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PHOTOCATALYTIC DEGRADATION OF TEXTILE DYE DIRECT BLUE 86 BY BIO-SYNTHESIZED ZNO NANOPARTICLES BY MODIFIED SOLUTION-COMBUSTION METHOD

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ABSTRACT

The ZnO nanoparticles were synthesized with zinc nitrate as a precursor and plant leaf powder as a fuel at 600˚C through the slightly modified solution-combustion method. The synthesized ZnO nanoparticles were subjected to XRD, FT-IR and UV-visible absorption. The XRD result shows that the synthesized ZnO nanoparticles has a main peak at 36.33° belongs to (101) plane implies that the ZnO has wurtzite structure with hexagonal cell unit. From the debye-scherrer formula the synthesized ZnO NPs possess the particle size calculated for (101) plane is 30.9 nm. The peak at 467 cm^{-1} and 675 cm^{-1} in the FT-IR spectra is the characteristic stretching mode vibration of Zn-O matrix. The synthesized nanoparticles was processed to the photocatalytic degradation activity on the dye direct blue 86 which was often used in the textile industries. The dye direct blue 86 was considerably degraded by as-synthesized ZnO surface under UV irradiation at degradation time 120 min with the maximum dosage 50 mg.

KEYWORDS: ZnO nanoparticles, solution combustion method, direct blue 86, photocatalytic degradation.

INTRODUCTION

The wastewater discharged from the industries like textiles, dye, paper and some other industries contains residual dyes. It has been estimated that more than 10% of the total dyestuff used in dyeing processes is released into the environment which are hazardous to aquatic system and surrounding ecosystem. Generally dyes are biodegradable and it inhibits the natural biological degradation of organic compounds occurring through bacterial processes, since they affect the availability of readily degradable nutrients necessary in the bacterial metabolism. Biological degradation processes compete with adsorption of the dye in the activated sludge. It clearly delivers that necessary steps would have to be taken for the degradation of such a hazardous dyes. For that there are numerous technologies involving physical, chemical and biological method. The above methods are cost effective, produce secondary sludge, simply transfer pollutants to another phase where it does not destroys and are not completely degrade the dyes. The advanced oxidation process is the efficient technology to degrade the recalcitrant dye pollutants. This technology is highly potent and produces strongly oxidizing radical to destruct the organic pollutant with no selectivity. Among AOPs, the heterogeneous photocatalyst degradation processes are the efficient technology to degrade both aquatic and atmospheric organic contaminants.[1,2] Generally photocatalytic degradation occurs when the semiconductor materials absorb photon energy hv equals or exceeds the band gap of semiconductor. Then the electron gets excited from the filled valence band of semiconductor to empty conduction band, forming a hole-electron pair which initiates the oxidation and reduction processes of adsorbed substrates. In addition the holes present in the aqueous solutions are scavenged by surface hydroxyl ions (OH^-) or H_2O which generate strong oxidizing hydroxyl radical (OH) and electrons combines with O_2 to form superoxide radicals ($^{\bullet}O_2^-$) and another active species H_2O_2 which promotes the oxidation of organic compounds.[3] Nowadays semiconductors such as TiO_2, ZnO, CdS, MgO, CdS and Fe_2O_3 are effectively employed in the AOP. In this consortium TiO_2 and ZnO are most widely used semiconductors for the advanced oxidation processes to degrade pollutants under UV irradiation.

ZnO is the most promising alternative instead of TiO_2 since its band gap very similar to TiO_2. ZnO is also advantageous over TiO_2 in the aspect of absorbing over the larger fraction of UV spectrum and the corresponding threshold of ZnO is 425 nm. It is less expensive and exhibits good efficiency to the degradation of dye in both acidic and basic medium.[4] The dye C.I.direct blue 86 was an important dye was frequently used in the textile industries. The direct blue 86 was colourful green light blue soluble in water which was mainly used to dyeing cellulose fiber, silk fabric and nylon. It was also used for leather, paper dyeing, paint industry, pulp dyeing and also used to manufacture of organic pigment sediment colour. Repeated exposure of this dye may produce general deterioration of health by an accumulation in one or many human organs. It may also causes acute effects such as irritating to eyes and skin on contact, Inhalation causes irritation of the lungs and respiratory system. The present work is performed to investigate the rate of degradation of direct blue 86 by biosynthesized ZnO NPs and also study the effect of pH, initial concentration of dye, catalyst dosage and irradiation time.

MATERIALS AND METHOD

Materials

Plant material

For the biosynthesis of ZnO, pachygone ovata leaf powder was used as a fuel. Earlier the leaf of pachygone ovata was collected and dried in shadow for a week. The dried leaf was powdered using domestic mixer. The powdered substance was subjected to mesh (Sieve No: 30) to obtain the fine powder and then it is stored in an air-tight container for further experiments.

Chemicals required

The C.I.direct blue 86 was purchased from the local dyeing industry with high purity. The chemicals zinc nitrate, sulphuric acid and sodium hydroxide (used to adjust the pH of solution prepared) were merck products. Distilled water was used for the preparation of stock solution and working solution.

Dye description

Colour index No: C.I.Direct Blue 86,

C.I. constitution no: 74180

CAS Registry No: 1330 - 38 – 7

Chemical Name: Sodium Salt of Mono and Disulphonated Copper Phthalocyanine Blue

Molecular formula: $C_{32}H_{14}CuN_8Na_2O_6S_2$

Molecular weight: 780.17

Molecular Structure: Phthalocyanine class

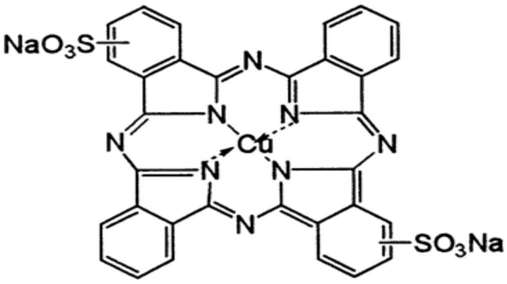

Fig 1: Molecular structure of Direct Blue 86

Preparation of dye stock solution

The stock solution of dye C.I.direct orange 39 was prepared by dissolving required amount of dye into distilled water. Different concentration for the degradation experiment was prepared by diluting the stock solution. The pH of the working solutions was maintained by using the diluted solution of HCl and NaOH.

Preparation ZnO Nanoparticle

For the biosynthesis of ZnO NPs: zinc nitrate and leaf powder of plant was taken at (w/w) ratio. The resultant mixture was stirred homogenously and heating the mixture upto 10 minutes. After completion, the resultant pale white precipitate was kept for calcination for about 6 hours.

Characterization of nanoparticles

The synthesized nanoparticles were characterized using XRD, FTIR and UV absorption spectra. The diffraction pattern of the synthesized nanoparticles was recorded by X-ray diffractmeter at room temperature Cu Ka (1.541 Å) radiation with nickel filter in the 2h range 20–70° at a scan rate of 2° min^{-1}. Functional groups present in the particles are analyzed by using Fourier transform infra-red spectrometer model schimadzu IR affinity 1. The UV-visible absorption spectrum was recorded by using the model lambda 35.

Experimental procedure

For studying the photocatalytic activity of ZnO NP against the degradation of dye namely C.I.direct blue 86 was carried out under the UV light consisting typical photocatalytic reactor. For irradiation of direct blue 86, 50 mg of biosynthesized ZnO NPs was added to desire concentration of dye solutions were about 100 ml under constant stirring, before irradiation the suspension was stirred using magnetic stirrer continuously for about 30 minutes to achieve the adsorption-desorption equilibrium between dye and ZnO NPs under dark conditions. The homogenous stable suspension was exposed to UV illumination under constant stirring at room temperature. The irradiated dye solution was periodically withdrawn for every 30 mins time interval and subjected to centrifugation to separate the catalyst. The clear solution of degraded dye obtained was measured by using UV-visible spectrophotometer. The rate of degradation of both dye solution was calculated by the following equation:

Rate of photodegradation = $\frac{C_0 - C_t}{C_0} \times 100$

where C_0 is corresponding to initial concentration at 0 min and C_t is corresponding to concentration at time t.

RESULT AND DISCUSSION

Characterization of ZnO nanoparticles

Functional group analysis by using FT-IR

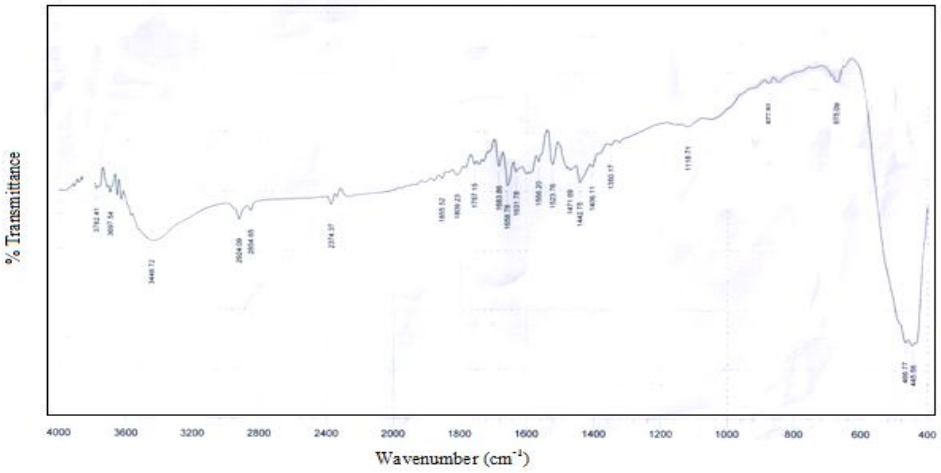

Fig: 2 FI-IR spectra for the biosynthesized ZnO nanoparticles.

Fourier transform infrared spectrum of biosynthesized ZnO nanoparticles are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm^{-1}. In the FT-IR spectra, the two peaks at the range of 467 cm^{-1} and 675 cm $^{-1}$ are the characteristic peak of ZnO stretching modes. The weak absorption peaks in the range 1100-1600 cm $^{-1}$ is attributed C-H stretching modes in C-OH groups. The peak at 1631 cm $^{-1}$ clearly indicates that the presence of hydroxyl groups. The peak appears at 2924 cm^{-1} are attributed to the C-H stretching in Alkane and the peak at 2854 cm^{-1} is the characteristic peak of O-H stretching in carboxylic acid. The broad peak at the range of 3448 cm^{-1} shows that O-H stretching vibration of intra-molecular hydrogen bonding in water molecules.

Diffraction pattern of ZnO nanoparticles

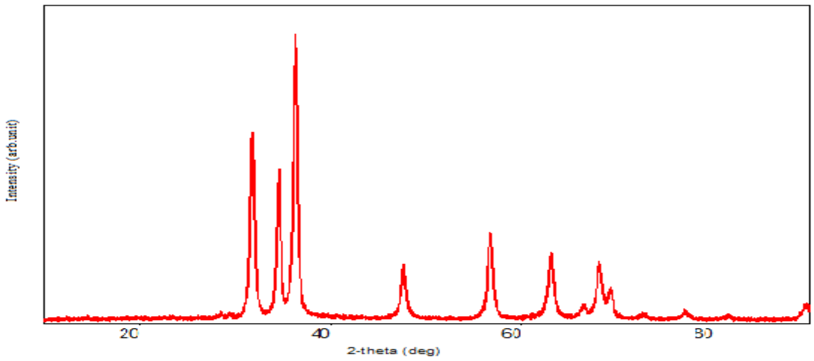

Fig 3: XRD pattern of ZnO nanoparticles.

Fig:3 shows that the X-Ray Diffraction patterns of ZnO in 2θ taken in the range from 20–75°. The XRD pattern of pure ZnO powders shows peaks at 2θ = 31.84°, 34.50°, 36.33°, 47.64°, 56.67°, 62.92°, 66.32°, 68.01° and 69.06° which can be index to (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes referred to wurtzite structure with hexagonal cell unit agreement to JCPDS No.36-1451. The crystalline size of as synthesized ZnO was determined by the X-ray line broadening method using the Debye-Scherrer's equation:

$$D = \frac{k\lambda}{\beta_D \cos\theta}$$

where D is the crystalline size in nanometers, λ is the wavelength of the radiation (1.542 Å), k is a constant equal to 0.94, β_D is the peak width at half maximum intensity and θ is the peak position. From Debye-Scherrer's formula particle size of biosynthesized ZnO nanoparticles for (101) plane is 30.9 nm

UV-visible Absorption spectrum

Fig 5 represents UV absorption spectrum of synthesized ZnO nanoparticles. The spectrum obtained has been concluded that the ZnO NPs has adequate transmission in entire visible and IR region. The band gap energy of the ZnO was calculated using the following simple conversion equation. The band gap equation is calculated using the Planck's equation as follows.

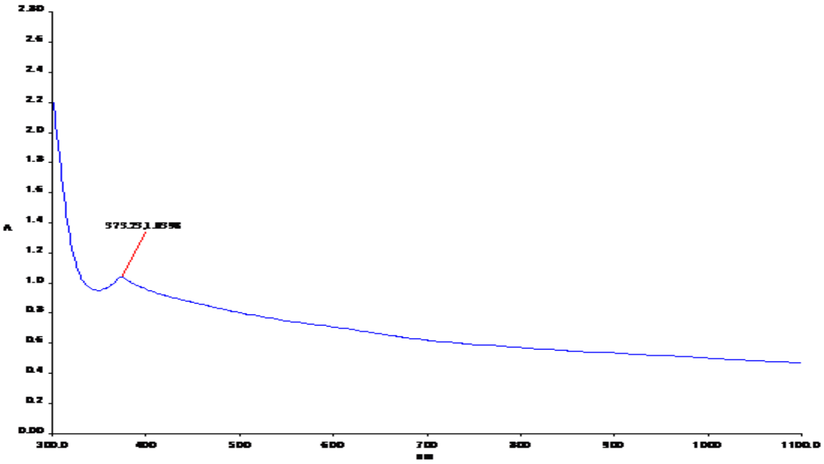

Fig 5: UV absorption spectrum of ZnO.

$$e = \frac{hC}{\lambda}$$

Where h is a Planck's constant ($h=4.135\times10^{-15}$ eV), C is the Velocity of light source ($C=3\times10^{8}$ m/s) and λ is the wavelength absorbed by the catalyst in the UV-visible region.

$$Band\ gap\ energy\ (eV) = \frac{1240}{wavelength\ (nm)}$$

From the above formula band gap energy (eV) of synthesized ZnO nanoparticles were found to be 3.32 eV. This inferred that the band gap of the ZnO nanoparticles depends on the particle size.

Photocatalytical activity

Effect of pH as a function of irradiation time

pH is an important operational parameter for handling the wastewater treatment.[5] Actually pH contributing the vital role in the rate of degradation in photocatalytic system but it is very difficult to interpret effects of pH on the efficiency of rate of degradation of dye since it has plays multiple purposes. This is because many of the semiconductor oxides are amphoteric in nature in such cases the pH plays main role in the rate of degradation thereby influencing the surface-charge properties of photocatalyst.[6] Hence effect of pH must be accounted on the rate of degradation. In order to find out the effect of pH, the experiment was carried out at three different initial pHs 4, 7 and 10.

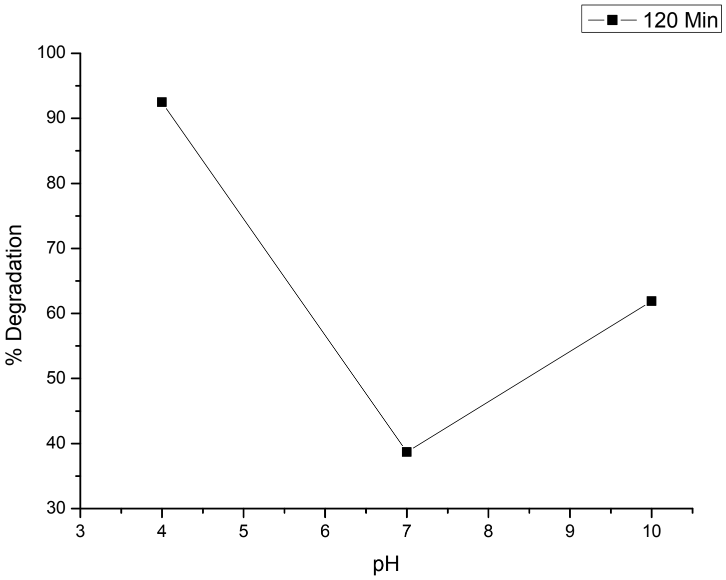

Fig 6: Effect of pH on photocatalytic degradation of direct blue 86 as a function of irradiation time.

Fig 6 shows that the effects of pH on photocatalytic degradation of C.I.direct blue 86 as a function of irradiation time. From the fig 6 it was observed that the rate of degradation of dye C.I.direct blue 86 attains maximum at acidic pH 4 in the contact time 120 min. Many earlier literature also obtained better degradation results in the acidic pH.[7, 8] The extent of rate of degradation decreases at neutral pH and then slightly increases at pH 10. The fact that acidic pH the surface of the photocatalyst is positively charged while at basic pH its surface would be negatively charged. Since dye C.I.direct blue 86 contains two sulphonic groups in its molecular structure, which is negatively charged so that the acidic pH favours that the adsorption onto catalytic surface. This clearly indicates that there is no dissolution Zn^{2+} ions takes place. The slight increase in the rate of degradation attributes that the hydroxyl ions which induces the formation of hydroxyl radical slightly favours the rate of reaction.

Effect of initial concentration as a function of irradiation time:

The initial concentration of dye is an important parameter to study the dependence of degradation efficiency on the initial concentration of dye as a function of irradiation time.[9] In order to investigate the effect of initial concentration of dye, the experiments were performed out by varying the initial concentration dye in the range 2-7 mg/dm^3 while the other parameters kept constant.

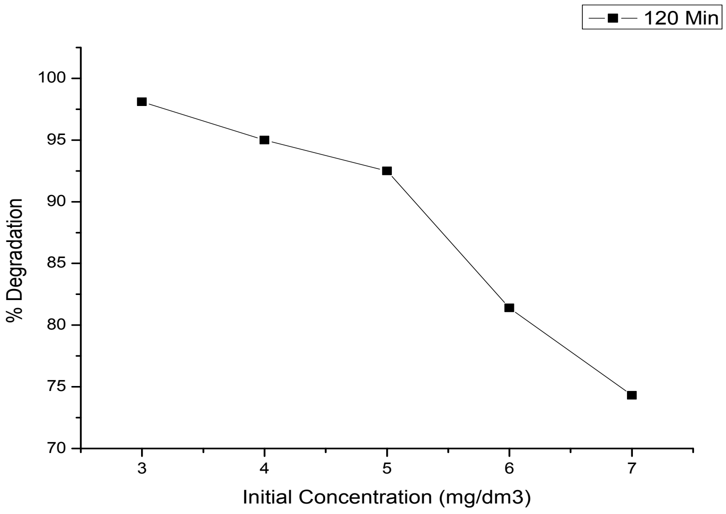

Fig 7: Effect of initial concentration on photocatalytic degradation of dye as a function of irradiation time.

Fig 6 represents the effect of initial concentration of dye on photocatalytic degradation rate as a function irradiation time. The rate of degradation of dye onto the catalytic surface increases with increase of irradiation time and reaches maximum at 120 min after that rate of degraded slowly. It was observed that as the concentration of dye increases, the percentage of degradation of dye decreases. The rate degradation of dye depends on surface i.e., the active sites provided by the photocatalyst. The decrease in the rate of degradation with the increase of initial concentration is due to decrease of active sites in the photocatalytic catalytic surface.

Effect of catalyst dosage as a function of irradiation time

The catalyst dosage is an important parameter because the there is direct relationship between the surface coverage of photocatalyst and dye. The catalyst plays main role in the rate of reaction thereby controls the number photons striking the photocatalyst.[10] To optimize the effect of catalyst dosage, the experiment was conducted with the catalyst dosage 10-60 mg while keeping other parameters constant.

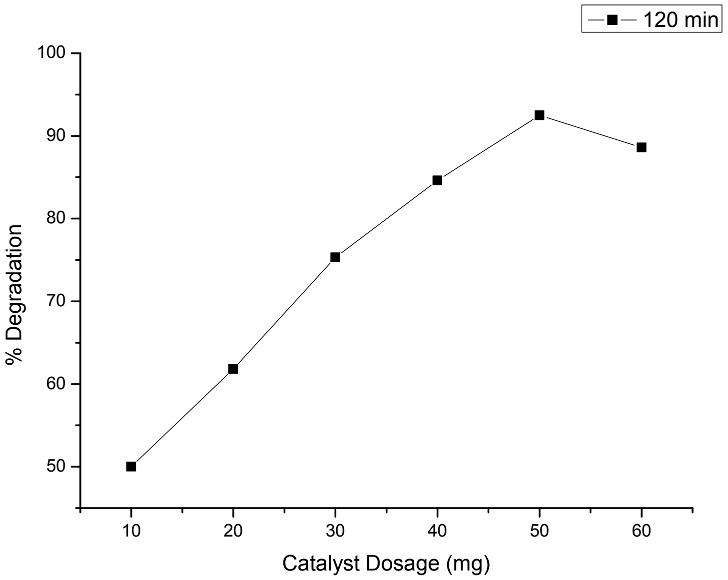

Fig 8: Effect of catalyst dosage on photocatalytic degradation of dye as function of irradiation time.

Fig 8: represents the effect of catalyst dosage on photocatalytic degradation of dye as a function of irradiation time. The result shows that as increases the amount of catalyst dosage, the rate of degradation was also increased from 50 to 92.5%. The maximum percentage degradation was achieved at irradiation time 120 min with the catalyst dosage 50 mg. The study indicates that the rate of degradation increases on increases of catalyst dosage. This phenomenon was explained on the aspect that when increasing the dosage, active sites provided by the catalyst become increases Further increase in catalyst dosage was not beneficial where the rate of degradation was decreased considerably. This fashion has been explained on the basis of increase in catalyst dosage increases the turbidity of the suspension and penetration of UV light penetration as a result of increased scattering effect. So those increases in catalyst dosage limiting the rate of degradation of dye C.I.direct blue 86.[11]

CONCLUSION

The porus ZnO NPs were bio-synthesized by slightly modified gel-combustion method from the plant source with zinc nitrate as a precursor which is very easy and quick process. The bio-synthesized ZnO NPs were characterized by XRD, FT-IR and UV Absorption. From the XRD data, the particle size for (101) plane of the synthesized ZnO NPs was in the range 30 nm and exhibit hexagonal wurzite structure. The band gap calculated by the plank's equation is 3.32 equals to the actual band gap of ZnO. The present also investigate the photocatalytic activity of ZnO synthesized by solution-combustion method on the degradation of dye C.I.direct dye 86 under UV illumination which was often used in the textile industries. The C.I.direct blue 86 was efficiently degraded over photocatalyst ZnO by using catalyst dosage 50 mg at the acidic pH 4 with irradiation time 120 min was found to be 92.5%.

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