Effective Adsorption and Photocatalytic Degradation of Toluidine Blue using Eco-Friendly Composite: A Comparative Study

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Abstract

Copper oxide nanoparticles were synthesized using powder of bamboo leaves and its composite was prepared with graphite powder. This composite was characterized using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive Spectroscopy (EDS). It was used for adsorption and degradation of Toluidine blue. The effect of operating parameter such as pH, contact time, amount of composite, concentration of dye and light intensity was observed to achieve optimum condition. Trapping experiments indicated that superoxide radical ($O_2^{\cdot-}$) is the active oxidizing species in photocatalytic degradation while electrostatic interactions and hydrogen bonding played a crucial role in the adsorption process.

It was observed that photocatalytic degradation achieved a higher degradation efficiency of 63.19% as compared to 42.19% adsorption. It was concluded that photocatalytic degradation was more effective than adsorption for removing toluidine blue.

Keywords: Photocatalysis, Adsorption Copper oxide, Toluidine blue, Bamboo leaves composite.

Introduction

The continuous and untreated discharge of textile dyes into the environment poses significant risks. These dyes persist in aquatic ecosystems, leading to harmful effects on aquatic flora and a decline in water quality. Due to various issues such as eutrophication, unpleasant odors, turbidity may arise. Additionally, the long-term hazards included carcinogenecity and mutagenicity[9]. Nanoparticles have been recently used in removing dyes from wastewater through adsorption or photocatalytic degradation. This includes the use of semiconductors, metal, metal oxides and magnetic nanoparticles[4,7].

Lanthanum-based nanocomposites $LaFeO_3$, $LaNiO_3$ and $LaCoO_3$, were synthesized in sol-gel method and used for photocatalytic degradation for methylene blue and toluidine blue (model pollutants) under visible light irradiation. It was observed that $LaCoO_3$ composite exhibited higher efficiency in degrading these dye as compared to others[6]. Green synthesis of multifunctional $MgO@AgO/Ag_2O$ nanocomposite was performed by using the leaves extract of Purslane and it was used for photocatalytic degradation of methylene blue and toluidine blue[13]. Iron oxide nanoparticles modified with tannic acid have also been reported to adsorb toluidine blue from an aqueous solution[2]. The catalytic oxidation of toluidine blue and methyl orange under UV light irradiation was also investigated using undoped as well as metal-doped titanium dioxide. It was reported that the degradation rate increases with longer wavelength (254nm) exposure and an increased amount of photocatalyst. The metal-doped titanium dioxide achieved a degradation of 98% at pH 11, while the undoped titanium dioxide exhibited negligible degradation in the absence of light[8].

Green-synthesized TiO_2 nanoparticles were prepared using leaf extracts of the as a usage and their performance in the photocatalytic degradation of toluidine blue was observed up to 99.59%[12]. The ZnO catalyst was synthesized using zinc nitrate and extract from the bark of *Terminalia arjuna*, in presence of microwave irradiation used for degradation of toluidine blue and safranin O in aqueous solution.

It was observed that 94% degradation of toluidine blue occurred in 190 min. while 87% safranin O degradation could be achieved in 310 min. respectively[3].A quaternary photocatalyst, $ZrCdPbO_4$ was synthesized using a co-precipitation method and was utilized for the degradation of toluidine blue, brilliant green and crystal violet[5].

The removal of safranin O and toluidine blue by clinoptilolite zeolite was evaluated in single and binary systems. It was indicated that the removal of toluidine blue was almost double as compared to safranin O[11]. The $Ag@Fe_3O_4$ nanocomposite was biosynthesized using the aqueous leaf extract of *Laurus nobilis* and used for the treatment of oily wastewater. It was reported that this nanocomposite exhibited degradation of 96.8% for Rose Bengal, 90.1% for methylene blue and 93.8% for toluidine blue[1]. The removal of toluidine blue was observed using a combination of kaolinite and halloysite in 1:1 layered clay mineral ratio. It was revealed that materials with high cation exchange capacity and large specific surface are most effective factors for removal of such cationic dyes from polluted water[10].

Material and Methods

Chemicals and Materials: The leaves of Bamboo were collected in June from the Pacific University Campus, Udaipur Rajasthan, India. Copper sulfate and graphite powder were purchased from Sigma-Aldrich and all other

chemicals were of analytical grades and used without further purification.

Synthesis of Composite: Dried leaves of bamboo were washed with distilled water. After drying with the help of sun light, a fine powder of this material was obtained by mechanical grinder, then this powder was passed through a 70 Mesh size. A graphite powder was added to this powder in a ratio of 1:2 (leaves: Graphite powder) and treated with 1% NaOH solution for 30 min by using a sonicator and then filtered using a vaccum filter.

0.1 M copper sulfate solution was added dropwise in the solid residual and it was stirred for 2h at 60°C. A brown precipitate was formed. Residual was placed in an oven for 12 h. at 50°C. The substance was dried in Muffle furnace and charcoal was prepared with dried material at 700°C for 8 h.

Structure of Toluidine blue: A field emission scanning electron microscope (FESEM-EDX) was used for surface morphology and the elemental analysis to determine crystalline structure of composite as shown in fig. 1.

X-Ray Diffraction (XRD): X-ray diffraction is a technique to assess crystalline structure. Anton Paar Model - Sax space was used in the scanning range from 5 to 80° with scan speed/duration time 10.00 °/min. The XRD pattern is presented in fig. 2. The Debye-Scherer's formula was used to determine crystal size:

$$D = k\,\lambda/\beta \cos\theta \qquad (1)$$

where D = Particle size, K = Scherer's constant (K = 0.94), λ = X-ray wavelength (1.54060) Å,) β = Full width at half maximum (FWHM) and θ is Bragg's angle. The crystalline size for composite was calculated to be 10.53 nm, which is in the nanoscale range.

Field Emission Scanning Electron Microscopy (FESEM): The composite was observed with the help of Hitachi, Japan (Model: Su8010 Series). The results are reported in fig. 3.

EDX (Energy dispersion X-Ray spectroscopy) The EDX of composite was obtained on the interaction between the X-ray excitation source and the sample. The results are presented in fig. 4.

Photocatalytic degradation and Adsorption: The results are presented in fig. 5 and table 1. 0.10gm of toluidine blue was dissolved in 100 mL of doubly distilled water to prepare a stock solution of the dye 1000ppm. Further, 2mL of this solution was taken out and made up to 100ml with water to prepare 20ppm of solution, then 0.12g composite was added and solution was exposed to 200 W tungsten lamp with Intensity of 60 mW cm^{-2}. The absorbance(A) of toluidine at 620nm was found to decrease with increasing time of exposure. A plot of 1 + log A vs time was found to be linear. The rate constant of the reaction was calculated with the equation k = 2.303 x slope.

The adsorption was also carried out in absence of light. A decrease in concentration of dye was observed by increasing time with (k) = 9.42 × 10^{-5} (s^{-1}). The results are presented in fig. 6 and table 2.

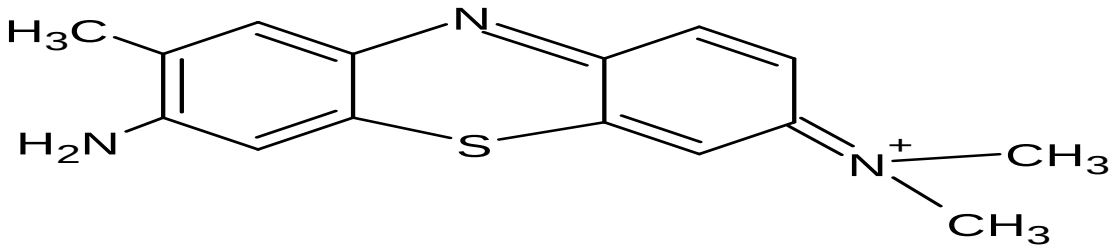

Fig. 1: Structure of Toluidine blue

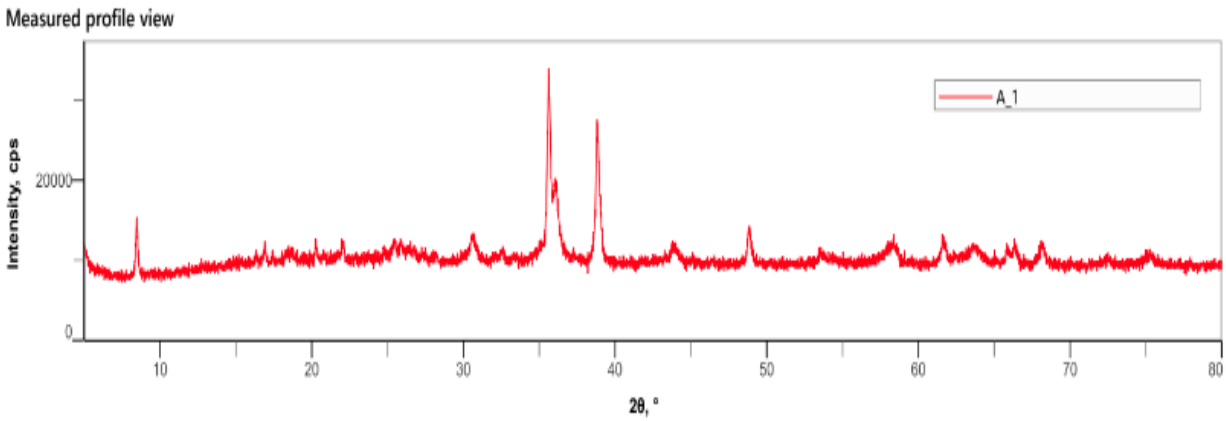

Fig. 2: XRD of Composite.

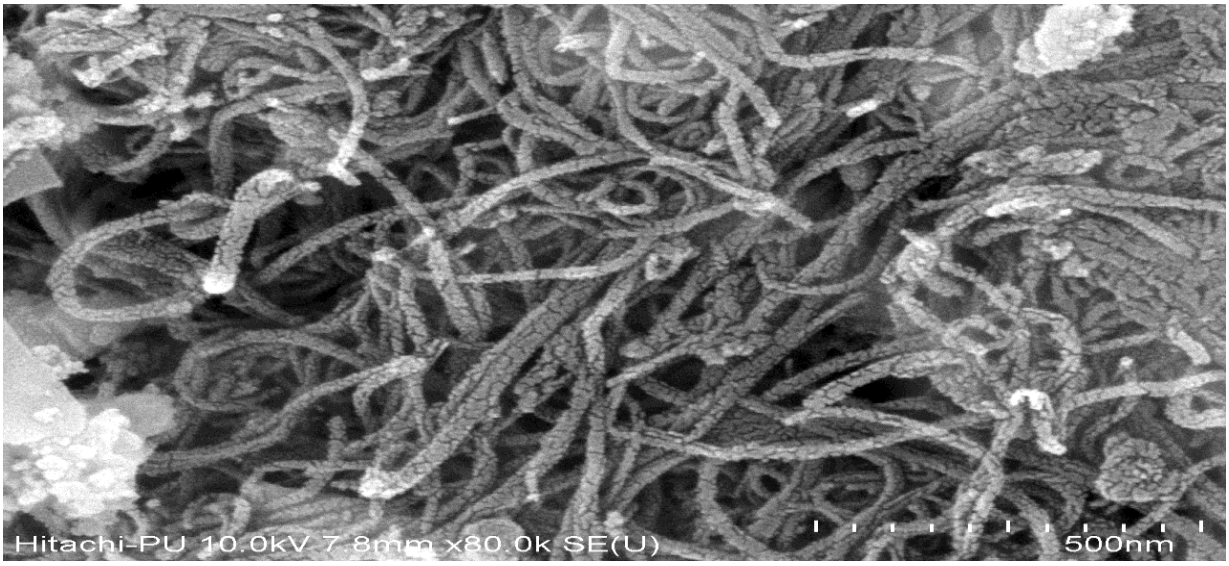

Fig. 3: FESEM of Composite.

Table 1
Typical run in photocatalytic degradation.

Time (Min)	Absorbance (A)	1+Log A
0	0.501	0.699
15	0.445	0.648
30	0.407	0.609
45	0.381	0.580
60	0.361	0.557
75	0.342	0.534
90	0.311	0.492
105	0.281	0.448
120	0.261	0.416
135	0.235	0.371
150	0.215	0.332
165	0.195	0.290
180	0.181	0.257

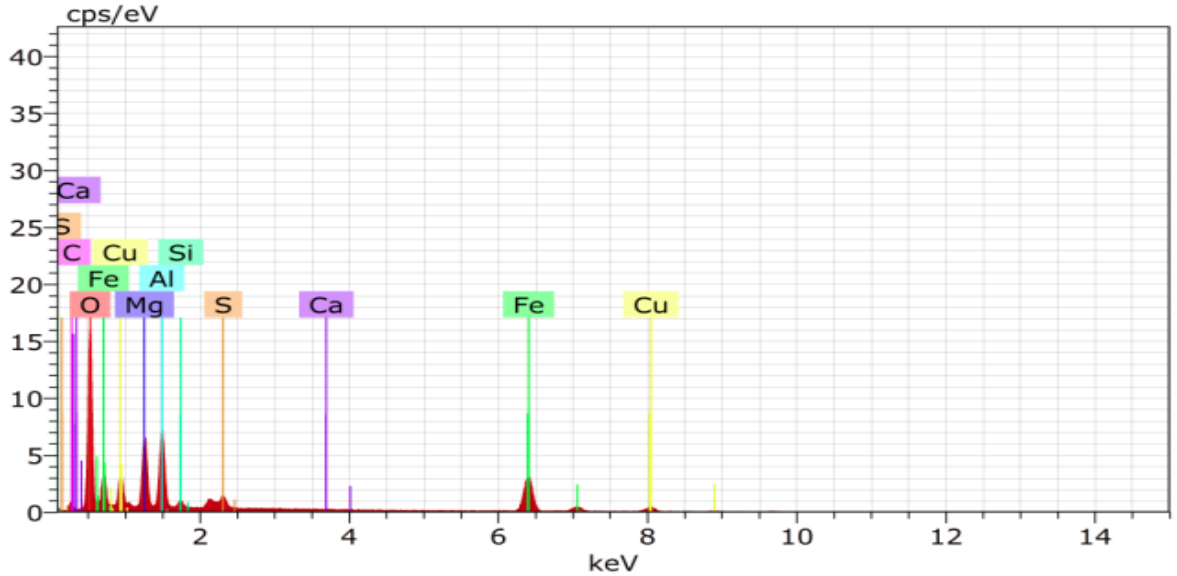

Fig. 4: EDX of composite

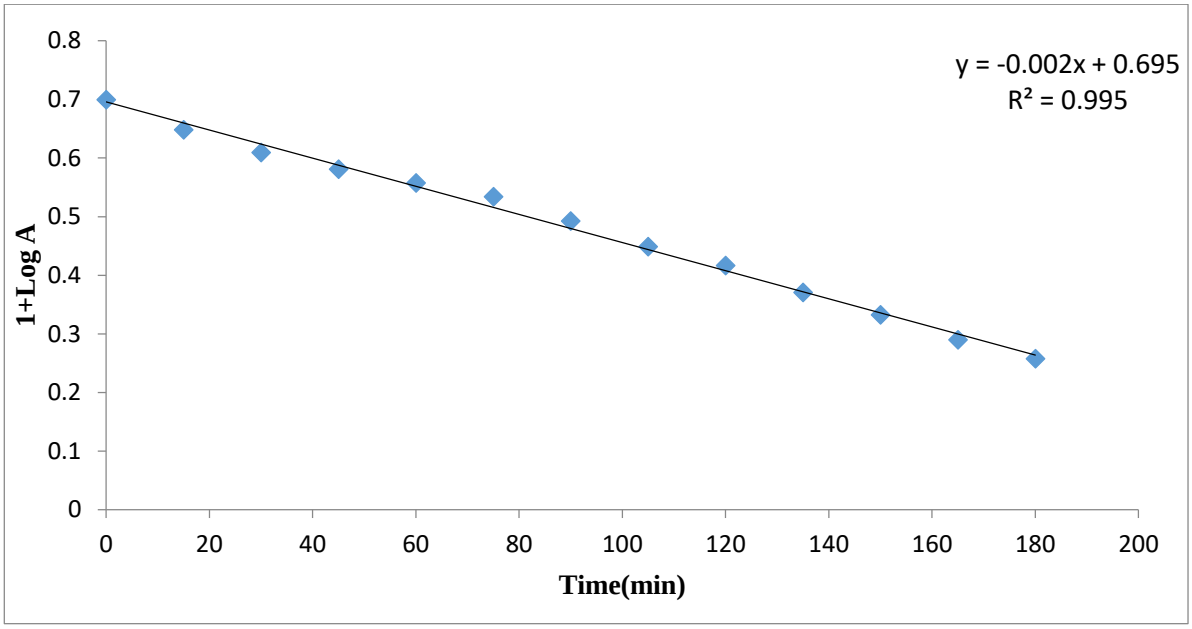

Fig. 5: Typical run in photocatalytic degradation

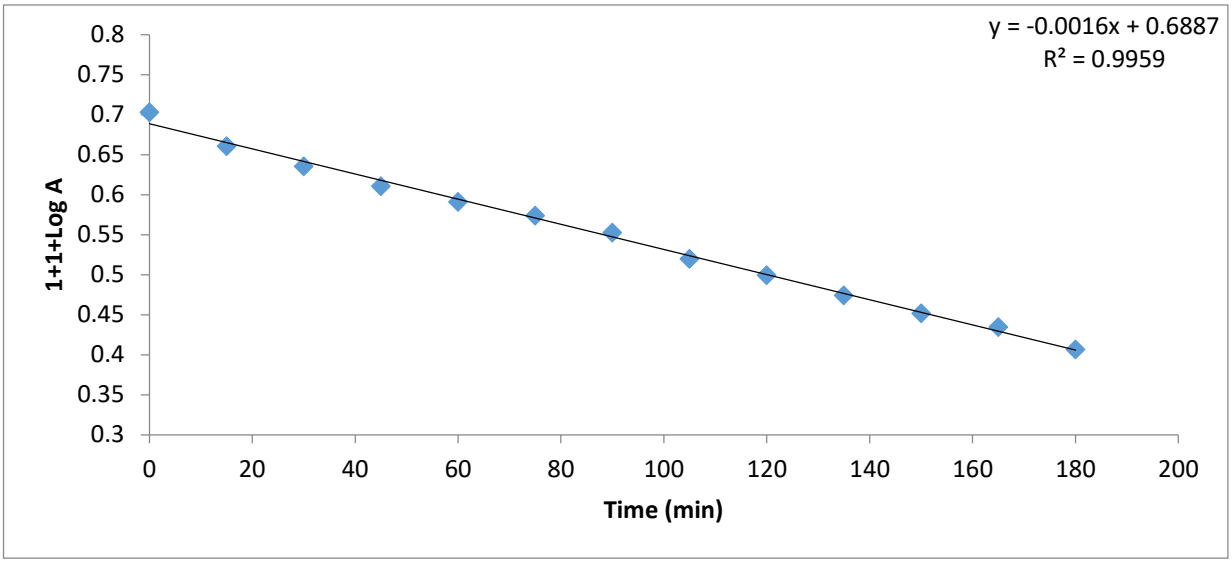

Fig. 6: Typical run for adsorption

Table 2
Typical run for adsorption

Time(min)	Absorbance (A)	1+Log A	Co(PPM)	Ce(PPM)	Removed	(qe) mg /L-1)	1+Log qe
0	0.505	0.7032	20	20	0	0.00000	0.00000
15	0.458	0.6608	20	18.8	1.2	0.50000	0.69897
30	0.432	0.6354	20	18.07	1.93	0.80417	0.90535
45	0.408	0.6106	20	17.37	2.63	1.09583	1.03974
60	0.39	0.591	20	16.81	3.19	1.32917	1.12358
75	0.375	0.574	20	16.33	3.67	1.52917	1.18445
90	0.357	0.5526	20	15.72	4.28	1.78333	1.25123
105	0.331	0.5198	20	14.79	5.21	2.17083	1.33663
120	0.316	0.4996	20	14.21	5.79	2.41250	1.38247
135	0.298	0.4742	20	13.49	6.51	2.71250	1.43337
150	0.283	0.4517	20	12.85	7.15	2.97917	1.47409
165	0.272	0.4345	20	12.36	7.64	3.18333	1.50288
180	0.255	0.4065	20	11.56	8.44	3.51667	1.54613

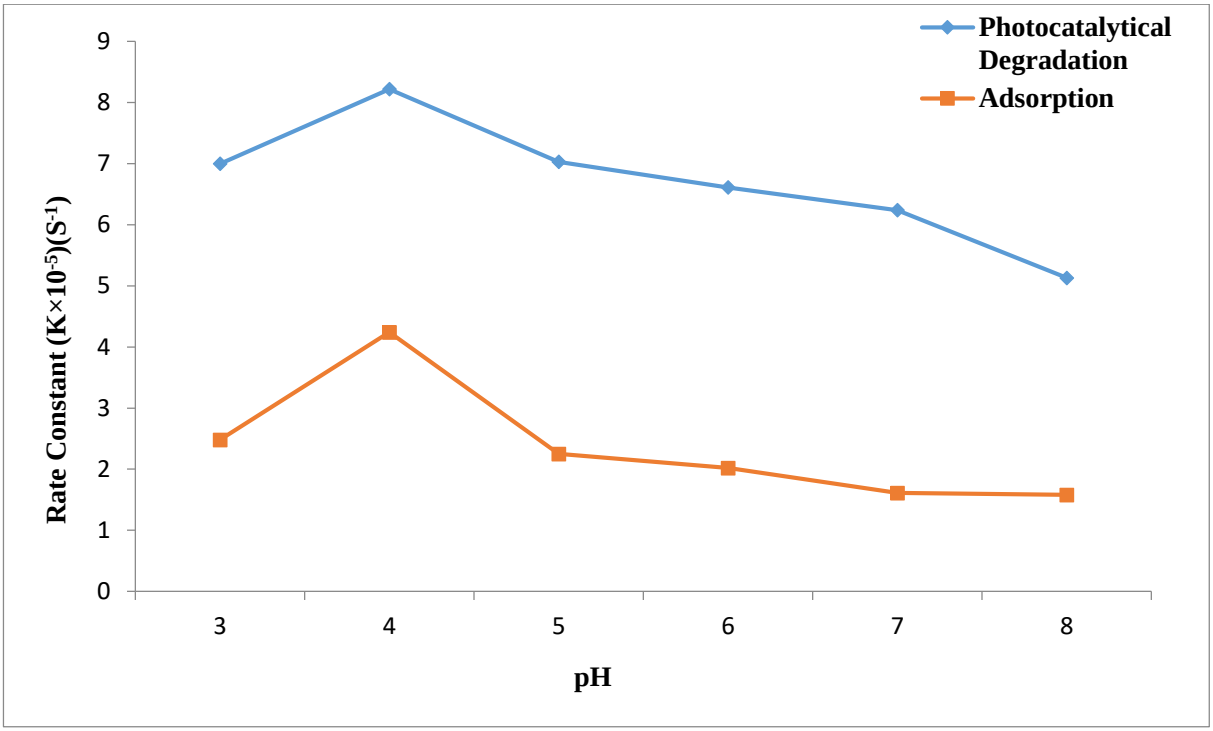

Fig. 7: Comparative Effect of pH in photocatalytical degradation and adsorption

Effect of pH in photocatalytic degradation: The effect of pH on photocatalytic degradation of toluidine blue was examined in the pH range of 3.0 to 8.0. The results are given in fig. 7. It was observed that degradation of toluidine blue decreases on increasing pH as the dye is positively charged in aqueous solution, which faces a repulsion from positively charged surface of composite due to adsorption of proton.

The rate of photo degradation was obtained at pH 4.0. An electron from conduction band is removed by dissolved oxygen to generate $O_2^{\bullet-}$ anion radical. Cationic form of toluidine blue was converted to its neutral form so when pH was increased above 4.0, anionic form experienced a force of repulsion with the negatively charged surface of the semiconductor due to the adsorption of more OH^- ions on the surface of the composite, so rate constant decreased at higher pH.

Effect of pH in adsorption: The effect of pH on adsorption was examined in the pH range of 3 to 8.0. The results are presented in fig. 7. The impact of pH is influenced on ionization of compound through Pka value of compound and creates a charge on the adsorbent material. The percent elimination of toluidine blue at equilibrium improved as pH increased. The negative charge density on the adsorbent surface causes the positively charged dye molecule to be electrostatically attracted to the adsorbent surface, so adsorption occurs at pH 4. Cationic dye repels with OH^- ions, there is no more adsorption above pH 4. Only desorption occurs.

Effect of dye concentration in photocatalytic degradation: The effect of dye concentration on the degradation has been observed in the range of 5 ppm to 35ppm. The results are given in fig. 8. The results revealed that as the concentration of the dye was increased above K value 8.31×10^{-5}, the reaction rate decreased. This might be because too many molecules have accumulated, preventing incident light from reaching the composite and slowing down the rate of disintegration as the dye concentration is increased.

Effect of dye concentration in adsorption: The impact of dye concentration on adsorption was examined in the range of 5 to 35 ppm. The results are presented in fig. 8. Dye adsorption increases by increasing the concentration of dye. After 20 ppm, sudden fall comes in the adsorption. This is mainly due to the unavailability of active sites responsible for adsorption.

Adsorption Isotherm: The relationship between the amount of adsorbate adsorbed onto the surface of an adsorbent and the concentration followed Langmuir isotherm rather than Freundlich.

Effect of amount of composite in photocatalytic degradation: The effect of composite dosage on dye degradation was examined between 0.02 to 0.12 g, the results are given in fig. 11. It was observed that as the amount of composite was increased from 0.02 to 0.12 g, the rate also increased but on further increasing the amount of composite, rate decreased. This could be explained due to the fact that on increasing the amount of photocatalyst, the exposed surface area of the composite also increases, which increases the rate. However, once this limiting value of 0.12 g reached, an increase in the amount of composite further will only increase the thickness of the composite layer, not the exposed surface area.

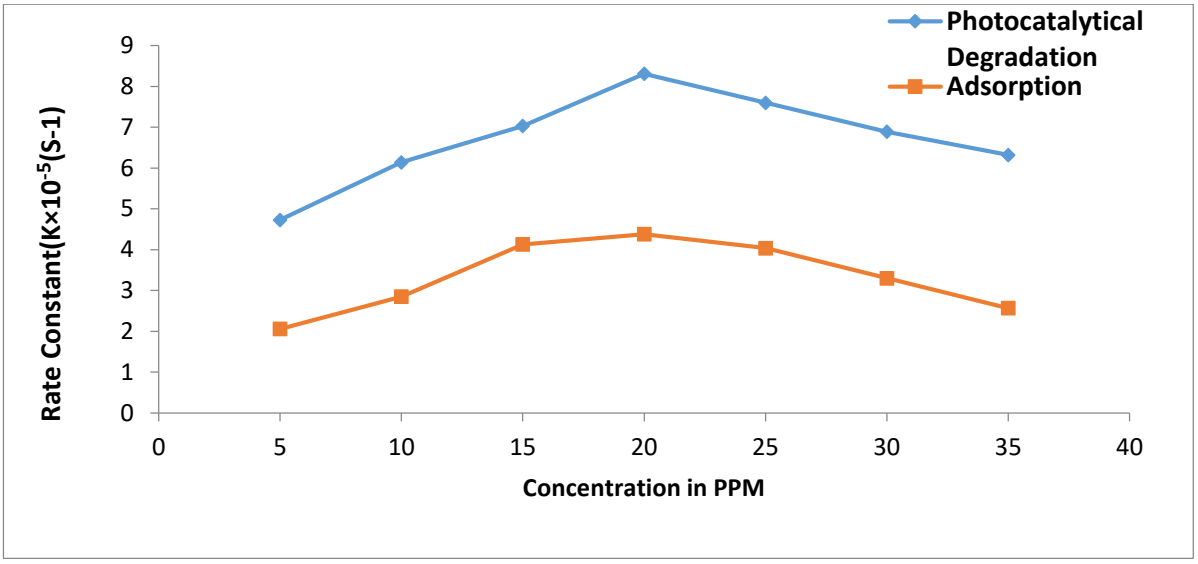

Fig. 8: Comparative effect of dye concentration in photocatalytical degradation and adsorption.

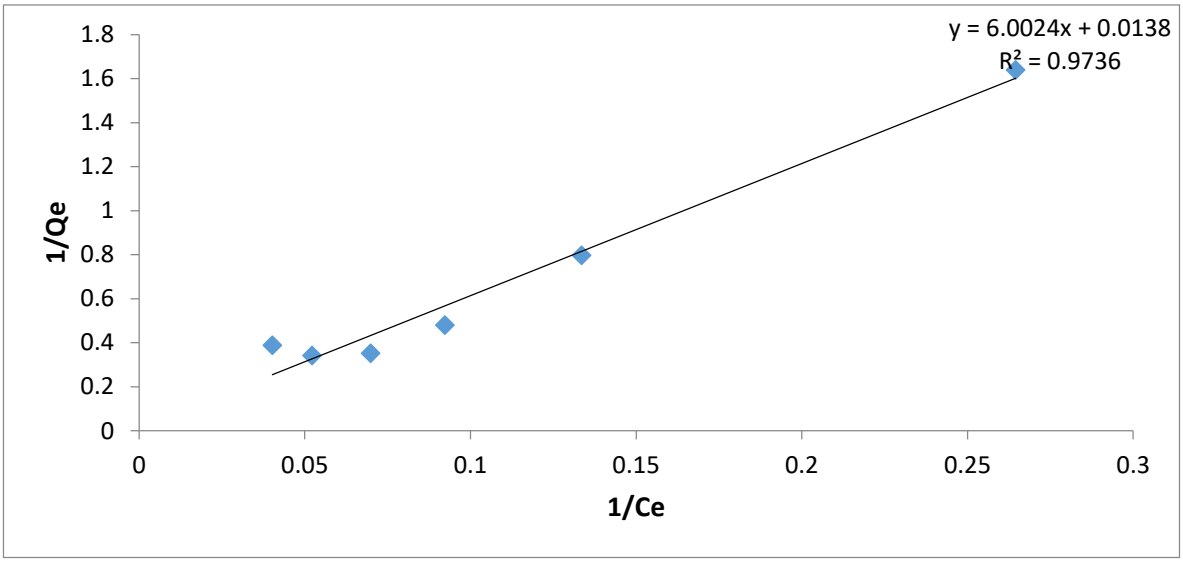

Fig. 9: Langmuir isotherm

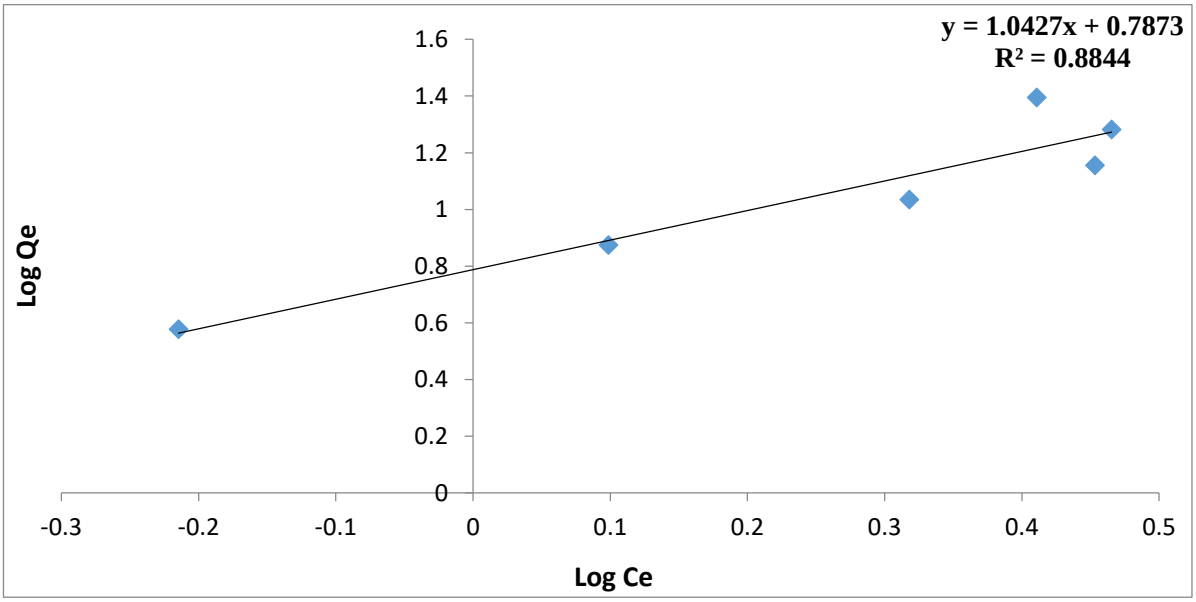

Fig. 10: Freundlich adsorption.

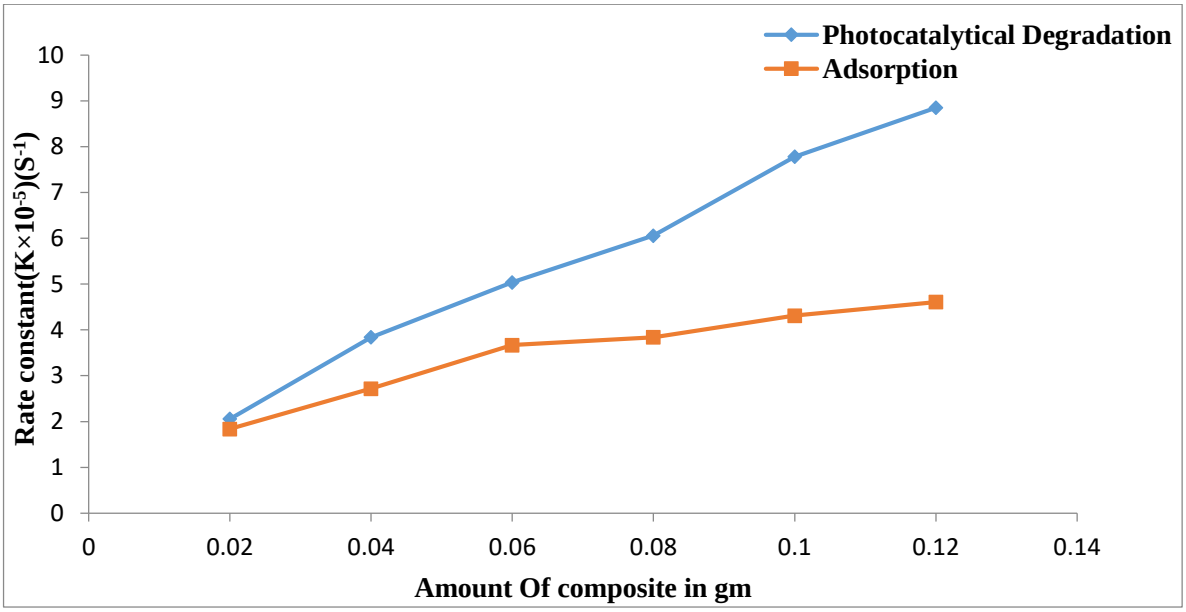

Fig. 11: Comparative effect of amount of catalyst for photocatalytic degradation and adsorption

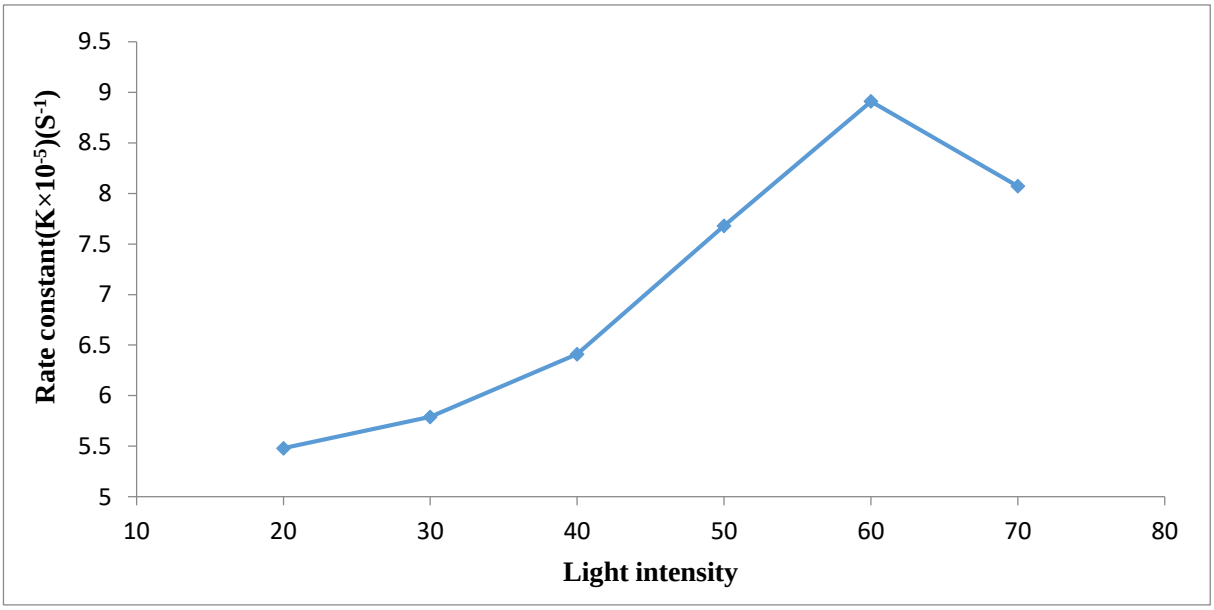

Fig. 12: Effect of light intensity in photocatalytic degradation

So multilayer permit the e and h + recombination as particles of the composite in close contact, as a consequence the rate of degradation decreases.

Effect of the amount of composite in adsorption: On increasing the amount of composite, the adsorption is increasing, because more surface area is available for binding the dye molecules as in fig. 11.

Effect of light intensity on photocatalytic degradation: In order to examine the effect of light intensity on dye degradation, the light intensity was changed from 20.0 to 70.0 mW cm^{-1}. The observation was reported in fig. 12 Maximum rate was found at 60.0 $mWcm^{-2}$. It may be due to fact that as the light intensity increased, the number of photons striking per unit time per unit area of composite also increase.

Mechanism

$^1TB_0$ hv ⟹ $^1TB_1$.
$^1TB_1$ ISC ⟹ $^3TB_1$.
G. C.Catalyst ⟹ h + (VB) + e - (CB).
O 2 (Dis.oxygen) + e - ⟹ $O_2^{\bullet -}$
$O_2^{\bullet -}$ + $^3TB_1$ ⟹ Leuco Dye.
Leuco Dye ⟹ Product.

After absorbing light with the suitable wavelength, toluidine blue is excited to its first excited singlet state, which is followed by intersystem crossover (ISC) to the triplet state. However, the composite also uses the energy of the incident light to excite its electron from the valence band to the conduction band and leaving a hole in the process. The dissolved oxygen absorbs the electron from the conduction band and it transforms into the superoxide anion radical, which transforms the toluidine blue into its leuco form. This

leuco dye is unstable and breaks down into smaller, nearly innocuous compounds.

Conclusion

A green synthesis method was used to successfully create an eco-friendly composite. Superoxide radicals ($O_2^{\bullet-}$) are the active species responsible for photo catalytic degradation. In contrast, electrostatic interactions and hydrogen bonding are the main factors influencing adsorption. The adsorption follows a Langmuir adsorption isotherm. The composite has been effectively utilized in the degradation of dye, achieving approximately 63.19% degradation, compared to around 42.19% for adsorption. Overall, the composite is more efficient in photocatalytic degradation than in adsorption.

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