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Research Article

PHOTOCATALYTIC DEGRADATION OF INDIGO CARAMINE FROM AQUEOUS SOLUTION BY TIO_2 NANOPARTICLE UNDER UV IRRADIATION

Swati Goyal*, Divya Patidar

Department of Chemistry, Dr. A. P. J. Abdul Kalam University, Indore, Madhya Pradesh, India

**Corresponding author: swatipc2011@gmail.com*

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ABSTRACT

Despite rising demand for chemical industry products and associated factories, the issues of environmental pollution have not improved, and the situation is rapidly deteriorating. The importance of dyeing companies in polluting the environment is evident in this regard. The photodegradation of Indigo caramine (IC) by Titanium dioxide (TiO_2) was studied using UV-absorption spectroscopy in this study. By adjusting the dye concentration, catalyst dose, pH, temperature, and H_2O_2 concentration, It was able to be determined the percentage of degradation of these nanoparticles on Indigo caramine. The Langmiur-Hinshelwood mechanism was used in this experiment. The percentage of degradation was exceptionally efficient at 4×10^{-5} M dye concentration with pH 2.5 and constant catalyst concentration for nanoparticle. This demonstrates that Titanium dioxide (TiO_2) nanoparticles may remove Indigo caramine (IC) from waste water. The outcomes of this investigation resulted in a ground-breaking, cost-effective water pollution remediation method.

Keywords: Indigo caramine, Titanium dioxide, Nanoparticles, Photodegradation, Wastewater.

1. INTRODUCTION

The water bodies are persistently contaminated due to the informal strategies received by the chemical, material, paper, and mash businesses, and so forward, amid the release of poisonous and dangerous chemicals [1-5]. The complexity of the color particles does not favor the natural process of degradation additionally during certain occurrences fragmented corruption or change may create carcinogenic byproducts [6-9]. In this manner, physical, chemical and biological strategies have been developed for the treatment of color effluents from industries [10]. In this think about, indigo dye is utilized as a targeted pollutant to undergo photo degradation. Indigo dye belongs in an ancient class of dyes called vat dyes. In advanced times, it is artificially created in huge amounts (20 million kg every year) and utilized primarily for coloring cotton materials such as denim cloth or jeans.

Indigo dye is an organic chemical with the molecular formula $C_{16}H_{10}N_2O_2$. This dye could be derived from the indigo plant (*Indigo feratinctoria*) and woad (*Isanti's tinctoria*). Photocatalysis, an improved oxidation process that uses semiconductors like TiO_2 as photocatalysts, could be a potential way for removing organic contaminants from water *in situ* [11]. Photocatalysis could be a heterogeneous catalytic reaction under the illumination of bright light within the presence of a light-activated photocatalyst [12]. Various studies have been published on the photocatalytic degradation of organic dyes in wastewater utilizing titanium dioxide [13-15]. Different innovations have been utilized to expel IC from water and wastewater. Physical treatments such as adsorption on chitin and chitosan [16], and on charcoal from the extracted residue of coffee beans have been tested [17]. In any case, these physical frameworks transferred the pollutants from the liquid to a solid phase, requiring further treatment and in this manner expanding the cost of the method. Other frameworks, such as incineration, are expensive and in most cases can lead to the generation of air pollutants and greenhouse gasses [18]. Hence, it is essential to look for economical and efficient alternative strategies for IC degradation. In recent years advanced oxidation processes (AOPs) have appeared as curious options for treating water containing natural pollutants [19-22].

The reuse of treated water is among the foremost suitable solutions to realize genuine sustainable use of water, particularly in water-deprived nations. One of

the most pertinent issues in wastewater reusing is the presence of micro contaminants, also known as emerging contaminants (ECs). Wastewater from industries and municipal treatment plants can be reused after the proper treatment. Among the distinctive advanced oxidation processes, the utilize of photo-catalysis based upon TiO_2 for water purification is getting expanding interest in recent years due to its high photo-stability, non-toxicity, and cost-effectiveness [23]. However, in spite of the fact that it may be a good catalyst, its wide band-gap (3.2eV) limits utilize of visible light as the light source. This has consequent suggestions for the utilization of titania materials as solar or room-light activated catalysts since the majority of sunlight consists of visible light and only a 3-5% of UV light. Subsequently, increasing the effectiveness of visible photocatalysis is vital for the practical application of this strategy [24]. Among physical, chemical, or biological waste treatment strategies, chemical course sand, in particular, the photocatalytic strategies are considered the most curious ones much appreciated to their wide applicability, low cost and environmental compatibility. Physical treatments primarily work to concentrate the pollutants instead of removing them; on the other hand, biological processes are of great significance in numerous applications, but the operational conditions got to be entirely controlled to protect the active bacterial colonials. Conventional chemical routes require the addition of dangerous or expensive chemical reagents [25] and the main objective of this study is the photocatalytic degradation of Indigo caramine dyes from aqueous solution using nano crystalline Titanium dioxide.

2. EXPERIMENTAL

The characteristics, structure and absorption spectra of Indigo Carmine dye derived from Loba Chemie (India) are listed in Table 1. Millennium Inorganic Chemicals provided the titanium dioxide, which was used without further purification. For the preparation of the various solutions, double distilled water was employed. 1 M HCI or 1M NaOH was used to modify the pH of the solutions.

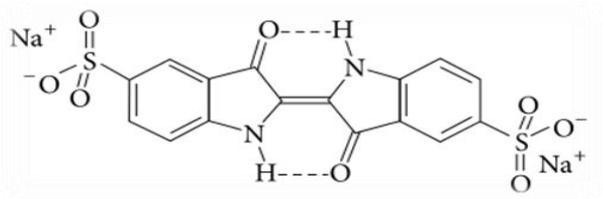


Fig 1: Structure of indigo carmine

Table 1: Properties of indigo carmine dye

Name	Indigo Carmine
Other name	5,5'-indigodisulfonic acid sodium salt or Indigotine
Empirical formula	$C_{16}H_8N_2Na_2O_8S_2$
Nature	Acidic dye
Maximum wave length (λ_{max})	608 nm
Formal charge	0
Formula weight	466.36 g mol-1
Density	1.01g/ml at 20°C
Water solubility	1g/100ml at 25°C
Color	Very dark blue to purple
Complexity	870
Solubility	Soluble in water, ethanol; insoluble in organic solvents

2.1. Reagents and solutions

Hydrogen peroxide (30% for analysis) was purchased from Meyer. Sodium sulfate (Na_2SO_4), sodium chloride (NaCl), potassium iodide (KI), ammonium hepta molybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$), ferrous sulfate hepta hydrate (reagent grade) and sodium bicarbonate ($NaHCO_3$) were obtained from Merck. Sulfuric acid and sodium hydroxide, used to adjust the pH as required, were purchased from Sigma Aldrich and Carlo Erba, respectively. A stock solution of IC was prepared in distilled water and diluted for individual experiments. The selection of dyestuff concentration was based on a suitable pollutant concentration for the analytical test (COD and dye evolution) over a significant timescale (neither too short nor too long).

2.2. Apparatus

Experiments on photocatalytic degradation were carried out in a 1000 ml Pyrex-glass cell in a UV chamber equipped with eight 18W (Philips) UV lamps, each with

a wavelength of 608 nm. UVA light metre (Model UVA-365, Lutron) was used to measure UV light intensity, which was found to be 0.5mW/cm^2. To achieve consistent mixing of the solution in the jar, a magnetic stirrer was used. The dispersions were magnetically agitated in the dark for 15 minutes before to irradiation to achieve adsorption/desorption equilibrium. WTW pH-720 digital pH metre was used to determine the pH of the solutions. The temperature in the jacketed wall reactor was kept constant during the reaction time by circulating water. The spectra were captured using a Shimadzu UV-vis spectrophotometer.

2.3. Photo-catalytic studies

The photocatalytic activity of TiO_2 nanocomposite was investigated on degradation of indigo carmine (IC) dye, a group of dark blue indigo caramine dye, from solution in various initial pH, photocatalyst mass, initial dye concentration and UV irradiation time. The UV light source was a 6 W UV lamp (608 nm) and was located 10 cm from the Pyrex glass vessel. Using a pH meter, the pH of the dye solution was changed by adding either 0.1 M HCl or 0.1 M NaOH solutions. Before irradiation, a combination of 25mL of IC solution and the appropriate amount of photocatalyst was magnetically agitated in the dark for 30 minutes to create adsorption-desorption equilibrium of the IC and the photocatalyst surface. The suspensions were subjected to UV light for another 120 minutes, and a tiny aliquot was removed from the system and centrifuged every 30 minutes throughout the experiment. The residual IC dye in the filtrate was measured using a UV-Vis spectrophotometer with a maximum wavelength of 608 nm. The experiment was also carried out in the dark (without UV irradiation) with the same parameters as the one with UV irradiation. All of the trials were carried out twice.

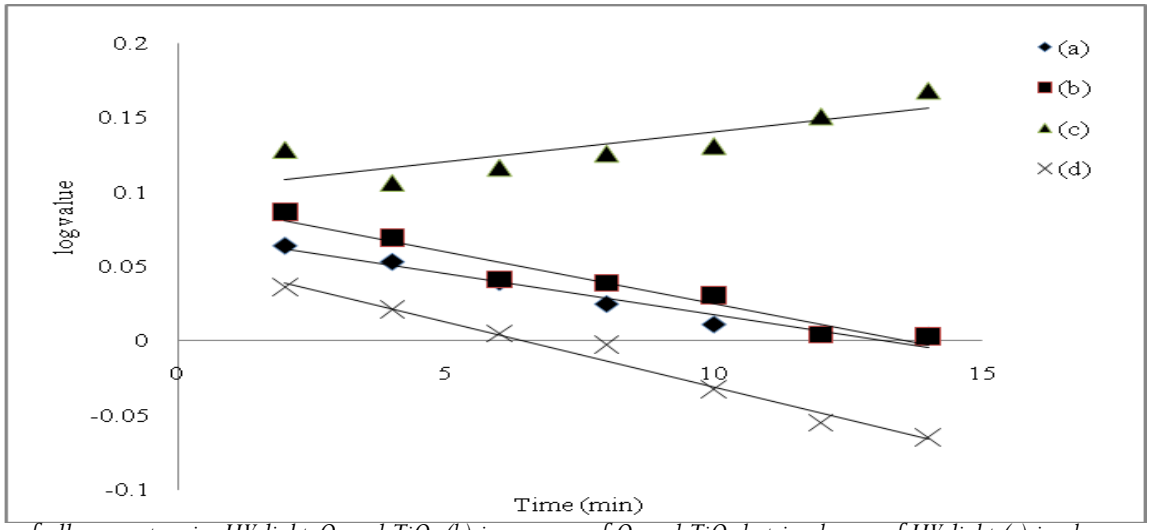
3. RESULTS AND DISCUSSION

3.1. Preliminary Observations

Preliminary photo-catalytic studies were carried out by taking TiO_2 containing indigo caramine solution in dark. In view of the existence of several degradation pathways, the photodegradation was studied under the following experimental conditions in order to define the system completely:

(a) Photo degradation of the dye in presence of all parameters viz. UV light, O_2 and TiO_2.
(b) Photo degradation of the dye in presence of O_2 and TiO_2 but in absence of UV light.
(c) Photo degradation of the dye in absence of TiO_2 but in presence of O_2 and UV light.
(d) Photo degradation of the dye in presence UV lightand TiO_2, but in absence of O_2.

It was observed from the above studies that decrease in absorbance of dye in absence of UV light was very slow. Presence of TiO_2 only does not catalyze the degradation of the dye. Only a minor loss of the dye on to TiO_2 surface was observed due to initial degradation of the dye on TiO_2 surface. Minor loss was found in presence and absence of O_2 and TiO_2 while better results were observed when small amount of TiO_2 is added to the solution in the presence of UV light and O_2 (Fig. 2).



(a) in presence of all parameter viz. UV light, O_2 and TiO_2 (b) in presence of O_2 and TiO_2 but in absence of UV light (c) in absence of TiO_2 but in presence of O_2 and UV light (d) in presence UV lightand TiO_2, but in absence of O_2 and, at concentration 4×10^{-5} M, pH 2.5, temp. 30±1°C

Fig. 2: Photocatalytic degradation of Indigo Carmine

3.2. Photodegradation Kinetics of MG (Langmuir -Hinshelwood model)

The Langmuir-Hinshelwood (L-H) model describes how a contaminant adsorbs on the catalyst surface, which is required for efficient oxidation. The adsorption-desorption process is defined by the transfer of reactants from the aqueous phase to the surface, their adsorption, reaction in the adsorbed phase, product desorption, and removal [26, 27]. While the L-H model appears to adequately describe the macroscopic kinetics of photodegradable contaminants in very dilute aqueous solutions, some of the model's inherent assumptions, such as its failure to account for simultaneous adsorption (or desorption), may not be valid at the microscopic level [28-30]. L-H model equation is represented by equation (1):

$$r = k\theta = -dC / dt = k (KC/1+KC) \quad (1)$$

Where r is the rate of degradation, t is the period, C is the concentration, K is the adsorption coefficient, and is the fractional site coverage for the reactant as KC1, the equation becomes (2) or (3).

$$C = C_0 e^{-kt} \quad (2)$$

$$Ln\ C = Ln\ C_0 - kt \quad (3)$$

k stands for the first-order photocatalytic reaction rate constant. The first-order rate constant is commonly calculated using relative aqueous concentration changes [31-33].

3.3. Effect of TiO_2 concentration

In slurry photocatalytic processes, catalyst dosage (5 to 40 mg/l) is an important parameter that has been extensively studied. Before treatment, the UV-vis spectra of indigo carmine exhibit three main absorption bands - two in the UV region and one in the visible region (608 nm). The UV band is characterized by two adjacent rings, and the visible band is associated with a long conjugated π system that is linked by two azo groups [34, 35]. The decolorization of indigo carmine was simultaneously monitored at 608 nm in the UV/TiO_2 system. The experiments were carried out using TiO_2 catalyst at a fixed dye concentration (25 mg/ L), and different catalyst loading (5 to 40) mg/L at 25 minute of irradiation. Fig. 3 displays the percentage decolorization of indigo carmine for 25 minute using TiO_2 photocatalysts. The results indicate that the optimum dose of TiO_2 is 25mg/L exhibits higher photo-catalytic activity than the others. The rate of photo-catalytic reaction is strongly influenced by concentration of the photocatalyst. Heterogeneous photocatalytic reactions are known to show proportional increase in photodegradation with catalyst loading [36].

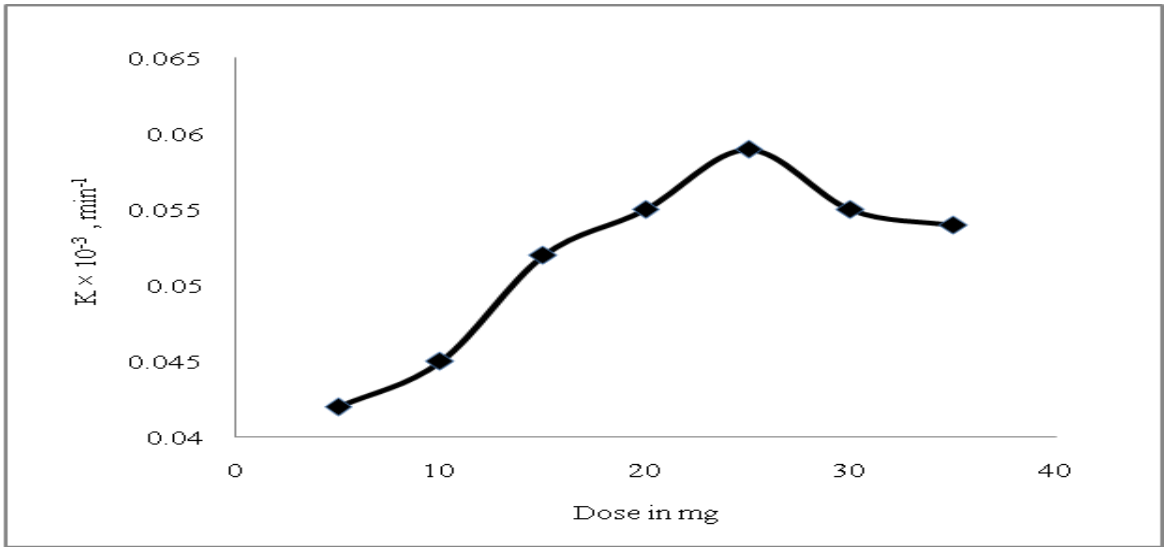


Fig. 3: Variation of rate constants with different concentrations of TiO_2 at Indigo Carmine concentration 4×10^{-5} M, pH 2.5, temp. 30±1°C

3.4. Influence of Initial Concentration on Photodegradation of MG

An essential part of the research is the effect of the dye solution's initial concentration on photocatalytic degradation. The initial concentrations of indigo carmine ranged from 1×10^{-5} M to 8×10^{-5} M, with 4×10^{-5} M being the best value. As shown in Fig. 4, as the initial concentration of the dye solution was increased after the optimal concentration, the photodegradation percent fell.

3.5. Influence of pH on Photodegradation of MG

The efficiencies of photocatalytic processes strongly depend upon the pH of the reaction solution. It was due to the amphoteric behavior of semi-conductor TiO_2. The surface charge-property of TiO_2 changes with the change of solution pH. Fig. 5 depicts the color removal efficiency of indigo carmine dye solution as a function of pH in the range varying from 4 to 11. The maximum decolorization was seen at lower pH (pH ~2.5). Fig. 5 represents Influence of pH on the decolorization rate for the decomposition of indigo carmine dye (catalyst dose 25 mg/l).

3.6. Effect of H_2O_2 concentration

Electron acceptors (H_2O_2) play an important role in photocatalytic degradation. Several researches have looked at the effects of H_2O_2, and it has been discovered that it speeds up the photodegradation of organic contaminants [37]. In this study, H_2O_2 accelerates the pace of indigo caramine degradation by removing surface-trapped electrons, lowering the rate of electron-hole recombination and boosting the efficiency of whole process usage. The enhancement of degradation with the addition of 2 is due to an increase in the hydroxyl radical concentration Eq. (4) and (5).

$$H_2O_2 + eCB^- \rightarrow {\bullet}OH + OH^- \quad (4)$$

$$H_2O_2 + h_VB \rightarrow OH + {\bullet}OH \quad (5)$$

The effect of H_2O_2 addition on indigo caramine degradation was studied with concentrations ranging from 0.001 to 0.006 mM. Low H_2O_2 concentrations were less effective for indigo caramine degradation, as seen in Fig. but the percentage of degradation of H_2O_2 concentrations increased.

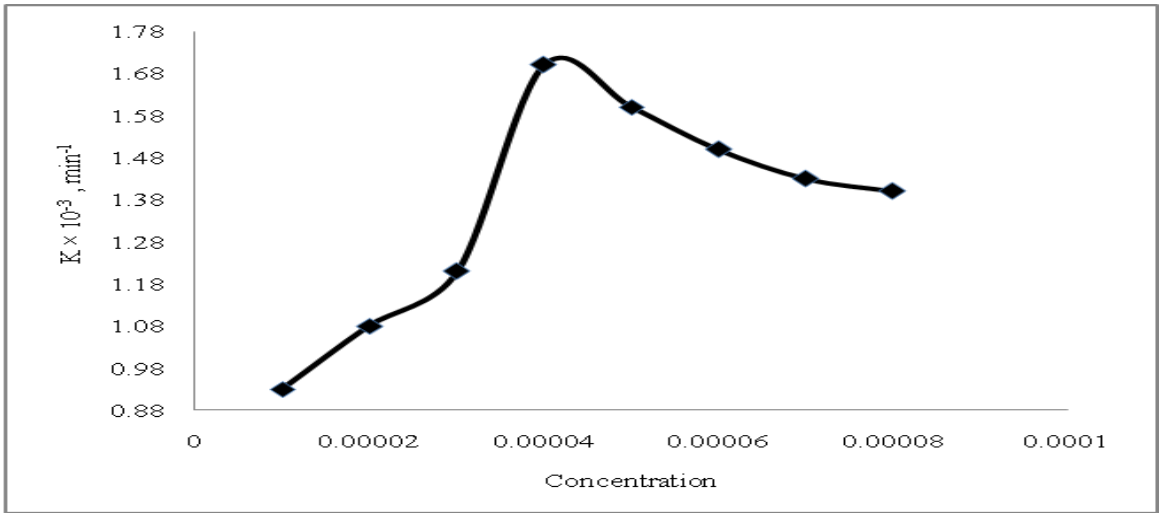


Fig. 4: Variation of rate constant with substrate concentrations at pH 2.5, temp. 30±1°C

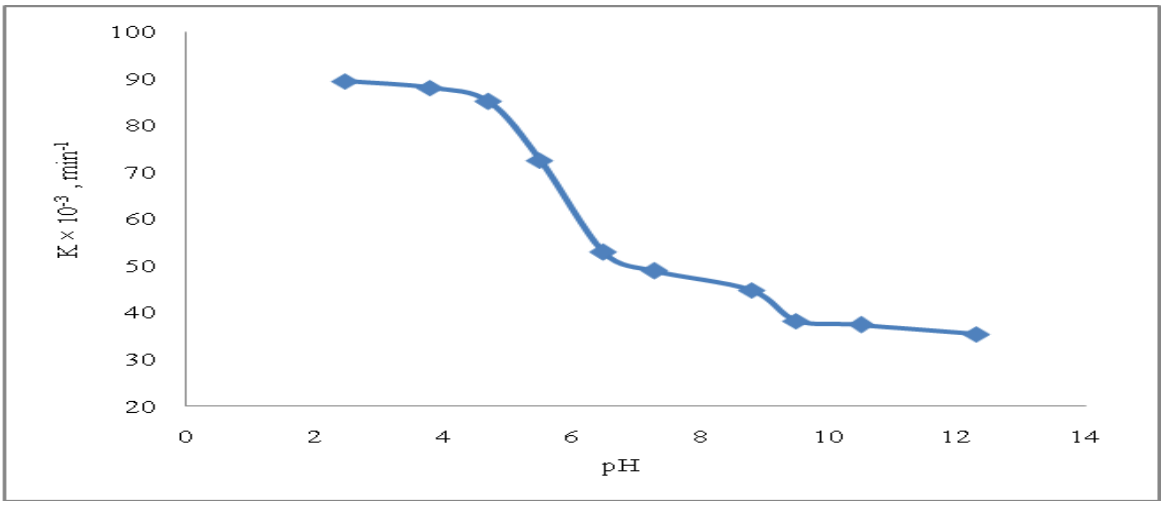


Fig. 5: Variation of rate constant with different pH at dye concentration 4×10^{-5} M, temp. 30±1°C

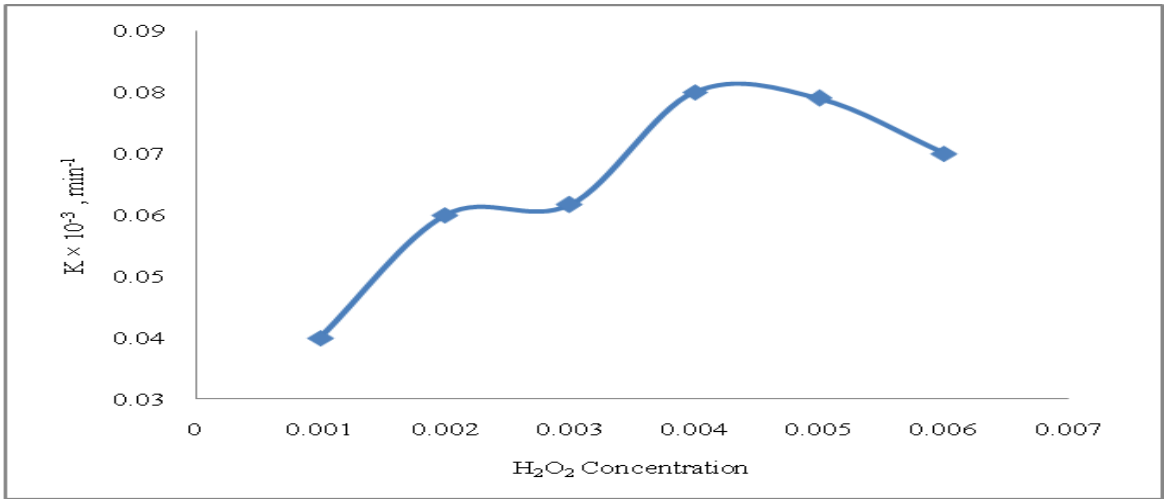


Fig. 6: Variation of rate constant with different concentration of H_2O_2 at conc. 4×10^{-5} M, temp. 30±1°C

4. CONCLUSION

This paper focuses on recent advances in photocatalysis systems for water and wastewater treatment. This article investigates the impact of various operating settings on the photocatalytic degradation of Indigo caramine. In the presence of UV light, TiO_2 has been proposed as an efficient and viable photocatalyst for the breakdown and mineralization of numerous hazardous organic contaminants in water. In this study, the efficacy of photocatalytic decolorization of indigo carmine dye solution utilizing TiO_2 suspended in aqueous media in the presence of UV light was investigated. Initial dye concentrations, pH, and metal doping on TiO_2 were all used to evaluate the catalyst impact. The perfect catalyst load was 25 mg, which was adjusted by diluted HCl solution, and the optimum operating pH was 2.5 with an indigo carmine dye concentration of 4×10^{-5} M, according to the experimental data. An average of 98 percent color removal was obtained with a comparatively short UV irradiation time of 25 minutes at pH 2.5 and the treatment of single component indigo carmine from wastewater using Photocatalytic degradation was taken up in the present study. The study may be extended for multi-component systems as wastewaters contain several contaminants. The experimental settings that have been developed will be beneficial in the treatment of effluent-containing colors.

Conflict of interest

There is no conflict of interest.

Source of funding

There is no funding agency. All expenditure has been done by authors only.

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