ABSTRACT

Advanced oxidation process (AOP) is a recently developed by the researchers for the wastewater treatment over a decade which has more advantages when compared with other conventional methods. Photocatalysis is the most efficient and attractive techniques for the degradation of organic pollutant using semiconductor nanostructured material in presence of solar energy. The researchers decided on the rising deprivation rate of pollutants by incorporating inorganic materials into conducting polymers to understand its synergistic and complementary behaviour among the polymer and inorganic materials. Based on this, the present study is to synthesize polymeric nanocomposite material ZnO with polyazomethine (PNZ) and TiO$_2$ with polyazomethine (PNT) through ultrasonication technique. The synthesized polymeric nanocomposites were used for the photodegradation of cationic and anionic dyes. These synthesized polymeric nanocomposites can act as a potential alternate in future due to its enhanced dye degradation ability and higher stability nature. By varying pH of the dye solution at different time interval the degradation efficiency of photocatalysts were analyzed and found that cationic dyes are removed more when compared to anionic dyes.

Keywords: Photocatalytic degradation, Polymer nanocomposite, Cationic dyes, Anionic dyes.
al. (2017) summarized that synthetic dyes are classified into two types: acidic dyes and basic dyes. Acidic dyes are water soluble anionic dyes used to impart colour to fabrics such as silk, wool, nylon etc. Basic dyes are water soluble cationic dyes mostly enforced in acrylic fibres. Major industries generally use these acidic and basic dyes for imparting colour to the finished products resulting in the release of toxic effluents during the end of the dyeing and finishing process. Methylene blue is an odourless, dark-green solid, imparting blue solution upon suspension in water. Methylene blue is a really unsafe chemical mainly used as a dyeing unit of textile industries. Balu et al. (2018) delivered that dyes are extremely carcinogenic causing serious harmful effects: vomiting, diarrhea, cyanosis, jaundice, quadriplegia, tissue necrosis, deformation of ecological community and discomfort in amphibians existence.

Malachite green dye is mainly utilised to impart colour to resources like silk, wool, cotton, and paper etc. Bandala et al. (2008) classified malachite green as a class (II) health hazard causing harmful effects on kidney, liver, gill, and gonads of aquatic animals. According to Chen et al. (2014) census in 2000, the utilize of malachite green for fish food was disqualified in the European Union since it harms organ, mutagenic, carcinogenic and irregularity to existing organisms. Bismarck brown is considered as a most important since it contains azo linkages, toxic to aquatic organisms. Djokic et al. (2012) summarized that direct contact of this dye in eyes can cause edema, hyperemia, purulent, necrosis, sloughing of the corneal stratum and has a capability of causing the individual using this bismarck dyed fabrics. These dyes are stable, non-biodegradable and highly soluble in nature. Extensive usage of these dyes in various industries maximizes its probability of its presence as pollutants in industrial effluents. To decrease the hazard of ecological contamination created from wastewater effluents, it is essential to remove them before releasing it into the living aquatic environment. According to Eskizyebek et al. (2012) census at present, more than 10,000 dyestuffs have been included in the colour index. Nearly 7 x 10^5 tons of synthetic dyes are annually produced worldwide.

Han et al. (2016) proposed the methods to defeat this difficulty, various schemes have been examined, inclusive of noble metal deposition, the doping of metal or non-metal ions, integrating with a different metal oxide, surface photosensitization with dye and producing composites with a conductive polymer. Polymeric nanocomposite (PNC’s) is the combination of a conducting polymer and inorganic or organic fillers with specific magnitudes like flakes, spheres, particulates etc. Nanostructured elements like clay, silica, CNTs, cellulose and graphene etc. were refined as efficient nanofillers. Enhancement in fiber flexibility creates the fiber to sustain its aspect ratio which results in high flexible nature and better mechanical properties. Moreover, when a polymer is incorporated with nanofillers, it shows enhanced mechanical, thermal and charge transfer property when compared with microfillers. The improved interfacial relations of the nanomaterials with the polymer matrix modify its entire morphology leading to the symbiotic enhancement in the composites. Hussein et al. (2010) recommended the PNCs precisely depend on the quantity portion of nanomaterials, aspect ratio, arrangement in matrix and other geometry. Jamal et al. (2014) summarized the major threatening in producing a good PNCs mainly falls on choosing a relevant nanostructured semiconductor particle and its compatible nature with the polymer matrix. Ijadpanah-Saravi et al. (2014) recommended the development of appropriate handling system to diffuse and disseminate the nanostructured semiconductor material inside the polymer matrix has become a main concern. The following cationic dyes like methylene blue (MB), bismarck brown (BB) & malachite green (MG) and anionic dyes like methyl orange (MO) and alizarin red S (ARS) are selected for the present research study using polyazomethine/ZnO (PNZ) and polyazomethine/TiO2 nanocomposites (PNT).
Where $C_0$ denotes the concentration of dye before irradiation and $C_t$ represents the concentration of the dye after a irradiation with respective time interval.

2.3 Mechanism of Photocatalytic Activity

In general, a photocatalytic reaction is explained as “redox mechanism” in terms of chemistry. A solid material is excited with the help of photon of energy using any light source and it should basically be a semiconductor material. For any photodegradation of any organic compound in water or air medium, bandgap plays a significant role. The bandgap position of a semiconductor material decides the effective oxidation and reduction potential of a photocatalyst. The bandgap of different semiconductors present in between the ranges of 0.7 eV to 5 eV respectively. For any photocatalyst to take part in an effective photocatalytic reaction the bandgap should be between the ranges of 2 eV to 3.3 eV (Jumat et al., 2017).

Fig. 1 represents the mechanism of a semiconductor materials employed in any photocatalytic reaction. When an effective photocatalyst absorbs light from any irradiation sources (UV light, light emitting diodes (LEDs) superior than its bandgap, electrons and holes are produced at the conduction and valence band due to excitation of an electron in the conduction band. The holes generated in the valence band absorb the water molecule to produce hydroxyl radicals ($\cdot OH$) and the electron reacts with the oxygen molecule to build superoxy radicals ($\cdot O_2^{-}$). These radical species are proficient to oxidize the organic compound to form organic intermediates. These organic intermediates undergo further oxidation in presence of atmospheric oxygen or by hydroxyl radicals resulting in carbon dioxide and water. On the other hand, the superoxy radical on further protonation results in the generation of hydroxyl radicals. These radical, further result in molecular oxygen and hydrogen peroxides (Kim et al., 2016).

Therefore, a semiconductor photocatalyst can take part in a redox reaction upon photo-excitation on its surface effectively. The general scheme of a photocatalytic reaction involving a semiconductor material used for the dye degradation is as follows Equation (1) to (7):

$$\text{Dye} + h\nu \rightarrow \text{Dye}^* \quad (1)$$
$$\text{Dye}^* + \text{TiO}_2 \rightarrow \text{Dye}^{\cdot +} + \text{TiO}_2 \quad (2)$$
$$\text{TiO}_2 (e^-) + \text{O}_2 \rightarrow \text{TiO}_2 + \text{O}_2^{-} \quad (3)$$
$$\text{O}_2^{-} + \text{TiO}_2 (e^-) + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 \quad (4)$$
$$\text{H}_2\text{O}_2 + \text{TiO}_2 (e^-) \rightarrow \text{OH}^{\cdot} + \text{OH}^- \quad (5)$$
$$\text{Dye}^{\cdot +} + \text{O}_2 (\text{O}_2^{-} \text{or OH}^-) \rightarrow \text{Organic intermediates} \quad (6)$$
$$\text{Organic intermediates} \rightarrow \text{Degraded or mineralized products} \quad (7)$$

3. RESULTS AND DISCUSSION

3.1 Cationic Dyes Degradation

Fig. 2 shows the effects of altering dye solution pH on the photodegradation of MB dye using synthesized PNT and PNZ catalysts. From the figures, it was clearly seen that all synthesized materials in acidic pH, show less photodegradation of MB dye. But with increase in pH value, photodegradation takes place at a higher rate. At basic condition pH 11, maximum degradation takes place. This is due to the reason that at basic pH, the catalyst becomes negatively charged, hence causing the cationic dye to attract resulting in complete degradation. Photodegradation efficiency was found to be low in acidic pH but with gradually rise in pH and efficient decolourization of the MB...
dye was attained at basic pH at 8. At basic pH, OH$_{-}$ radical shall mix with the holes situated in the photocatalyst exterior, creating additional OH$_{-}$ radical (Pradeeba et al., 2018, 2019). While the OH$_{-}$ radical are the mainly domineering oxidizing group in the photo deprivation method, elevated deprivation of MB dye occurs at the basic medium. Hence optimized pH of 8 was selected for further photocatalytic studies. When the synthesized materials were compared, the titanium doped PAZ polymeric nanocomposite (PNT) shows excellent dye deprivation of methylene blue dye (Shoubin et al., 2011).

Fig. 2. The results of varying dye solution pH onto photodegradation of MB dye using PNT(left) and PNZ (right) polymeric nanocomposite

Fig. 3. The results of varying dye solution pH onto MG dye degradation using PNT(left) and PNZ (right) polymeric nanocomposite

Fig. 4. The results of varying dye solution pH onto photodegradation of BB dye using PNT (left) & PNZ (right) Polymeric nanocomposite

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The results of varying dye solution pH onto photodegradation of malachite green (MG) dye using synthesized PNT and PNZ were shown in Fig. 3. It was found that dye elimination proportion improved gradually with rise in the pH from 3 to 11. At lesser pH values the quantity of positively charged energetic sites on the surface of the photocatalyst are more. Therefore, the electrostatic relation among the negatively charged dyestuff molecules and the energetic sites on the surface of the sample photocatalyst increases the deprivation of cationic molecule. Comparatively, at elevated pH values the surface of the sample photocatalyst turns to more negatively charged and so the electrostatic repulsion among the dye molecule and the photocatalyst surface sites improved which led to degradation of dye molecules to a maximum extent (Suganya et al., 2015).

The results of varying dye solution pH onto degradation of bismarck brown (BB) dye using PNT and PNZ were shown in Fig. 4. Since, bismarck brown (BB) is a cationic dye, lower degradation rate was observed at acidic pH. But with rise in pH from acidic medium to basic, photodegradation rate increases steadily and finally reaches the maximum at pH-11. This indicates that the photocatalyst should be a negative charged to degrade the cationic dye molecules present in the solid-liquid interface. It was found that the degradation rate of synthesised photocatalysts PNT & PNZ was greater (Khan et al. 2016).

3.2 Anionic Dyes Degradation
Fig. 5 shows the effects of altering dye solution pH on photodegradation of methyl orange dye using PNT and PNZ. From the results, the photodegradation takes place in acidic pH and gradually decreases with increase in pH causing a shift into basic medium. These outcomes revealed that elevated photodegradation rates acquired at lesser dye solution pH. Since the amino groups present in the synthesized material gets protonated at a lesser pH, then the sulfonic acid groups of methyl orange (MO) would stay ionized at the tested pH values. This is due to the powerful electrostatic attraction among anionic MO molecules and cationic protonated amino groups of photocatalyst enhance the photodegradation at low pH value (Kazeminezhad and Sadollahkhani, 2016).

Fig. 5. The results of varying dye solution pH onto photodegradation of MO dye using PNT (left) & PNZ (right) Polymeric nanocomposite

Fig. 6. The results of varying dye solution pH onto photodegradation of ARS dye using PNT (left) & PNZ (right) Polymeric nanocomposite
When comparing the photodeprivation of methyl orange dye with the synthesized photocatalysts, the PNZ polymeric nanocomposite degrades the methyl orange dye at a higher pace than PNT in visible light.

The results of varying ARS dye photodegradation using synthesized catalysts PNT and PNZ were revealed in Fig. 6 correspondingly. With rise in pH of the dye solution, the photodegradation gradually decreases. At acidic pH maximum degradation was observed for all the catalyst used for the photodeprivation of ARS dye in the existence of natural sunlight irradiation. From this it was found that less acidic condition are more constructive against the development of the reactive intermediates that is hydroxyl radicals is broadly enhanced, that additionally supports in enlarging the reaction rate. Moreover in extremely acidic conditions for the making of reactive intermediates is fairly low agreeable and not naturally occurring process (Suresh and Annadurai, 2013).

From Table 1, it is found that, the maximum deprivation efficacy of the photocatalysts is in the order as follows, PNZ ≥ PNT. The maximum degradation efficiency for cationics dyes MB (97%), MG (95%), BB(96%) occurs at dye concentration 10mg/L at pH = 11 with photocatalyst (PNT, PNZ) dosage 500mg at time period 5 h. Simultaneously for anionic dyes MO (94%) and ARS (92%) occurs at dye concentration 10mg/L at pH = 3 with photocatalyst (PNT, PNZ) dosage 500mg at time period 5 h. On the other hand, the synthetic cationic and anionic dyes were compared and analyzed to find out the maximum degraded dye by the

### Table 1. Photocatalytic efficiency of synthesized photocatalyst used for the photodeprivation of natural dyes in solvent intermedium

| Dyes             | Optimized parameter | Synthesized photocatalyst | PNT | PNZ |
|------------------|---------------------|---------------------------|-----|-----|
| Methylene blue (MB) | 500 mg              | 95.46                     | 97.08 |
|                  | 10 mg/L             |                           |     |
|                  | pH 11               |                           |     |
| Bismarck brown (BB) | 500 mg              | 85.00                     | 96.66 |
|                  | 10 mg/L             |                           |     |
|                  | pH 11               |                           |     |
| Malachite green (MG) | 500 mg              | 93.22                     | 95.93 |
|                  | 10 mg/L             |                           |     |
|                  | pH 11               |                           |     |
| Methyl orange (MO) | 500 mg              | 92.46                     | 94.08 |
|                  | 10 mg/L             |                           |     |
|                  | pH 3                |                           |     |
| Alizarin red S (ARS) | 500 mg              | 90.22                     | 92.93 |
|                  | 10 mg/L             |                           |     |
|                  | pH 3                |                           |     |

**Fig. 7. Efficacy of synthesized catalyst for the photodeprivation of natural dye pollutant in aqueous intermedium**

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influence of synthesized photocatalysts and it was observed that the cationic dyes are degraded more than anionic dyes. The order of dye removal is as follows, MB ≥ MG > BB > MO > ARS and it was presented in Fig. 7.

4. CONCLUSION

In this study, the photocatalytic elimination of different dyes cationic and anionic from the wastewater using PNT & PNZ nanocomposites was examined. The result of various parameters like pH alteration of photocatalyst, reaction time was studied. The solution pH was found to be 11 with initial dye concentration of 10 mg/L of methylene blue dye solution using 500 mg of PNZ photocatalyst for the time period of 5 h for maximum dye degradation. It was observed that PNZ nanocomposite was showing higher efficacy photocatalyst in eliminating dyestuff in waste-water. It was found that the cationic dyes are degraded more than anionic dyes.

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