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Removal of Methylene blue Dye from water through Photocatalytic Activity Using Polymer-Metal Oxide Nanocomposites – a Comparative Study

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ABSTRACT

The dye-containing effluent from the textile, paper, and food sectors is brightly coloured and has extremely negative impacts on living creatures. Dye degradation into a non-toxic state is useful for reducing water pollution. A variety of treatment strategies have been used to maximize dye deterioration process. Furthermore, because of its small size and high reactive nature, nanocomposites have attracted a lot of interest in the elimination of harmful dye pollution. In this present research work Methylene blue dye was selected for photocatalytic degradation using synthesized photocatalysts. In the presence of synthetic photocatalysts, we irradiated an aqueous solution of methylene blue dye with sunlight and UV radiation. This study compares photocatalytic methylene blue degradation in the presence of Poly (aniline-Co-O-aminophenol)/ZnO nanocomposite and Polyazomethine/ZnO nanocomposites. The outcomes showed that Poly (aniline-Co-O-aminophenol)/ZnO nanocomposite has a higher photocatalytic productivity than Polyazomethine/ZnO nanocomposites.

Key words : Methylene blue, Nanocomposites, Photocatalytic degradation efficiency, UV light, Natural sunlight.

Introduction

Organic dyes are colored aromatic organic compounds that ingest light and transmit color to the visible region. Over 100,000 commercial dyes have been reported around the world, weighing between 7×10^8 to 1×10^9 kg. Material enterprises produce 100-170 litre color profluent per kg of fabric handled which might be described by heavy scent, elevated COD and wide scope of pH. Methylene blue, which is extensively used to shading silk, fleece, cotton and paper is one of the most highly consumed ingredients in the dye trading (Patil *et al.*, 2017; Kamil *et al.*,

2015). The scopus database demonstrates that MB is broadly utilized for different applications. The quantity of articles on MB color corruption has been consistently expanding beginning around 2010-2020 (Abdiriyum *et al.*, 2014).

Methylene blue dye is generally utilized in coloring paper, hair, cotton materials etc. It is a cationic dye. Although MB is not regarded a particularly dangerous dye, it has the potential to cause serious harm to living organisms (Govindhan and Pragathiswaran, 2016; Kim *et al.*, 2016). Frequent exposure of this dye causes hurdles in breathing, nausea and dysentery in human beings (Baeissa, 2016).

Photocatalytic oxidation has gained popularity as an improved oxidation performance because of its efficacy and low energy usage (Eskizeybek *et al.*, 2012). Furthermore, photocatalytic technology is environmentally friendly because organics can be mineralized fully into CO₂ and H₂O during the photocatalytic process. ZnO seems to be an appropriate option in contrast to TiO₂ since its photo deprivation component has been shown to be like TiO₂ (Jamal 2014). ZnO is a n-type semiconductor with numerous appealing highlights. Zinc oxide has a wide band gap of 3.17 eV when contrasted with TiO₂ (anatase = 3.2 eV). It has the ability to produce enough hydroxyl radical extremists (Jenwheng *et al.*, 2012). The photo oxidation of pulp mill bleaching and textile industry effluents has been demonstrated to be particularly effective using ZnO (Liuxue, 2006).

In most cases, the goal of combining polymer/inorganic material crossover is to create a new composite material with synergetic or integral behaviours between the polymer and the inorganic material (Yong *et al.*, 2015). Chelating polymers with an azomethine group (-CH=N-) in the fundamental chain have acquired a great deal of interest nowadays. Polyazomethines, polyamides, polyimides and polyurethanes with Schiff base chelators in the polymer backbone are of significant interest because of important properties (Pathania *et al.*, 2016; Mzoughi *et al.*, 2016; Ansari *et al.*, 2015; Al-Kahtani 2017). Such polymers are thermally steady, has great mechanical strength, semiconducting practices, electronic, optoelectronic, nonlinear optics and electrochemical properties (Wahyuni *et al.*, 2018). Compared with crosslinked or synthetically changed polymers, polyazomethines, basically a leading polymer is reachable with magnificent properties under gentle reaction domain in most extreme amount and high production (Moosvi *et al.*, 2016).

The photocatalytic performance of synthesized materials like Poly (aniline-Co-O-aminophenol)/ZnO nanocomposite and Polyazomethine/ZnO nanocomposites employed for MB degradation was examined in this study. FT-IR, SEM, TEM, UV-visible, TGA, and XRD are some of the techniques used to characterise the composites. The photocatalytic degradation of MB is also studied.

Materials and Methods

Synthesis of ZnO Nano particles

Under vigorous stirring, an aqueous solution of

KOH (0.4 M) is gradually discharged into azinc nitrate solution (0.2 M) at room temperature, resulting in the formation of a white suspension. After being rinsed three times with filtered water, the whitish substance was centrifuged. Finally, the produced product was rinsed in pure alcohol before being calcined for 3 hours at 500 °C (Sivakumar *et al.*, 2015).

Synthesis of Poly (Ani-co-oAP)

Aniline (0.93 g, 0.1 M) and o-aminophenol (1.09 g, 0.1 M) were dissolved in 100 ml of 0.1 M hydrochloric acid. To the above mixture dripping ammonium persulfate (2.28 g, 0.1M) in 100 ml of 0.1 M HCl solution and stirring constantly for 24 h. The finished product was extensively cleaned with clean water until it became colourless. The product was dried in a vacuum oven at 50 °C for 24 h (Sivakumar *et al.*, 2015).

Synthesis of Poly (Ani-co-oAP)/ZnO Nanocomposite

From the above preparation of Poly(Ani-co-oAP), add ZnO nanoparticles (5-10% w/w, depending on the comonomer concentration). The finished product was extensively cleaned with deionized water until it became colourless. In a vacuum at 50 °C, the product was dried for 24 h. The composition of metal oxide with polymer to make effective nano composite was 10% ZnO (Sivakumar *et al.*, 2015).

Synthesis of polyazomethine (PAZ)

The polymer synthesis is based on the reference work carried out (Vasanthi and Ravikumar, 2013; Tripathi *et al.*, 2014). About 0.5 mol of 4, 4'-diformyl biphenyl monomer is taken in DMF medium added slowly into a mixture of toluene solution of 0.5 mol *p*-phenylenediamine. The contents of the reaction were refluxed for 6 hours, then allowed to cool before being discharged into methanol. The resultant precipitate was filtered and dried (Pradeeba and Sampath, 2018, 2022).

Synthesis of polyazomethine/ Zn O nano composite (PNZ)

500 mg polyazomethine is dissolved in 100 mL DMF solution and sonicated for 48 h under constant stirring. Under sonication, ZnO nanoparticles are liberated in acetone and simultaneously added to the polymeric solution. The precipitated ZnO integrated polyazomethine (PNZ) composite material is filtered, cleaned frequently in acetone and dehydrated

(Pradeeba *et al.*, 2022).

Photocatalytic Activiy using Poly(Ani-co-oAP)/ ZnO Nanocomposite under UV light

To measure the photocatalytic capabability of synthesized nanocomposite, the dye methylene blue (MB) was used as a test particle. The process was done in normal temperature using stimulated UV light having a wavelength 365 nm with 10 ppm dye concentration. With standard agitation synthesized photocatalysts was added to dye solution. To obtain the MB adsorption/desorption equilibrium, the suspension was mechanically shaken for 30 min in the dark before irradiation. 10 ml sample was collected every hour for testing. Initially suspended particles are removed by centrifuge process and then dye residue solution was found using a UV-visible spectrophotometer (Jumat, 2017).

Photocatalytic Activiy using polyazomethine/ ZnO nanocomposite under natural sunlight

The experiment under the solar irradiation was carried out on 6th April 2015 for 3 h. The building's roof top was used to store test samples. 3 ml supernatant samples of photoreaction aliquots were taken after each 30 minute irradiation to be measured on the UV-vis spectrometer. A pyranometer was used to measure the intensity of solar radiation. During the day, the total accumulated irradiance was 45.13 MJ/m², the mean duration of sunlight was 12.5 h, and the highest solar radiation was 705 W/m² with a mean sunlight intensity of 160 W/m². During the process, the average temperature was around 29 °C (Yan *et al.*, 2018).

Results and Discussion

FT-IR spectroscopy characterization

The FT-IR spectrum of synthetic photocatalysts is discussed in the table below (Table 1).

When the FTIR spectra of Poly(Ani-co-oAP)/ ZnO Nanocomposite and Polyazomethine /ZnO nanocomposite (Fig. 1,2) are compared with its pure copolymer both are found to be similar with minor changes in the peak magnitude.

UV-Spectroscopy Characterization

In the tabular column below, the UV-Vis spectrum of synthesized photocatalysts is shown (Table 2).

These absorption bands are gently displaced in

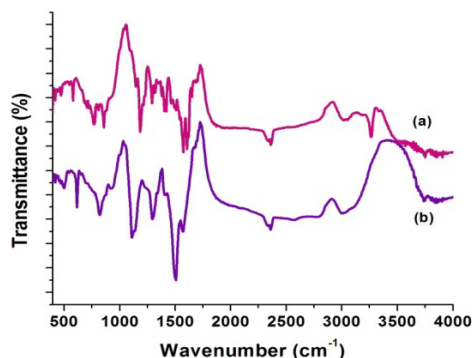


Fig. 1. FT-IR Spectrum of Poly (Ani-co-oAP) (a) and Poly (Ani-co-oAP)/ZnO Nanocomposite (b)

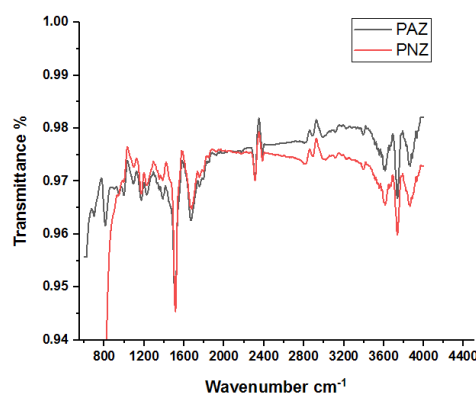


Fig. 2. FT-IR Spectrum of Polyazomethine (a) and Polyazomethine/ZnO Nanocomposite (b)

the nanocomposite. The synergy of polymer and metal oxide shows higher electron delocalization. The UV spectrum of polymer and nanocomposites was depicted in Fig. 3,4.

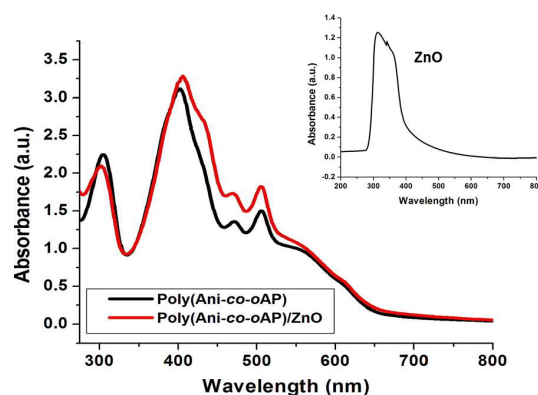


Fig. 3. UV Spectrum of Poly(Ani-co-oAP) (a) and Poly(Ani-co-oAP)/ZnONanocomposite (b)

Thermogravimetric Analysis

The thermal stability of the Poly(Ani-co-oAP)/ZnO nanocomposite was tested by TGA in nitrogen, and

Table 1. FT-IR data and interpretation of synthesized photocatalysts

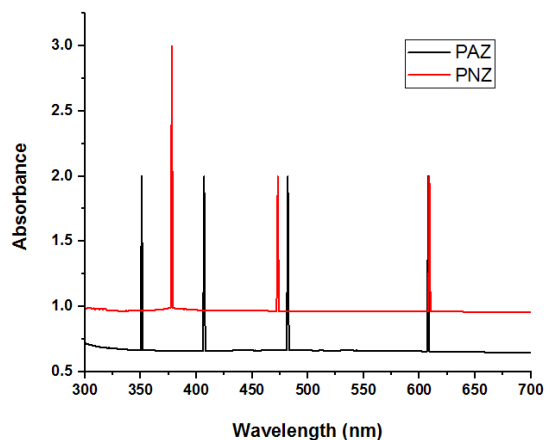
S.No.	Wavenumber (cm ⁻¹)	Group presence in Polyazomethine/ZnO
1	1512cm ⁻¹	azomethine linkage (-CH-N)
2	3736 cm ⁻¹	N-H stretching vibration
3	3555 cm ⁻¹	C-H stretching in aromatic ring
4	1387 cm ⁻¹ & 1352 cm ⁻¹	C=C stretching in benzene ring
5	500 cm ⁻¹ to 600 cm ⁻¹	stretching vibration frequency of ZnO
6	1629 cm ⁻¹	HOH bending vibration
7	2863 cm ⁻¹	CH bond
8	2924 cm ⁻¹ & 2843 cm ⁻¹	CH stretching vibration of the alkane groups

S.No.	Wavenumber (cm ⁻¹)	Group presence in Poly(Ani-co-oAP)/ZnO
1	3272 cm ⁻¹	N-H stretching vibration of secondary amine
2	1587 cm ⁻¹ and 1516 cm ⁻¹	C=C stretching vibrations of quinoid and benzenoid rings
3	1414 cm ⁻¹	C-O-H deformation vibration of o-aminophenol
4	1303 cm ⁻¹	C-N stretching vibration of secondary amine
5	3749 cm ⁻¹	stretching vibration of -OH group in o-aminophenol
6	590-700 cm ⁻¹	C-Cl stretching band
7	464 cm ⁻¹	M-O bond of ZnO

Table 2. UV spectral data and interpretation of synthesized photocatalysts

S.No.	Wavelength (nm)	Group presence in Polyazomethine/ZnO
1	400 nm to 460 nm	π - π^* and n- π^* transition between the benzenoid segments
2	490 nm to 500 nm	Electron move from valence band to the antibonding π - π^* type of PAZ
3	510 nm to 700 nm	
4	375 nm	ZnO nanoparticle

S.No.	Wavelength (nm)	Group presence in Poly(Ani-co-oAP)/ZnO
1	300 nm	π - π^* transition of the benzenoid rings
2	400 nm	localized polarons
3	500 nm	oxidation state of PoAP
4	570 nm	n- π^* transition in the quinoid structure
5	375 nm	ZnO nanoparticle

**Fig. 4.** UV Spectrum of Polyazomethine (a) and Polyazomethine/ZnO Nanocomposite (b)

the findings were compared to the pure copolymer (Fig. 5). The TGA curves in show that the 10% weight loss of Poly(Ani-co-oAP) was in the range of 370-530 °C, revealing that Poly(Ani-co-oAP) were thermostable. Differential scanning calorimetry (DSC) was used to estimate the glass transition temperatures (T_g) of Poly(Ani-co-oAP), which were found to be in the region of 204-206 °C. The thermal stability of nanocomposite was found to be higher than that of pure copolymer, which was linked to the presence of thermally stable ZnO (Min and Chang, 2011).

Thermogravimetric analysis was utilized to evaluate the thermal properties of polyazomethines/ZnO in a nitrogen environment at a temperature increase of 10 °C/min (Fig. 6). Temperatures were taken at the commencement of de-

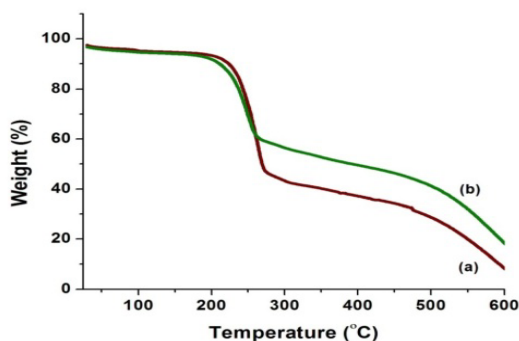


Fig. 5. TGA curve of Poly (Ani-co-oAP) (a) and Poly(Ani-co-oAP)/ZnO Nanocomposite (b)

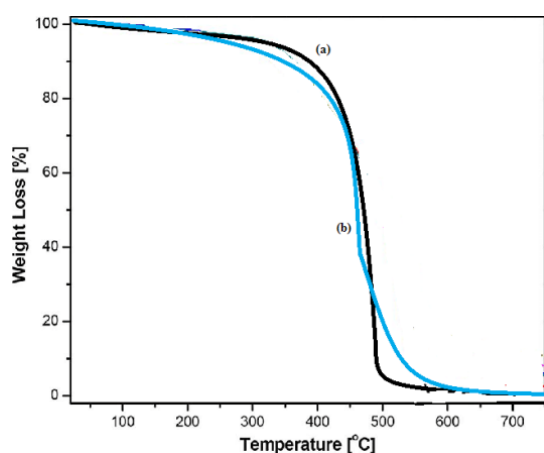


Fig. 6. TGA curve of Polyazomethine (a) and Polyazomethine/ZnO Nanocomposite (b)

composition and at 10% weight loss (T10). The TGA curves in show that the 10% weight loss of polyazomethines was in the range of 398-425°C, revealing that polyazomethines were thermostable. Differential scanning calorimetry (DSC) was used to estimate the glass transition temperatures (Tg) of polyazomethine, which were found to be in the region of 110-125 °C. Polyazomethines have low glass transition temperatures due to the internal plasticization action of the lengthy pentadecyl group pen-

dant chain (Alkaim *et al.*, 2014)

The TGA curve of both synthesized photocatalysts were compared, from the results it was observed that thermal stability of Poly(Ani-co-oAP)/ZnONanocomposite is higher than Polyazomethine/ZnO Nanocomposite.

X Ray Diffraction characterization

The XRD characterization studies of synthesized photocatalysts materials were explained in the below tabular column (Table 3).

The peaks of ZnO in pure copolymer matrix are present in the XRD pattern, confirming the synthesis of Polyazomethine/ZnO and Poly(Ani-co-oAP)/ZnO nanocomposites (Fig. 7-8).

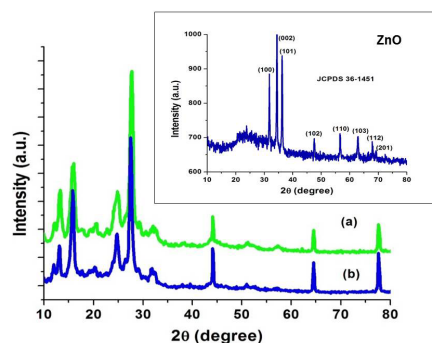


Fig. 7. XRD spectrum of Poly(Ani-co-oAP) (a) and Poly(Ani-co-oAP)/ZnO Nanocomposite (b)

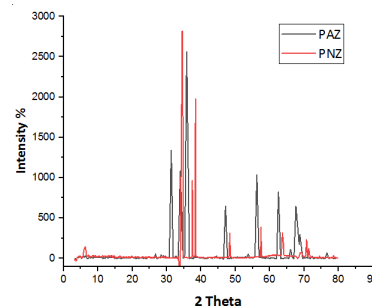


Fig. 8. XRD spectrum Polyazomethine (a) and Polyazomethine/ZnO Nanocomposite (b)

Table 3. XRD spectral data and interpretation of synthesized photocatalysts

S.No.	2θ Values	Interpretation
1	Sharp narrow peaks in Polyazomethine	Recommend the material is crystalline with a little amorphous component.
2	29.21, 35.27, 40.08, 44.27, 49.09, 58.19, 63.67, 70.40°	ZnO with hexagonal crystal structure
3	sharp peaks at 27.7, 32.1, 44.1, 64.4 and 77.7°	suggested that the copolymer Poly(Ani-co-oAP) is crystalline
4	five peaks 2θ = 10–30°	Attributed to copolymer chain
5	peak at 20.2°	Denotes the typical distance between the ring planes of consecutive benzene rings.

Scanning Electron microscope

The particle size of photocatalysts synthesized was listed in the table below (Table 4).

Table 4. Particle size of synthesized photocatalysts

S.No.	Photocatalysts	Particle Size
1	ZnO	32nm
2	Polyazomethine/ZnO	33 nm
3	Poly(Ani-co-oAP)/ZnO	34 nm

The metal oxide nanoparticle (ZnO) and copolymer were present in the intersection of polymer network of nanocomposite. Nanocomposites are generally made up of globular polymer and inorganic filler clusters. The morphology of the poly(Ani-co-oAP)/ZnO nano composite was spherical in shape with ZnO nanoparticles evenly distributed throughout the copolymer matrix (Fig. 9a,9b).

Polyazomethine (PAZ) aggregate particles were visible in SEM micrographs as microporous aggregates. The particles, which had an irregular shape and were in sufficient numbers, could be employed to adsorb dye molecules from the solution interface onto the pores on the surface of the PAZ polymeric resin (Fig. 9c,9d). The presence of functional group carrying donor atoms in the polymeric main chain

per unit volume causes high density agglomerations of particles. The homogeneous dispersion of ZnO nanoparticles in SEM micrographs revealed a cohesive nature. Smooth grains of nanosized particles have been detected all over the surface of the mesosized pores in between the grains. This is mostly due to the nucleation and coalescence of smaller particles, which causes the porous aspect of the material.

Transmission electron microscope

ZnO nanoparticles were found to be mildly aggregated during TEM examination due to their high surface energy. The ZnO nanoparticles were equally distributed throughout the copolymer matrix, giving the poly (Ani-co-oAP)/ZnO nanocomposite a spherical shape. The metal oxide nanoparticles (ZnO) resemble as dark in colour which was enclosed by polymer matrix resemble as lighter in colour which was shown in Fig. 10a,10b.

Polyazomethine polymer aggregate particles with irregular shape were visible in TEM images. In the TEM images, the existence of a pendant azomethine structure was shown by the appearance of dark patches with high intensities at regular intervals. The TEM image of ZnO nanoparticles revealed

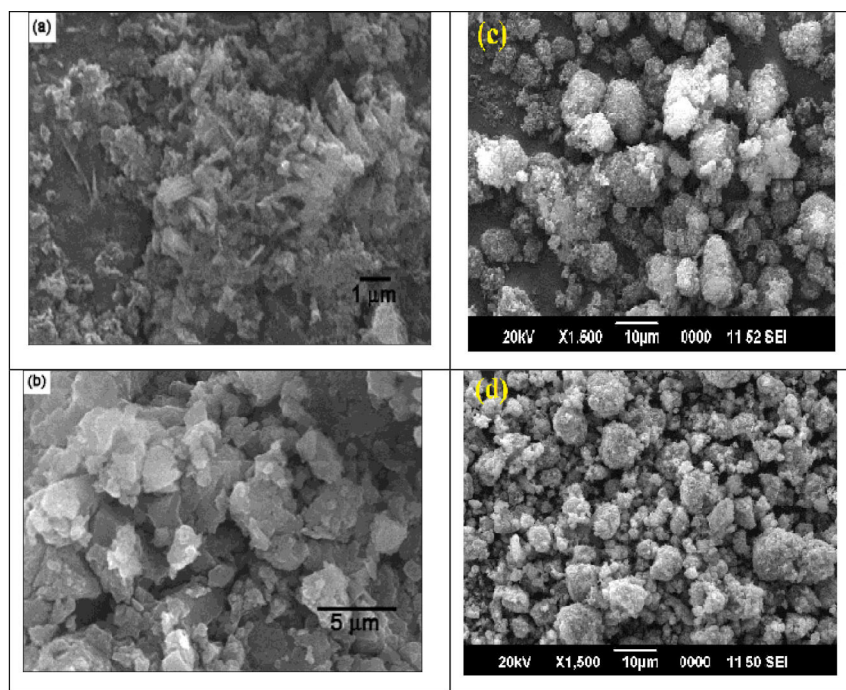


Fig. 9. SEM image of Poly (Ani-co-oAP) (a), Poly(Ani-co-oAP)/ZnO Nanocomposite (b), Polyazomethine (c) and Polyazomethine/ZnO Nanocomposite (d)

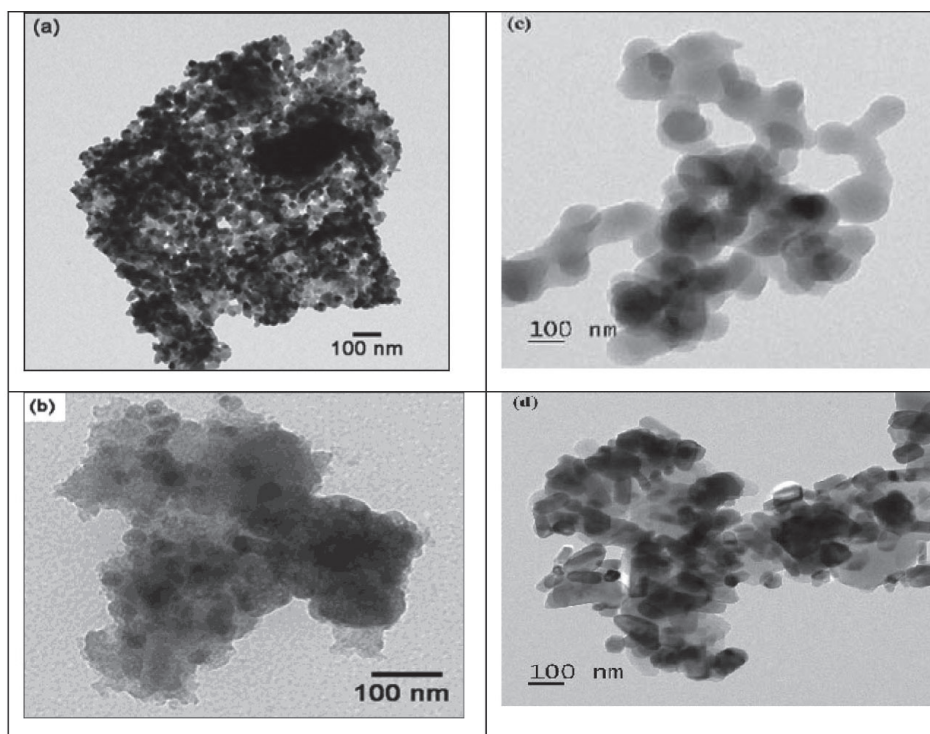


Fig. 10. TEM image of Poly(Ani-co-oAP) (a), Poly(Ani-co-oAP)/ZnO Nanocomposite (b), Polyazomethine (c) and Polyazomethine/ZnO Nanocomposite (d)

a combination of ellipsoidal nanoparticles (Fig. 10c, 10d).

Mechanism of Photocatalytic degradation of MB dye using synthesized photocatalysts

UV-visible spectra of MB solution with the photocatalyst poly(Ani-co-oAP)/ZnO under stimulated UV irradiation and polyazomethine/ZnO

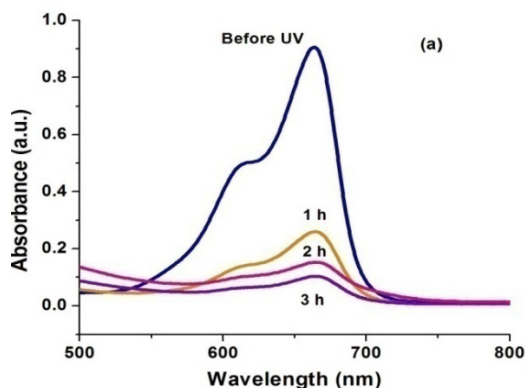


Fig. 11. Efficacy of time variation photodegradation of MB dye using Poly(Ani-co-oAP)/ZnO Nanocomposite

nanocomposites under natural sunlight were recorded before and after varying durations. The highest absorbance at 663 nm (A) is proportional to the concentration of MB (C), hence we examined at the difference in concentration (C/C_0) from the variation in absorbance (A/A_0), where C_0 and A_0 are the initial concentration and absorbance of MB, corre-

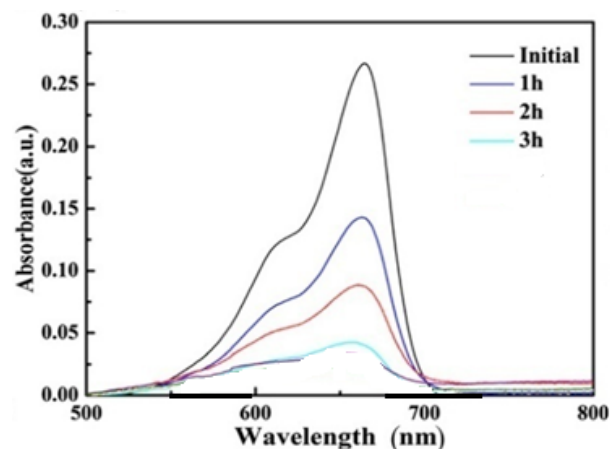


Fig. 12. Efficacy of time variation photodegradation of MB dye using Polyazomethine/ZnO Nanocomposite

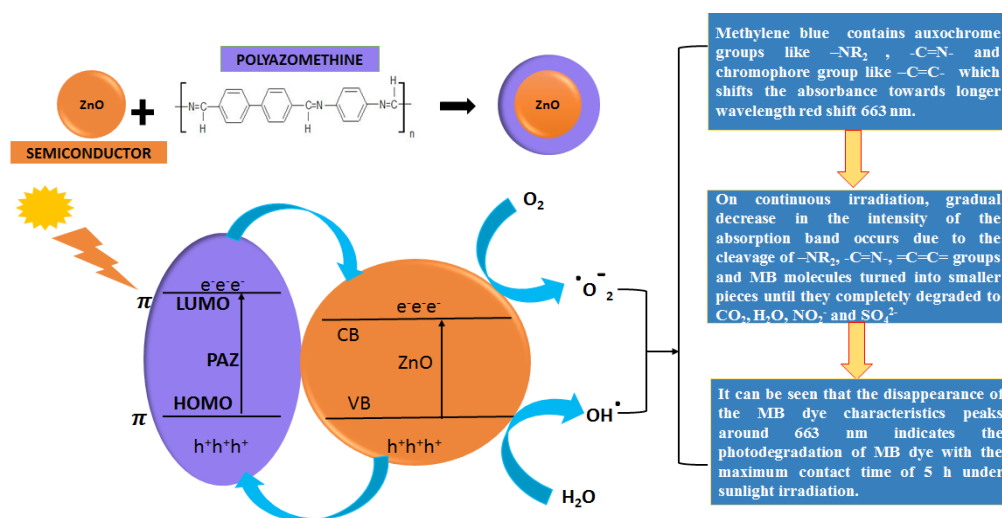
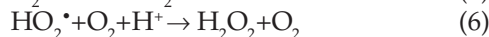
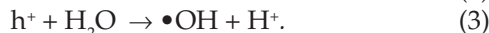


Fig. 13. Schematic diagram of photodegradation mechanism

spondingly. The intensity of the absorption peak at 653 nm, which corresponds to the MB dye, decreased with increased UV exposure duration, implying that the MB dye deteriorated (Chen *et al.*, 2014). The progress of MB photodegradation by photocatalyst is depicted in Fig. 11. Under UV irradiation, poly (Ani-co-oAP)/ZnO nanocomposite degraded around 88 % of the MB in 3 h (Fig. 11), whereas polyazomethine/ZnO nanocomposites degraded approximately 82 % of the MB in 3 h (Fig. 12). When methylene blue dye was exposed to stimulated UV light and natural sunlight irradiation in the presence of synthesised photocatalysts, the results showed that stimulated UV light had a higher photocatalytic efficiency using poly(Ani-co-oAP)/ZnO than natural sunlight using polyazomethine/ZnO because the intensity of UV light remains constant throughout the experiment because it is highly focused, whereas the intensity of natural sunlight may vary due to weather condition. Further the synthesised photocatalyst poly (Ani-co-oAP)/ZnO nanocomposite has high thermal stability than polyazomethine/ZnO nanocomposites which helps to increase the photodegradation efficiency.

ZnO is a well-known photocatalyst that has been widely employed in solar cells and wastewater treatment. Its photocatalytic activity is based on the formation of electron-hole pairs via band-gap radiation, which can lead to redox reactions involving species adsorbed on the catalysts surface (Fig. 13). In the photocatalytic process, the active material is

commonly hydroxyl free radicals ($\bullet\text{OH}$), which are formed when photogenerated electron-hole pairs which oxidise OH^- or H_2O in the presence of oxygen. They are strong oxidants that can cause organic dyes to fade by oxidising them. The following is a description of a probable formation process.



Conclusion

The degradation of MB dye was studied using poly(Ani-co-oAP)/ZnO nanocomposites exposed to UV light and polyazomethine/ZnO nanocomposites exposed to natural sunlight. The metal oxide ZnO were evenly disseminated in the polymer matrix, according to TEM measurements. The nanocomposite was crystal-like in nature, identical to the pure polymer, as revealed by XRD patterns. In comparison to the pure polymer, the nanocomposite showed better heat stability. FT-IR and UV-visible spectra confirmed the interaction between metal oxide and the polymeric network. Both synthesized nanocomposites catalyst showed a high photocatalytic activity by 88% for the photodegradation of the MB dye under UV light irradiation using poly (Ani-

co-oAP)/ZnO within 3 h and 82% for the photodegradation of the MB dye under natural sunlight irradiation using polyazomethine/ZnO nanocomposites within 3 h. The degradation of MB dye was better for poly(*Ani-co-oAP*)/ZnO nanocomposite than polyazomethine/ZnO nanocomposite due to its high thermal stability.

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