



Kinetic Study of Photocatalytic Degradation of Tolonium Chloride Under High Pressure Irradiation in Aquatic Buffer Systems

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Received 6 January 2011; Accepted 1 March 2011

Abstract: Anatase titanium dioxide catalyzed photodegradation of tolonium chloride at various bufferic pH of 2, 7, 9 and 12 in aqueous solution is presented. The effect of some physicochemical parameters such as initial concentration of dye, catalyst amount and reaction time on photocatalytic degradation has been investigated in a photo-reactor cell containing high pressure mercury lamp to obtain the optimum conditions in each bufferic pH at constant temperature. A complete spectrophotometric kinetic study of tolonium chloride under high pressure irradiation at buffer media was performed. The photocatalytic degradation observed rate constants (k_{obs}) were found to be 2.90×10^{-3} , 3.30×10^{-3} , 3.20×10^{-3} and $5.20 \times 10^{-3} \text{ min}^{-1}$ for buffer pH of 2-12 respectively. It was found that a pseudo-first-order kinetic model based on Langmuir-Hinshelwood one is usable to photodegradation of this compound at all considered buffer pH. In addition to these, the Langmuir-Hinshelwood rate constants, k_r , for the titled compound at various pH are reported.

Keywords: Degradation, Tolonium chloride, Photocatalytic, Anatase titanium dioxide

Introduction

It is well known that some dyes and degradation products are highly toxic and carcinogenic. The removal of pollutant compounds from aqueous media can be done using various techniques including biological treatments such as biofiltration and bioscrubbing; physical absorption methods for example use of activated carbon adsorption and destructive process such as wet chemical scrubbing, thermal oxidation, water hydrolysis by aqueous alkalis and oxidative chlorination¹⁻⁹. Each of these processes has some advantages, but production of large volumes of toxic solutions or toxic gaseous derivatives is one common disadvantage of

them that need next treatments. Heterogeneous photocatalysis based on the use of suitable semiconductor materials is known as another destructive technical process leading to the efficient degradation and in most cases the complete mineralization of a variety of organic or inorganic toxic pollutants present at aqueous waste waters. Among semiconductor oxides, titanium dioxide is the most applicable one because of some its properties such as stability and non-toxicity¹⁰⁻¹⁴. Therefore the use of TiO₂ as photocatalyst for the degradation of organic pollutants in water has been found as a highly promising universal method in the economically and environmental friendly processes point of view¹⁵. Previously photocatalytic decomposition of toloum chloride in the presence degussa-type titanium dioxide under medium pressure mercury lamp irradiation at non-bufferic system has been reported¹⁶. In continuation of our previous works¹⁷⁻²⁰ in this work kinetic study of photodegradation of toloum chloride (also known as Toluidine Blue) in the presence of anatase titanium dioxide under high pressure mercury lamp at various buffer system is described and compared with previous reported conditions.

Experimental

All compounds were purchased from Merck and Aldrich. Anatase titanium dioxide(99.9%) was analytical grade. The pH of solution was adjusted using diluted aqueous buffers that were prepared by the following compounds: KH₂PO₄, Na₂HPO₄, NaOAc, HOAc, Na₂B₄O₇, HCl, H₂SO₄ and NaOH. In all experiments doubly distilled water was used

Apparatus

Photochemical set containing 400W high pressure mercury lamp was used for photodegradation experiments. UV- VIS spectrophotometer, JASCO-V570, was used for spectral monitoring of toloum chloride concentrations. A parsazma SH-12 model of centrifuge was used for separation of photocatalysts from solution. Metrohm -620 model of pH-meter was applied for controlling of pH of solution.

Analytical determinations

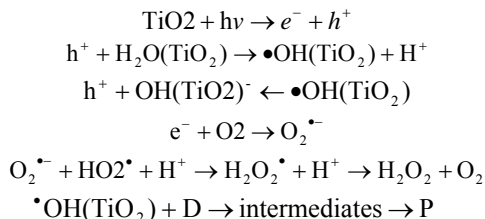
Spectrophotometric method was used for determination of concentration of toloum chloride via calibration curves at λ_{\max} =588, 590, 588 and 580 nm for buffer pHs of 2, 7, 9 and 12 repectively.

General procedure for photodegradation process

The photodegradation experiments were performed by irradiation of 20 mL of 70 and/or 80 ppm oxygenated (5 minutes bubbled) and stirred aqueous solution of toloum chloride as well as considered amounts of photocatalysts in photoreactor cell under 400W high pressure mercury lamp at room temperature. After requested time for photodegradation, photocatalyst was separated by centrifugation and photolyte was analyzed by UV-Vis spectrophotometric method.

Results and Discussion

Photocatalytic decomposition of a pollutant by use of a photocatalyst in presence of UV irradiation is illustrated by the mechanism²¹ shown in Scheme 1. The mechanism indicate that UV radiation, transfer one electron from conduction band to the valence band of the photocatalyst generating electron/hole(e⁻/h⁺) pairs. The e⁻/h⁺ pairs produce active oxidant species such as hydroxyl radicals, superoxide anion radicals and hydrogen peroxide that degrade target molecules (D) into decomposed products (P):



After introductory expression about the photocatalytic processes, the effect of effectual parameters and kinetics model in photocatalytic degradation of titled compound is presented in the next sections. By designing the blank experiments, it was found that degradation percents in the presence of agents such as photocatalyst, oxygen and irradiation simultaneously were non-comparable with those ones that each one of above agents is absence. Therefore at first, optimization of parameters was done in the presence of these three agents and then kinetic study performed.

Calibration curves for the standard solutions

Tolonium chloride is chemically stable in the range buffer pH, 2-12 therefore the standard solutions with the range of 0-100 ppm of tolonium chloride at buffer pH of 2, 7, 9 and 12 were prepared. Then the plots of absorbance *versus* concentration at λ_{max} were drawn in Figure 1.

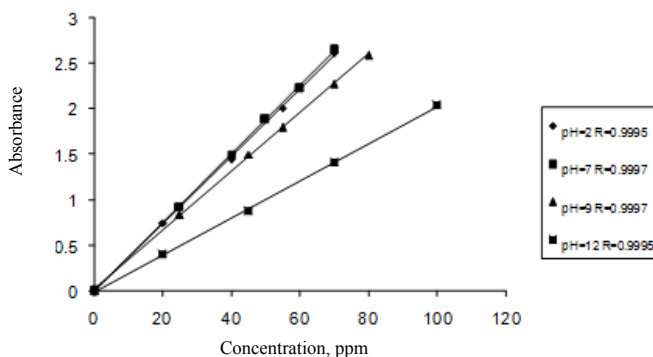


Figure 1. Calibration curve of tolonium chloride at buffer pH of 2, 7, 9 and 12

Optimization of anatase titanium dioxide loading on residual concentration

Decomposition of the compounds takes place on both active surface of the catalyst particles followed by adsorption and in bulk solution by photocatalyst generated active oxidant species. Therefore photocatalyst loading has an important role in decomposition. In our conditions, the effect of the catalyst loading has been presented by the plotting of residual concentration of tolonium chloride in each buffer pH after photodecomposition using various amounts of anatase titanium dioxide within the same reaction times. The plots are shown in Figure 2. As seen in the Figure 2, the amount of 30, 40, 40 and 20 mg were found to be optimum amount of catalyst at pH of 2, 7, 9 and 12 respectively for effective degradation of compound and higher amounts decrease the percent of degradation due to high scattering of UV-light by dispersed catalyst and therefore low formation of active sites and oxidant species²²⁻²³. It is to be noted that the optimum amount of photocatalyst is different at various buffer pH. This observation reveals that catalyst dispersion is different at various pH. It seems that in our conditions, dispersion at high acidic and high basic media is more than two other pH,

so that the lower the amount of photocatalyst is optimum in these pH. In previous report¹⁶ the effect of catalyst (Degussa titanium dioxide) loading only at non-bufferic pH of 5 has been reported that amount of 1 g/L catalyst was selected as optimum. In this work the higher amounts of catalyst for buffer pH 2, 7, 9 and the same amount are optimum for effective degradation. Other bufferic pH were not investigated because the lack of a suitable absorption wavelength for spectrophotometric analysis and monitoring.

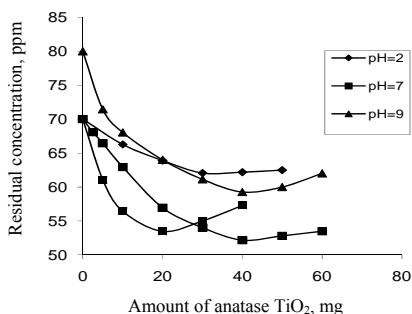


Figure 2. The effect of anatase titanium dioxide loading on residual concentration of tolonium chloride after irradiation (Time= 60 min. V=20 mL)

The effect of bufferic pH

Photodegradation of tolonium chloride in the presence of anatase titanium dioxide was affected by pH of the solution. The results as depicted in Figure 3 shows the more dye degradation was found to be at buffer pH= 9 when the dye concentration is 40 ppm and catalyst amount is 40 mg. This result can be explained based on adsorption mechanism under the influence of initial solution pH. Titanium dioxide usually has an isoelectric point of charge at a pH about 6.8, its surface has a positive charge at pHs lower than 6.8 via protonation and a negative charge at pHs higher than 6.8 via deprotonation. It seems that among the pH 2, 7, 9 and 12; at pH=9, there are more dye adsorption on or migration to near the catalyst surface favorable due to electrostatic interaction between tolonium chloride as cationic dye and catalyst. On the other hand, it is to be noted that in more alkaline solution $\cdot\text{OH}$ is easier to be generated by oxidizing of more hydroxide ions available on photocatalyst surface that diffuse to bulk solution leading to more effective photodegradation at basic medium²⁴. But also as will be seen in the next section when the optimum amount of catalyst at each pH is used, the higher photodegradation rate obtained at buffer pH=12. This trend also was observed in previous report when degussa titanium dioxide has been used at non-buffer pH.

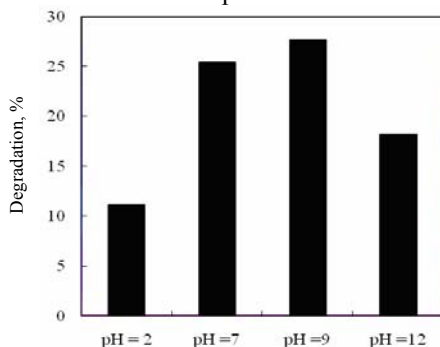


Figure 3. The effect of bufferic pH on % photodegradation (Anatase TiO₂: 40 mg; V=20 mL; irradiation time=60 min)

Kinetics study

The plots of residual concentration-time of tolonium chloride for each buffer pH using optimum amount of anatase titanium dioxide as mentioned in section 2.2 are drawn in Figure 4. As shown in this Figure for pH of 2, 7 and 9, the dye residual concentration reach to very low value after about 750 minutes while it is occurred after 500 minutes at pH= 12. In compared with degussa titanium dioxide catalyzed degradation at non buffer pH¹⁶, anatase titanium dioxide catalyses degradation after longer times. This can be related to both lower catalytic activity and bufferic conditions of medium during the reaction. The photodegradation of Tolonium chloride at bufferic pH obeys the pseudo-first order kinetics:

$$-\frac{dc}{dt} = kc$$

Where c is the concentration of Tolonium chloride and k is the observed first-order rate constant(k_{obs}). From the integration of this equation, the concentration-time equation of $\ln(C_0/C_t) = k_{obs}t$ will be derived.

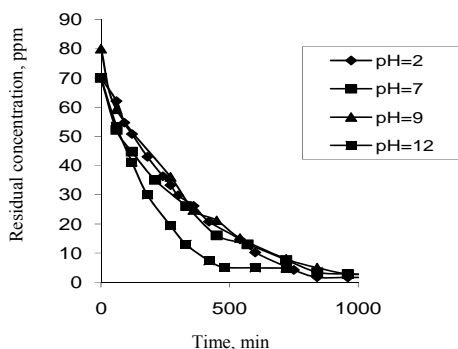


Figure 4. Residual concentration- time plots of tolonium chloride at various bufferic pH by use of optimum amount of anatase TiO_2 (V=20 mL)

A plot of $\ln(C_0/C_t)$ versus time lead to a straight line, the slope of which upon linear regression equals the observed first-order rate constant of photodegradation k_{obs} (Figure 5, Table 1).

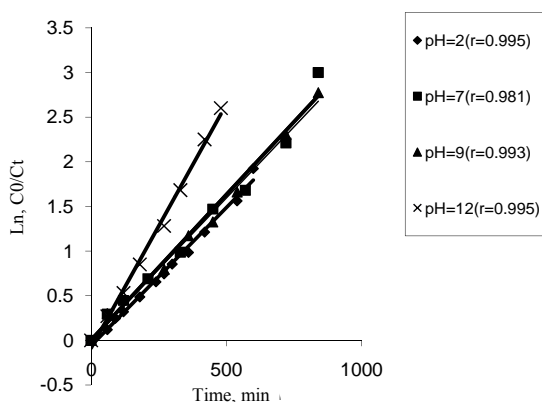


Figure 5. Kinetics of the tolonium chloride degradation ($\ln(C_0/C_t)$ vs. Time) at various buffer pH

Table 1. Kinetic parameters in photodegradation of tonium chloride at various buffer pH in the presence of anatase titanium dioxide

Kinetic parameters	pH=2	pH=7	pH=9	pH=12
$k_r, \text{mg. min}^{-1} \cdot \text{L}^{-1}$	0.46	0.77	0.46	1.38
$k_{\text{obs}}, \text{min}^{-1}$	2.9×10^{-3}	3.3×10^{-3}	3.2×10^{-3}	5.2×10^{-3}
$t_{1/2}, \text{min}$	239	210	216	133

The tonium chloride adsorption on catalyst surface can be explained by Langmuir-Hinshelwood (L-H) kinetic model²⁵⁻²⁷. Modified to accommodate the reaction occurring at a solid-liquid interface. In this model the rate of reaction is proportional to the surface coverage θ :

$$\theta = \frac{KC_0}{1 + KC_0 + K_s C_s}$$

Where K is the adsorption coefficient of substrate; K_s , the adsorption coefficient of solvent; C_0 , the initial concentration of substrate and C_s solvent concentration. The rate of photodegradation can then be written as a single-component L-H kinetic rate equation as following in which k_r is the apparent reaction rate constant occurring at catalyst surface.

$$\text{Rate} = R = \frac{-dc}{dt} = k_r \theta = k_r \frac{KC_0}{1 + KC_0 + K_s C_s}$$

If K_A is defined as:

$$K_A = \frac{K}{1 + K_s C_s}$$

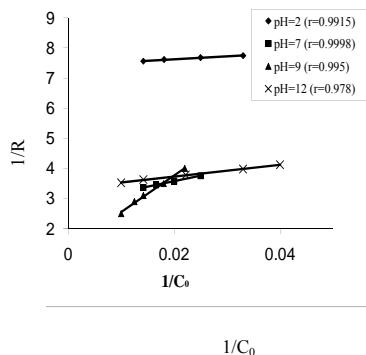
The rate expression will be as:

$$\text{Rate} = R = \frac{-dc}{dt} = k_r \theta = k_r \frac{K_A C_0}{1 + K_A C_0}$$

And ultimately the equation $1/R$ in $1/C_0$ will be obtained:

$$\frac{1}{R} = \frac{1}{k_r K_A C_0} + \frac{1}{k_r}$$

The linear plots of $1/R_{\text{L-H}}$ versus $1/C_0$ for tonium chloride on at various buffer pH is shown in Figure 6, which confirms the L-H model. In range of used concentration, photodegradation kinetic is in agreement to L-H model.

**Figure 6.** The plots of $1/R$ vs. $1/C_0$ at various buffer pH (Langmuir-Hinshelwood kinetics for degradation of tonium chloride in the presence of anatase TiO_2)

As seen in Table 1, observed photodegradation rate constant, k_{obs} (related to total reaction) and apparent reaction rate constant, k_r increase while dye degradation half time, $t_{1/2}$ decreases as solution pH is raised. The maximum value of k_{obs} and k_r is related to bufferic pH of 12. A comparison between photodegradation rates of tolonium chloride at current work with ones previously reported under medium pressure irradiation using degussa titanium dioxide at non-bufferic pH is performed in Table 2.

Table 2. A comparison between photodegradation rates of tolonium chloride at different two conditions

Phodegradation rate, k_{obs}	pH=2	pH=7	pH=9	pH=12
^a Ref ¹⁶ , $k_{\text{obs}} \text{ min}^{-1}$	-	6.0×10^{-2}	$(6.0-7.0) \times 10^{-2}$	-
^b Present study, $k_{\text{obs}} \text{ min}^{-1}$	2.9×10^{-3}	3.3×10^{-3}	3.2×10^{-3}	5.2×10^{-3}

^aRefers to condions: Degussa TiO_2 ; 125W medium pressure mercury lamp; non-bufferic medium.

^bRefer to conditions: anatase TiO_2 (99.9%); 400W high pressure mercury lamp; bufferic medium

Finally as seen in Table 2, the order of photodegradation rates of tolonium chloride based on conditions is as degussa titanium dioxide/medium pressure irradiation/non-bufferic pH > anatase titanium dioxide/high pressure mercury lamp/bufferic pH. The plots of $1/R$ versus $1/C_0$ show that rate are decreased with increase of the initial concentration while in the presence of degussa type titanium dioxide the rate increase with increase of dye concentration and after a maximum is decreased. A comparison between the apparent reaction rate constants, k_r , at two conditions in Table 2 is not possible because this parameter has not been reported previously. This observed different between observed rates, k_{obs} at two conditions may be related to a) more photoactivity of degussa titanium dioxide with respect to anatase titanium dioxide b) bufferic media in our current work that causes covering the surface of photocatalyst leading to reduction of the active sites for degradation. Also the current work indicates the optimum amount of catalyst is dependent to pH and may be different in different pH.

Conclusion

In this research kinetic study of photodegradation of tolonium chloride at various bufferic pH of 2, 7, 9 and 12 in aqueous solution was presented. The effect of some physicochemical parameters such as initial concentration of dye, catalyst amount and reaction time on photocatalytic degradation has been investigated in a photo-reactor cell containing high pressure mercury lamp to obtain the optimum conditions in each bufferic pH at constant temperature. A complete spectrophotometric kinetic study of Tolonium chloride under high pressure irradiation at buffer media was performed and compared with previous Degussa type titanium dioxide phodegradation of the titled compound.

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