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Photodegradation, thermodynamic and kinetic study of cationic and anionic dyes from effluents using polyazomethine/ZnO and polyazomethine/TiO_2 nanocomposites

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Water is a life-giving and energising substance. People all around the world are struggling due to the deficiency of fresh and hygienic potable water. Clean water is a significant resource for human civilization on Earth and one of the most crucial requirements for all living species to survive. Contamination of water due to synthetic dye is one of the most serious threats to human health. The photocatalystspoly(azomethine), ZnO, TiO_2, poly(azomethine)/TiO_2 and poly(azomethine)/ZnO were synthesized and used to remove cationic and anionic dyes from contaminated water.The band gap of photocatalysts, reaction kinetics, isotherm studies and thermodynamic studies were assessed and the photocatalytic studies revealed that polyazomethine/ZnO and polyazomethine/TiO_2 nanocomposites had significantly higher photocatalytic activity and are more efficient at removing dyes from effluents than PAZ, ZnO, and TiO_2 in natural sunlight.

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1. Introduction

Textile industries are the biggest producer of effluents causing problem with major impact on the quality of available water resources. According to the World Bank, textile treatment and dyeing contributes between 17 and 20 percent of overall industrial water pollution [1-2].Owing to the complex nature of the synthetic dyes, it is hard to remove. Colour of these dyes is a pollutant in wastewater which should be cleared and then it is released into water bodies or in landfills. This huge entry of unprocessed organic chemicals into the water bodies not only disturbs aesthetic concerns, significantly it stimulates eutrophication and it gives undesirable effects to environment health. Synthetic dyes are believed to be chemically and photolytically stable ; therefore, once they have been released into the environment, they will present for an extended time due to their persistent properties in the natural environment. Few synthetic dyes are created from petroleum by-products, thus they may contain chemical structures that are harmful to humans. Over time, prolonged exposure to chromium-based synthetic dyes can affect the central nervous system, kidneys, and other organs [3]. The adoption of acidic and basic dyes to lend colour to completed products is common in major industries, resulting in the discharge of hazardous sewages at the end of the dyeing and finishing processes.

Over the last decade, researchers have developed an advanced oxidation process (AOP) for wastewater treatment that has more advantages than other conventional approaches. This process are commonly termed as “Adjacent well-ordered temperature and pressure method sare taking part in the creation of sufficient quantity of hydroxyl radicals for the wastewater treatment practices”. The process takes place in presence of reactive species which includes hydroxyl radicals used for the destruction of toxic organic pollutants. These hydroxyl radicals, on the other hand, are exceedingly sensitive and unstable. Therefore constant creation of these vastly sensitive hydroxyl radicals is essential for the photochemical process to complete. These hydroxyl radicals

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are, chemical oxidant, non-selective, extremely sensitive to organic pollutants [4]. When plotted with 2.8 V oxidation potential against NHE, the hydroxyl radical is the second hardest radical after fluorine (included in table 1).

These reactive species have an ability to oxidize and mineralize all organic molecules into simple inorganic ions with the evolution of CO_2. The pathway of the AOP process is as follows, the first step is the formation of hydroxyl radical from the release of hydrogen from the organic molecule. With the addition of ambient oxygen, the process proceeds to produce hydrogen peroxide radicals (Eqn. 2).

Table 1. List of Oxidation Potential of oxidants.

Species	Oxidation Potential (V) vs NHE
Fluorine	3.03
Atomic oxygen	2.42
Ozone	2.07
Hydrogen Peroxide	1.78
Perhydroxyl radical	1.70
Permanganate	1.68
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Hypoiodous acid	1.45
Chlorine	1.36
Bromine	1.09
Iodine	0.54

The oxidative degradation heat reaction, which produces carbon dioxide, water, and inorganic salt, is initiated by these intermediates. An electron transfer to the hydroxyl radical (Eqn. 3) with subsequent proton transfer can be distinguished from (Eqn. 1).

$$HO^{\bullet} + RH \rightarrow H_2O + R^{\bullet} \quad (1)$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \rightarrow \text{Products} \quad (2)$$

$$HO^{\bullet} + RX\rangle \rightarrow RX^{\bullet} \rightarrow HO^{-} \quad (3)$$

Some of the advantages of AOPs, over other conventional processes used for the removal of toxic pollutants are

- In any temperature and pressure condition, the photocatalytic technique can be applied.
- No expensive chemical are required for effective oxidation to take place since atmospheric oxygen, itself act as an effective oxidant.
- The oxidant is very reactive and helps to fully mineralize organic contaminants into inorganic salts.
- No secondary sludge is produced after the treatment process hence no secondary disposal is required.
- The catalyst is inexpensive, harmless, chemical inactive, consistent and extremely reactive.

- Even in low concentrations of organic pollution, the approach is proven to be effective.

Photocatalytic degradation of hazardous organic compounds in wastewater discharged from the textile industry using semiconductor materials has gained a lot of interest because it is the most competitive technology [5]. When the light of suitable wavelength falls on the photocatalyst, electron-hole pairs are generated which actively takes part in the photocatalytic reaction. For effective photocatalysis reactions, recombination of electron-hole pairs must be avoided. For complete photodegradation of dyes semiconductor nanostructured metal oxides are widely used as catalyst for the removal of organic pollutants from water [6].

An inorganic semiconductor material must meet the following conditions to function as a photocatalyst: the catalyst material must be photoactive (able to absorb sunlight or UV light); it must be photostable; it must be chemically and biologically inactive; and it must be inexpensive and harmless in nature. Semiconductor metal oxides such as ZnO, TiO_2, MnO_2 and ZrO_2were widely used as metal oxide and hybrid materials as a photocatalyst and for other potential applications. ZnO has been employed in a variety of applications [7-8].

Because of their high absorption coefficients in the visible portion of the spectrum, high flexibility of charge carriers, and remarkable stability, conjugated polymers like Polythiophene, Polypyrroles Polyaniline, Poly(p-phenylenevinylene), Poly(3,4-ethylenedioxythiophene)/ZnO and their derivatives are commonly used as antenna layers in photovoltaic devices for photoconversion of solar energy [9-13] .Semiconductor nanostructured material when incorporated with polymers was utilised as a photocatalyst for the deprivation of organic dyes in aqueous medium.

Chelating polymers with an azomethine group (–CH=N–) in the main chain have received much interest recently because of their importance. Polyazomethines, polyamides, polyimides and polyurethanes with Schiff base chelators in the polymer backbone are of considerable interest due to valuable properties [14]. Such polymers are thermally stable, has good mechanical strength, semiconducting behaviour, electronic, optoelectronic, nonlinear optics and electrochemical properties [15] .Compared with crosslinked or chemically modified polymers, polyazomethines, simply a conducting polymer is attainable with outstanding properties under mild reaction environment in maximum quantity and high yield [16].

Nowadays heterogeneous polymeric nanocomposites plays more attention among scientists due to its wide charge carrier properties [17-18]. Polymers exhibit higher stability and flexibility are generally chosen as good host materials. Nanocomposites due to its charge transfer potential act as a efficient photocatalyst in their nanostructured interface and microstructural properties [19-22].

The scope of the present research is to synthesize a polymeric nanocomposite which can act as an effective photocatalyst for the degradation of organic toxic dye effluents in aqueous medium.

2. Materials and methods

All chemicals used in the synthesis were obtained and utilised as such from Sigma Aldrich.

2.1. Synthesis of Polyazomethine (PAZ)

The polymer synthesis is based on the reference work carried out by B Joy vasanthi in 2013 [23]. 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 (Fig 1).

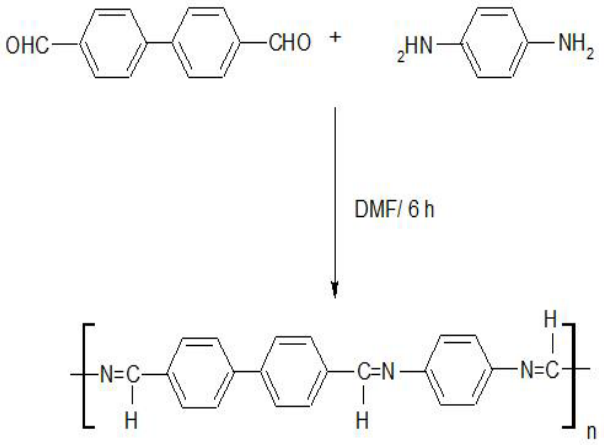


Fig .1. Synthesis of polyazomethine (PAZ).

2.2. Synthesis ofZnO nanoparticle

Under vigorous stirring, an aqueous solution of KOH (0.4 M) is gradually discharged into a zinc 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 degrees Celsius.

2.3. Synthesis of TiO_2 nanoparticle

In an ice bath, $TiCl_4$ was gradually added to clean water with stirring until it was entirely dissolved simultaneously add NH_4OH (30%) solution was added. After 1 hour, the white TiO_2 nanoparticle was filtered. Obtained TiO_2 nanoparticles were washed in clean water and dehydrated for 3 h under vacuum at 100°C.

2.4. Synthesis of ZnO/TiO_2 incorporated polyazomethine polymeric nanocomposite

500 mg polyazomethine is dissolved in 100 mL DMF solution and sonicated for 48 hours under constant stirring. Under sonication, ZnO or TiO_2 nanoparticles are liberated in acetone and simultaneously added to the polymeric solution. The precipitated ZnO incorporated polyazomethine (PNZ) or TiO_2 incorporated polyazomethine (PNT) composite material is filtered, washed repeatedly in acetone and dried out [24].FT-IR spectroscopy, UV-Vis spectroscopy, scanning electron microscopy, transmission electron microscopy and Energy Dispersive Analysis X-ray powder X-ray diffraction were used to verify the synthesised polyazomethines (PNT & PNZ) [25-31].

2.5. Photocatalytic experiment

In the presence of a visible light source, batch mode photocatalytic investigations were carried out for the effective degradation of MB, BB, MG, MO, and ARS synthetic dyes utilising synthesised photocatalysts (PAZ, PNT, PNZ, TiO_2, and ZnO). Prior to irradiation, the suspension (50 mL dye solution + 20 mg photocatalyst) is stirred for 30 minutes with a magnetic stirrer (300 rpm) until adsorption-desorption equilibrium is achieved. After reaching adsorption-desorption equilibrium, the suspension was held in visible light irradiation to ensure efficient photodegradation. The dye solution was pipetted out once at regular intervals and the absorbance was measured using a UV-Visible spectrophotometer. Fig 2 depicts the setup for the photodegradation experiment.

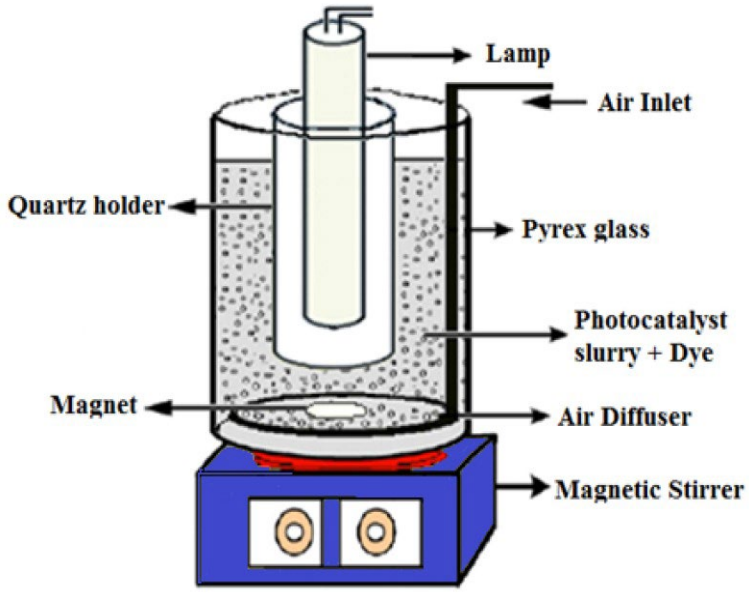


Fig. 2. Setup for a photodegradation experiment with synthesised material.

The photo deprivation efficacy R (%) was calculated using the equation (4):

$$R(\%)=\frac{C_0 - C_t}{C_0} \tag{4}$$

where C_0 symbolizes the dye concentration before irradiation and C_t indicates the dye concentration after a set period of time.

2.6. Effect of contact time

The effect of contact duration was investigated using 100 mL of MB, BB, MG, MO, and ARS dye solutions in optimal initial dye concentrations, pH, and photocatalyst dosage (PAZ, PNT, PNZ, TiO_2 and ZnO). The contact time was varied from 0 to 5 h with definite regular time intervals.

2.7. Isotherm studies for decolourization of dyes

When a saturated monolayer of solute molecules attaches to the sorbent's surface, there is no sorbate molecule movement on the surface plane, and the sorption energy remains constant, the hypothesis of maximum sorption is established. The non-linear Langmuir isotherm model (5) is commonly written like this:

$$q_e = \frac{q_{max} b_L C_e}{1 + b_L C_e} \tag{5}$$

where q_e is the amount of metal adsorbed (mg/g) and C_e is the equilibrium concentration of the solution (mg/L). The adsorption capacity and energy are shown by the Langmuir constants q_m and b_L.

The Freundlich isotherm is a well-known relationship that symbolises non-ideal, reversible adsorption that is not really confined to monolayer formation. This realistic model can be utilised to simulate multilayer adsorption with non-uniform adsorption heat and affinity distributions across a heterogeneous surface. The non-linear formula for Freundlich isotherm (6) is as follows:

$$q_e = K_f C_e^{1/n} \tag{6}$$

where K_F symbolizes the Freundlich isotherm constant (mg/g), n exemplifies the adsorption intensity, C_e signifies the adsorbate equilibrium concentration (mg/L), and q_e is the amount of metal adsorbed by the adsorbent at equilibrium b [32-33].

The Temkin isotherm model implies that all molecules adsorption heat reduces linearly as the adsorbent surface is covered more, and that adsorption is characterised by a uniform distribution of binding energies up to a maximum binding energy. Equation (7) can be used to describe the Temkin isotherm.

$$q_e = B_T \ln(AC_e) \tag{7}$$

BT = RT/b, where b symbolizes the adsorption heat (kJ/mol), R is the gas constant (8.314 J/mol.K), T the temperature (K), and A is the adsorption equilibrium binding constant proportional to the maximal binding energy (L/mg) [34-35].

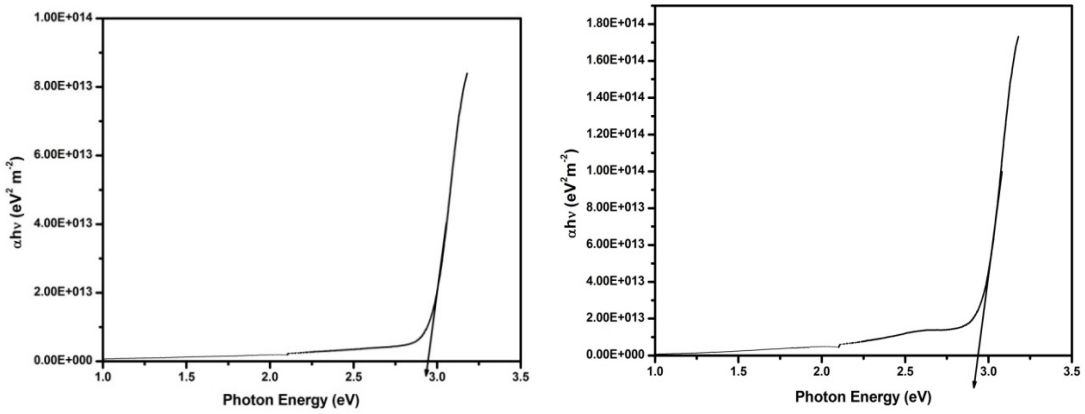
2.8. Kinetic Studies for photodegradation of dyes

The pathway of the photodegradation of MB, BB, MG, MO and ARS dyes using synthesized PNT, PNZ, TiO_2 and ZnO photocatalyst was calculated using photodegradation kinetics. All dye photodegradation experiments with associated photocatalysts were performed out under predicted optimal conditions. Using the Langmuir-Hinshelwood kinetic model, the rate of photodegradation reaction with each photocatalyst independently with corresponding dye solutions was measured [36]. The mathematical equation of Langmuir-Hinshelwood kinetic model is (8):

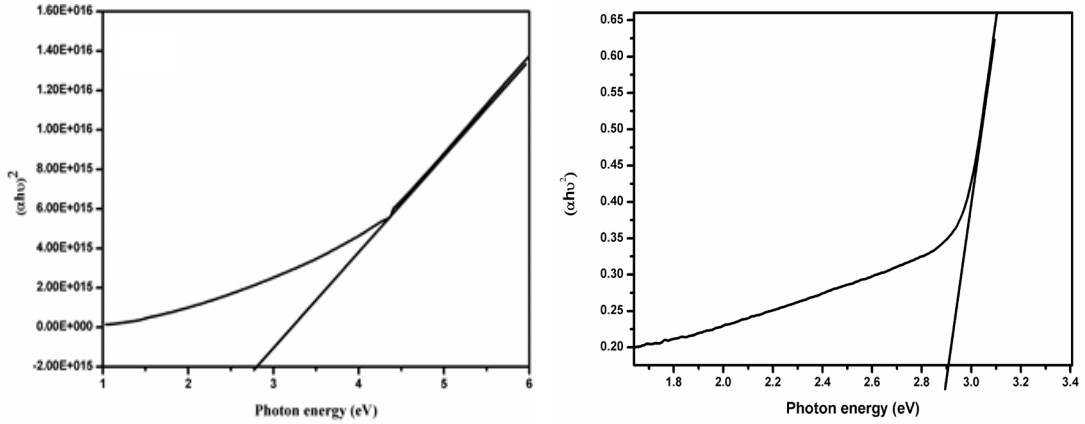
$$-\ln\frac{C}{C_o} = kt \tag{8}$$

3. Result and discussion

The characteristics absorption of ZnO/TiO_2 and the PAZ absorption band in the UV light region may be assigned to the band from 200 nm to 400 nm, and the characteristics absorption of PAZ in the visible region can be assigned to the band from 400 nm to 700 nm. PNT and PNZ composites have the same absorption spectrum as PAZ composites, with the same distinctive bands [37]. Furthermore, as compared to PAZ polymer, the absorption intensity of PNT and PNZ nanocomposite was higher. However unlike ZnO/TiO_2 photocatalyst, which can only be photoactivated by harmful UV light, the synthesised PNT and PNZ nanocomposite can be photoactivated by visible light or available natural solar irradiation, which has no negative impact on human health. The wavelength at the absorption band edge was determined for the PAZ, TiO_2, ZnO, PNT, and PNZ using UV absorption spectra. The photon energy (eV) was plotted against the hv (eV^2 m^{-2}). A straight line was drawn to the X-axis from the outer edge of the curve obtained in the plot. PAZ, TiO_2, ZnO, PNT, and PNZ band gap energies were determined (Table 2) and displayed in fig 3 to 7.



Figs. 3 and 4. Polyazomethine (PAZ)(left) & TiO_2 (right) nanoparticles shows Bandgap energy curve.



Figs. 5 and 6. ZnO (left) &PNT (right) nanocomposite shows Bandgap energy curve.

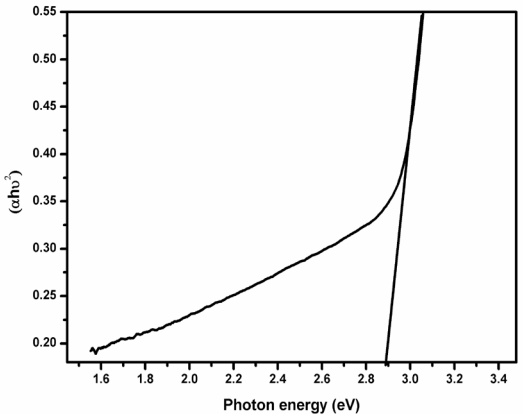


Fig. 7. Shows Bandgap energy curve of PNZ composite material.

Table 2. Wavelength and Band gap values of photocatalysts.

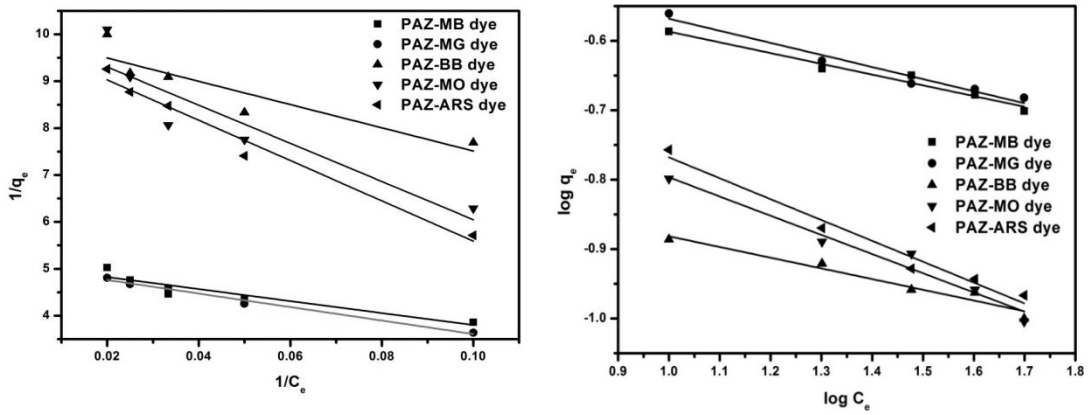
S.No.	Synthesized materials	Wavelength (nm)	Band gap (eV)
1.	PAZ (Azomethine polymer)	530	2.93
2.	TiO_2 Nanoparticles	380	2.96
3.	ZnO Nanoparticles	483	2.94
4.	PNT (Polymeric nanocomposite)	665	2.89
5.	PNZ (Polymeric nanocomposite)	760	2.9

The calculated band gap energy of PNT and PNZ was 2.89 eV and 2.9 eV respectively (table 2), which was inferior than the reckoned band gap energy of TiO_2 and ZnO nanoparticles of 2.96 eV and 2.94 eV. Therefore, addition of PAZ polymer onto TiO_2 and ZnO matrix resulted in the red shift in the wavelength of the adsorption to visible region. This shift makes it possible to carry out the photodegradation of dye molecules in the presence of sunlight proving to as visibly active photocatalyst. It was revealed that photocatalyst absorption is influenced by electron-hole pair mobility, which determines the possibility of electrons and holes attaining reaction sites on the photocatalyst surface [38].

3.1. Isotherms studies

Since the azomethine polymer (PAZ) has only unshared pair of electrons which effectively takes part in the decolourization of the organic dyes before reaching equilibrium. There was an assumption that this effect was caused by the adsorption of dye molecules over the surface of the polymeric resin PAZ. Hence to deduce the effect of adsorption in the decolourization process, the isotherm studies, thermodynamic studies and kinetic studies were done only for the PAZ resin and the outcomes are discussed. The effect of Langmuir, Freundlich and Temkin isotherms for the decolourization of MB, MG BB, MO and ARS dyes using PAZ is presented in Fig 8 to 10.

Since isotherm studies were carried out to find only the influence of unshared pair of electrons for the decolourization of organic dyes before reaching equilibrium. Hence a linear plot of $1/C_e$vs $1/q_e$ was plotted for Langmuir isotherm, log $C_e$vs log q_e plotted for Freundlich isotherm and log $C_e$vsq_e plotted for Temkin isotherm. The R^2 value was calculated from the plot. Since, if the R^2 value (correlation coefficient) is nearer to 1, it plays a significant role in the decolourization process [39].Table 3 shows the isotherm parameters for dye decolorization utilising PAZ polymer.



Figs. 8 and 9. Shows the decolorizing of dyes utilising PAZ polymer Langmuir isotherms (left) and Freundlich isotherms (right).

From the results, it was evident that Freundlich isotherm R^2 values were close to 1, suggesting that the unshared pair of electrons present in the polymer binds with the dye molecule causing significant effect in the decolourization of organic dyes.

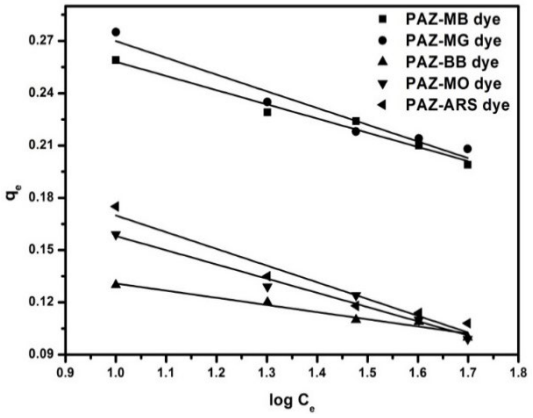


Fig. 10. Decolorizing of dyes utilising PAZ polymer Temkin isotherms.

Freundlich isotherm refers to the multilayer deposition of dye molecules on a material's surface. This denotes that physical attraction and chemical attraction took place between the dye molecules and the PAZ polymer causing effective decolourization of dyes. Hence electrostatic force of attraction and weak vanderwaals force of attraction plays a significant role, causing the dye decolourization [35].

Table 3. Shows the isotherm parameters for dye decolorizing utilising PAZ polymer.

Dyes	*PAZ polymer*		
	Langmuir	*Freundlich*	*Temkin*
MB	*0.8526*	*0.9730*	*0.9677*
MG	*0.9864*	*0.9770*	*0.9410*
BB	*0.7816*	*0.9807*	*0.9560*
MO	*0.7919*	*0.9953*	*0.9677*
ARS	*0.9697*	*0.9972*	*0.9410*

3.2. Thermodynamic studies

The thermodynamic studies were performed for the removal of organic dyes using PAZ polymer to check whether the reaction if possible and nature of the reaction rate.

Table 4. Thermodynamic parameter for PAZ-based dye decolorization.

Dyes (10 mg/L)	ΔH^o *(kJ/mol)*	ΔS^o *(J/mol/K)*	ΔG^o *(kJ/mol)*						
			303 K	*308 K*	*313 K*	*318 K*	*323K*	*328K*	*333K*
MB	*-50.55*	*-153.02*	*-1.950*	*-1.502*	*-1.139*	*-0.818*	*-0.518*	*-0.218*	*-0.0755*
MG	*-46.53*	*-142.11*	*-1.552*	*-1.183*	*-0.861*	*-0.563*	*-0.274*	*-0.023*	*0.032*
BB	*-43.76*	*-135.93*	*-1.120*	*-0.807*	*-0.516*	*-0.233*	*0.513*	*0.354*	*0.670*
MO	*-43.19*	*-135.96*	*-0.852*	*-0.562*	*-0.282*	*-0.002*	*0.287*	*0.602*	*0.941*
ARS	*-43.22*	*-136.41*	*-0.797*	*-0.510*	*-0.232*	*0.048*	*0.338*	*0.657*	*1.002*

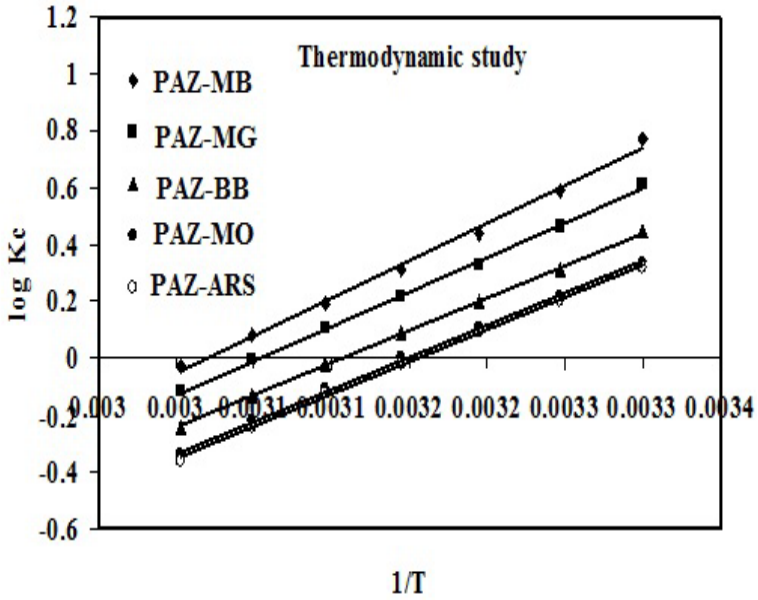


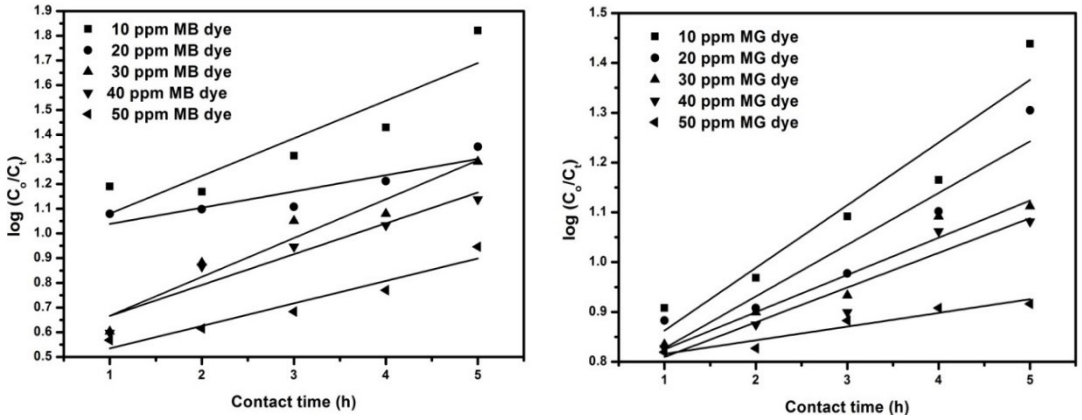
Fig. 11. Thermodynamic curve of dye decolorizing with PAZ polymer.

The temperature 1/T vs log (Kc) was plotted (Fig 11). The reckoning of the thermodynamic parameter of PAZ are shown in Table 4.

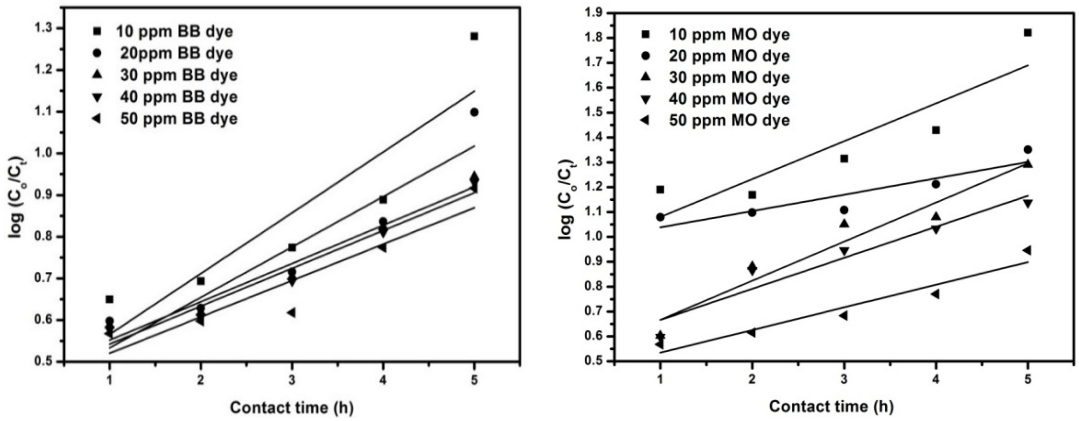
The results showed that as the temperature rises, the decolorization process becomes less favourable The negative values of ΔG, ΔH and ΔS indicates that the decolourization of dyes using PAZ polymer is more preferred, reaction is exothermic and spontaneous [1].

3.3. Kinetics for the decolourization of dyes

In order to find the nature and type of interaction existing between the dye molecule and the PAZ polymer, kinetic studies were carried out. The sort of interaction between the dye molecule and the PAZ responsible for the decolorization of organic pollutants was determined using a pseudo first-order and second kinetic model and intraparticle diffusion model. The kinetic models were plotted for the decolourization of organic dyes with PAZ polymer and showed in Fig 12 to 22 respectively.



Figs. 12 and 13. Show Pseudo-first-order kinetic model for PAZ polymer decolorizing of MB (left) and MG (right) dyes.



Figs. 14 and 15. Show Pseudo First-order kinetic model for PAZ polymer decolorizing of BB (left) & MO (right) dyes.

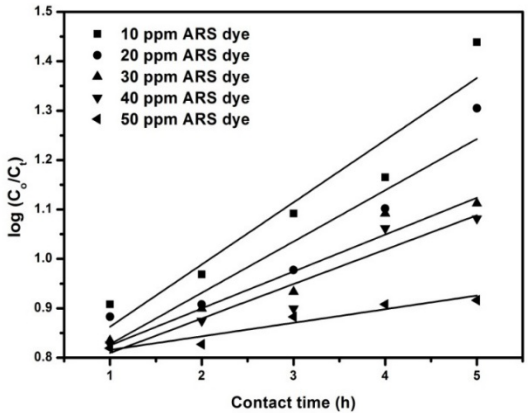
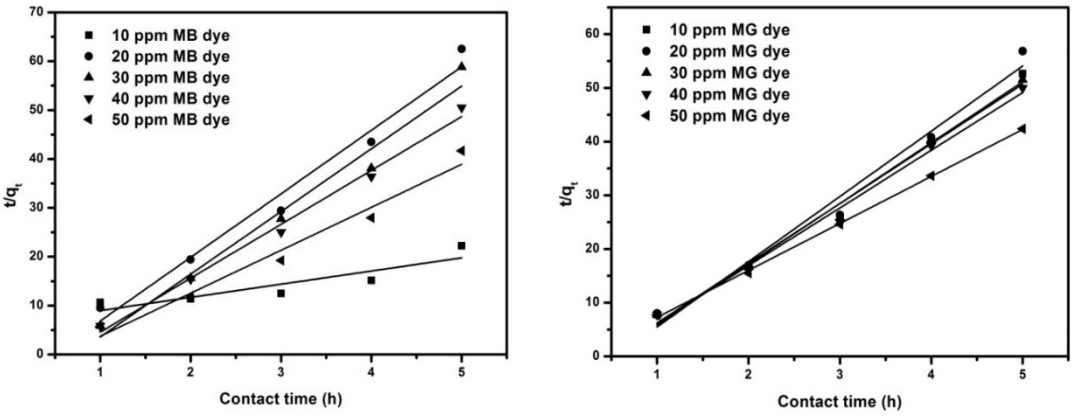
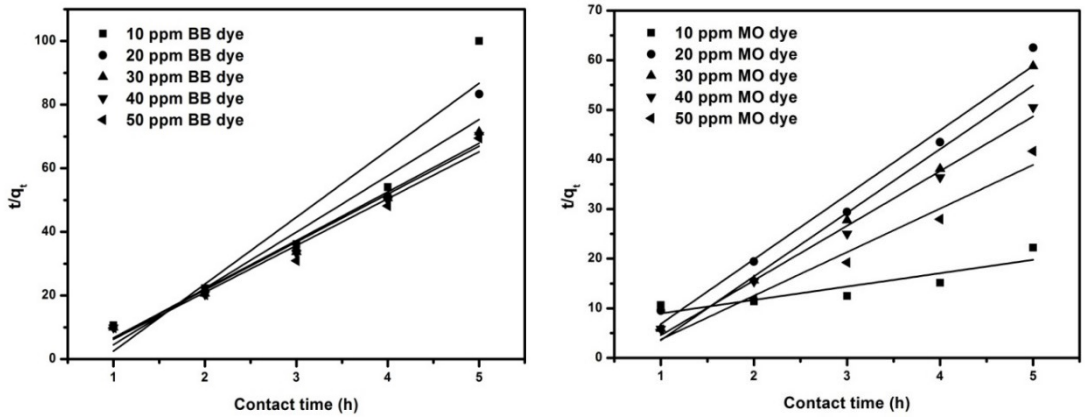


Fig. 16. Shows Pseudo First-order kinetic model for PAZ polymer decolorizingof ARS dye.



Figs. 17 and 18. Show Pseudo Second-order kinetic model for PAZ polymer decolorizing of MB (left) & MG (right) dyes.



Figs. 19 and 20. Show Pseudo Second-order kinetic model for PAZ polymer decolorizing of BB (left) & MO (right) dyes.

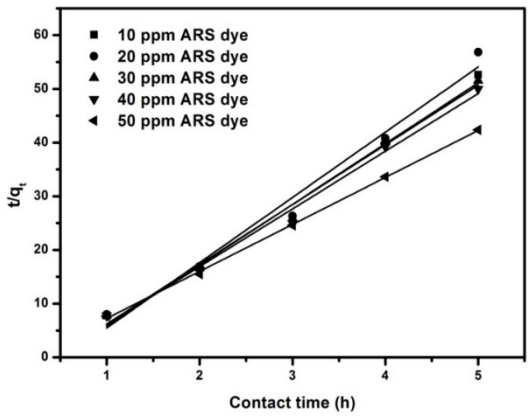


Fig. 21. Shows Pseudo Second-order kinetic model of PAZ polymer decolorizing for ARS dyes.

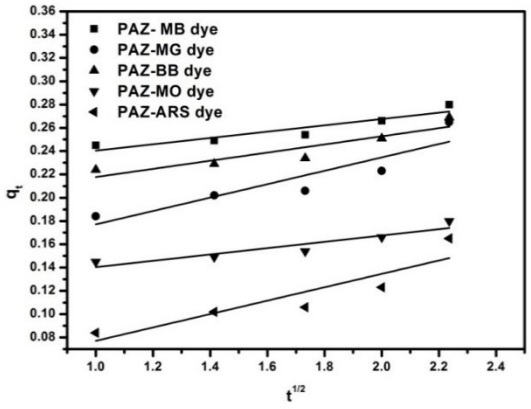


Fig. 22. Show. Intra-particle diffusion model for PAZ polymer decolorizing of organic dyes.

The R^2 values for the decolourization of organic dyes using PAZ polymer was calculated and presented in Table 5.

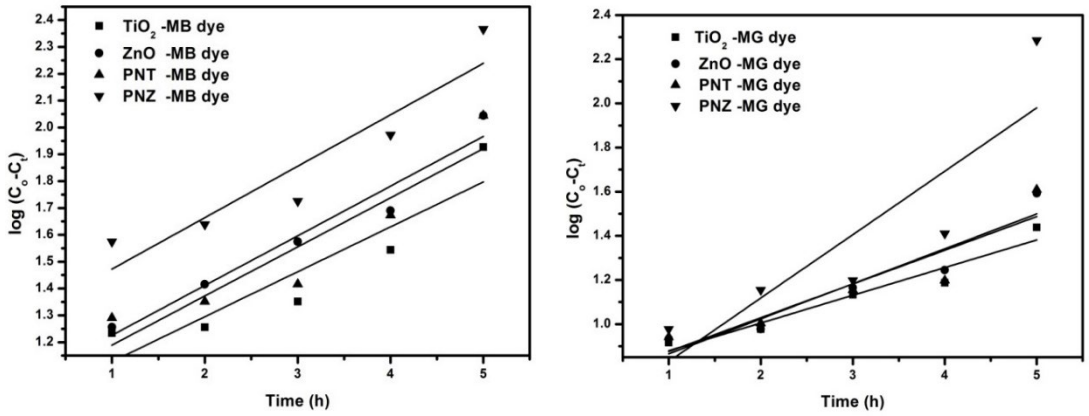
Table 5.Kinetic parameter for decolorizing of organic dyes using PAZ polymer.

PAZ	*Dyes*	*10 ppm*	*20 ppm*	*30 ppm*	*40 ppm*	*50 ppm*
Pseudo first order Kinetic model	*MB*	*0.7632*	*0.7990*	*0.9203*	*0.9009*	*0.9105*
	MG	*0.8928*	*0.8645*	*0.9162*	*0.8822*	*0.9011*
	BB	*0.7680*	*0.8494*	*0.9459*	*0.9461*	*0.8385*
	MO	*0.7632*	*0.7790*	*0.9203*	*0.9046*	*0.9103*
	ARS	*0.8928*	*0.8645*	*0.9162*	*0.8822*	*0.9011*
Pseudo second order Kinetic model	*MB*	*0.7585*	*0.9706*	*0.9688*	*0.9897*	*0.9650*
	MG	*0.9869*	*0.9991*	*0.9839*	*0.9755*	*0.9880*
	BB	*0.8769*	*0.9307*	*0.9764*	*0.9769*	*0.9644*
	MO	*0.7585*	*0.9706*	*0.9688*	*0.9897*	*0.9650*
	ARS	*0.9839*	*0.9755*	*0.9881*	*0.9869*	*0.9991*
Intraparticle Diffusion model	*MB*	-	-	-	-	*0.8250*
	MG	-	-	-	-	*0.7734*
	BB	-	-	-	-	*0.8004*
	MO	-	-	-	-	*0.8250*
	ARS	-	-	-	-	*0.7734*

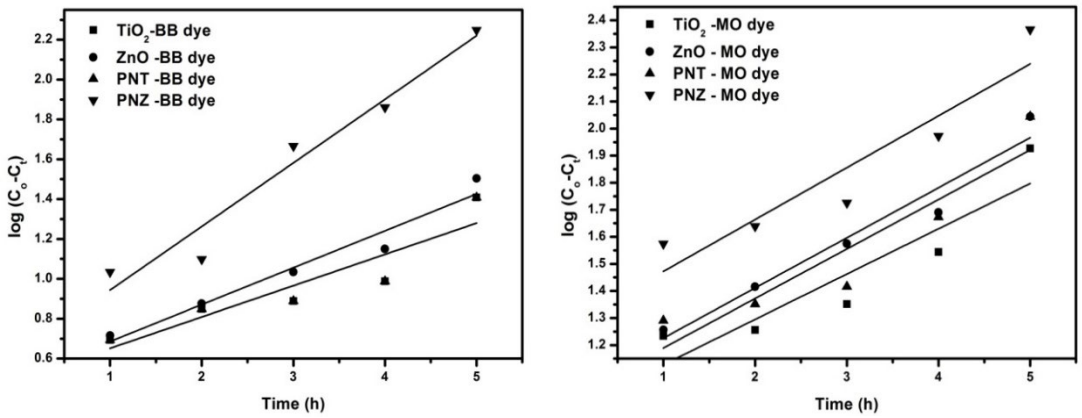
From the R^2values obtained from the kinetics calculations, the R^2 value of organic dyes (50 ppm) using synthesized materials for decolourization, showed that the reaction is feasible and spontaneous. The unshared pair of electrons and the functional groups present in the polymer effectively makes a bond with the dye molecules resulting in the decolourization of dyes. Decolorizing occurs when the chromophore in a dye molecule disintegrate. This effective decolourization causes considerable change while using PAZ polymer as photocatalyst before reaching equilibrium.

3.4. Langmuir–Hinshelwood (LH)

Organic dyes such as methylene blue (MB), malachite green (MG), Bismarck brown (BB), Methyl orange (MO), and Alizarin blue S (ARS) were used to test the photocatalytic activity, feasibility, and pathway of photodegradation of the synthesised semiconductor nanomaterials and polymeric nanocomposite such as TiO_2, ZnO, PNT, and PNZ. Fig 23 to 27 depict the outcomes of L-H kinetic model.



Figs. 23 and 24. Show an L-H kinetic model for photodegradation of MB (left) and MG (right) dyes using a sample photocatalyst.



Figs. 25 and 26. Show an L-H kinetic model for the photodegradation of BB (left) & MO (right) dye using sample photocatalyst.

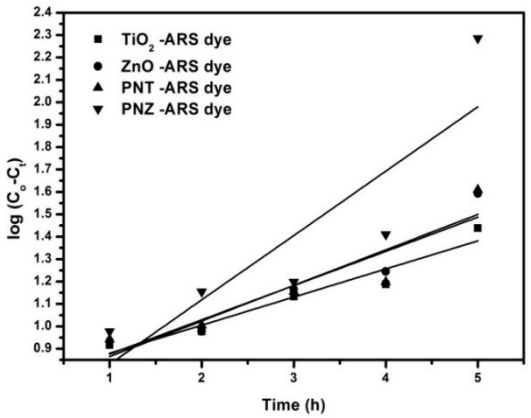


Fig. 27. Depicts An L-H kinetic model is used to model the photodegradation of ARS dye using a sample photocatalyst.

The kinetic parameters derived from the L-H kinetic models are tabulated and shown in Table 6.

Table 6 The photodegradation of organic dyes was studied using synthetic materials to establish kinetic parameters.

Materials	*Parameters*	*MB*	*MG*	*BB*	*MO*	*ARS*
TiO_2	*R^2*	*0.8906*	*0.9195*	*0.7981*	*0.8006*	*0.9195*
	$K(min^{-1})$	*0.6243*	*0.6155*	*0.6299*	*0.6321*	*0.6132*
	K_{ads}	*8.5135*	*8.7922*	*8.7910*	*8.3156*	*8.4132*
ZnO	*R^2*	*0.9543*	*0.8789*	*0.9413*	*0.9416*	*0.8780*
	$K(min^{-1})$	*0.6133*	*0.5990*	*0.6146*	*0.6129*	*0.5936*
	K_{ads}	*8.9321*	*8.9260*	*8.9530*	*8.4592*	*8.5269*
PNT	*R^2*	*0.9888*	*0.9808*	*0.9781*	*0.9278*	*0.9096*
	$K (min^{-1})$	*0.6012*	*0.5413*	*0.6010*	*0.6003*	*0.5432*
	K_{ads}	*8.9990*	*9.1532*	*9.1520*	*8.5510*	*8.9362*
PNZ	*R^2*	*0.9215*	*0.9006*	*0.9439*	*0.9411*	*0.9001*
	$K(min^{-1})$	*0.5411*	*0.5008*	*0.5430*	*0.5432*	*0.4999*
	K_{ads}	*9.0120*	*9.4523*	*9.4153*	*9.0165*	*9.1052*

The statistics showed that when the K_{ads} value increased, the K value decreased. This exhibits that the photodegradation reaction is more agreeable and effective at 30 °C. When the R_2 values of the synthesized materials were compared, it was clear that PNT and PNZ had a superior R_2 value than other synthetic materials used to photodegrade organic dyes in existence of visible light. The order of photocatalyst's reactivity was observed to be PNT≥PNZ>ZnO>TiO_2>PAZ. Increased reactivity and a decrease in the bandgap of the material resulted from the amalgamation of semiconductor nanomaterial into the mesoporous polymer, making the polymeric nanocomposite PNT and PNZ effective photocatalysts. As the bandgap shrinks, electrons can freely migrate from the valence to conduction bands, resulting in effective deterioration.

In existence of visible light radiation, the recombination of electron-hole pairs occurs at a slower rate, resulting in the eventual destruction of organic dyes.

4. Conclusion

The photocatalytic activity of the newly synthesized catalysts PNT and PNZ was exceptional, with maximum dye degradation. With the use of isotherm analyses and kinetic models, the main explanation for the dyes' maximal decolorization before achieving equilibrium in the presence of PAZ polymeric material was revealed. Both the studies project the fact that the lone pair of unshared electrons present in the polymer backbone adsorbs the dye molecule causing a considerate change in colour. The thermodynamic studies carried out for PAZ polymeric resin also confirmed that such chemical interaction is feasible, spontaneous and release energy from the system to the surroundings (exothermic) as proceeds.

The photodegradation kinetics were carried out for TiO_2, ZnO, PNT and PNZ catalyst materials and explained the nature of the mechanism involved in the photodegradation of organic pollutant dyes. All the studies finally concludes with the similar outcome that PNT and PNZ catalyst materials exhibit outstanding performance in the photodegradation of dyes with increased electron mobility due to the addition of dopants Ti atom and Zn atom into the polymeric matrix.

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