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Photocatalytic Activity of TiO₂/POT core-shell nanocomposite on Eosin yellow dye

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ABSTRACT

Poly(o-toluidine) [POT] has been used to prepare TiO₂/poly(o-toluidine) nanocomposite with core-shell structure as photocatalyst. Titanium dioxide (TiO₂) nanoparticles prepared from sol-gel technique were used for the preparation of TiO₂/POT nanocomposite. The nanocomposite is synthesized via chemical oxidative polymerization technique. XRD, UV-Vis, SEM and TEM techniques were used to characterize the TiO₂/POT core-shell nanocomposite. The particle size was found to be 54.5 nm. The particles of the nanocomposite were found to be spherical in shape. Photocatalytic activity of TiO₂/POT nanocomposite on Eosin yellow (EY) dye was investigated under both visible and UV light irradiations. Effects of various parameters such as catalyst dosage, initial concentration of the dye and pH on degradation have been determined. Results indicated deposition of POT on the surface of TiO₂ nanoparticles which improved the photocatalytic activity of TiO₂ nanoparticles.

KEYWORDS. Photocatalyst, TiO₂ nanoparticles, poly (o-toluidine), chemical oxidative polymerization, core-shell nanocomposite.

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1. INTRODUCTION

An attractive subject of research was initiated with the discovery of conducting polymers (conjugated polymers). In recent years development of inorganic/polymer hybrid materials on nanometer scale have been receiving significant attention due to their wide range of potential applications in optoelectronic devices¹⁻³. Titanium dioxide (TiO₂), a semiconductor with a band-gap of 3.0–3.2 eV, has been widely studied for photocatalytic degradation of organics due to its high activity, high stability, and toxicity-free nature⁴⁻⁶. When, a conducting organic polymer gets polymerized on the surface of the TiO₂ nanoparticles its photocatalytic activity gets enhanced due to the prevention of aggregation of nanoparticles.

As a result of an excellent and remarkable properties of conducting organic polymer PANI and its substituted derivative POT, have great scientific and industrial importance⁷⁻⁹. Though the unique properties of PANI provide a great scope for applications in various fields, but poor processibility due to insolubility in most of the common solvents and brittleness restrict its use as a commercial polymer¹⁰⁻¹². To overcome these limitations, change in the physical and chemical properties through substitution of specific groups on aromatic rings of polymer chains is one of the well-known route¹³⁻¹⁴. MacDiarmid and co-workers suggested that substitution of methyl group at ortho position, increases steric interactions between benzenoid rings along the polymer chains, resulting decrease in the extent of conjugation¹⁵. Shama Islam studied the dopant effect and characterization of Poly (o-toluidine)/Vanadium pentoxide composites prepared by insitu polymerization process¹⁶. The synthesis and Characterization of Poly(o-toluidine) doped with Camphor Sulphonic acid is reported by Dhanavelet al¹⁷. Polyaniline based polymeric nanocomposite containing TiO₂ and SnO₂ for environmental and energy applications¹⁸. Since, organic dyes are carcinogenic they have to be degraded. In this paper, TiO₂/POT Nanocomposite is synthesized, characterized and used for the photocatalytic study of Eosin Yellow, an anionic dye.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis of Nano TiO₂

All the reagents used were of analytical grade and no further purification was done before use. The TiO₂ nanoparticles obtained by sol-gel method from Titanium (IV) isopropoxide (TTIP). TTIP was dissolved in absolute ethanol and distilled water was added to the solution in terms of a molar ratio of Ti: H₂O=1:4. Nitric acid was used to adjust the pH and for restrain the hydrolysis process of the solution. The solution was vigorously stirred for 30 min in order to form sols. After aging for 24 hrs, the sols were transformed into gels. In order to obtain nanoparticles, the gels were dried under 120°C for 2 hr to evaporate water and organic material to the maximum extent. Then the

dry gel was sintered at 300°C for 1h were subsequently carried out to obtain desired TiO₂ nanoparticles.

2.2. Synthesis of TiO₂/POT nanocomposite

TiO₂/POT nanocomposite is prepared by chemical oxidative polymerization technique. Nano TiO₂ (1g) is dispersed in 100 ml of HCl aqueous solution (1M). 2 ml of o-toluidine monomer is added to the above solution. Then about 5 g of potassium peroxydisulphate as the oxidant is dissolved in 25ml of distilled water and added to the reaction mixture. The reaction mixture was allowed to polymerize under stirring for 3 hrs at room temperature. The obtained precipitate was filtered and washed with ethanol followed by water and then dried at 110°C for 1 h to get TiO₂/POT nanocomposite.

2.3. Measurement of Photocatalytic Activity

The photocatalytic activity of the TiO₂/POT nanocomposite was evaluated by photo degradation of an aqueous Eosin Yellow (EY) dye. The experiment was carried out in a cylindrical double walled hollow photoreactor with water circulation facility. A 20W UV lamp [wave length of 365 nm] and visible lamp was placed inside the reactor. The catalytic experiments were carried out with 100 ml solution of EY [5×10^{-5} M] and 20 mg of the catalyst under constant stirring. About 3 ml of the aliquot solution was withdrawn at predetermined time intervals from the reaction mixture, centrifuged and the decrease in absorbance value was measured.

$$\text{Decolourization \%} = [(C_0 - C) \div C_0] \times 100 \text{ ----- (2)}$$

where,

C₀, is the initial concentration of dye solution and

C, is the concentration of dye solution after photocatalytic degradation.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

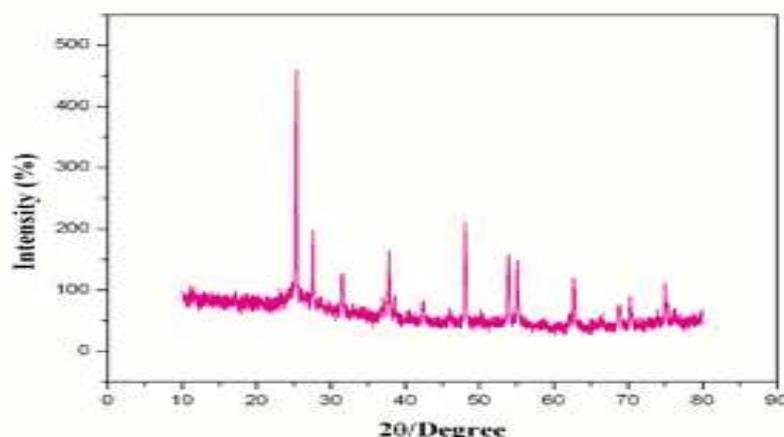


Fig.1 XRD pattern of TiO₂/POT nanocomposite

XRD pattern of the prepared photocatalyst is shown in the Fig. 1. The XRD pattern shows the diffraction peaks at $2\theta = 25.31^\circ$, 37.84° , 48.05° , 53.93° and 62.69° with the corresponding (101), (004), (200), (105) and (204) planes respectively. All the peaks are indexed to anatase phase of the TiO_2 nanoparticles and the diffraction data were in very good agreement with the JCPDS files 21-1272. The peak at 27.56° indicates the polymerization of o-toluidine corresponding to (110) plane.

The particle size obtained in the above XRD pattern is 54.5 nm.

3.2 UV-Visible Absorption spectrum

The optical property of the sample was characterized by UV-Vis spectroscopy. The optical absorption spectrum of the TiO_2/POT nano composite sample was recorded at room temperature, with the wavelength range between 300 and 700 nm and is shown in Fig. 2. The first absorption band at 320 nm is attributed to the $\pi - \pi^*$ transition relative to the bond of conjugation between the neighboring phenylene rings of the polymer network. This band of absorption ensured the hypsochromic shift assigned to POT. The next absorption band located around 500 – 550 nm was attributed to the $n - \pi^*$ transition and also attributed to the exciton band as a result of inter band charge transfer associated with the shifting of electrons from benzenoid ring to quinoid ring²⁰.

The absorption data were analyzed using the following classical relation for near edge optical absorption of semiconductors.

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad \text{----- (2)}$$

Where $h\nu$ is the photon energy. A and n are constants. Where n is 2 for a direct energy gap and $\frac{1}{2}$ for an indirect energy gap. The E_g value can be estimated by extrapolating the straight portion of $(\alpha h\nu)^2$ vs $h\nu$ plot. The band gap energy value for the nanocomposite is found to be 3.4 eV.

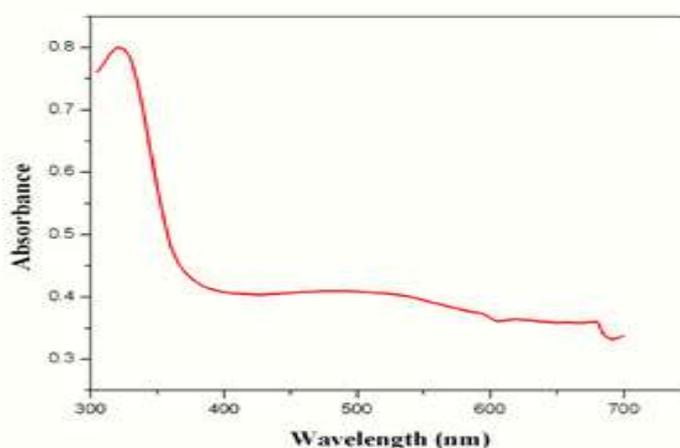


Fig.2 UV-Vis absorption spectrum of TiO_2/POT nanocomposite

3.3 SEM Analysis

SEM image of TiO₂/POT nanocomposite is shown in the fig. 3. TiO₂ nanoparticles were tend to aggregate due to high surface energy, which is the unique property of nanoparticles. This aggregation reduces the photocatalytic activity through the reduction of effective surface area of TiO₂ nanoparticles. From the SEM image of the nanocomposite it is very clear that aggregation of TiO₂ nanoparticles were prevented and they were in well separated state due to the polymerization of o-toluidine on the surface of TiO₂ nanoparticles. Formation of POT shell on the surface of the TiO₂ nanoparticles causes repulsion between nanoparticles and prevented their aggregation. Similar trend was observed by Ali Olad in the formation of TiO₂/polyaniline core-shell nanocomposite²¹.

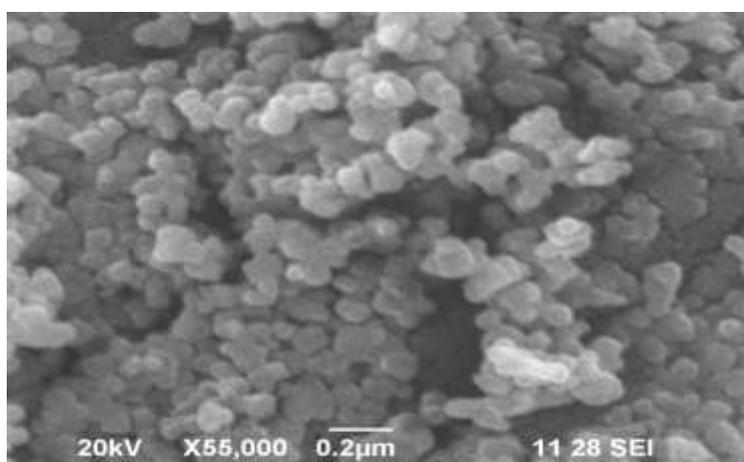


Fig. 3 SEM image of TiO₂/POT Nanocomposite

3.4 TEM Analysis:

It is interesting to note that, polymerization of o-toluidine on the surface of the TiO₂ nanoparticles prevented the aggregation of nanoparticles. As seen in the HRTEM image, most of the particles of the TiO₂/POT nanocomposite were found to be spherical in shape. All the spherical shaped nanoparticles are monodispersed. The nanoparticles were clearly well identified and no effective aggregation of bulk particle is formed. The core-shell structure of the TiO₂/POT nanocomposite was well observed in the HRTEM image as shown in the fig. 4.

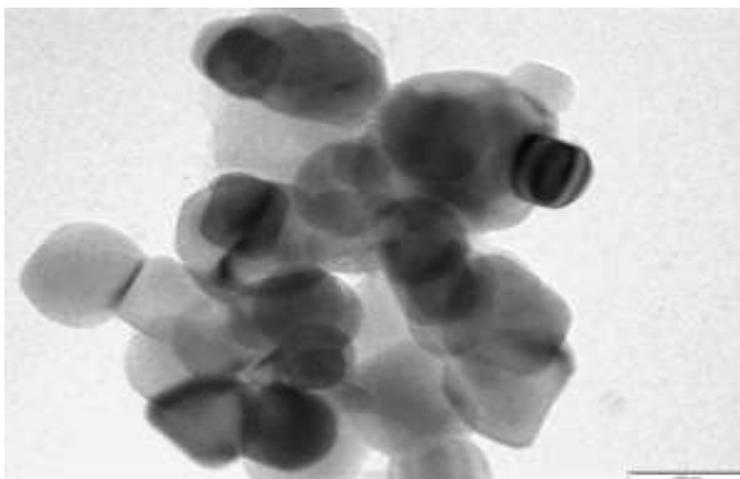


Figure 4. TEM image of TiO₂/POT Nanocomposite

3.5. Photocatalytic removal of Eosin Yellow dye using TiO₂/POT Nanocomposite in the presence of Visible and UV light irradiation:

3.5.1. Effect of Contact time:

For different contact times, the percent removal of the EY dye was recorded under UV and Visible light irradiation. The results for the effect of contact time on adsorption was studied and shown in fig. 5. With increase in the contact time, removal efficiency of the dye increases which may be due to the fact that the dye molecule get chance to make an attraction with the nanoparticles more times. Initial removal occurs immediately as soon as the dye and nanoparticles comes in contact. But after that when some of the easily available active sites engaged, dye needs to find out more active sites for binding. So it is concluded that dye and nanoparticles should be in contact for 80 min for visible light irradiation and 60 min for UV light irradiation. The photocatalytic degradation of EY dye obeys apparently pseudo first order kinetics and the rate expression is given by the following equation.

$$\ln (C_0/C_t) = k_t \text{ ----- (3)}$$

Where,

C₀ = initial concentration of dye solution

C_t = final concentration of dye solution in various time interval

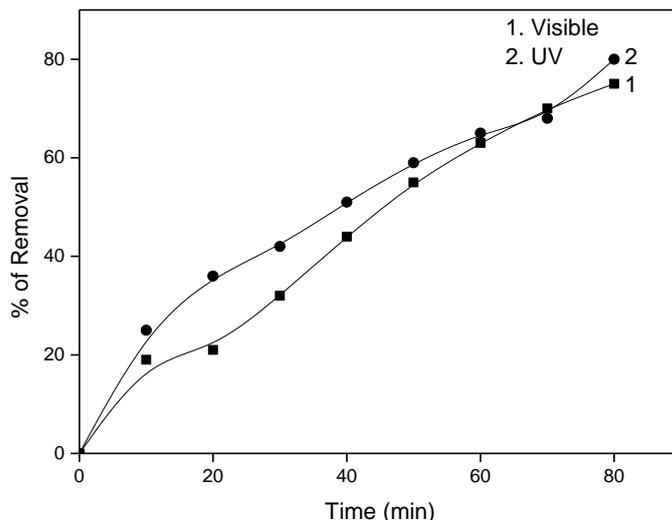


Fig. 5 Effect of Time

3.5.2. Effect of Catalyst dosage:

The experiments were performed by taking different amount of catalyst varying from 10 mg to 20 mg under visible and UV light irradiations. The results are shown in fig. 6. Compared to visible light irradiation, UV light irradiation has maximum dye degradation efficiency which is well shown in the figure. The percentage removal of dye was found to enhance linearly with increase in the dose of the catalyst. This linear relationship is may be due to the following factors. The factors are increase in the extent of dye adsorption molecules on the catalyst surface, increase in the number of surface active sites and enhanced generation of hydroxyl radicals due to increase in the concentration of charge carriers²²⁻²⁵.

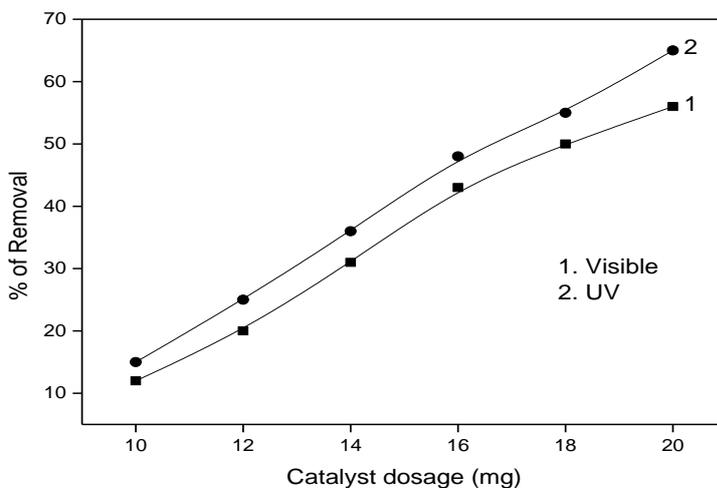


Fig. 6 Effect of catalyst dosage

3.5.3. Effect of initial concentration of Eosin Yellow dye:

The reaction was performed with different concentration of Eosin Yellow dye with constant weight of the catalyst under visible and UV light irradiation. The effect of initial concentration of Eosin Yellow dye on photocatalytic activity was studied by varying the initial dye concentration from 10 ppm to 50 ppm. This trend is shown in Fig. 7. UV light irradiation has maximum dye degradation efficiency than visible light irradiation. The samples were taken in 100 ml of dye solution and percentage of decolourization was calculated after experiment. The Percentage removal of the dye is decreased with increase in dye concentration. This is because with increase in the dye concentration, the solution became more intense colored and the path length of the photons entering the solution is decreased thereby few photons reached the catalyst surface. This leads to the reduction of photo degradation efficiency.

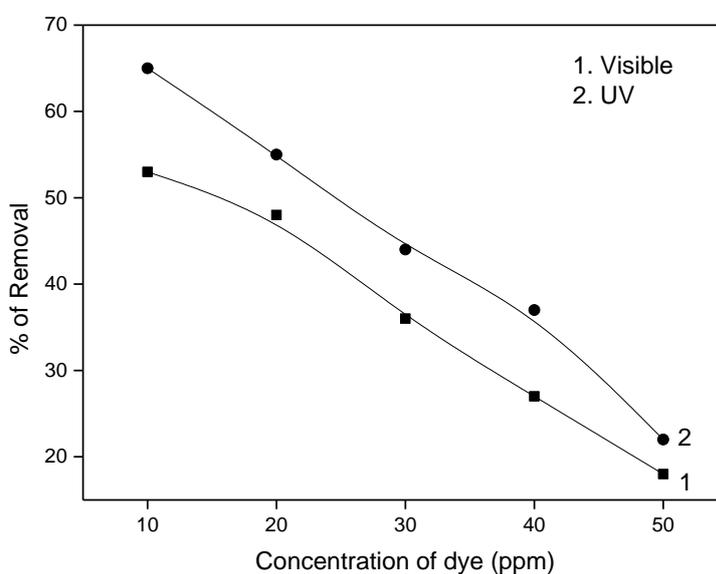


Fig. 7 Effect of initial concentration of the dye.

3.5.4. Effect of pH

The wastewater from textile industries usually have a wide range of pH values. pH of the solution is one of the important factors in evaluating the photodegradation reaction in aqueous medium. In the present work, the pH of the solution was adjusted by adding HCl and NaOH solution. The effect of pH was studied at pH 2 to 10 for EY dye under UV and Visible light irradiation and the results are shown in fig. 8. The zero point charge for TiO₂ is 6.25. Since EY is an anionic dye, higher percentage removal occurs at acidic condition. At lower pH, the presence of H⁺ ions increases the number of positively charged adsorbent sites and the increase in the number of positively charged surface sites probably favor the adsorption of negatively charged dye (Eosin Yellow dye). Because, there is increase in electrostatic attraction with decreasing pH, thus resulting of dye adsorption.

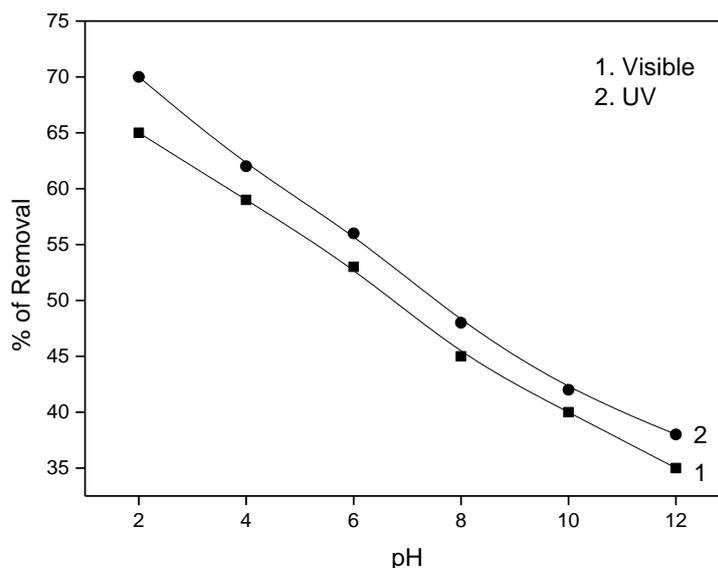


Fig.8 Effect of pH

4. CONCLUSION

TiO₂/POT nanocomposite was successfully synthesized by chemical oxidative polymerization by chemical oxidative polymerization method. Deposition of POT on the surface of TiO₂ nanoparticles and formation of a core-shell nanocomposite were confirmed by XRD, UV-Vis, SEM and TEM techniques. Results showed that POT is a promising material for increasing the photoactivity of TiO₂ nanoparticles under both visible and UV light irradiations. Therefore, surface modification of TiO₂ nanoparticles by POT via the polymerization is a facile method for increasing the photocatalytic activity of TiO₂ nanoparticles.

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