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Article

BIOLOGIC AND PHOTOCATALYTIC DEGRADATION OF UV PRETREATED MIXTURE OF DYES BY *CALOCYBE INDICA*

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ABSTRACT

The degradation of a mixture of dyes by photocatalytic process (TiO_2/UV) and as a pre-treatment to biologic degradation by *Calocybe indica* (milky white mushroom) was investigated. The fungus was capable of degrading 52.6% of the dye's mixture, within 10 days under static conditions at pH 7.5 and 30°C temperature and having 150 µg/ml dye concentration. The photocatalytic process was capable of degrading only 16.2% dye mixture when exposed to UV for 4 h at continuous stirring at 30°C temperature and 150 µg/mL dye concentration. A two-step treatment process, namely, photocatalytic treatment followed by biologic degradation, was assessed. The visual observations and ultraviolet-visible (UV-VIS) spectral analysis showed that the combined effects were most efficient in the removal of the dye (94.6%), which involved a complex interaction of enzyme activity, biosorption, and photocatalytic action. The biotransformation of the synthetic dye mixture was confirmed by UV-Vis spectroscopy analyses of samples before and after decolorization. The strain showed a high correlation between the dry weight and color removal percentage. Thus, the biodegradation of complex synthetic dye mixture to non-toxic metabolites using *C. indica* would be a better option for the biologic treatment of textile effluents.

Keywords: Mixture of dyes, Photocatalytic pre-treatment, Mycoremediation, TiO_2/UV

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INTRODUCTION

Synthetic dyes find extensive usage across industries, notably in textile dyeing, contributing significantly to wastewater pollution (Grassi *et al*., 2011b). The color imparted by these dyes is a visible contaminant in water, with even minimal amounts (10–15 mg/L) affecting water esthetics and transparency (Robinson *et al*., 2001). Textile industries are major consumers, accounting for two-thirds of the global dye and pigment production (Vijayaraghavan *et al*., 2015). The inherent stability of synthetic dyes against light, water, and oxidizing agents poses challenges for their environmental degradation (Georgieva *et al*., 2010). Their complex aromatic molecular structure renders biodegradation in aquatic systems arduous (Grassi *et al*., 2011b), with untreated discharges posing hazards to both human health and aquatic ecosystems (Rajhans *et al*., 2021). The colored effluents from the textile industries affect the photosynthetic processes of aquatic plants which reduce oxygen levels in water, and in severe cases, result in the suffocation of aquatic flora and fauna (Janaki *et al*., 2015). Effluent treatment typically involves chemical and physical methods such as adsorption and coagulation, but these generate substantial sludge and incur high costs (Mechichi *et al*., 2006). Consequently, there is a pressing need for cost-effective decolorization methods. Fungi have garnered attention for their efficient and economical degradation of organic pollutants, including synthetic dyes, through mycoremediation (Grassi *et al*., 2011b; Perelo, 2010).

The treatment of dye effluents encompasses a range of chemical and physical methods, including adsorption, coagulation, oxidation, precipitation, photodegradation, filtration, and ionizing radiations, each with distinct decolorization capabilities, capital costs, and operational speeds. While coagulation and adsorption are commonly employed, they often yield large quantities of sludge, posing disposal challenges, and chemical degradation methods tend to be costly, time-consuming, and methodologically demanding (Grassi *et al*., 2011b; Mechichi *et al*., 2010). Hence, there exists a pressing need to develop an economically viable and efficient approach to decolorize textile dyeing waste.

In this regard, fungi have garnered significant attention for their capacity to efficiently and affordably degrade organic pollutants, including synthetic dyes. Mycoremediation emerges as an eco-friendly, non-invasive, cost-effective solution capable of reducing or transforming environmental hazards into non-toxic forms (Perelo, 2010). Mushrooms, recognized as powerful decomposers of by-products and integral components of the food web, exhibit remarkable prowess in interacting with recalcitrant substrates such as fats, chitin, and keratin, breaking them down into starches, hemicelluloses, celluloses, pectins, and other sugar polymers (Rhodes, 2012).

Recent interest has surged in heterogeneous photocatalytic oxidation processes for dye degradation, wherein irradiation of TiO_2 particles proves highly competent for wastewater treatment. This method facilitates the complete mineralization of organic compounds under mild conditions, sans sludge, or harmful by-products (Huang *et al*., 2006). The TiO_2 catalyst, characterized by its affordability, high surface area, non-toxicity, chemical stability across a broad pH range, photostability, and capacity to utilize sunlight and air to generate reactive species such as hydroxyl radicals (HO), demonstrates efficacy in converting organic compounds into harmless species such as CO_2 and H_2O (Adams *et al*., 2006; Su *et al*., 2016).

While varying percentages of decolorization have been reported for different textile dyes, investigations into combined biologic-photocatalytic effects remain scarce. Hence, the primary objective of the present study was to optimize degradation conditions for the fungus *Calocybe indica* and explore the photocatalytic degradation of dye mixtures as a pre-treatment to enhance biodegradability. This holistic approach seeks to harness both biologic and photocatalytic mechanisms for effective wastewater treatment.

METHODS

Microorganism and cultivation conditions

The fungal strain *C. indica* was stored on PDA slants (potato dextrose agar consisting of glucose [10 g/L], agar [15 g/L], and 40% potato

extract) at 4°C. After transferring mycelium from a slant tube to potato dextrose broth (PDB), it was allowed to grow for 3 days. Subsequently, 8 mL of this inoculum was introduced into a 500 mL flask containing 200 mL of liquid culture medium (PDB).

Chemicals and dyes

The following dyes – acid red G183, basic violet 10, vat blue 4, reactive orange 16, basic violet 3, reactive yellow 135, reactive blue 25, reactive red HE3B, acid orange 11, basic blue 9, reactive red HE7B, and Remazol Blue R – were procured from Sri Devi Dyes & Chemicals, a local company in Bangalore, India, and used directly without additional purification. These dyes are commonly utilized by textile industries in India. All chemicals and reagents were of the highest available purity and analytical grade. Nano TiO_2 was synthesized in-house using TiCl4 through acid-hydrolysis (Swetha *et al*., 2010).

Biologic experiments and decolorization procedures

Microbial dye decolorization

The decolorization and biodegradation capabilities of *C. indica* were examined in a synthetic medium (potato dextrose broth) comprising potato extract (40%), glucose (1%), and wheat flour (0.5%), along with 150 mg/L RB 25 dye. Before autoclaving, the pH of the medium was adjusted to 7.5±0.2. A 6% (v/v) suspension of *C. indica* culture derived from the inoculum was introduced into 250 mL of medium in 500 mL flasks. These flasks were then incubated in a shaking incubator at 150 rpm and 30°C for a duration of 10 days.

Control flasks with identical media but lacking inoculum were retained to observe abiotic decolorization. At regular intervals, a 5 mL aliquot of the culture medium was withdrawn from the flasks, and centrifuged at 10,000 rpm for 10 min at 10°C, and the dye concentration in the supernatant was determined. The decolorization of the dye was measured by the absorbance of the culture supernatant at λ max (518 nm). The percentage of decolorization was calculated according to the following formula:

D = (A1-A2)/A1×100%.

where A1 represented the absorbance of the control, A2 represented the absorbance of the corresponding untreated sample, and D was the dye decolorization efficiency (%).

Effect of pH and temperature on microbial dye decolorization

The impact of pH and temperature on microbial dye decolorization was investigated across a range of pH values (from 5 to 9) with 0.5-unit increments and at various temperatures (25°C, 28°C, 30°C, 32°C, 35°C, and 40°C). Each experiment was conducted twice in triplicate. Visual observations and UV-VIS spectroscopic analysis were employed to monitor the decolorization and degradation of dyes. The absorbance at 518 nm, measured using a UV-Vis spectrophotometer (Shimadzu, Japan), served as an indicator of dye decolorization, whereas spectral scanning between 200 and 800 nm was performed to assess peak removal.

Photocatalytic experiments

Photocatalytic apparatus

Experimental procedures involving photocatalysis were conducted in a batch setup with a total capacity of 1 l. The dye solution occupied 500 mL of the apparatus throughout the experiment. To ensure thorough mixing, the reactor, housing the reaction solution consisting of the dye solution and TiO2 photocatalyst powder, was positioned on a magnetic stirrer. Illumination was provided by a medium-pressure mercury lamp (UV-C), emitting light at a maximum wavelength of 247.3 nm, with a power of 150 W. Within the reactor, a glass tube containing the UV lamp was centrally located parallel to the length of the cylinder. To shield the reactor from UV radiation, aluminum foil was carefully placed over it.

Analytical procedures

The working solution for the photocatalytic tests was prepared using tap water, with a dye mixture concentration of 150 mg/L and a TiO2 concentration of 0.2 g/L. Before initiating the photocatalytic process, the suspensions were magnetically agitated in darkness for 30 min to ensure adsorption–desorption equilibrium between the dye and TiO2. Subsequently, samples were subjected to centrifugation at 10,000 rpm for 10 min and then filtered through a 0.45 μm syringe filter to separate TiO2 particles. Absorbance measurements were conducted at the maximum wavelength of the dye mixture (λ_{max}=518 nm), whereas UV–vis spectra of the samples were recorded between 200 and 800 nm.

Combined biologic-photochemical process

Studies on the combined effects were conducted to assess the efficiency of UV radiation as a pre-treatment of dye before microbial degradation. The aim was to render recalcitrant dye molecules biodegradable and achieve maximum degradation.

Data analysis

The amount of degradation of mixed dye by *C. indica* (ml/L) was obtained using the following expression:

$$q = \frac{[(C_o - C_I)\,V}{M} \quad (1)$$

where q is the amount of dye degradation onto the unit amount of the adsorbents (ml/L) and C_o and C_t are the concentrations of the mixed dye in the aqueous solution (ml/L) before and after degradation, respectively; V is the volume of the aqueous phase and M is the amount of the fungal culture (ml).

Pseudo – first and second-order equation

The study of degradation kinetics describes the adsorbate uptake rate and evidently, this rate controls the residence time of adsorbate at the solid–liquid interface (Lagergren, 1898). The kinetics of mixed dye degradation on fungal culture was analyzed using the pseudo-first order and pseudo-second order.

The pseudo-first-order equation (Demirbas *et al*., 2004) is generally expressed as follows,

$$\log(q_{eq} - q_t) = \frac{\log \mathbf{q_{eq}} - (k_1 t)}{2.303} \quad (2)$$

The applicability of the kinetic first-order model is confirmed by the straight line against Log ($q_{eq} - q_t$) against *t*. The first-order process q_{eq} should be equal to the intercept of a plot of Log ($q_{eq} - q_t$) against *t*.

The second-order mechanism for the degradation of mixed dye by *C. indica* (Ho *et al*., 1998) is expressed as Equation 4

$$\frac{t}{q_t} = \frac{1}{(k_2 q^2 eq)} + \frac{1}{q_{eq}}\, t \quad (3)$$

The applicability of the kinetic second-order model is confirmed by the plot of t/q_t versus *t* gives a linear relationship between dye degradation and fungal culture. From the intercept and slope, the rate constant (k_2) and adsorption at equilibrium (q_{eq}) are calculated, respectively.

Adsorption isotherms

The Langmuir isotherm relates the degradation density *q*e (dye degradation per ml of the fungal culture) to equilibrium degradation in the bulk fluid phase, *C*e. The Langmuir isotherm is described by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_a} + \frac{C_e}{q_m} \quad (4)$$

where q_e is the amount of fungal culture (ml/L), C_e is the equilibrium concentration of degradation (ml/L), q_m is the equilibrium degradation capacity for complete monolayer (ml/L), and K_a is the degradation equilibrium constant (ml/L). When C_e/q_e was plotted against C_e, a straight line with slope $1/K_a$ qm and an intercept of $1/q_m$ were obtained.

The Freundlich equation is described by the following equation

$$q_{eq} = K_F \ Ce^{1/n} \quad (5)$$

q_e – dye degradation at equilibrium concentration (ml/L); C_e – equilibrium of mixed dye concentration, (ml/L); K_F – Freundlich's constant of degradation capacity; n – Freundlich's constant of degradation intensity. The K_F was estimated from the y-intercept and n was calculated from the slope.

Thermodynamics of dye degradation by *C. indica*

In the present study, the mixed dye degradation experiments were carried out at the temperature (25, 28, 30, 32, 35, and 40°C). The values of the thermodynamic parameters such as ΔG°, ΔH°, and ΔS°, describing mixed dye degradation by *C. indica*, were calculated using the thermodynamic equations. The apparent equilibrium constant for the process has been shown to be

$$K_{c=\frac{K_{pd}}{C_e}} \quad (6)$$

The change in Gibbs free energy process is given as

$$\Delta G^\circ = -RtlnK_c \quad (7)$$

where ΔG° is the standard Gibbs free energy change for the biosorption (J/mol), R is the universal gas constant (8.314 J/mol/K), and T is the temperature (K). From thermodynamics,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

Or

$$\Delta G^\circ = -\Delta S^\circ(T) + \Delta H^\circ \quad (9)$$

A plot of T against ΔG° gives a straight line with slope –ΔS° and an intercept of ΔH° was obtained.

RESULTS AND DISCUSSION

Decolorization of dye mixture by *C. indica* in batch liquid cultivation

Initial experiments in liquid media indicated partial decolorization of a dye mixture by *C. indica* after 10 days of incubation. The decolorization rate was initially slow during *C. indica* cultivation, with approximately 50% of the dye removed by the 10th day. The decolorization rate was assessed in culture filtrates, revealing a removal of about 40–50% of color in cultures containing 150 mg/L dye mixture after 10 days. No further degradation was observed as cultivation progressed, and the dye concentration in abiotic control flasks remained unchanged. Decolorization was attributed to either biodegradation by the fungus and/or adsorption on fungal biomass. Spectral analysis of dye samples indicated incomplete disappearance of absorption peaks in the visible region (Fig. 1), suggesting *C. indica* alone is not effective in complete dye removal. Previous studies have also shown decreased dye degradation efficiency at higher concentrations due to potential toxicity to metabolic activity (Zhuo *et al*., 2011; Laksmi *et al*., 2021).

Effect of pH and temperature on degradation

The effect of pH on the decolorization of the dye mixture was monitored at pH ranging from 5 to 9 at 30°C. The results revealed an appreciable decolorization of dye over a pH range of 6.5–8 which is

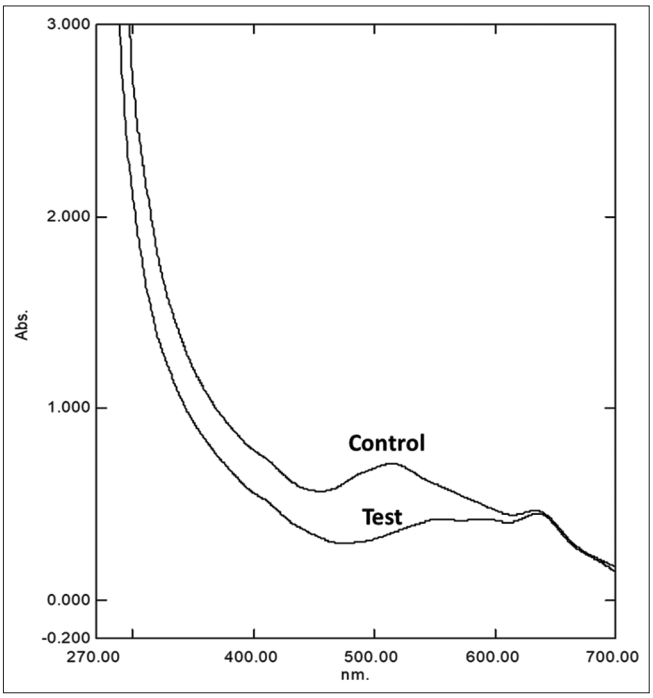

Fig. 1: UV-Vis spectra of dye mixture in the presence (Test) or absence (Control) of *C. indica* (Filtrates obtained from the control cultures grown in the absence of dye mixture were used as blanks while obtaining these spectra)

desirable for industrial applications since it can be used for textile dye effluent treatment without a previous pH adjustment stage. The dye decolorization rate increased with pH up to 7.5, above which it slightly decreased. The decolorization rates (40–50%) in the basic pH range of 7–8 were higher than those (5–20%) in the acidic pH range of 5–6. The most suitable pH for the dye mixture for maximum decolorization efficiency was around pH 7.5 (Fig. 2). The obtained result indicates that the initial media pH is one of the important factors influencing the biodegradation process. This finding is in line with Kunjadia's work, which investigated the decolorization of azo dye from an aqueous solution by a ligninolytic-producing fungi strain of *Pleurotus* spp. They found that the maximum color removal was obtained at pH 6. Syafiuddin and Fulazzaky (Syafiuddin *et al*., 2021) also examined the effect of pH on the ability of *Trichoderma citrinoviride, Trichoderma koningiopsis,* and *Pestalotiopsis* sp. to decolorize the Remazol Brilliant Blue R dye in aqueous solution. They suggested that the favorable pH to change the color of this dye was in the pH range of 3–5. The higher dye removal efficiency on slightly acidic media was associated with the stability of the MnP enzyme under acidic conditions (Asses *et al*., 2018).

The impact of temperature on dye decolorization was assessed by subjecting the culture to various temperatures ranging from 25°C to 40°C. Optimal decolorization was observed at 30°C with agitation rates of 150 rpm, using an initial dye concentration of 150 mg/L (Fig. 3). Similarly, *Pleurotus sajor-caju* exhibited the highest levels of decolorization at 35°C and pH 3.2 for 19 out of the evaluated dyes, with 13 of them showing a color reduction exceeding 50% post-enzymatic treatment. Conversely, *Coriolopsis sp*. demonstrated varying levels of azo dye decolorization, with percentages ranging from 22.24% to 14.35% across temperatures of room temperature, 30°C, 35°C, 40°C, and 45°C, respectively. However, this degradation pattern was not consistent across all dyes tested, despite the statistically significant effects of different incubation temperatures ($p<0.001$) (Cheng *et al*., 2016).

Dye decolorization by photocatalytic process

Photocatalytic degradation of the dye mixture at 150 mg/L concentration showed only 14% decolorization with 5 h of illumination time. UV-Vis

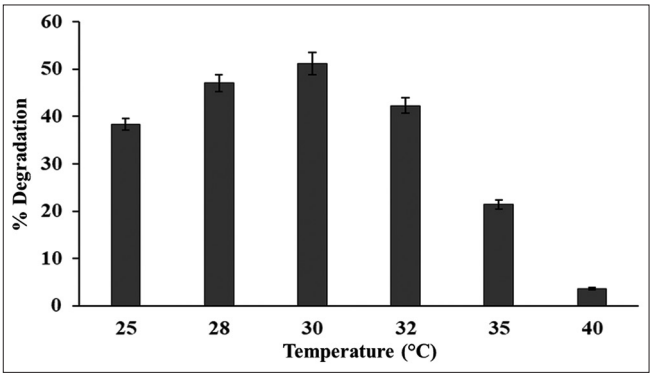

Fig. 2: Effect of temperature on percent decolorization of dye mixture of *C. indica*

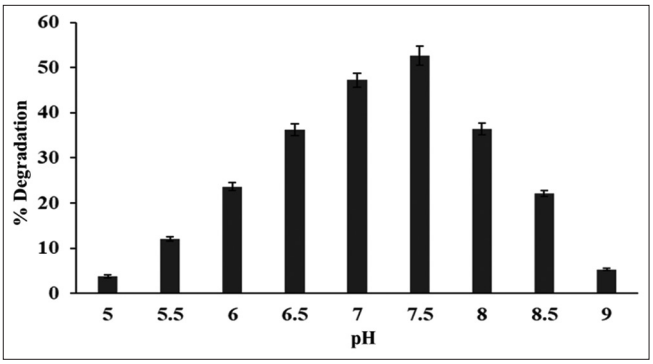

Fig. 3: Effect of pH on percent decolorization of dye mixture of *C. indica*

spectral analysis indicated ineffective removal of absorbance peaks. Findings (Fig. 4.) indicated that this method in isolation exhibited limited efficacy in degrading the dye mixture, with only a 14% decolorization achieved after 5 h of illumination at 150 mg/L. UV-Vis absorption spectra revealed that absorbance in both the visible and UV spectral ranges was ineffective in eliminating two absorbance peaks in the visible spectrum. However, heterogeneous photocatalysis utilizing TiO_2 as a catalyst proved to be a promising technique for decolorizing PBS and RB160 dyes. Notably, the decolorization of RB160 was hindered at lower H_2O_2 dosages, contrary to the trend observed in the $UV/H_2O_2/TiO_2$ process, whereas $KBrO_3$ enhanced decolorization across all dosages. The efficiency of the catalytic reaction may diminish at higher dye concentrations due to a significant portion of UV being absorbed by the dye molecules rather than the TiO_2 particles. In addition, interference from intermediates generated during the breakdown of the original dye molecules is a potential explanation. These intermediates could compete with dye molecules for the limited catalytic and adsorption sites on the TiO_2 particles, hindering decolorization. With increased initial dye concentration, the presence of elevated levels of degradation intermediates could exacerbate such interference (Karimi *et al*., 2014). However, challenges such as dye molecule absorption of UV and interference from degradation intermediates may limit efficacy at higher dye concentrations.

Combined effects of biologic and photocatalytic process

In the mitigation of aromatic byproducts, the amalgamation of a biologic-photocatalytic process showcased superior efficacy compared to employing either the photocatalytic or biologic process in isolation. Findings (Fig. 5.) underscored that utilizing a photocatalytic process as a preliminary treatment for dye, particularly at a concentration of 150 mg/L, yielded superior outcomes compared to employing a combination of photocatalytic and microbiologic degradation solely for aromatic remediation. As the cultivation progressed, no further degradation was observed, with degradation rates measured at

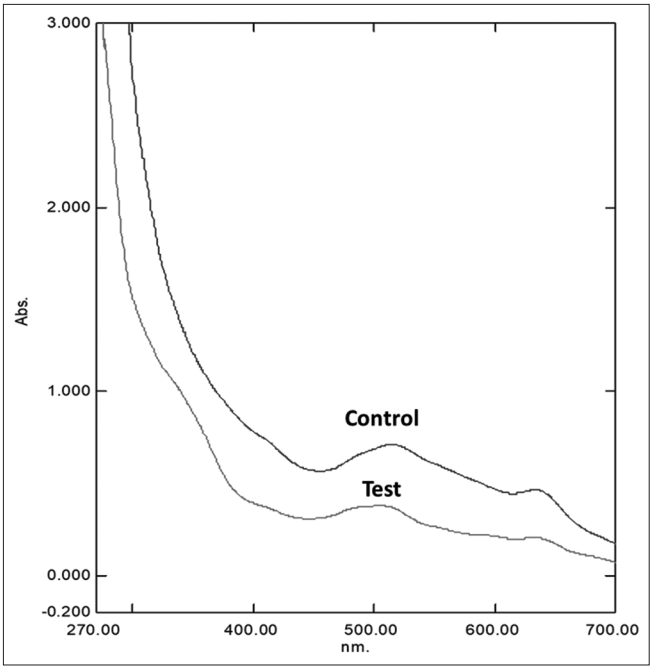

Fig. 4: UV-Vis spectra of dye mixture in the presence (Test) or absence (Control) of UV/TiO_2 (filtrates obtained from the control in the absence of dye mixture were used as blanks while obtaining these spectra)

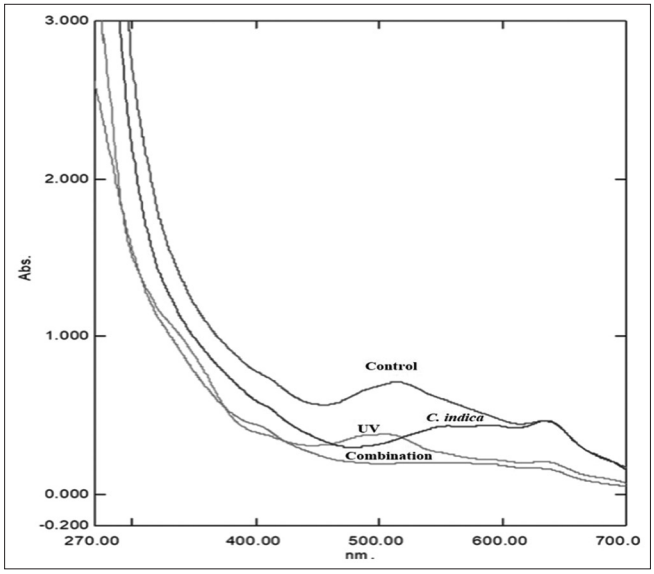

Fig. 5: UV-Vis spectra of untreated sample (Control), dye mixture treated with *C. indica*, UV/TiO2, and both in combination (filtrates obtained from the control cultures grown in the absence of effluents were used as blanks while obtaining these spectra)

various intervals revealing the peak rate occurring on the 7th day of cultivation, reaching 94.6% (Fig. 6.). In a study by Gonzalez *et al*. (González *et al*., 2010), the efficacy of *Trametes pubescens* and TiO2/UV-based sequential biologic-photochemical processes in degrading chlorophenols was evaluated. This approach was suggested due to the partial oxidation of original chemicals and the potential formation of intermediate byproducts through biologic processes, which could pose greater risks than the original molecules (Venkata *et al*., 2022a).

Degradation kinetic modeling

The pseudo-first- and second-order rate constant for mixed dye degradation by *C. indica* at different pH are shown in Tables 1 and 2. The

Table 1: The pseudo-first- and second-order kinetic constants for degradation of mixed dye by *Calocybe indica* at different pH

pH	Experimental	Pseudo First Order			Pseudo Second Order		
	q_{ex} (ml/L)	Qe (ml/L)	$k_1 \times 10^{-1}$ (1/min)	R^2	qe (ml/L)	$k_2 \times 10^{-4}$ (1/min)	R^2
5	3.81	3.72	0.301	0.9517	72.46	0.426	0.6192
5.5	12.1	12.9	1.690	0.9466	15.36	8.300	0.613
6	23.6	22.5	2.168	09767	45.66	1.372	0.6048
6.5	36.3	35.9	2.544	0.9723	36.76	1.315	0.7474
7	47.2	47.8	3.869	0.9751	72.46	4.266	0.6192
7.5	52.6	52.2	3.869	0.9761	400.00	0.476	0.1576
8	36.4	35.5	3.045	0.9124	116.28	2.850	0.5956

Table 2: The pseudo-first- and second-order kinetic constants for the degradation of mixed dye by *Calocybe indica* at different temperatures

Temperature (°C)	Experimental	Pseudo First Order			Pseudo Second Order		
	q_{ex} (ml/L)	Qe (ml/L)	$k_1 \times 10^{-1}$ (1/min)	R^2	qe (ml/L)	$k_2 \times 10^{-1}$ (1/min)	R^2
25°C	38.4	38.50	3.983	0.987	3.374	5.587	0.634
28°C	47.1	46.87	3.332	0.980	4.304	7.407	0.614
30°C	52.2	52.50	2.808	0.936	3.310	8.486	0.892
32°C	42.3	41.89	2.643	0.987	4.184	6.027	0.637
35°C	21.4	20.90	2.233	0.964	8.695	1.502	0.629
40°C	13.6	15.10	0.338	0.932	625	0.007	0.004

Table 3: Langmuir and Freundlich Isotherm model constant and correlation co-efficient for degradation of mixed dye by *Calocybe indica* at different pH

pH	Experimental	Langmuir Constant			Freundlich Constant		
	q_{ex} (ml/L)	qm (ml/L)	k_d	R^2	k_F	N	R^2
5	3.81	5.39	0.081	0.9925	0.319	0.875	0.9473
5.5	12.1	15.23	0.912	0.9920	0.064	0.777	0.9770
6	23.6	26.07	4.101	0.9944	0.0807	0.871	0.9768
6.5	36.3	43.13	9.201	0.9996	0.1034	0.747	0.9949
7	47.2	41.19	12.86	0.9895	0.1723	0.809	0.9800
7.5	52.6	53.64	1.078	0.9905	0.2326	0.934	0.9870
8	36.4	30.18	3.839	0.9984	0.1644	0.880	0.9953

experimental values and correlation coefficients were lower than the theoretical value at different pH and temperature which gives different values for second-order kinetics. The correlation coefficients of second-order kinetics at different pH and temperature by *C. indica* were lower than 0.990. The experimental and theoretical values were very close in first- and second-order kinetics. Thus, the first-order mechanism was predominant in the degradation of mixed dye by *C. indica*.

Langmuir and Freundlich adsorption isotherms

Tables 3 and 4 show the Langmuir constant and correlation coefficients calculated from the plots for mixed dye degradation by *C. indica* at different pH and temperature. The maximum degradation capacity by *C. indica* of mixed dye is determined from the Langmuir isotherm constant. The maximum capacity (q_m) for the degradation of mixed dye was found to be at pH 7.5 and temperature 32°C. The Langmuir constant measures the stability of the intricate between the mixed dye and the fungal biomass in experimental conditions. The high degradation affinity of the fungi is due to the presence of small k_d values. The favorable degradation of mixed dye from aqueous solution by fungal biomass is shown by the Freundlich constant k_F and n. The high degradation capacity of mixed dye by the fungal biomass is shown by the n values calculated from the slope. In the present investigation, it is clear that the Langmuir model fits better than the Freundlich isotherm model at different pH and temperature.

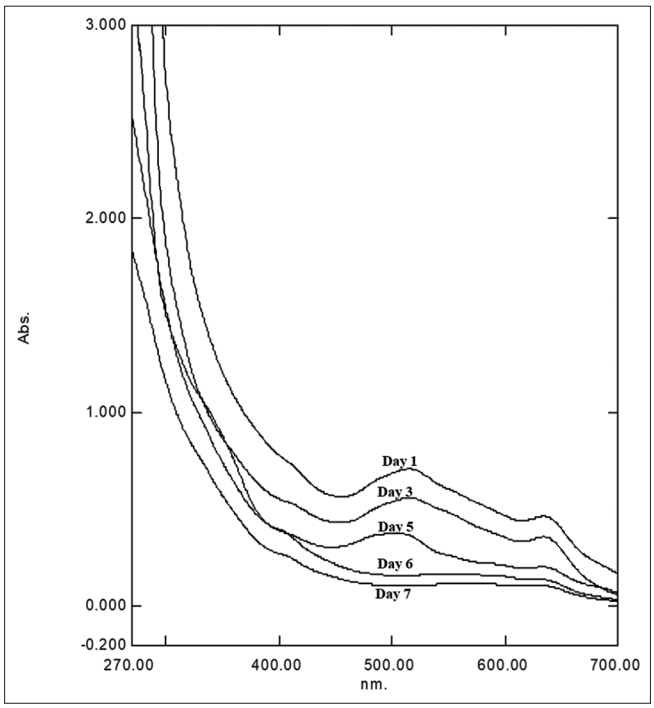

Fig. 6: UV-Vis spectra of time course studies on the decolorization of UV pre-treated dye mixture by *C. indica*

Thermodynamics of biodegradation of mixed dye

The thermodynamic parameters for the degradation by the fungal biomass at different temperatures are present in Table 5. The spontaneous degradation of mixed dye by the fungal biomass is shown by the negative values of ΔG°. The Gibbs energy of the interactions demonstrated that the processes are favorable for the formation of electrostatic interaction and/or mixed dye-fungal biomass complexes. However, the negative value of ΔGº decreased with an increase in temperature, indicating that the spontaneous nature of degradation of mixed dye by *C. indica* is inversely proportional to the temperature. The negative value of ΔG° shows

Table 4: Langmuir and Freundlich Isotherm model constant and correlation co-efficient for degradation of mixed dye by *Calocybe indica* at different temperature

Temperature (°C)	Experimental q_{ex} (ml/L)	Langmuir Constant			Freundlich Constant		
		qm (ml/L)	$k_d \times 10^{-2}$	R^2	k_F	N	R^2
25°C	38.4	35.24	10.02	0.9967	0.08888	0.6900	0.9746
28°C	47.11	41.74	3.632	0.9837	0.172428	0.8099	0.9799
30°C	52.2	49.45	6.853	0.9976	0.158302	0.7658	0.9964
32°C	42.3	43.19	11.72	0.9952	0.118099	0.7197	0.9822
35°C	21.4	25.24	11.35	0.9985	0.014605	0.7329	0.9822
40°C	3.6	4.39	6.796	0.9863	0.22775	0.9362	0.9565

Table 5: Free energy values obtained from the degradation of mixed dye by *Calocybe indica* at different temperatures

S. No	Kelvin (K)	ΔG°(J/mol/K)
1	298	−431.12
2	301	−435.46
3	303	−438.35
4	305	−441.25
5	308	−445.59
6	313	−452.82

that the degradation of mixed dye by the fungal biomass is an exothermic process.

CONCLUSION

In this study, UV-vis analysis served as a pivotal tool for gauging the degradation and decolorization of the dye mixture by both photocatalytic and biologic treatments. However, standalone employment of these methods yielded insignificant decolorization and failed to substantially remove aromatic rings resulting from the breakdown of dye molecules. Consequently, a combined approach was adopted to achieve optimal decolorization and degradation, proving notably effective for this purpose. Our findings suggest that through the utilization of combined effects, it is feasible to decolorize high concentrations of textile-related dyes swiftly and economically, presenting a significant advantage in textile effluent treatment. While the combined process showcased superior efficacy compared to individual biologic or photocatalytic treatments, further refinement of the system is warranted. Notably, our results underscored the heightened effectiveness and cost-efficiency (in terms of time utilization) of the combined approach over standalone treatments. While degradation of dyes has primarily been associated with white-rot fungi, limited studies have explored the potential of *C. indica* in this regard. Our study highlighted the profound influence of pH, temperature, and dye concentration on the overall degradation and decolorization of mixed dye. Moreover, the degradation kinetics of dye removal appeared to adhere to first-order kinetics. To elucidate the degradation equilibrium data on *C. indica* across varying pH, temperature, and heavy metal concentrations, both Freundlich and Langmuir adsorption models were employed. Encouragingly, our findings demonstrated that the Freundlich model aptly described the degradation of dye, suggesting promising avenues for further research and optimization of this combined treatment approach.

AUTHORS' CONTRIBUTIONS

Dr. Venkata Krishna B played a pivotal role in the project by conducting extensive microbial and UV degradation studies. He designed and executed experiments to evaluate the photocatalytic degradation of dye mixtures using TiO_2 under UV light. His efforts were crucial in establishing the comparative efficiency of the combined treatment approach and in optimizing conditions for maximal dye degradation.

Dr. S. Maheswari and Dr. Malaiyarasa Pandian contributed significantly through their work on kinetic modeling studies. Their work provided insights into the rate-determining steps and the overall efficiency of the biodegradation pathway, thereby enhancing the scientific robustness of the study.

The authors declare that they have no conflict of interest.

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