Section A-Research paper

PHOTOCATALYTIC DEGRADATION OF TOLUIDINE BLUE USING BISMUTH VANADATE–MWCNTS COMPOSITE

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Abstract

Advanced oxidation processes (AOPs) have been used as an alternative and effective option for treatment of wastewaters especially in case of non–biodegradable compounds. It is well known that bismuth vanadate shows photocatalytic activity. In the present work, bismuth vanadate–MWCNT composite was used for degradation of toluidine blue. The degradation was monitored spectrophotometrically. Effect of different operational parameters like pH, concentration, amount of composite, light intensity, etc. was studied on the rate of degradation. A suitable mechanism for the photocatalytic degradation of toluidine blue dye has been proposed. It is an eco-friendly method for the treatment of polluted water. The catalyst can be recycled and used again.

Keywords: Photodegradation, Bismuth vanadate, Photocatalytic, MWCNTs, Toluidine blue.

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Doi: 10.48047/ecb/2023.12.5.105

1. Introduction

Nanoparticle technology is becoming an increasingly popular choice for treatment of hazardous and toxic wastes (remediation of contaminated water). The smaller particle size of nanoparticles and their large specific surface area correspond to enhanced reactivity for wastewater treatment. Recent trends in nanoparticle synthesis and production have resulted in substantial reductions of cost and increased availability of nanoscale particles for large scale applications. Dyes are a major pollutant of water worldwide and special attention to be degraded effectively. Photochemical technique is considered to be the most useful technique involving oxidative degradation processes among various treatment method.

Lanthanum based nanocomposites LaFeO3, LaNiO3, and LaCoO3 were synthesized by Mocwana et al.1 via sol-gel method using several metals such as Fe, Ni, or Co in different ratios. They studied the photocatalytic degradation activity of as-synthesized composites using methylene blue and o-toluidine blue as model pollutants under visible light. They observed that LaCoO3 composite was more efficient as compared to LaFeO3 and LaNiO3 for both these dyes. BiPO4/Bi2S3-HKUST-1-MOF was synthesised by Mosleh et al.2 and used as a photocatalyst for the degradation of toluidine blue and auramine-O. They found that as-synthesised photocatalyst exhibited 99.37 and 98.44% degradation of toludine blue and auramine-O, respectively.

Parsoya and Ameta3 synthesised ZnFe2O4 via precipitation method and investigated its photocatalytic activity for degradation of toluidine blue. They concluded that superoxide anion radical is the active oxidizing species for the photocatalytic degradation in presence of zinc ferrite. Sadia et al.4 studied the catalytic oxidation of toluidine blue and methyl orange under UV light irradiation using undoped and metal-doped TiO2. They observed that rate of degradation increases with increasing light exposure and amount of photocatalyst. They found that metal-doped titania displayed a degradation of 98% atpH 11; while, it shows a negligibilty degradation in absence of light source.

Kangralkar et al.5 synthesized ZnO catalyst using zinc nitrate and Terminalia arjuna bark extract in presence of microwave irradiation. As-synthesised photocatalyst was used to reduce Cr(VI), & degrade toluidine blue and safranin O in aqueous solution. They observed that 94 and 87% degradation of toludine blue and safranin O was there in 190 and 310 min, respectively using 0.1 g photocatalyst. A quaternary photocatalyst ZrCdPbO4 was prepared by Lohar et al.6 via co-precipitation method. They used as-synthesised photocatalyst for the degradation of toluidine blue, brilliant green and crystal violet. The order of degradation rate followed the order:

Crystal violet, Brilliant green, > Toluidine blue

Photocatalytic degradation of toluidine blue dye in aqueous solution was also studied by Salim et al.7 under fluorescent light in presence of zinc oxide. They observed that the rate of removal of toluidine blue increases with increase in dose of catalyst from 20 to 60 mg L-1; while it decreases with increase in concentration of dye. Liu et al.8 synthesized single crystalline LiNb3O8 nanoflakes via a facile thermal annealing process. They observed that as-prepared nanoflakes exhibited great photocatalytic activities for the degradation of toluidine blue O dye and chemical stability.

Jiang et al.9 fabricated monoclinic BiVO4 with multiple morphologies using hydrothermal strategy. They observed that pH and surfactant had a great effect on the morphology and pore structure of the BiVO4. They evaluated the photocatalytic activities of as-synthesised for the degradation of methyl orange in the presence of visible light. Shen et al.10 prepared bismuth vanadate via hydrothermal method using NaVO3 and Bi(NO3)3 as starting materials. They evaluated the photocatalytic activities of as-synthesised photocatalyst for degradation of methylene blue (model pollutant) in presence of visible light. They observed that as - prepared composite exhibited the highest photocatalytic activity for the degradation of dye (96.4%) in presence of visible light in 200 min.

Novel Ag2O@Ag-modified BiVO4 composites having Z-scheme heterojunction were prepared by Yang et al.11 they evaluated the photocatalytic activity of as-synthesised composite using methylene blue, rhodamine B and their mixture. They observed that as–synthesized composite and composite displayed a high photocatalytic activity as compared to its individual components BiVO4 and Ag2O due of the efficient separation of electron–hole pairs in

the heterojunction construction. Adepu et al.12 prepared a mesoporous titanosilicate/bismuth vanadate (BVTS) inorganic heterostructures. They evaluated the photocatalytic efficiency and found that as-prepared composite displayed 3.5 and 6.5 times higher photocatalytic activity as compared to its individual components, titanosilicate and bismuth vanadate, respectively for the degradation of rhodamine B dye under sunlight.

Liu et al.13 prepared monoclinic BiVO4/MWCNT nanocomposites. They evaluated their photocatalytic activities for degradation of methylene blue in presence of visible light. They observed that photodegradation was enhanced on using BiVO4/MWCNT composite as compared to BiVO4 particles alone and concluded that this enhancement in activity was due to the effective charge transfer from BiVO4 nanocrystals to MWCNT, which promoted the migration efficiency of photogenerated electron–hole pair. Zhang et al.14 prepared a carbon nanotubes (CNTs)/Bi4VO8Cl composite and evaluated its photocatalytic properties for degradation of methyl orange and bisphenol A solutions under visible light irradiation in water. They found that as-prepared composite with 4 wt% CNTs exhibited highest photocatalytic activity, which was 30% higher as compared to pure Bi4VO8Cl.

2. Experimental

2.1 Materials

Bismuth nitrate, citric acid, nitric acid, and ammonia were used in synthesis of bismuth vanadate, which was mixed with MWCNTs. All chemicals used were of analytical grade and used without further purification. Toluidine blue was purchased from Himedia Chemicals.

2.2 Synthesis of Composite

The BiVO4–MWCNTs NPs were synthesized by sol-gel method and characterized as reported earlier15.

3. Photocatalytic Degradation

A stock solution of toluidine blue (1.0 × 10−3 M) was prepared by dissolving 0.0270 g of dye in 100 mL double distilled water. This stock solution was further diluted. The absorbance (A) of toluidine blue solution was determined with the help of a spectrophotometer (Systronics Model 106) at λmax= 630 nm. The photocatalytic degradation of toluidine blue was studied after addition of 0.06 g of BiVO4–MWCNTs in 50.0 mL dye solution (6.5 × 10–5 M). The reaction mixture was exposed to visible light with a 200 W tungsten lamp. Absorbance of solution was measured with the help of a spectrophotometer at different time intervals. The intensity of light was varied by changing the distance between the light source and reaction mixture. A digital pH meter (Systronics Model CL-54) was used to measure pH of the solution. pH of the dye solution was adjusted by addition of previously standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. Control experiments were carried out to confirm that the degradation of toluidine blue was photocatalytic in nature.

A graph was plotted between log A v/s time, which was a straight line showing that photocatalytic degradation of dye followed pseudo-first order kinetics. The rate constant for degradation of dye was calculated by the following equation–

$$k = 2.303 \times \text{slope}$$

A typical run has been drawn for the photocatalytic degradation of toluidine blue using BiVO4–MWCNTs composite, keeping all other parameters constant. The results are reported in Table 1 and Fig. 1.

Table 1: A typical run

pH = 8.5

[Toluidine blue] = 6.5 × 10–5 M

Amount of composite = 0.06 g

Light Intensity = 60.0 mWcm–2

Time (min.)	Absorption	1 + log A
0.0	1.08	1.033
10.0	1.04	1.020
20.0	1.03	1.012
30.0	0.99	0.995
40.0	1.02	1.008
50.0	1.01	1.004
60.0	0.98	0.991
70.0	0.97	0.986
80.0	0.96	0.982
90.0	0.94	0.973

Rate constant (k) = 1.43 × 10–5 s–1

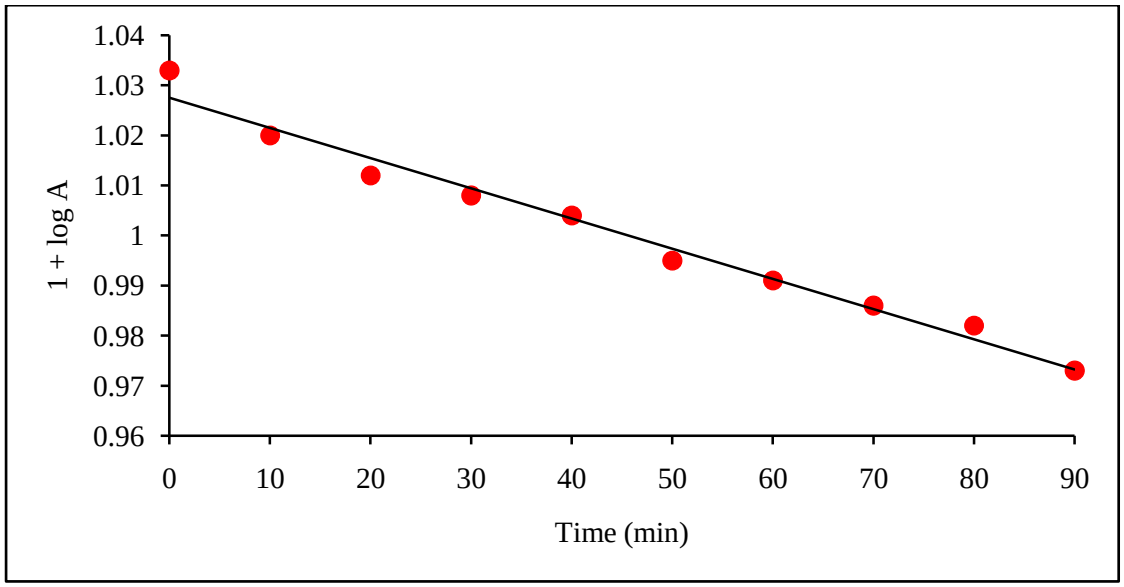

Figure 1: A typical run

3. Results and Discussion

3.1 Effect of working parameters

pH Variation

The effect of pH was investigated by varying the initial pH of solution from 4.0 to 9.5. The results are given in Table 2. It was found that degradation efficiency increases with pH up to 8.5 and then decreases on a further increase. An electron from conduction band is removed by dissolved oxygen to generate O2•– anion radical. An increase in rate of degradation with increase in pH may be due to availability of more O2•– (more oxidising) radicals. A decrease in rate of photocatalytic degradation may be due to neutral form of toluidine blue at higher pH, which faces no attraction/repulsion from negatively charged surface of composite due to adsorption oh OH– ions.

Table 2: Effect of pH

[Toluidine blue] = 6.50 × 10–5 M
Amount of composite = 0.06 g Light intensity = 60.0 mWcm–2

pH	$k \times 10^{-5}$ (s^{-1})
4.0	0.28
5.0	0.32
5.5	0.43
6.0	0.73
6.5	0.92
7.0	1.00
7.5	1.09
8.0	1.25
8.5	1.43
9.0	1.33
9.5	1.26

Concentration Variation

The effect of variation of concentration of toluidine blue has been observed in the range from 3.0 × 10–5 to 7.5 ×10–5 M. The results are reported in Table 3. It has been observed that rate of degradation increases with increasing concentration of dye but decreases after a certain value. On increasing the concentration of dye, the degradation rate increases due to fact that more molecules are available for excitation and energy transfer, but after a certain concentration (6.50 × 10–5 M), the rate of photocatalytic degradation was observed to decrease. This may be due to accumulation of excessive molecules, which do not allow incident light to reach the composite and thus, resulted in a decrease in rate of degradation on further increase in the concentration of dye.

Table 3: Effect of dye concentration

pH = 8.5
Amount of composite = 0.06 g
Light Intensity = 60.0 mWcm–2

[Toluidine blue] × 10^5 M	$k \times 10^5$ (s^{-1})
3.0	0.46
3.5	0.58

4.0	0.65
4.5	0.73
5.0	0.98
5.5	1.14
6.0	1.28
6.5	1.43
7.0	1.15
7.5	0.69

Amount of Composite Variation

The effect of dosage of composite on dye degradation was investigated in the range of 0.02 to 0.12 g and results are summarized in Table 4. It was observed that rate of degradation increases on increasing the amount of composite, further but up to a certain amount of composite for BiVO4–MWCNTs (0.06 g). After this point, the rate of reaction decreases. It may be explained on the basis that as the amount of composite was increased, the exposed surface area of composite. But will also increase. As a result, the rise in the rate of reaction has been observed, but on increasing amount of composite further, there is no increase in exposed surface area of composite, only the thickness of the layer will increase, which allowed e– – h+ recombination and hence, a decrease in rate of photocatalytic degradation was observed.

Table 4: Effect of amount of composite

pH = 8.5

[Toluidine blue] = 6.50 × 10–5 M

Light Intensity = 60.0 mWcm–2

$BiVO_4$–MWCNTs (g)	**$k \times 10^{-5}$ (s^{-1})**
0.02	0.71
0.04	0.99
0.06	1.43
0.08	1.00
0.10	0.80
0.12	0.71

Light Intensity Variation

An influence of light intensity on rate of degradation of dye was also investigated by changing the light intensity from 20.0 to 70.0 mW cm–2. The observation was reported in Table 5. The data indicated that rate of reaction increases with increasing light intensity and maximum rate was found at 60.0 mWcm-2. It may be due to fact that as the light intensity was increased, the number of photons striking per unit time per unit area of composite will also increase, resulting in higher rate of degradation. Further increase in the light intensity may initiate some side thermal reactions and therefore, higher intensities of light have been avoided.

Table 5: Effect of light intensity

pH = 8.5

[Toluidine blue] = 6.50 × 10–5 M

Amount of composite = 0.06 g

Light intensity (mW cm^{-2})	**$k \times 10^5$ (s^{-1})**
20.0	0.38
30.0	0.55
40.0	0.82
50.0	1.07
60.0	1.43
70.0	1.18

4. Mechanism

It was confirmed that •OH radicals do not participate as an active oxidising species in the present investigation as confirmed by using hydroxyl radical scavenger (2–propanol), where the rate of degradation was not retarded appreciably. On the basis of the observation, a tentative mechanism for photocatalytic degradation of TB has been proposed as –

$^1TB_0 \xrightarrow{h\upsilon} {}^1TB_1$ (1)

$^1TB_1 \xrightarrow{ISC} {}^3TB_1$ (2)

$BiVO_4$–MWCNTs $\xrightarrow{h\upsilon}$ (h^+ (VB) + e^- (CB)) (3)

O_2 (Dissolved Oxygen) + $e^- \longrightarrow O_2^{\bullet -}$ (4)

In basic medium-

$^3TB_1 + O_2^{\bullet -} \longrightarrow$ Leuco TB (5)

Leuco TB $\longrightarrow$ Products (6)

Toluidine blue absorbs radiation of suitable wavelength and it is excited to its first excited singlet state, which was followed by intersystem crossing (ISC) to triplet state. On the other hand, the composite BiVO4–MWCNTs also utilize the incident light energy to excite its electron from valence band to conduction band; thus, leaving behind a hole. The dissolved oxygen accepts the electron from

conduction band and it is converted to superoxide anion radical, which converts the TB in to its leuco from. This leuco form of dye is unstable and degrades to smaller almost harmless products.

5. Conclusion

The BiVO4–MWCNTs samples were synthesized by sol-gel method. The experimental results showed that degradation efficiency of toludine blue was affected by various working parameters like pH, concentration, dose of semiconductor and light intensity. Photocatalytic degradation has emerged as an advanced technology for wastewater treatment, because it is an eco-friendly approach. This technique will replace all other existing methods of wastewater treatment in year to come.

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