

Photocatalytic Degradation of Textile Dye (ACID Red 114) from Aqueous Solution using Immobilized Tube Reactor

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Abstract— In this study the Photocatalytic degradation of textile dye (Acid Red 114) from aqueous solution has been investigated using immobilized nano TiO₂ photocatalyst under UV light. Nano sized Titanium dioxide (TiO₂) powder was synthesized by sol-gel method using titanium tetra chloride (TiCl₄) as the precursor. The prepared photocatalyst were characterized by scanning electron micrographs (SEM). The investigated nanoparticle of titanium dioxide was immobilized on Quartz surface using heat attachment method. Photocatalytic degradation experiments were carried in a circulation photo reactor with a 15 W UV lamp radiating around 365 nm. All the experiments were carried out as a function of irradiation time, pH, initial dye concentration, and Catalyst concentration. The optimum condition for AR 114 removal were found to be pH = 2, adsorbent dosage = 0.6 gm/l of solution and dye degradation equilibrium was rapidly attained after 80 minutes of the irradiation time and it was described by the Langmuir and Freundlich adsorption isotherms over the entire concentration range from 20-100 mg/l. Adsorption data's are used for modeling, from the first and second order kinetic equation.

Keywords: Acid Red 114, NanoTiO₂, Photocatalytic degradation, Immobilization.

I. Introduction

Dyes are used extensively in various industries such as dyestuffs, textile, paper, leather, foodstuffs, cosmetics, rubber and plastics are using enormous quantity of synthetic dyes in order to give color for their products and consume substantial volumes of water [1]. About 7×10^5 dyes are produced annually in the global market. It is estimated that about 2% of these dyes are discharged into the water system with most of the sources generated from textile industries [2]. Most of the dyes are toxic and potentially carcinogenic in nature and their removal from the industrial effluents is a major environmental problem [3]. Various methods have been suggested to handle the dye removal from water these includes the biodegradation, coagulation, adsorption, advance oxidation process and membrane process [4]. In recent years, advanced oxidation processes (AOPs) have been proposed as an alternative to conventional methods. Heterogeneous photo catalysis via combination of nanoparticles of TiO₂ and UV light is considered to be one of the promising advanced oxidation processes for of water-soluble organic pollutants found in water and wastewater .It causes complete decomposition of toxic and bio resistant compounds into harmless species such as CO₂, H₂O, etc. [5]. Semiconductors are the commonly used material in the degradation process of azo dyes [6]. Titanium dioxide (TiO₂) is a functional semi conducting material used for various applications as it has a lot of merits like, being environmental friendly, chemically stable and less costly as compared to the other metal oxides and absorbs only in UV region because of its large band gap (3.2 eV) [7-8]. Most of the literature studies related to photo degradation have been carried out using the suspension of Nano crystals of TiO₂ in aqueous solution. However, the use of aqueous suspension is not suitable for

industrial applications due to the inconvenient and expensive separation of nano-particles of titanium dioxide for reuse. Moreover, suspension of fine particles limits the penetration of light leading to reduced efficiency of photodegradation. Therefore, there is a need to immobilize the photocatalyst onto an appropriate inert support in an efficient way, which eliminates the need of filtration of catalyst for reuse.[9]

In the present work the photocatalytic degradation of textile dye (Acid Red 114) from aqueous solution has been investigated using immobilized nano TiO₂ photocatalyst under UV light. Nano sized Titanium dioxide (TiO₂) powder was synthesized by sol-gel method using titanium tetra chloride (TiCl₄) as the precursor. The prepared photo catalysts were characterized by scanning electron micrographs (SEM). The investigated nanoparticle of titanium dioxide was immobilized on Quartz surface using heat attachment method. Photo catalytic degradation experiments were carried in a circulation photo reactor with a 15 W UV lamp radiating around 365 nm. All the experiments were carried out as a function of irradiation time, pH, initial dye concentration, and catalyst concentration.

II. EXPERIMENTAL

Materials and reagents

The commercial Diazo dyes Acid red 114 was used without purification ($\lambda_{max}=524$ nm). TiCl₄ was obtained from LOBAL chemie, ethanol (absolute alcohol) solution was purchased from Jiangu Huaxi International Trade Co. Ltd, and All other reagents were of analytical reagent grade and were obtained from Sisco Research Laboratories Pvt Ltd. Mumbai. A calculated amount of the dye was dissolved separately in 1L of deionized water to prepare stock solutions (1000 mg/l), which were kept in dark coloured glass bottles.

Synthesis of TiO₂ nano material by sol-gel method

The TiO₂ colloidal solution was prepared by hydrolysis of titanium tetra chloride (TiCl₄). In a typical process, 3.5 ml of titanium tetra chloride was added to 50 ml of deionized water in ice bath and the process was done under fume hood followed by the addition of 35 ml of ethanol with vigorous stirring for 30 min at room temperature. Drop of ammonium hydroxide were added into the solution to neutralize it and precipitate was filtered. After stirring vigorously, the solution was made to settle for twelve hours. Then, precipitate was centrifuged. The obtained precipitate was washed with deionized water until the removals of chloride ion and was centrifugally separated. Then, using oven, the precipitate was dried at 200°C to remove part of the absorbed water for 4 hours and finally amorphous TiO₂ was obtained. The obtained amorphous TiO₂ was calcinated at 700° C four hours step by step. Finally, the powder TiO₂ nanomaterial was obtained [10].

Characterization of TiO₂ Nano materials

There are a large number of methods to characterize TiO₂ nanomaterials. The microstructure of the TiO₂ nanoparticles synthesized by sol gel in the present study was observed by FESEM which is shown in figure.1 . The size of the particle is around 47.23 nm. The shape of the particle is uniform and it looks like spherical in shape and Also the size distribution is almost uniform.

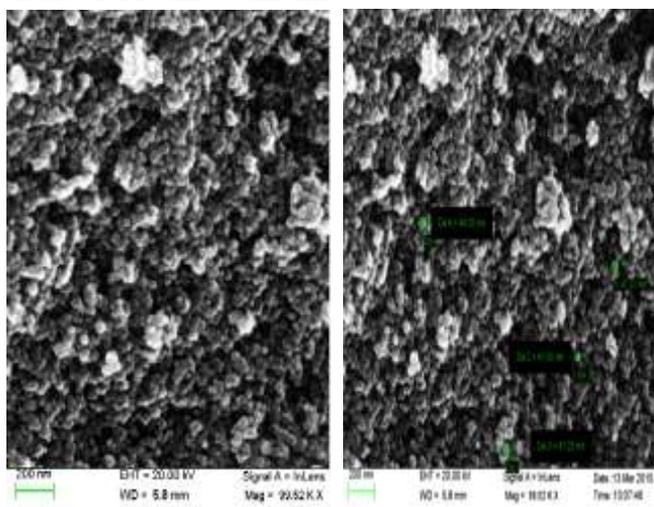


Fig1. (A) SEM image of nano TiO₂ particles, (B) SEM image of nano TiO₂ particles with particles size.

Immobilization of nano TiO₂ on Quartz surface

TiO₂ nano particles were fixed on quartz surface by a heat attachment method. The suspension of nano TiO₂ was chosen so as to get thin adequate deposition. the pH of the solution was adjusted to about 3 using dilute HNO₃ and the

solution was sonicated for 15 minutes. Then quartz tube surface was washed in a basic solution of 1 N NaOH in order to increase the number of OH groups and proper volume of solution was carefully transferred on the quartz surface and allowed to dry out at room temperature for 12 hours. After drying is completed, the quartz tube was calcinated at 475°C for 4 hours. The first coating does not cover all the surface but additional coats gives to a complete coverage. Therefore, this deposition process was carried out twice in order to increase the total thickness. The photocatalysis of the dye has been tested in this quartz surface[11].

2.5. Photoreactor

The experiments were carried out in circulation photocatalytic reactor. The reactor consists of quartz tube which was placed inside the glass reactor fitted with standard joint. The solution to be treated (350 ml of dye solution) was stored in a reservoir and was continuously circulated in the system by a pump at a constant flow rate of 160 ml/min that permitted an optimal distribution of the liquid on the catalytic support. The reservoir was open to air to give sufficient oxygenation. The irradiation was provided by a 15W UV lamp radiating around 365 nm and the lamp was placed inside the quartz tube. Lamp was turned on at the beginning of the each experiment. The reactor was washed after every run by circulating deionized water with few drops of 30% hydrogen peroxide under UV irradiation. So that the immobilized photocatalyst was regenerated.

The degradation was monitored by UV-Visible spectrophotometer in the range of 400-800 nm. A liner correlation was established between the concentration of dye (C) and the absorbance (A) at λ max (524 nm) in the range of dye concentration (C dye) 20-100 mg/l.

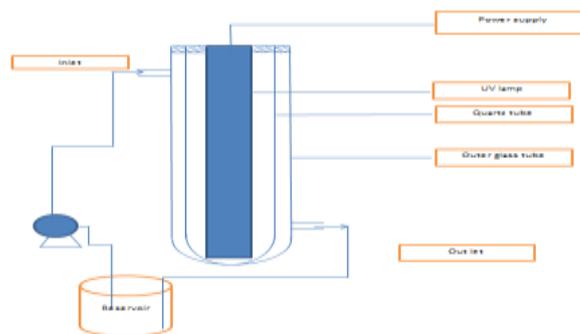


Figure 2. Immobilized circulation photocatalytic reactor used for degradation of textile dyes.

III. Results and Discussion

Effect of irradiation time

The initial concentration of Acid Red was kept at 20 mg/L and the catalyst concentration was 0.6 g/350 ml at pH =

2. At the end of each time, the concentration of solution was determined.

The result showed that the percentage of dye degradation increased when the irradiation time was increased and equilibrium was reached after 80 minutes. The percentage degradation of Acid Red 114 on nanoTiO₂ was found to be fast at the beginning and became slower as the irradiation time was increased until equilibrium was reached. This trend is because the concentration driving force continuously decreases with time t.

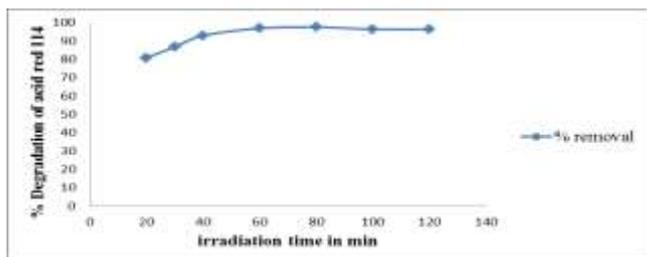


Fig 3. Effect of irradiation time on dye removal (%Degradation vs. Irradiation time)

Effect of pH of the solution

The effect of pH on the degradation of Acid Red 114 on nanoTiO₂ was investigated. The initial dye concentration was kept at 20 mg/L and catalyst concentration at 0.6 g/350 mL. The desired initial pH of the solutions was adjusted by adding 0.1 M HCl or 0.1 M NaOH to vary the pH range from 2 to 12. The suspensions were irradiated for 80 minutes at room temperature of 25°C.

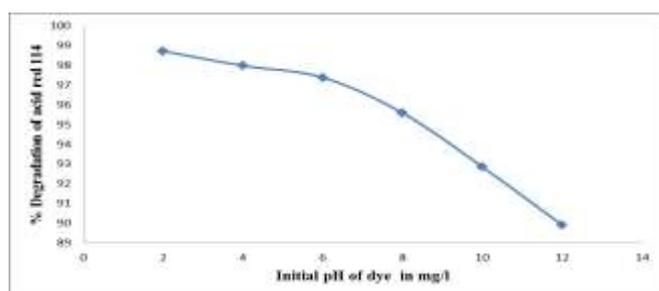


Fig 4. Effect of pH of the solution (%Degradation Vs. Initial pH)

The effect of pH on degradation of Acid Red 114 is given in figure 4. The maximum degradation of Acid Red 114 occurred at pH 2.0 (98.72%) and as the initial pH was increased, the percentage degradation decreased. This is because at low pH, the nanoTiO₂ surface is positively charged and this will lead to a significantly strong electrostatic attraction between the positively charged nanoTiO₂ surface and the anionic dye molecules thus resulting in an increase in dye degradation. Also by increasing the pH of the solution, the number of negatively charged sites on the surface increases. Thus the nano TiO₂ with negatively charged sites will repel the

anionic dye. pH value of 2 was selected for all subsequent studies.

Effect of catalyst concentration

The effect of the concentration of TiO₂ on the degradation of Acid Red 114 was studied by irradiating 350 mL of 20 mg/ L dye solutions with varying catalyst mass from 0.2 g to 1.0 g. All experiments were carried out at constant pH of 2.

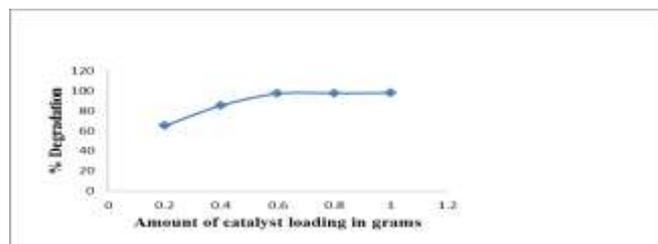


Fig 5. Effect of catalyst loading (% Degradation Vs. Catalyst loading)

The result showed that as the adsorbent mass was increased from 0.2 g to 1.0 g, removal of dye also increased from 64.97% to 97.83%. The increasing trend is because of catalyst increases might be attributed to the increase of surface area and presence of additional available sites. After reaching the equilibrium, the catalyst concentration was inversely proportional to the degradation capacity of TiO₂. This is because of increase in catalyst concentration; UV light does not penetrated into the solution.

Effect of initial dye concentration

Degradation was conducted with series of initial dye concentrations ranging from 20 to 100 mg/L at pH = 2 and catalyst loading of 0.6g in 350 mL of dye solution.

The degradation of Acid Red 114 for different initial concentrations range 20 – 100 mg/L at pH 2 as a function of irradiation time. An decrease in the percentage degradation was observed when the initial concentration of solution was raised.

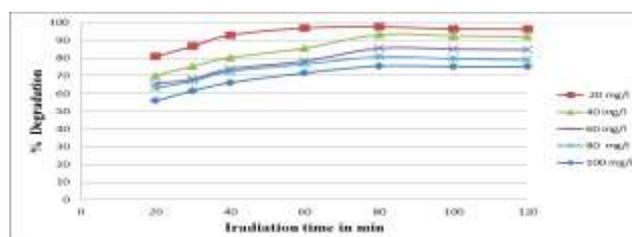


Fig 6. Effect of initial concentration (% Degradation VS. Initial dye concentration)

As initial dye concentration was increased from 20 to 100 mg/L, the percentage degradation decreased from 93.15 %

to75.43. This indicates that the initial concentration strongly affects degradation capacity, Hence the degradation process is improved at lower initial concentration of dye.

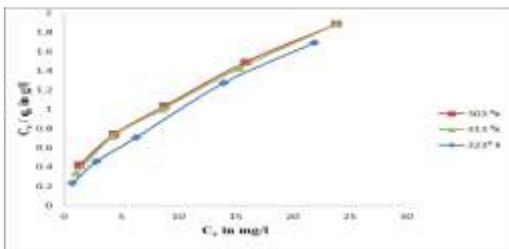
3.5. Adsorption isotherms

3.5.1. Langmuir adsorption isotherm

A well-known linear form of the Langmuir equation can be expressed

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \quad (1)$$

According to above Equation 1, when the adsorption obeys the Langmuir equation, a plot of C_e/q_e versus C_e should be a straight line with a slope of $1/q_m$ and intercept $1/q_m b_L$.



7. Langmuir plot for AR114 on nano TiO₂
 From graph

Temp (K)	Energy of adsorption (b _L) L/mg	q _m in mg/g	R ²	R _L for 20 mg/L
303	0.1502	67.935	0.879	0.249
313	0.1727	0.983	0.839	0.040
323	0.2783	0.971	0.819	0.152

3.5.2. Freundlich adsorption isotherm

The well-known expression for the Freundlich model is given as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

The Freundlich isotherm constants are calculated from the plot of $\ln Q_e$ versus $\ln C_e$.

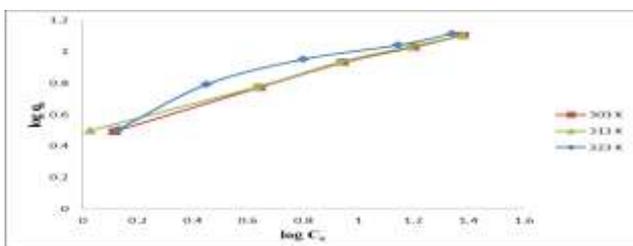


Fig 8. Freundlich plot for AR114 on nano TiO₂

From graph

Temp (K)	K _f	n	R ²
303	3.055	2.220	0.995

313	2.846	2.037	0.997
323	2.566	1.707	0.986

3.6. Kinetic studies

3.6.1. Pseudo-first-order

The linear form of Lagergren's first order rate equation is as follows

$$\ln (q_e - q_t) = \ln q_e - K_1 t \quad (4)$$

K_1 (min⁻¹) is the rate constant of the pseudo-first-order adsorption which can be calculated from the slope of the linear plot of $\ln (q_e - q_t)$ vs. t (slope= K_1 , $q_e = \exp$ intercept).

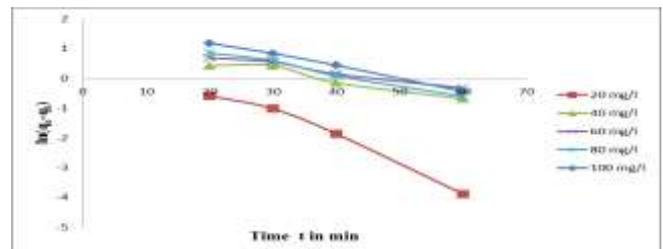


Fig 9. Pseudo first order kinetic plot for Acid Red 114 onto TiO₂.

From graph

Initial conc in mg/l	Pseudo first order			
	q _e exp	k ₁	q _e calc	R ²
(C ₀)				
20	3.251	0.0848	3.825	0.877
40	6.210	0.0301	3.116	0.834
60	8.545	0.0264	3.510	0.881
80	10.753	0.0374	5.138	0.891
100	12.571	0.0409	7.684	0.897

Pseudo second order

The linearized form of the pseudo-second-order model as follows.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

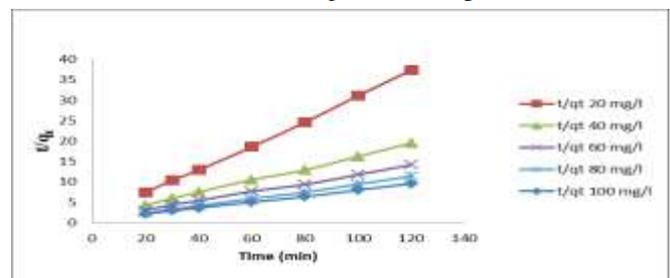


Fig 10. Pseudo second order kinetic plot for Acid Red 114 onto TiO₂.From graph

initial conc in mg/l	Pseudo second order		
	k ₂	q _e	R ²
C ₀			

20	0.010	17.798	0.998
40	0.032	14.428	0.998
60	0.023	19.679	0.99
80	0.009	33.915	0.998
100	0.015	30.102	0.998

The calculated value of k_1 , k_2 , q_e and their corresponding regression coefficient values (R^2) are present in Table. The correlation coefficient are closer to unity for Pseudo second order kinetics than pseudo first order model. This suggests that the adsorption system can be better represented by the pseudo second order model.

4.0. CONCLUSION

This study investigated the degradation of Acid Red 114 onto nano TiO_2 as a function of catalyst concentration, initial dye concentration, pH and irradiation time. The equilibrium and kinetics for the removal of AR 114 by nano titanium dioxide from aqueous solution were studied. The adsorption data fitted best in Freundlich adsorption model. The fitness of Freundlich's model indicated the formation of multilayer coverage of the adsorbate on the outer surface of the adsorbent. The kinetic data agreed well with the pseudo-second order rate equation.

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