Scientific Research

Factors Influencing the Photocatalytic Degradation of Reactive Yellow 145 by TiO₂-Coated Non-Woven Fibers

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Abstract

The photocatalytic degradation of the synthetic textile dye Reactive Yellow 145 (RY 145) in aqueous solution, using TiO₂ coated non-woven fibers as photocatalyst, under UV-lamp irradiation, was studied. The effects of the operational parameters such as initial dye concentration, pH, addition of oxidant hydrogen peroxide and addition of ethanol on the reaction rate were investigated. The effect of some inorganic ions such as SO_4^{2-}, Cl^-, NO_3^-, CH_3COO^-, HCO_3^- and HPO_4^{2-}, commonly present in real effluents, on the photodegradation of RY 145 was also examined. The experimental results showed that the photocatalytic degradation rate was favoured by a high concentration of solution in respect to Langmuir-Hinshelwood model. The maximum rate of complete decolorization of RY 145 was observed in the acidic medium at pH 3. The presence of SO_4^{2-} and Cl^- anions led to an increase of the effectiveness of the photocatalytic degradation. However, the presence of CH_3COO^-, HCO_3^- and HPO_4^{2-} anions decreased differently the photodegradation reaction rate. TiO₂/UV process was proved to be capable of the complete degradation of the RY 145.

Keywords

Photocatalytic Degradation, Immobilized TiO₂, Reactive Yellow 145, Water Treatment

1. Introduction

Reactive dyes have been most commonly used due to their advantages such as better dyeing processing condi-
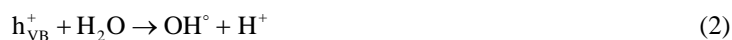
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tions and bright colors. Generally, reactive dyes exhibit a wide range of different chemical structures, primarily based on substituted aromatic and heterocylic groups [1] [2]. However, the release of these colored wastewaters in the environment is a considerable source of non-aesthetic pollution and eutrophication [3]. It is well known that some azo dyes and degradation products such as aromatic amines are highly carcinogenic [4]. Since reactive dyes are highly soluble in water, their removal from wastewater is difficult by conventional coagulation and activated sludge processes [5]. Recently, there has been a considerable interest in the utilization of advanced oxidation processes (AOPs) for the complete destruction of dyes [6]-[11].

Heterogeneous photocatalysis (one kind of AOPs) has been considered as a cost effective alternative for the purification of dye containing wastewater [8] [9]. Moreover, recent studies have demonstrated that photocatalysis can be used to mineralize organic compounds or degrade dyes under UV irradiation [12]-[15]. Titanium dioxide (TiO_2) is one of the most preferable semiconductors for the photocatalytic process [16]-[19]. The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed extensively in the literature [20] [21]. When titanium dioxide (TiO_2) is illuminated with light of band gap energy (3.2 eV), electrons in conduction band $\left(e_{CB}^-\right)$ and holes in valence band $\left(h_{VB}^+\right)$ are produced according to:

$$TiO_2 + h\nu \rightarrow h_{VB}^+ + e_{CB}^- \tag{1}$$

These charge carries can recombine, or the holes can be scavenged by oxidizing species (for example, H_2O, OH^-), and electron by reducible species (for example, O_2) in the solution:

$$h_{VB}^+ + H_2O \rightarrow OH^\circ + H^+ \tag{2}$$

$$h_{VB}^+ + OH^- \rightarrow OH^\circ \tag{3}$$

$$e_{CB}^- + O_2 \rightarrow O_2^{\circ -} \tag{4}$$

The hydroxyl radical (like OH°) is a highly reactive oxidizing reagent and can decompose most organic contaminants [22] [23].

However, the obligation to separate the small TiO_2 particles from the suspension after treatment limits the process development. Alternatively, the catalyst may be immobilized onto a suitable solid inert material, which eliminates the catalyst removal step [4] [24].

In this work, the photocatalytic degradation of Reactive Yellow dye (RY 145), selected as a model organic pollutant, was investigated using a new photocatalytic material, which consists of TiO_2 supported on natural and synthetic non-woven fibers. The investigation of factors that influenced the dye photocatalytic removal was carried out.

2. Materials and Methods

2.1. Materials

All chemicals used in the investigation were of reagent grade and were used without further purification.
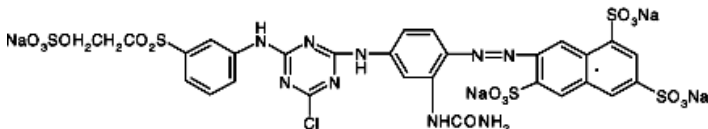
The immobilized photocatalyst used in this study consists in PC500 titania by Millennium inorganic chemicals (anatase: >99%, specific surface area 350 - 400 m^2/g, crystallites mean size = 5 - 10 nm). Titania PC500 was coated on non-woven fibers (natural and synthetic fibers 254 μm of thickness) using an inorganic binder. The binder was an aqueous dispersion of colloidal SiO_2. A specific surface area extender (zeolite, 2000 m^2/g) was used to increase adsorption properties of the photocatalyst.

The RY 145 was obtained from a textile firm as a commercial available dye (C.I. Reactive Yellow 145). The molecular structure and other properties of RY 145 are given in **Table 1**. Solutions were prepared by dissolving requisite quantity of the dye in distilled water. The pH was adjusted to a given value in the range 3 - 11.5 by addition of HNO_3 (1 N) or NaOH (1 N) and was measured using a Schott Titroline pH-meter. The H_2O_2 solution (30%) was obtained from Merck.

2.2. Photocatalytic Reactor

Irradiation was performed in a cylindrical batch reactor opened at air, 8 cm in diameter and 12 cm in working height. The water jacket has a diameter of 5 cm, contains a UV lamp, and permits water circulation. The photocatalytic reactor was covered inside with (11 cm × 25 cm) of the photocatalyst and was exposed to a luminous

Table 1. Properties of RY 145 dye.

Name	Reactive Yellow 145 (RY 145)
Nature	Anionic reactive dye
λ_{max} (nm)	419
Molecular weight (g/mol)	1026.2
Reactive group	Sulfatoethyl sulfone
Molecular structure	

source (an HPK 125 W Philips ultraviolet lamp with a wavelength maximum of 365 nm), placed in axial position inside the water jacket. The reactor was stirred continuously at a low setting, 100 rpm, by a magnetic stirrer.

2.3. Procedure and Analysis

The photodegradation experiments were carried out by loading 500 ml of the dye solutions in the photocatalytic reactor. The effect of initial concentration was obtained with different initial dye concentrations (5 - 40 mg/l) at initial pH. The effect of pH was carried out by varying the initial pH of aqueous solution from 3 to 11.5, with an initial concentration of 30 mg/l. In all experiments, the solution of RY 145 L was magnetically stirred in presence of TiO$_2$ in the dark during 45 min to reach the adsorption equilibrium before UV irradiation. The temperature was maintained at 20°C.

The RY 145 aqueous solutions were filtered by Millipore membrane filter type 0.45 μm, and the concentrations were determined from UV-Vis absorbance characteristic with the calibration curve method. A Jasco V-630 UV/Visible spectrophotometer was used.

The percentage decolorization was calculated as follows:

$$\% \text{ Decolorization} = 100 \times (C_o - C)/C_o$$

where C$_o$ = initial concentration of dye solution, C = concentration of dye solution after photoirradiation.

3. Results and Discussion

3.1. Effect of Initial Concentration

The effects of the initial concentration of RY 145 dye on the photocatalytic efficiency were investigated with concentrations from 5 to 40 mg/l (**Figure 1**).

It was found that on increasing the dye concentration the degradation efficiencies of dye decreases. Hence, the photo-oxidation process will work faster at a low concentration of pollutants. These results are in agreement with previous reports [17] [25] [26] that photodegradation of textile dye RY 145 decreased with increasing concentrations. At high concentrations of dye, the deeper colored solution would be less transparent to UV light and the dye molecules may absorb a significant amount of UV light causing less light to reach the catalyst and thus reducing the OH° radical formation.

The effect of the initial concentration of the initial rate of the photocatalytic degradation of RY 145 is represented by curve of **Figure 2**. These initial results indicate that the degradation rate increases with the initial concentration. The shape of the curves is similar to that obtained in the kinetic model of Langmuir-Hinshelwood (L-H) [27] and expression of the initial rate of which is given by the following equation:

$$r_o = \frac{k K C_o}{1 + K C_o} \tag{5}$$

where r$_o$ is the initial degradation rate of RY 145 (mg/l min), *k* is the observed degradation rate constant relating to TiO$_2$-catalysed primary oxidation events on a surface monolayer (mg/l min), and K is a pseudo-equilibrium
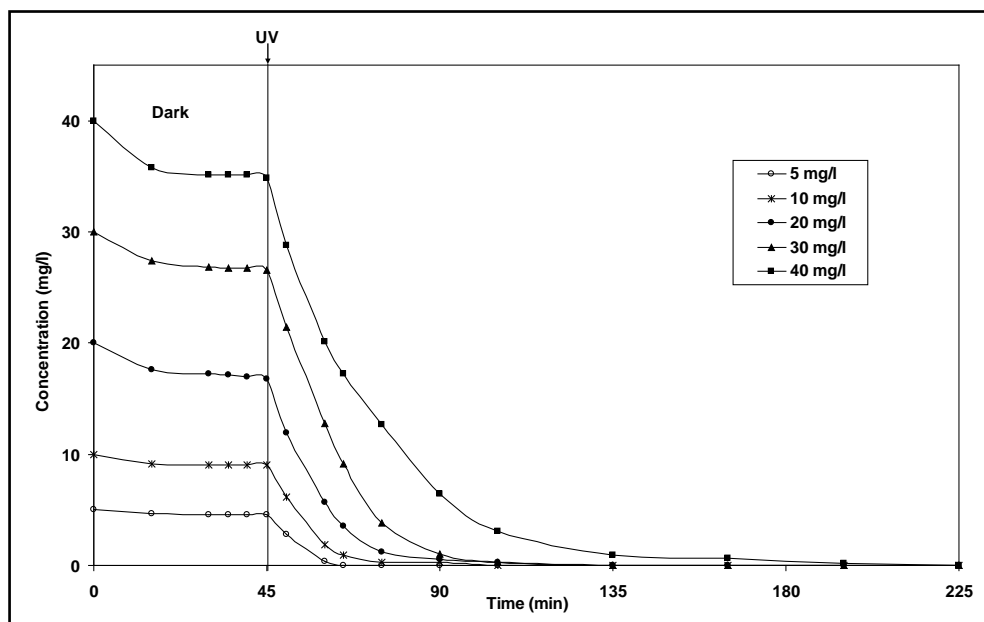
Figure 1. Effect of the initial RY 145 concentration on photodegradation efficiency.
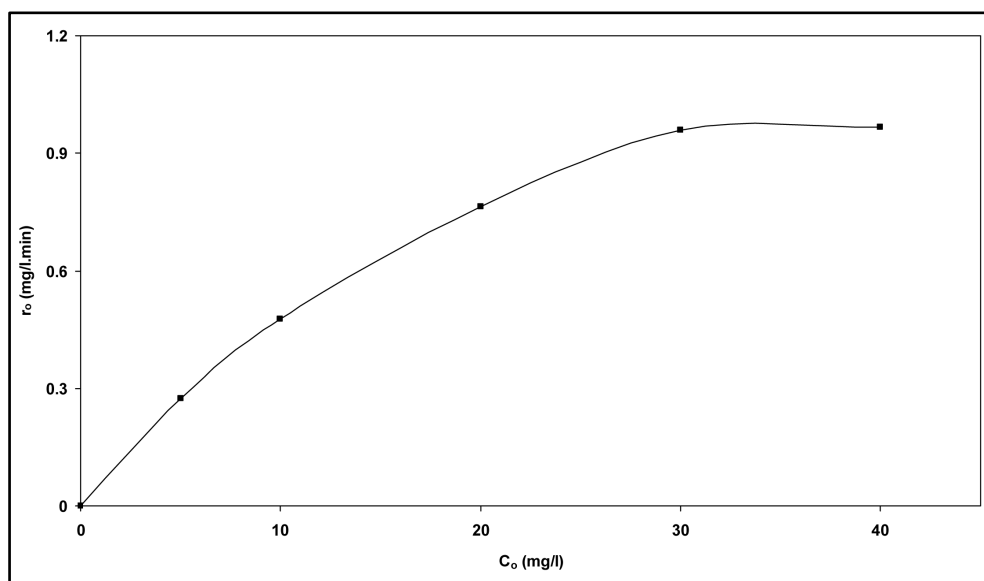

Figure 2. Effect of initial RY 145 concentration on the initial rate of degradation.

constant related to the monolayer adsorption (l/mg). Rearrangement Equation (5) it can be observed that linear relationship exists between the reciprocal initial rate and the reciprocal initial substrate concentration (Equation (6)):

$$\frac{1}{r_o} = \frac{1}{k} + \frac{1}{kKC_o} \tag{6}$$

In **Figure 2**, it is shown that the initial degradation rate (r_o) increases at the beginning of the run, when the concentration of RY 145 is increased until it attains a plateau, at around 30 mg/l. This behaviour indicates saturation-type Langmuir kinetics. This is confirmed by the linear plots of $1/r_o$ versus $1/C_o$ (see **Figure 3**). The calculated value of K and *k* were 0.037 l/mg and 1.74 mg/l.min, respectively. Such a Langmuir-Hinshelwood type relationship between the initial degradation rate and the concentration, has been also reported by other au-
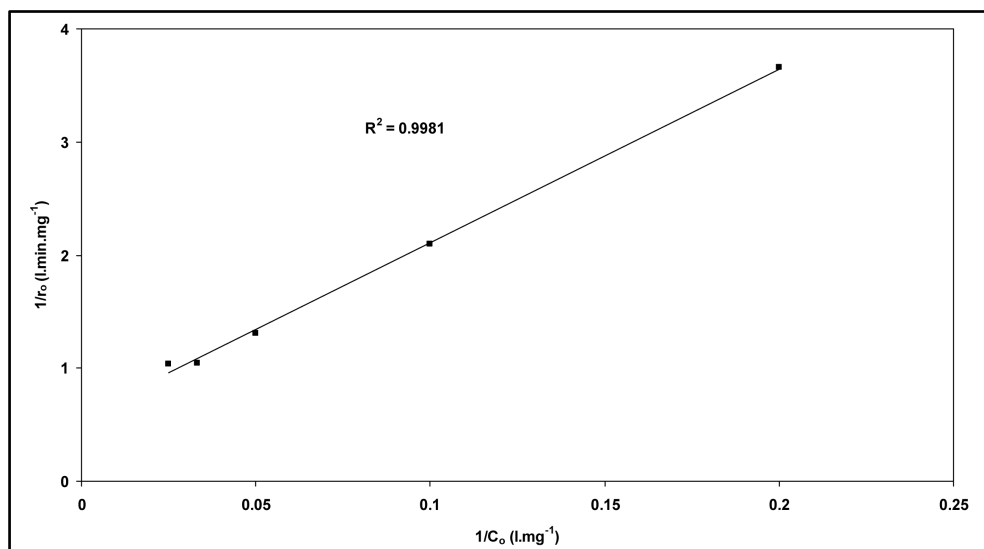
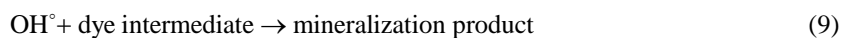**Figure 3.** The linear transformation of $1/r_o$ vs. $1/C_o$.

thors [27] [28]. This type of reaction kinetics suggests that the adsorption plays a key role in the photocatalytic degradation mechanism.

3.2. Effect of pH

An important parameter in the photocatalytic reactions taking place on the particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms. It is well known that pH value has an influence on the kinetic of degradation of some organic compounds in photocatalytic processes [27]-[29]. Therefore, the degradation of the pollutant was studied at different pH values (in the range 3 - 11.5). **Figure 4** shows the color removal efficiency of RY 145 as a function of pH. The experimental results revealed that higher degradation of RY 145 was found to be in acidic conditions. The maximum decolorization was observed at pH 3. This may be attributed to the electrostatic interactions between the positive catalyst surface and dye anions leading to strong adsorption of the latter on the metal oxide support. Similar behavior has also been reported for the photocatalytic efficiency of TiO_2 for decolorization of azo dyes [16] [29] [30]. Moreover, the positive holes are considered as the major oxidation species at low pH which react with hydroxide ions forming hydroxyl radicals, thus the efficiency of process is enhanced. At increased pH, there is a columbic repulsion between negatively charged surface of catalyst and the hydroxide anions which prevent the formation of $OH°$ and decrease the photocatalytic degradation [31].

3.3. Effect of Addition of H_2O_2

The addition of H_2O_2 was regarded as a good parameter for enhancement of photocatalytic degradation process [32]. The results as shown in **Figure 5**, indicate that the hydrogen peroxide had accelerated the photocatalytic degradation of RY 145. The photocatalytic degradation rate of RY 145 increased when hydrogen peroxide concentration increased from 0 to 3 mol/l. The maximum degradation is achieved at H_2O_2 concentration of 3 mol/l. This could be due to the production of hydroxyl radical $OH°$ by photodissociation of H_2O_2 which is acting as strong oxidant and as electron scavengers [33].

$$H_2O_2 + e^- \rightarrow OH^- + OH° \tag{7}$$

$$OH° + dye \rightarrow dye\ intermediate \tag{8}$$

$$OH° + dye\ intermediate \rightarrow mineralization\ product \tag{9}$$

Moreover increasing of hydrogen peroxide concentration, more than 3 mol/l, decreased the rate of photocatalytic degradation that could be due to by scavenging effect. However, High concentration of H_2O_2 inhibits catalytic activity as H_2O_2 is adsorbed onto TiO_2 [11].
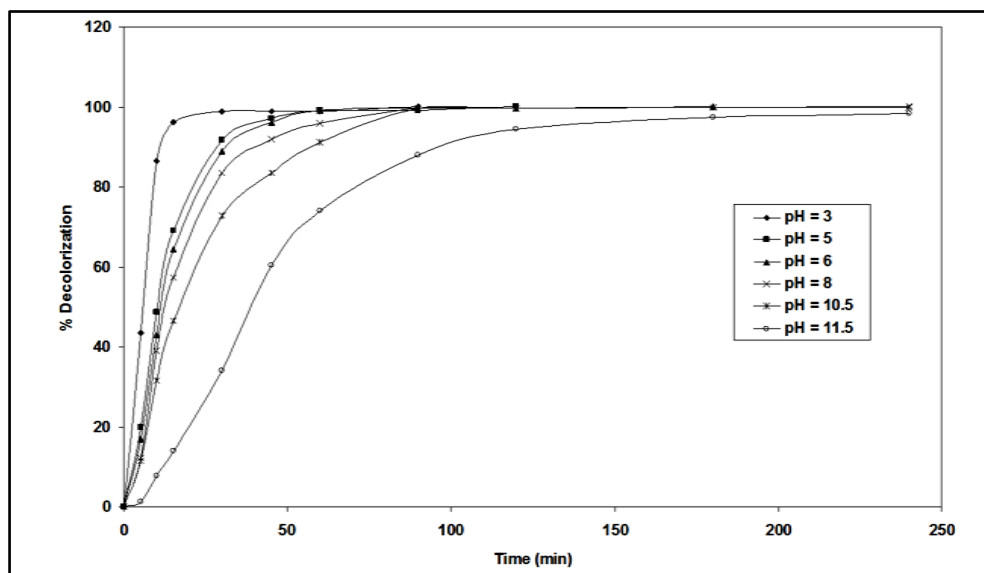
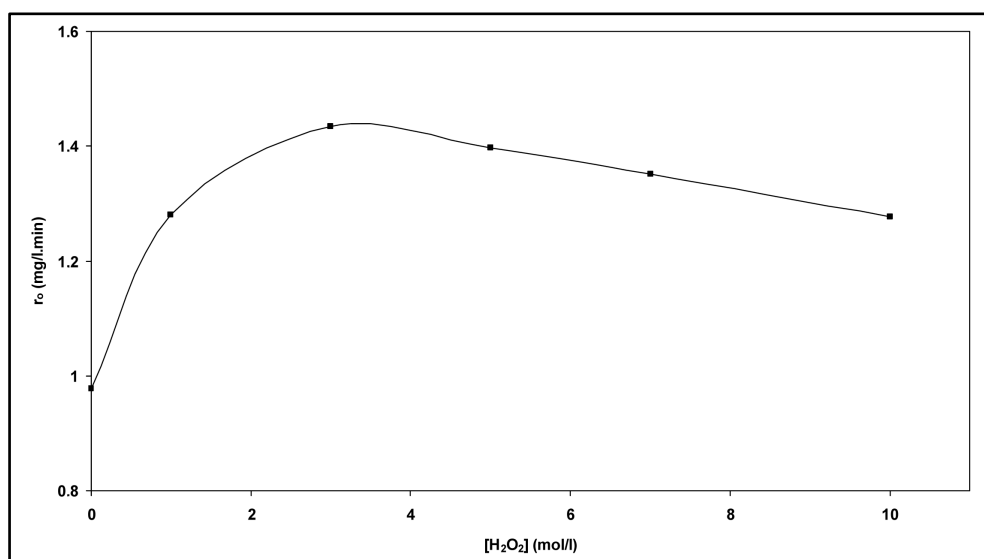**Figure 4.** Effect of pH on decolorization rate of RY 145 dye (C_o = 30 mg/l).

Figure 5. Effect of H_2O_2 concentration on photocatalytic degradation of RY 145 (C_o = 30 mg/l).

$$H_2O_2 + OH^° \rightarrow H_2O + HO_2^° \tag{10}$$

$$HO_2^° + OH^° \rightarrow H_2O + O_2 \tag{11}$$

3.4. Effect of Ethanol

It is well known that in the photocatalytic degradation process two main species have the major contributions; electrons and holes $\left(h_{VB}^{+}, e_{CB}^{-} \right)$ and hydroxyl radicals. In order to evaluate these two paths, experiments were performed by adding different amounts of ethanol to the solution. Alcohols such as ethanol are commonly used to quench hydroxyl radicals [11] [32] [34]. As it is observed from **Figure 6**, adding small amounts of ethanol, up to 2 ml of ethanol, decreases the degradation efficiency of RY 145. On the other hand, adding extra amount of ethanol leads to a mild increase in the process efficiency due to the formation of ethoxy radicals ($C_2H_5O^°$) from direct photocatalytic oxidation of ethanol; meanwhile, the ethanol molecules can produce hydroxyl radicals in direct photolysis with respect to the level of C-O energy bond.
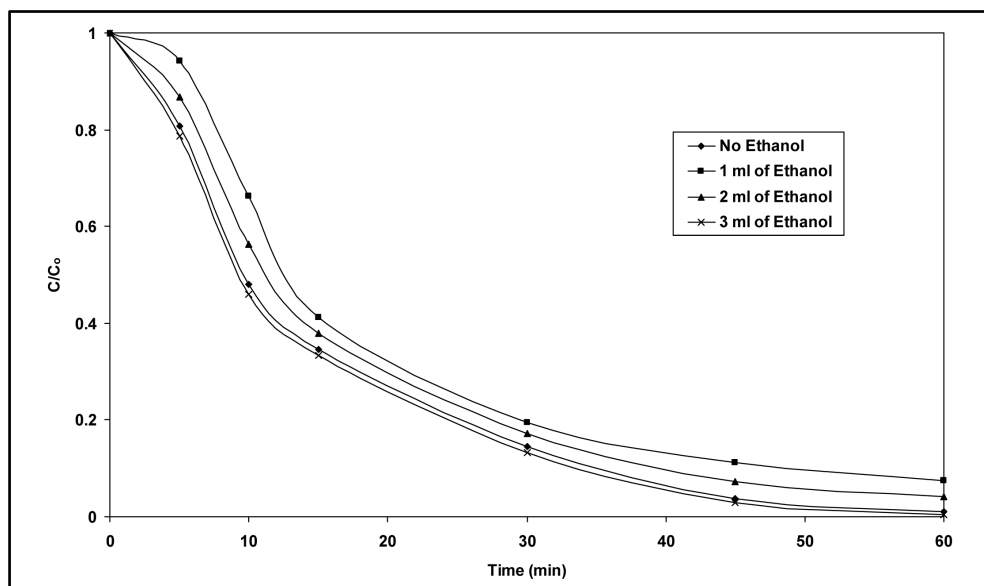
Figure 6. Effect of ethanol on the photocatalytic degradation of RY 145 (C_o = 30 mg/1).

3.5. Effect of Some Ions

The photocatalytic degradation of dyes is also performed in the presence of inorganic anions [35] [36]. They are generally present in industrial discharges with values depending on the nature of the effluent. In this study, the effect of SO_4^{2-}, Cl^-, NO_3^-, CH_3COO^-, HCO_3^- and HPO_4^{2-} (sodium salts) in the order of 10^{-3} mol/l was investigated. As shown in **Figure 7**, the presence of SO_4^{2-} and Cl^- anions leads to an increase of the effectiveness of the photocatalytic degradation. However, the presence of CH_3COO^-, HCO_3^- and HPO_4^{2-} anions decreases differently the photocatalytic efficiency.

For HPO_4^{2-} ions, it's well known that they are strongly adsorbed on the surface of TiO_2, and therefore, they compete with the adsorption of RY 145 on the surface of the photocatalyst. They can also scavenge OH° to form the corresponding anion radicals $HPO_4^{-\circ}$, which leads to the decrease of the oxidation process [36].

The inhibitory effect of HCO_3^- ions can be explained by a competition with the adsorption of dye on the surface of TiO_2 (capture OH° radicals to produce $CO_3^{-\circ}$ less reactive).

$$HCO_3^- + OH^\circ \rightarrow CO_3^{-\circ} + H_2O \tag{12}$$

Some authors explain this effect by blocking the active sites of the catalyst [37].

The reduction of the photocatalytic degradation in presence of CH_3COO^-, which is used to reduce the alkalinity of the effluent in dyeing section, can be explained by the "photo-kolbe" reaction (Equation (13)) [38], which inhibits the formation OH° radicals via Equations (14) and (15) on the surface of the photocatalyst.

$$CH_3COO^- + h^+ \rightarrow CH_3^\circ + CO_2 \tag{13}$$

$$h^+ + H_2O \rightarrow OH^\circ + H^+ \tag{14}$$

$$h^+ + OH^- \rightarrow OH^\circ \tag{15}$$

The effect of Cl^- on the oxidation process can be explained by the result of the reaction of photo-produced OH° with Cl^- [28]:

$$OH^\circ + Cl^- \rightarrow Cl^\circ + OH^- \tag{16}$$

The Cl° radicals are in principle also capable of oxidizing pollutants and to participate in process of degradation. However, the generation of Cl° radicals leads also to the formation of chlorinated organic compounds, which are known as very harmful substances.

For SO_4^{2-} ions, they are adsorbed in the surface of TiO_2 and consequently react with photo-induced holes (h^+) [38]:
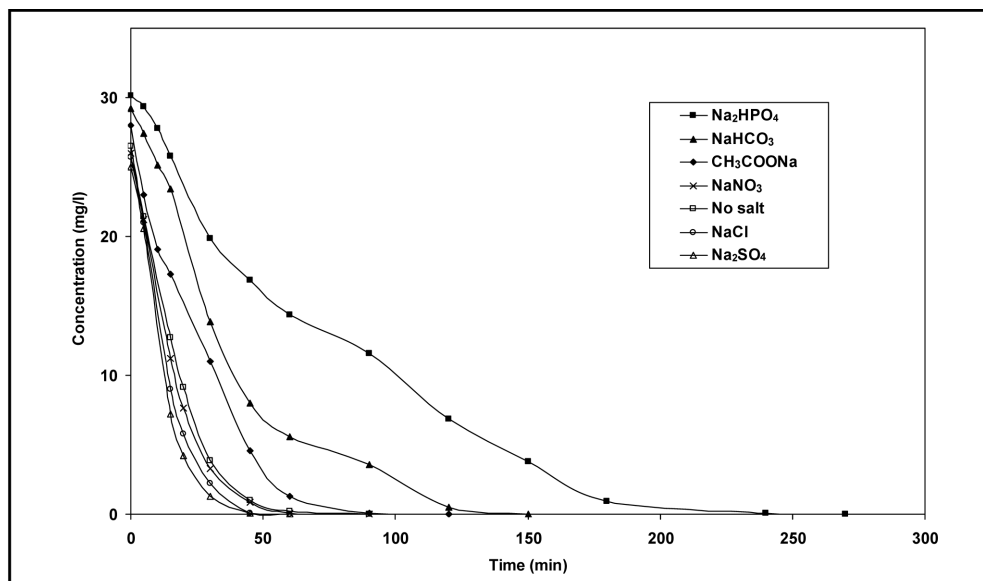
Figure 7. Effect of anions on the photodegradation of RY 145 (C_o = 30 mg/l).

$$h^+ + SO_4^{2-} \rightarrow SO_4^{-\circ} \tag{17}$$

The sulphate radical anion $\left(SO_4^{-\circ}\right)$ formed is a strong oxidant, and engages in the three possible modes of reactions with organic compounds: 1) by abstracting a hydrogen atom from saturated carbon; 2) by addition to unsaturated or aromatic carbon; and 3) by removing one electron from the carboxylate anion and from certain neutral molecules.

Regarding nitrate ions, it has been shown that they adsorb weakly on the surface of titanium dioxide and, thus, little effect on photodegradation of RY 145. According to Lucas Vaz *et al*. [39], these ions generate OH° radicals in the presence of sunlight according to the following equation:

$$NO_3^- \xrightarrow{h\nu} \left(NO_3^-\right)* \xrightarrow{H_2O} NO_2^\circ + OH^\circ + OH^- \tag{18}$$
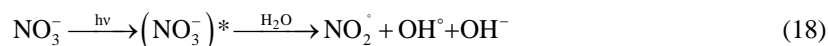
4. Conclusion

Photocatalysis has been ascertained to be a promising technique for the removal of dyes from industrial effluents. In the present investigation, a complete removal of reactive yellow 145 on TiO_2 coated non-woven fibers has been processed with the help of Langmuir-Hinshelwood model. The study reveals that the photocatalytic degradation of synthetic wastewater of RY 145 dye made with TiO_2 coated non-woven fibers depends on the initial concentration of dye, pH, concentration of hydrogen peroxide, addition of the ethanol and inorganic ions. It was shown that complete degradation can be achieved. The maximum efficiency of decolorization is at acidic pH. The maximum amount of dark surface adsorption is observed at pH of 3. Moreover, with addition of oxidant H_2O_2 into illuminated TiO_2, a synergistic effect that leads to an enhancement and improvement of the efficiency of the process is observed. Our results showed that ethanol (2 ml) inhibited the photodegradation of dye; we concluded from the inhibitory effect of ethanol that hydroxyl radicals played a major role in photocatalytic degradation of RY 145 in the time. The presence of SO_4^{2-} and Cl^- ions increased the photodegradation rate while, CH_3COO^-, HCO_3^- and HPO_4^{2-} decreased the reaction rate. The use of TiO_2 coated on non-woven fibers is an efficient photocatalyst to degrade textile dye avoiding the tedious filtration step.

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