS₂) and were 2.47 eV and 2.48 eV respectively. The composite exhibited a band gap of 2.42 eV. The rate of recombination was evaluated by PL measurements, whereby the suppression of recombination was observed in the composite as depicted by (Figure S1(CIb)) and a Nyquist plot (Figure S1(CIc)), and photocurrent response (Figure S1(CId)) further evidenced the PL measurements of the composites.

2.2. Surface Charge Analysis

The surface charges of the prepared photocatalysts were investigated by measuring the zeta potential. The zeta potentials for bare WS₂, metal doped, and composite measured in deionized water are shown by Figure 1. A negative zeta potential for all prepared photocatalysts was observed. No point of zero charge (pzc) was depicted, and this is often experienced by 2D materials [11]. The zeta potential of pristine WS₂ at acidic medium, pH = 1 was −8.1 mV, and the incorporation of dopants gadolinium and cerium made the zeta potential more negative, which stands at −11.9 mV and −12.9 mV, respectively. The composite exhibited a zeta potential of −16.2 mV. The zeta potential increases with an

increase in pH. This was observed at basic medium, pH = 11, whereby pristine WS₂ zeta potential was −21.2 mV, −33.5 mV for Gd-WS₂, −39.5 mV for Ce-WS₂, and −42.1 mV for the composite (3% Ce/Gd-WS₂). Dibutyl phthalate has a pK_a value of 2.9 [12]. The zeta potential of the materials is low at low pH but gradually increases toward higher pH. This is attributed to a weak electrostatic repulsion force at low pH and higher electrostatic repulsion force at high pH between dibutyl phthalate and the photocatalysts [13].

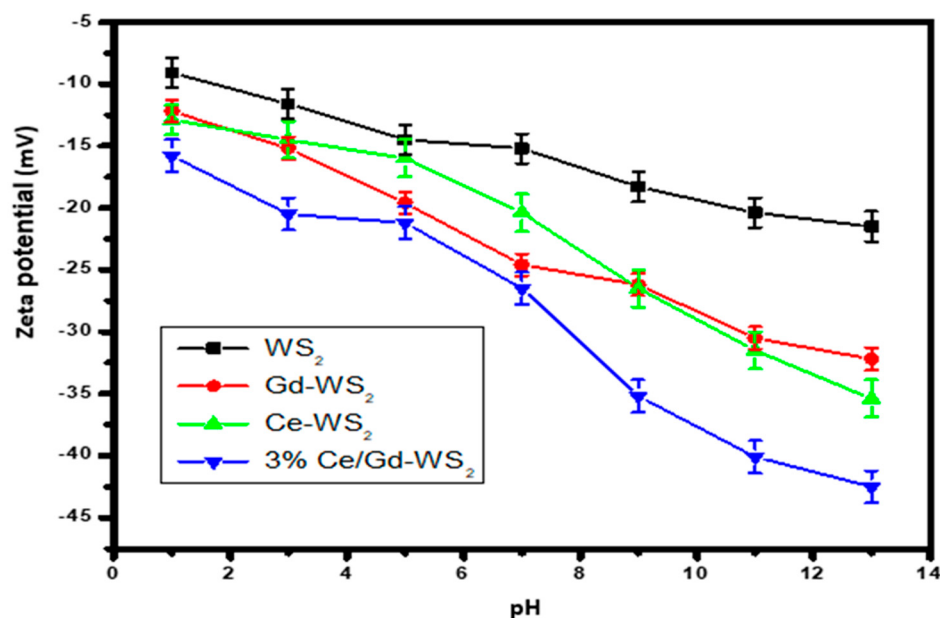


Figure 1. Pristine, metal doped, and co-doped WS₂ zeta potential.

2.3. The Effect of pH

The pH studies of the solution with pH ranging from 1 to 11 of the photocatalytic degradation experiments of dibutyl phthalate were investigated. The degradation efficiencies of pristine WS₂, metal doped, and co-doped WS₂ toward DBP at different pH values are shown in Figure 2a–d. The highest photocatalytic efficiency of DBP was observed at neutral pH using pristine WS₂, as shown in Figure 2a. In the acidic medium, pH = 1 depicted the highest degradation efficiency after 60 min of 56% higher as compared to pH = 3 and pH = 5, which was 52% and 43%, respectively after 60 min of irradiation. The photodegradation at pH = 9 and pH = 11 was 40% and 36%, respectively. The optimal degradation efficiency is in the acidic medium, and this is due to a pK_a value of 2.9 of DBP. This illustrated that dibutyl phthalate is weak at basic pH, hence its ability to be protonated at acidic pH. The highest photodegradation of 60% at neutral conditions, pH = 7, is because different pH values have the ability to alter catalyst properties, which affect the adsorption behavior of DBP on the surface of the photocatalyst [14].

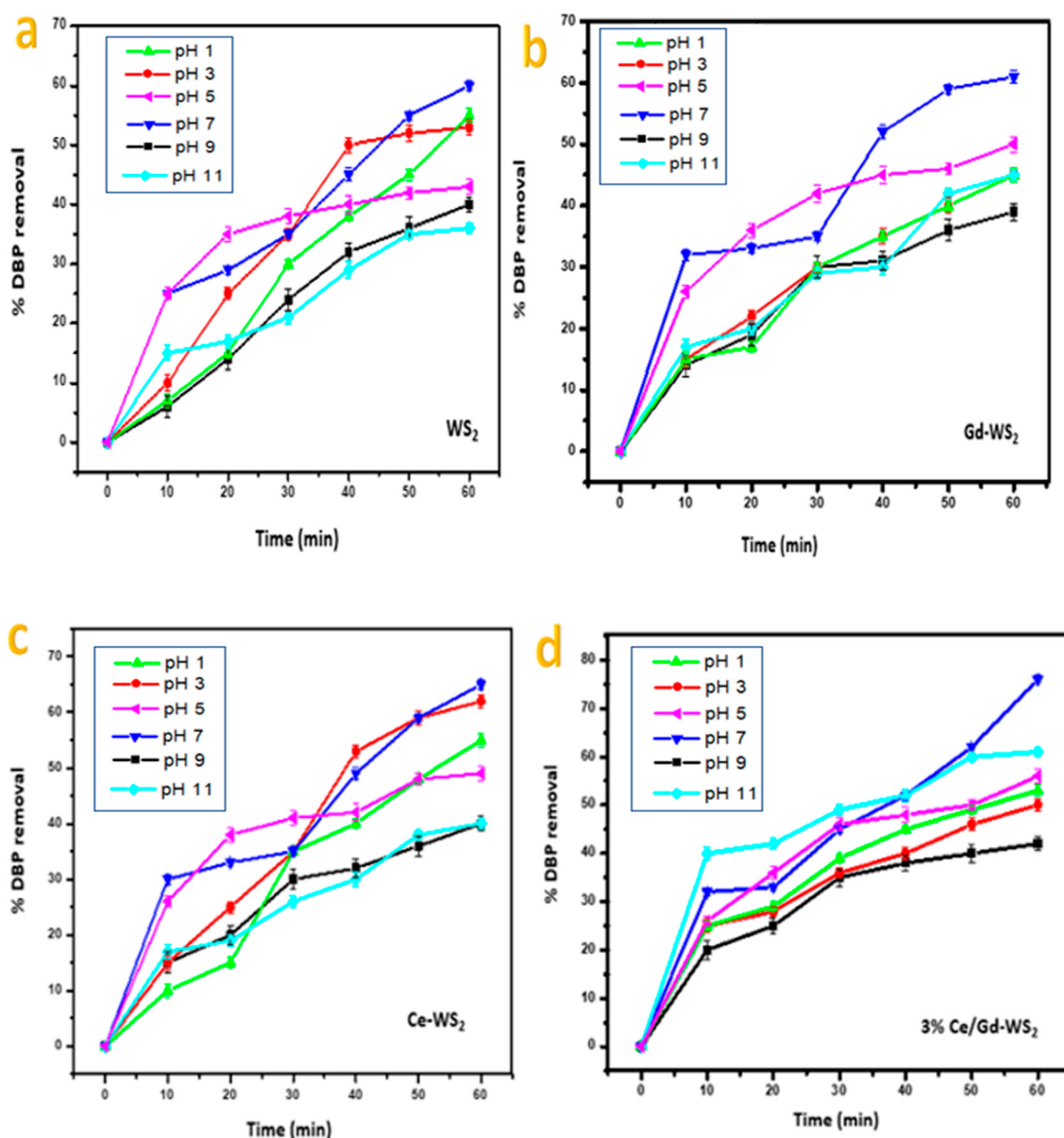


Figure 2. The effect of pH effect on the photodegradation of DBP using (a) WS₂, (b) Gd-WS₂, (c) Ce-WS₂ and (d) 3% Ce/Gd-WS₂.

The incorporation of dopants on the surface of WS₂ was also investigated. A similar mechanism was observed when incorporating with gadolinium (Figure 2b) and cerium (Figure 2c). The degradation efficiency was low at acidic medium and lowest at basic medium. The degradation efficiency of Gd-WS₂ and Ce-WS₂ at pH = 1 was 44.2% and 47%, respectively. Moreover, in basic mediums with a pH = 11, the degradation was 43% and 40.8% respectively. The surface charge analysis of the as prepared at high pH revealed to be more negative, which resulted in the electrostatic repulsion of DBP and the photocatalysts, thus leading to decreased photodegradation. The degradation efficiency at neutral pH of Gd-WS₂ and Ce-WS₂ was 61% and 62%, respectively. As compared to pristine WS₂, metal-doped WS₂ had a high % degradation of DBP. This is due to the formation of heterojunction, which sufficiently separates photoinduced electrons preventing recombination.

The degradation results of the composite 3%_Ce/Gd-WS₂ are displayed in Figure 2d. The degradation of 54% and 63% was observed at low pH = 1 and pH = 3, respectively. The degradation of DBP decreased at pH = 9 and pH = 13 and was found to be 41% and 48%, respectively. This is due to the photocatalyst's surface charge being more negative.

The optimal photodegradation was observed at neutral pH and found to be 76%. This is attested to the negative charge of the composite and more pronounced attractive forces on the photocatalysts surface due to the ionized form of dibutyl phthalate. Furthermore, PL and EIS measurements affirmed that dual doping forms an ideal heterojunction, which prevents charge recombination and showed excellent charge transfer. Moreover, neutral pH was selected as the optimal pH condition as most industrial organic pollutants such as dibutyl phthalate exist in neutral pH in water [15].

2.4. The Effect of Initial Concentration

To study this aspect, the pH was kept constant at pH = 7, at constant photocatalyst loading of 10 mg for all the photocatalysts while varying DBP concentrations from 1, 3, 5, 7, and 10 ppm. The obtained results are shown in Figure 3a–d. Bare WS₂ depicts the highest dibutyl phthalate degradation of 60% at 5 ppm DBP concentration, as shown by Figure 3a. The photocatalytic degradation at 1 ppm and 3 ppm DBP concentrations was obtained to be 51% and 46%, respectively. The lowest degradation of 43% and 39% was obtained at high concentrations of 7 ppm and 10 ppm, respectively.

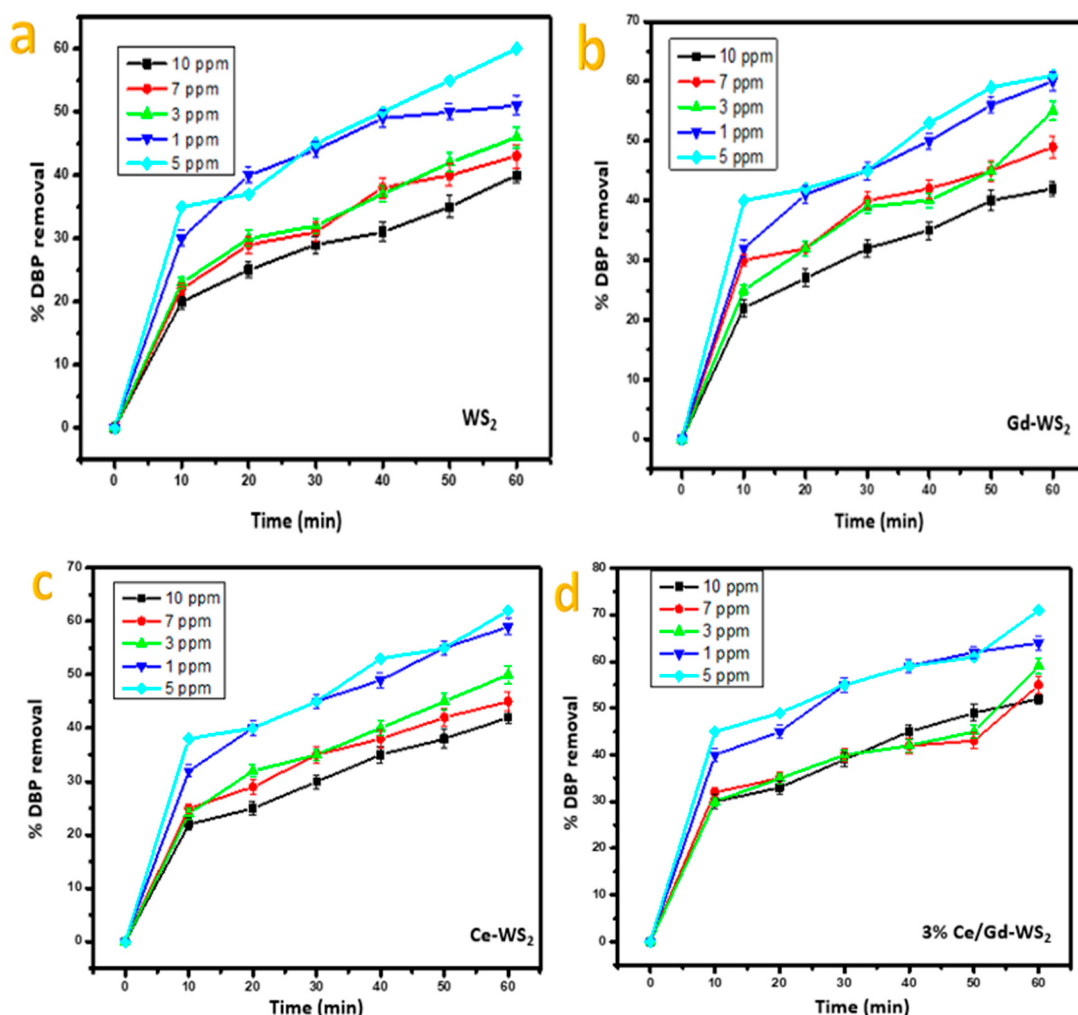


Figure 3. The influence of initial concentration on the degradation of DBP with (a) pristine WS₂, (b) Gd-WS₂, (c) Ce-WS₂, and (d) 3% Ce/Gd-WS₂.

Photocatalytic degradation was further enhanced upon the incorporation of rare earth metal gadolinium (Figure 3b) and cerium (Figure 3c) WS₂. The optimal photocatalytic efficiency was obtained at 5 ppm DBP concentration at percentage removal of 61% and 64% for Gd-WS₂ and Ce-WS₂, respectively. The lower degradation of Gd-WS₂ compared

to Ce-WS₂ was due to a higher rate of recombination of photoinduced charge carriers and high resistance of electron transfer, as supported by PL and PES measurements. The enhanced degradation as compared to pristine WS₂ is due to more active sites present on the surface of the catalysts. Similarly, the lowest degradation efficiency was obtained at high DBP concentrations. This is due to the active site being clogged, blocking photons from reaching the surface of the catalyst. Moreover, this is due to less adsorption sites because of the increased adsorption of DBP on the catalyst's surface. Figure 3d shows dual doping on the surface of WS₂. The highest DBP removal of 72% was also obtained at initial concentrations of 5 ppm. Moreover, the lowest photodegradation of 51% and 55% was obtained at high initial concentrations of 7 ppm and 10 ppm, respectively. At low dibutyl phthalate concentration of 1 ppm and 3 ppm, the photodegradation efficiency was 64% and 59%, respectively.

2.5. Influence of Photocatalyst Loading

The efficiency of the organic pollutant removal can be affected by the amount of catalyst added. The working condition of constant concentration of 5 ppm and pH = 7 was used while varying the loading of catalysts added from 5 mg to 25 mg with an increment of 5. The photodegradation experiments results are shown by Figure 4a–d. Pristine WS₂ exhibited the highest photocatalytic efficiency of 55% using 10 mg catalyst loading as depicted by Figure 4a after 60 min of irradiation. The use of 5, 15, 20, and 25 mg of catalyst loading exhibited photodegradation removal at 45%, 49%, 51%, and 41%, respectively. The incorporation of dopants onto WS₂ also affected the removal efficiency of DBP. The degradation efficiency of Gd-WS₂ (Figure 4b) and Ce-WS₂ (Figure 4c) with 10 mg catalyst loading increased by 10% and 13%, respectively. Photocatalytic degradation decreased to 58% and 60% for Gd-WS₂ and 59% and 64% for Ce-WS₂ upon the use of 15 mg and 20 mg respectively. Furthermore, a decrease in efficiency removal was observed with the catalyst loading of 25 mg and 5 mg. Gd-WS₂ exhibited a removal of 42% (25 mg) and 46% (5 mg), while Ce-WS₂ exhibited removal efficiencies of 45% and 48% using 25 mg and 5 mg catalyst loadings, respectively. The composite removal efficiency was also investigated, and the obtained findings are depicted in Figure 4d. A similar mechanism was observed with 3%Ce/Gd-WS₂. The highest dibutyl phthalate photodegradation efficiency of 75% was depicted with 10 mg catalyst loading, and the lowest photodegradation of 43% was observed with 25 mg catalyst loading. These findings indicate that the use of the lowest amount of catalyst loading forms defects, resulting in less photodegradation efficiency and high catalyst loading causes agglomeration, thus hindering active sites and resulting in ineffective photodegradations of DBP. Moreover, the excess use of catalyst loading inhibits light penetration, resulting in less photoinduced charge carries [16].

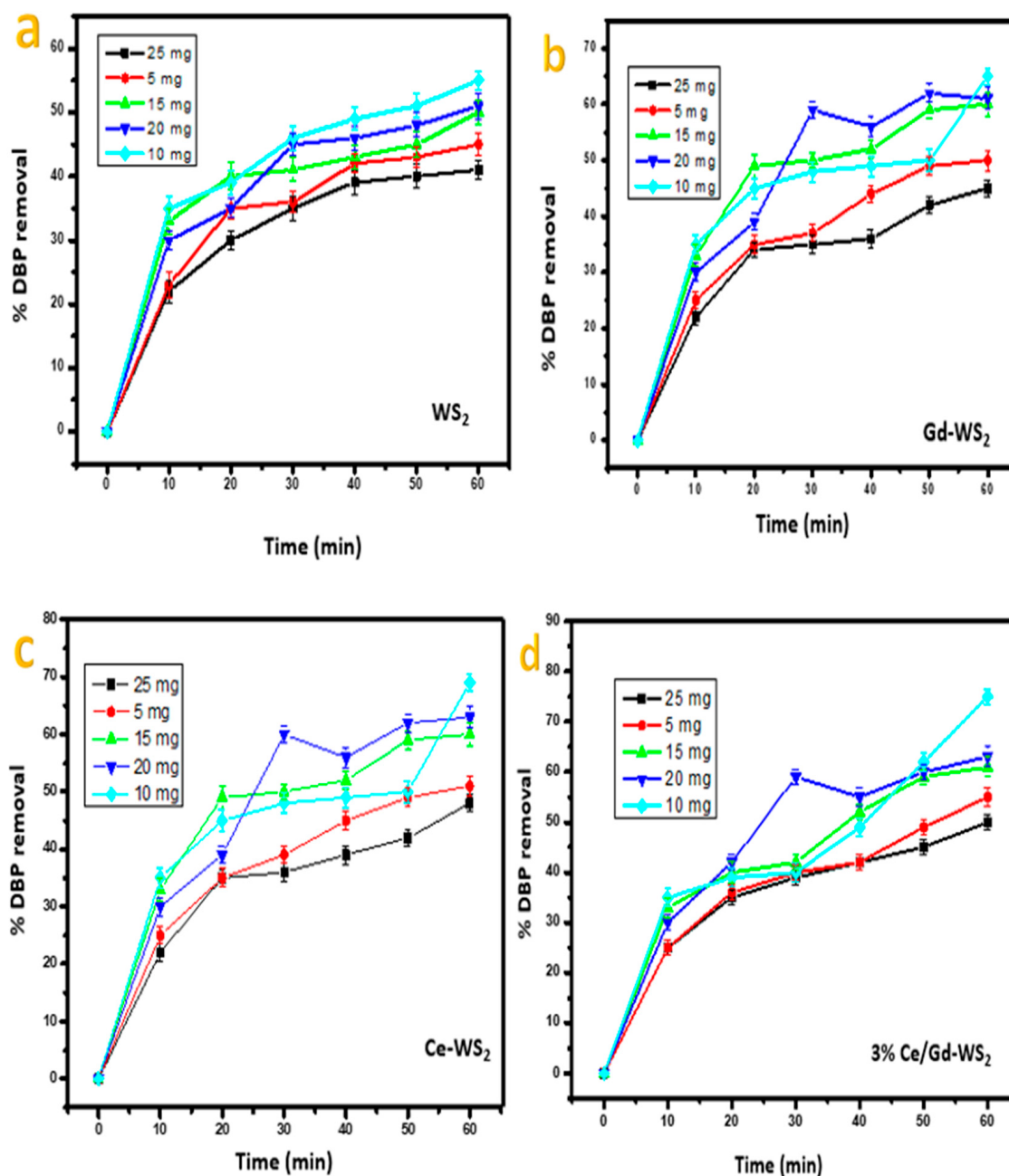


Figure 4. The effect of photocatalyst loading using (a) pristine WS₂, (b) Gd-WS₂, (c) Ce-WS₂, and (d) 3% Ce/Gd-WS₂ towards the photodegradation of dibutyl phthalate.

2.6. Acclimatization of Activated Sludge

The acclimatization of microorganisms was performed for a period of 39 days. The treatment plant was run at 100% synthetic wastewater at day 31. Several working parameters were monitored during the acclimatization period. These parameters include pH, dissolved oxygen (DO), chemical oxygen demand (COD), mixed liquor volatile suspended solids (MLVSS), mixed liquor suspended solids (MLSS), conductivity, and temperature. These were monitored for the survival and growth of microorganisms. The removal COD efficiency during the acclimatization state was illustrated by Figure 5. The COD removal efficiency is regarded as valid when COD removal is above 80% according to Organization for Economic Co-operation and Development (OECD 303A) [17]. The chemical oxygen demand of >50% was removed during the first days (7 days) of sludge retention time one (SRT 1). An increase in COD removal efficiency on STR 2 was observed due to a new source

of food, which comprises synthetic wastewater. A drastic decrease in COD removal was detected when the system was run with 50% secondary (2°) influent and 50% synthetic wastewater. This is caused by “shock” experienced by the system microorganisms in the aeration chamber [18]. Since the ratio of MLVSS/MLSS is above 0.75 illustrating microorganisms’ survival, the system was not hindered. At the last stage of acclimatization, SRT 5, when the system was run with 100% synthetic wastewater, the COD removal reached >80%. Other parameters are tabulated in Table 1. The average temperature of 23 °C was monitored. Moreover, in a wastewater treatment plant, the MLVSS/MLSS ratio should be over 0.75, and it was achieved [19]. The ratios of MLVSS/MLSS were 0.83(SRT 1), 0.82(SRT 2), 0.93(SRT 3), 0.84 (SRT 4), and 0.88(SRT 4). The growth of the microorganisms depends on the amount of dissolved oxygen [18]. Low oxygen content in the aeration chamber can prevent the growth of microorganisms’ growth. The oxygen content was all above 2.0 mg/L. Moreover, the pH of the activated sludge microorganisms was monitored at an ideal pH of 6.0–8.0. The degradation efficiency using wastewater treatment plant and determination of water quality as a function of the amount of salt dissolved was investigated by measuring conductivity.

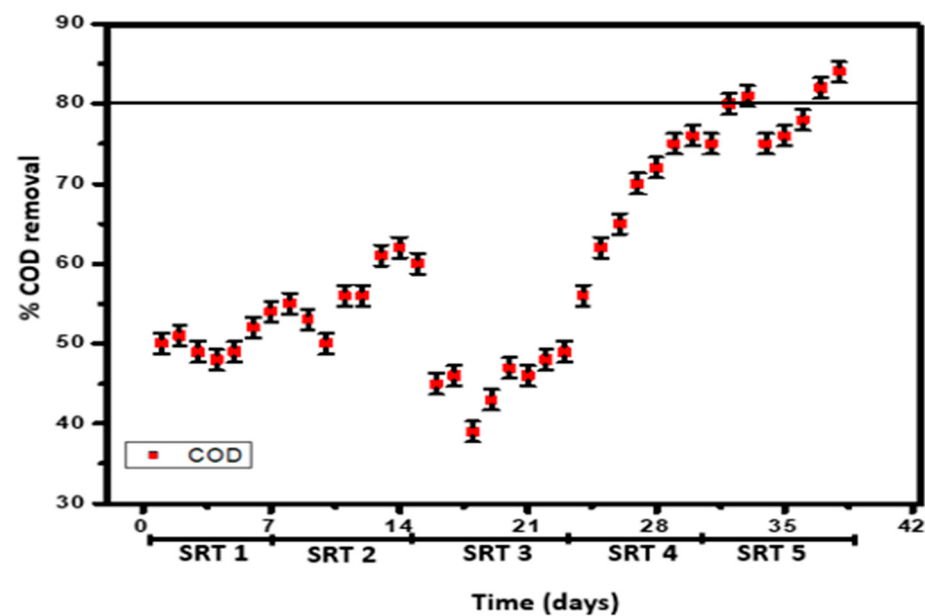


Figure 5. The acclimatization of microorganisms.

Table 1. Other monitored parameters during the acclimatization of microorganisms.

	SRT 1	SRT 2	SRT 3	SRT 4	SRT 5
Parameters	Mean SD	Mean SD	Mean SD	Mean SD	Mean SD
pH	7.1 ± 0.3	6.9 ± 0.3	7.2 ± 0.3	7.0 ± 0.3	7.3 ± 0.3
DO (mg/L)	4.0 ± 0.3	3.5 ± 0.4	3.8 ± 0.3	4.2 ± 0.4	4.3 ± 0.4
Temperature (°C)	22.5 ± 0.5	23.4 ± 0.6	23.1 ± 0.6	23.5 ± 0.7	23.0 ± 0.6
Conductivity (µS/cm)	820.9 ± 29.5	875.2 ± 40.1	891.1 ± 51.2	858.5 ± 35.4	860.2 ± 36.1
MLSS (mg/L)	1620.5 ± 102.1	1550.2 ± 185.5	1750.2 ± 179.5	1680.9 ± 150.2	1702.5 ± 179.2
MLVSS (mg/L)	1350.2 ± 156.8	1275.5 ± 145.6	1640.6 ± 129.3	1420.5 ± 179.5	1500.2 ± 196.5
COD (mg/L)	50.5 ± 5.8	58.2 ± 14.5	47.5 ± 11.5	75.2 ± 8.6	82.1 ± 7.8

SD: Standard deviation.

2.7. Biological Degradation of Dibutyl Phthalate

Biological degradation is considered one of conventional process for metabolic breakdown of organic pollutant in water [20]. After acclimatization, the microorganisms were put to test for biological degradation of t dibutyl phthalate in water under aerobic conditions at various concentration of 1 ppm, 3 ppm, 5 ppm, 7 ppm, and 10 ppm, as depicted by Figure 6a. Furthermore, total organic carbon measurements were further investigated to validate the biological degradation of DBP. The COD removal efficiency on sludge retention time 6 and 7 was >80% using 1 ppm and 3 ppm dibutyl phthalate concentration; meanwhile, TOC removal was at 58% and 64%, respectively. At DBP concentrations of 5 ppm and 7 ppm, a decrease in COD removal was observed by 10% for SRT 8 and SRT 9, but TOC removal increased to 70%. This illustrates the microorganism's tolerance to break down DBP even at high concentrations. A similar mechanism was observed at highest DBP concentrations of 10 ppm (SRT 10), with efficient TOC removals of >70%. The biological efficiency was further monitored using UV-Vis spectrophotometers at a wavelength of 230 nm, as illustrated in Figure 6b. The biological degradation of 62% was obtained at SRT 6(1 ppm). Lowest biological degradations of 35% of SRT 10(10 ppm) followed by 45% and 51% of SRT 9(7 ppm) and SRT 7(3 ppm) were observed, respectively. The optimal metabolic breakdown with 69% removal was depicted by SRT 8 using 5 ppm DBP concentration.

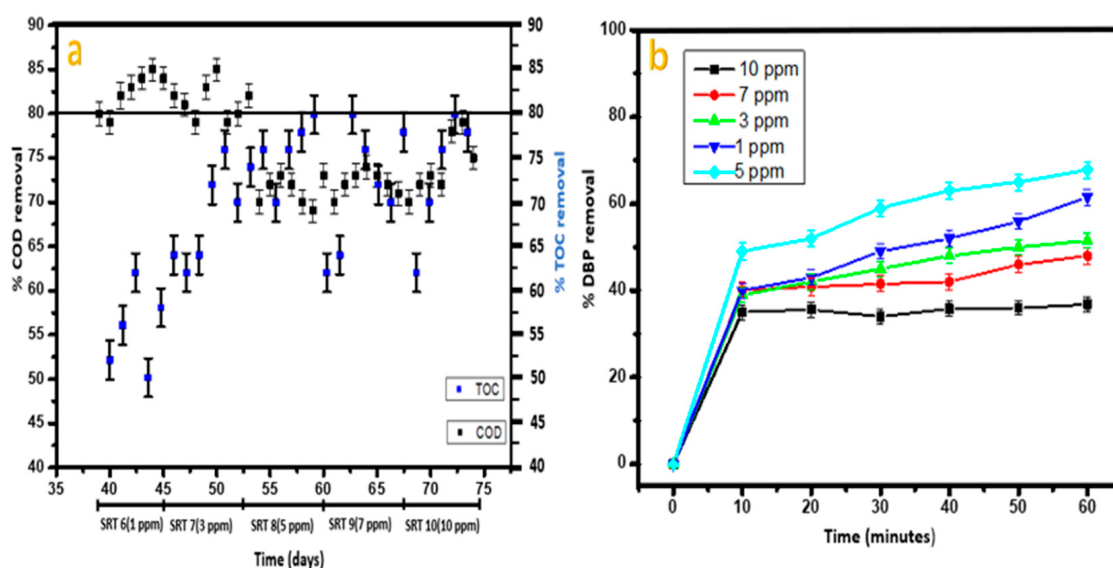


Figure 6. (a) Biological percentage removal of COD and TOC towards DBP removal. (b) The removal efficiency by microbes monitored on UV-Vis spectrophotometer.

The obtained degradation data were further fitted into Equation (1) for kinetics reaction studies.

$$\ln(C_0/C) = -kt \quad (1)$$

The plot of $\ln(C_0/C)$ versus time is shown in Figure 7 with a slope correlating to pseudo first-order constants. The biological degradation of SRT 8 showed the highest rate constant of $7 \times 10^{-2} \text{ min}^{-1}$. This is due to optimal COD and TOC percentage removal by microbes. Lowest rate constants of $3.2 \times 10^{-3} \text{ min}^{-1}$ were depicted on SRT 10. These obtained finding are tabulated in Table 2.

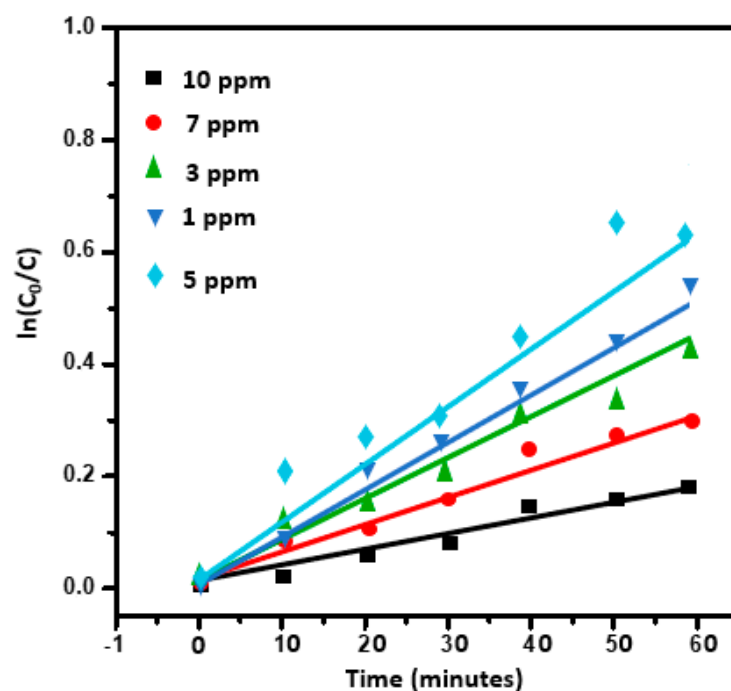


Figure 7. Biological degradation kinetics of dibutyl phthalate degradation at different concentration.

Table 2. DBP degradation kinetics reaction values.

Sludge Retention Time (Days)	K Values(Min^{-1})	R ²
6 (1 ppm)	1.1×10^{-2}	0.9852
7 (3 ppm)	1.0×10^{-2}	0.9704
8 (5 ppm)	1.7×10^{-2}	0.9825
9 (7 ppm)	2.4×10^{-3}	0.9692
10 (10 ppm)	3.2×10^{-3}	0.9650

2.8. Combined Photocatalytic and Biological Degradation of Dibutyl Phthalate

The optimized parameters, which includes a working pH of 7, 5 ppm DBP initial concentration, and the addition 10 mg catalyst loading, were employed in a simulated wastewater treatment plant for the photocatalytic degradation of dibutyl phthalate. The obtained data are shown in Figure 8a,b. The lowest photocatalytic degradation of 46% after an hour of irradiation using WS₂ was obtained, as shown by Figure 8a. This is because the use of pristine WS₂ suffers from excellent charge separation; hence, low degradation was obtained [21]. Photodegradation was enhanced upon the introduction of dopants. The degradation efficiency of Gd-WS₂ and Ce-WS₂ was found to be 75% and 79%, respectively. This is due to excellent charge separation and low recombination rate as further validated by EIS and PL measurements [10]. The degradation efficiency of Gd-WS₂ and Ce-WS₂ increased by 6% and 10%, respectively, as compared to biological degradation; hence, the combined system serves as an ideal system for the effective removal of DBP. The highest photocatalytic removal using co-doped system 3% Ce/Gd-WS₂ of 85% was achieved after 60 min of illumination. The use of co-dopants on the surface of WS₂ further increased degradation efficiency by 16% as compared to biological activity. This is due to the successful formation of Schottky barrier, facilitating excellent charge separation while being irradiated in the visible range of the spectrum. Furthermore, 3% Ce/Gd-WS₂ showed low recombination rates of photoinduced charge carriers, thus preventing the recombination of photoexcited electrons and holes when compared to bare WS₂ and metal doped WS₂.

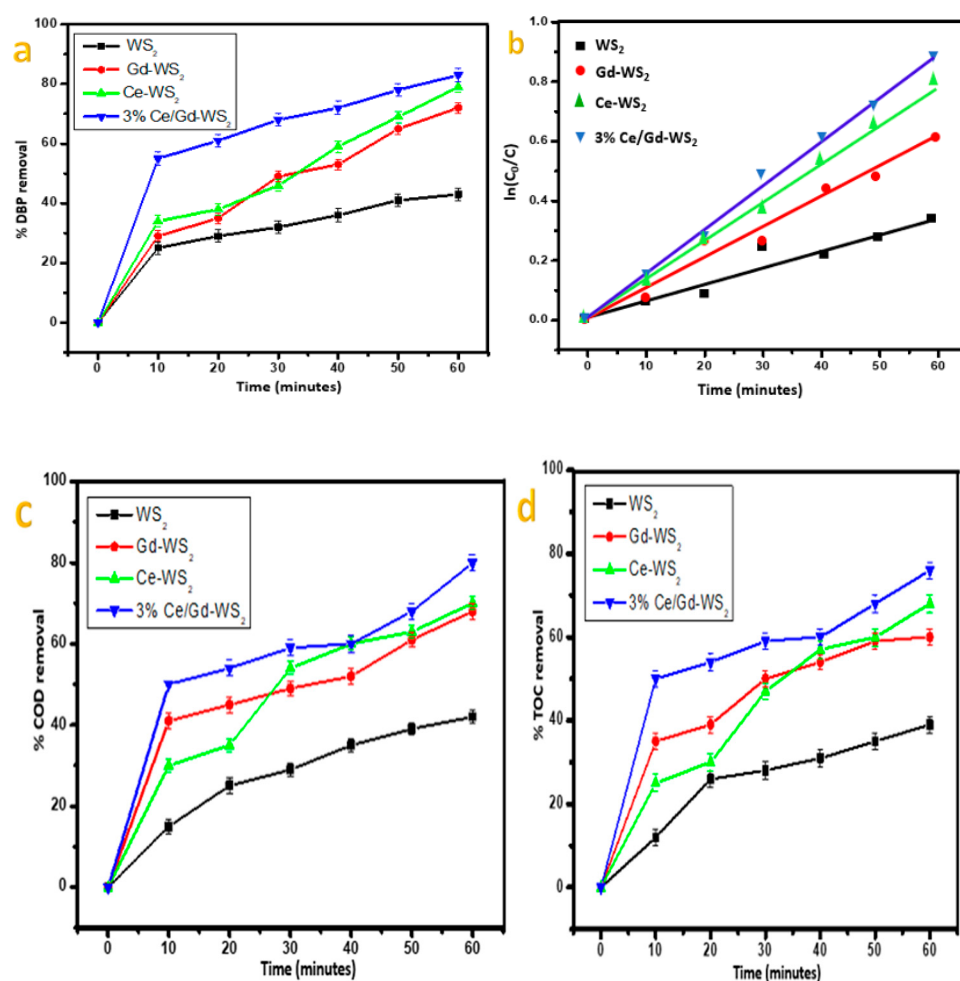


Figure 8. (a) The effect of photocatalysts degradation of DBP, (b) kinetic studies of DBP, (c) % COD removal, and (d) % TOC removal efficiency during photocatalytic degradation of DBP.

The kinetics studies were evaluated, as shown by Figure 8b. The obtained data were fitted to Equation (1). The 3% Ce/Gd-WS₂ exhibited the highest rate constant of $1.9 \times 10^{-2} \text{ min}^{-1}$ ($R^2 = 0.9821$), while pristine WS₂ exhibited a lowest rate constant of $3.4 \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.9681$). These results depict the excellent photocatalytic degradation of 3% Ce/Gd-WS₂ and, thus, complement photometrics studies. The composite displayed an excellent charge separation emerged upon the formation of heterojunction as exhibited by PL and EIS obtained data. The COD and TOC data further complimented the sufficient photodegradation of DBP, as shown by Figure 8c,d, respectively. The lowest COD (Figure 8c) removal of 42% was achieved using WS₂ while metal doped depicted a COD removal of 67% and 74% upon the use of Gd-WS₂ and Ce-WS₂, respectively. The composite exhibited the highest COD removal of 80%. Furthermore, the total organic carbon shown by Figure 8d was further evaluated. The highest TOC removal of 77% using 3% Ce/Gd-WS₂ was achieved. This shows a successful breakdown of organic pollutant dibutyl phthalate into organic intermediated materials, which mineralized into less harmful intermediates [1]. Pristine WS₂ exhibited the lowest TOC removal of 39%, while metal doped Gd-WS₂ and Ce-WS₂ had TOC removals of 60% and 69%, respectively. These results indicate the successful combination of biological and photocatalytic systems, which serves as an ideal system to enhance microorganisms' activity toward the degradation of dibutyl phthalate.

2.9. Proposed Dibutyl Phthalate Photocatalytic Degradation Mechanisms

The proposed mechanism of DBP degradation is depicted, as represented by Figure 9.

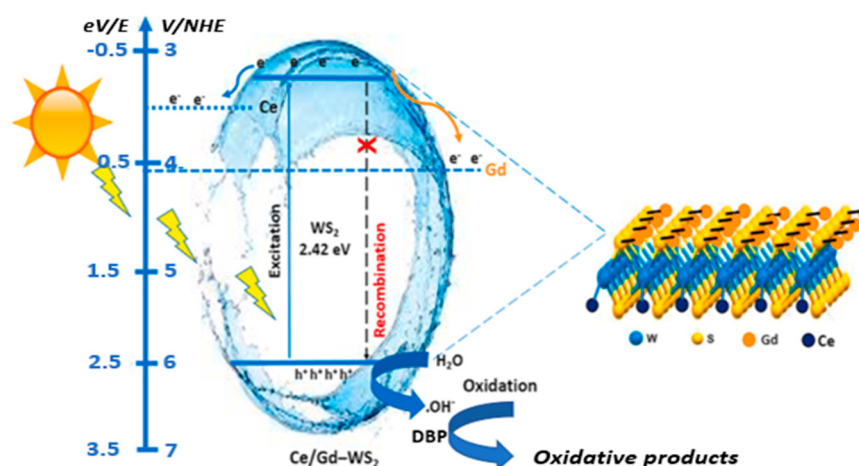
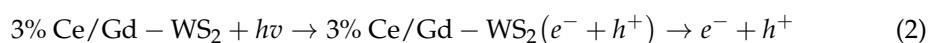
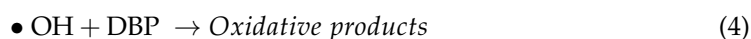


Figure 9. Proposed DBP degradation mechanism.

When the light source of energies greater than 2.42 eV 3% Ce/Gd-WS₂ is irradiated, the electrons (e[−]) are photoexcited migrating from valence band (VB) to conduction band (CB), while holes (h⁺) are generated on the valence band as illustrated by Equation (2).



When electrons lose energy, they tend to recombine with holes generated on the surface of VB, then Ce and Gd trap them as these act as electron traps. The generated holes react with H₂O, forming hydroxyl radicals with oxidized DBP into less toxic molecules.



2.10. Recyclability Studies

The stability of the material for multiple use was studied when performing a recyclability experiment for the photocatalyst, as displayed in Figure 10. After dibutyl phthalate degradation, the catalyst is filtered and rinsed several times with deionized water and ethanol and oven dried at 60 °C overnight. The degradation performance using 3% Ce/Gd-WS₂ after the seventh run was 56%.

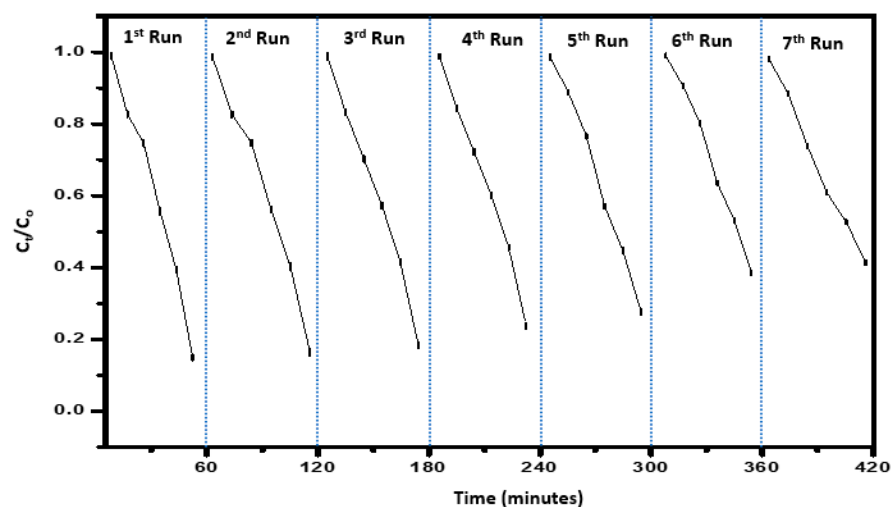


Figure 10. Recyclability experiments of the composite.

3. Materials and Methods

3.1. Materials

All purchased materials are used without further characterization. These chemicals were thioacetamide (Sigma-Aldrich Co., Burlington, MA, USA, 98%, reagent grade), tungsten (VI) chloride (Sigma-Aldrich Co., Burlington, MA, USA, $\geq 99.9\%$ trace metal basis), sodium sulfate anhydrous (Associate Chemical Enterprises, Johannesburg, South Africa), gadolinium (III) acetate hydrate (Sigma-Aldrich Co., Burlington, MA, USA, 99.9% trace metal basis), Nafion perfluorinated resin, aqueous dispersion (10 wt% in H₂O, eq. wt. 1.100 Sigma-Aldrich Co., Burlington, MA, USA), cerium (IV) sulfate (Sigma-Aldrich Co., Burlington, MA, USA), dibutyl phthalate (99% pure), ethanol (Sigma-Aldrich Co., Burlington, MA, USA), and 1-methyl-2-pyrrolidinone (NMP) (Sigma-Aldrich Co., Burlington, MA, USA).

3.2. Methods

3.2.1. Synthesis and Characterization of the Nanoparticles

A slightly modified hydrothermal synthesis route was followed for the preparation of nanoparticles, as reported in our last publication [10]. The synthesized nanoparticles exhibited hexagonal phases with an average particle size of 20 nm. The characterizations of the as-synthesized nanoparticles were performed with various characterization techniques. Functional group determination used a Fourier Transform Infrared spectra (PerkinElmer, Johannesburg, South Africa) of 4 cm⁻¹ resolution. Prior to analysis, a pellet was prepared with potassium bromide (KBr) and scanned in a range 4000 cm⁻¹ and 400 cm⁻¹ at 23 °C and used air as the background. The material's morphology was determined using JOEL-JEM 2010 (United Kingdom) transmission electron microscopy (TEM) at an acceleration voltage 200 kV coupled with energy-dispersive X-ray spectroscopy detectors for the elemental composition of the nanoparticles. TEM carbon copper grids were dispersed in ethanol to coat samples prior to analyses. Moreover, morphology was determined by scanning electron microscopy (SEM) (TESCAN Vega TC, Czech republic) using TESCAN VEGA 3 software with nitrogen flowing at 20 kV voltage. Imagery was improved by coating samples with copper before analyses. The polymorph nature, crystallite size, and phase of the nanoparticles were evaluated using a powder X-ray diffractogram (X'Pert Philip, Germany) operated at 2 θ between 10° and 80° at 40 mA with step size of 0.1017(2 θ) and 4°/min scan rate and a step time of 87.63 with 0.1540 nm CuK α radiation. Raman Micro 200 was further used to evaluate the nature of the sample. UV-Vis spectrometer (Shimadzu UV-2450, Johannesburg, South Africa) was used to deduce the optical properties of the nanoparticles. The atomic composition and chemical states of the material and valence band analyses were determined using X-ray photoelectron spectroscopy (ESCA lab 250 Xi, Thermo Fischer Scientific, Johannesburg, South Africa) using a light monochromator (1486.7 eV of Al K α) as the excitation source at a pressure of $<10^{-8}$ mBar. The characterization of samples' recombination ability was deduced from photoluminescence emission spectra with a light source Xe 300 W at 420 nm. Charge transfer resistance analyses were determined using an Autolab (Nova, Utrecht, The Netherlands) 2.0 potentiostat using three electrodes, namely reference, counter, and working electrode. The reference electrode was a Ag/AgCl, platinum wire as counter and working electrodes constructed from using fluorine-doped tin oxide glass (FTO) coated with samples mixed with NMP and nafion. The nanoparticles surface charge measurements were evaluated using Malvern Zetasizer (The Netherlands). The Shimadzu UV-2450 UV-Vis spectrophotometer at a wavelength of 230 nm was used to monitor the degradation efficiency of dibutyl phthalate. The total organic carbon (TOC) measurements using CO₂ for quantitation were performed on Tekmar Dohrmann Apollo 9000 TOC analyzer (California, USA).

3.2.2. Secondary Wastewater Sampling

The secondary influent was sampled at Daspoort wastewater treatment plant, Pretoria. The plant collects domestic wastewater. The lifespan of wastewater was seven days according to OECD 303A guidelines; hence, sampling was performed weekly. The sampled

wastewater was stored at 4 °C in a refrigerator. To formulate the complete run of the synthetic influent, secondary wastewater and synthetic influent were mixed to attain acclimatization

3.3. Wastewater Treatment Plant

3.3.1. Optimization of Wastewater Treatment Plant

The simulated coupled wastewater treatment plant as shown in Figure 11 consists of 3 L aeration chamber, 1.5 L working volume secondary clarifier, 1 L working volume photoreactor, and 20 L influent tank. The wastewater treatment plant was operated with mean hydraulic retention time (HRT) of 6 h and mean retention time of 0–6 days until a steady state was reached. The 6 h HRT was obtained with a flow rate of 0.5 L/h. The secondary influent was circulated into the aeration chamber using peristaltic pump (120S/DV, Watson Marlow). The influent tank was stirred continuously to keep the contents in suspension using the stirrer (RW 20 digital stirrer, IKA). The oxygen content of 2 mg/L was supplied into the aeration chamber using perforated tube from the compressor. This helps to keep flocs in suspension. The sludge in the secondary clarifier was recycled into the aeration chamber using a 323S (Watson Marlow) peristaltic pump. The water bath was used to maintain the temperature of the lamp jacket between 10 and 20 °C.

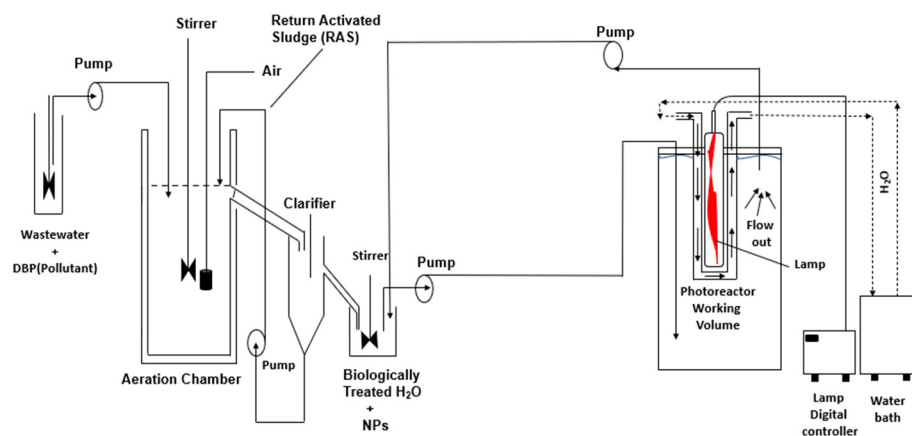


Figure 11. Simulated wastewater treatment plant.

3.3.2. Inoculation of Wastewater Treatment Plant

The return activated sludge (RAS) sampled from Daspoort wastewater treatment plant was used as an inoculum. Prior to inoculation, 12 L of sludge was aerated overnight using compressed air. After the aeration process, the supernatant was removed, and 5 L secondary influent was added and further aerated for 4 h, and the resulting supernatant was reserved. The secondary influent was then mixed with the reserved supernatant and used for the first three days of sludge retention time (SRT 1). The sludge was then partitioned in the aeration chamber in the treatment plant as shown by Figure 11.

3.3.3. Formulation of Synthetic Wastewater Influent

The OECD 303A guideline was followed to prepare the synthetic wastewater influent, as shown in Table 3 [17].

Table 3. Synthetic wastewater influent compositions.

Composition	mg/L
Peptone	160
Meat extract	110
Urea	30
Anhydrous dipotassium hydrogen phosphate	28
Sodium chloride	7
Calcium chloride dehydrate	4
Magnesium sulphate heptahydrate	2

3.3.4. Activated Sludge Acclimatization to Synthetic Wastewater Influent

The wastewater treatment plant was run at 100% raw wastewater (secondary influent) mixed with the reserved supernatant after the inoculation of the aeration chamber with the activated sludge. Following OECD 303A guidelines, MLSS was monitored and expected to be about 2500 mg/L. This was monitored by extracting 50 mL from aeration chamber and filtered and oven dried overnight at 105 °C. The MLSS ranged from 1200 to 2500 mg/L for the first three days of SRT 1. Then, during remaining days of sludge retention time 1, the system was run with 100% secondary influent. This was performed to allow the acclimatization of microorganisms to new sources of food. The secondary influent was decreased gradually while increasing synthesized wastewater until the system was run with 100% synthetic wastewater influent. Table 4 shows the concentration changes of secondary influent relative to the synthetic influent until day 38 when 100% synthetic wastewater was reached. The system was further run for 5 days with 100% synthetic wastewater prior to the introduction of dibutyl phthalate pollutant (5 mg/L).

Table 4. Secondary (2°) and synthetic wastewater (SWW) influent composition [18].

Sludge Retention Time	Days	% Influent
1	0–7	100% 2° influent
2	15–8	75% 2° influent + 25% SWW
3	16–23	50% 2° influent + 50% SWW
4	23–30	25% 2° influent + 75% SWW
5	31–38	100% SWW

3.3.5. Monitored Parameters on Wastewater Treatment Plant

Several chemical and physical tests were conducted. These tests involved chemical oxygen demand (COD) with the use of a COD kit (1.14541.0001, Merck) analogous to DIN EN ISO 7393 and determined using a spectrophotometer (Spectroquant Pharo 300, Merck, Germany) and total organic carbon (TOC) measurements performed on a TOC analyzer (Tekmar Dohrmann Apollo 9000), mixed liquor suspended solids (MLSS), and mixed liquor volatile suspended solids (MLVSS). Prior to the analyses of COD and TOC, the samples were filtered through 0.45 µm and 0.22 µm PVDF filters (Sigma-Aldrich, Burlington, MA, USA), respectively. Moreover, pH, dissolved oxygen, temperature, and conductivity in the aeration chamber were measured using Starter pH 300, Starter DO, Starter conductivity 300C (OHAUS, Parsippany, NJ, USA).

3.4. Optimization of Photodegradation Parameters

The photodegradation activity of the as-synthesized nanoparticles was evaluated in a photoreactor irradiated with 250 W Xe lamp as a light source for the photocatalytic degradation of dibutyl phthalate. The optimization was studied monitoring three parameters, which includes the pH, the initial concentration of the pollutant, and catalyst loading. For all photocatalytic degradation experiments, the varied DBP concentrations and amount of photocatalysts were added into 500 mL solutions while water bath regulates the temperature.

3.4.1. The Effect of pH

The pH studies were conducted in a photoreactor for photodegradation of dibutyl phthalate in a range of pH 1 to pH 11 with an increment of 2 at constant 10 mg catalyst loading and 5 ppm (500 mL) DBP concentration. The pH solution was adjusted dropwise using NaOH and HCl. The solution was stirred for an hour in the dark and further irradiated for an hour using 250 W Xe lamp as a source of light, and 2 mL was sampled; then, it was filtered with 0.22 μ m PTFE membrane filter at an interval of 10 min for an hour. The degradation rate was measured using a UV-Vis spectrophotometer at a wavelength of 230 nm.

3.4.2. The Effect of DBP Initial Concentration

The effect of the initial concentration of dibutyl phthalate was studied with the optimized pH = 7. The concentration of DBP varied between 1 ppm and 10 ppm with an increment of 2. The solutions were then transferred into a photoreactor, with the constant addition of 10 mg photocatalyst.

3.4.3. The Effect of Catalysts Loading

At this stage, the optimized pH = 7 and initial concentration of 5 ppm were employed. Therefore, 5 sets of 5 ppm DBP solutions were prepared and different amounts of catalyst were added ranging from 5 mg to 25 mg in an increment of 5. From these, the solutions were treated following the procedure in Section 3.4.1.

4. Conclusions

The incorporation of biological and photocatalytic setups for the degradation of dibutyl phthalate was successful. A degradation efficiency of 69% and TOC removal of 70% were obtained using biological degradation. This is due to the ability of microorganisms to mineralize DPB into less toxic molecule. The use of the photocatalytic setup under optimization, which includes pH = 7 with 10 mg photocatalyst loading in 5 ppm DBP solution (500 mL), revealed significant photodegradations of 85% using the composite with COD and TOC removal efficiencies of 80% and 77%, respectively. The enhanced biological activity by the composite is attested to the formation of heterojunctions, exhibiting excellent charge separation exhibited by the composite and metal-doped WS₂. Moreover, these findings depict the potential use of the incorporated photocatalytic and biological system for the degradation of toxic organic pollutants such as DBP in the environment. The composite was re-used seven times and still achieved photodegradation efficiencies of 56%.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12050504/s1>, Figure S1: (A) Pristine WS₂, metal doped and co-doped WS₂ characterization with (I) XRD pattern, (II) Raman bands and (III) FT-IR, and (IV–V) TEM and SEM morphological analyses; (B) chemical composition of I(a) survey spectrum, I(b) 4f W, I(c) 2p, I(d) 3d Ce, I(e) 3d Gd, I(f) 1s O and I(g) VB edge position of as-prepared nanomaterials. (C): WS₂, Ce-WS₂, Gd-WS₂, and 3% Ce/Gd-WS₂ characterizations with I(a) band gap measurements, I(b) PL, I(c) Nyquist plots, and I(d) Photocurrent response.

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