Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1079248

57 (2016) 16514–16521
July

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Synthesis of ZnO photocatalyst via ZnO_2 precursor and its application for dye degradation from effluent under solar irradiation

Ramdas A. Pawar[a], Dnyaneshwar R. Shinde[b,*], Popat S. Tambade[b]

[a]*Department of chemistry, P.D.E.A's. Baburaoji Gholap College, Savitribai Phule Pune University, Sangavi, Pune 27, India*
[b]*Department of Chemistry, P.D.E.A's. Prof. Ramkrishna More College, Savitribai Phule Pune University, Akurdi, Pune 44, India, Tel. +91 9881350383; email: drshinde1970@yahoo.com (D.R. Shinde)*

Received 3 August 2014; Accepted 29 July 2015

ABSTRACT

Nanosized ZnO crystallites were prepared by a new route from ZnO_2 as a precursor. In turn, the precursor was synthesized from $Zn(CH_3COO)_2·2H_2O$ and H_2O_2 by a simple mechanochemical method. The synthesized photocatalysts was characterized by XRD, SEM, FTIR, and UV–visible spectroscopic methods. The X-ray diffraction data suggest that the synthesized ZnO crystallite has the hexagonal wurtzite structure with crystallite size ~13 nm. ZnO-mediated photocatalytic degradation of the dyes from an effluent has been investigated under solar irradiation. Experimental conditions for degradation of dyes including pH of the effluent, dose of the catalyst, and height of the effluent column in reaction vessel were optimized. Nearly 100% decolorization and more than 95% degradation of the dyes from the effluent were achieved under optimized conditions under solar irradiation within 90 min time.

Keywords: Degradation; Solar irradiation; Dyes; Photocatalyst; ZnO; Effluent

1. Introduction

In recent years, TiO_2 and ZnO have attracted considerable attention as photocatalysts due to their ability to degrade many organic pollutants from water or air in the presence of UV or visible irradiations [1,2]. ZnO with wurtzite crystal structure is an n-type semiconductor having a band-gap around 3.3 eV, abundant in nature and environment-friendly [3]. It is used as a photocatalyst as well as in the production of many optoelectronic devices such as transparent conducting oxides (TCO), solar cells, and flat panel displays. [4–6]. The biggest advantage of ZnO over TiO_2 is that it shows higher photocatalytic activity under sunlight [7–9]. This is due to better efficiency of ZnO toward generation of hydroxyl free radicals ($^{\cdot}OH$) than TiO_2 [10,11]. Various chemical and physical methods for synthesis of ZnO nanoparticles, such as chemical precipitation, sol–gel, process, microwave irradiation-based methods, mechanical milling, spray pyrolysis, thermal evaporation, mechanochemical synthesis, hydrothermal methods, and sonochemical method, have been reported in the literature [12]. There are no reports on the synthesis of ZnO from ZnO_2 as a precursor, where ZnO_2 was prepared by mechanochemical method by grinding $Zn(CH_3COO)_2$ and H_2O_2 together. The preparation of ZnO photocatalyst via ZnO_2 is a simple low-temperature route, hence could be employed for large-scale and economic preparation of ZnO photocatalyst. In this study, we have prepared

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*Corresponding author.

ZnO by this method and studied photocatalytic activity toward the degradation of the dyes from industrial effluent.

Nowadays, more than ten thousand synthetic dyes are known and have been employed by textile, leather, paper, food, petroleum, etc. industries for dyeing of the products [13]. Due to widespread uses of the dyes, they emerged as predominant water pollutants. It is a well-known fact that textile industries utilize vast amount of synthetic dyes and in the dyeing process, invariably 10–20% dyes are released into the effluent either in solution or in suspended form [14]. The effluent containing dyes when mixed with natural water sources cause many issues regarding the water pollution. The dyes and their degradation products are considered to be toxic, mutagenic, and carcinogenic in nature [15]. The dyes in the effluent possess high absorbance, hence they are clearly visible though present in small amount. This property of the dyes affects aquatic life (phytoplanktons) by limiting passage of light through water [16]. Therefore, it is of prime importance to remove the dyes from industrial effluent before they are being allowed to release into natural water reservoirs. Removal of organic compounds from the industrial effluents could be performed by biological methods. However, biological methods are less effective for removal of dyes, since many dyes are designed so that they are stable to light and resistant to attack by the micro-organisms [17–19]. On the other hand, advanced oxidation processes proved to be more effective than biological methods for the degradation of dyes from the effluents [20–23]. Conversely, the advanced oxidation processes like Fenton's oxidation process and persulfate oxidation process lead to the formation of undesirable side produces such as $Fe(OH)_3$, and $(NH_4)_2SO_4$. In this context, one of the best emerging alternatives to eliminate the dyes from the effluent is mineralization of the dyes via photocatalytic degradation method. Review of the literature shows that ZnO is the better alternative as a photocatalyst for the oxidative degradation of the dyes. However, in many of these studies, schemes employed for the synthesis of ZnO catalyst and reactor system for photodegradation are technically complicated. Such methods remain as a part of academic interest as they are not cost-effective. The present work focuses on the development of a cost-effective method for the synthesis of ZnO photocatalyst and its application for the degradation of the dyes from the effluent under solar irradiation.

2. Materials and method

In the present investigation, all AR grade chemicals were procured from Merck Chemicals and used without further purification.

2.1. Synthesis and characterization of ZnO photocatalyst

In the synthesis of ZnO_2, 10 g of zinc acetate and 0.5 ml of 20% H_2O_2 were mixed and grinded in the mortar with pestle till the smell of acetic acid disappeared. Addition of 0.5 ml H_2O_2 and grinding step were repeated 25 times which resulted in the formation of ZnO_2. If necessary, during this process, the reaction mixture was dried under IR lamp. Finally, synthesized ZnO_2 was dried in an oven at 130˚C for 30 min. Then thermal decomposition of ZnO_2 to ZnO was achieved in an open atmosphere at 190–210˚C in a controlled manner as ZnO_2 decomposes to ZnO violently. Then the resulted product was annealed in a muffle furnace at 450˚C for 90 min.

2.2. Characterization of ZnO

Chemical analysis of ZnO for Zn(II) was performed by complexometric titration using standard solution of Na_2EDTA. The crystalline phase of ZnO was identified by powder X-ray diffraction (XRD) using Cu-Kα radiation. The crystallite size was calculated by Debye–Scherrer's formula [24]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \tag{1}$$

where D—crystallite size (nm), λ—0.15405 nm, β—full width at half height of the peak in radians, θ—Bragg diffraction angle.

The particle morphology was determined by scanning electron microscope (SEM) imaging. The diffuse reflectance spectra (DRS) of the ZnO photocatalyst was recorded over the range of 250–660 nm and the band gap was estimated using the Kubelka–Munk plot [25,26]. Fourier transforms infrared (FTIR) spectrum of ZnO was recorded in the range of 400–4,000 cm^{-1}.

2.3. Source of dye effluent

An untreated dye effluent of a particular batch was procured from a small scale cotton dying unit located in Malegaon (Maharashtra, India). The effluent was analyzed for chemical oxygen demand (COD), Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, and SO_4^{2-} content as per the prescribed methods [27]. The UV–visible absorbance spectrum of the effluent as received was recorded over the range of 330–800 nm.

2.4. Photocatalytic degradation of dyes from the effluent

The photocatalytic degradation of the dyes from the effluent was performed under solar irradiation.

Experiments were carried out in a Petri dish of 125 cm^2 surface area under unstirred condition of the effluent and at a solar irradiation of intensity in the range of 4.5×10^3–6.8×10^3 Lux.

The effect of pH on the degradation of dyes was investigated over the pH range 5–10 (at one unit interval). The pH of 100 ml effluent was adjusted to requisite value by addition of either 0.1 N NaOH or 0.1 N H_2SO_4 and absorbance was recorded at λ_{max}. In the effluent, 50 mg of ZnO was added and the solution was sonicated for 2 min. Resulted suspension was poured in the Petri dish and placed under sunlight for 25 min. Subsequently, the effluent was centrifuged and absorbance was recorded at λ_{max}. Percent degradation was calculated using Eq. (2):

$$\text{Percent degradation} = \frac{A_0 - A}{A_0} \times 100 \qquad (2)$$

where A_0—Initial absorbance of effluent at λ_{max} and A—absorbance of dye solution after experiment at λ_{max}.

To optimize the catalyst dose, the procedure was repeated as above using 20–100 mg ZnO dose at pH where optimum degradation of the dyes was observed. Time required for complete decolorization was determined by performing experiment on 100 ml of effluent at an optimum dose of ZnO and pH of the effluent. In this experiment, during irradiation of the effluent, 3 ml of the effluent was successively withdrawn at definite time interval, ZnO was separated by centrifugation, and absorbance was recorded at λ_{max}. The effect of column height of the effluent in the Petri dish on the percent degradation of the dyes was determined at optimized pH and quantity of ZnO. The column height of the effluent in the Petri plate was varied from 0.75 to 3.75 cm and percent degradation was determined at 30 min irradiation time. The degradation of the dyes is also accounted in terms of the COD and it was determined by the prescribed method [27] after complete decolorization of the effluent. With each of the above experiments, one control experiment was also carried out.

3. Results and discussion

3.1. Synthesis of ZnO

$Zn(CH_3COO)_2$ and H_2O_2 react with each other to form ZnO_2 and acetic acid (Eq. (3)). Acetic acid escapes from the reaction mixture during grinding process as a gas and can be detected by its typical smell. The loss of acetic acid from reaction mixture is a driving force for this reaction.

$$Zn(CH_3COO)_2 + H_2O_2 \rightarrow ZnO_2 + 2CH_3COOH \uparrow \qquad (3)$$

The thermal decomposition of ZnO_2 at 190–210˚C resulted into the formation of amorphous ZnO. The decomposition reaction of ZnO_2 to ZnO takes place violently with evolution of heat, hence must be carried out in a controlled way (Eq. (4)).

$$2ZnO_2 \xrightarrow{\Delta} 2ZnO + O_2 \qquad (4)$$

Then ZnO obtained at this stage is amorphous in nature and cannot be used as photocatalyst. To obtain active catalyst, it was annealed in a muffle furnace at 450˚C for 90 min.

The overall reaction of synthesis of ZnO was monitored by FTIR spectroscopic analysis. The FTIR spectrum (Fig. 1) of ZnO showed a broad peak below at 550 cm^{-1} and minor peaks at 1,340, 1,615, and 3,330 cm^{-1}. The major broad peak below 550 cm^{-1} belongs to Zn–O stretching frequency, while minor peak at 1,340 cm^{-1} may occurr due to O–O bonds [28]. The peaks at 1,631 and 3,375 cm^{-1} in the FTIR spectrum can be attributed to adsorbed H_2O. The FTIR spectrum of ZnO does not show any characteristic peak belonging to the acetate group of $Zn(CH_3COO)_2$ indicating that annealing temperature 450˚C is sufficient to decompose residual zinc acetate present in the ZnO_2 precursor.

3.2. Characterization of ZnO photocatalyst

3.2.1. Compositional analysis

The chemical analysis of as-synthesized ZnO showed that it contains 78.86 ± 0.92% Zn(II). The calculated purity of ZnO depending on Zn content becomes 98.03 ± 1.14%.

3.2.2. XRD studies

The XRD pattern (Fig. 2) shows the peaks at 2θ values 31.9˚, 34.6˚, 36.2˚, 47.64˚, 56.8˚, 63.0˚, 66.4˚, 68.1˚,

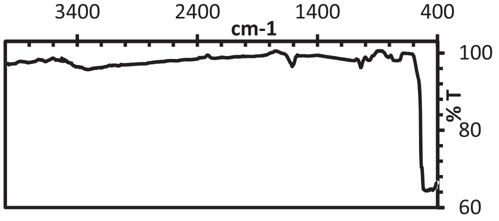

Fig. 1. FTIR spectrum of ZnO photocatalyst.

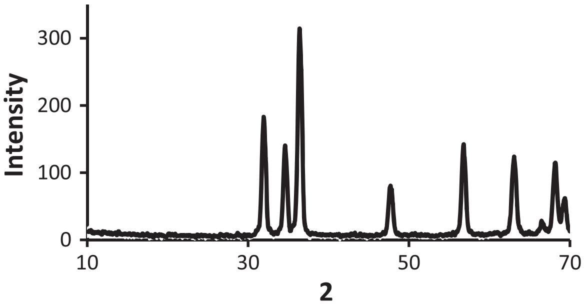

Fig. 2. XRD of ZnO photocatalyst.

and 69.2°, and can be indexed to the planes [1 0 0], [0 0 2], [1 0 1], [1 0 2], [1 1 0], [1 0 3], [2 0 0], [1 1 2], and [2 0 1] of the ZnO crystal as in the standard data file (JCPDS, card No. 36-1451). The observed diffraction pattern is a characteristic of crystalline ZnO having hexagonal Wurtzite structure. The sharp and intense peaks in the XRD point out that the synthesized ZnO is highly crystalline in nature. No extra peak was detected in the XRD of ZnO which indicates the complete decomposition of ZnO_2 precursor to ZnO. Furthermore, the crystallite size of ZnO photocatalyst was estimated by Debye–Scherrer's equation and found in the range of 10–16 nm.

3.2.3. UV–visible spectrum

Typical DRS of ZnO is represented in Fig. 3. The band gap energy was obtained from the Kubelka–Munk plot (Fig. 4) and it is found to be 3.2 eV. Such band gap is useful for solar irradiation-mediated photocatalysis as it helps to absorb the light of longer wavelength [10].

3.2.4. SEM analysis

The typical SEM image of ZnO (Fig. 5) indicates that ZnO grains are quite uniform in size and morphology, and show agglomeration to some extent. The ZnO grains acquired roughly spherical shape of an average diameter ~82 nm.

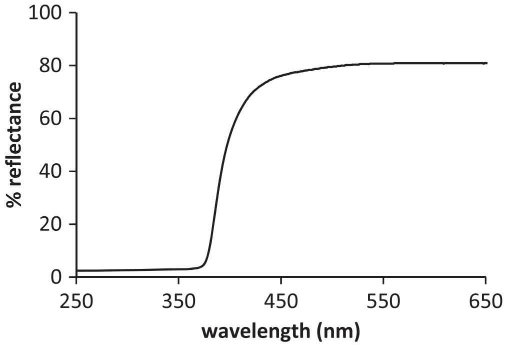

Fig. 3. Diffuse Reflectance Spectrum of ZnO photocatalyst.

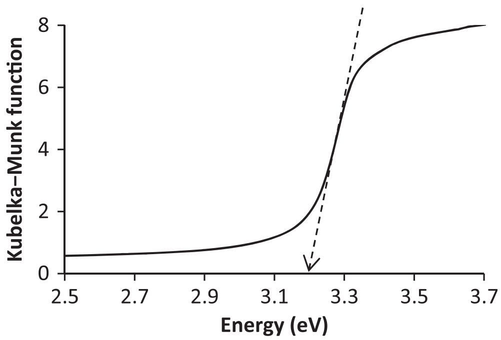

Fig. 4. Kubelka–Munk plot.

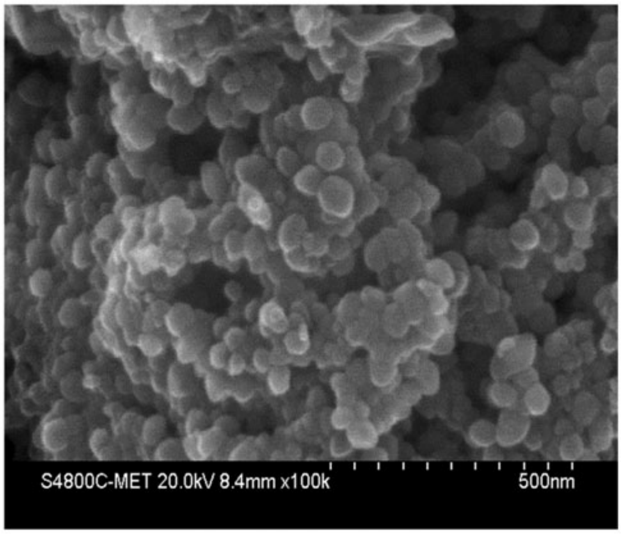

Fig. 5. SEM image of ZnO photocatalyst.

Table 1
Characteristics of dye effluent

Characteristic	Value
Color	Pink–purple
COD	359.2 ppm
Cl^-	1,623 ppm
SO_4^{2-}	55 ppm
Na^+	1,830 ppm
Ca^{2+}	89 ppm
K^+	20 ppm
pH	8.96
λ_{max}	534 nm
Absorbance at λ_{max}	0.402

3.3. Characteristics of the effluent

The physicochemical analysis of the dye effluent as received was carried out by the prescribed methods and results are depicted in Table 1. The high Na^+ and Cl^- contents, and alkaline pH of the effluent are as a result of the salt and caustic requirement of the dyeing process.

3.4. Photocatalytic degradation of dye from the effluent

3.4.1. Effect of pH

The pH of the effluent is an important parameter, which directly influences the rate of photocatalytic degradation of the dyes [29]. The effect of pH on degradation of dyes was examined over the pH range 5–10 (Fig. 6). At $pH < 4.5$, the ZnO undergoes dissociative corrosion, hence the study was not performed below pH 5 [30,31]. The results of this experiment show that an increase in the pH of the effluent from 5 to 10 resulted in an increase in the percent degradation of dyes from 49.65 to 81.77%. These results demonstrate that in an alkaline medium, higher degradation of the dyes takes place than in the acidic medium. Hydroxyl free radical ($^{\cdot}OH$) is the primary oxidizing species responsible for the photocatalytic activity of ZnO. In the acidic medium, the formation of $^{\cdot}OH$ radical takes place as represented in Eqs. (5) and (6) [29,32,33]:

$$ZnO + h\upsilon \rightarrow ZnO + e^-_{(cb)} + h^+_{(vb)} \tag{5}$$

$$H_2O + h^+_{(vb)} \rightarrow {}^{\cdot}OH + H^+ \tag{6}$$

In the alkaline medium, the $^{\cdot}OH$ free radicals are generated by different mechanism than in the acidic medium which is assisted by OH^- ions in the solution [34].

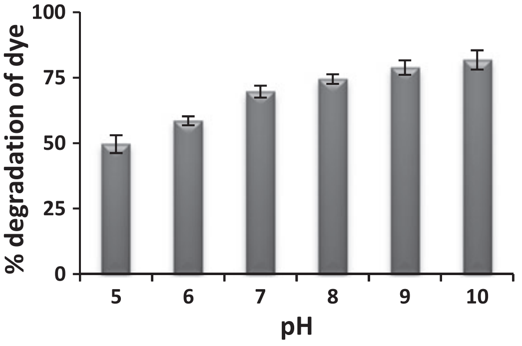

Fig. 6. Effect of pH of effluent on percent degradation of dye from the effluent.

$$OH^- + h^+_{(vb)} \rightarrow {}^{\cdot}OH \tag{7}$$

The pH of a solution is a function of OH^- ion concentration. When the pH is raised from 7 to 10, OH^- ion concentration also increases which in turn enhances $^{\cdot}OH$ free radicals. Therefore, enhanced degradation of the dyes was observed in alkaline condition as compared to acidic and neutral pH of the effluent. The general reaction responsible for the degradation of the dye molecules via free radical mechanism can be represented as in Eqs. (8)–(11):

$$^{\cdot}OH + R - H\ (\text{dye}) \rightarrow R^{\cdot} + H_2O \tag{8}$$

$$R^{\cdot} + {}^{\cdot}OH + O_2 \rightarrow \text{degradation products } CO_2 \text{ and } H_2O \tag{9}$$

$$e^-_{(CB)} + O_2 \rightarrow {}^{\cdot}O_2 \tag{10}$$

$$^{\cdot}O_2 + \text{dye} \rightarrow \text{dye} - O_2^{\cdot} \rightarrow \text{degradation of dyes to } CO_2 \text{ and } H_2O \tag{11}$$

Similar results were reported by Daneshvar et al. [2], Krishnakumar et al. [9], Pardeshi and Patil [32], and Chen et al. [35] on the degradation of the dyes using ZnO as a photocatalyst.

3.4.2. Effect of catalyst loading

A series of experiments were performed by varying catalyst dose to assess the optimum catalyst loading. It is observed that (Fig. 7) the percent degradation of the dyes is a function of catalyst dose. The percent degradation of the dyes increases with increase in catalyst dose from 20 to 60 mg per 100 ml and then remains constant. The enhancement of the dye degradation is due to increase in population of the catalyst particles within illumination area. The experiments were carried out under unstirred condition, hence the ZnO particles settle at the bottom of the Petri dish forming a layer. With increase in the catalyst dose, more uniform layer of ZnO occupying whole bottom surface of the Petri dish could be obtained. This has resulted in an increase in the number of reaction sites for the degradation reaction. At and above 60 mg of catalyst dose, nearly the same percent degradation has been observed indicating that 60 mg of ZnO is sufficient to occupy the whole surface of the Petri dish uniformly. The catalyst dose required to attain an optimum rate of degradation of the dyes depends upon the geometry, working conditions of

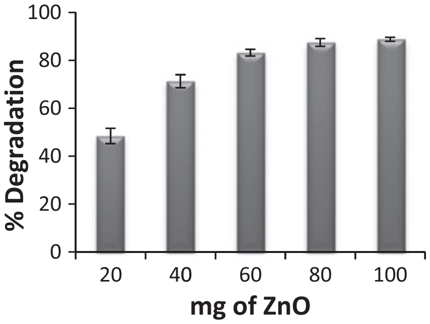

Fig. 7. Effect of dose of ZnO on percent degradation of dye from effluent.

the photoreactor, and resistivity of molecules to degradation [31]. Daneshwar et. al., found that the optimum catalyst loading for the highest rate of degradation of vanillin is 160 mg L^{-1} [36]. In other studies, the optimum catalyst dose was reported in the range of 1–5 g L^{-1} [9,37,38]. In the present study, the projected dose of the ZnO is about 0.6 g L^{-1} of the effluent.

3.4.3. Effect of irradiation time

The percent degradation of dyes from the effluent is a function of irradiation time. Fig. 8 represents the percent degradation of dyes with time under optimized condition of pH and catalyst dose. The observed rate of degradation is high in the first 20 min and then decreases with time. In the first 20 min, approximately 84% degradation was observed while about 60 min were required for nearly 100% degradation of the dyes. Higher rate of degradation at initial stage could be attributed to the higher initial concentration of dyes in the effluent. With increase in irradiation time, concentration of the dyes in the effluent goes on decreasing which reflects in terms of decrease in the rate of degradation reaction. Fig. 9 shows the absorbance spectra of the effluent at different time intervals during photocatalytic degradation which also support the observations. In the literature, time ranging from 20 to 600 min were reported for the complete decolourization of the dyes [10,11,31,35,39–41]. The experimental results demonstrate that ZnO photocatalyst prepared from ZnO_2 precursor possesses sufficiently high photocatalytic activity and becomes a good candidate for the solar energy-based degradation of the organic pollutants. However, one must keep in mind that the type of dye and a reactor design also plays an important role in deciding the rate of photocatalytic degradation reaction.

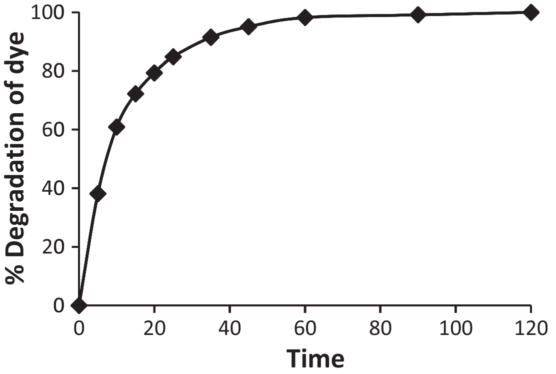

Fig. 8. Effect of time on percent degradation of dye from effluent.

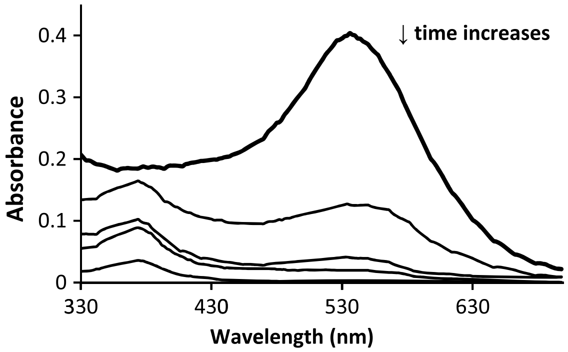

Fig. 9. Absorbance spectra of the effluent at different time intervals.

3.4.4. Effect of column height of the effluent

The effect of effluent column height on the percent degradation of dyes under the sunlight was studied over a range of column heights 0.75–3.75 cm. The results of this experiment (Fig. 10) show that percent degradation of the dyes is a function of the column

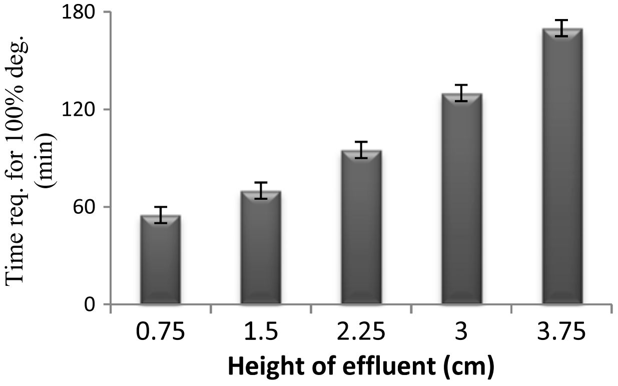

Fig. 10. Effect of height on percent degradation of dye from effluent.

height of effluent in the reaction vessel. With increase in the column height of the effluent, less flux of the solar irradiation reaches over the surface of the catalyst. Thus, with increase in column height of the effluent, greater time is required for nearly 100% degradation.

3.4.5. COD of effluent

The degradation of the dyes can be accounted in terms of decolorization and/or COD of the effluent [9]. The decolorization of the effluent may take place due to fragmentation of dye molecules via free radical mechanism. Hence, 100% decolorization may not have been achieved at complete decolourization stage. The COD of the effluent is more appropriate parameter as in this parameter all organic species in the effluent are monitored. Therefore, in the present investigation the COD of the effluent was determined at the complete decolorization stage. It was found to be 16.42% with respect to the COD of an untreated effluent. The experimental result indicates that when the decolorization was 100%, the degradation was only 83.58%. To achieve more degradation, irradiation of the effluent was continued for further 30 min after decolourization stage. Then further decrease in the COD was observed (4.98% of the untreated effluent). Shanthi and Kuzhalosai [34] also reported the similar results on the degradation of methyl orange dye by ZnO photocatalyst. The results of the present study demonstrated that the degradation reaction should not be stopped at 100% decolorization stage but must be continued beyond it till the COD decreases nearly to zero.

3.4.6. Recycling of photocatalyst

The ZnO photocatalyst was recovered by centrifugation and dried at 110℃ for 1 h and reused. It has been observed that there was no appreciable decrease in the catalytic activity of ZnO up to the fifth catalytic cycle (95.34% degradation). It indicates that the reuse of ZnO photocatalyst is possible for a number of catalytic cycles which makes the process economically viable. Similar results were reported by Patil et al. [7], Krishnakumar and Imane [42], and Neppolian et al. [43].

4. Conclusions and future plans

ZnO_2 can be synthesized by mechanochemical method at room temperature by grinding zinc acetate and H_2O_2 together. In turn, ZnO photocatalyst which is active under solar light can be synthesized from ZnO_2 as precursor by thermal decomposition and by annealing at 450℃ for 90 min. The method of synthesis of ZnO photocatalyst proposed in this study is simple, therefore, can be adopted for the large-scale synthesis of ZnO photocatalyst. The synthesized ZnO by the method proposed in the study possesses appreciable photocatalytic activity toward the degradation of the dyes.

Depending on the results of the present research work, we are designing a continuous-flow channel reactor for the treatment of dye effluent using ZnO photocatalyst.

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