



Application of TiO₂/UV-C Photocatalytic Process in Removal of Reactive Red 198 Dye from Synthetic Textile Wastewater

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Owing to high volume of dye in their wastewater, textile industries are one of the main industries which pollute the environment. Reactive dyes which are widely used in textile industries have complex structure, are mainly toxic and cannot be purified using classical methods of wastewater treatment. The aim of this research was to study the effects of operating parameters on photocatalytic degradation of reactive red 198 (RR198) using TiO₂/UV-C photocatalytic process. This study was carried out in laboratory scale and in batch system. The synthetic wastewater was prepared from dissolution of reactive red 198 dye in city drinking water and the effect of initial dye concentration, TiO₂ dose, pH solution and contact time were examined. The dye concentration was determined using spectrophotometer in wavelength of 518 nanometers. The results revealed that as TiO₂ dose increases from 0.4-1.0 g/L, the dye removal efficiency increases from 97-100 %. However, as initial dye concentration increases from 100-250 mg/L and as pH increases from 4-10, the removal efficiency decreases from 100-97 and from 100-94, respectively. The best dye removal efficiency was achieved in pH solution: 4. The highest removal efficiency of reactive red 198 dye is best achieved through photochemical and photocatalytic processes in acidic conditions; among them, photocatalytic processes are the most effective ones. The kinetic study showed that the reactive red 198 by TiO₂/UV-C photocatalytic was followed to first order kinetic as well as other kinetic models.

Key Words: Photocatalytic degradation, UV-Ray, TiO₂, Reactive red 198 dye.

INTRODUCTION

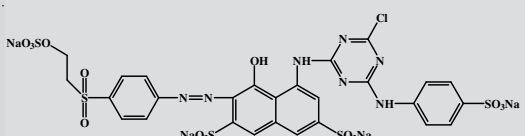
Textile industries consume a huge amount of water during dyeing, printing and washing. Their water consumption is between 25 and 250 m³ per ton of product (regarding the type of production process)^{1,2}. Studies show that about 40 million tons of textiles are produced every year in the world and the annual effluents produced in these industries³ are about 4-8 million m³. Dye is the most prominent pollutant of wastewater produced in textile industries and other similar industries; due to its undesirable health and environmental effects, it is taken into high consideration⁴. Two main dyeing and finishing steps in textile industries create significant volume of effluents with high dye concentration. During dyeing process, more than 50 % of dyes may enter the effluents^{5,6}. Due to various consumed dyes and production methods, textile industries produce effluents with different chemical quality and quantity. Wastewater

produced by these industries have significant levels of dye which is mainly toxic, non-biodegradable and resistant in environment. Thus, most conventional biological processes are not effective in removing synthetic dyes available in these effluents due to complex aromatic structure and resistant nature of dyes⁷⁻¹⁰. Other treatment processes like adsorption process, coagulation and flocculation processes aren't suitable methods because they produce solid waste or sludge with high concentrations of dye; for, unsuitable removal of this waste can cause serious environmental problems^{11,12}. One of the newest methods used to remove various pollutants from wastewater is advanced oxidation processes. Among these processes, photocatalytic process (which uses nano-particles) is a new technology which has successfully been used in several studies to remove dyes from textile industries. The work basis of advanced oxidation processes is the production of active hydroxyl radicals. This oxidant radical has a very strong affinity *i.e.*, if

hydroxyl radicals react with organic materials, carbon dioxide and water are produced as harmless final products¹³⁻¹⁷. In photocatalytic oxidation process, when a high energy photon collides with TiO₂, one electron from outside orbital of valence layer is transferred to the conductive layer. Potential difference of these two layers is called band gap, whose level is 3.2 electron volts for TiO₂. Then, various reactions occur to produce very active types of hydroxyl radicals; these radicals have high oxidation powers and can oxidize most dyes to final mineral products^{18,19}. The aim of this research was to study the efficiency of TiO₂/UV-C in removing reactive red 198 dye from synthetic textile wastewater, to determine the effect of pH, radiation time, TiO₂ mass, initial dye concentration and to determine optimal conditions for removing the above-mentioned dye using this process.

EXPERIMENTAL

All chemicals were used in this study purchased from Merck Company with analytical grade. In this work, the chemical solutions were prepared using deionized water and the stock of dye solution using city drinking water. The amount of dye was measured by spectrophotometer (Optima SP-3000 Plus, model UV/VIS, Japan) according to "Standard Methods for the Examination of Water and Wastewater". For pH measurement and homogenize TiO₂ suspension in aqueous solutions, the electronic pH meter (Hach-HQ40D) and ultrasonic bath equipment (Starsonic model 18-35) was used, respectively. The characteristics of reactive red 198 dye was summarized in Table-1.

| TABLE-1 CHARACTERISTICS OF ANIONIC REACTIVE RED 198 (RR-198) DYE | |
|--|--|
| Chemical structure |  |
| m.f. | C ₂₇ H ₁₈ ClN ₇ Na ₄ O ₁₅ S ₅ (m.w. 967.5) |
| λ _{max} | 518 |

The characteristics of TiO₂ nanoparticles (P 25) that was prepared from German Degussa Company were listed in Table-2.

| TABLE-2 CHEMICAL AND PHYSICAL CHARACTERISTICS OF TiO ₂ NANOPARTICLES | | |
|---|-------------------|---------|
| Characteristics | Unit | Value |
| Specific surface level | m ² /g | 15 ± 40 |
| Particles initial size | nm | 21 |
| pH (4 % mixture) | – | 4.5-3.5 |
| Purity | % | ≥ 99.5 |
| Al ₂ O ₃ | W (%) | ≤ 0.3 |
| SiO ₂ | Weight per cent | ≤ 0.2 |
| Fe ₂ O ₃ | Weight per cent | ≤ 0.1 |

TiO₂/UV-C photocatalytic reactor set up: All the experiments were performed in a batch system and Fig. 1 illustrating

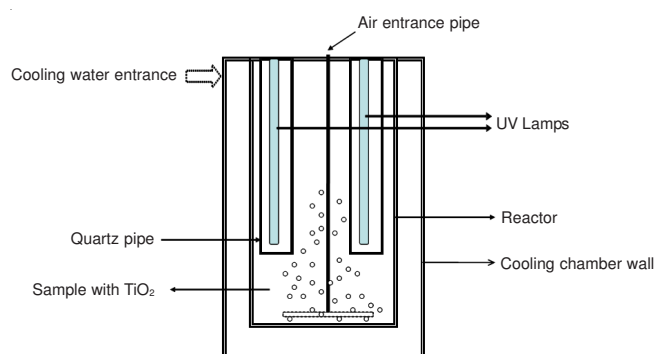


Fig. 1. Schematic of photocatalytic reactor

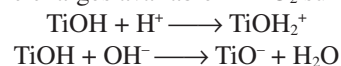
the schematic design of the photocatalytic reactor. The reactor was made of plexiglass with working volume of 1.7 L that equipped with two UV-C (15 W) lamps with quartz coating (diameter: 30 mm, length: 490 mm). For prevention of the temperature variation, whole body of reactor was placed in a cooling chamber.

Experiments: In order to determination optimum conditions of TiO₂/UV-C photocatalytic process on reactive red 198 dye, effect of TiO₂ dose (0.4, 0.6 and 1.0 g/L), initial concentrations of reactive red 198 dye (100, 150 and 200 mg/L), contact times (30, 60, 90, 120, 150 and 180 min) and pH solutions (4, 7, 10) was tested. All the experiments were conducted at laboratory temperature (25 ± 0.5 °C). In order to separation TiO₂ from solution, the cellulose acetate membrane filter (0.2 μm pores size) was used.

RESULTS AND DISCUSSION

Effect of pH solution: The obtained results from the effect of pH on removal efficiency of reactive red 198 dye are shown in Fig. 2. It is showed that with increasing the pH solution, the reactive red 198 dye removal efficiency by UV-C photooxidation was decreased. The highest removal efficiency was observed at pH solution of 4. Moreover, as contact time increases from 0-180 min, the dye removal efficiency was increased. Concerning the application of TiO₂ nanoparticle, as pH decreases, dye removal efficiency increases. The highest removal efficiency is observed at pH: 4 and as contact time increases, the efficiency increases too. Results obtained from application of TiO₂ and UV-C photocatalytic oxidation revealed almost equal trend in all three pH ranges. They also showed that as the contact time increased to 100 min, efficiency trend increased and then reached a plateau and was equal in all pH range.

The pH value of the solution is one of the most important parameters which affect pollutant removal efficiency through the effects on pollutant ionization status and surface properties of catalytic factors used in systems. Results showed that changes in pH had significant effects on dye removal level. The reason may be related to the effects that pH has on surface properties of TiO₂ nanoparticles and pollutant ionization conditions. Studies have shown that changes in pH can, according to the following equations, affect the surface properties or electric charges available in TiO₂ surface.



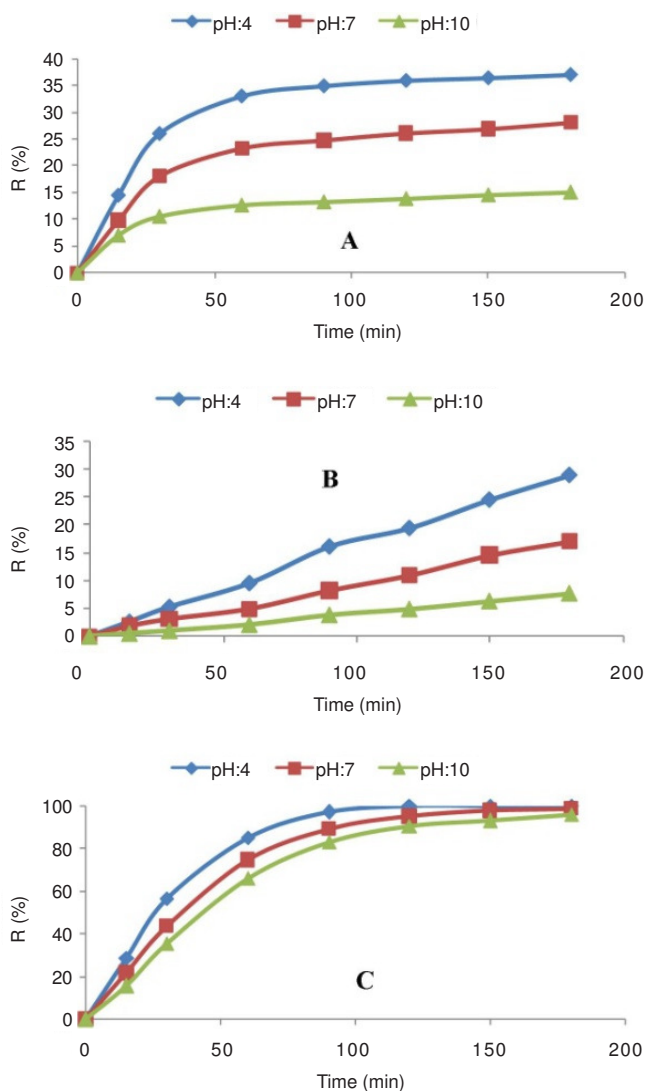


Fig. 2. Effect of pH on reactive red dye 198 removal: (A) TiO₂ adsorption (TiO₂ dose: 0.4 g/L, C₀: 100 mg/L), (B) UV-C photooxidation (C₀: 100 mg/L) (C) TiO₂/UV-C photocatalytic

As shown in Fig. 4, as pH increases from 4-10, dye removal level decreases. The reason can be related to the effect of this factor on changing dominant electric charge on TiO₂ surface. Since pH ZPC of TiO₂ used in this research was 6.3, it can be concluded that pH < pH ZPC (e.g., pH: 4) of electric charge on the surface of TiO₂ was positive and resulted in more adsorption of this pollutant on TiO₂ surface. Since hydroxyl free radical is produced as a result of stimulation of TiO₂ surface, more adsorption of pollutant on its surface will cause the radicals (produced at TiO₂ surface) to affect dye molecules sooner and to remove it²⁰. In higher pH, however, dominant electric charge on TiO₂ surface is negative and it creates electrical repulsive force between reactive red dye 198 and like electric charges available on photocatalyst surface; thus, dye removal efficiency decreases. Such results have also been reported by Kaur and Singh¹. Reviewing the effect of pH on removal level of reactive red dye 198, other researchers like Wu²⁰ concluded that as pH increased from 4-10, removal efficiency decreased from 98-35 % which conforms to the results of this research. He also believed that high efficiency in acidic conditions was related to effect of pH in surface charge of TiO₂ particles. The reason

is related to the nature of photocatalytic process in various pH. Accordingly, it can be concluded that TiO₂/UV-C is more effective in degradation of reactive red dye 198 than UV-C single process and this effect increases in acidic conditions. Thus, other parts of the study were performed in acidic conditions and pH: 4. Although pollutant removal level in acidic conditions is more than that of other pH conditions, synergic effect of UV-C/TiO₂ mixed process in this pH is less than other pH conditions. The reason of low synergy in acidic pH than in alkaline and neutral conditions is that in this condition UV-C single process affects dye removal significantly [reaction rate consonant proves these results (Table-3)].

TABLE-3
SYNERGY EFFECT OF TiO₂/UV-C
PHOTOCATALYTIC PROCESS ON DYE REMOVAL

| pH | C ₀ (mg/L) | TiO ₂ (g/L) | k _{TiO₂} | K _{UV-C} | k _{TiO₂+UV-C} | Synergy |
|----|--------------------------|---------------------------|------------------------------|----------------------|-----------------------------------|---------|
| 4 | 100 | 0.4 | 2×10 ⁻³ | 1.9×10 ⁻³ | 3.8×10 ⁻² | 0.89 |
| 7 | 100 | 0.4 | 1×10 ⁻³ | 1.1×10 ⁻³ | 2.6×10 ⁻² | 0.92 |
| 10 | 100 | 0.4 | 5×10 ⁻⁴ | 4.0×10 ⁻⁴ | 2.1×10 ⁻² | 0.96 |

Kinetics of reaction of UV-C photooxidation process, TiO₂ adsorption process and TiO₂/UV-C photocatalytic are shown in Fig. 3. According to this figure, TiO₂/UV-C photocatalytic reactions are done much faster than that of UV-C photooxidation process and TiO₂ adsorption process.

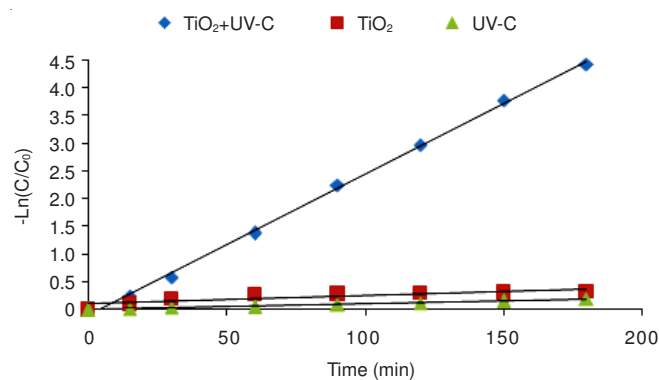


Fig. 3. Kinetics of reactive red dye 198 removal: (▲) UV-C photooxidation (C₀: 100 mg/L, pH: 7), (■) TiO₂ adsorption, (◆) TiO₂/UV-C photocatalytic (TiO₂ dose: 0.4 g/L, C₀: 100 mg/L, pH: 7)

The synergy between UV-C photolysis and TiO₂ adsorption can be calculated by following formula as the normalized difference between the rate constants obtained under TiO₂/UV-C photocatalytic and the sum of those obtained under separate process.

$$\text{Synergy} = \frac{k_{\text{TiO}_2+\text{UV-C}} - (k_{\text{TiO}_2} + k_{\text{UV-C}})}{k_{\text{TiO}_2+\text{UV-C}}}$$

The obtained results from the survey of synergy effect of TiO₂/UV-C photocatalytic are shown in Table-3.

These results showed that TiO₂/UV-C photocatalytic has more effects than UV-C photooxidation and TiO₂ adsorption process. As shown in Table-3, the degradation was negligible in the presence of only UV-C without TiO₂. A further increase in reaction rate was observed with rising the pH solution.

Effect of TiO₂ concentration: Fig. 4 shows the results related to the effect of TiO₂ concentration on removal of reactive red dye 198 in two various conditions: TiO₂ adsorption (Fig. 4A) and TiO₂/UV-C photocatalytic (Fig. 4B). As shown in Fig. 4, increased concentration of TiO₂ causes dye removal level to increase too. According to results, as TiO₂ mass increases from 0.4 to 1.0 g/L, dye removal efficiency increases from 68 to 85 % at 1 h contact time.

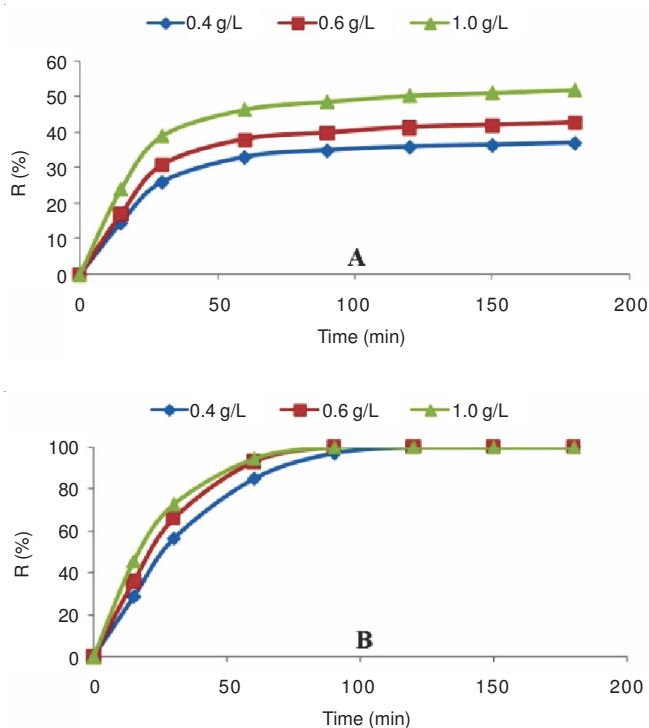


Fig. 4. Effect of TiO₂ concentration on reactive red dye 198 removal: (A) TiO₂ adsorption (B) TiO₂/UV-C photocatalytic (C₀: 100 mg/L, pH: 4)

Photocatalyst concentration is one of the most important, fundamental and economical parameters in degradation of dyes. To prevent the application of extra catalyst, determining optimum concentration of catalyst is essential for removing dye effectively. Regarding the effect of TiO₂ concentration on dye removal, results of this research conform, to some extent, to the results obtained by Kaur and Singh¹. These researches reviewed removal of reactive red using sono-photocatalytic process in the presence of TiO₂. They reported that removal of the mentioned pollutant is low in ultrasonic system and changes in TiO₂ concentration has no effect on efficiency of the above system. However, in conditions where ultrasonic and visible lights were used, dye removal efficiency was affected by TiO₂ mass so that as TiO₂ level increased to 300 mg/L, removal efficiency increased too, while in higher levels removal efficiency decreased. The reason is related to increased solution turbidity, decreased UV penetration and increased path passed by light photons^{5,21}. Such reasons are true for a single system studied in this research because as dye concentration level increases from 100-200 mg/L, light penetration level is influenced significantly and reduces dye removal level.

Effect of initial dye concentration: Results obtained from the effect of dye initial concentration on removal

efficiency of reactive red dye 198 are shown in Fig. 5 (in various conditions: UV-C photooxidation (Fig. 5A), TiO₂ adsorption (Fig. 5B) and TiO₂/UV-C photocatalytic (Fig. 5C)). Dye concentration in this step of the experiment varied from 100 to 200 mg/L, pH: 4 and TiO₂ dose: 0.4 in TiO₂/UV-C photocatalytic process. As shown in part A of Fig. 5, in UV-C photo-oxidation process with various initial dye concentration, as dye concentration increases, removal efficiency decreases. Concerning the application of TiO₂ nano-particle, as initial dye concentration increases, dye removal efficiency decreases. Results obtained from application of TiO₂ and UV-C photocatalytic oxidation reveals that at the beginning of reaction and contact time of 0-150 min, as dye initial concentration increases, removal efficiency decreases, while as contact time increases to more than 150 min, initial dye concentration has no effect on removal efficiency. The efficiency changes is equal in all three concentrations and all three concentrations have equal removal efficiency. The initial concentration of dye in a given photocatalytic reaction is also another factor which needs to be taken into account. It is generally found that percentage

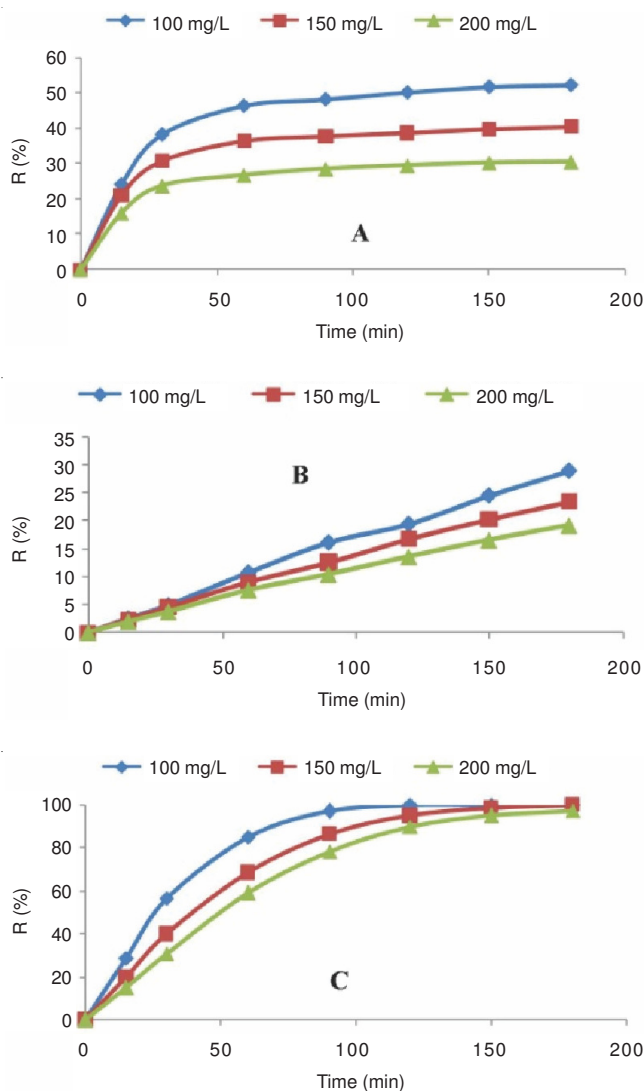


Fig. 5. Effect of initial dye concentration on reactive red dye 198 removal: (A) TiO₂ adsorption (TiO₂ dose: 0.4 g/L, pH: 4) (B) UV-C photooxidation (pH: 4), (C) TiO₂/UV-C photocatalytic (TiO₂ dose: 0.4 g/L, pH: 4)

degradation decreases with increasing amount of dye concentration, while keeping a fixed amount of catalyst. This can be rationalized on the basis that as dye concentration increases, more organic substances are adsorbed on the surface of TiO₂, whereas less number of photons are available to reach the catalyst surface and therefore less •OH are formed, thus causing an inhibition in degradation percentage.

Variation of dye spectral during TiO₂/UV-C photocatalytic: By changing in dye molecular structure, the adsorption spectral of reactive red 198 dye changes during photocatalytic process. Fig. 6 shows the variation of adsorption spectral of reactive red 198 dye and reduction of adsorption peak in different radiation times. As shown in Fig. 6, the high amount of reactive red 198 dye (100 mg/L initial concentration) was removed in 1 h contact time; it shows rapid degradation of reactive red 198 dye.

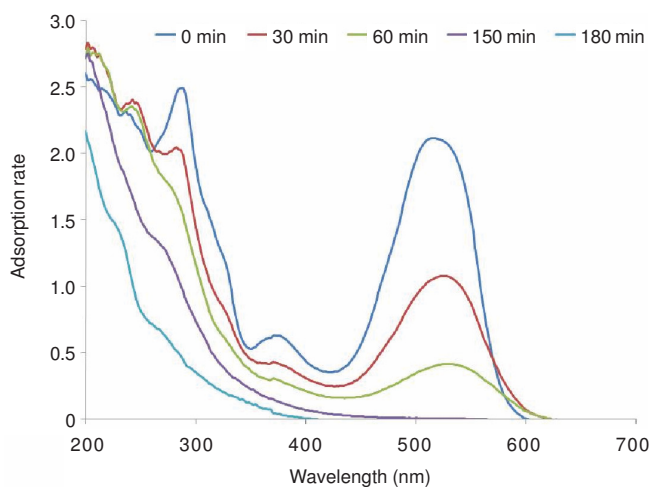


Fig. 6: Spectral changes of reactive red dye during the TiO₂/UV-C photocatalytic (C₀: 100 mg/L, TiO₂ dose: 0.4 g/L, pH: 4)

The results from changes in adsorption peak were showed that dye removal during photocatalytic process was relatively quick. The reason of this rapid removal is related to dye structure and chemical bonds available in its structure. It's depicted that the relatively low energy of chemical bonds in dye structure may be broken during photocatalysis with emitting high energy photons from TiO₂ surface by UV-C radiation.

Kinetic studies of TiO₂/UV-C photocatalytic process:

All processes related to purification of water and wastewater is done in a volume called special borders; this volume is called reactor. Various combination and concentration of materials in reactor are the main factors of purification of water and

wastewater. These variation are resulted from hydraulic transfer of materials into and out of the reactor as well as from reactions occur in reactor. To completely describe a reactor system and its design, rate and level of changes occur in the reactor must be specified. These rate directly affect on reactor size. Therefore, study the kinetic reactions to prediction of pollutant removal rate, which is important in designing and modeling the process, is very useful. The most conventional kinetic models were applied to reactive red dye 198 removal from aqueous solution.

A kinetic analysis was conducted by fitting the time-course performance data with zero, first and pseudo-second order kinetic equations as shown in Table-4 and Fig. 7.

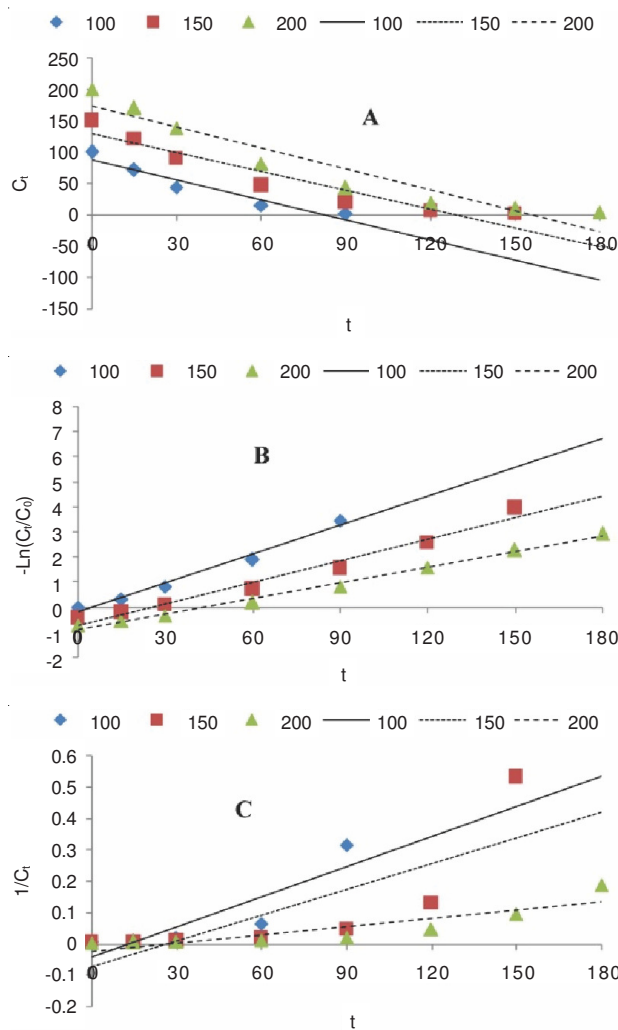


Fig. 7. Kinetics of TiO₂/UV-C photocatalytic processes on reactive red dye 198

| TABLE-4 EQUATIONS AND RESULTS FROM THE KINETIC CALCULATIONS | | | | | | |
|--|--------------------------------|--------------------------------------|----------------|--------------------------|---------------|---------------|
| Kinetic model | Equation | Linear form | Constant | Dye concentration (mg/L) | | |
| | | | | 100 | 150 | 200 |
| Zero-order | $r_c = \frac{dC}{dt} = k_0$ | $C - C_0 = -k_0t$ | k_0 R^2 | 1.06 0.92 | 0.99 0.91 | 1.11 0.91 |
| First-order | $r_c = \frac{dC}{dt} = k_1C$ | $\ln \frac{C}{C_0} = -k_1t$ | k_1 R^2 | 0.038 0.98 | 0.028 0.97 | 0.02 0.99 |
| Second-order | $r_c = \frac{dC}{dt} = k_2C^2$ | $\frac{1}{C} - \frac{1}{C_0} = k_2t$ | k_2 R^2 | 0.003 0.77 | 0.002 0.63 | 0.001 0.77 |

Where r_c is the rate of conversion, k_0 , k_1 and k_2 are reaction rate coefficients, t is time and C_0 and C are the initial and final concentration of the constituent in the liquid, respectively. The data were correlated well (higher R^2) by first order kinetic model and revealing the first model can successfully simulate the reactive red 198 removal in the $TiO_2/UV-C$ photocatalytic process. The first order reaction showed that the reaction progressed at a rate directly proportional to the concentration of each reactant.

Conclusion

The advanced oxidation process ($TiO_2/UV-C$) has more suitable effects than photooxidation process ($UV-C$) due to the creation of synergy in degradation of reactive red 198. The reason is due to the production of hydroxyl free radical (OH) which oxidizes and decomposes a broad range of pollutants rapidly and randomly. Results of this research show that degradation/removal of reactive red 198 with photo-oxidation process and $TiO_2/UV-C$ mixed process is a first-order reaction. Dye removal speed is as follows: acidic conditions > neutral conditions > alkaline conditions.

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