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Photocatalytic Degradation of Dye in Aqueous Solution using Metal Oxide/Activated Carbon Nanocomposite

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Abstract
The removal of dyes from water is a matter of great interest due to its environmental health concerns. In this study activated carbon (AC) was prepared from Indian Jujube (Ziziphus mauritiana) seeds as an agricultural waste by chemical activation using $ZnCl_2$ as an activating agent at carbonaization temperature 500^0C for 3 hours. Further, the Jujube activated carbon (JAC) was used to fabricate Zinc oxide/ activated carbon (ZnO/JAC) nanocomposites by one step facile hydrothermal process. The as-synthesized activated carbon (JAC) and metal-oxide composites were characterized by SEM, FTIR, and UV-Vis Spectroscopy. The SEM and XRD results showed successful hexagonal nanorods of zinc oxide dispersed on the surface of activated carbon. The degradation effect of nanocomposites on methylene blue (MB) was studied under UV-light irradiation. The ZnO/AC showed efficient degradation of MB about 97.25% in 2 hours and followed pseudo first order kinetics.

Keywords
ZnO/JAC nanocomposite, Photocatalytic degradation, CuO/JAC nanocomposite, MB

1. Introduction

In recent years, surface and ground water contamination has become a problem due to population growth. The rapid development in industries and urban areas has led to hazardous contamination in water resources such as organic compound pollutants, heavy metals, and many other complex compounds. It has been reported that, annually, about 300 to 400 million tons of untreated organic pollutants are produced and without prior treatment discharged into water resources[1]. Then they remain in water resources and soil for long period of time posing serious health risks to living organisms. It also reduces the soil fertility as well as the photosynthetic activity of aquatic plants. Among these chemicals, the dye is considered as the primary pollutant due to their stability and low biodegradability. The dyes can have also various toxic effects on human life such as cancers of the kidney, urinary bladder, and liver [2]. Thus, removal of such dyes from the wastewater effluents is of great concern.

In recent years, various methods have been reported for dye removal from industrial wastewater such as adsorption, electrochemical precipitation, coagulation flocculation, ozonation. However, these treatments are not effective in the removal of dye from effluents as they only transfer pollutants from one phase to another phase and therefore lead to secondary pollution.

In this context, Photocatalytic advance oxidation processes (AOPs) are considered as highly competitive technology as they are capable of complete elimination of non-biodegradable organic pollutants from wastewaters. For the photocatalytical removal of organic pollutants from air and water, metal oxide semiconductors have been widely used. In the photocatalytic process, the metal oxides are activated by suitable photon energy that generates the active sites of electron-hole [3]. Thus, many of materials have been studied such as TiO_2, ZnO, CuO, ZrO_2. CdS, MoS_2, and WO_3 as photocatalysts for degradation of pollutants. Among these materials, TiO2 is common photocatalyst and has had a maximum application so far.Nonetheless, TiO_2 has defects such as high cost and adsorption band at ultraviolet area. Hence, recently ZnO as a good replacement for TiO_2 at the photocatalytic process is noteworthy. However, Its low quantum effieciency leads to large band gap and rapid recombination of photo generated electron-hole pairs. So, it is

important to prevent the recombination of electron-hole pair. [4].

However, there are some disadvantages of these photocatalyst materials used in advanced oxidation process. These photocatalyst powder is easy to agglomerate with poor adsorption capacity, and is difficult to be separated and recycled from the solution. For the purpose of overcoming the drawbacks of these two approaches the combination of adsorption and photocatalytic process was reported as a very promising technology for the treatment of wastewater. Activated carbon possesses a large specific area, high adsorption capacity, and suitable pore structure [5]. The studies have shown that combining the suitable band gap materials leads to improvement in the separation and transfer efficiency of photogenerated e- and h^+ pairs, which enhance the photocatalytic activity. Albiss et al. recently synthesized Zinc oxide nanorods grown on activated carbon fibers (ZnO-NR/ACF) via a sequential sol-gel and hydrothermal method. Characterization showed that the ZnO nanorods were effectively grown on the surface of ACF. The photocatalytic properties of synthesized material were better than those of ZnO or ACF [5]. Similarly, Shrestha et al. synthesized ZnO/AC nanocomposite via one-pot hydrothermal method using lapsi seed stone as precursor of activated carbon. The results showed that ZnO/AC had better photocatalytic property than that of pristine ZnO nanorods [6]. Hence, the current study will explore the dispersion of the ZnO nanoparticles doped activated carbon for removal via. photocatalytic degradation of MB (cationic) dye from aqueous solution.

2. Materials and Methods

This study is focused on carbonization of jujube seed stone, fabrication of metal oxides on activated carbon and then photocatalytic activity of as synthesized metal oxide/ activated carbon nanocomposites.

2.1 Synthesis of JAC from the Jujube seed

The precursor powder was mixed with $ZnCl_2$ in the ratio 1:1 by weight using sufficient amount of distilled water. Then, the mixture was kept in a hot air oven at 70^0 C for 24h h in an electric oven. Then, activated precursor was transferred to a quartz tube in a tubular furnace and carbonized at 500°C for 3 hrs. As synthesized activated carbon was characterized by iodine number which was determined according to ASTM D4607-94 method [7], methylene blue number was determined method [8] and surface area. The surface area of activated carbon was estimated by multiple regrassions method using the result of iodine and methylene blue numbers [9].

2.2 Preparation of Zinc oxide/activated carbon nanocomposite

The sample was prepared by dissolving 0.063M $Zn(NO_3)_2.6H_2O$ in 40 mL and 0.071M hexamethylenetetramine in 50 mL of distiled water and stirred for one hour. The pH of the solution was adjusted to 11 and agin stirred for one hour. Then, 25 mg of AC was added, stirred for 3 hrs and final solution was transferred into a Teflon crucible and kept inside an autoclave at 150°C for 2h. . After cooling at room temperature, the obtained product was filtered and washed repeatedly using distilled water and ethanol and dried in hot oven at 60°C for 6 hours and 140°C for 12 h respectively. For comparison, ZnO nanoparticles were also prepared under identical conditions without using JAC in the above process.

2.3 Photocatalytic activity study

The photocatalytic activity of the ZnO/JAC nanocomposites were studied by observing the photodegradation of MB dye solution under a mild UV radiation at room temperature. Dye stock solution were prepared by dissolving 1g dye in 1L distilled water. Then, 25 mg of photocatalysts (ZnO, and ZnO/JAC) were added to the 50mL of 10ppm dye solution. The solution was followed by 45 minutes to achieve adsorption-desorption equilibrium prior to UV light irradiation. UV light irradiation was done by a mercury vapor lamp and the distance between the tip of the light guide and the solution was 10cm. After one hour, 5mL of the sample was withdrawn from the solution and centrifuged. From the centrifuged sample, the supernatant solution of MB dye was observed using a UV-visible spectrophotometer at 664 nm wavelength.

3. Results and Discussions

3.1 Characterization of Activated Carbon

The MBN, IN, and S.A. of the agro-based JAC (Series1) and commercial activated carbon (series2)

are presented in the figure 1. As shown in figure 1, iodine number and surface area of the activated carbon is high whereas methylene blue number is low as compared to others. The iodine number, methylene blue number and surface area of activated carbon are 824 mg/g, 368 mg/g and 872 m^2/g respectively. Iodine number and methylene blue number resembles the adsorption of molecules into micropores and mesopores respectively. These values were also compared with commercial activated carbon which showed similar results. The availability of these pores on the surfaces of carbons could be due to the evaporation of ZnCl2 as an activating agent while carbonization. During carbonization, activating agent leaves the space which results in formation of pores. These pores can be regarded as channel to the porous systems which increases the surface area for adsorption.

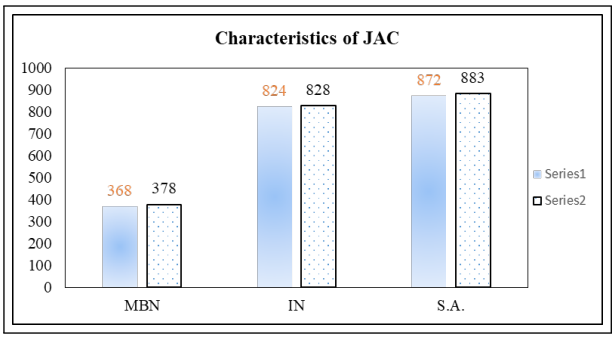

Figure 1: Results from Iodine and Methylene Blue number experiment

3.2 Characterization of Zinc oxide/ activated carbon nanocomposite

The SEM image of zinc oxide/activated carbon agro-based Indian jujube seed stones is shown in figure 3. As shown in below figure 2 and 3, it revealed the smidge porous structure of agro-based AC prepared from Indian jujube seed stone which indicates the adequate adsorption nature of JAC. As indicated in figure 2c) & d), it showed the deposition of ZnO wurtzite structure nano-rods in the porous structure of JAC. Thus, the SEM image of ZnO/JAC nano-composite confirmed the successful growth and dispersion of ZnO nanorods on the surface of JAC and formation of ZnO/JAC nano-composite. It also showed immense porous structure of ZnO/JAC nano-composite which also includes cylindrical shape pores on the surface of composite. The growth of zinc oxide nanorods on the surface can be explained as the presence of functional groups on the surface of JAC acted as nucleation site. Analogous results were obtained from SEM image in case of zinc oxide growth on the surface of AC from agro-based Lapsi seed stone [7].

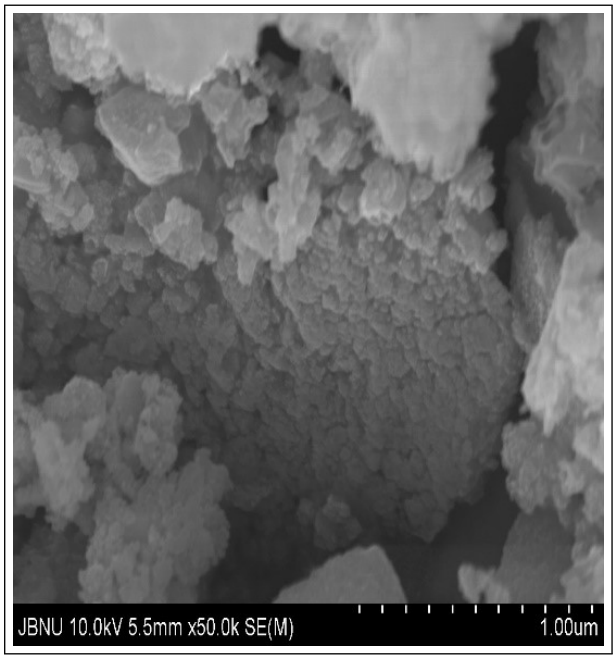

Figure 2: SEM image of Jujube activated carbon (JAC)

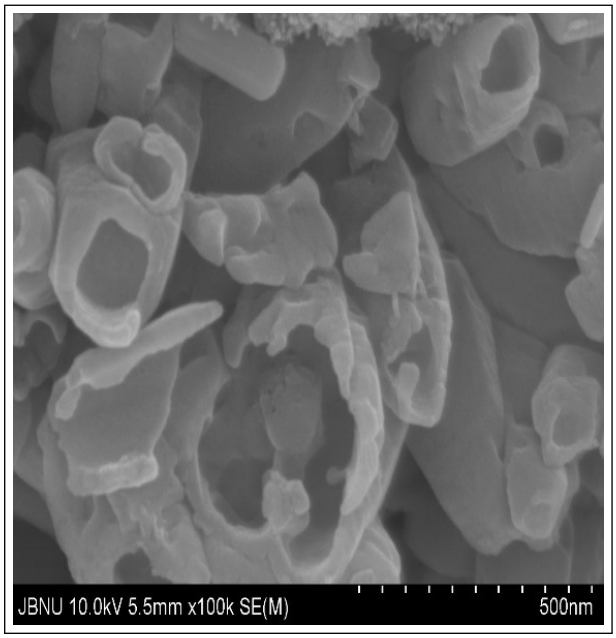

Figure 3: SEM image of ZnO/JAC nano-composite

The XRD pattern of ZnO and ZnO/JAC nano-composite is presented in figure 4.

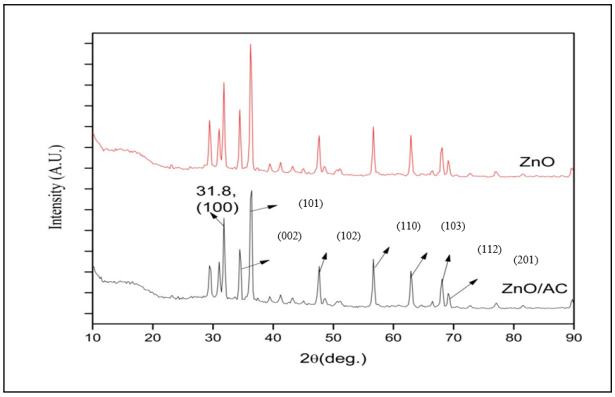

Figure 4: XRD spectra of ZnO and ZnO/JAC nano-composite

The XRD pattern of pure ZnO and ZnO/JAC nanocomposite are shown in figure 10 and the main peaks were indexed with Miller indices (h k l) which correspond to interplanar spacing of ZnO and JAC. As illustrated in figure, the sharp peaks can be observed at the 2θ angles of 31.7, 34.4, 36.2, 47.4, 56.5, 62.8, 66.3, 67.9, 68.9, 72.5, 76.9, 81.3, and 89.5° which corresponds to the crystallites plane (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1), (0 0 4), (2 0 2), (1 0 4), and (2 0 3) of ZnO respectively (ICSD-01-080-0075). This indicates the formation of pure ZnO with wurtzite structure. Furthermore, the diffraction peaks of ZnO/JAC nano-composite corresponds with the wurtzite structure of pure ZnO which confirmed the favorable growth of ZnO nano-particles on the surface of agro-based JAC. However, the existence of zenith peak of zinc oxide in case of ZnO/JAC nano-composite which might supressed the broad peak of JAC. The average crystallite size calculated was 18.36 nm for pure and 17.42 nm for ZnO/JAC nanocomposite using Debye-Scherrer equation. Analogous results of X-ray diffraction were obtained in deposition of ZnO onto the surface of agro-based AC from Lapsi fruits [7] and graphitic carbon nitride [4].

3.3 Optical band gap analysis

This can be defined as the gap between the conduction band and valence band. This can be measured as the energy required to excite an electron from valence band (VB) to conduction band (CB). In case of semiconductor minimum energy is required to excite the electrons from VB to CB, thus photon could excite these electrons on the absorption of photon. Further, these band gaps are divided into two types which depends on the momentum of VB and CB. If the momentum of both band is similar than i.e., direct band gap and vice-versa [5]. This can be calculated by using Tauc's equation:

$$(a\,h\,v)n = A(h\,v - Eg) \tag{1}$$

Where,

A = Energy independent constant,

h = Planck's constant,

v = Frequency of incident photon,

a = Absorption coefficient of material and also given as f(r),

Eg = Optical band gap,

n = index that depends upon nature of electronic transition responsible for optical absorbance.

The band gap characterization of zinc oxide/ activated carbon was characterized by UV-Vis spectroscopy. The band gap of semiconductors can determined by using Tauc Plot and Kubelka-Munk relation. The optical band gap measurement in case of photo-catalyst is an important parameter to determine the photocatalytic property. Due to the photocatalytic property, semiconductors are used in various opto-electronics devices (Jubu, 2022).Thus, the band gap of JAC, ZnO, ZnO/JAC nano-composites were evaluated by plotting the (ahv)n v/s hv graph. The results are presented in figure 5,and 6 respectively. The result of band gap analysis by Tauc plot showed higher energy band gap in case of JAC, which can be inferred as the absence of free electrons in bands. However semiconducting nature of activated carbon can be ascribed by presence of sp2 hybridization state of Carbon.

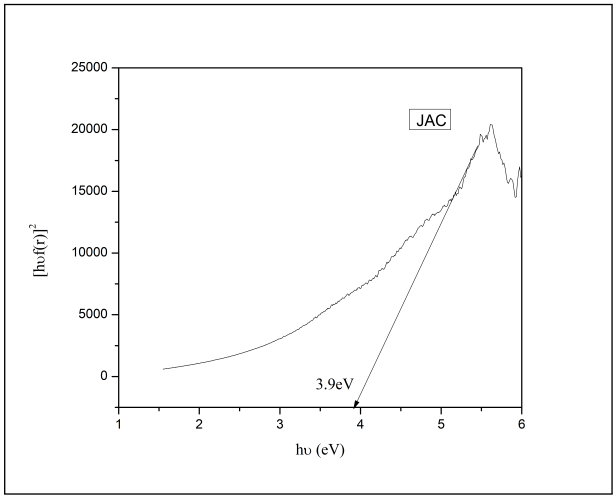

Figure 5: Optical band gap of Jujube activated carbon (JAC)

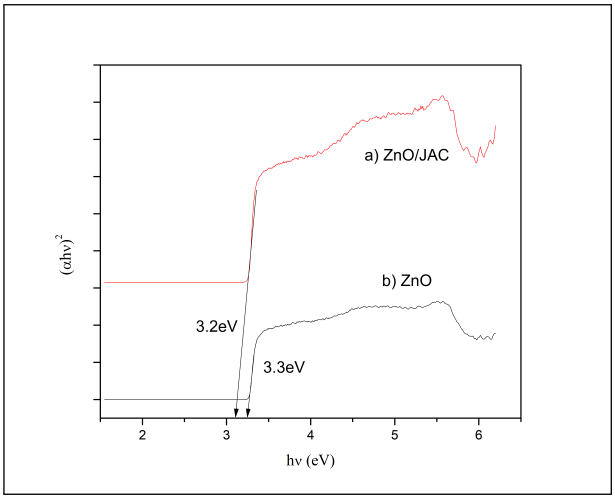

Figure 6: Optical band gap of ZnO and ZnO/JAC nano-composite

As illustrated in figure 6, the band gap of pure ZnO and ZnO/JAC nanocomposite are 3.3 eV and 3.2 eV respectively. Thus, this showed the decrease in band gap of pure ZnO nanocrystals on addition of activated carbon. This can be interpret as the increment of oxide radicals on the surface of the ZnO/JAC nano-composite, which lower the recombining rate of electrons from CB to holes in VB. Analogous results was observed when increasing the weight (%) of activated carbon to synthesize ZnO/AC led to decrement in band gap of ZnO/AC [4].

3.4 Photocatalytic degradation of MB dye

As synthesized photocatalyst degradation activity was performed through the degradation activity of MB dye as the organic pollutant target from aqueous solution under UV light irradiation. A comparison study was also done between synthesized nanocomposites, pristine zinc oxide nano-particles and commercial TiO_2 -P25. The self degradation of MB dye under UV irradiation was also studied. The comparative study of photocatalytic degradation of MB dye from aqueous solution is shown in figure 7.

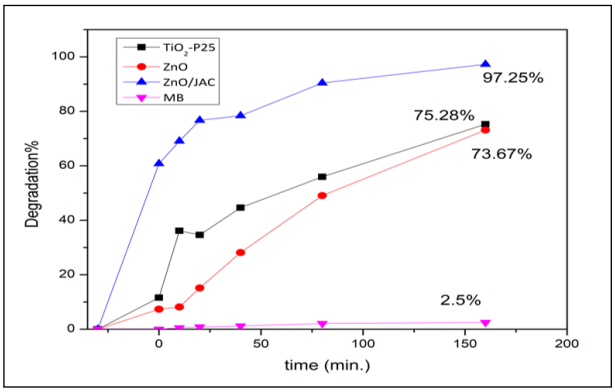

Figure 7: Photocatalytic degradation of MB dye by different photocatalyst under UV light irradiation

As presented in figure 7, self degradation of MB dye is negligible as these dyes are stable organic compounds and consists toxic nature.The result implied the higher degradation of MB dye by ZnO/JAC $\sim$ 97.25% than pristine zinc oxide and commercial TiO_2-P25. The photocatalytic degradation of MB dye by ZnO and TiO_2-P25 were 75.28% and 73.67% respectively. It can be inferred as the addition of AC with ZnO led to the decrease in recombination of e- and h+ pairs. Initially, the figure iterates the increasing straight line which is due to the adsorption and desorption of dye in the porous structure of photo-catalysts during shaking in dark conditions. The initial adsorption of dye on the porous surface of photo-catalysts also revealed that the porosity of metal oxide particles increased on fabrication with agro-based activated carbon from Indian Jujube seeds. Furthermore, the increased photo-catalytic activity of ZnO/JAC nanocomposite can be inferred as the availability of electrons from the conduction-band of JAC. However, absence of electron donor from conduction-band in case of JAC, there was no change in fast recoupling of pair e- & h+. Analogous results were observed in the case of MB dye degradation using ZnO/AC and ZnO [7].

3.5 Kinetic study of MB dye degradation

The kinetics models were applied in order to study the kinetics of photodegradation of MB and MO. The pseudo-first order and pseudo-second order kinetic models were used to validate the photocatalytic degradation of MB and MO dye. The first-order kinetic model is given in equation (2):

$$\ln(C/C0) = -kt \tag{2}$$

The second-order kinetic equation is given in equation (3) as per widely known expression (Mahmoodi, 2013):

$$1/C = Kt + 1/C0 \tag{3}$$

In which,

C = concentration of dye after time t,

$C0$ = initial concentration of dye,

k = rate constant, and can be evaluated from the plots of ln(C/C0) v/s time for first-order, and the plots of 1/C v/s time for second-order kinetics.

t = time.

The result of kinetics model fitting of MB dye degradation by ZnO/JAC nanocomposite is presented in figure 8 and 9.

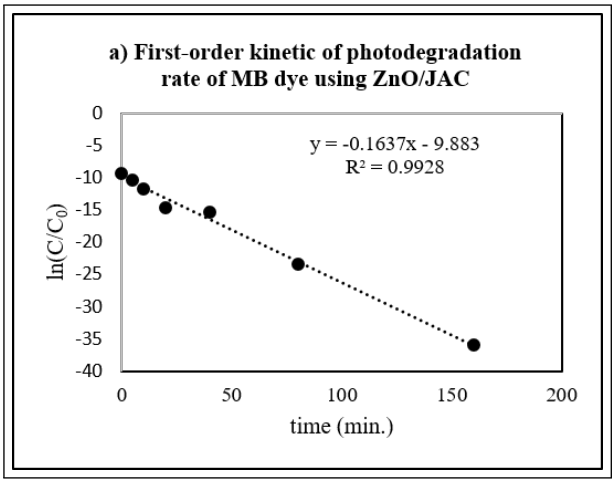

Figure 8: Pseudo First-order Kinetics of MB dye degradation using ZnO/JAC nano-composite

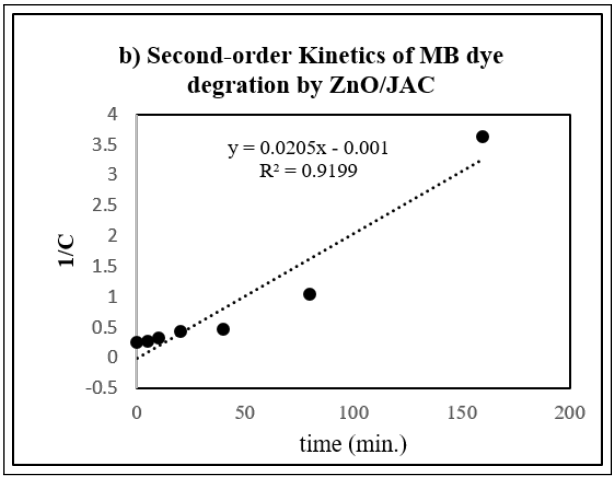

Figure 9: Pseudo Second-order Kinetics of MB dye degradation using ZnO/JAC nano-composite

The As illustrated in given figure 8 and 9, it showed that photocatalytic dye degradation of MB dye followed Pseudo first-order kinetics than Pseudo second-order kinetics. The rate constant (k) in case of pseudo first-order kinetics for MB dye degradation using ZnO/JAC was 0.163 min^{-1}. The present work of MB dye degradation efficiency was also compared with previous research studies which is shown in figure 10. The result showed good agreement with other research studies which confirmed the dispersion of zinc oxide nanorods on the surface of Indian jujube activated carbon.

Table 1: Comparative analysis of Photodegradation efficiency of Zinc oxide based composite

Catalyst	Light source	Dye	Degradation %	Time (min)	References
MWCNTs / Zno / Chitosan	UV	MB	98.76	300	3
ZnO-NR/ACF	UV	MB	99.0	120	5
ZnO-AC	UV	MB	95.0	180	7
ZnO/AC	UV	MB	97.52	160	Present Work

4. Conclusions

In summary, ZnO nanorods were dispersed successfully on the surface of activated carbon via one step hydrothermal synthesis method.The SEM images confirmed the highly porous nature of Zinc oxide/ activated carbon nanocomposite. The XRD pattern confirmed the crystalline nature and presence of hexagonal structure of Zinc oxide in ZnO/JAC nanocomposite. The optical band gap analysis showed the decrease in band gap of ZnO/JAC nanocomposite than pristine ZnO from 3.3 eV to 3.2 eV. The comparative study pf photocatalytic degradation of MB dye showed higher degradation efficiency of ZnO/JAC nanocomposite than that of pristine ZnO. The Kinetic study of photocatalytic MB dye degradation using ZnO/JAC nanocomposite followed pseudo first-order kinetics. Ergo, as synthesized Zinc oxide/ jujube activated carbon nanocomposite can be used as photocatalyst for dye contaminated waste water treatment.

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