

PHOTOCATALYTIC DEGRADATION OF TEXTILE DYE REACTIVE YELLOW 17 IN AQUEOUS SOLUTION BY TiO₂

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Abstract

The Sanganer (Jaipur) has been a pioneer in the textile industry over the last decade. Sanganer is the center of the Rajasthan state's textile industries. Textile industry is one of the world's most water-intensive and chemical industries. In the textile industry, approximately 300 to 500 liters of water are required to make 1 kg of textile fabric. Textile industries include raw material processing and conversion into finished cloths involving a wide range of processes and operations and consume a large amount of water and produce highly polluted waste effluents. In dissolved, colloidal or suspended forms textile effluent contains both inorganic and organic material, and is usually colored due to the presence of dyestic dies. While various physical, chemical and biological treatment methods for textile waste water according to their characteristics are employed.

In the present work, the Photolytic degradation of Commercial Azo Dye (Reactive Yellow 17) was examined by heterogeneous photocatalysis. First of all, we have studied the adsorption of this dye on non-woven TiO₂-coated fibers, to determine optimum conditions for degradation of the dye, the results show that an adsorption balance is reached after 30 minutes of the adsorption cycle. We then discussed the influence of certain experimental parameters, such as initial dye levels, the initial pH for aqueous solution and the addition of H₂O₂ in the solution degradation.

Keywords : Photochemical Treatment , TiO₂Catalyst , Reactive Yellow 17 , Azo Dye , Textile Wastewater

Introduction

The main cause of water contaminations is the textile dyeing process. Wastewater containing processed textile dyes is growing by over 7 x 10⁵ tons, with about 10,000 different types of dyes and pigments being manufactured around the world each year. In effluents during the dyeing processes, 10 to 15 % of the dyeing is estimated to be lost. The regulation of water pollution is critical for both water-borne and productive species. Many dyes to the source of water are hard to break down and cause a lot of cancer problems. Therefore, before final discharge these pollutants are removed from the wastewater.

Azo dyes make up around 50-70% of the available dyes on the market. These can be classified into monoazo, diazo, triazo, and pigments in various groups, according to the existence of one or more azo-bonds (-N = N-). Several studies showed the toxic effect and carcinogenic Azo-dyes. Their non-biodegradability is also due to the high molecular weight and the complex structure of the azo dyes which, due to their electronic deficiencies, are generated by the electric attraction of azo groups, reject oxidant catabolism under aerobic

environmental conditions. These dyes are present in the presence of more than 3.1 µg/L in drinking water which creates health problems for the human being. Different conventional processes for decontamination, whether in physical or chemical processes or in bio-electrical processes, present a major disadvantage in dyeing aqueous pollution into the new phase by the formation of concentrated sludge, thus creating a problem of secondary waste, or leading to a regeneration of materials, often very expensive.

The new development has been made in water treatment with the oxidation of "biologically recalcitrant" organic compounds strongly present in textile release effluent. Such approaches are the advanced oxidation processes (AOPs) which depend on the creation of highly reactive chemical entities that decompose the recalcitrant molecules into biologically degradable molecules or into mineral compounds such as H₂O and CO₂.

Heterogeneous photocatalysis is an important part of these processes. The probability of cleaning up the water and effluents shutting down biological contaminants and to disinfect them. The goal of this study is to display the interest in the degradation of textile dye by heterogeneous

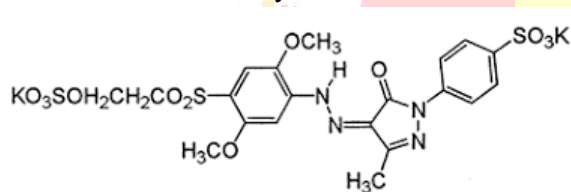
photocatalysis. In this context, the study focuses in view of the application of real effluent cleaner from the textile industry on oxidation of the azo dye RY17 solution.

This dye, due to its high use in the Moroccan textile industry, was selected. The effects on photodegradation in kinetics were also investigated by several experimental parameters (initial RY17 concentration, initial medium pH and addition of H₂O₂).

Materials and methods

Reagent

Without previous purification, the various reagents used in this study were used. The Reactive Yellow 17 is the azo dyeing synthetic organic used by Sigma – Aldrich in the textile industry. Its chemical structure is as following. The following table summarizes the main physico-chemical characteristics of the dye used in this work



Structure of Reactive Yellow 17

Physico-chemical properties of the Remazol Red 133 dye

Dye	Reactive Yellow17
Family	Reactive dye
Brute formula	C ₂₀ H ₂₀ N ₄ O ₁₂ S ₃ .2K
Molecular weight (g/mol)	682.77
λ _{max} (nm)	408
Origin	Sigma-Aldrich
Purity (%)	99.9

The immobilized photocatalyst used in this analysis is titanium dioxide PC500 of the Millennium inorganic chemicals company S.A (anatase: > 99%, special area 350-400 m²g⁻¹). Titania PC500 was filled with an inorganic binder on nonwoven fibers (natural and plastic fibers 254 μm thick). The binder was a colloidal SiO₂ aqueous. For increasing adsorption properties of the photocatalyst a specific area expander (zeolite, 2000 m²g⁻¹) has been used.

Experimental setup

The Reactive Yellow 17 adsorption experiments were conducted at different initial levels between 5 mgL⁻¹ and 40 mgL⁻¹ on the TiO₂ surface. The adsorbed amount is calculated by using the following equation to measure the concentration of the solution before and after adsorption:

$$Q_e = \frac{\Delta C \cdot V}{m}$$

When Q_e (mgL⁻¹) implies the adsorbed quantities of Reactive Yellow 17, the difference is between the original (C₀) concentration and the balances (C_e), V (L) is the volume of the solution and m (g) is the photocatalyst mass. Where Q_e is adsorbed by Q_e (mgL⁻¹) is the amount per unit weight of the photocatalyst in the adsorption balance.

Photodegradation experiments were carried out by loading 500ml of the known photoreactor tin-pin solutions Reactive Yellow 17 (Figure 2) with photocatalytic non-woven tile fibers TiO₂ (11 cm x 25 cm) (equivalent to 1 g of TiO₂) inside of the dye solutions. In the range from 3 to 11,5 the pH was adjusted to a given value with HNO₃. The Merck was obtained by (1N) or NaOH (1N). During one hour and half of this mixture, the Reactive Yellow 17 adsorption equilibrium is formed on the catalyst surface by constant magnetic stirring in the darkness. The reaction mixture is then exposed to UV radiation. At room temperature experiments were performed.

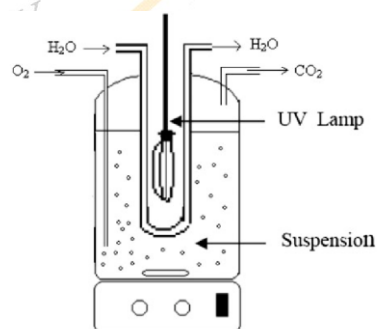


Figure 2 :Photocatalytic reactor used for degradation of textile dyes

The collected samples were filtered with 0.45 μm pore-sized cellulose filters. Using a UV-Vis Spectrophotometer (Jasco V-630), the remaining concentration in the solvent Reactive Yellow 17. The average absorption wavelength (μ_{max}) is 408 nm. The dye curve was calibrated with RY17 concentrations ranging between 5 and 40 mg.

Result and Discussion
adsorption Study

An important step in the process of photocatalytic degradation is the adsorption of the pollutant on the surface of photocatalytic material. We began by researching the adsorption of the titanium-dioxide coated media with the goal of stressing the optimum conditions for the degradation of our colour. Figure 3 displays the adsorption kinetics. The findings show that adsorbed amounts increase with the initial concentration of the photocatalyst (Table 2). This is because a large number of molecules are present which spread towards the locations of the TiO₂ surface.

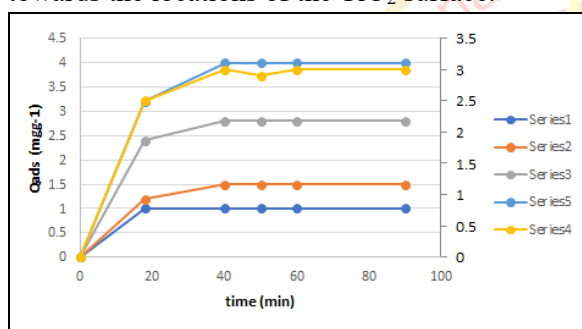


Figure 3 adsorption kinetics of RY17

Series 1 = C₀ = 05 mgL⁻¹ ; Series 2 = C₀ = 10 mgL⁻¹
Series 3 = C₀ = 20 mgL⁻¹; Series 4 = C₀ = 30 mgL⁻¹
Series 5 = C₀ = 40 mgL⁻¹

The figure also shows that the quantity of Reactive Yellow 17 adsorbed in mg gm⁻¹ TiO₂ for the first ten minutes has increased steadily, reaching a constant value of some initial concentration after 30 minutes. Therefore this 30 minute contact time is the time for adsorption balance. The development of repulsive forces between the thinning molecules on the catalyst surface in solution may explain this, preventing the occupation of the vacant surface sites on the surface. On the contrary, the average dimensions of the Reactive Yellow 17 molecules promote quick and easy dissemination into internal pores to saturation, leading to a reduction in mass transfers between liquid and solid phases over time and a subsequent decrease in the amount of adsorption. Therefore, it is important, at least before continuing with photodegrading, to leave the agitation of the mixture.

Table 2. Adsorbed Quantity of Reactive Yellow 17 on the TiO₂ at different initial dye concentration.

Initial Concentration of RY 17	5	10	20	30	40
Q _{max} (mg _{RY17} /g _{TiO2})	1	1.83	2.8	3.25	4

Adsorption Isotherms:

The adsorption isothermal expresses the existing relation between the adsorbed amount and Reactive Yellow 17 concentration in a solvent at a constant temperature at the adsorption equilibrium. Diverse initial concentrations (5, 10, 20, 30 and 40 mgL⁻¹) were carried out in Reactive Yellow 17 adsorption on the TiO₂ surface (Figure 4). In order to understand the adsorption pattern of a solid-liquid system, the adsorption pattern is very important [6]. The adsorption activity of Reactive Yellow 17 was evaluated in this analysis on models Langmuir and Freundlich.

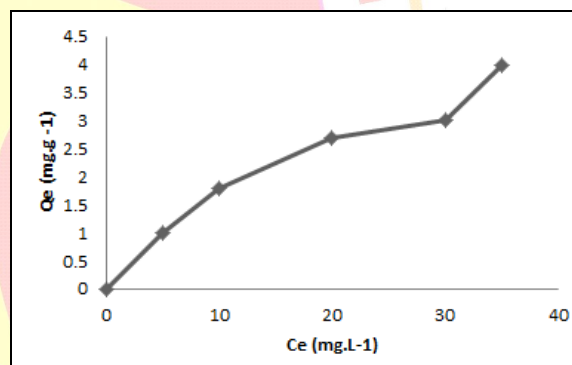


Figure 4: adsorption isotherm of RY17

Several works [7, 8] have shown that the Langmuir model, which is given below, describes the adsorption of a large number of organic compounds on TiO₂:

$$Q_e = Q_{\max} \left(\frac{K_{ads} C_e}{1 + K_{ads} C_e} \right)$$

Where, Q_{max} (mg.gm⁻¹) is the maximum adsorbed quantity and K_{ads} is the equilibrium constant for adsorption.

The linear form of the Langmuir isotherm is given as follows:

$$\frac{1}{Q_e} = \frac{1}{Q_{\max} K_L C_e} + \frac{1}{Q_{\max}}$$

The values of K_L, Q_{max} are calculated from the plot of figure 5, these kinetic constants of equilibrium adsorption are shown in table 3.

The adsorption isotherm of Freundlich is based on the following empirical equation:

$$Q = K_f C_e^{1/n_f}$$

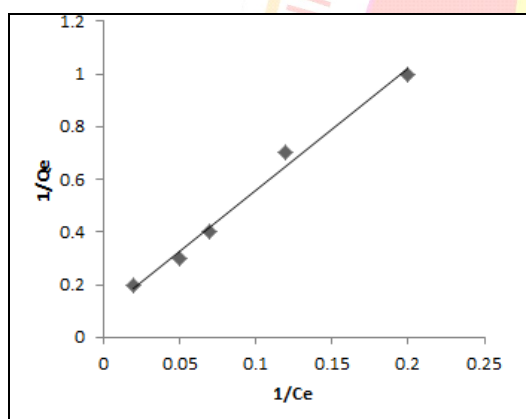
Where, K_f and n are Freundlich constants

The transformed linear allows you to check the validity of the equation we got by using the logarithmic scale

$$\ln Q_e = \ln K_f + \frac{1}{n_f} \ln C_e$$

By plotting $\ln Q_e$ versus $\ln C_e$, we obtain a straight line of slope $1/n_f$ and the intercept $\ln K_f$ (Figure 6).

In the absence of UV light, the adsorption of Reactive Yellow 17 with a TiO_2 obedience, according to its two straight lines, to the Langmuir model, as it has a greater correlation rate than those obtained in the Freundlich model, suggesting an adsorption of a single-layer model.



$$y = 4.0402x + 0.1348$$

$$R^2 = 98.88$$

Figure 5 : Linear transformation of the Langmuir isotherm

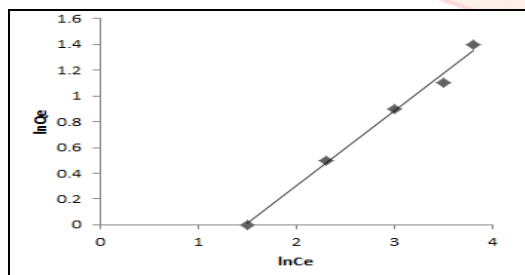


Figure 6 : Linear transformation of the Freundlich isotherm

$$y = 0.6641x - 0.9525$$

$$R^2 = 98.88$$

Table 3. Kinetics Constants of Langmuir and Freundlich

Iso The m	Langmuir isotherm			Freundlich Isotherm		
	Q_{max} (mg.g ⁻¹)	K_L (L.mg ⁻¹)	R_L^2	K_f (mg. g ⁻¹)	n_f	R_f^2
Para metr s	7.418	0.033	99.72	0.386	1.506	98.88

Degradation of Reactive Yellow 17 by heterogeneous photocatalysis

1. Effect of initial dye concentration

The concentration of contaminants is a very important parameter in the procedure, the effect on the photocatalytic degradation rate of the initial concentration of Reactive Yellow 17 was studied at various initial concentrations of the colouration from 5 to 40 mg L⁻¹, and the test results in Figure 7 are shown. With the following exponential function, all concentration profiles may be associated with good consent:

$$C = C_0 \exp(-k_{app} \cdot t)$$

With, C and C_0 (mg.L⁻¹) are the concentration at time t and initial time, K_{app} (min⁻¹) is the apparent rate constant and t (min) is the illumination time.

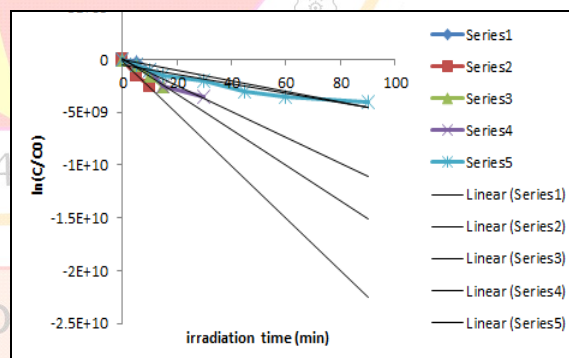


Figure 7: effect of initial RY17 concentration on the removal efficiency; (TiO_2) = 1g.L⁻¹; pH=5; T=22°C
 Series 1 = $C_0 = 05 \text{ mgL}^{-1}$; Series 2 = $C_0 = 10 \text{ mgL}^{-1}$
 Series 3 = $C_0 = 20 \text{ mgL}^{-1}$; Series 4 = $C_0 = 30 \text{ mgL}^{-1}$
 Series 5 = $C_0 = 40 \text{ mgL}^{-1}$

When other parameters remain unchanged, the apparent rate of constant k_{app} above has decreased, with the first concentration of Reactive Yellow 17 increasing. Therefore, the pseudo-first order degradation rate was Through referring to the experimental spectrum of concentration.

2. Effect of pH

Both tests have been conducted in the Reactive Yellow 17 solution natural pH of 5. In order to determine the degradation efficiency assisted by TiO₂, solutions with several value pH (3, 5, 6, 8, 10.5 and 11.5) were tested. Furthermore, the actual industrial effluent that cover a broad range of pH. Figure 8 shows the relation between the apparent constant rate and pH.

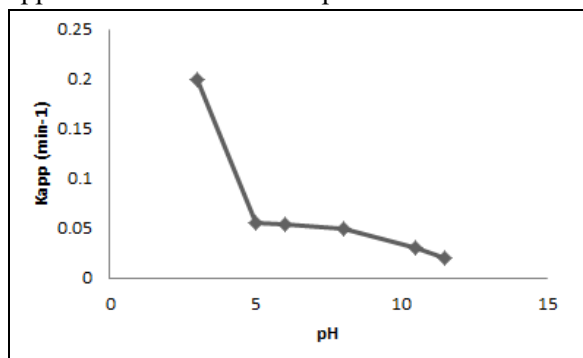
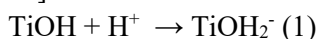


Figure 8: effect of pH on the photodegradation of RY17; (RY17)₀ =30 mgL⁻¹; (TiO₂) = 1gL⁻¹; pH=5; T=22°C

It is clearly seen that the apparent rate constants decreases when pH values increase in order: (pH) 3> 5> 6> 8> 10> 11.

It is known that the metal oxide particles in water present an amphoteric behavior and react readily with the dye by a mechanism which can be described by the following chemical equilibria [10-12]:



The pH of the solution is dependent on the TiO₂ charge. The pH for TiO₂ is approximately 6.3 [13], with zero charge points (PH_{PZC}). Thus, in the acid (pH<pH_{PZC}), TiO₂ is positive and in alkaline conditions negative (pH >pH_{PZC}) charged in the TiO₂ surface (Figure 9)

At a pH below pH_{PZC} the positive charge (1) of TiO₂ surface attracts the Reactive Yellow 17 skeleton negatively charged, resulting in the attraction of (or adsorption) large numbers of coloring molecules on the surface of the paper. When dye concentrations in the surface increases, the tendency for photodegradation also increases, when observed in pH 3 at a pH above pH_{PZC} electrostatic repulsion between negative paper surface charge as shown in (2) and anionic dye skeleton retards dyeing on the surface leading to a

lowering of the photodegradation activity[14]. The effect of dye repulsion on the surface is to increase.

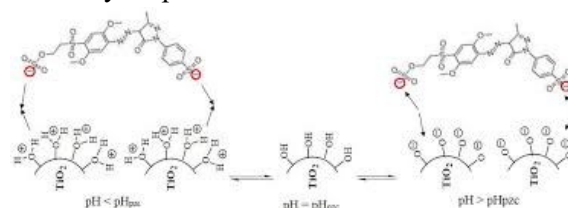


Figure 9: Scheme of interaction between RY17 and TiO₂ as a function of pH

3. Effect of Addition of H₂O₂

The photocatalytic tests in presence of hydrogen peroxide, which were considered a significant generation source of these radicals, were used to highlight the role of hydroxyl radicals (•OH) in color decay[13]. Specific concentrations of H₂O₂ were analyzed in terms of the effect of the concentrations of H₂O₂ on the photocatalytic action of TiO₂ for the photodegradation of Reactive Yellow 17 (Figure 10).

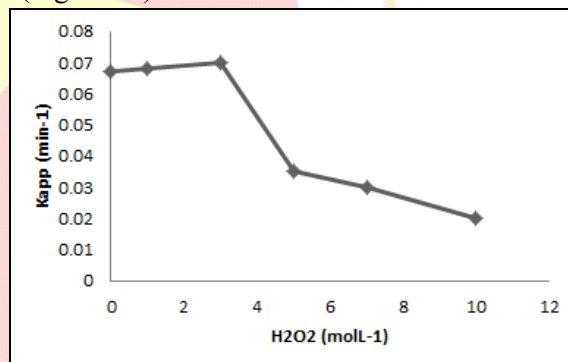
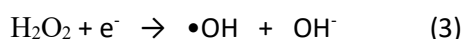
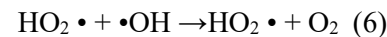
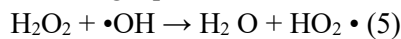


Figure 10: effect of addition of H₂O₂ on the apparent rate constant of photodegradation of RY17; (RY17)₀ =30 mgL⁻¹; (TiO₂) = 1gL⁻¹; pH=5; T=22°C

The results show that with the increase in H₂O₂ concentration from 0 to 3 mol. L⁻¹ then OH decreased 3 to 10 mol. L⁻¹ (Figure 10), which represent the increased development of •OH radicals and also inhibits hole-electric recombination in the following equation [16, 17]: The apparent rate constant increased



While, at high concentrations of H₂O₂, the photocatalytic processes decrease because H₂O₂ is a scavenger for •OH radicals, according to the following equations [18]:



The rate of photocatalytic degradation was decreased at higher concentration of H₂O₂, this negative effect of H₂O₂ at higher concentration may occur due to inhibition of •OH, because at high concentration of H₂O₂, the amount of •OH formed on the surface was increased quickly and hence the annihilation •OH + •OH → H₂O₂ rate which consider faster than the degradation rate of RY17 [19].

Conclusion

The results of this analysis suggest that:

- Langmuir isotherm is a better description of the adsorption balance.
- A pseudo-first order kinetics follows the photocatalytic degradation of Reactive Yellow 17 in aqueous solution by TiO₂-coated non-woven fiber.
- With an increase in pH, the rate of photodegradation decreases, the efficiency is very high at high acidity pH. Because TiO₂ surface adsorption releases OH, which is essential for photocatalysis.
- The additive of an electron acceptor (H₂O₂) increases the decay rates to 3, while the addition of H₂O₂ decreases the rate of photocatalytic decomposition in concentrations over 3.

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