

Photodegradation of 2-naphthol Using Nanocrystalline TiO₂

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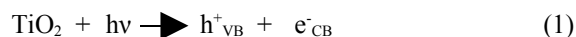
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The kinetics of the photocatalytic degradation of 2-naphthol has been investigated in aqueous suspensions of titanium dioxide (TiO₂) under a variety of conditions, which is essential from application point of view. The degradation was studied using different parameters such as types of TiO₂, catalyst concentration, substrate concentration, reaction pH and in the presence of different electron acceptors such as hydrogen peroxide (H₂O₂), potassium bromate (KBrO₃) and potassium persulphate (K₂S₂O₈) besides molecular oxygen. The degradation rates were found to be strongly influenced by all the above parameters. The photocatalyst "Degussa P-25" was found to be more efficient as compared with other photocatalysts. The results indicate the process follows Langmuir-Hinshelwood-type kinetics and inference is made of the reaction taking place on the semiconductor particle surface. An analysis of Total Organic Carbon (TOC) showed that a complete mineralization of 2-naphthol can be easily achieved.

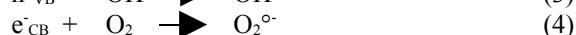
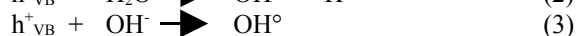
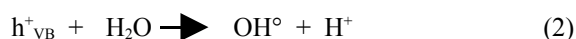
Keywords: Photocatalysis, Titanium dioxide, 2-naphthol, Water treatment.

I. INTRODUCTION

One of the most important challenges for science is to develop efficient methods to control environmental pollution. Several specific new technologies, called Advanced Oxidation Processes (AOPs), have been developed to eliminate dangerous chemicals such as organics from polluted waters. The photocatalytic process, based on UV-irradiated semiconductor, represents one of AOPs that provide an interesting route to the destruction of many organic substances to CO₂, H₂O and corresponding mineral acids [1-3]. Nanocrystalline TiO₂ is one of the most preferable semiconductors for the photocatalytic process [4,5]. The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed extensively in the literature [6,7]. When titanium dioxide (TiO₂) is illuminated with light of band gap energy (3.2 eV), electrons in conduction band (e⁻_{CB}) and holes in valence band (h⁺_{VB}) are produced according to:



These charge carries can recombine, or the holes can be scavenged by oxidizing species (for example, H₂O, OH⁻), and electron by reducible species (for example, O₂) in the solution:



The hydroxyl radical (like OH[•]) is a highly reactive oxidizing reagent and can decompose most organic contaminants.

In this work, we present the results of our investigation on the photodegradation kinetics of 2-

naphthol in aqueous TiO₂ suspensions. The impacts of various parameters on the reaction rate, such as type of photocatalyst, substrate and catalyst concentrations, initial pH of the solution and addition of several electron acceptors, were investigated to determine the optimum treatment conditions. The analysis of Total Organic carbon (TOC) was also determined.

II. EXPERIMENTAL DETAILS

II.1. Materials

All the chemicals that were used in the experiments were of laboratory reagent grade and used as received without further purification. 2-naphthol was obtained from Aldrich. The water employed in all the studies was double distilled. The photocatalyst, TiO₂ "Degussa P-25" was used for the degradation of 2-naphthol in most of the experiments. Other catalyst powder namely, TiO₂ "Hombikat UV-100" and TiO₂ "Millennium PC-500" (inorganic chemicals) were used for comparative study. "Degussa P-25" consists of 80% anatase and 20% rutile with a specific BET-surface area of 50 m²/g and primary particle size of 20 nm [8]. "Hombikat UV-100" consists of 100% anatase with a specific BET-surface area > 250 m²/g and primary particle size of 5 nm [9]. The photocatalyst Millennium PC-500" has a BET-surface area of 287 m²/g with 100% anatase and primary particle size of 5-10 nm [10]. The other chemicals used in this study such as K₂S₂O₈, H₂O₂ and KBrO₃ were obtained from Merck.

II.2. Photoreactor and light source

The static batch photoreactor was a cylindrical flask of ca. 0.5 l, opened to air and fitted with a

bottom optical Pyrex window *ca.* 4 cm in diameter. It was mounted at a distance of 3 cm from the top of the lamp assembly, which consisted of an HPK 125 W mercury lamp supplied by Phillips and a circulating-water cuvette (*ca.* 2.2 cm thick). A filter (Corning 0-52) was used to cut off the wavelengths shorter than 340 nm which can cause a direct photochemical transformation of 2-naphthol. The temperature during the experiment was maintained at $20 \pm 2^\circ\text{C}$.

II.3. Procedure-Analysis

In the experiments, 250 ml of 2-naphthol at natural pH (6) were magnetically stirred in presence of TiO_2 in the dark during 30 min to reach the adsorption equilibrium before UV irradiation. The suspensions were continuously purged with oxygen throughout in each experiment. Samples of 0.5 ml were collected at regular intervals, filtered through 0.45 nylon filters (Millipore) and analysed by HPLC.

Substrate conversions were monitored by HPLC, using a Varian Polychrom 9065 Photodiode Array Detector and Waters 510 pump. A good separation of the products was achieved using the reverse-phase column ODS2-Spherisorb-Chrompack (length 25 cm; internal diameter, 4.6 mm; particle diameter, 5 μm) and the detector with a wavelength at 280 nm. The mobile phase was composed of acetonitrile and doubly distilled water. The v/v ratio $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ was 80/20 and the flow rate was 0.4 ml/min. Total Organic carbon (TOC) analysis of the liquid samples was performed on a Shimadzu carbon analyzer model 5000 A.

III. RESULTS AND DISCUSSION

III.1. Comparison of different photocatalysts

Titanium dioxide has turned out to be the semiconductor with the highest photocatalytic activity, being non-toxic, stable in aqueous solution and relatively inexpensive too. Several reviews have been made regarding the mechanistic and kinetic question as well as the influence of experimental parameters [11,12]. The aim of the present study was to determine the best photocatalyst among different TiO_2 material and find further means to accelerate the efficiency of the photocatalytic process. Hence the degradation of 2-naphthol was tested with three different photocatalysts, namely, "Degussa P-25", "Millennium PC-500" and "Hombikat UV-100". Fig. 1 shows the degradation rate obtained for the decomposition of 2-naphthol in the presence of different photocatalysts. It was observed that the degradation of the compound proceeded much more rapidly in the presence of "Degussa P-25" as compared to other employed photocatalyst powders. The better photocatalytic activity of "Degussa P-25" could be explained on the basis of the fact that "Degussa P-25" being composed of small nano-crystallites of rutile

disperses within an anatase matrix. The smaller band gap of rutile "catches" the photons, generating electron/hole pairs. The electron transfer, from the rutile CB (conduction band) to electron traps in anatase phase, takes place. Recombination is thus inhibited, allowing the hole to move to the surface of the particle and react [6].

In all following experiments, TiO_2 "Degussa P-25" was used as the photocatalyst since this material exhibited the highest overall activity for the degradation of the model compound under investigation.

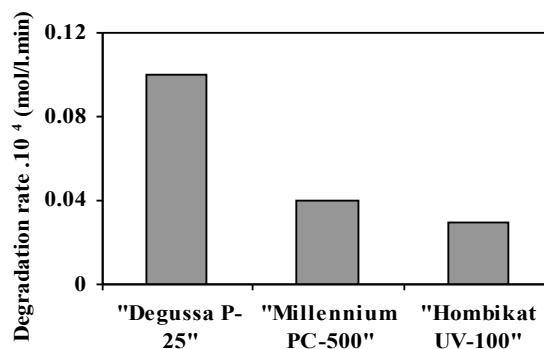


FIG. 1: Comparison of degradation rate for the decomposition of 2-naphthol ($C_0 = 5 \cdot 10^{-4}$ mol/l) in the presence of different photocatalysts. Experimental conditions: "Degussa P-25" (1 g/l), "Millennium PC-500" (1 g/l), "Hombikat UV-100" (1 g/l), irradiation time 60 min.

3.2. Kinetics of 2-naphthol disappearance

The elimination of 2-naphthol was studied at three different experimental conditions: (i) under UV illumination in absence of TiO_2 (photolysis), (ii) in the dark with TiO_2 and (iii) under UV illumination in presence of TiO_2 (photocatalysis). In Fig. 2, the concentration of 2-naphthol is plotted as a function of reaction time.

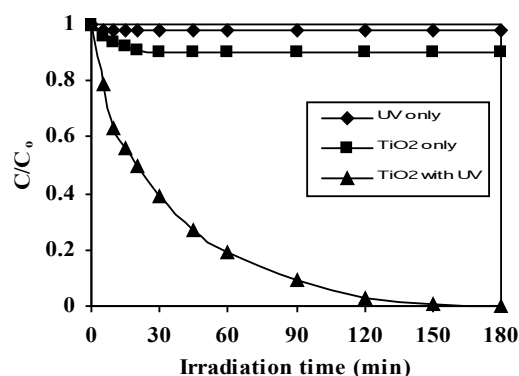


FIG. 2: Photocatalytic disappearance of 2-naphthol ($C_0 = 5 \cdot 10^{-4}$ mol/l) degradation under the control conditions (TiO_2 only and UV only) and photocatalytic condition. Experimental conditions: TiO_2 "Degussa P-25" = 1 g/l.

There was no observable loss of 2-naphthol when the irradiation was carried out in the absence of TiO₂. In non-irradiated suspensions, there was a slight loss, ca. 10%, due to adsorption onto TiO₂ particles. However, in the presence of TiO₂, a rapid degradation of 2-naphthol occurred by irradiation. The 2-naphthol concentration was completely removed after 180 min. Therefore, it can be concluded that 2-naphthol degradation in photocatalysis proceed by the oxidation of 2-naphthol by hydroxyl radical.

3.3 Effect of photocatalyst dosages

To optimize the TiO₂ suspension concentration, the effect of photocatalyst dosages on the degradation of 2-naphthol in aqueous solution was studied. The results were illustrated in Fig. 3. The degradation efficiency increased with increasing the amounts up to 1 g/l. Then, the efficiency decreased slightly, and above 1.25 g/l of TiO₂ became nearly flat. The increase in the efficiency seems to be due to the increase in the total surface area, namely number of active sites, available for the photocatalytic reaction as the dosage of photocatalyst increased. However, when TiO₂ was overdosed, the number of active sites on the TiO₂ surface may become almost constant because of the decreased light penetration, the increased light scattering and the loss in surface area occasioned by agglomeration (particle-particles interactions) at high solid concentration [13]. Therefore, 1 g/l of TiO₂ was selected as the optimal amounts of photocatalyst for the sequential experiment.

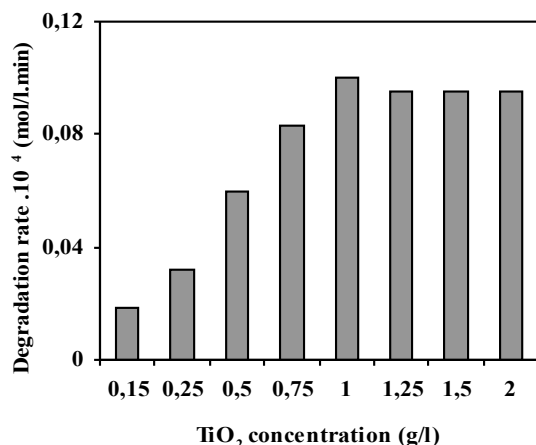


FIG. 3: Influence of catalyst concentration on the degradation rate for the decomposition of 2-naphthol ($C_0 = 5 \cdot 10^{-4}$ mol/l). Experimental conditions: Photocatalyst TiO₂ "Degussa P-25" (0.15 g/l – 2 g/l), irradiation time 60 min.

3.4. Effect of substrate concentration

As the effect of pollutant concentration is of importance in any process of water treatment, it is

necessary to investigate its dependence. The effect of initial concentration on the photocatalytic degradation rate was investigated over the concentration range of $2 \cdot 10^{-4}$ mol/l to $10 \cdot 10^{-4}$ mol/l of 2-naphthol, and the experimental results are presented in Fig. 4. Fig. 4 (a) shows that the degradation rate decreases as the initial 2-naphthol concentration increases. Furthermore, all the concentration profiles could be correlated by the following exponential function with good agreement:

$$C = C_0 \cdot \exp(-k_{\text{obs}}t) \quad (5)$$

where C_0 is the initial reactant concentration (mol/l) and t the illumination time (min). Based on Eq. (5), the straight-line relationship of $\ln(C/C_0)$ versus irradiation time was observed as indicated in Fig. 4(b). The apparent rate constant k_{obs} (min⁻¹) in above equation decreased with the increasing of initial concentration of 2-naphthol when other parameters are kept unchanged. Therefore, the degradation rate was pseudo-first-order with respect to the concentration within the experimental range.

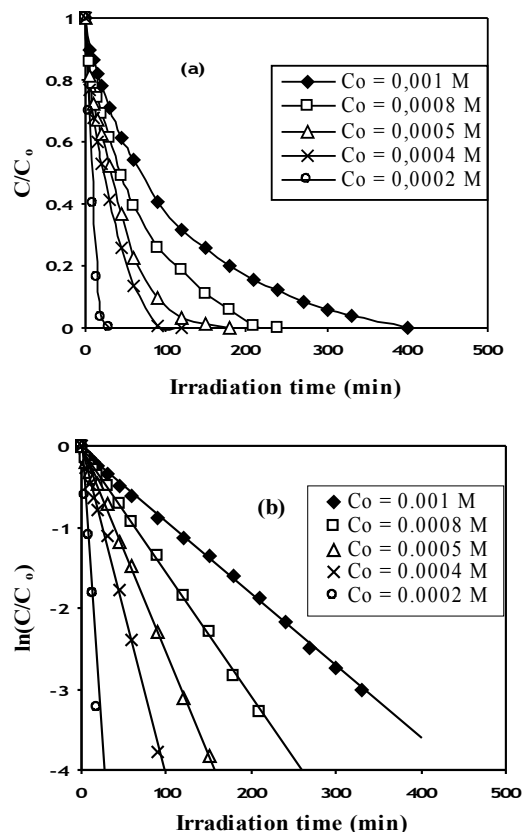


FIG. 4: Effect of initial 2-naphthol concentration on the removal efficiency: (a) the percent removal of 2-naphthol at the different initial 2-naphthol concentration and (b) the plot of $\ln(C/C_0)$ versus irradiation time. Experimental conditions: Photocatalyst TiO₂ "Degussa P-25" (1 g/l).

In recent years the Langmuir-Hinshelwood (L-H) rate expression has been used successfully for heterogeneous photocatalytic degradation to describe the relationship between initial oxidation rate r_o (mol/l.min) and initial concentration [1,14]. A linear expression can be conveniently obtained by plotting reciprocal initial rate against reciprocal initial concentration:

$$\frac{1}{r_o} = \frac{1}{k} + \frac{1}{kKC_o} \quad (6)$$

where k is the reaction rate constant (mol/l.min) and K is the adsorption coefficient of the reactant (l/mol). A reasonable fit of above equation was obtained with values of $0.03 \cdot 10^4$ l/mol, $0.55 \cdot 10^{-4}$ mol/l.min for K and k respectively. This indicates that the degradation of 2-naphthol occurred mainly on the surface of TiO_2 .

3.5. Effect of pH

An important parameter in the photocatalytic reactions taking place on the particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms. Therefore, the degradation of the pollutant was studied at different pH values (in the range 3-11). The pH of the reaction mixture was adjusted by adding a dilute aqueous solution of HNO_3 or $NaOH$. The degradation rate for the decomposition of 2-naphthol as a function of reaction pH is shown in Fig. 5. It was found that the rate decreases first and then increases with the increase in reaction pH and highest efficiency was observed at pH 11. The highest efficiency of degradation in alkaline pH could be attributed to more efficient generation of hydroxyl radicals by TiO_2 with increasing concentration of hydroxide ion.

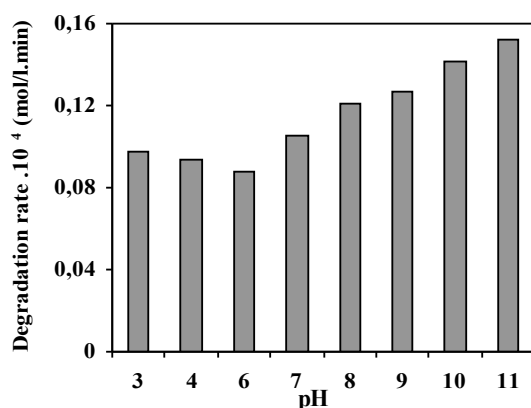


FIG. 5: Influence of pH on the degradation rate for the decomposition of 2-naphthol ($C_o = 5 \cdot 10^{-4}$ mol/l). Experimental conditions: Photocatalyst TiO_2 "Degussa P-25" (1 g/l), irradiation time 60 min.

3.6. Effect of electron acceptors

Since hydroxyl radical appears to play an important role in photocatalysis, electron acceptors such as hydrogen peroxide, potassium bromate and potassium persulphate were added into the solution in order to enhance the formation of hydroxyl radicals and also to inhibit (e^-/h^+) pair recombination. The degradation rate for the decomposition of 2-naphthol in the presence of various electron acceptors is shown in Fig. 6. All the additives showed a beneficial effect on the degradation of the model compound.

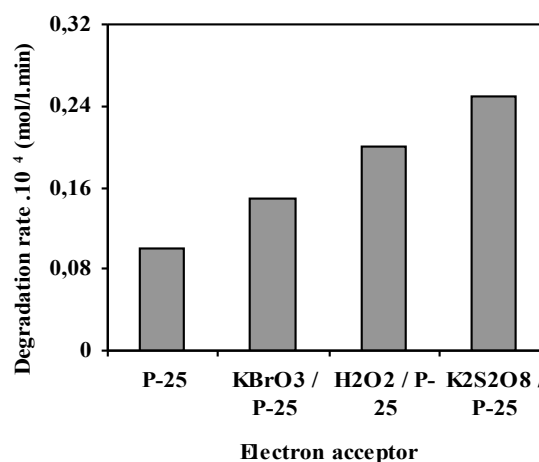
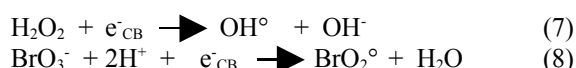
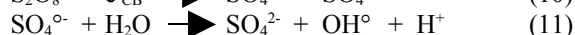
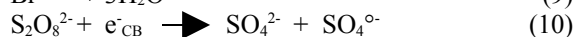
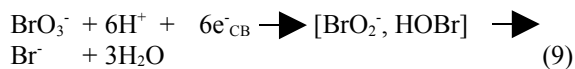


FIG. 6: Comparison of degradation rate for the decomposition of 2-naphthol ($C_o = 5 \cdot 10^{-4}$ mol/l) in the presence of different electron acceptors. Experimental conditions: Photocatalyst TiO_2 "Degussa P-25" (1 g/l), electron acceptors: $KBrO_3$ ($5 \cdot 10^{-4}$ mol/l), H_2O_2 ($5 \cdot 10^{-4}$ mol/l) and $K_2S_2O_8$ ($5 \cdot 10^{-4}$ mol/l), irradiation time 60 min.

One practical problem in using TiO_2 as a photocatalyst is the undesired electron/hole recombination, which, in the absence of proper electron acceptor or donor, is extremely efficient and thus represents the major energy-wasting step thereby limiting the achievable quantum yield. One strategy to inhibit electron-hole pair recombination is to add other (irreversible) electron acceptors to the reaction. In highly toxic wastewater where the degradation of organic pollutants is the major concern, the addition of additives to enhance the degradation rate may often be justified. In this connection, we have studied the effect of electron acceptors such as H_2O_2 , $KBrO_3$ and $K_2S_2O_8$ on the photocatalytic degradation of the model compound under investigation. These acceptors are known to generate reactive species according to the following Eqs. (7-11):





As expected, all the additives markedly influence the degradation rate for the decomposition of the compound. These results indicate that all the additives are more effective electron acceptors than molecular potential oxygen as indicated by the one electron reduction potential of different species formed from these additives: $E(\text{O}_2/\text{O}_2^{\cdot-}) = -155$ mV, $E(\text{H}_2\text{O}_2/\text{OH}^\cdot) = 800$ mV, $E(\text{BrO}_3^-/\text{BrO}_2^-) = 1150$ mV, $E(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{\cdot-}) = 1100$ mV [15]. From the thermodynamic point of view all employed additives should therefore be more efficient electron acceptors than molecular oxygen.

3.7. Mineralization

A preliminary experiment was carried out to study the photocatalytic mineralization of 2-naphthol in aqueous solution ($5 \cdot 10^{-4}$ mol/l) with TiO₂ (1g/l of solution), UV light and a flow of 100 ml/min of pure oxygen. The composition changes in the reaction mixture were monitored by both HPLC and TOC (Fig. 7). Experimental HPLC results show that 2-naphthol is quickly oxidized into organic compounds. TOC results also show that the intermediate organic species remain in the solution for several hours and are eventually mineralized into CO₂ and H₂O. Comparing HPLC and TOC curves it is apparent that the organic intermediate species degrade at a much slower rate than 2-naphthol.

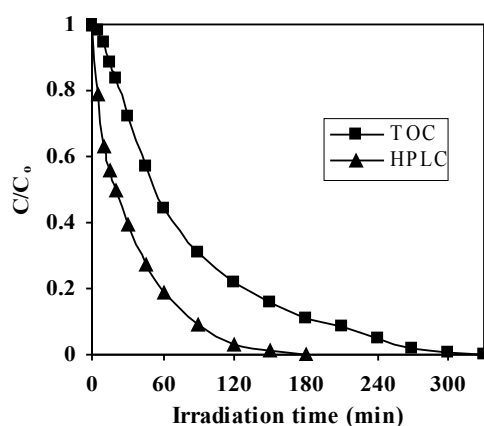


FIG. 7: Comparison of removal efficiency between photocatalytic degradation and TOC mineralization of 2-naphthol ($C_0 = 5 \cdot 10^{-4}$ mol/l). Experimental conditions: Photocatalyst TiO₂ "Degussa P-25" (1 g/l).

4. CONCLUSION

The results of this study show that the TiO₂ can efficiently catalyze the decomposition of 2-naphthol

in the presence of light and oxygen. The photocatalyst "Degussa P-25" was found to be more efficient as compared with other TiO₂ powders. The photocatalytic degradation of 2-naphthol in aqueous TiO₂ suspensions follows a pseudo-first-order kinetics. The apparent rate constant depends on the initial 2-naphthol concentration. A linear dependence of the rate constant upon the reciprocal of the initial 2-naphthol concentration has been obtained. The addition of electron acceptor markedly enhances the degradation rate of the pollutant. The final mineralization product was carbon dioxide during the degradation of 2-naphthol in aqueous solution. The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain high degradation rate, which is essential for any practical application of photocatalytic oxidation processes.

References

- [1] I. K. Konstantinou, V. A. Sakkas and T. A. Albanis, *Applied Catalysis B: Environmental*, 34 (2001) 227-239.
- [2] K.-H. Wang, Y.-H. Hsieh and L.-J. Chen, *Journal of Hazardous Materials*, 59 (1998) 251-260.
- [3] D. Bahnemann, *Solar Energy*, 77 (2004) 445-459.
- [4] Y. Hu and C. Yuan, *Journal of Crystal Growth*, 274 (2005) 563-568.
- [5] G. Sivalingam and G. Madras, *Applied Catalysis A: General*, 269 (2004) 81-90.
- [6] D. Robert and S. Malato, *The Science of the Total Environment*, 291 (2002) 85-97.
- [7] J.-M. Herrmann, *Catalysis Today*, 24 (1995) 157-164.
- [8] R.I. Bickley, T.G. Carreno, J.S. Lees, L. Palmisano and R.J.D. Tilley, *Journal of Solid State Chemistry*, 92 (1992) 178-190.
- [9] M. Lindner, D. Bahnemann, B. Hirthe and W.D. Griebler, *Journal of Solar Energy and Engineering*, 119 (1997) 120-125.
- [10] K.V.S. Rao, B. Lavédrine and P. Boule, *Journal of Photochemistry and Photobiology A: Chemistry*, 154 (2003) 189-193.
- [11] M. Trillas, J. Peral and X. Domènech, *Applied Catalysis B: Environmental*, 5 (1995) 377-387.
- [12] N. San, A. Hatipoğlu, G. Koçtürk and Z. Çinar, *Journal of Photochemistry and Photobiology A: Chemistry*, 146 (2002) 189-197.
- [13] S. Kaneco, H. Katsumata, T. Suzuki and K. Ohta, *Chemical Engineering Journal*, 125 (2006) 59-66.
- [14] H.-S. Son, S.-J. Lee, I.-H. Cho and K.-D. Zoh, *Chemosphere*, 57 (2004) 309-317.
- [15] M. Faisal, M.A. Tariq and M. Muneer, *Dyes and Pigments*, 72 (2007) 233-239.