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Impregnation of ZnO onto activated carbon under hydrothermal conditions and its photocatalytic properties

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Zinc oxide photocatalyst was impregnated onto the activated carbon under mild hydrothermal conditions (T=150°C, P = 20–30 bars) to form a ZnO:AC composite material. The ZnO:AC composite was characterized using powder X-ray diffraction (XRD), Fourier infrared spectroscopy (FTIR), BET surface area measurements and scanning electron microscopy (SEM). As-prepared ZnO:AC composite exhibited higher photocatalytic activity when compared to the commercial ZnO and untreated activated carbon; this was testified by the degradation of acid violet dye using ZnO:AC and commercial ZnO. The effect of various parameters such as initial dye concentration, catalyst loading, pH of the medium, source and intensity of illumination on the photocatalytic degradation of acid violet using ZnO:AC were investigated. Real time textile effluents have also been considered for the degradation using ZnO:AC composites. The reduction in the chemical oxygen demand (COD) values of the treated effluents revealed a complete destruction of the organic molecules along with the color removal.

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1. Introduction

Semiconductor based photocatalysis has gained much importance due to its incomparable ability in the environmental detoxification [1–4]. In any photocatalytic process absorption of the near-UV light by the semiconductor is followed by electron (e^-) hole (h^+) pair generation. These charge carriers can migrate rapidly to the surface of catalyst particles where they are ultimately trapped and poised to undergo redox reaction with suitable substrates. Thus the trapped hole can react with chemisorbed OH^- or H_2O to produce OH radical species [5, 6]. The reason for the increased interest in the photocatalytic process is the fact that the process is carried out under ambient conditions, and it does not require expensive oxidants and catalyst is inexpensive, nontoxic and can be activated by UV and visible light. Most of the photocatalytic studies use TiO_2 as a photocatalyst. In comparison with other promising semiconductors, ZnO appears as a very potential photocatalyst. The design and development of highly efficient photocatalytic materials have attracted the interest owing to their potential applications in the degradation of toxic organic molecules and industrial effluents. In the recent years, the design of photocatalysts impregnated or embedded onto porous materials with a large

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surface area is of great significance, which provides high concentration environments of target substances around TiO_2 photocatalyst [7, 8]. The most promising support is the activated carbon, because of its high surface area and a well-developed porosity [9, 10].

In the present work the authors have employed mild and environmentally benign technique, viz. hydrothermal method for the impregnation of ZnO onto the activated carbon. The ZnO:AC composite was characterized by various techniques like powder X-ray diffraction (XRD), Fourier infrared spectroscopy (FTIR), BET surface area measurements and scanning electron microscopy (SEM). The photocatalytic degradation of acid violet dye using ZnO:AC has been reported. The influence of various parameters like initial dye concentration, catalyst amount, pH of the aqueous medium, source and intensity of the illumination on the photocatalytic degradation of acid violet has been discussed in great detail. In view of the complexity of a real time textile effluent for containing a range of dyes and other chemicals, the present authors have considered a textile effluent for the photodegradation study. The effluent was collected from a silk weaving and dyeing plant located in Mysore city, India.

2. Experimental

2.1. Hydrothermal impregnation

In the preparation of ZnO:AC composite material, commercially available activated carbon and ZnO were taken in a definite ratio in a Teflon liner. A required amount of an effective mineralizer (1.5 M NaOH) was added into this mixture in the Teflon liner, which was later placed inside an autoclave. The autoclave assembly was then placed inside the furnace and the temperature of the furnace was set to 150°C. A schematic representation of the hydrothermal autoclave used in the present work has been shown elsewhere [11]. After the experimental run, the autoclave was quenched and the liner was taken out. The resultant product inside the liner was separated from the solution and washed with a double distilled water, soaked in 0.2 M HCl to remove the residual alkalinity and once again repeatedly washed with double distilled water till the pH of the wash becomes neutral, and then ultrasonicated. Then the product was centrifuged in three or more cycles to remove the undesired components and finally dried at 35 to 40°C in a dust proof environment.

The ratio of AC and ZnO considered for the hydrothermal impregnation plays a major role as the increased ZnO concentration may block the activated carbon pores reducing its surface area and in turn the adsorption capacity. In the present study an optimum ratio of ZnO to AC has been determined by carrying out the hydrothermal impregnation with various ZnO to AC ratios. In all the experiments the weight of AC was taken constant as 1 g and the weight of ZnO was varied from 0.1 g to 1 g. For convenience in the interpretation AC = 1 g and ZnO = 0.1 g is coded as ZnO:AC(0.1 g), similarly when AC = 1 g and ZnO = 0.2 g it is ZnO:AC(0.2 g) and so on.

2.2. Characterization

The X-ray powder diffraction patterns were obtained using Rigaku Miniflex X-ray diffractometer, Model IGC2, Rigaku Denki Co. Ltd., Japan. The scanning range was 10–60° (2θ). The crystalline phase of ZnO was identified by comparing with JCPDS files (PCPDF WIN-2.01). The SEM photographs of TiO_2-AC were obtained using a high-resolution scanning electron microscope (Hitachi, Model S-4000, Japan). The BET surface area measurements were carried out using Shimadzu Flowsorb II Model No. 2305, Japan. The FTIR spectrum of ZnO:AC was recorded by FTIR spectroscopy (JASCO-460 PLUS, Japan).

2.3. Photocatalytic experiment

In a typical photocatalytic degradation experiment on acid violet dye, a certain amount of the catalyst (ZnO:AC) was added into 50 ml of the aqueous dye solution taken in a beaker. Then the beaker containing the dye solution was exposed to the light source, it should also be noted that no external supply of oxygen was employed. Dye samples of about 2 to 3 ml were taken out at a regular interval from the test solution, centrifuged for 4 to 5 min at 950–1000 rpm and their % transmittance was recorded at 540 nm using a visible spectrophotometer (Model: Minispec SL 171, Elico, India). Light source used for illumination in the photodegradation experiments was a UV tube (8W, Sankyo Denki, Japan), for comparison studies mercury vapor lamp (MVL, 300 W) and sunlight was used. The intensity of all the light sources was estimated by photolysis of uranil oxalate [12]. In case of textile effluent treatment, effluent from two different textile plants were collected and labeled as E1 and E2. The same photocatalytic experimental setup employed in the degradation of acid violet was employed. As-received effluent was used without any preliminary treatment, unless that the effluent was suitably diluted in order to facilitate the light penetration. The photodegradation path of the effluents was followed by the estimation of chemical oxygen demand (COD) and percentage transmission (%T).

The acid violet dye was received as compliments from a textile industry located in Mysore, India. ZnO used in the impregnation work was reagent grade procured from M/s Loba Chemie, India. Activated carbon and other reagents were procured from M/s Ranbaxy, India. The precursors were prepared using double distilled water.

3. Results and discussion

3.1. Characterization of ZnO:AC composite materials

The X-ray powder diffraction pattern of ZnO:AC composite is shown in Fig. 1. The identification of crystalline phase of ZnO was accomplished by comparison with JCPDS file (PDF: 800075) and there was no change in the ZnO phase after the hydrothermal experiment. The ZnO:AC (ZnO from 0.1 g to 0.5 g) and ZnO:AC (ZnO from 0.1 g to 1 g) was considered for BET and FTIR measurements respectively. Fig. 2 shows the FTIR spectra for commercial activated carbon and reagent grade ZnO. Fig. 3 shows the FTIR spectra for ZnO:AC (ZnO = 0.1 g to 1 g). The FTIR spectra of ZnO:AC (0.1 g) to ZnO:AC (0.3 g) are similar to that of untreated activated carbon and on further increasing ZnO%, ZnO:AC (0.4 to 0.5 g), the gradual shift of FTIR absorption bands in the range of 400–1500 cm^{-1} towards ZnO can be noticed, which is more dominantly seen in ZnO:AC(1 g) (Fig. 3). The possible explanation for this is, when the ZnO% is low (ZnO:AC (< 0.5 g)), most of the ZnO particulates during the impregnation enter into the pores of the activated carbon and only fewer ZnO particles are deposited on the outer surface, which is not detected by the FTIR. But when the ZnO% is increased beyond 0.5 g (ZnO:AC (> 0.5 g)), the excess of ZnO that cannot enter the activated carbon pores remains in the system, which is detected by the FTIR as can be seen in the ZnO:AC (1 g) (Fig. 3). To confirm this, AC and ZnO were thoroughly mixed in a similar proportion (AC = 1 g and ZnO = 0.2 g) and FTIR was recorded (Fig. 4) for this mixture, which resembles the ZnO pattern. The FTIR bands in the region 400–1500 cm^{-1} of ZnO:AC (0.2 g) mixed and ZnO:AC (0.2 g) hydrothermally treated (Fig. 4), clearly indicate that the ZnO is available in the system and impregnation cannot take place without the hydrothermal treatment. The BET surface area measurement of ZnO:AC is represented in Fig. 5. The average specific surface area of the activated carbon is strongly dependent on the weight of ZnO. It is observed that upto ZnO:AC (0.2 g), it shows only a marginal decrease in the average specific surface area, beyond which it decreases rapidly. This is because of the blocking of pores by the excess ZnO particulates. It was then considered that 0.2 g of ZnO was optimum for impregnation. From the nitrogen gas adsorption (BET) and FTIR spectroscopic studies, it can be concluded that the ZnO particles are deposited in the macro- and mesopores of activated carbon blocking the micropores, which in turn decreases the surface area.

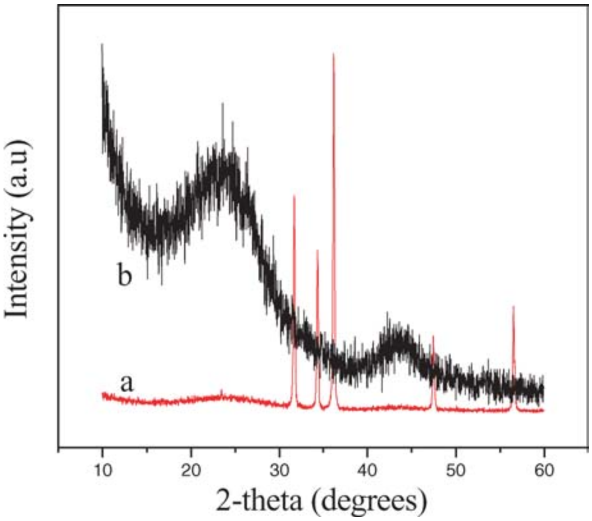


Figure 1 XRD pattern: (a) ZnO:AC; (b) commercial activated carbon.

High-resolution SEM studies have shown the impregnation of the ZnO particulates onto the carbon surface. Fig. 6 shows the external morphology of the ZnO:AC composites. Figs. 6a and b clearly show the ZnO particulates deposited on the surface and much in the pores of the activated carbon particle. Fig. 6d shows the enlarged portion of the pores. Fig. 6c shows the EDX spectrum of representative parts of the Fig. 6a and b.

3.2. Photocatalytic activity of ZnO:AC

The initial experiments were conducted in order to test the activity of ZnO:AC obtained in the degradation of acid violet (5×10^{-5} M) and also to compare its efficiency with commercial ZnO. The efficiency of dye decomposition over each catalyst (ZnO:AC and commercial ZnO) after 75 min of exposure to sunlight has been presented in Fig. 7a and b. It appeared that ZnO:AC was more active when compared to commercial ZnO, which confirms the possible synergism between activated carbon and ZnO. In order to check the decomposition of acid violet occurs only upon exposure to light, an experiment without light illumination (in total darkness) has been conducted (Fig. 7c), where only adsorption takes place. But in the presence of light, adsorption and degradation takes place concurrently, which indicates that there is a synergetic effect between ZnO and AC. This stands as an evidence to confirm the efficiency of the prepared ZnO:AC is not only due to the strong adsorption properties of AC, but also because of the photocatalytic behavior of ZnO.

Any semiconductor assisted photocatalytic reaction depends on various parameters like nature and concentration of the organic substrate, concentration and type of the semiconductor, nature of the light source and its intensity, pH of the reaction medium, etc [13–16]. The influence of such rate determining factors on the photodegradation of acid violet has been studied in detail and discussed. In all these studies to ensure a constant illumination and intensity, a UV light was considered as the source of light.

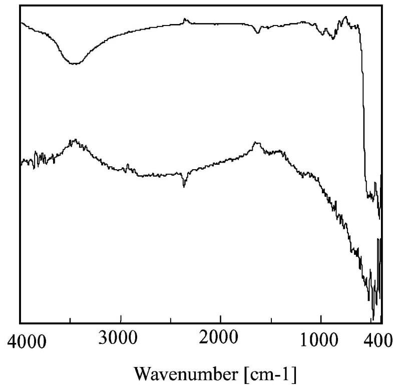


Figure 2 FTIR spectra: (a) commercial AC; (b) reagent grade ZnO.

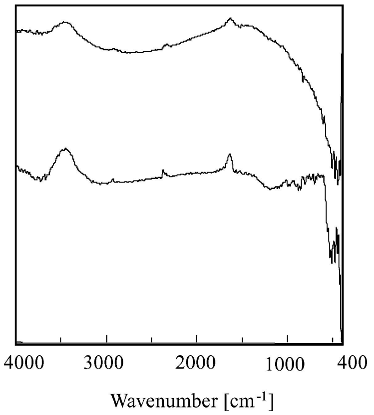
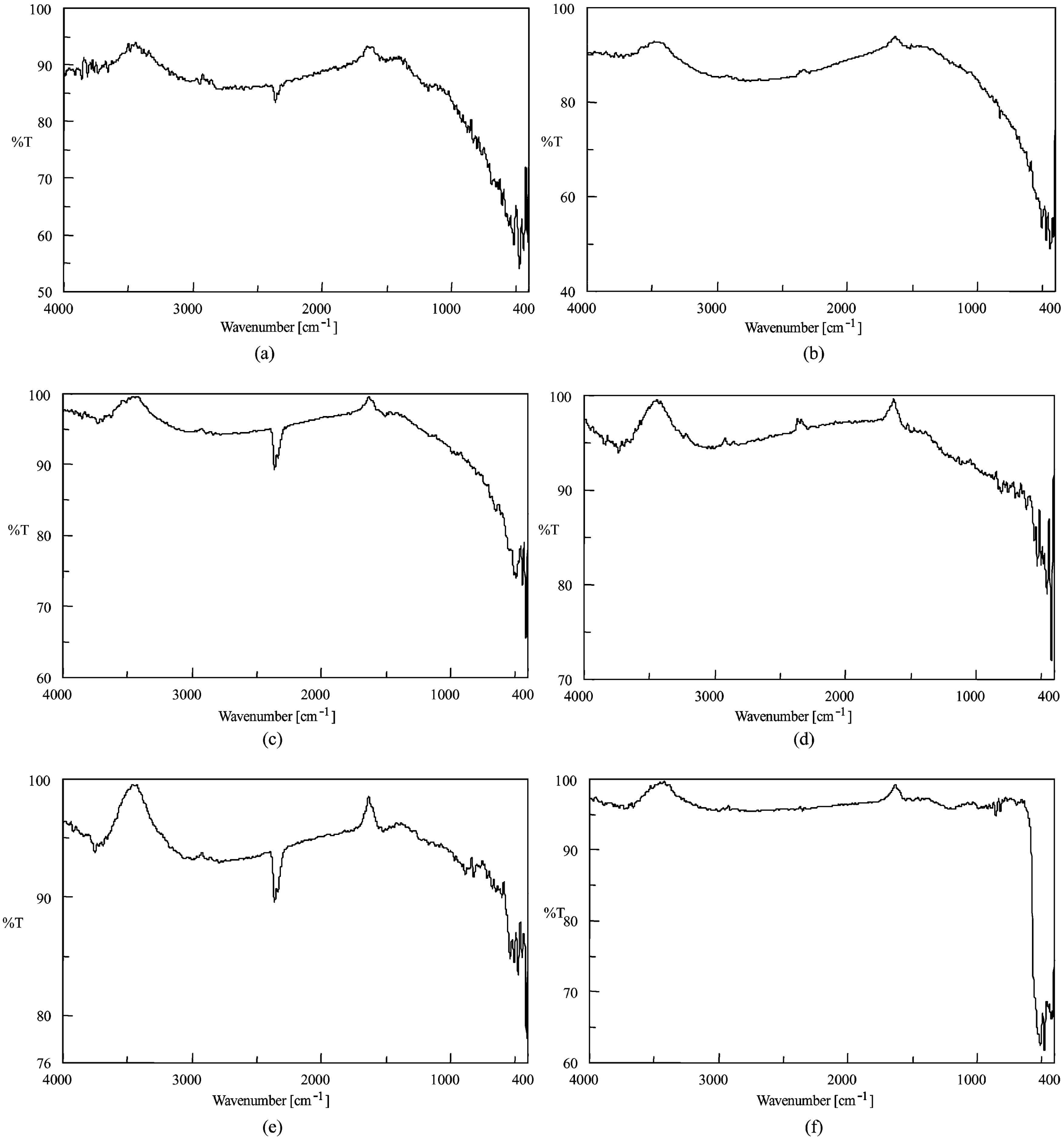


Figure 4 FTIR spectra. (a) ZnO:AC (0.2 g) just mixed; (b) ZnO:AC (0.2 g) impregnated.



(a) (b)

(c) (d)

(e) (f)

Figure 3 FTIR spectra: (a) ZnO:AC (0.1 g); (b) ZnO:AC (0.2 g); (c) ZnO:AC (0.3 g);(d) ZnO:AC (0.4 g); (e) ZnO:AC (0.5 g); (f) ZnO:AC (1 g).

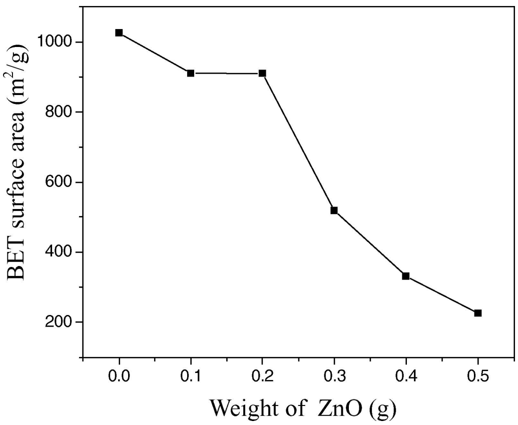


Figure 5 Average BET specific surface area of ZnO:AC composite with varying ZnO to AC ratio.

3.2.1. Effect of initial dye concentration

The effect of initial dye concentration on the photocatalytic process has been examined. The initial concentration of acid violet was varied from 1×10^{-5} M to 9×10^{-5} M. The results of these experiments are shown in Fig. 8. For the concentration of 1×10^{-5} M the decomposition was almost complete after 120 min of illumination, whereas for the higher concentration (9×10^{-5} M) the photocatalytic efficiency was lower (60%). However, better results can be obtained by increasing the light illumination duration. As the initial concentration of the dye is increased, more dye molecules are adsorbed onto the surface of ZnO:AC. But the adsorbed dye molecules are not degraded immediately because the intensity of the light and the catalyst amount is constant and also the light penetration is less. Hence the production of hydroxyl and super oxide radicals are limited or reduced. Therefore, the photodegradation efficiency is reduced. Still at higher concentration of the dye, the path length was further reduced and the photodegradation was found to be negligible.

3.2.2. Effect of catalyst content

In order to determine the optimal amount of the photocatalyst, a series of experiments with a varied amount of ZnO:AC composites have been conducted. The amount of the catalyst was varied between 10–50 mg/50 ml of the aqueous dye solution. The results of these experiments are shown in Fig. 9. The degree of decolorization of the dye solution increases with increasing amount of the catalyst, and the highest efficiency was attained when the catalyst was 20 mg /50 ml and then decreases. An increase in the efficiency is due to an increase in the number of active sites on ZnO:AC available for the reaction, which in turn increases the rate of radical formation.

The reduction in the decomposition efficiency may be due to the reduction in the penetration of light with surplus amount of ZnO:AC. The excess addition of the catalyst makes the solution more turbid and the light reaching the catalyst surface is reduced. Further the addition of surplus catalyst also results in the deactivation of activated molecules by collision with ground state molecules and the photodegradation efficiency drops down.

3.2.3. Effect of pH

The efficiency of the photocatalytic process strongly depends upon the pH of the aqueous solution [17]. The pH of the solution was adjusted using varying concentrations of HNO_3 or NaOH. The results of the study are presented in Fig. 10. The maximum efficiency was observed either at extreme acidic or basic condition. This is in agreement with most of the previous studies [16, 18]. The change in pH of the solution varies the dissociation of the dye molecule and also the surface properties of the ZnO. Also the initial adsorption of the dye molecules onto the activated carbon greatly depends on the solution pH [19]. Increase in the degradation efficiency under alkaline condition could be attributed to the increase of hydroxyl ions, which induces more hydroxyl radical formation. In acidic condition, the perhydroxyl radical can form hydrogen peroxide, which in turn gives rise to the hydroxyl radical. The equations 1–6 indicate the possible radical formation reactions both at acidic and basic pH conditions. The degree of photodegradation efficiency of acid violet does not increase for more than 10% under strong acidic and alkaline conditions; hence all the other photocatalytic experiments were carried out at the natural pH of acid violet (pH = 6.5).

$$O_2 + e^- \xrightarrow{h\gamma} O_2^{\bullet -} \tag{1}$$

$$O_2^{\bullet} + H^+ \longrightarrow HO_2^{\bullet} \tag{2}$$

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \tag{3}$$

$$H_2O_2 + e_{CB}^- \xrightarrow{h\gamma} HO^{\bullet} + HO^- \tag{4}$$

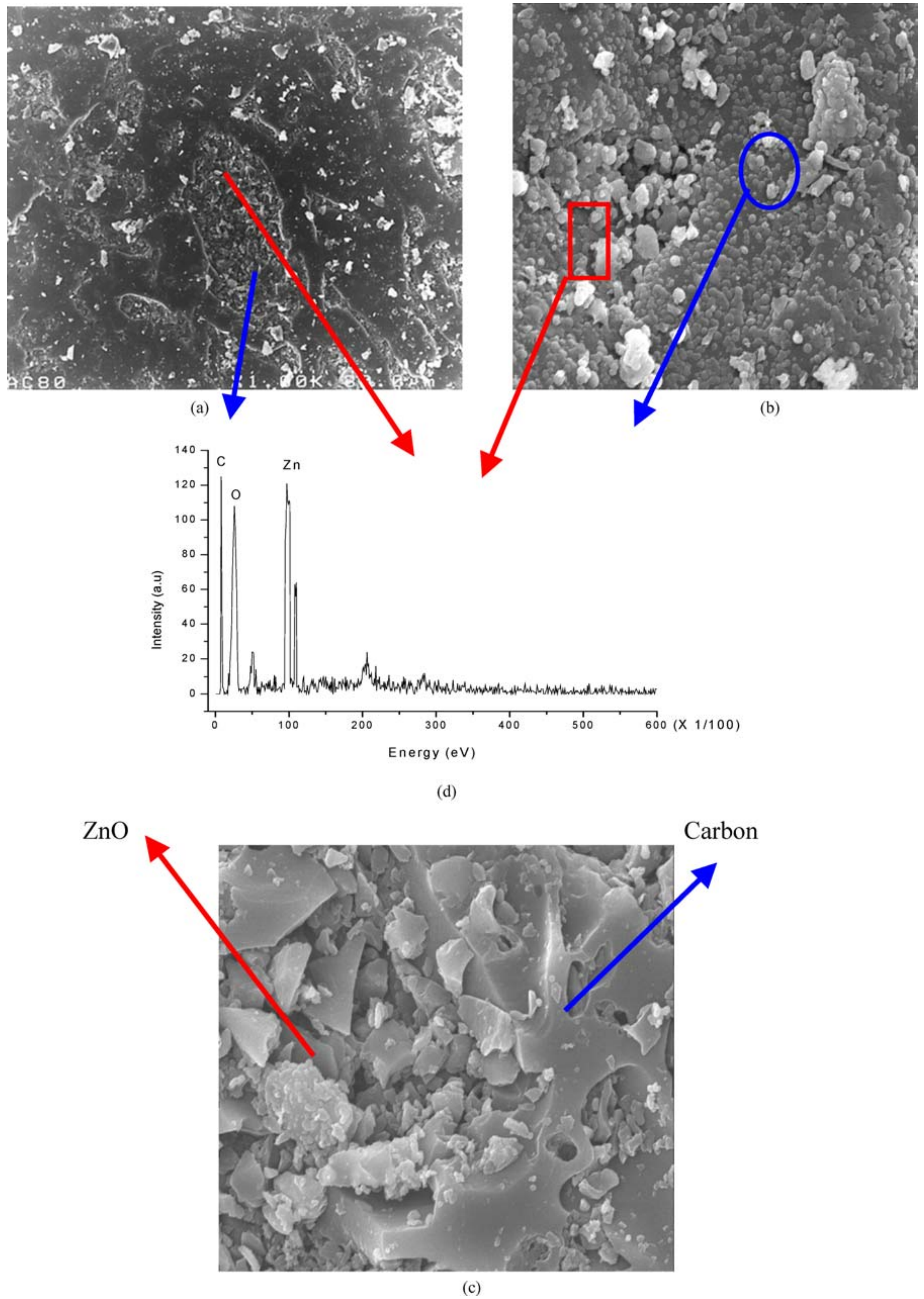
$$H_2O_2 + O_2^{\bullet} \longrightarrow HO^{\bullet} + HO^- + O_2 \tag{5}$$

$$H_2O_2 \xrightarrow{h\gamma} 2HO^{\bullet} \tag{6}$$

$$O_2 + HO^- \xrightarrow{h\gamma} O_2^{\bullet -} + HO^{\bullet} \tag{7}$$

3.2.4. Effect of light source

In order to study the effect of the type of light source on the degradation efficiency, sunlight (intensity: 8.425×10^{15} quanta/s), UV light (intensity: 2.3775×10^{15} quanta/s) and mercury vapor lamp (300 W, intensity: 3.31×10^{15} quanta/s) illumination were considered. It was observed that the degradation of acid violet was rapid under sunlight illumination, when compared to UV and mercury



(a)

(b)

(d)

(c)

Figure 6 SEM photograph of ZnO:AC sample with EDX spectra: (a) Pores of activated carbon surface with deposited ZnO particles; (b) and (c) An enlarged portion of the pore of the activated carbon on which ZnO crystals were deposited; (d) EDAX spectrum of representative portion of the Figs (a) and (b).

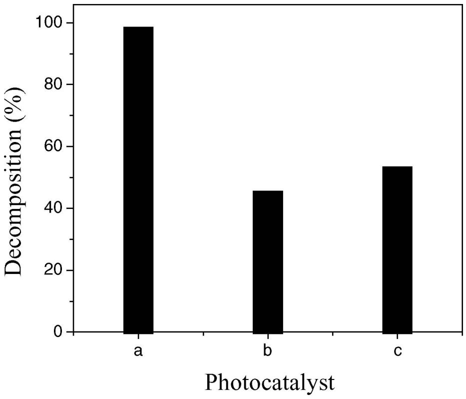


Figure 7 Photocatalyst efficiency: (a) ZnO:AC composite; (b) commercial ZnO; (c) ZnO:AC in total darkness.

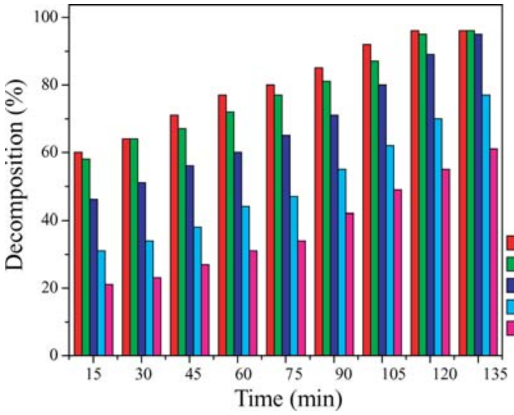


Figure 8 Effect of initial dye concentration on the photodegradation efficiency.

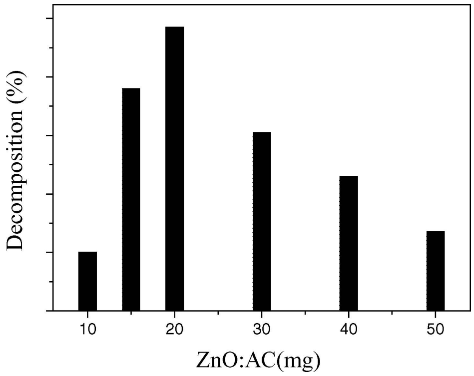


Figure 9 Effect of ZnO:AC weight on the rate constant of the photodegradation reaction.

vapor lamp (MVL). The experimental results are shown in Fig. 11.

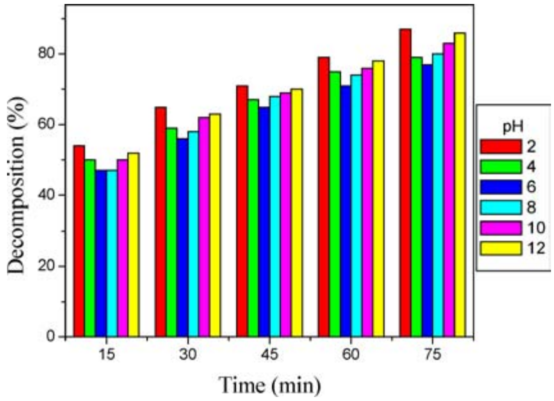


Figure 10 Effect of pH on the photodegradation of acid violet.

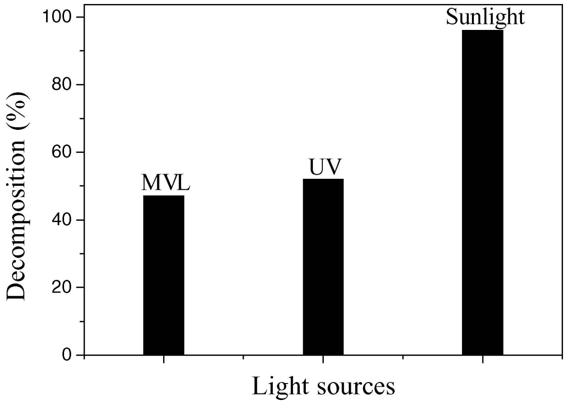


Figure 11 Effect of different light source on the photodegradation of acid violet.

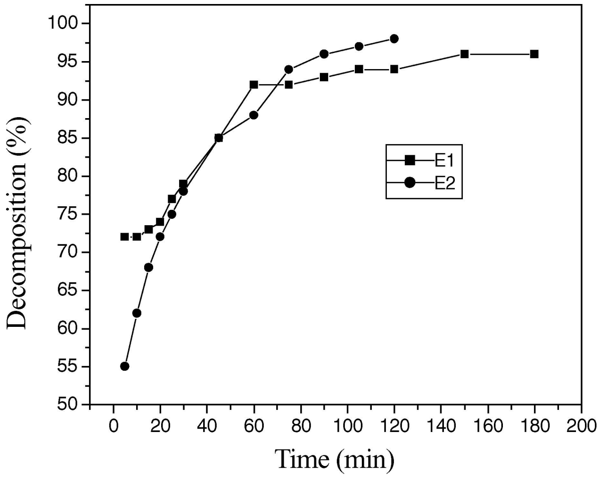


Figure 12 Degradation of the textile effluent using ZnO:AC.

3.3. Photocatalytic degradation of textile effluent

The λ_{max} for the effluents E1 and E2 was found to be 425 nm and 360 nm respectively. Fig. 12 shows the decomposition rate for the effluents and Fig. 13 shows the reduction in the COD for the effluents. The reduction in the COD confirms the destruction of the organic molecules in the effluents along with the color removal.

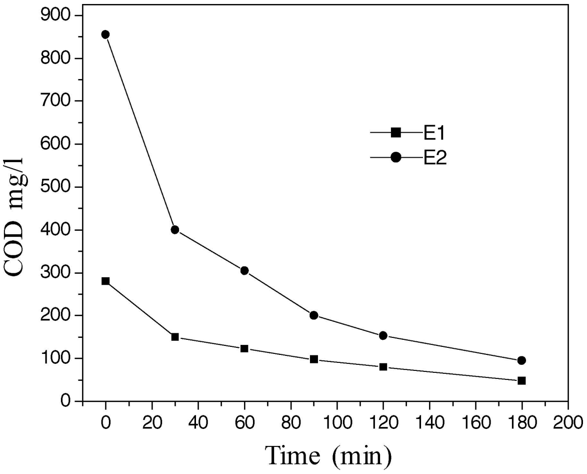


Figure 13 COD of the effluents at different time intervals.

4. Conclusion

A unique ZnO photocatalyst impregnated onto the activated carbon (ZnO:AC composite) was developed for the photocatalytic degradation. Mild hydrothermal conditions were used for the impregnation experiments. The FTIR and BET study resulted in the recognition of optimum impregnation conditions. The ZnO:AC composite was found to be very effective in the degradation of acid violet dye. The synergism between the ZnO photocatalyst and activated carbon was clearly demonstrated. In order to obtain an optimum treatment condition various reaction parameters on which the rate of decomposition is dependent have been studied in detail. The textile effluents were treated successfully. The decrease in COD values demonstrates the destruction of the organics present in the effluent.

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