Research Article

Preparation of BSA-ZnWO₄ Nanocomposites with Enhanced Adsorptional Photocatalytic Activity for Methylene Blue Degradation

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This study explains the effect of adsorption on dye degradation using bovine serum albumin and ZnWO₄ based nanocomposite (BSA-ZnWO₄). The synthesis of BSA-ZnWO₄ was performed by a hydrothermal method involving the encapsulation of ZnWO₄ with BSA. BSA-ZnWO₄ was characterized by SEM, TEM, XRD, FTIR, and UV-Vis spectral techniques. The photocatalytic experiments were performed under solar light. The dye removal was investigated under different reaction conditions. The photocatalytic efficiency of solar/BSA-ZnWO₄ process was higher compared to solar/ZnWO₄, dark/BSA-ZnWO₄, solar/BSA, dark/ZnWO₄, and solar light systems. The simultaneous adsorption and photodegradation process (A + P) was the most efficient process due to rapid destruction of adsorbed dye molecules. BSA-ZnWO₄ showed superior degradation efficiency and reusability over ZnWO₄ for MB degradation.

1. Introduction

Synthetic dyes have significant impact on the ecosystem and can change the physical and chemical properties of water resulting in adverse effect on aquatic flora and fauna. For example, the dyes containing waste water reduce the light penetration and may prevent the photosynthesis resulting in hindrance of microbial activity of submerged plants [1–3]. In addition some dyes may degrade to toxic and stable compounds which are harmful to human beings and living organisms. Therefore, dye removal from waste water is one of the crucial environmental issues for researchers and environmentalists working on water management [4].

Many physicochemical methods such as coagulation, flocculation combined with flotation, ozonation, chemical oxidation, membrane separation process, electrochemical, aerobic, and anaerobic microbial degradation, precipitation, adsorption, and photocatalysis have been reported for the removal of dyes from the aqueous phase [1, 2, 5, 6]. Among these methods, adsorption has been considered as a low-cost and simple technology for environmental engineers. Biological materials with various functional groups (–COOH, –OH)

have an affinity for dyes. Various biomaterials such as pine-wood powder, pineapple peel, cotton stalk, bamboo, coffee grounds, peanut, guava leaf powder, and peat have been used as adsorbents for methylene blue dye from the aqueous phase [7–9].

Bovine serum albumin (BSA) is an important blood protein with a molecular weight of 66500 Da and is composed of 580 amino acid residues [10]. It is a versatile carrier protein with wide hydrophobic, hydrophilic, anionic, and cationic properties. BSA is weakly reducing and can act as a shape directing agent to promote anisotropic growth [11]. Singh et al. prepared silver and gold and their alloy nanoparticles using BSA as a stabilizer agent [12]. Rostogi et al. reported BSA capped gold nanoparticles for the effective delivery of amino-glycoside antibiotics [13].

The photocatalytic degradation process occurs on the surface of the catalyst. Initial adsorption of pollutants on the catalyst surface is essential for a highly efficient process [14, 15]. Jo et al. (2011) claimed that adsorption of dimethyl sulphide onto activated carbon fiber supported TiO₂ enhanced the photodegradation rate [16]. However, the adverse effect of

adsorbed compounds on the photodegradation process was found by Xu and Langford [17]. The excessive adsorption of organic pollutants hinders the penetration of light and causes a reduction in photoactive volume. Recently, ZnWO_4 has been used for degradation of organic pollutants under UV light irradiation. Various methods, such as hydrothermal crystallization process, calcination at elevated temperatures, molten salt, self-propagating combustion, and microwave solvothermal [18, 19], have been developed for the preparation and fabrication of ZnWO_4 . C. Yu and J. C. Yu synthesized ZnWO_4 nanorods using an ultrasonic radiations assisted hydrothermal method and explored its photocatalytic activity for the degradation of rhodamine B dye [19]. Song et al. (2012) reported a novel coupled Cu- ZnWO_4 system and combined it with a Fenton's like reaction for degradation of organic dyes [20]. However, practical application of ZnWO_4 is hindered due to low adsorptional photocatalytic activity. Therefore, it is still a main challenge to enhance the adsorptional photocatalytic activity of ZnWO_4 .

The present work is focused on the applicability of BSA- ZnWO_4 nanocomposite for methylene blue (MB) degradation with ability of bovine album serum as a bioadsorbent and ZnWO_4 as a photocatalyst. BSA- ZnWO_4 was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR), and ultraviolet-visible (UV-Vis) spectroscopy. The influence of adsorption on photocatalysis was studied to understand the real photodegradation process.

2. Experimental

2.1. Chemicals. All the chemicals used were of analytical grade. Bovine serum albumin and $\text{Zn}(\text{NO}_3)_2$ and Na_2WO_4 were purchased from SD Fine Company (India) and used without further purification. CH_3COOH and NaOH were obtained from CDH Company, India. Methylene blue was obtained from Sigma Aldrich Company (India). The double wall cylinder (borosilicate glass), magnetic stirrer, digital thermostatic water bath, pH meter, thermometer, halogen lamp, and aluminium reflectors were used to construct the photoreactor. All the solutions were prepared in doubly distilled water.

2.1.1. Preparation of BSA- ZnWO_4 Nanocomposite. The synthesis of BSA- ZnWO_4 was performed by a hydrothermal method involving the encapsulation of ZnWO_4 with BSA. Different solutions were prepared by dissolving 1 M bovine serum albumin (10 mL), 0.1 M $\text{Zn}(\text{NO}_3)_2$ (50 mL), and 0.1 M Na_2WO_4 (50 mL) with doubly distilled water. $\text{Zn}(\text{NO}_3)_2$ solution was added to bovine serum solution with continuous stirring for 30 minutes at room temperature. To the resulting mixture, Na_2WO_4 solution was added dropwise. The obtained solution was stirred for six hours at 70°C to obtain precipitates. The mixture was centrifuged at 10000 rpm to obtain precipitates. The obtained precipitates were washed several times with ethanol and distilled water to remove unreacted chemicals. Finally, precipitates were heated at 78°C for 8 hours to obtain BSA- ZnWO_4 nanocomposite.

2.2. Photocatalytic and Adsorption Experiments. Adsorption and photocatalytic experiments were performed in a slurry type batch reactor (ht. 7.5 cm $\times$ dia. 6 cm) (Figure 1). A double walled Pyrex vessel was surrounded by thermostatic water circulation arrangement to keep temperature in the range of $30 \pm 0.3^\circ\text{C}$. During adsorption experiments, slurry composed of dye solution and catalyst suspension was stirred magnetically and placed in dark for adsorption and desorption of dye molecule on surface. In case of photocatalytic studies, a suspension composed of MB and catalyst was stirred for ten minutes. Then the suspension was exposed to solar light with continuous stirring. At specific time intervals, aliquot (3 mL) was withdrawn and centrifuged for 2 minutes to remove catalyst particles from aliquot. MB concentration in supernatant was determined on a double-beam UV-Vis spectrophotometer at 653 nm, corresponding to the maximum absorption wavelength of MB. The average intensity of solar light was measured by a digital lux meter ($35 \times 10^3 \pm 100$ lux). All the experiments were performed in triplicate with errors below 5% and average values were reported. The decolorization efficiency of MB was calculated using the following equation:

$$\% \text{ removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100, \quad (1)$$

where C_0 is the initial concentration and C_t is instant concentration of dye sample. The pseudo first order rate constant (k) was used to explore the kinetics of dye degradation (3):

$$k = 2.303 \times \text{slope}, \quad (2)$$

where the slope was obtained from the plot of $\ln(c)$ versus t .

The amount of MB adsorbed onto catalyst surface is calculated by the following equation:

$$q_e = (C_0 - C_e) \frac{V}{M}, \quad (3)$$

where V is volume of dye solution and M is the mass of adsorbent.

3. Results and Discussion

3.1. Characterization of BSA- ZnWO_4

3.1.1. FTIR Analysis. In BSA- ZnWO_4 spectrum, the peaks at 3580 and 3300 are due to N-H stretching and O-H stretching vibrations of amides functionalities present in BSA Figure 2. The absorption peaks at 1830 and 1600 cm^{-1} are due to C=O and COO^- stretching bands of amides in BSA [21, 22]. The band at 1458 corresponds to C-N stretching of amides [22]. The bands at 730 cm^{-1} are assigned due to symmetrical vibrations of the bridge oxygen atom of the Zn-O-W groups [23, 24]. The absorption peaks at 458 and 420 cm^{-1} are due to W-O and Zn-O bonds stretching in WO_6 and ZnO_6 octahedra, respectively [23, 24].

3.1.2. X-Ray Diffraction Pattern. Figure 3 depicts the X-ray diffraction pattern of BSA- ZnWO_4 . The diffraction peaks at

FIGURE 1: Schematic diagram of photoreactor.

FIGURE 2: FTIR spectrum of BSA-ZnWO₄. FIGURE 3: XRD pattern of BSA-ZnWO₄.

20°, 30°, 34°, 38°, and 55° are well matched to the monoclinic structure of ZnWO₄ [23–25]. Slightly broad peaks between 10° and 20° indicate the presence of biological BSA in the nanocomposite [26].

3.1.3. SEM Analysis. SEM micrographs of BSA-ZnWO₄ are shown in Figure 4. SEM images revealed that ZnWO₄ particles were irregularly attached to BSA. ZnWO₄ has spherical, rod like, and plate like submicron particles. These particles tend to aggregate into microsphere (~10 μm), resulting in a rough and porous surface (Figure 4).

3.1.4. TEM Analysis. Figure 5 depicts the TEM image of the BSA-ZnWO₄ composite. The TEM image shows the dispersed homogeneous particles with diameters of around 50 nm, which is in agreement with the result of the XRD. The different contrast on every particle indicates its different composition and structure. The dark part is BSA wrapped ZnWO₄ and the gray part indicated a polymeric backbone of BSA.

3.1.5. Optical Properties and Gel Electrophoresis. Figure 6 depicts UV-Vis absorption spectrum of BSA-ZnWO₄ in ethanol. The absorption maximum of BSA-ZnWO₄ was about 350 nm. The band gap energy E_g was calculated by using the equation $E_g = 1240/\lambda_{\max}$. The band gap energy of BSA-ZnWO₄ was found to be 3.54 eV.

The polarity of BSA-ZnWO₄ nanocomposite was determined in pH range 6.0–7.0 using gel electrophoresis. BSA-ZnWO₄ showed a displacement towards the positively

FIGURE 4: SEM images of ZnWO_4 . FIGURE 5: TEM image of BSA-ZnWO_4 nanocomposite (inset is TEM image at higher magnification). FIGURE 6: UV-Vis spectrum of BSA-ZnWO_4 nanocomposite.

charged electrode under the applied potential, suggesting that the surface of BSA wrapped ZnWO_4 is negatively charged.

3.2. Photodegradation of MB. The results of photodegradation of MB are depicted in Figure 7. Direct photocatalysis

FIGURE 7: Degradation of MB under different reaction conditions: $[\text{MB}] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$, catalyst dosage = 50 mg/100 mL, pH = 5, temperature: $30 \pm 0.5^\circ\text{C}$.

in the absence of a catalyst showed insignificant changes in MB concentration. The decrease in MB concentration was observed both in solar/ BSA-ZnWO_4 and in dark/ BSA-ZnWO_4 systems. MB was completely decolorized in 60 min using the solar/ BSA-ZnWO_4 photocatalytic system. However, 50% of MB was decolorized using dark/ BSA-ZnWO_4 . The higher MB removal efficiency was found in case of suspension under the solar/ BSA-ZnWO_4 system. These experiments clearly indicated that the photocatalytic activity of BSA-ZnWO_4 is quite different from that of common photocatalysts due to high adsorption of MB onto BSA-ZnWO_4 . So photodegradation of dye depends on dye concentration in bulk solution and on the catalyst surface [27, 28]. Hence, the adsorption of MB onto BSA-ZnWO_4 is an important

TABLE 1: Comparison of removal efficiency of BSA-ZnWO₄ in different reaction systems. [MB] = 6.0×10^{-5} mol dm⁻³, catalyst dosage = 50 mg/100 mL, pH = 5, temperature: $30 \pm 0.5^\circ\text{C}$.

Reaction system	Overall removal efficiency (%)	k_{ORE} (10^{-4} s^{-1})	Removal efficiency due to adsorption (%)	k_a (10^{-4} s^{-1})
BSA-ZnWO ₄ /A + P	99	9.0	46.9	4.3
BSA-ZnWO ₄ /A - P	75	6.0	45	4.1
BSA-ZnWO ₄ /DA	45	3.0	45	4.1

A + P means simultaneous adsorption and photocatalysis.

A - P means adsorption followed by photocatalysis.

DA means dark adsorption.

k_{ORE} means rate constant for overall reaction.

k_a means rate constant for adsorption process.

FIGURE 8: Photodegradation of MB under different reaction conditions: [MB] = 6.0×10^{-5} mol dm⁻³, catalyst dosage = 50 mg/100 mL, pH = 5, temperature: $30 \pm 0.5^\circ\text{C}$.

parameter for the photocatalytic activity evaluation of the nanocomposite. The real photodegradation can be explained on the basis of the decrease in dye concentration both in bulk solution and in catalyst surface. Total MB concentration in the present slurry batch reactor is given as

$$C = C_b + C_s, \quad (4)$$

where C_b is the MB concentration in bulk solution and C_s is adsorbed MB on the catalyst surface.

As indicated in Figure 7, the removal efficiency trend follows the order solar/BSA-ZnWO₄ > solar/ZnWO₄ > dark/BSA-ZnWO₄ > solar/BSA > dark/ZnWO₄ > solar light. The results clearly point out the adsorptional photocatalytic activity of BSA-ZnWO₄ as compared to other systems. ZnWO₄ showed insignificant adsorptional removal of MB under chosen experimental conditions.

3.3. Role of Adsorption in Photodegradation of MB. To study the effect of adsorption on the photodegradation of MB onto BSA/ZnWO₄, MB solution was subjected to three reaction conditions. The three reaction systems, that is, equilibrium adsorption in dark, equilibrium adsorption followed by photodegradation, and simultaneous adsorption and degradation, were denoted by BSA-ZnWO₄/DA, BSA-ZnWO₄/A - P, and BSA-ZnWO₄/A + P, respectively, unless otherwise specified. During the simultaneous adsorption and degradation process (A + P), 99% of MB in bulk solution

was degraded under solar light for 60 minutes while in case of dark adsorption (DA) only 33% of MB was removed (Figure 8). BSA-ZnWO₄/A + P system was highly more efficient than BSA-ZnWO₄/A - P (75%) for the degradation of methylene blue dye.

Commonly, adsorption of adsorbate onto catalyst results in the enhancement of its photocatalytic degradation [29, 30]. In the present study, the role of adsorption might be complicated for BSA-ZnWO₄ nanocomposite. The unexpected photocatalytic degradation behavior over BSA-ZnWO₄ was ascribed to the extent of adsorption of MB. BSA-ZnWO₄ had far higher adsorption of MB than ZnWO₄ (Figure 7 and Table 1). The difference in adsorption capacity might be due to surface charge. The surface of BSA-ZnWO₄ was negatively charged in the pH range of 6.0–7.0 causing high adsorption of cationic MB molecules. On the other hand, no net charge on the surface of ZnWO₄ resulted in low adsorption of MB dye onto ZnWO₄. The adsorption of dye onto BSA-ZnWO₄ PCSNC increased with increasing pH value. Increased pH resulted in higher negative charge density on adsorbent surface leading to enhancement in cationic dye adsorption. In contrast, dye adsorption was suppressed at a lower pH value due to competitive adsorption between the hydrogen ion and cationic dye molecule onto BSA-ZnWO₄. The solution pH value after dye uptake was lower than initial pH. This was due to the release of H⁺ ions PCSNC surface by an ion exchange mechanism between the dye molecule and H⁺ ions of the carboxylic acid on the PCSNC surface [17].

During BSA-ZnWO₄/A - P, the catalyst particles were highly covered by MB molecules. Such high coverage by MB dye molecules might cut off the sunlight, resulting in lower degradation of MB. In case of the simultaneous adsorption and photocatalytic degradation process (BSA-ZnWO₄/A + P), the instant amount of MB adsorbed onto BSA-ZnWO₄ at each time was not too much, which weakened the screening effect to sunlight and offered adequate active sites to generate valence-band holes and conduction band electrons [31]. In the mean time, the adsorbed dye molecules could be degraded rapidly in simultaneous photodegradation. This concurrent photodegradation of MB could increase the sunlight transmittance to catalyst surface and improve the degradation efficiency enormously.

3.4. Recycling Efficiency of BSA-ZnWO₄. The filtration of BSA-ZnWO₄ was quick and easy due to the gel formation ability of BSA, whereas the separation of ZnWO₄ was slow

FIGURE 9: Recycle efficiency of BSA-ZnWO₄ and ZnWO₄: [MB] = 6.0×10^{-5} mol dm⁻³, catalyst dosage = 50 mg/100 mL, pH = 5, temperature: $30 \pm 0.5^\circ\text{C}$.

and difficult. 20% of ZnWO₄ was lost during each catalytic process. These studies revealed that recovery of CSNP is difficult and reapplication is not effective. The efficiency of ZnWO₄ was decreased to 15% after 10 catalytic cycles due to catalyst loss during the recovering procedure Figure 9. On the other hand, BSA-ZnWO₄ was easily recycled with 75% efficiency after 10 catalytic cycles confirming the reusability of BSA-ZnWO₄ in the photodegradation process.

4. Conclusion

In this study, BSA-ZnWO₄ nanocomposite was successfully prepared by a hydrothermal method. The photocatalytic activity of BSA-ZnWO₄ was tested for the adsorptional removal of methylene blue from the aqueous phase. BSA-ZnWO₄/A + P exhibited higher photocatalytic activity for the removal of MB due to a high adsorption capacity compared to other investigated systems. In case of the A – P system, too high adsorption on catalyst surface resulted in low rate of the degradation process. However, in the A + P system, the promoting effect was relatively lower in adsorption followed by simultaneous photocatalytic degradation. The superior recycle efficiency of BSA-ZnWO₄ showed a promising vision for its large scale application in water purification.

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