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Enhanced dynamics characterization of photocatalytic decolorization of hazardous dye Tartrazine using titanium dioxide

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ABSTRACT

Advanced oxidation process is a promising technology for remediation of organic pollutants at ambient conditions. Several experiments of photocatalytic decolorization of Tartrazine compound using TiO_2 and UV light have been carried out for enhancing the characteristic of the oxidation kinetics. The experimental results revealed that photo oxidation process was strongly dependent on UV light intensity, and an improvement of 98% was achieved for 75% increase in the light intensity. The reaction rate constant in respect to UV light intensity was larger by order of 10 compared to other considered parameters. The second important parameter that affecting the decolorization rate was the hydraulic time constant (τ) showed an improvement of 79.4% of the decolorization process. The catalytic oxidation process is considered similar to a batch chemical reactor and covered by the first-order reaction rate. A negative impact of 66.67% was obtained by increasing the dye concentration. The results showed that the increased level of TiO_2 concentration did not necessarily improve the rate of degradation of pollutant. The repeatability of photocatalytic process was also tested and after reusing the recycled TiO_2, the rate of color degradation was still efficient with respect to initial dye concentration. It appeared that the photo-oxidation process was favorable at neutrality conditions or slightly higher pH for solutions consisting of anions.

Keywords: Dynamic behavior; Photocatalyst; TiO_2; Tartrazine

1. Introduction

Organic contaminants present in industrial wastewater are of major concern with respect to the health of the general public. There are several established methods of removing organic waste. The most widely used of these methods is biological treatment [1–3]. Other important applied methods include adsorption on activated carbon, hydrogen peroxide/UV-light, Ozone/UV/hydrogen peroxide, and γ-radiolysis [4]. Many chemical wastes are very toxic, difficult for biological degradation, and therefore, advanced oxidation process has become attractive to many researchers for treating chemical organic wastes [5–8].

Heterogeneous photocatalytic oxidation, one of the advanced oxidation processes (AOPs), has proved to be a promising technology for remediation of organic pollutants at ambient conditions. The main advantage of photocatalytic oxidation is the complete destruction of organic pollutants. Most of the literatures stated that the AOP has the advantage of complete destruction compared with the other more established water purification processes [9,10].

Photocatalysis is an advanced oxidation process in which the reaction is initiated by UV light illumination on a catalyst. It is an environmentally friendly technology in terms of (i) material: the photocatalyst, i.e. titanium dioxide (TiO_2) is safe to handle as it is not a toxic material and can be regenerated, (ii) reaction: a complete aerobic degradation of organic compounds yields carbon dioxide, water, and simple mineral acids, (iii) operation: photocatalysis does not require addition of chemical oxidants, (iv) localized treatment: its application does not have an effect on its vicinity as it will only be activated upon UV light illumination, and (v) controllable: there is no reaction with photocatalyst when the UV lamps are switched off except adsorption [11].

In this regard, AOPs have been described as efficient procedures for obtaining high oxidation yields from several kinds of organic compounds based on the generation of very reactive agents such as hydroxyl radicals (OH) that are extremely reactive and capable of mineralizing organic pollutants [11]. For enhancement in efficiency, the use of TiO_2 catalyst has gradually attracted more interest. TiO_2 is the most acceptable catalyst because it is cheap and it can be recovered from treated waste solution [12]. The more activity of the TiO_2/UV process is due to the well-known fact that when TiO_2 is illuminated with UV light, electrons are promoted from the valance band to the conduction band of the semi-conducting oxide to give electron–hole pairs [13]. Direct UV light exposure increases the rate of reaction and oxidation of the substrates to CO_2 [14,15]. Konstantinou and Albanis [16] presented a comprehensive review paper to assist researchers in the field of decolorization of azo dyes. This review paper discussed the photocatalytic decolorization mechanisms in details and reviewed the influences of many factors, such as initial dye concentration, TiO_2 loading, pH, UV light intensity, and humic substances, on the photocatalytic treatment using TiO_2. They concluded that a focus on quantitative data of intermediates and product evaluation will help in mechanistic studies of the photocatalytic process.

Despite the agreement on the outcomes of all these works that the photo-oxidation process offers great potential as an industrial technology for detoxification or remediation of organic wastewater, there are still disagreements about other issues such as the amount of catalyst loading. Most authors have stated that the increase in degradation rate is limited to a certain level of catalyst [9,13,15,17,18].

The effect of acidity or alkalinity of the solutions is not fully clarified. Some authors indicate that the increase in pH value increases the rate of degradation [17,19], while, other state the decrease in pH increase degradation rate [13,20,21]. However, others indicate that the pH value has a little effect on the degradation rate [11].

Many researchers have demonstrated the use of titanium dioxide (TiO_2) as a photocatalyst for decomposition of organic compounds, because of its photochemical stability, non-toxicity, and low cost [22,23]. All of those researchers have demonstrated the ability of oxidation process in degradation of organic compounds. Some researchers tried to model the photo-oxidation process, most of them have reported that the process can be represented by first-order reaction rate or their data are fitted to a first-order rate model [9,11,13,14,17,19,23–25]. Other researchers tried to fit their kinetic data to the Langmuir–Hinshelwood model and Langmuir isotherm (19, 24). Most of those researches have been carried out with different operating conditions and procedures such as concentration of TiO_2, types of organic compounds, UV light intensity, process capacity and flow rate, pH of medium, adding air and adding H_2O_2, etc. However, there is no general model for the process is presented; different kinetic models were developed for each process. These kinetic behaviors are similar to that of real chemical reactions at which different reaction rates and kinetics are obtained depending on reactants, catalyst, operating conditions, etc. Thus, a focus has to be placed on other parameters which may lead to greater understanding of the kinetics of the oxidation process, and can help enhance the operation and reduce the cost of photocatalytic oxidation, compared with alternate technologies.

Although several models have been proposed for the photocatalytic process, they still lack of considering all parameters that affect the dynamics of the process such as light intensity, circulating flow rate, ratio of titanium dioxide to number of carbon atoms in the treated solutions.

Another important factor that has to be considered for analysis of the photo-oxidation process is the hydraulic time constant, which can be calculated as the ratio of liquid volume in the reactor to its feed flow rate. This factor has second major impact after intensity of UV light on the reaction time constant, and in turn the degradation rate.

The aim of the present work was to evaluate the impact of reaction and hydraulic time constants on the decolorization rate of the dye along with other parameters; UV light intensity, catalyst concentration, dye initial concentration, pH, and temperature. Series of experiments have been carried out. By selecting Tartrazine dye as organic pollutant, which has a wide application in food, non-food, and drug industries, in the present photo-catalyst process, TiO_2 is freely suspended and circulated through the reactor. Different conditions such as TiO_2 concentration, dye concentration, pH, and circulated liquid flow rate were studied. Artificial UV powers were selected in order to obtain UV power lower and similar to that of the natural solar UV (sunlight) [26].

2. Materials and methods

2.1. Reagent

The selected photocatalysis was titanium dioxide TiO2 (P25, Degussa AG, Germany) with a surface area of 50 m^2/g and a primary particle size of 20 nm. Degussa P25, a commercially produced form of titanium dioxide and reference catalyst is composed of both phases 80% anatase and 20% rutile [27]. The organic pollutant, Tartrazine dye, is chosen due to its wide application in food, non-food, and drugs industries. The chemical structure of the Tartrazine dye is shown in Fig. 1.

2.2. Photocatalytic reactor

Experiments were performed in a (26.7 × 13.5 × 6.5 cm) transparent glass flat vessel as a photoreactor. The photoreactor is connected by a set of tubes as a series with pump to beaker, as shown in Fig. 2. During operation, liquid height in the reactor was about 1.25 cm and UV lamps were placed 10 cm above the liquid surface of the vessel and both vessel and lamps were covered with aluminum foil to reflect UV light; therefore, maximum light utilization was achieved. The available UV radiation sources were giving range of light intensity around the lamp from 0.53 to 2.2 mW/cm^2 at a wavelength of 365 nm.

2.3. Procedure and analysis

The experimental tests were carried out using 1 l of dye solution of concentration varying from 25 to 75 mg/l, and a desired amount of titanium dioxide catalyst varying from 200 to 700 mg/l. The solution was circulated at desired flow rates varying from 0.8 to 2.4 l/min. The reactor was then exposed to the UV light in order to provide the suitable energy for exciting the TiO_2 particles. Samples were taken every 30 min from the circulated solution in the beaker. The disappearance of color was measured using UV–vis spectrophotometer model UV-1800 Shimadzu.

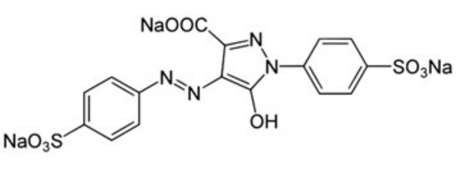

Fig. 1. Tartrazine chemical structure.

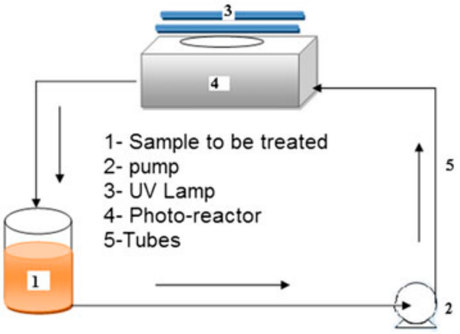

Fig. 2. Schematic diagram of photocatalytic process.

The effect of photocatalyst concentrations on the degradation kinetics was found to follow the pseudo-first-order kinetics modeled by Eq. (1):

$$\ln\left(C_t/C_0\right) = -kt \tag{1}$$

where C_0 = dye concentration (mg/l) at time $t = 0$; C_t = dye concentration (mg/l) at time $t = t$; k = first-order rate constant (min^{-1}). The slope of the plot of ln (C_t/C_0) vs. time represents rate time constant of decolorization [19].

3. Results and discussion

3.1. Effect of catalyst concentration

Results obtained from experiments on dye decolorization using different concentrations of titanium dioxide are illustrated in Fig. 3. The rates of decolorization have been found to improve as catalyst concentration increases up to a certain amount; however, the decrease in color is faster with using 500 mg/l of TiO_2 compared to that of 200 and 700 mg/l. A possible explanation is that increasing catalyst concentration increases turbidity of the solution which in turn reduces the light transmission through the solution. Results, also, show that the variation of decolorization was occurred between two typical times of 60 and 300 min.

It was found that disappearance of dye followed the pseudo–first-order kinetics as shown in Fig. 4.

3.2. Effect of initial dye concentration

Applying the catalyst concentration of 500 ppm for decolorizadation of different dye solutions with concentrations varying from 25 to 75 mg/l, it was shown that degradation rate decreased as initial dye concentration increased, as illustrated in Fig. 5. From Figs. 3 and 4, it can be seen that the increase in TiO_2 and dye concentrations led to a lower rate of decolorization, which attributed to decrease in absorbance of UV light. This was clearly indicated in the dye discolorization using 700 ppm TiO_2 catalyst. The pseudo-first-order kinetics was utilized for these data and shown in Fig. 6.

3.3. Effect of circulating feed flow rate

The dye decolorization results with different circulating flow rates using three of catalyst concentrations were summarized in Figs. 7–9. The results indicated that the disappearance of dye was less by increasing circulating flow rate with range from 0.8 to 2.4 l/min; however, all results of decolorization were following the pseudo–first-order kinetics as shown in Fig. 10.

Results showed that less decolorization rate was obtained at smaller hydraulic time (τ), and hence, larger operation time was required for complete decolorization.

3.4. Effect of UV light intensity

A series of experiments was carried out to find the influence of intensity of UV light on the decolorization rate of Tratazine dye using three different concentrations of dye; 25, 50, and 75 mg/l and catalyst concentration of 200 ppm. The results for experiments using

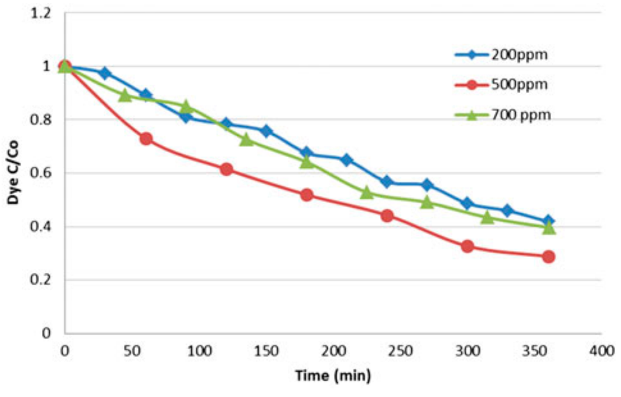

Fig. 3. Effect of TiO_2 concentration on decolorization of dye solution with initial concentration = 50 mg/l, UV = 0.53 mW/cm^2.

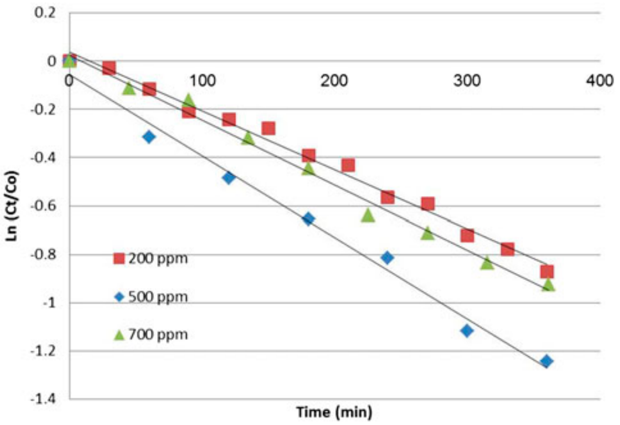

Fig. 4. Plot $\mathrm{Ln}(C_t/C_0)$ vs. t of different catalyst concentrations using dye solution with initial concentration = 50 mg/l, UV = 0.53 mW/cm^2.

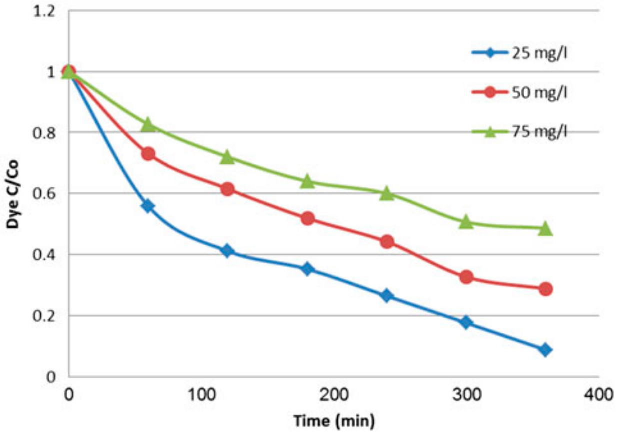

Fig. 5. Effect of dye concentration on the decolorization of dye using 500 mg/l TiO_2, UV = 0.53 mW/cm^2.

UV light intensity ranging from 0.53 to 2.2 mW/cm^2 were illustrated in Fig. 11.

The pseudo–first-order model was utilized for the obtained data at different UV light intensities, the results indicated that the model was applicable for all the decolorization of the solution as shown in Fig. 12.

3.5. Reusing recycled TiO_2

One of the advantages of the photocatalytic treatment is that the catalyst can be reused, and thus, TiO_2 catalyst was used and recycled for consecutive reuse for decolorization, and the results were presented in Fig. 13. These results indicated that TiO_2 demonstrated an acceptable stability after recovery and that catalyst reuse was efficient. However, comparing to results

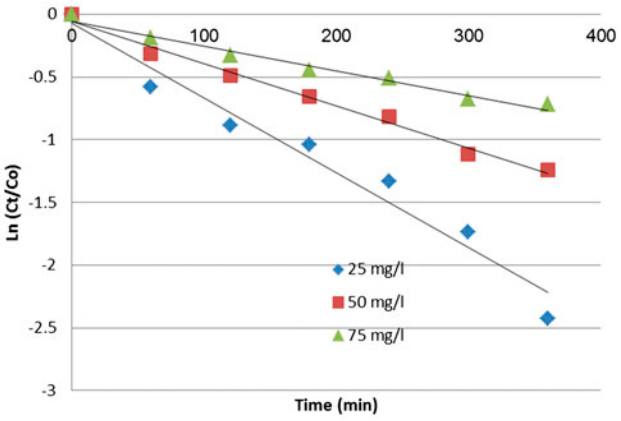

Fig. 6. Plot Ln (C_t/C_0) vs. t at different dye concentrations using catalyst concentration = 500 ppm, UV = 0.53 mW/cm^2.

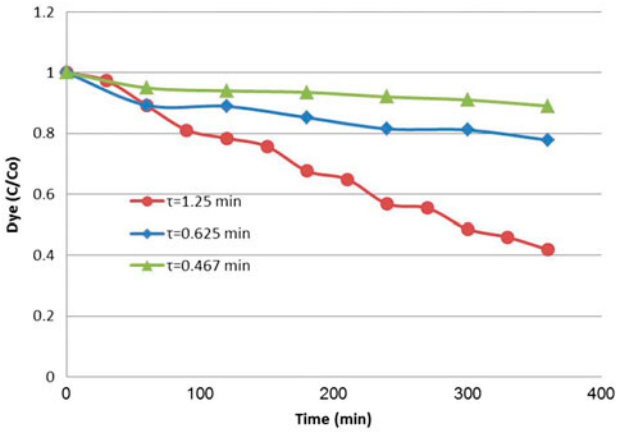

Fig. 7. Effect of circulating flow rate on decolorization of solution with dye concentration = 50 mg/l and TiO_2 = 200 ppm, UV = 0.53 mW/cm^2.

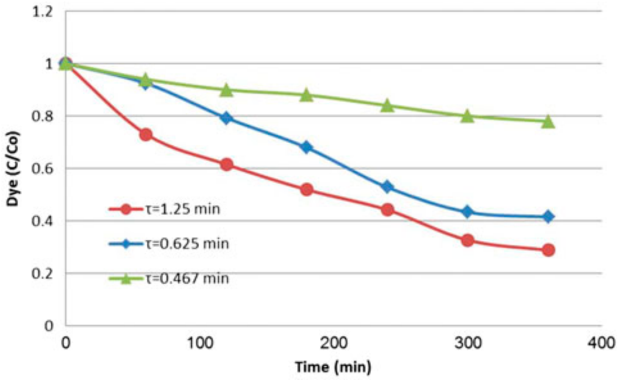

Fig. 8. Effect of circulating flow rate on decolorization of solution with dye concentration = 50 mg/l and TiO_2 = 500 ppm, UV = 0.53 mW/cm^2.

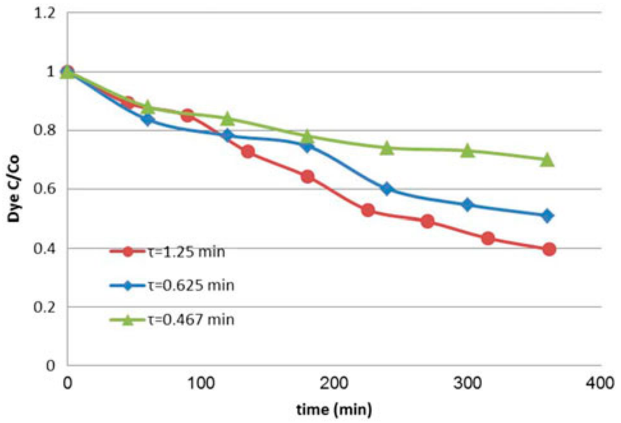

Fig. 9. Effect of circulating flow rate on decolorization of solution with dye concentration = 50 mg/l and TiO_2 = 700 ppm, UV = 0.53 mW/cm^2.

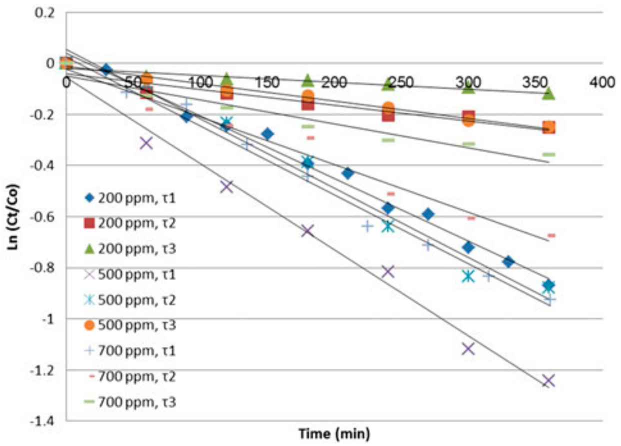

Fig. 10. Plot ln (C_t/C_0) vs. t for different circulating flow rates ($\tau 1$ = 1.25 min, $\tau 2$ = 0.625 min, $\tau 3$ = 0.467 min) using dye concentration = 50 mg/l with three different catalyst concentrations, UV = 0.53 mW/cm^2.

shown in Fig. 11, it can be seen that a slower decolorization rate was obtained. This may be due to insufficient illumination time of UV light for regeneration purposes.

3.6. *Effect of pH*

pH value was measured during all the experiments. It was found that at increased TiO_2 concentrations, higher pH values showed an increased oscillatory behavior as illustrated in Fig. 14. pH for the fresh deionized water was about 6.9, and for solution with 200 mg/l of TiO_2 was 7.4, while it was 8.2 for solution with 700 mg/l of TiO_2. However, the pH

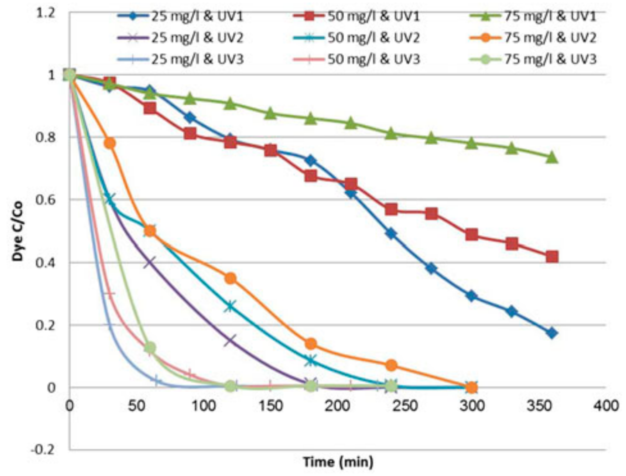

Fig. 11. Effect of UV light intensity (UV1 = 0.53, UV1 = 1.82, and UV3 = 2.2 mW/cm^2) on decolorization of solution with three different dye concentrations and TiO_2 = 200 ppm.

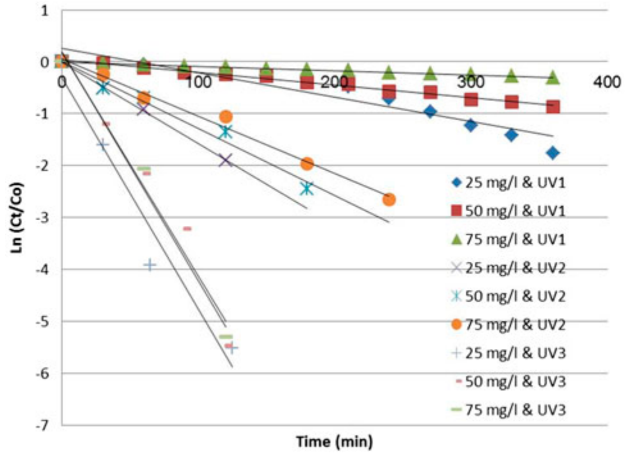

Fig. 12. Plot Ln (C_t/C_0) vs. t for different UV light radiations (UV1 = 0.53, UV1 = 1.82, and UV3 = 2.2 mW/cm^2) using three different dye concentrations.

value started to oscillate after decolorization of dye. Results showed that the higher the concentration of TiO_2 in the solution, the stronger the oscillation was achieved especially when dye concentration was reduced. This pH behavior could be due to the presence of H ions and OH radical by the illumination of TiO_2 by proton with energy higher than 3.2 eV (360 nm), this presence seemed to be high at low decolorization process, which led to an oscillatory behavior. However, the slight change in pH would not be considered to have an impact on the photocatalyst process.

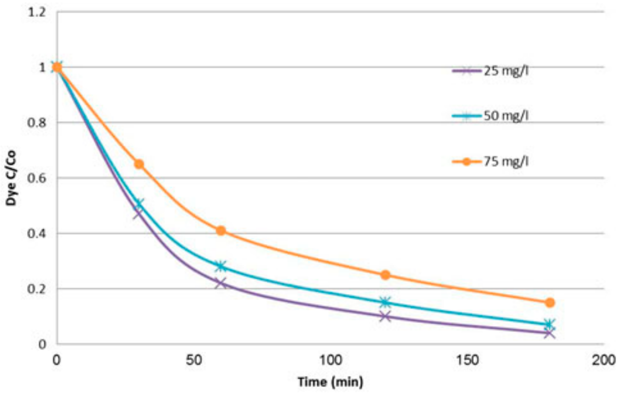

Fig. 13. Effect of reused TiO_2 (200 ppm) on decolorization of dye under UV light intensity = 2.2 mW/cm^2.

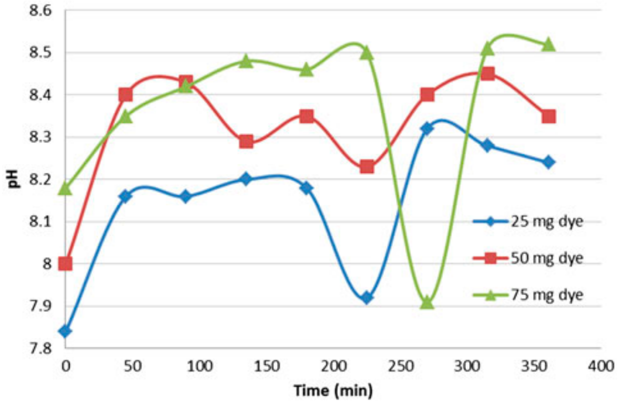

Fig. 14. Effect of TiO_2 concentration on pH using different dye concentrations and TiO_2 = 500 ppm.

The impact of the pH effect on the photo-oxidation process is still not well clarified by researchers. However, it can be seen from previous research works that the most oxidation processes were favorable near neutrality or slightly at a higher pH, except those operated with solution having no anion present in it [13]. This phenomenon can be referred to during oxidation process where TiO_2 are illuminated, OH radicals were present and thus, the pH of the solution will rise above neutrality. For solutions that have no anions, acid solution may be added to accelerate the oxidation process, and thus, pH value will be decreased and the process is favorable of acidity.

3.7. Effect of temperature

During all experimental tests, the temperature of the solution was raised only by 3˚C (from 22 to 25˚C). At this range of temperature, there was no much effect

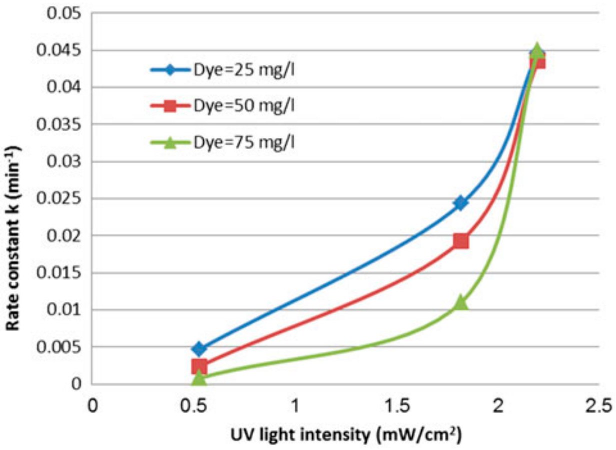

Fig. 15. Effect of UV light intensity on the decolorization rate of dye using TiO_2 = 200 ppm.

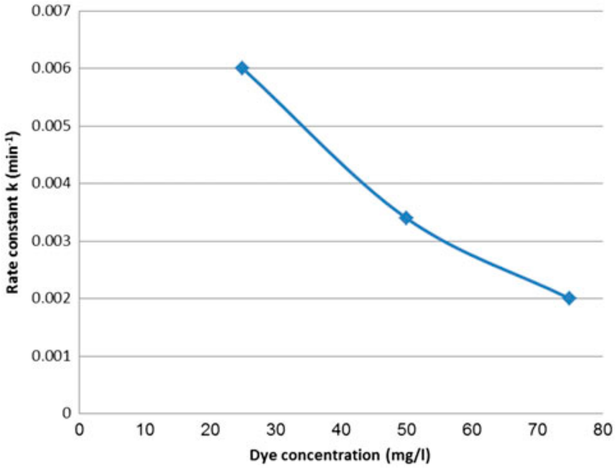

Fig. 17. Effect of initial dye concentration on the decolorization rate of dye using TiO_2 = 500 ppm.

on the process of photo-oxidation. Also, there was no work suggesting to be carried out at a very high temperature; such condition would have a significant effect on dye decolorization due to the solution evaporation and reduction in O_2 concentration during the experiment.

4. Process kinetics

The kinetics and dynamic model of photocatalytic process can be evaluated using its dynamic responses based on four major contributing factors on the photo-oxidation process—hydraulic time constant, UV light intensity, initial of organic concentration, and catalyst concentration. The effects of these terms on the decolorization rate constant have been determined and illustrated in Figs. 15–18.

Analyzing and evaluating data presented in these figures indicated that: (1) UV light intensity has the greater effect on the degradation of the organic compounds compared to other terms as an almost 10 times larger reaction rate constants were obtained. Results presented in Fig. 15 showed that decolorization rate constant has been improved by 98.2% in respect to 75% increase in light intensity. (2) Hydraulic time constant has the second great effect on the decolorization rate; results presented in Fig. 16 showed that the decolorization rate constant has been improved by 79.4% in respect to 66.67% increase in hydraulic time constant. Slow circulating or no circulation may give a

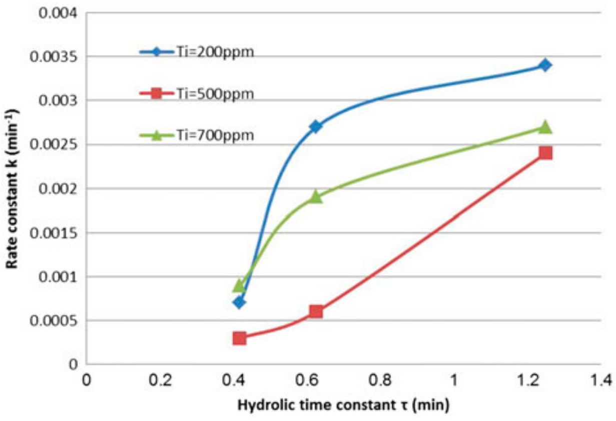

Fig. 16. Effect of hydraulic time constant on the decolorization rate of dye using different TiO_2 concentrations and dye = 50 mg/l.

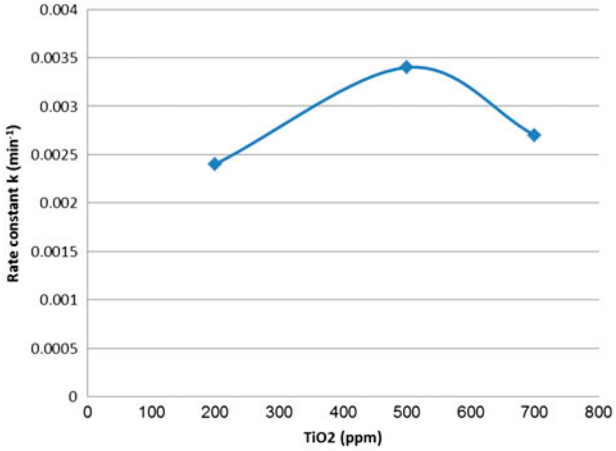

Fig. 18. Effect of TiO_2 concentration on the decolorization rate using dye = 50 mg/l.

better degradation of organic compound. (3) The increase in initial dye concentration in the treated solution has a negative impact on the decolorization rate as illustrated in Fig. 17. An increase in 66.67% of dye concentration caused a decrease 66.67% of the reaction rate constant. (4) The concentration of catalyst, TiO_2, has shown to be the least affected parameter on the degradation process. Initially, the increase in catalyst concentration has improved the decolorization rate; however, further increase in catalyst concentration has a negative impact on the decolorization as illustrated in Fig. 18. At the optimum catalyst concentration, maximum improvement of 29% was achieved.

5. Conclusion

This work was focused on studying and evaluating the effect of most important parameters on the degradation of organic compounds in wastewater using photocatalytic oxidation process. Based on the analysis of obtained results, the following conclusions can be drawn:

(1) Hydraulic time constant and UV light in the presence of catalyst have the greater impact on the dye decolorization rate compared to other process parameters.
(2) The larger the value of UV light and/or hydraulic time constant gave lager improvement for dye decolorization rate.
(3) For a cheap oxidation process, large hydraulic time constant may compensate the power of the UV that was needed for a large degradation rate. This suggestion would be benefited where UV light intensity was low.
(4) Dye concentration has a considerable negative impact on the decolorization rate.
(5) The increase in concentration of catalyst up to certain amount has lower influence on the decolorization rate; however, larger concentration has a negative impact on rate constant.
(6) Most of the processes with solutions-containing anions were favorable at a neutral and a slightly higher pH.

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