



# Photo-catalytic degradations of methylene blue, malachite green and Bismarck brown using poly(azomethine)/TiO<sub>2</sub> nanocomposite

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## Abstract

The poly(azomethine), TiO<sub>2</sub> and poly(azomethine)/TiO<sub>2</sub> nanocomposites were prepared and exemplified by Fourier Transform-Infra red spectroscopy, UV–Visible spectroscopy, Powder X-ray diffraction, EDAX, SEM and TEM techniques. Methylene blue, malachite green and Bismarck brown were debased from water using poly(azomethine) (PAZ), titanium di oxide (TiO<sub>2</sub>), poly(azomethine)/titanium di oxide (PAZ/TiO<sub>2</sub>) nanocomposites as photo-catalyst in presence of natural sunlight. The deprivation efficiency and reaction kinetics was calculated and the outcome of the photo-catalytic experiments proved that the PAZ/TiO<sub>2</sub> nanocomposites reveals excellent photo-catalytic activity and efficient for achromatize the dyestuff present in the waste water than PAZ and TiO<sub>2</sub> in presence of normal sunlight. The maximum degradation efficiency 95, 93 and 95% was obtained for PAZ/TiO<sub>2</sub> nanocomposites at optimum dosage of catalyst as 500 mg and 50 ppm of methylene blue, malachite green and Bismarck brown dye concentration respectively. The maximum deprivation time was 5 h. After photo-catalytic study the samples were portrayed by FT-IR and UV–Visible spectroscopy. The main aim of this research was to protect our environment from the contamination of water due to the effluence released from dyestuff industries, to resolve this crisis effective nanocomposite were synthesized.

**Keywords** Poly(azomethine) · TiO<sub>2</sub> · Photo-catalyst · Nanocomposites · Advanced oxidation process · Degradation efficiency

## 1 Introduction

Manmade dyes are poisonous and heavy chemicals that can produce concentrated colors are dangerous to the surroundings. These dyes are opposed to bio-decomposition and have pernicious effect on human health. Adsorption, ultra filtration, extraction, oxidation ozone and hydrogen

peroxide are some of the conservative technique utilized to eliminate color from industrial runoff noxious materials [1]. Advanced oxidation processes (AOPs) are substitute to all other techniques, of which the photo-catalysis is the most popular one. In current scenario, heterogeneous photo-catalysis technique can direct to the full deterioration of various inorganic, organic dyes in industrialized operations. There are many semiconductor components are available which acts as photo-catalyst such as TiO<sub>2</sub>, MnO<sub>2</sub>, ZnO etc. The system depends on the concept of decaying various organic hazardous substances speedily and not a particular one. Among many photo-catalyst element, TiO<sub>2</sub> and ZnO are the best photo-catalyst because they have broad band gap [2]. TiO<sub>2</sub> is the extensively favored because it is harmless, steady, biologically static, excellent absorption/desorption properties, safety and photo corrosion stability [3]. A TiO<sub>2</sub> photo-catalyst has achieved several significant in the ancient times due to its outstanding quality of degrading the huge variety of ecological pollutants such as bacteria, organics, viruses and the

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subsequent discovery of photo activated for water separating of  $\text{TiO}_2$ .

Lot of Interest has been created on this technique because solar radiation is used as main source for the removal of contaminant from these industrial runoff noxious materials [4]. Investigation in the synthesis of creative photo-catalyst has been provoked by two major problems: (i) the enhancement of the effectiveness in the presence of solar light by changing the consumption of  $\text{TiO}_2$  placed in the near UV to the visible wavelength range and (ii) the restriction of the active semiconductor elements to promote the removal of the catalyst once the reaction has been completed. Huge hard works have been dedicated to the study of  $\text{TiO}_2$  material, which directs to several challenging functions in the various fields from photo-voltaics and photo-catalysis to electro chromic and sensors. Innovative physical and chemical characteristics appear while the dimension of the  $\text{TiO}_2$  turns into lesser and lesser and down to the nanometer size [5]. The outcome of the photo-catalytic deprivation of biphenyl by  $\text{TiO}_2$  with UV light illumination in the year 1976 has created more interest in the ecological application of the  $\text{TiO}_2$  as photo-catalyst. Though the band gap of  $\text{TiO}_2$  (anatase) is 3.2 eV so it can only absorb and be energized by UV illumination with a wavelength below 387 nm UV light accounts for < 5% of solar illumination. The intrinsic property of anatase limits realistic application.

To beat this discrepancy, polymer hybridizing, semiconductor coupling, ion doping and various other procedures were introduced. Conjugative polymer/ $\text{TiO}_2$  hybrid stuff reveals more effectiveness in deterioration of organic contaminants in presence of both UV light and visible illumination. By means of this blending technique, it was found to be complicated to attain electric contact among the metal oxide particles and the conjugative polymer layer, because the polymer chain might hinder with the correlation produced inside the metal oxide. Entire hybridization might not be achieved using the diffusion technique as the polymer may not be filled because of the inadequate penetration power of the conductive polymer film. Since the conjugative polymers merely placed on the  $\text{TiO}_2$  nanoparticles, but the boundary linking the  $\text{TiO}_2$  semiconductor and the conjugative polymer layer does not balance. A steady border for the hetero function composite is extremely advantageous since it promotes the speed of charge injection when accelerates by light or electrical motivation. UV accelerates the  $\text{TiO}_2$  produce conduction band electrons ( $e^-$ ) and valence band holes ( $h^+$ ) in couples provide surface –mediated reduction–oxidation activities. In recent times, it has been revealed that photo energized  $\text{TiO}_2$  nanoparticles are qualified of catalyzing the free radical polymerization of alkenes such as in methyl methacrylate and acrylic acid. This polymerization technique

directs to excellent bonding nature for the inorganic stuff. The polymers synthesized by this method have good electronic contact with the inorganic semiconductor segment since the polymerization reaction is narrowly started by charge transfer across the inorganic semiconductor–monomer boundary.

Conjugative polymers and their derivatives are widely engaged in photovoltaic conversion of solar illumination owing to their absorption coefficients in the visible fraction of spectrum, elevated movement of charge carries and outstanding constancy. Recently, there is rising interest in using polythiophenes, polyaniline, polypyrrole and their derivatives to sensitive  $\text{TiO}_2$  produce polymer/ $\text{TiO}_2$  nanocomposites. Like this several nanocomposites such as polypyrrole/ $\text{TiO}_2$  composite particles polythiophene/ $\text{TiO}_2$  composite particles, polyaniline/ $\text{TiO}_2$  composite particle, poly (3-hexyl thiophene)/ $\text{TiO}_2$  nanocomposite were also prepared and its effective deprivation of dye stuffs like methyl orange, methylene blue, rhodamine-B under UV and visible sunlight have been recorded in the past decades [1, 3–16].

Recently derivative of polythiophene, polyterthiophene—type conjugative polymers have quickly achieved significant consideration owing to the pre-subsistence of  $\alpha$ - $\alpha'$ -linkages in their monomers, which makes the whole polyterthiophene-type chain grow frequently and directs to remarkable electrochromic and optical properties [11]. Polydopamine (PDA) is a biocompatible and biodegradable polymer and has powerful solar absorption and weak fluorescence upon excitation of UV light owing to its chemical disarray. In terms of its electronic properties, PDA is similar to shapeless organic semiconductor or electronic –ionic hybrid conductors due to its  $\pi$ -system, leads to electrical conduction ability which is significantly exaggerated by temperature, morphology and ecological moisture. PDA/ $\text{TiO}_2$  nanocomposites were prepared and showed absorption in the visible region, which favors the photo-catalytic activity of  $\text{TiO}_2$  under visible light and expected the  $\text{TiO}_2$ /PDA nanocomposites exhibit better photo-catalytic activity in the deprivation of methyl orange under sunlight compared with PDA/ $\text{TiO}_2$  this is owing to the synergetic effect between  $\text{TiO}_2$  and PDA [12]. The maximum photo-catalytic activity for the deprivation methylene blue aqueous solution under UV illumination by  $\text{TiO}_2$ –graphene nanocomposite was obtained [13]. Phenolic compounds are normally present in the effluents discharged from various industries and other every day feature of existence. They are one of the familiar and hazardous contaminants present in water bodies. Elevated toxicity and pernicious compounds are undesirable and leads to severe consequences on the aquatic ecosystem and human health. The exposure of phenolic compounds also ascribed to their accumulations which widen their occurrence in the

ecological sequence which merely gives additional harm to the surroundings it is removed by using TiO<sub>2</sub>/graphene nano compounds.

By analyzing the previous studies [17–22], there have been no reports on nanocompounds of poly(azomethine) PAZ/TiO<sub>2</sub> as a photo-catalyst. So conjugative polymer poly(azomethines) are used to make composite with TiO<sub>2</sub> to acts as photo-catalyst. Moreover, the poly(azomethines) present the advantages to be p- and n-doped, due to their reversible oxidation and reduction, correspondingly [23]. Conjugated poly(azomethine)s (PAZ), polyamines or poly (Schiff bases) are an additional fascinating class of conjugative polymers holding nitrogen atom (CH=N) in a polymer backbone is used in this study for producing nanocomposites along with TiO<sub>2</sub>.

Based on the above concept, in this article, poly(azomethine) PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> nanocomposites were prepared and structural characterization such as FT-IR, UV–Vis, SEM, TEM, XRD and EDAX were conferred. The photocatalytic experiments with poly(azomethine) PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> nanocomposites were examined by elimination of methylene blue, malachite green and bismarck brown present in waste water was carried out in presence natural sunlight. Deprivation efficiency of photocatalyst such as poly(azomethine) PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> nanocomposites were evaluated.

## 2 Materials and methods

### 2.1 Reagents and materials

Highly uncontaminated chemicals were purchased from in Sigma Aldrich, India they are p-phenylene diamine (99.98), Hexamethylene tetramine (99.98), ethanol(99.98), 4,4'-bis (chloro methyl) biphenyl (99.98), toluene, DMF(99.98), methanol (99.98), titanium tetra chloride, ammonium hydroxide, methylene blue, malachite green and Bismarck brown.

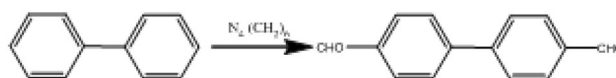
### 2.2 Experiments

Preparation of poly(azomethine)

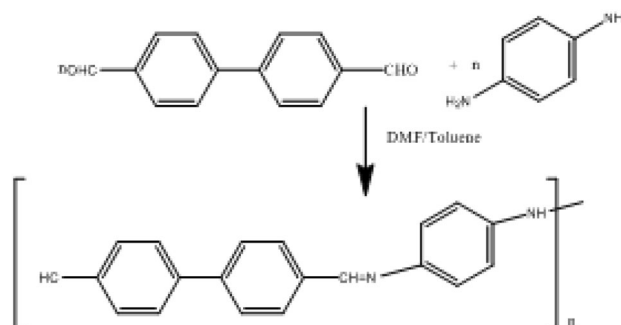
Monomer preparation

Synthesis of 4,4'-diformyl biphenyl

Hexamethylene tetramine (6.8, 48 mmol) was dissolved in ethanol (90 ml) and 4,4'-bis (chloro methyl) biphenyl (3.00 g, 12 mmol) was added at 40 °C. The combination was stirred 1.5 h at 45–50 °C and precipitate was collected, washed with ethanol for two times. Then acetic acid (40 ml) 50% was added. Reflux the substance for 10 h and



**Scheme 1** Synthesis of 4,4'-diformyl biphenyl



**Scheme 2** Synthesis of polyazomethine

filtrated. The filtrate was cooled overnight. The crystals (Scheme 1) were accomplished.

#### 2.2.1 Synthesis of poly(azomethine)

In a 25 ml of RB flask with a magnetic stirrer a condenser and inlet–outlet dean stark system 0.1536 g (0.5 mmol) of 4,4'-diformyl biphenyl and 0.05456 g (0.5 mmol) of p-phenylene diamine, 7 ml of DMF and 2 ml of toluene were introduced. The reaction mixture was refluxed at the boiling temperature of toluene for 6 h. After cooling at room temperature the reaction mixture was added in a huge amount of methanol and the polymer precipitate (Scheme 2) was filtered and dried.

#### 2.2.2 Synthesis of nano TiO<sub>2</sub>

TiCl<sub>4</sub> was slowly introduced into deionised double distilled water in an ice bath (0 °C) under constant stirring until it was completely dissolved and then 18 ml of 30% ammonium hydroxide was added to this suspension. The formed white titanium hydroxide was allowed to stand for 1 h. Then, the obtained TiO<sub>2</sub> nanoparticles were filtered, washed with deionised double distilled water and dried at 100 °C in a vacuum oven for 3 h [15].

#### 2.2.3 Preparation of making polymer nanocomposite

Only a small amount of polymers were taken to prepare the composites. The polymer (250 mg) was dissolved in 100 ml DMF by stirring in 250 ml Stoppard conical flask kept in a shaker and sonicated to obtain a dispersed polymer solution. The polymers were incompletely soluble in DMF and continued finely dispersed after 48 h. The

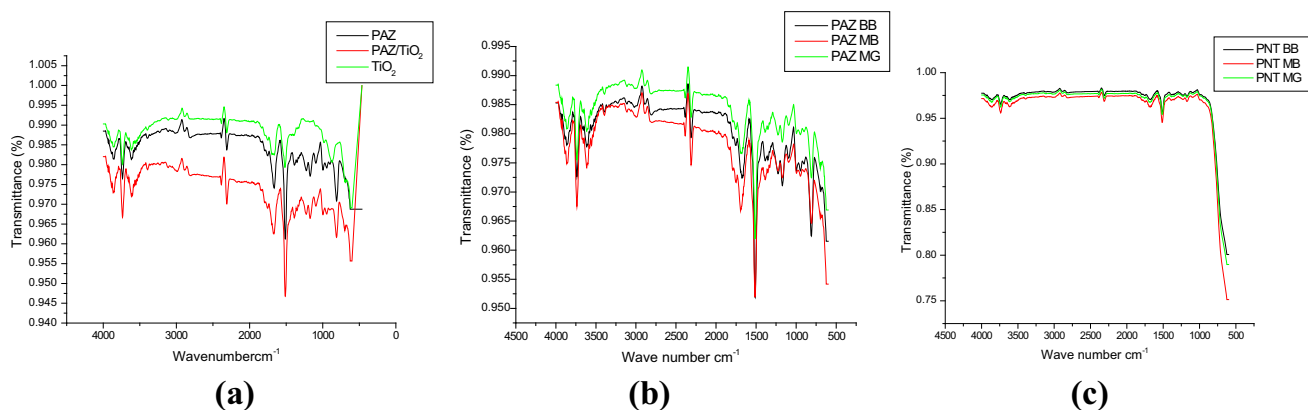
relevant nanoparticles dispersed in acetone were sonicated and instantaneously added to the polymer in DMF under sonication. The polymers were permitted to precipitate out. While precipitating, the nanoparticles got encapsulated into the polymer matrix. The composites thus acquired were filtered and washed systematically with acetone and dried [24].

### 2.3 Characterization

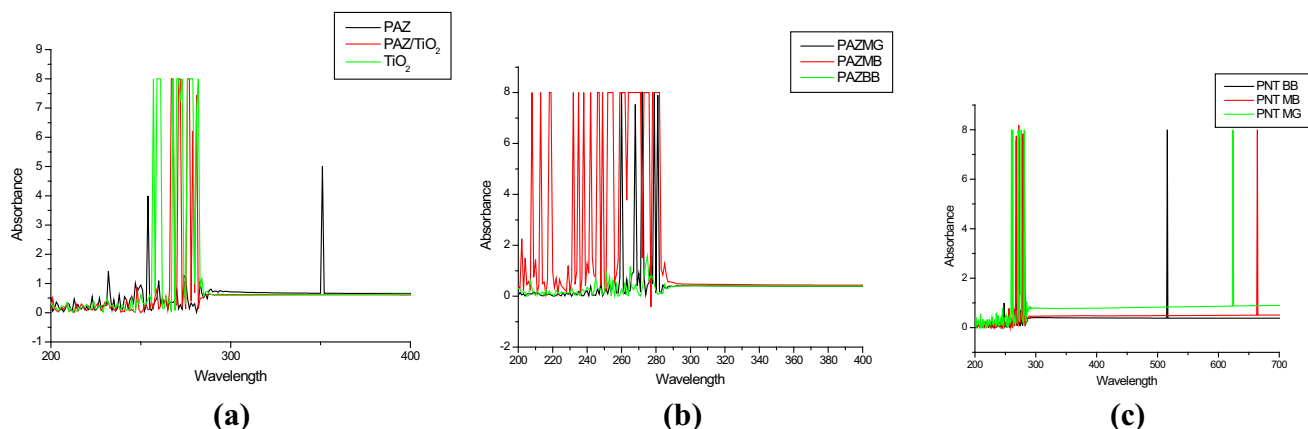
FT-IR spectroscopy (BRUKER EQUINOX-55), UV-Vis spectroscopy (SHIMADZU), Powder X-ray Diffraction (Scintag-XDS-2000m), Scanning Electron microscope (JSM-7600F Japan), Transmission Electron Microscopy TEM (JEOL model 2100) and EDAX of the sample were recorded for structural characterization.

### 2.4 Photo-catalytic experiments

The photo-catalytic activities of poly(azomethine) PAZ,  $\text{TiO}_2$  and PAZ/ $\text{TiO}_2$  nanocomposites were performed using methylene blue, bismarck brown and malachite green dyes in presence of normal sunlight. Before irradiation the suspension was mixed magnetically for 30 min in absence of light until adsorption–desorption equilibrium was recognized and then suspension were illuminated by light source with stirring. Dye stock solution was produced by 4 mg of dye is soluble in 500 ml of DI water. The different amount of catalyst (PAZ,  $\text{TiO}_2$  and PAZ/ $\text{TiO}_2$ ) was added to remove methylene blue, malachite green and Bismarck brown dyes (MB, MG and BB) and kept in ordinary sunlight. Initial and final concentrations of dye solution were measured by recording absorbance on a double beam UV-Vis spectrophotometer at 516, 624 and 668 nm respectively. The samples were received at different time period and concentration of the dye was calculated using UV-Vis



**Fig. 1** FT-IR characterization of PAZ,  $\text{TiO}_2$  and PAZ/ $\text{TiO}_2$  nanocomposite before (a) and after (b, c) removal of methylene blue, Bismarck brown and malachite green (Color figure online)



**Fig. 2** UV Vis characterization of PAZ,  $\text{TiO}_2$  and PAZ/ $\text{TiO}_2$  nanocomposite before (a) and after (b, c) removal of methylene blue, Bismarck brown and malachite green (Color figure online)

spectroscopy. The photo degradation efficiency  $R$  (%) was calculated by the employing the following equation

$$R(\%) = \frac{C_0 - C_t}{C_0}$$

where  $C_0$  symbolize the concentration of dye before irradiation and  $C_t$  denotes the concentration of the dye after a definite illumination time correspondingly [16, 25–28].

## 3 Results and discussion

### 3.1 Characterisation of photocatalyst

#### 3.1.1 Fourier transform-infra red spectroscopy

A representative FT-IR spectrum of poly(azomethine) (PAZ),  $\text{TiO}_2$  and PAZ/ $\text{TiO}_2$  (PNT) nanocomposites are reproduced in (Fig. 1a, b, c). The characteristics band of azomethine or imine linkage ( $-\text{CH}=\text{N}$ ) appeared at  $1512 \text{ cm}^{-1}$ . The absorption band at about  $3736 \text{ cm}^{-1}$  is

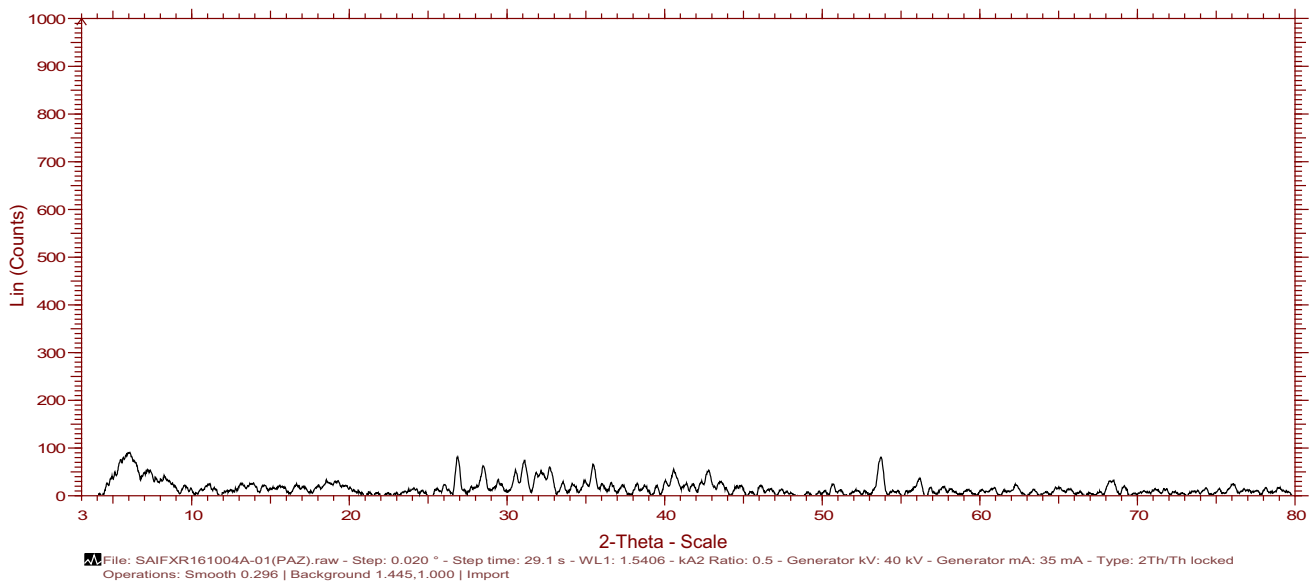


Fig. 3 XRD of poly(azomethine)

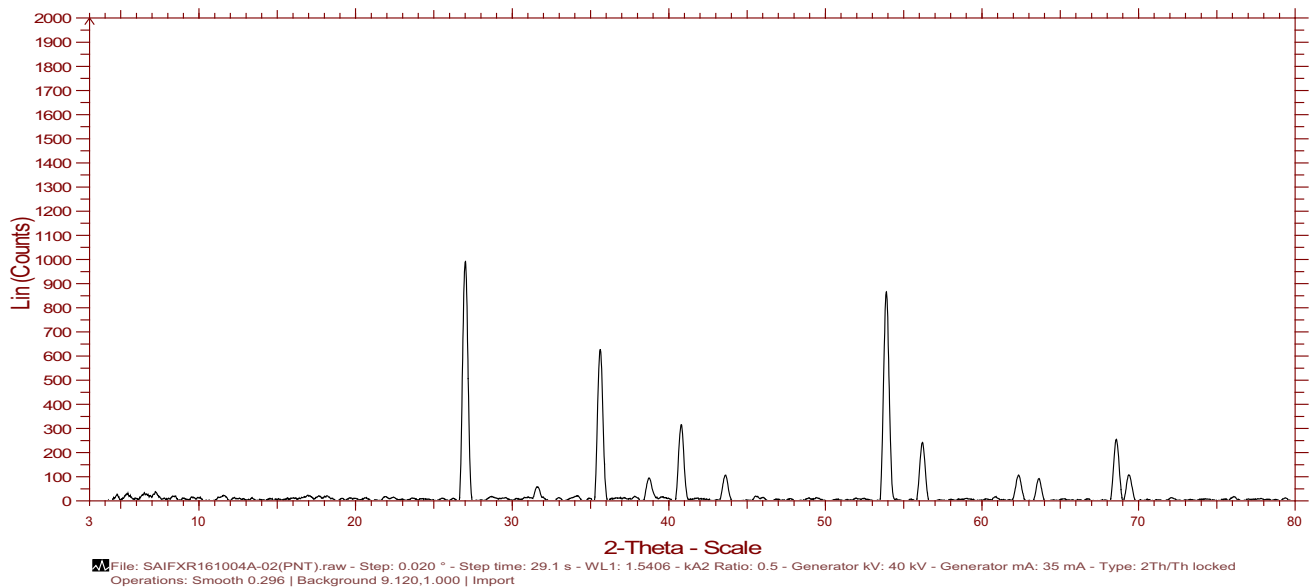


Fig. 4 XRD of poly(azomethine)/ $\text{TiO}_2$

related with the N–H stretching vibration in the aromatic unit. The absorption spectrum at  $3555\text{ cm}^{-1}$  is attributed to the C–H stretching in aromatics. The peaks at  $1387$  and  $1352\text{ cm}^{-1}$  are endorsed to C=C stretching in benzene ring. The peaks visible at  $809$ ,  $811$ ,  $872\text{ cm}^{-1}$  are the region for N–H stretching vibration respectively. The absorption peak at  $800\text{ cm}^{-1}$  corresponds to the Ti–O–Ti stretching mode [16] and the same peak was observed in PAZ/TiO<sub>2</sub> (PNT) composite but the intensity of that peak is not observed in PAZ spectrum.

The PAZ/TiO<sub>2</sub> (PNT) nanocomposites displays related distinctive peaks like PAZ, moreover it shows the quality absorption of Ti–O–Ti at about  $800\text{ cm}^{-1}$  (Fig. 1a). Slight alteration in high peak magnitude and wave numbers may

be the outcome of the interaction with PAZ chains and TiO<sub>2</sub> particles [29–34].

After the photo-catalytic process respective FT-IR spectrum of PAZ and PAZ/TiO<sub>2</sub> (PNT) were observed (Fig. 1b, c). The peaks are similar for PAZ only and slight variation due to absorption of methylene blue (PAZMB), malachite green (PAZMG) and bismarck brown (PAZBB) dye. In case of PAZ/TiO<sub>2</sub> (PNT) the peaks remains same position like PAZ but there is change in the intensity of peaks, it shows the deprivation efficiency of methylene blue (PNTMB), malachite green (PNTMG) and bismarck brown (PNTBB) is more for PAZ/TiO<sub>2</sub> (PNT) than PAZ.

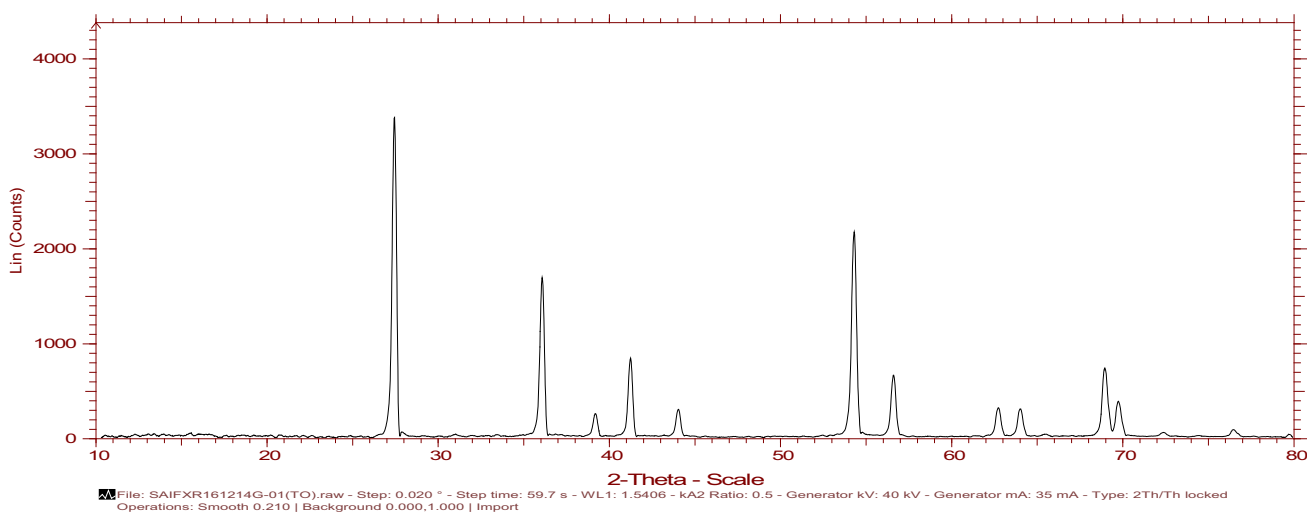


Fig. 5 XRD of TiO<sub>2</sub>

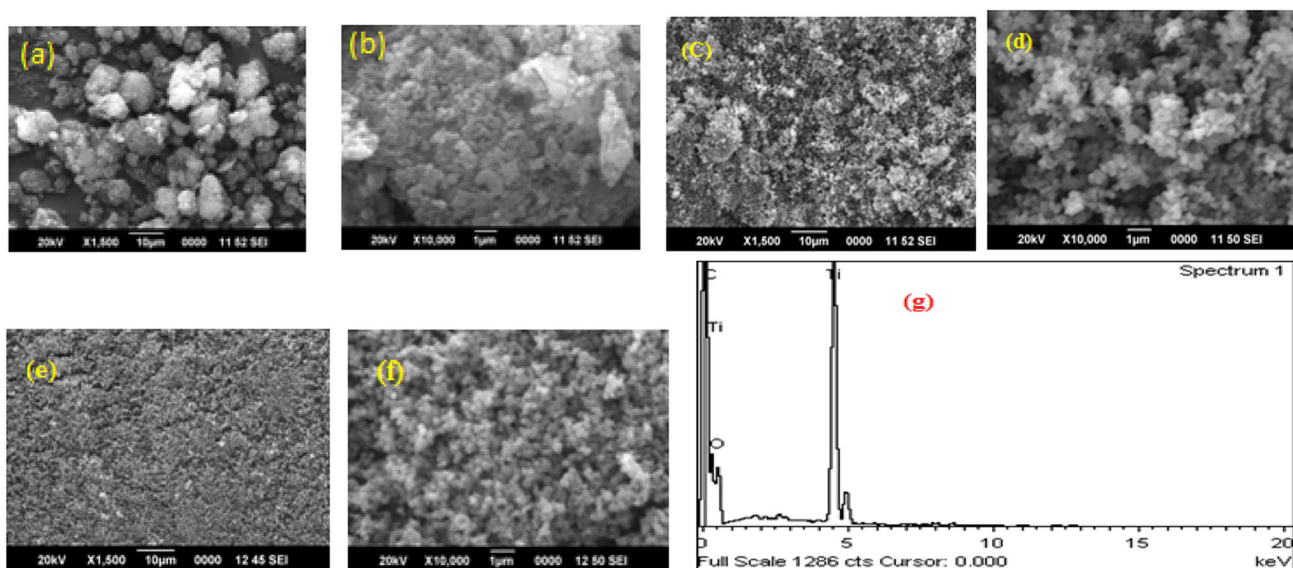


Fig. 6 SEM of PAZ (a, b), PAZ/TiO<sub>2</sub> nanocomposite (c, d) and ZnO (e, f) and EDAX of PAZ/TiO<sub>2</sub> nanocomposite (g)

### 3.1.2 UV–Visible spectroscopy

The UV–Vis spectrum (Fig. 2a) displays the absorption band in the series of 280–290 nm was designated to the  $\pi$ – $\pi^*$  and  $n$ – $\pi^*$  transition in the conjugated chain present in the structure of PAZ and PAZ/TiO<sub>2</sub> (PNT) nanocomposites. TiO<sub>2</sub> has shown strong absorption at 296 nm when TiO<sub>2</sub> nanoparticles were incorporated into the polymer matrix, a slight shift in the absorption band of TiO<sub>2</sub> from 296 to 300 nm was observed which indicated the formation of PAZ/TiO<sub>2</sub> (PNT) nanocomposite (Fig. 2a). Sudden change in the absorption peak at around 350–390 nm is due

to the electron transition from the valence band to the conduction band [13]. The peak in the range of 296 nm is present in TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> (PNT) nanocomposites but not observed in PAZ (Fig. 2a). It was noticed that peak intensity was higher for the entire three spectrums (Fig. 2a) it shows hyperchromic effect which indicated presence of auxochrome group like –NH<sub>2</sub> and –O in the structure. Therefore the prepared nanocomposite can be photo stimulated by visible light or existing natural sunlight illumination which has no destructive effect on human health [35–39].

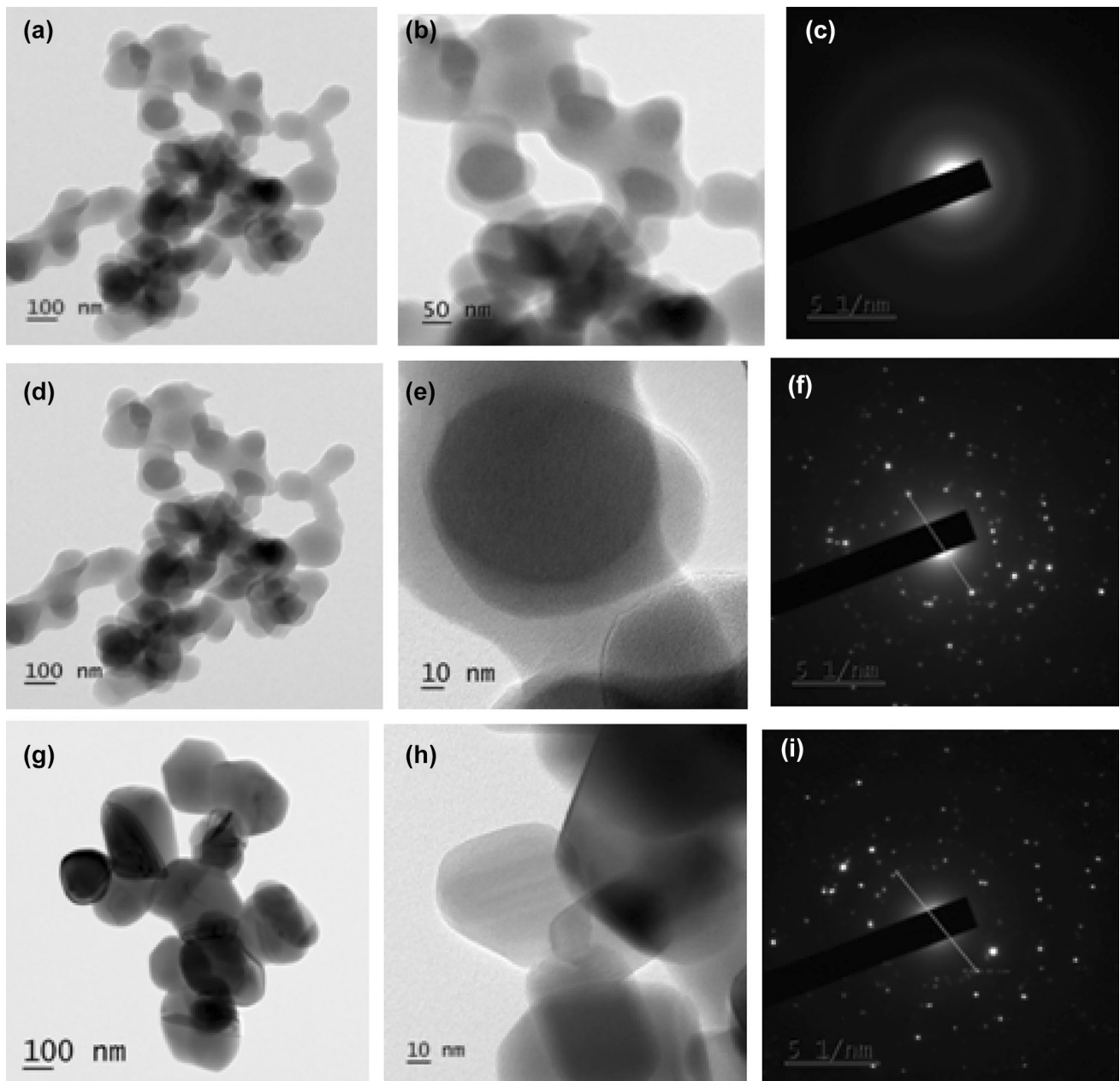
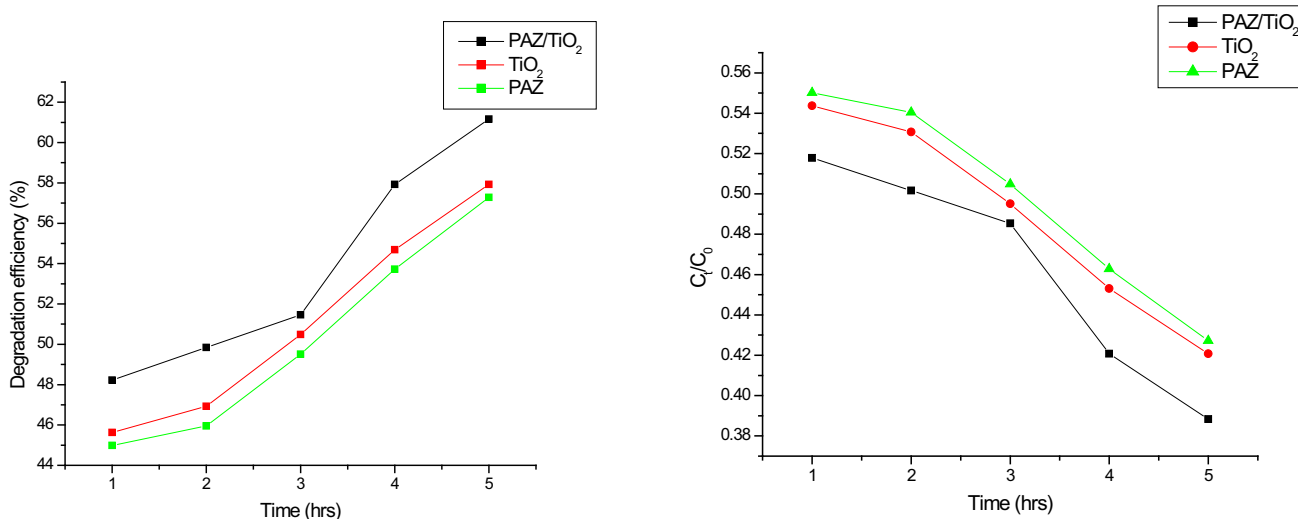


Fig. 7 TEM of PAZ (a, b, c), PAZ/TiO<sub>2</sub> nanocomposite (d, e, f) and TiO<sub>2</sub>(g, h, i)

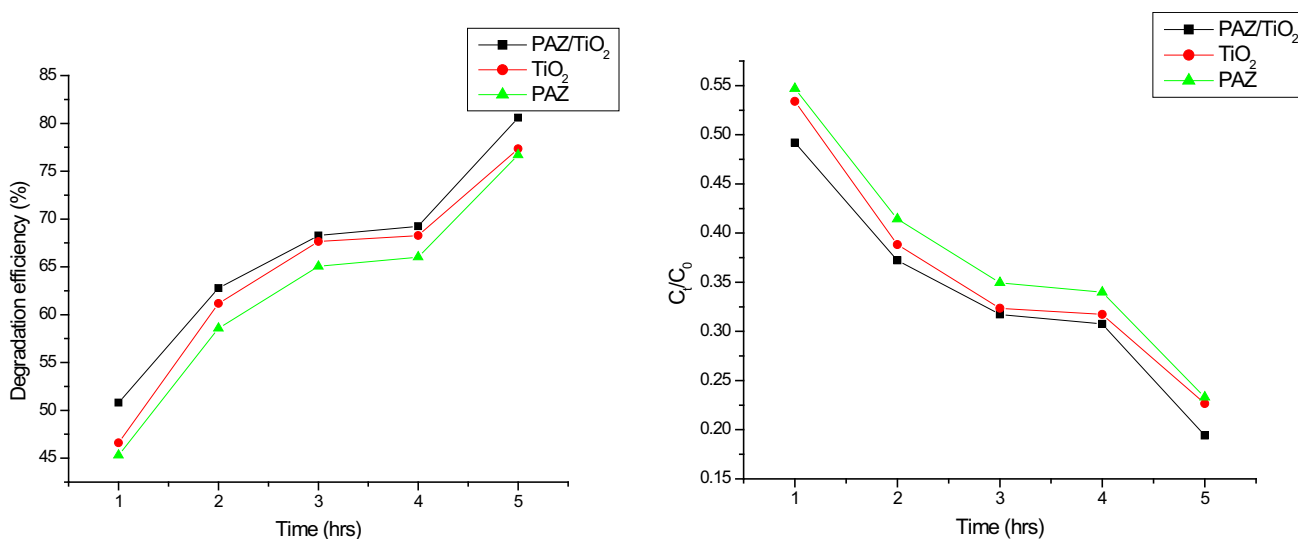
After the photo-catalytic process respective UV–Vis spectrum of PAZ and PAZ/TiO<sub>2</sub> were observed (Fig. 2b, c). The appearance of absorption band in the range 500–700 nm PAZ/TiO<sub>2</sub> (PNT) nanocomposites is due to the colour absorption of methylene blue (PNTMB) Malachite green (PNTMG) and Bismarck brown (PNTBB) present in water. But, absorption band in the range of 500–700 nm was not observed in PAZ (Fig. 2b) it shows the dye removal of methylene blue (PAZMB), malachite green (PAZMG) and Bismarck brown (PAZBB) is less when compared to PAZ/TiO<sub>2</sub> (PNT) nanocomposites (Fig. 2c)

### 3.1.3 X-ray diffraction

Figures 3, 4 and 5 shows the XRD pattern of PAZ, PAZ/TiO<sub>2</sub> and TiO<sub>2</sub>. Generally polymers exhibited a broad halo in the wide angle region (at about  $2\theta = 20^\circ$ ) indicating that the polymers were shapeless. The peak at  $2\theta = 20^\circ$  also symbolizes the distinctive interval linking the ring planes of aromatic units in neighboring chains or the convenient association with inter-chain distance. Further, the sharp peak centered at  $2\theta = 25^\circ$  might be consigned to the spreading from PAZ chains at inter planar interval distance



**Fig. 8** The result of degradation efficiency and kinetics of MB solution at normal sunlight irradiation using 100 mg catalyst (PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> (PNT) and 50 ppm dye concentration (Color figure online)



**Fig. 9** The result of degradation efficiency and kinetics of MB solution at normal sunlight irradiation using 200 mg catalyst (PAZ, TiO<sub>2</sub> & PAZ/TiO<sub>2</sub> (PNT) and 50 ppm dye concentration (Color figure online)



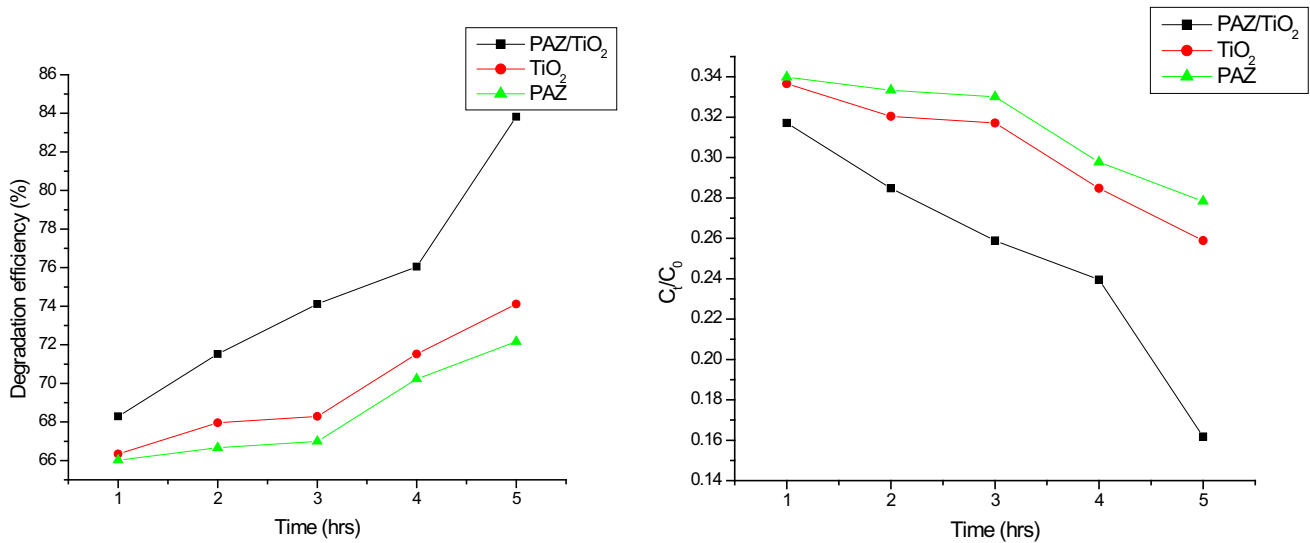
and specify the PAZ had also same degree of crystalline [40].

The XRD pattern of  $\text{TiO}_2$  shows diffraction peaks at  $2\theta$  values of 25.53, 38.34, 48.38, 54.61, 55.64, 63.21, 69.21, 69.14, 75.42 corresponding to the (101), (004), (200), (105), (211), (204), (116) and (215) which could be attributed to the anatase phase in the  $\text{TiO}_2$  (JCPDS-87-0598) [15]. In Figs. 4 and 5 the major diffraction peaks of PAZ/ $\text{TiO}_2$  composites are parallel to those of clean  $\text{TiO}_2$  particles. This concludes that the PAZ placed on the exterior of  $\text{TiO}_2$  particles and the crystalline structure of  $\text{TiO}_2$  was not influenced by the alteration of poly(azomethine) PAZ. The addition of PAZ species did not change the crystalline phases of  $\text{TiO}_2$ . However the intensity of the

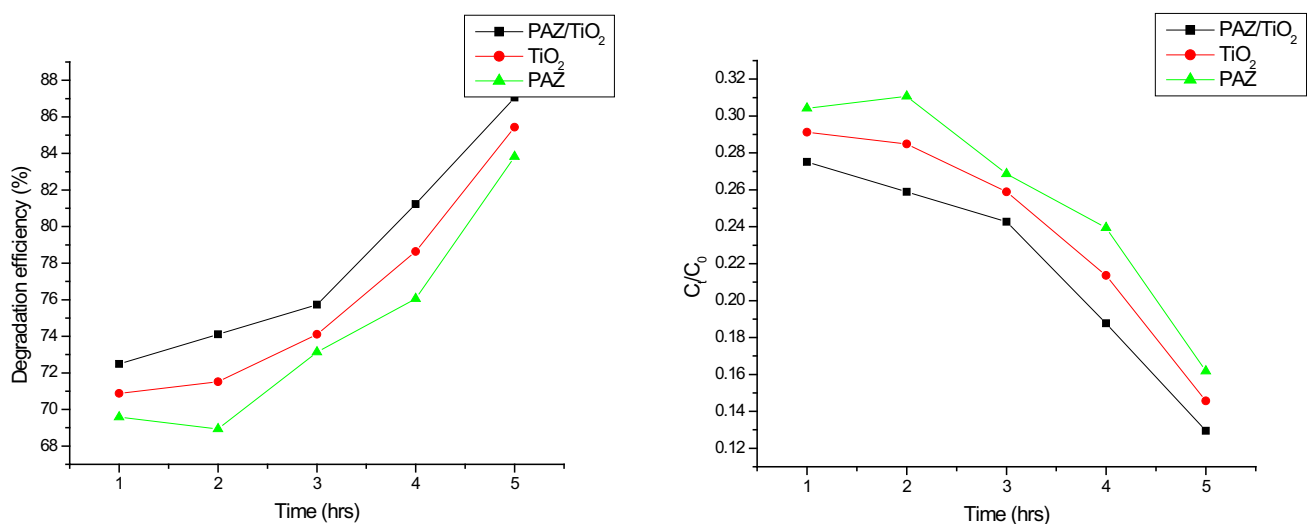
peaks of  $\text{TiO}_2$  is lower in the case of PAZ/ $\text{TiO}_2$  nanocomposite than that of nano  $\text{TiO}_2$  suggesting that the  $\text{TiO}_2$  particles are uniformly embedded in the polymer matrix of PAZ/ $\text{TiO}_2$ . Therefore, the XRD patterns of composites propose a flourishing merging of nano-  $\text{TiO}_2$  in PAZ composites [23].

### 3.1.4 Morphological studies

The structural modification of  $\text{TiO}_2$ , poly(azomethine)PAZ and PAZ/ $\text{TiO}_2$  nanocomposites were exemplified by TEM method and the outcomes are exhibited in Fig. 7. As shown in the Fig. 7d, e the nature of the TEM images revealed that all nanoparticles are spherical in shape with uniform



**Fig. 10** The result of degradation efficiency and kinetics of MB solution at normal sunlight irradiation using 300 mg catalyst (PAZ,  $\text{TiO}_2$  & PAZ/ $\text{TiO}_2$  (PNT) and 50 ppm dye concentration (Color figure online)



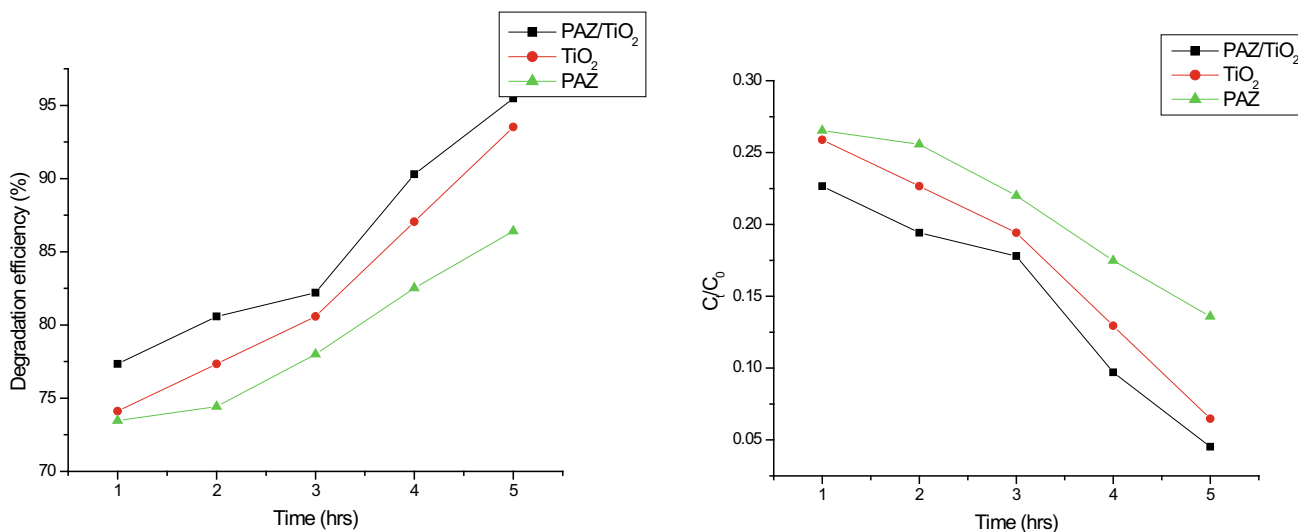
**Fig. 11** The result of degradation efficiency and kinetics of MB solution at normal sunlight irradiation using 400 mg catalyst (PAZ,  $\text{TiO}_2$  and PAZ/ $\text{TiO}_2$  (PNT) and 50 ppm dye concentration (Color figure online)

structure. The morphology of the composites is related to that of precise TiO<sub>2</sub> (Fig. 7g, h). However the constituent part in the composites tends to aggregate and lump tightly than precise TiO<sub>2</sub>. This might be owing to the PAZ (Fig. 7a, b) chains performing as folder in the composite, which hold together or lump the composite particle together. A same outcome was found in another research article [40]. Moreover, the TiO<sub>2</sub> particles (dark shaded nanoparticle) are determined that they get captured in polymer (light shaded) matrix. These outcomes expose that the TiO<sub>2</sub> particles are not merely mixed up or merged with the polymer, signifying that the TiO<sub>2</sub> particles are implanted in

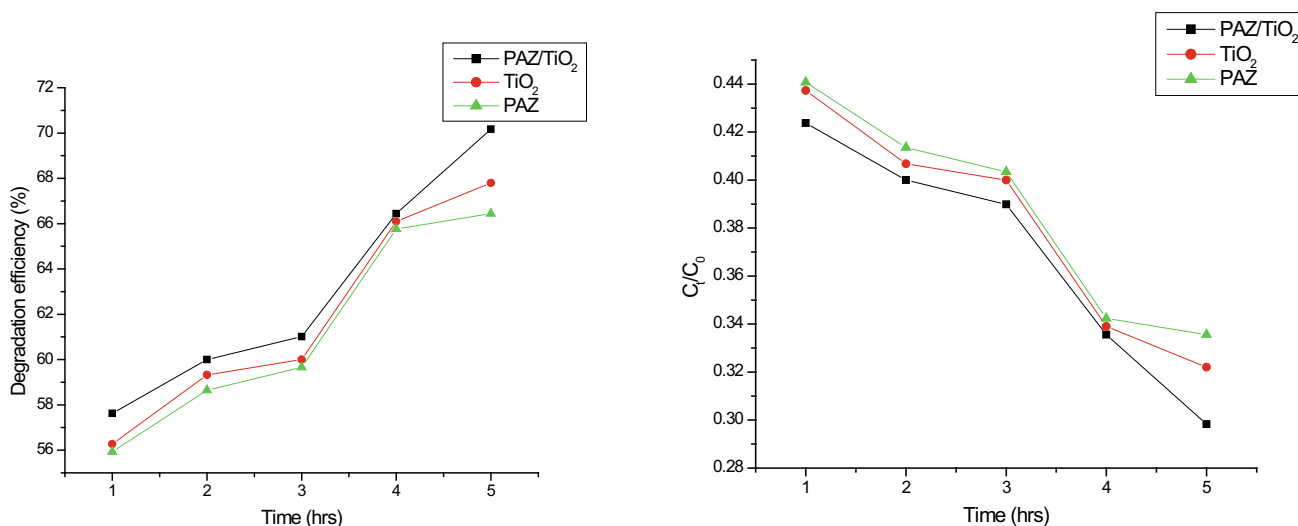
the polymer matrix, which is fairly in conformity with the outcomes of the XRD analysis [12].

The selected area electron diffraction (SAED) pattern of PAZ/TiO<sub>2</sub> and TiO<sub>2</sub> (Fig. 7c, f, i) also confirms the binding of composites material together [40].

The SEM image of TiO<sub>2</sub> nanoparticles (Fig. 6e, f) with a diameter of nearly 10 nm and a crystalline structure confirm the SEM images of PAZ/TiO<sub>2</sub> nanocomposite (Fig. 6c, d) with low and high exaggeration images correspondingly. Surface alteration of TiO<sub>2</sub> (Fig. 6e, f) particles by poly(azomethine) PAZ (Fig. 6a, b) chain show minor change in the morphology of PAZ/TiO<sub>2</sub> nanocomposite (Fig. 6c, d).



**Fig. 12** The result of degradation efficiency and kinetics of MB solution at normal sunlight irradiation using 500 mg catalyst (PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> (PNT) and 50 ppm dye concentration (Color figure online)



**Fig. 13** The result of degradation efficiency and kinetics of MG solution at normal sunlight irradiation using 100 mg catalyst (PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> (PNT) and 50 ppm dye concentration (Color figure online)

The EDAX spectrum (Fig. 6g) proves the presence of Ti and O in the catalyst PAZ/TiO<sub>2</sub> nanocomposite (Fig. 7).

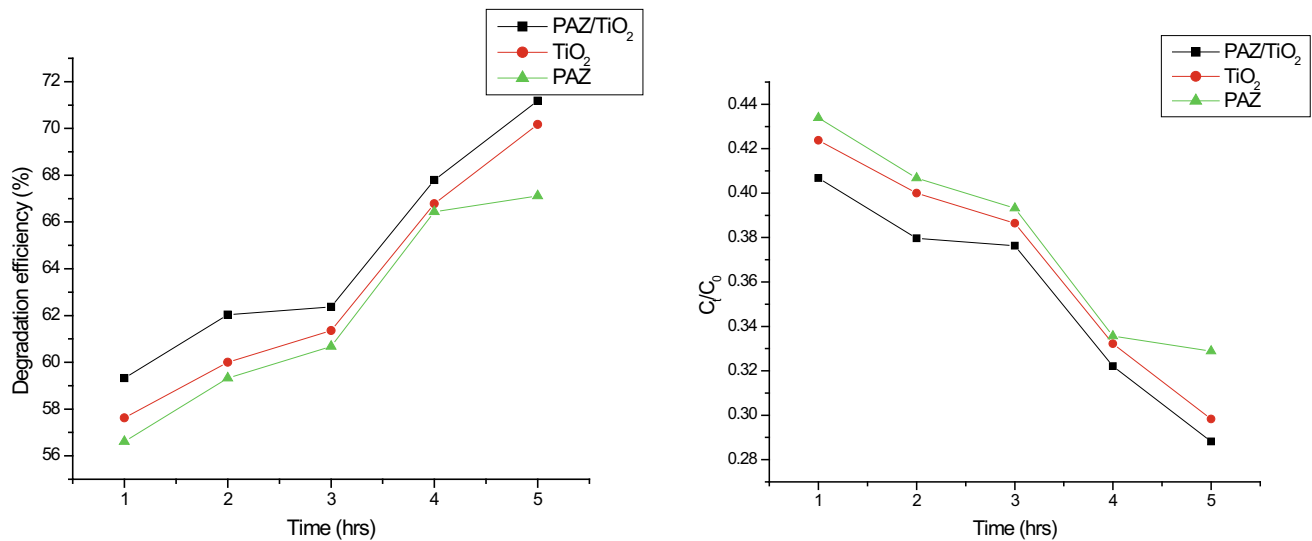
### 3.1.5 Photo-catalytic behavior of PAZ/TiO<sub>2</sub> nanocomposites under normal sunlight

The photo-catalytic deprivation of methylene blue, malachite green and bismarck brown using poly(azomethine) PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> (PNT) as a catalyst under sunlight irradiation were investigated. By varying the dosage of photo-catalyst such as 100,200,300,400 and 500 mg at

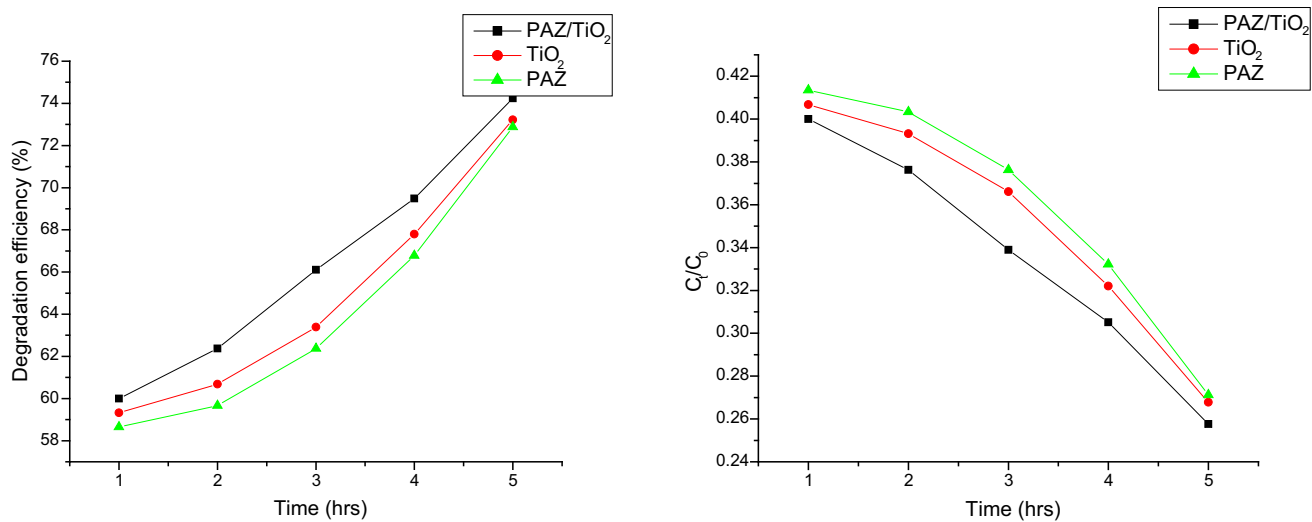
different time intervals (1–5 h) are shown in the Figs. 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21 and 22 at constant concentration (50 ppm) of dye.

The variation of decomposition vs irradiation time of methylene blue (Figs. 8, 9, 10, 11, 12), malachite green (Figs. 13, 14, 15, 16, 17) and Bismarck brown (Figs. 18, 19, 20, 21, 22) dye solutions are represented.

The maximum removal of Methylene blue (95%), Malachite green (93%) and Bismarck brown (95%) dye in water is achieved at 500 mg of PAZ/TiO<sub>2</sub> (PNT) at 50 ppm



**Fig. 14** The result of degradation efficiency and kinetics of MG solution at normal sunlight irradiation using 200 mg catalyst (PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> (PNT) and 50 ppm dye concentration (Color figure online)



**Fig. 15** The result of degradation efficiency and kinetics of MG solution at normal sunlight irradiation using 300 mg catalyst (PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> (PNT) and 50 ppm dye concentration (Color figure online)

of dye concentration under ordinary sunlight radiation in the duration of 5 h are shown in Table 1.

The rate constants of photo-catalytic deprivation of methylene blue (MB), malachite green (MG) and Bismarck brown (BB) dye was determined ( $C_t/C_0$  vs. time; Figs. 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22) using the following equation [11–14]

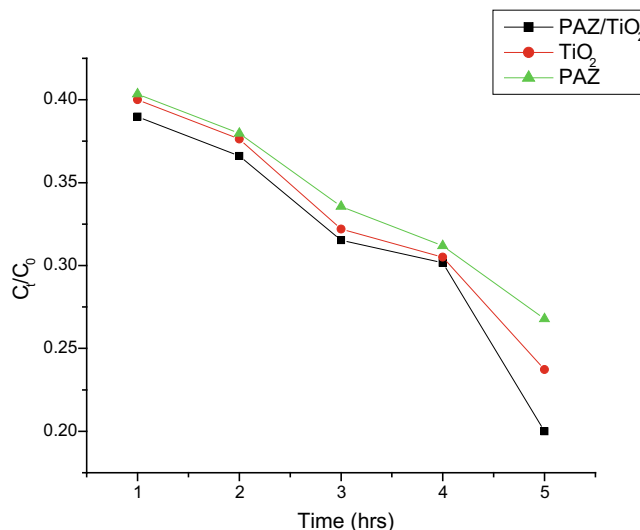
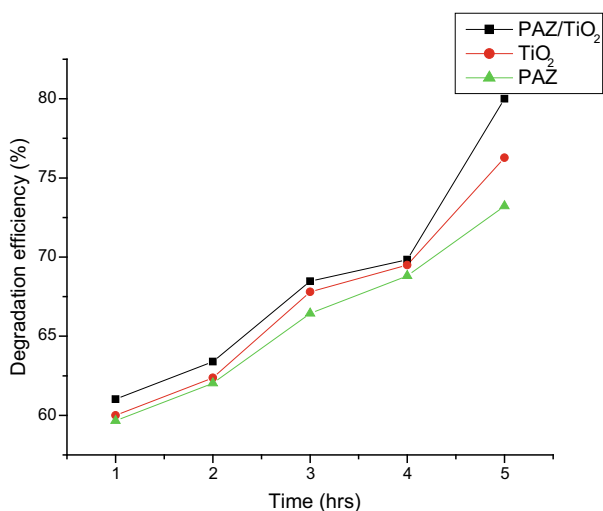
$$\ln \frac{C_0}{C} = K_{App}^t$$

$K_{App}$  ( $\text{min}^{-1}$ ) is the first order kinetics of rate constants. The rate constant for photo-catalytic deprivation composition of methylene blue (MB), malachite green (MG) and

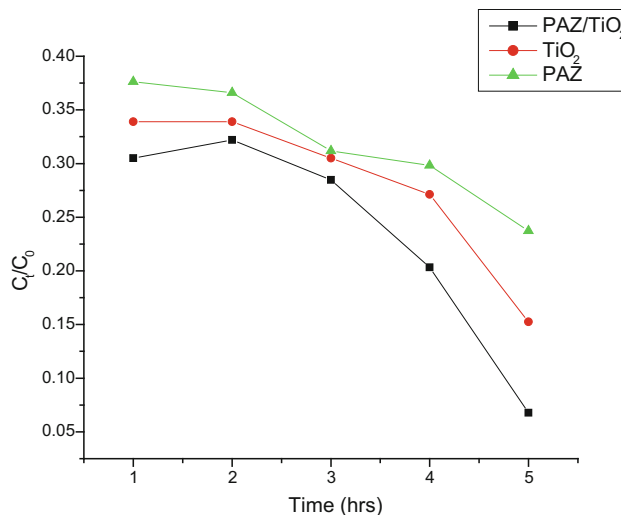
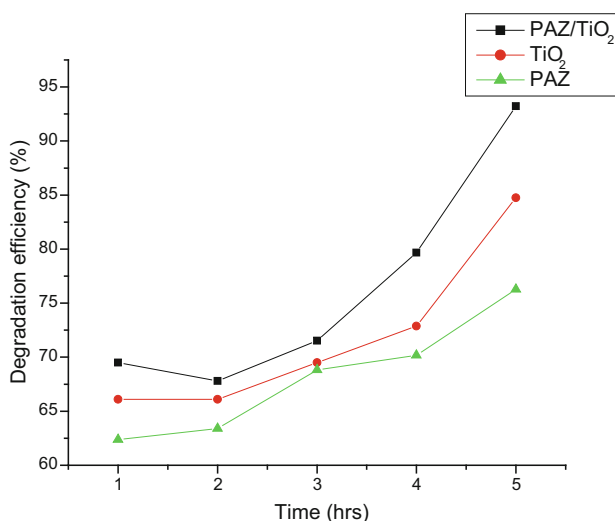
Bismarck brown (BB) dyes were regulated to be  $k = 0.2803 \text{ min}^{-1}$ ,  $k = 0.3232 \text{ min}^{-1}$  and  $k = 0.3762 \text{ min}^{-1}$  correspondingly.

### 3.2 Mechanism of photo-catalytic activity

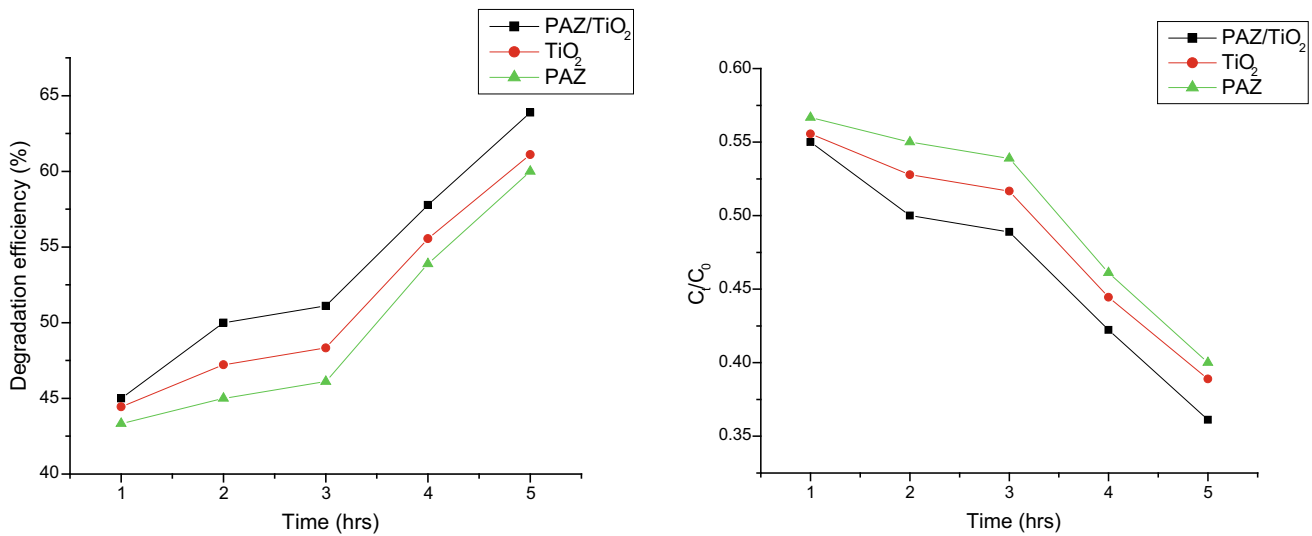
In a normal semiconductor photo-catalytic design, electrons of the photo catalyst are energized from the valence band lower energy level to the conduction band higher energy level by the absorbing illumination, an electron energy level conversion happens which directs to the creation of electron-hole pairs. At this point, 2 divergent passages are produced: the created electron hole ( $h^+$ )



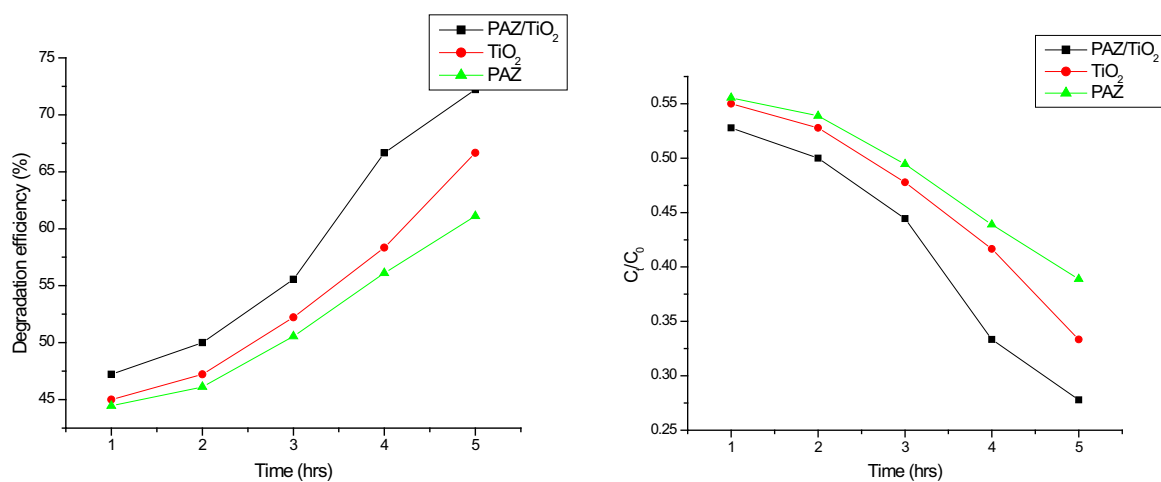
**Fig. 16** The result of degradation efficiency and kinetics of MG solution at normal sunlight irradiation using 400 mg catalyst (PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> (PNT) and 50 ppm dye concentration (Color figure online)



**Fig. 17** The result of degradation efficiency and kinetics of MG solution at normal sunlight irradiation using 500 mg catalyst (PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> (PNT) and 50 ppm dye concentration (Color figure online)



**Fig. 18** The result of degradation efficiency and kinetics of BB solution at normal sunlight irradiation using 100 mg catalyst (PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> (PNT) and 50 ppm dye concentration (Color figure online)

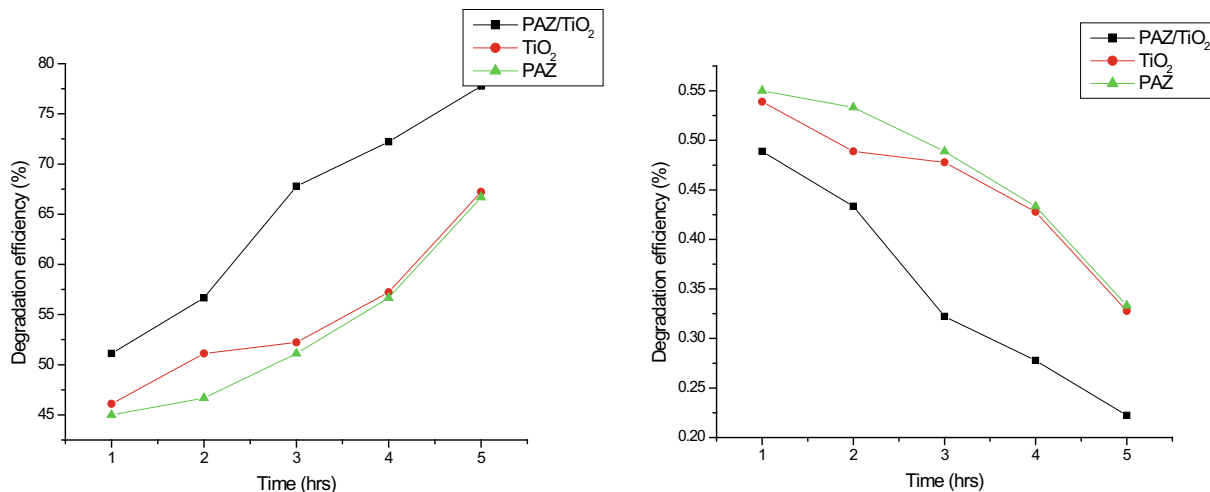


**Fig. 19** The result of degradation efficiency and kinetics of BB solution at normal sunlight irradiation using 200 mg catalyst (PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> (PNT) and 50 ppm dye concentration (Color figure online)

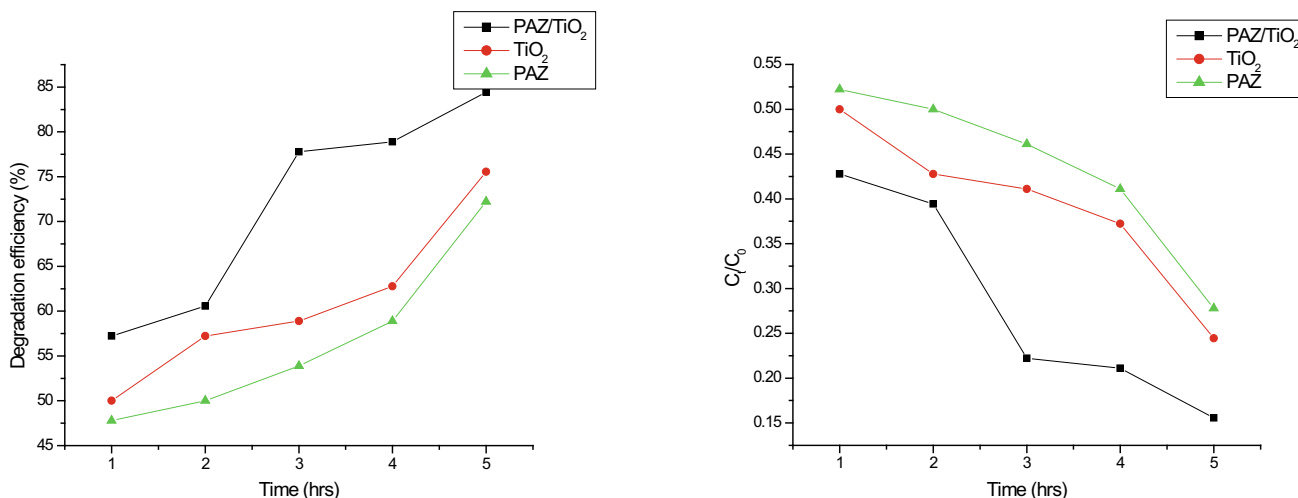
influencing with another particle is able to be utilized for oxidation reactions and the energized electrons ( $e^-$ ) are able to contribute for reduction reactions (Fig. 23).

A conjugated structure consists of linked  $\pi$ -orbitals by means of delocalized electrons are responsible for absorbing radiation from sunlight. Because of this, conjugated polymers are large organic molecules their structures are described as different single and multiple bonds with overlapping  $\pi$ -orbitals in their back bone which leads to

delocalization. Numerous resources such as PEDOT, polyaniline and polypyrrole have been examined as possible visible light active photo-catalysts. Recently, clean detectable luminous active conjugated polymer photo catalysts have been established, including polyazomethines and polyphenylenes were communicated for H<sub>2</sub> evolution, however the polymer materials were typically energetic in presence of UV–Visible radiation with moderate study [40].



**Fig. 20** The result of degradation efficiency and kinetics of BB solution at normal sunlight irradiation using 300 mg catalyst (PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> (PNT) and 50 ppm dye concentration (Color figure online)



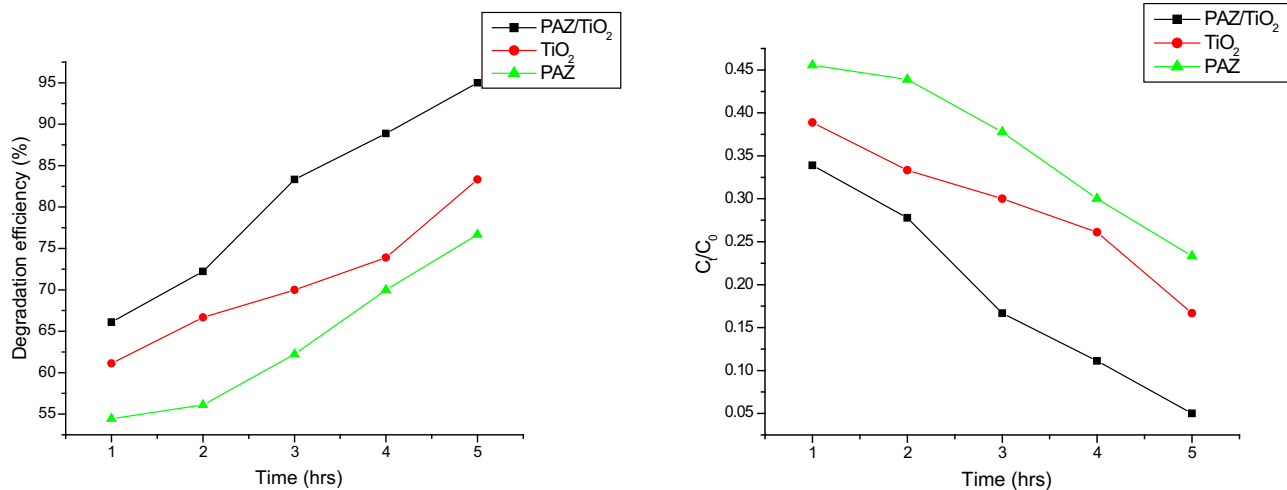
**Fig. 21** The result of degradation efficiency and kinetics of BB solution at normal sunlight irradiation using 400 mg catalyst (PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> (PNT) and 50 ppm dye concentration (Color figure online)

### 4 Conclusion

In this study, the photo-catalytic deprivation of the dye stuff from textile industries by PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> nanocomposites as catalyst was examined. The experiments were carried out using different catalyst by varying parameters such as the dosage variation of photo-catalyst and reaction time. The decolonization times was decreased by increasing the amount of PAZ/TiO<sub>2</sub> nanocomposites in the range of the test conducted in 100, 200, 300, 400 and 500 mg of methylene blue, malachite green and bismarck brown. The optimum dosage of catalyst was found to be

0.500 g. The optimum time of the tests in those dosage variation tests of PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> nanocomposites was 5 h.

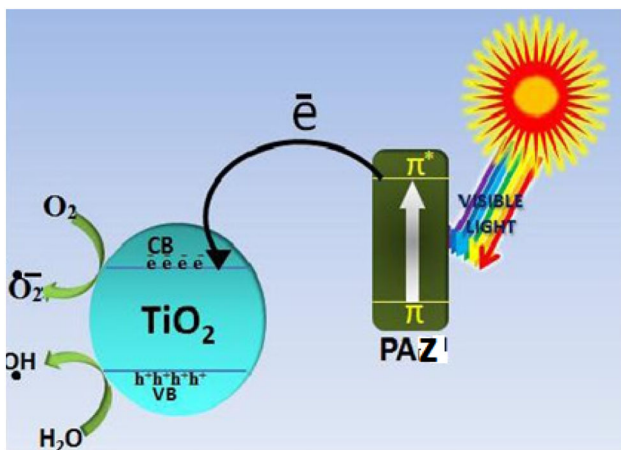
This practice may be employed effectively in the treatment of fabric dye waste matter which are hazardous to the environment, as this synthesized photo catalyst is economically feasible compared to other oxidative process. The present study demonstrates that the synthesized PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> nanocomposites could be used as efficient photocatalyst using the natural sunlight which contributes towards the remediation of pollution.



**Fig. 22** The result of degradation efficiency and kinetics of BB solution at normal sunlight irradiation using 500 mg catalyst (PAZ, TiO<sub>2</sub> and PAZ/TiO<sub>2</sub> (PNT) and 50 ppm dye concentration (Color figure online)

**Table 1** Maximum degradation efficiency at 500 mg catalyst dosage and 50 ppm dye concentration

Catalyst	Dye		
	Methylene blue	Malachite green	Bismarck brown
Degradation efficiency (%)			
PAZ	86	76	76
PAZ/TiO <sub>2</sub> (PNT)	95	93	95
TiO <sub>2</sub>	93	84	83



**Fig. 23** Diagrammatical representation of photo-catalytic reaction of PAZ/TiO<sub>2</sub> nanocomposite

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