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ORIGINAL ARTICLE

Removal of Ortho-Toluidine from Industrial Wastewater by UV/TiO_2 Process

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KEYWORDS

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Batch recirculating photo reactor;
Ortho-Toluidine (OT)

ABSTRACT: In this research degradation and mineralization of Ortho-Toluidine (OT) in the wastewater of petrochemical industries was investigated by UV/TiO_2 process in a batch recirculating photo reactor. The influence of different variables such as initial pH, amount of TiO_2 and initial concentration of OT on the reaction rate was investigated. In optimum conditions (1.75 g/l of catalyst, pH at 7 and initial concentration of OT at 20 mg/l), 93.5% of pollutant and 57% of COD were removed in 180 min of reaction. The reaction rate represented by the mechanism of Langmuir-Hinshelwood was found to follow pseudo first-order kinetics. Degradation and mineralization of the OT were tested by HPLC and COD tests.

INTRODUCTION

Wastewaters containing toxic compounds were produced by various chemical industries. These pollutants persist in the environment even after exposing to conventional processes [1]. O-Toluidine is probably considered carcinogenic to humans [2]. Ortho-Toluidine has been in creation above 100 yr [3] and furthermore, it initiated renal pelvis cancer or urinary bladder [4]. There are three ways for treatment of industrial wastewater, containing: physical, chemical and biological techniques [5–8]. Though, these methods have great operational costs, have secondary pollution and want longer reaction time, subsequently solid wastes would be created in these processes, which can convey other environmental difficulties of sludge treatment and disposal [9–10]. Thus, a cheap and easy-operated control technology without the formation of sludge is required [9].

Newly, the advanced oxidation processes (AOPs) have offered a favorable treatment option for industrial wastewaters compared to other treatment technologies. These techniques were based on the production of very reactive species such as hydroxyl radicals that oxidize a wide range of pollutants non-selectively and rapidly

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[11]. Semiconductor photo catalytic processes are a branch of AOPs that they have begun a significant treatment technology leading to the mineralization of most of the organic compounds [12]. The foundation for the improved interest in this process is the use of oxygen as an oxidant under mild conditions. Furthermore, this process employs low-cost obtainable nontoxic semiconductors (TiO_2, ZnO) and leads to total mineralization of organic pollutants to CO_2, water and mineral acids.

The purpose of this study was that to obtain the optimum conditions for degradation of O-Toluidine in the presence of TiO_2 Degussa p-25, nano catalyst and to investigate the effect of various operational variables on degradation of this pollutant.

MATERIALS AND METHODS

Materials

O-Toluidine (99%) was purchased from Merck. Titanium dioxide was Degussa P-25 and in the form of Anatase (approximately 80% Anatase, 20% Rutile). It had an average particle diameter of 21 nm and BET surface area of 50 ±15m^2 g^{-1}. NaOH and H_2SO_4 (0.1M) were reagent grade from Merck. Distillates water was used throughout this work.

Table 1. The molecular properties of O-Toluidine[13].

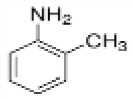
Pollutant	Molecular formula	Molecular structure	Molecular Mass	Solubility in water	Density
O-Toluidine	C_7H_9N		107.15 (g/mole)	1.5 g/100 ml (25 ºC)	1.004 at 20/4 ºC (water = 1)

Photo reactor

In this project, experiments were carried out in two series Teflonic cylindrical reactors (each of them with one liter of capacity) and equipped with a sampling system (Figure 1). The light source was two mercury lamps, Philips 15W (UV-C), immersed vertically in the center of the reactors. The reactors were equipped with a water-flow exchanger, using an external circulating flow of a thermostatic bath (BW20G model from Korean Company) for adjusting temperature about 25 ºC. The solution in reservoir mixed well by magnetic stirrer and pumped with a flow rate of 1.25 l/min and entered from beneath to the reactor. After radiation the solution recycled to the reservoir from the top of the second reactor. The volume of solution in the loop was 2.5 l. The initial pH of the solution was adjusted using a Basic pH Meter PT-10P Sartorius Instrument Germany Company. Oxygen was achieved from a capsule and injected from the bottom of the reservoir.

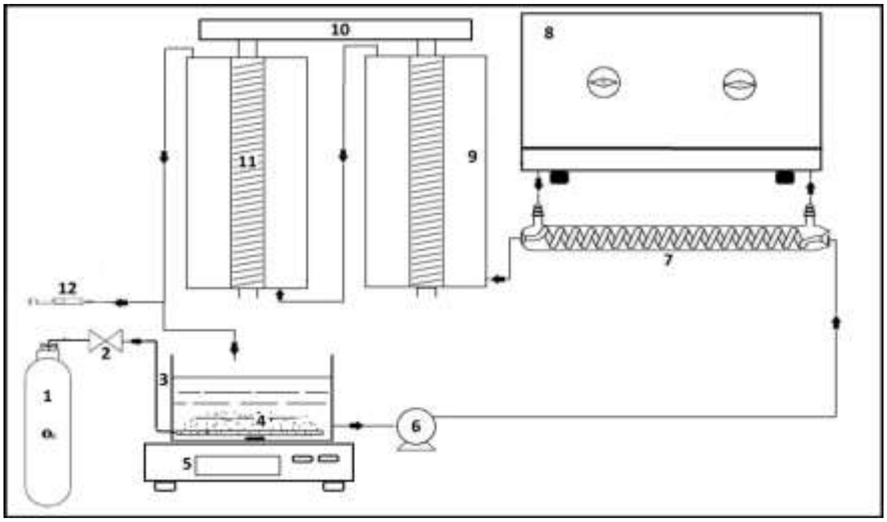


Figure 1. Schematic diagram of laboratory-scale experimental set-up.1-Capsule of Oxygen, 2-Cut off valve, 3-Reservoir, 4-Oxygen diffuser, 5- Magnetic Stirrer, 6-Recirculation pump, 7- Heat exchanger, 8- Thermo bath, 9-Reactor, 10- Electric supply, 11-UV lamp, 12-Sampling port

Analytical Procedure

A solution containing known concentration of the OT and TiO_2-P25 was prepared and permitted to equilibrate for 30 min by circulating in the reactor without irradiation to equilibrate the adsorption- desorption reactions, after circulating and regulating the temperature, oxygen was added from the bottom of the reservoir through a Sparger with the flow rates of 0.5 l/min to saturate the solution with oxygen. Dissolved oxygen has been essential for heterogeneous photo catalysis and is electrophilic and reacts very easily with the generated electrons from the surface of the catalyst in Conduction band, so reducing the unwanted electron–hole recombination.

During the experiment, the amounts of the oxygen in the solution remained adequate by injecting oxygen continuously to cause generating hydroxyl radicals responsible for the degradation of OT.

The lamps were switched on to initiate the reaction. The solution in the reservoir was mixed by a stirrer to avoid settling of nano catalyst particles and kept the suspension homogenous. The pH was adjusted by addition of NaOH or H_2SO_4 (0.1 M) and studied in the range from 4 to 11.

Five ml of samples were taken at certain reaction intervals, centrifuged and filtered, then analyzed by a UV–Vis spectrophotometer (Agilent, 5453, American) at 234 and 281 nm. For more validation, samples were tested by HPLC (Knauer, Germany) equipped with Spectrophotometer (Platm blue Germany). A reverse phase column, filled with 3 µm Separon C_{18}, was 150 mm in length and 4.6 mm in diameter. The isocratic method with a solvent mixture of 60% acetonitrile and 40% deionized water with a flow rate of 1 ml/min were used.

The COD was measured according to the standard methods [14], a closed reflux with the Colorimetric method was developed and spectrophotometer (DR5000, Hach, USA) was used for measuring the absorbance of COD samples in 600 nm.

RESULTS AND DISCUSSION

Effect of pH

The influence of pH on the photo catalytic degradation of various compounds is significant [15–16]. The results showed that pH had a main effect and degradation rates were slow at low and high pH values. The finest pH for the degradation was near the zero point of charge (ZPC) of TiO_2 and this theory was explained that the effect of pH on degradation rate was depended on its impact on TiO_2 particles itself.

The ZPC for TiO_2 photo catalyst was at pH values between 5.6 and 6.4 [17]. Therefore, the catalyst surface is positively charged at more acidic pH values, but it is negatively charged at pH values above 6.4.

$$TiOH + H^+ \rightarrow TiOH_2^+ \qquad pH < pH_{pzc} \quad (1)$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \qquad pH > pH_{pzc} \quad (2)$$

TiO^-, TiOH and $TiOH_2^+$ are the negative, neutral and positive surface hydroxyl groups, respectively [18]. These properties were caused changes in the structure of pollutant at different pH and adsorption on TiO_2 surface [19]. The influence of pH on photo degradation of the OT was investigated in the range of 4 to 11and presented in Figure 2. Degradation of the OT was low in acidic solution (pH=4). The degradation was improved by an increase in pH and reached its maximum amount (53.5%) at pH of 7.

The more increase in pH led to decrease in the degradation. In alkaline condition Columbic repulsion between OH^- and the negatively charged surface of TiO_2 particles could avoid the formation of hydroxyl radicals and decreasing the degradation.

The pH of six tests (pH 4, 5, 6, 7, 9 and 11) was examined and pH fallen in all experiments, although in the cases of pH 5 and pH 4 this decrease was not so manifest, but the most significant decrease observed in the case of pH 11, since it decreased to 7 at the end of the treatment, because mineral acids formed as the reaction was advanced.

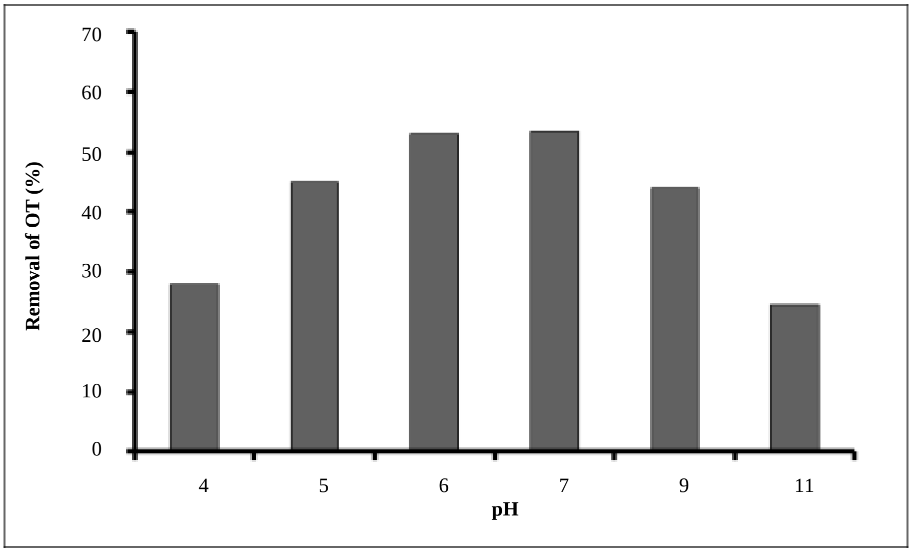


Figure 2. Effect of pH on the degradation of O-Toluidine ([OT] =40 mg/l, $[TiO_2]$= 2.25 g/l, irradiation time= 180 min).

Effect of TiO_2 concentration

Degradation tests were performed by changing TiO_2 concentration from 0.75 to 3.75 g/l, whereas the other parameters remained fixed ($[OT]_0$ = 40 mg/l, V_L = 2.5 L, Q = 1.25 L/min and pH =7). The optimum concentrations stated for TiO_2 were depended on contaminants and the photo reactor geometry [20]. Experiments showed that the degradation was increased (from 29 to 55%) whit increase in TiO_2 concentration (from 0.5 to 1.75 g/l) until it reached a plateau, and then it remained flat and somewhat decreased (Figure 3).

Above 1.75 g/l of catalyst, the rate of O-Toluidine decomposition was not affected further by an advanced increase in TiO_2 concentration because of the accumulation of TiO_2 particles at high dosages, causing a decrease in the number of active sites on the surface of catalysts. Moreover, the more increase in catalyst loading may cause opacity, increase light scattering and reduction of light penetration [21–22]. Therefore, 1.75 g/l of TiO_2 was selected as the optimal amount of photo catalyst and by an increase in dosage of catalyst to 3.75 g/l, decomposition dropped to 48.5%.

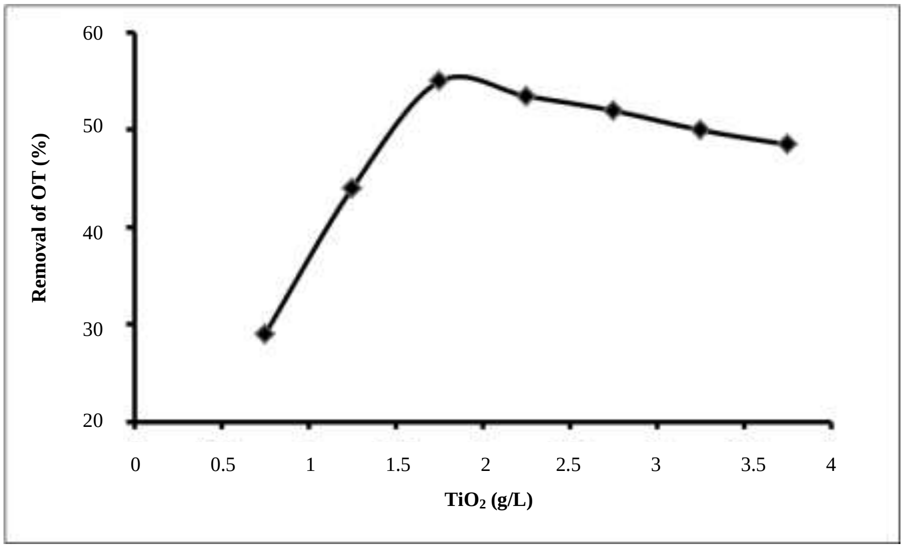


Figure 3. The effect of concentration of TiO_2 on degradation of OT (pH=7, [OT] =40 mg/l).

Effect of initial concentration of O-Toluidine in UV/TiO_2 process

Since the pollutant concentration was a very significant parameter in water treatment, so the effect of initial concentration of OT on the photo catalytic degradation rate was inspected over the concentration range of 10 to 40 mg/l (Figure 4).

The degradation reaction occurred to TiO_2 particles, so photo degradation rate depends on the initial concentration of OT and decreased with an increase in the initial concentration of contaminant [23]. The reaction was happening between the hydroxyl radicals produced by active OH^- sites on the surface of TiO_2 and the OT molecules from the solution. When the initial dosage of the pollutant was high (40 mg/l), the number of these available active sites was decreased by OT molecules, because of their competitive adsorption on TiO_2 surface and only 55.3% of the pollutant was degraded after 180 min of reaction. In this condition, the transfer rate of OT molecules from the solution was not affected on the removal rate, because with an increase in the initial concentration of OT, a large number of molecules were reacted with hydroxyl radicals originated from the process and hydroxyl radicals decreased. When the concentration of the OT was increased, more photons were adsorbed by pollutant and degradation rate decreased, because most of active site was covered by pollutant molecules.

However, when the initial concentration of the OT was low (10 mg/l), although there was more active sites and hydroxyl radicals, but the transfer rate of pollutant to catalyst surface was low, so in 10 and 20 mg/l of concentration, the removal percent of OT were 91.3 and 93.5%, respectively.

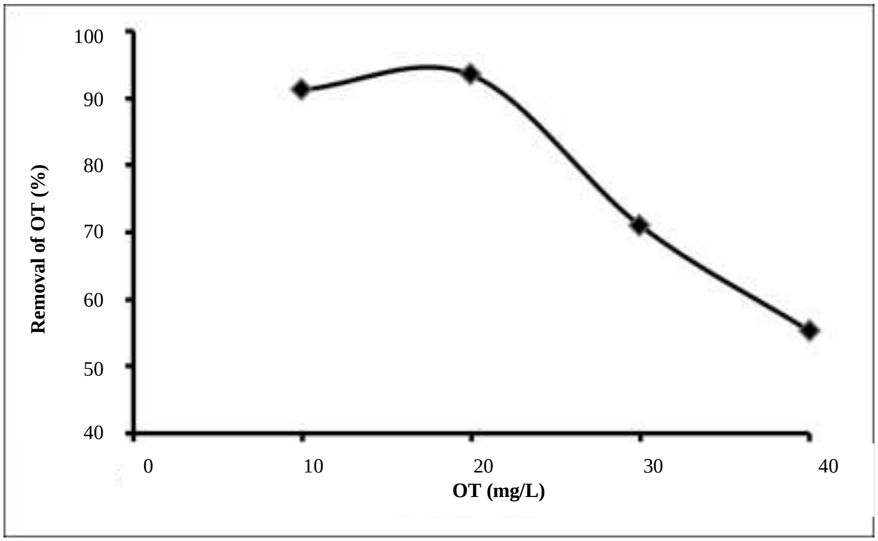


Figure 4. Effect of initial concentration of OT on photo catalytic degradation (pH=7, $[TiO_2]$ = 1.75 g/l).

Photo catalytic degradation of OT

When the pollutant irradiated with UV light for 180 min, slight degradation (3%) happened. The same experiments were performed in the presence of TiO_2 without UV light and only 5.5% of OT were disappeared because of adsorption of pollutant on the surface of the catalyst. Almost 93.5% of OT was degraded in the presence of TiO_2 along with UV light at 180 min of reaction. The hydroxyl radical was a really strong, non-selective oxidant that result in the degradation of organic contaminant [24–25] and this occurred only in catalyst together with UV irradiation. As it can be seen from the following equations, when TiO_2 illuminated by UV light, degradation and mineralization of the OT happened.

$$\mathrm{TiO_2} + h\nu < 387\ \mathrm{nm} \rightarrow e^-_{CB} + h^+_{vb} \quad (3)$$

$$h^+_{vb} + \mathrm{OT} \rightarrow \text{intermediates} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \quad (4)$$

$$\mathrm{H_2O} + h^+_{vb} \rightarrow OH^\bullet_{\mathrm{ads}} + \mathrm{H}^+ \quad (5)$$

$$\mathrm{OH}^\bullet + \mathrm{OT} \rightarrow \text{intermediates} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \quad (6)$$

$$h^+_{vb} + \mathrm{H_2O}_{\,(\mathrm{ads})} \rightarrow OH^\bullet_{\mathrm{ads}} + \mathrm{H}^+ \quad (7)$$

$$h^+_{vb} + OH^-_{\mathrm{ads}} \rightarrow OH^\bullet_{\mathrm{ads}} \quad (8)$$

$$OH^\bullet_{\mathrm{ads}} + \mathrm{OT}_{\,(\mathrm{ads})} \rightarrow \text{intermediates} + OH^\bullet_{\mathrm{ads}} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \quad (9)$$

Degradation of OT by Degussa TiO_2-P25 catalysts in optimum conditions is shown in Figure 5.

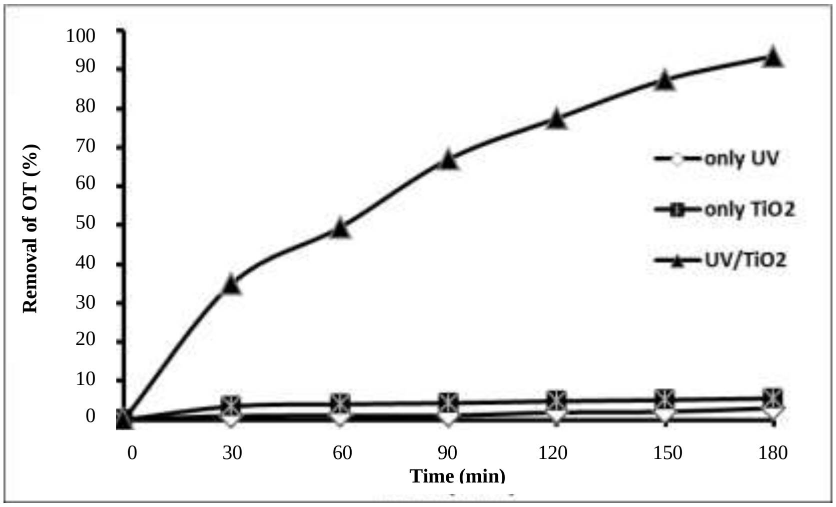


Figure 5. Effect of various processes upon degradation of OT in optimum conditions ([TiO_2] = 1.75 g/ l, [OT] =20 mg/l, pH = 7).

Removal of COD

COD was decreased in each process during treatment, but with a slower rate (Figure 6). These values were lower (35% in 180 min) than the ones corresponding to the OT degradation (93.5% in 180 min), because of intermediates were produced in the treatment process. In addition, in the first 120 min of reaction the rate of COD removal was slow which means that the intermediates produced continuously and they were persistent to photo catalytic degradation. However, in the final of treatment, the amounts of intermediates were reduced and their degradation rate was increased, subsequently the removal of COD increased. After 180 min of irradiation 57% of COD was removed in optimum condition for degradation of OT.

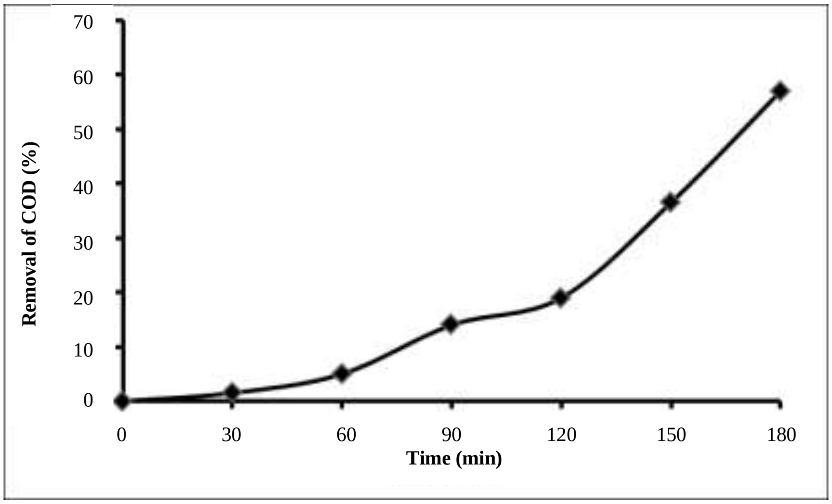


Figure 6. Removal of COD in optimum conditions ([TiO_2] = 1.75 g/l, [OT] =20 mg/l, pH = 7).

Kinetics of O-Toluidine degradation

Commonly the Langmuir–Hinshelwood model was used to describe the kinetics of photo catalytic degradation in aqueous suspensions [26]. It relates the degradation rate (R_{OT}) and the concentration of organic compound (C_{OT}), which is expressed as follows:

$$R_{OT} = \frac{k_r K_{ad} C_{OT}}{1+K_{ad} C_{OT}} \qquad (10)$$

k_r and K_{ad} are the rate constant and adsorption equilibrium constant, respectively. In this project, the adsorption was relatively weak and the concentration of OT was low (20mg/l) so Eq. 10 can be simplified to the pseudo first-order kinetics with an apparent rate constant, k_{app} [27]:

$$R_{OT} = k_r K_{ad} C_{OT} = k_{app} C_{OT} \qquad (11)$$

From the experimental results, kinetic constants of reaction were gained by fitting the experimental data using Pseudo first order kinetic equation. However, when the experimental data is plotted it looked like a first order reaction with respect to the OT decomposition. Therefore, a method to this kinetic study was done assuming that the degradation reaction followed first order kinetics. This achievement was in agreement with studies by several authors [28–29]. As shown in Figure 7, the experimental setup includes a mixed reactor (reservoir) and tow series cylindrical tubular photo reactors. In UV/TiO_2 process the degradation only occurs in the presence of both light and catalyst (as described in experimental section) so it can be proposed that the chemical reaction only happens in the photo reactors, but in the reservoir, exchanger and tube connections, very slight or no reaction were happening. The degradation rate was slow and the flow rate of recirculating pump was high (1.25 l/min) so we can assume that the OT concentrations in the photo reactor are really the same as in the reservoir. After integration from Eq.11 and multiplying the correction coefficient (V_L/V_R) the following equation was obtained:

$$\left(\frac{V_L}{V_R}\right).ln\left(\frac{[OT]_0}{[OT]}\right)= K_{app} \times t \qquad (12)$$

V_L and V_R are the total volume of the circulating liquid in the loop and the volume of the photo reactor, respectively. This expression is very similar to the normal one applied to a batch reactor. To evaluate these rate constants, the terms $\left(\frac{V_L}{V_R}\right).ln\left(\frac{[OT]_0}{[OT]}\right)$ versus reaction time was plotted, and after linear regression analysis, the first order rate constants (k=$19\times 10^{-3} min^{-1}$) and half-life of reaction ($t_{1/2} = 45.6\, min$) were determined [17].

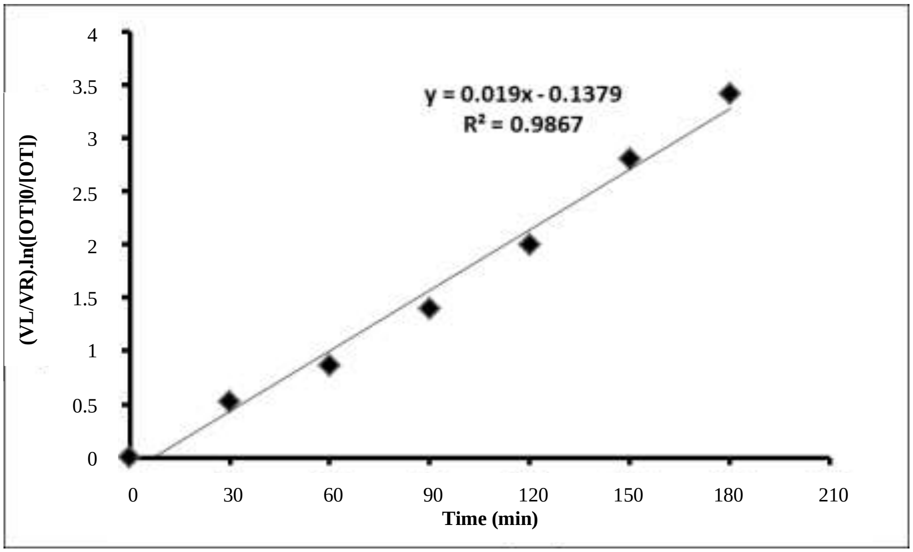


Figure 7. Kinetic fit for degradation of O-Toluidine in optimum conditions ([TiO_2] = 1.75 g/l, [OT] =20 mg/l, pH = 7).

CONCLUSIONS

The results of this study showed that:

- UV/TiO_2 process could efficiently be used to degrade the OT in a batch recirculating photo reactor with system light and oxygen, but UV light and TiO_2 had a negligible effect when they were used on their own.
- Experiments obviously were demonstrated the importance of choosing the optimum condition to gain high degradation rates, which is essential for photo catalytic processes.
- The degradation of the OT was clearly affected by irradiation time, initial concentration of pollutant, pH and the dosage of TiO_2. It was obtained that optimal condition of degradation was 1.75 g/l of photo catalyst, 20 mg/l of OT and neutral solution (pH=7).
- Removal of COD (57% in 180 min) was slower than removal of OT (93.5% in 180 min) because of persistent intermediates produced during degradation.
- Photo catalytic degradation of O-Toluidine in aqueous TiO_2 suspensions was followed a pseudo-first-order kinetics and the apparent rate constant (k_{app} =19× $10^{-3} min^{-1}$) depended on the initial concentration of O-Toluidine.

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