

Photooxidation: A Decolorization Procedure and a Pre-Treatment Step for Biodegradation of Reactive Azo Dye

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Received: June 3, 2004

Accepted: June 29, 2005

Abstract

In this study, by using a different variety of TiO_2 catalyst, photocatalytic oxidation of reactive azo dye used in textile industry and an improvement in the biodegradability of the dye by photocatalytic oxidation are investigated. It was found that the addition of TiO_2 in the photooxidation of dye increased color removal by 30.84 %, the addition of H_2O_2 in the presence of TiO_2 also increased color removal by 33.98 %. The study also examined the effect of TiO_2 obtained from different companies in color removal and it was found that TiO_2 obtained from Merck and Degussa displayed similar effectiveness in color removal. It was further found that, depending on the chemical composition of dye used, the ions, SO_4^{2-} , Cl^- and NH_4^+ emerged and that NH_4^+ was oxidized to NO_2^- . As a result of the 42 h long photocatalytic oxidation, a COD removal of about 85.3 % was achieved. In this study, Langmuir-Hinshelwood kinetic constants were examined and it was found that $k=0.971$ mg/L min and $K=0.176$ L/mg. By analyzing respirometric measures of raw and photocatalyzed dyes, it was determined that photocatalyzed dye had higher biodegradability than raw dye. Improvement in biodegradation was proven by the rise of BOD_5/COD ratio from 0.06 to 0.29.

Keywords: azo dye, biodegradability, Langmuir-Hinshelwood kinetics, photooxidation

Introduction

Most synthetic dyes commonly used in textile and other industries consist of azo dyes that contain azo chromophore. Since the fixation of dyes is poorly made in the textile industry, the concentration of azo dye in wastewater varies from 5 to 1500 mg/L [1]. Due to high stability of dyes and the existence of high levels of aromatic compounds in their molecular structure, conventional biological treatment methods remain insufficient in terms of color removal and dye degradability [2]. It is stated that these substances that remain unchanged after conventional treatment constitute 50 to 90 percent of total waste [3]. Dye which reaches the environment creates serious

environmental problems. Besides aesthetic deterioration in the environment, it is well known that dyes as well as their biotransformed by-products are quite harmful to living organisms.

Effluents from textile industries are highly variable in composition with relatively low BOD and high COD contents and are typically characterized by strong color and are recalcitrant due to the presence of residual dyes. Increasing environmental concerns regarding the treatment of textile effluents have led to the introduction of strict discharge limits all over the world. Given the complex and bioresistant character of textile effluents, their effective treatment usually requires a combination of various physical, chemical and biological technologies. In view of this, several advanced oxidation processes have been employed as a pre-treatment method aimed at reducing

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effluent color and biorecalcitrance. The photocatalytic oxidation that is currently used is one of the various advanced oxidation processes. In general, a chemical oxidation method aimed at complete mineralization might become extremely cost-intensive since the highly oxidized end-products that are formed during chemical oxidation tend to be refractory to total oxidation by chemical means. A potentially attractive alternative to complete oxidation through chemical means is the use of a chemical oxidation pre-treatment step to convert initially bio-recalcitrant organics to more readily biodegradable intermediates [4].

Using the photooxidation process as a pre-treatment step for the improvement of biodegradability has been subjected to numerous investigations by researchers. Pulgarin et al. [5] have used combined systems of photooxidation as a method of pre-treatment previous to the biodegradation of *p*-NTS and come up with satisfactory results in terms of optimal use of time and energy [5]. The influence of ultraviolet photolysis as a pre-treatment step to the aerobic and anaerobic biological mineralization of polyacrylamide was investigated by El-Mamouni et al. [6]. A positive correlation between the time of irradiation and the degree of its biological mineralization was determined. Aerobic and anaerobic biomineralization of the unphotolyzed polyacrylamide was 0.6% and 0.7%, respectively. Aerobic mineralization of photolysed samples was 5%, 17%, 29% and anaerobic mineralization was 3%, 5%, 17% after 12, 24 and 48 h, respectively [6]. Another study to determine the efficiency of photochemical pre-treatment was conducted for two different non-biodegradable herbicides (metabromuron and isoproturon). BOD₅/COD ratio of metabromuron was increased from 0.0 to 0.1 by photochemical pre-treatment. Furthermore the BOD₅/COD ratio of solution resulting from photocatalytic treatment of isoproturon was increased from 0.0 to 0.65 [7]

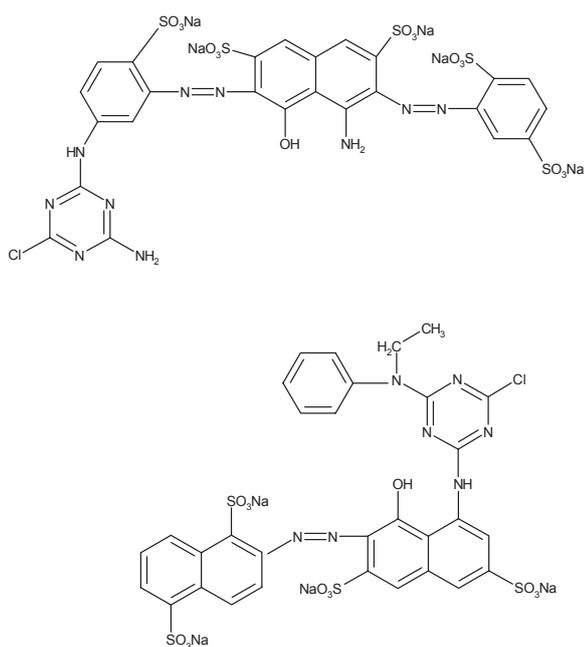


Fig. 1. Chemical structure of azo dye mixture.

Table 1. Properties of TiO₂ used in the photooxidation process.

Parameter	Degussa P-25	Merck/Sigma
Specific surface area (m ² /g)	50±15	-
Density at 20 °C (g/cm ³)	~3.8	3.9-4.2
Solubility in water	Insoluble	Insoluble
Average particle size (nm)	21	-

The present paper dwells on the photooxidation of reactive azo dye and improvements in biodegradability as a result of photooxidation.

Materials and Method

Dye Used

In the present study a reactive dye which is commonly used in the textile industry and manufactured by the Ciba Specialty Chemicals was used. The dye was not exposed to any treatment process. The reactive dye used was the mixture of sulphonated 2 azo group dye (at the ratio of 10-20%) and sulphonated 1 azo group dye (at the ratio of 1-5%). The chemical composition of the dye is shown in Fig. 1.

Catalyst

TiO₂ was obtained from three different companies, i.e., Sigma, Merck and Degussa. The samples from Merck and Sigma have similar characteristics. Table 1 gives the properties of TiO₂ used in the process. All other chemical substances used in the process were of analytical grade.

Experimental Equipment

The experimental work was carried out by illumination of synthetic dye solution prepared with distilled water in a glass vessel of capacity 4.5 L. Two 15W UV-C

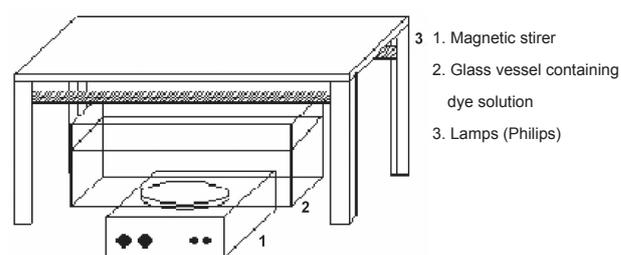


Fig. 2. Experimental setup.

Table 2. Series used in respirometric measurement.

Series	Content
Series I	The Mixture (1.05 mL of glucose solution+0.1 mL nutrient A+0.1 mL nutrient B+5 mL activated sludge) made up to a volume of 105 mL with distilled water.
Series II	The Mixture (99.8 mL raw dye solution+0.1 mL nutrient A+0.1 mL nutrient B+5 mL activated sludge)
Series III	The Mixture (99.8 mL photocatalytically treated dye solution+0.1 mL nutrient A+0.1 mL nutrient B+5 mL activated sludge)

Note: Additions were made so as to have the Nutrient A with buffering properties as well as Nutrient B that contained various trace elements correspond to 10 mL for COD of 1000 mg.

Composition of nutrient A and B are given below:

Nutrient A: 320 g/L K_2HPO_4 , 160 g/L KH_2PO_4 , 120 g/L NH_4Cl

Nutrient B: 15 g/L $MgSO_4 \cdot 7H_2O$, 0.5 g/L $FeSO_4 \cdot 7H_2O$, 0.5 g/L $ZnSO_4 \cdot 7H_2O$, 0.5 g/L $MnSO_4 \cdot H_2O$, 2.7 g/L $CaCl_2 \cdot 2H_2O$

Glucose solution containing 10 mg of COD in 1 mL was used in the experiment.

Sludge: Aerobic activated sludge from the recycling line of İzmit Industrial and Domestic Wastewater Treatment Plant was washed out three times with tap water, then centrifuged at 5000 rpm 3 times for a period of 10 min and separated completely from its upper supernatant. The solid content of activated sludge was 20 g/L.

lamps (Philips®-TUV model) were used for light. Experiments were performed in an open batch system (Fig. 2). 15 W low-pressure mercury lamps emitted UV-C light at 254 nm and the light intensity was 3.0 mW/cm² at approximately 10 cm.

Experimental Procedure

Effect of Oxidant and Catalyst in the Photooxidation Process

H_2O_2 was used as the oxidant and TiO_2 was used as the catalyst in the experiment. Effects of the oxidant and catalyst were investigated in the series UV, UV/ H_2O_2 , UV/ H_2O_2/TiO_2 (Degussa), UV/ H_2O_2/TiO_2 (Merck), UV/ H_2O_2/TiO_2 (Sigma) and UV/ TiO_2 (Degussa) in terms of color removal of illuminated dye solution. 1 g/L TiO_2 and 0.02 M H_2O_2 were used for 100 mg/L dye solution in all series.

Examination of Photooxidation Products

In the series UV/ H_2O_2/TiO_2 (Degussa), changes in the concentration of SO_4^{2-} , NO_2^- -N, NH_4^+ -N and Cl^- ions were examined in the samples taken from the dye solution throughout the process of photooxidation that lasted for 42 h.

Examination of Kinetic Photooxidation

To determine kinetic oxidation, dye solutions at different initial concentrations (25, 50, 75, 125 mg/L) were made subject to photooxidation in the presence of 1 g/L TiO_2 and 0.02 M H_2O_2 in the series UV/ H_2O_2/TiO_2 (Degussa). Color removal was determined for the samples taken during the oxidation process.

Effect of Photooxidation Process in terms of its Effects on Dye Biodegradation

Short and long duration degradability tests were applied in order to assess improvements in the biodegradation of treated dye by the photooxidation process. In short duration test, respirometric analyses were used. The series which are listed in Table 2 were investigated to estimate biodegradation by the activated sludge of the treated dye solution that was photocatalyzed for 42 h in the presence of a catalyst and oxidant and the untreated dye solution. For this purpose, changes in the concentration of dissolved oxygen (DO) in the treated and untreated dye solutions which were kept in containers of 105 mL with no oxygen entry were observed in series given in Table 2 [8]. Oxygen uptake rate (OUR, mg/L min) was determined by dividing abatement rates in DO by the time period. Maximum activity of the sludge was observed with the addition of glucose, a substrate easily consumed by activated sludge in Series I. The activity of sludge in decomposition of raw and photocatalyzed dye was observed in Series II and Series III, respectively.

In long duration degradability test, BOD_5 and COD of both raw dye solution and photocatalyzed dye solution illuminated for a period of 42 h were measured. The improvement of biodegradability was determined by observing the BOD_5/COD ratio.

Analysis

Prior to spectrophotometric analysis on photocatalyzed samples, TiO_2 was separated by a centrifuge at 5000 rpm for 10 min. In treated samples, visible colors of which were removed by photocatalytic oxidation, Cl^- , NO_2^- , NH_4^+ , SO_4^{2-} ions were analyzed using Hach DR/2000 spectrophotometry. For the raw dye solution, the same ions were analyzed using ion chromatography (Dionex DX 100). A CADAS 200 spec-

trophotometer was used to measure the absorbance of the dye solution by scanning in the wavelength range of 200 to 800 nm. Dissolved oxygen was analyzed by using WTW OXI 3000. BOD analysis was made by using Lovibond BOD-Sensor and Inductive Stirring System. The COD analysis was conducted on the sample where TiO_2 was centrifuged according to 5220 C "Close Reflux, Titrimetric Method" as given in Standard Methods [9].

Results and Discussions

Effect of the Oxidant and Catalyst

By means of estimating the changes in absorption spectrum with respect to illumination time during the photocatalytic oxidation of the studied dye, it was found that the solution yielded maximum absorbance in two wavelength range (range 260 to 290 nm in UV region and range 580 to 590 nm in visible region dependent on illumination time) (Fig. 3).

Compounds containing at least one chromophoric group like quinoid carbonyl, vinyl groups ($\text{CH}_2=\text{CH}-$), azo ($-\text{N}=\text{N}-$), nitro ($-\text{NO}_2$), nitroso ($-\text{NO}$) and carbonyl, leads to absorption in the visible spectral region. These substances in the visible region are seen as colored by naked eye [10]. Considering the chemical composition of dye used in the experiment, it can be inferred that the group giving visible color was azo ($-\text{N}=\text{N}-$) and the absorbance peak at range 580 to 590 nm originated from the presence of this chromophore group [8]. Examining Fig. 3, we may conclude that absorbance in the visible area decreased in a short illumination period. For example, color removal in 20 min illumination was 63.31 % at 580 nm and 10.65 % at 290 nm. Since the absorption peak in the UV region derives from aromatic rings, it can be concluded that short duration illumination is insufficient to fracture such structures while it may well be effective in fracturing azo ($-\text{N}=\text{N}-$) links.

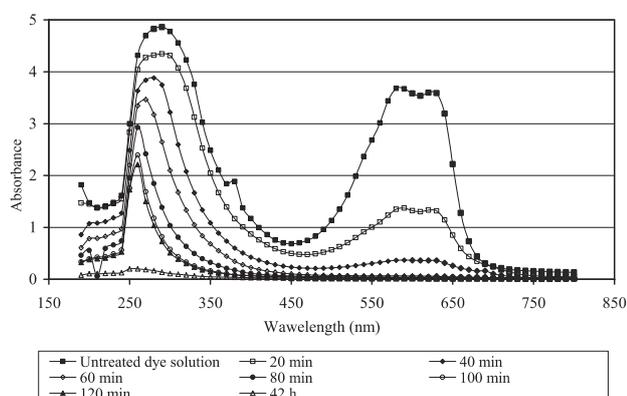


Fig. 3. Variation in absorbance with respect to wavelength for different period of photooxidation in $\text{UV}/\text{H}_2\text{O}_2/\text{TiO}_2(\text{Degussa})$ series.

The respective activities of catalyst and oxidant in the photooxidation process are explained by color removal of dye solution in different series. Change in absorbance observed in visible region is examined for the UV, $\text{UV}/\text{TiO}_2(\text{Degussa})$, $\text{UV}/\text{H}_2\text{O}_2/\text{TiO}_2(\text{Degussa})$, $\text{UV}/\text{H}_2\text{O}_2/\text{TiO}_2(\text{Merck})$ and $\text{UV}/\text{H}_2\text{O}_2/\text{TiO}_2(\text{Sigma})$ series (Fig. 4). In this series a photooxidation period of 120 minutes yielded the following rates of color removal: 34.28%, 65.12%, 99.10%, 98.41% and 70.21%. The increase by 30.84 % that emerged with the addition of TiO_2 can be attributed to two factors. The first is that a part of dye molecules are absorbed by the TiO_2 surface. The second factor is related to the fact that the active $\cdot\text{OH}$ radicals formed by the photolysis of water molecules played their part in the oxidation mechanism. The addition of H_2O_2 to the system with $\text{TiO}_2(\text{Degussa})$ led to an increase of 33.98 %. This increase may be attributed to the role of $\cdot\text{OH}$ radicals formed by H_2O_2 photolysis in accelerating the process of photooxidation. Evaluating color removal with respect to TiO_2 types, we observed that Merck and Degussa-P25 is more effective than Sigma.

Evaluation of Photooxidation Products

The degradation mechanism of dyes by photooxidation has similar characteristics with the degradation of mechanisms of other aromatic compounds. Here the possible mechanism was discussed [8]. In studied dye that is of anionic character, the most important factor that makes dye soluble in water is the presence of $-\text{SO}_3\text{Na}$. In water solutions, dye is ionized to sodium cations and colored sulphonate anions. Sulphonic groups linked to the aromatic ring in the structure break apart as a result of photocatalytic processes and turns into SO_4^{2-} ion [11]. This rupture is also possible for the $-\text{Cl}$ group that is attached to the triazine ring [12]. Experiments conducted by Ma and Chu [13] showed that Cl^- ion is formed as a result of degradation in aromatic disperse dye. Amino groups existing in dyes become subject to oxidation after their rupture from the main body [13]. It is in the light of this information that we observed and examined changes in SO_4^{2-} , Cl^- , NH_4^+-N and NO_2^- ions during the photooxida-

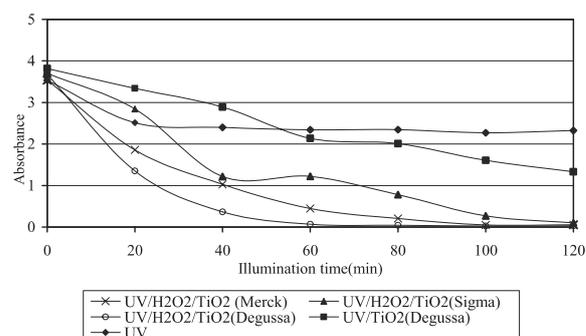


Fig. 4. Absorbance variation of treated dye in visible region with respect to illumination time for different series.

Table 3. Changes in COD concentration with respect to the illumination time in UV/H₂O₂/TiO₂ (Degussa) series.

Illumination time (h)	COD (mg/L)
0	92.9
21	25.8
28	24.3
35	21.3
42	13.68

tion process of the series UV/H₂O₂/TiO₂(Degussa) (Fig. 5). Since the dye mixture used had not been subject to any process for purification, initial concentration of the ions examined in raw dye solution were found at a specific level. No significant increase was observed since there was limited amount of -Cl group in the composition. The concentration of Cl⁻ ions increased from 9.3 mg/L to 12.8 mg/L after illumination of 7 h. However, since the dye was rich in its -SO₃ content, there was an increase in SO₄²⁻ throughout the process of illumination. 7 h long illumination led to a rise in SO₄²⁻ from 5.2 mg/L to 27 mg/L. Meanwhile, with the same amount of illumination time (7 h) NH₄⁺-N was rose from 0.728 mg/L to 2.2 mg/L accompanied by a rise in NO₂⁻-N, which occurred by the oxidation of NH₄⁺, was rose from 0.0237 mg/L to 1.217 mg/L.

COD analysis conducted on treated samples in UV/H₂O₂/TiO₂ (Degussa) series indicates that this process is as effective in COD elimination as in color removal (Table 3). Specific COD removal rate was 2.1 mg/Lh in the interval 0-35 h, later falling to 1.1 mg/Lh in the interval 35-42 h. In this series, after illumination period of 42 h, COD and color removal for dye solution came out to be 85.3 % and 99.6%, respectively. The fact that color removal ratio was greater than COD removal ratio showed that the photooxidation mechanism has started with the breaking of structure that gives color in the organic matter, and with the prolonged illumination time, by breaking down the main structure of molecule, it became proper for mineralization.

Evaluation of Reaction Kinetics

Langmuir-Hinshelwood (L-H) kinetics have been used successfully as a qualitative model to describe solid-liquid reactions. In heterogenous photocatalysis, the presence of TiO₂ particulates brings about the interaction of the surface with the solvent and the substrates. The substrate and water molecules could be absorbed on the surface and their competition for the same active sites can not be ignored. These simultaneous adsorptions influence the observed reaction kinetics. In such a case, modified form of the Langmuir-Hinshelwood (L-H) equation has been successful as a quantitative model to describe solid-liquid interactions. According to the Langmuir-Hinshelwood (L-

H) kinetic treatment, the rate of a surface reaction can be calculated by Equation (1) [14],

$$R = \frac{-dC}{dt} = k\theta = k \frac{K[C_0]}{1 + K[C_0]} \quad (1)$$

where; R , is the rate of the oxidation, k is the reactivity constant, θ is the fraction of surface covered, K is the adsorption equilibrium constant, C_0 is the initial concentration of the substrate.

This kinetic model is especially useful when the intermediate products of oxidation accumulate on the catalyst surface by adsorption at relatively high substrate concentrations, which limits the reaction rate.

The obtained expression by integration of Equation (1) was given in Equation (2),

$$t = \frac{1}{kK} \ln \frac{[C_0]}{[C_1]} + \frac{1}{k} ([C_0] - [C_1]) \quad (2)$$

The half life of the reaction ($t_{1/2}$) was given in Equation (3)

$$t_{1/2} = \frac{0.693}{kK} + \frac{0.5[C_0]}{k} \quad (3)$$

a plot of $t_{1/2}$ versus C_0 should yield a straight line whose slope is $0.5/k$ and whose intercept is $0.693/kK$.

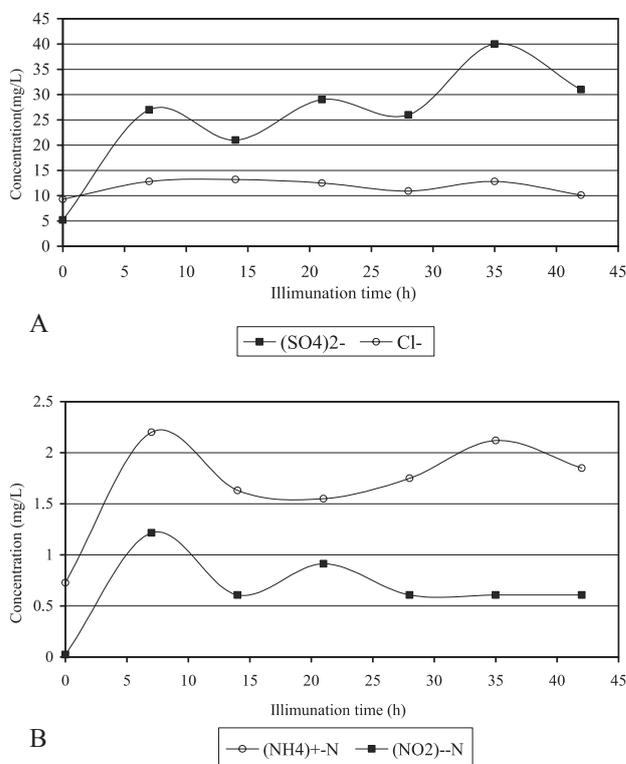


Fig. 5. Changes in concentrations of NH₄⁺-N, NO₂⁻, SO₄²⁻, Cl⁻ ions with respect to illumination time in UV/H₂O₂/TiO₂ (Degussa) Series: A) SO₄²⁻, Cl⁻; B) NH₄⁺-N, NO₂⁻-N.

Table 4. Relationship between absorbance and illumination time and $t_{1/2}$ values for different initial dye concentrations.

Initial dye concentration (mg/L)	The linear relation between absorbance and illumination	Correlation constant (R^2)	$t_{1/2}$ (min)
25	$C = -0.2799t + 18.04$	0.703	19.79
50	$C = -0.4423t + 37.521$	0.7821	28.31
75	$C = -0.7423t + 66.631$	0.9059	39.24
125	$C = -0.7862t + 117.96$	0.9205	70.54

k_{ap} (kK) gives the apparent first order reaction constant [15,16,17,18].

Hence by determining the L-H kinetic constants of a reactive dye used, it is possible to estimate the rate of reaction corresponding to a given specific concentration. To do this, dye solutions of different initial concentration (C_0) were photocatalyzed in the series UV/H₂O₂/TiO₂ (Degussa). For each C_0 by graphing C , the dye concentration with respect to t , the illumination time, the expression giving the relationship between C and t was obtained. In this expression, $t_{1/2}$ is the illumination time value corresponding to $C=C_0/2$. The equation and $t_{1/2}$ values thereby calculated are given in Table 4.

The relationship between C_0 and $t_{1/2}$ is expressed by the linear equation (4) given below (Fig. 6),

$$t_{1/2} = 0.515C_0 + 4.0626 \quad (4)$$

According to Equation (3), there was a linear relation between $t_{1/2}$ and C_0 . Correlation coefficient for this linear relation was found to be $R^2=0.9819$. By using this relation, for any C_0 concentration, the value for $t_{1/2}$ can be calculated. By considering the constants of Equation 4, k , K and k_{ap} constants were calculated according to equations 5, 6 and 7.

$$\frac{0.5}{k} = 0.515 \quad k = 0.971 \text{ mg/Lmin} \quad (5)$$

$$\frac{0.693}{kK} = 4.0626 \quad K = 0.176 \text{ L/mg} \quad (6)$$

$$kK = k_{ap} = 0.171 \text{ 1/min} \quad (7)$$

Evaluation of Biodegradability Results

The importance of respirometric measurement within the biodegradability tests is well known. In this study, respirometric measurements were made to assess the biodegradability of raw and treated dye solution.

The respirogram of activated sludge with photocatalytically treated and untreated dye solution is given in Fig. 7. Considering the OUR values for the first 10 min., we observed that while there is no change in OUR values in Series II, a decrease in OUR values was observed which was from 1.58 to 0.17 mg/Lmin in Series I and from 1.13 to 0.12 mg/Lmin in Series III. This clearly shows that it is

impossible to biologically degrade raw dye in short time intervals. This becomes possible, however, by introducing the process of photocatalysis. In Series II and III, the sludge could not reach the maximum activity level that was reached in Series I. BOD₅/COD ratio was used in order to decide whether this improvement generated by photocatalytic oxidation was sufficient for treatment in activated sludge systems. BOD₅ value was measured as 6 mg/L and 4 mg/L for raw dye solution and photocatalyzed dye solution by 42 h illumination, respectively. A 42 h long photocatalysis raised the BOD₅/COD ratio of raw dye from 0.06 to 0.29. Nevertheless, this increase is still not enough to support treatment in conventional activated sludge unit since it is stated that a BOD₅/COD ratio of

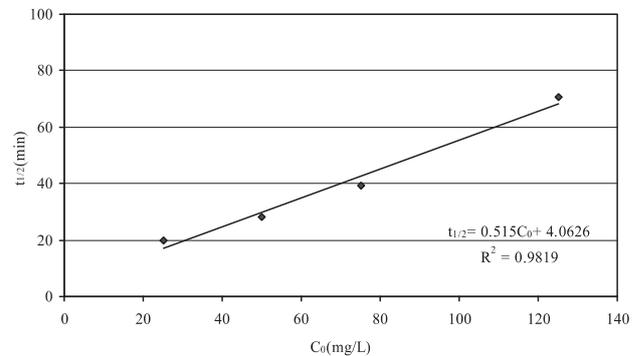


Fig. 6. Changes in $t_{1/2}$ with respect to different initial dye concentrations.

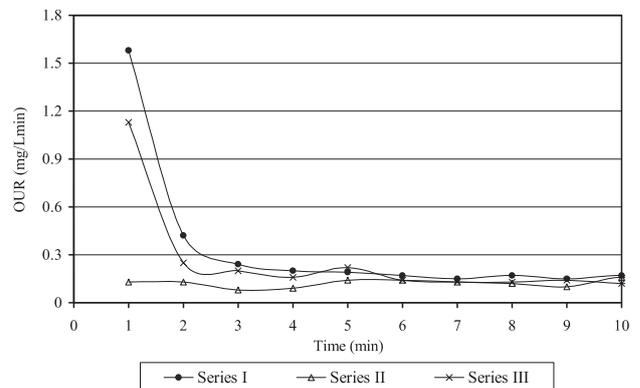


Fig. 7. Changes in OUR with respect to time.

at least 0.5 is required for the treatment of wastewater in conventional biological treatment plants [19].

Conclusions

The photooxidation process is as much effective in the elimination of organic substances as it is in the removal of color. It was found that the addition of TiO_2 in the photooxidation of dye increased color removal by 30.84%, and the addition of H_2O_2 given the presence of TiO_2 , increased by 33.98%. After a process of photooxidation for 7 h, it was found that, depending on the chemical composition of the dye in treated dye solution, concentrations of SO_4^{2-} and Cl^- ions increased from 5.2 mg/L to 27 mg/L and from 9.3 mg/L to 12.8 mg/L, respectively. As a result of the rupture of amino groups, the concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ increased from 0.728 mg/L to 2.2 mg/L and from 0.0237 mg/L to 1.217 mg/L, respectively. Langmuir-Hinshelwood kinetic constants were found as $k=0.971$ mg/Lmin and $K=0.176$ L/mg. It would be possible to determine the rate of color removal in a specific dye concentration by means of the constants. Measures indicate that the photocatalyzed dye is more prone to biodegradation than raw dye. This improvement in biodegradation was proven by the rise of BOD_5/COD ratio from 0.06 to 0.29. This ratio is not appropriate for treatment in conventional activated sludge systems. This ratio, however, can be further improved by extending the period of illumination. It should not be forgotten that such an extension would necessarily increase costs.

Acknowledgements

The financial support of Kocaeli University Research Foundation under Project Number: 2002/67 is gratefully acknowledged.

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