

Photocatalytic degradation of textile dye CI Basic Yellow 28 wastewater by Degussa P25 based TiO₂

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Abstract. Wastewaters of textile industry cause high volume colour and harmful substance pollutions. Photocatalytic degradation is a method which gives opportunity of reduction of organic pollutants such as dye containing wastewaters. In this study, photocatalytic degradation of C.I. Basic Yellow 28 (BY28) as a model dye contaminant was carried out using Degussa P25 in a photocatalytic reactor. The experiments were followed out at three different azo dye concentrations in a reactor equipped UV-A lamp (365 nm) as a light source. Azo dye removal efficiencies were examined with total organic carbon and UV-vis measurements. As a result of experiments, maximum degradation efficiency was obtained as 100% at BY28 concentration of 50 mgL⁻¹ for the reaction time of 2.5 h. The photodegradation of BY28 was described by a pseudo-first-order kinetic model modified with the langmuir-Hinshelwood mechanism. The adsorption equilibrium constant and the rate constant of the surface reaction were calculated as $K_{dye} = 6.689 \cdot 10^{-2} \text{ L mg}^{-1}$ and $k_c = 0.599 \text{ mg L}^{-1} \text{ min}^{-1}$, respectively.

Keywords: photocatalytic degradation; Degussa P25; textile dye wastewaters; Basic Yellow 28; Langmuir-Hinshelwood mechanism

1. Introduction

Synthetic dyes are widely used in the textile, biomedical or dyestuff industries for textile dyeing, paper printing, cosmetics, pharmaceutical and color photography. Dyehouse effluents from the textile and the dyestuff industries cause serious environmental problems by destroying many life forms and consume dissolved oxygen due to its strong color, a large amount of suspended solids and highly fluctuating pH (Vandevivere *et al.* 1998, O'Neill *et al.* 1999).

There are more than 100,000 commercially available dyes and more than 7×10^5 metric tons of dyes are produced worldwide annually (Nigam *et al.* 2001, Pearce *et al.* 2003). Recent studies indicate that approximately 12% of synthetic dyes are lost during manufacturing and processing operations and that 20% of the resultant color enters the environment through effluents from industrial wastewater treatment plants (Essawy *et al.* 2008). Dyes are organic compounds with a chemical complex structure that are stable to light and heat, and resistant to aerobic digestion (Sun

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and Yang 2003, Gupta *et al.* 2004). Discharge of dye wastewater into ambient streams can be toxic to the aquatic lives. Color influences the nature of water and disturbs the sunlight penetration into the stream. In addition it reduces photosynthetic activity (Kumar *et al.* 2006). Azo dyes constitute a major class of environmental pollutants accounting for 60-70% of all dyes and pigments used. These compounds are characterized by aromatic parts linked together with azo groups ($-N=N-$) (Gupta *et al.* 2007). Cationic dyes like C.I. Basic Yellow 28 (BY28), generally known as basic dyes and included in a complex dye family and used in acrylic, wool and nylon dyeing (Marungrueng and Pavasant 2006). The release of azo dyes into the environment is a concern due to not only the property coloring natural waters but also harmfulness (toxicity, mutagenicity, and carcinogenicity) of these dyes and their bio-transformation products (Gupta *et al.* 2007). In particular, BY28, one of the cationic azo dye, studied in this work is among the most commonly used dyestuff to dye cotton and polyacrylonitrile and is therefore common industrial pollutant (Méndez *et al.* 2008).

Organic pollution and color in textile wastewater are the main pollutants, which make difficult their treatment. Especially, the organics are resistant to biological degradation in nature because of their complex aromatic molecular structure. Therefore, researches have been conducted to decolorize the wastewater and minimize the concentration of the azo dye in effluent. Conventional methods of dyeing wastewater treatment include adsorption (Can *et al.* 2003, Morais *et al.* 1999), flocculation (Ciardelli and Ranieri 2001), electrochemical methods (Szpyrkowicz *et al.* 2001, Vlyssides *et al.* 2000, Xiong *et al.* 2001), membrane separation (Tan *et al.* 2006), ozonation (Dogruel *et al.* 2006, Ciardelli and Ranieri 2001), advanced oxidation using UV/H₂O₂ or wet air oxidation (Kusvuran *et al.* 2004, Balli *et al.* 2004, Donlagic and Levec 1997) and biological oxidation (Ghoreishi and Haghghi 2003, Zissi and Lyberatos 1996, Knapp *et al.* 1995). Physical methods do not degrade the pollutants but they only transfer them from the liquid phase to the solid phase, and this causes secondary pollution (Gupta *et al.* 2006). On the other hand, the biological techniques are more natural and easy to application but their inconveniences are the requirement of long treatment times and the production of sludge proportionally to the volume of treated water. When the volume to treat is huge, recycling is essential (Silva *et al.* 2006). Besides, most of the dyes are non-biodegradable in nature and pollutants which are difficult removal from wastewater by aforementioned methods (Peternel *et al.* 2007). All techniques aforementioned are versatile and useful, but they all end up in producing a secondary waste product which needs to be processed further. Advanced oxidation processes (AOPs), which are relatively newer, more powerful and very promising, have been developed and employed to treat dye-contaminated wastewater effluents (Rauf *et al.* 2011). Among AOPs, heterogeneous photocatalysis using TiO₂ as photo-catalyst appears as the most emerging destructive technology. The key advantage of the technology is its inherent destructive nature: it does not involve mass transfer; it can be carried out under ambient conditions (atmospheric oxygen is used as oxidant) and may lead to complete mineralization of organic carbon into CO₂. Moreover, TiO₂ photocatalyst is largely available, inexpensive, non-toxic and show relatively high chemical stability. Finally, TiO₂ photocatalytic process is receiving increasing attention because of its low cost when using sunlight as the source of irradiation (Sahel *et al.* 2007, Li *et al.* 2013). The utilization of combined photocatalysis and solar technologies may be developed to a useful process for the reduction of water pollution by dyeing compounds because of the mild conditions required and their efficiency in the mineralization (Konstantinou and Albanis 2004).

Crystalline TiO₂ has anatase phase wholly and anatase TiO₂ presents much more catalytic activity compared with rutile phase. Degussa 25, which is a commercial type of TiO₂, has higher

anatase phase than other commercial TiO₂ products. There are many studies dealing with the photocatalytic degradation of specific textile dyes, some hazardous chemicals such as chlorophenols, toluene and benzen, and microorganism (*Escherichia coli*) (Panniello *et al.* 2012, Sahel *et al.* 2007, Gummy *et al.* 2008, Zhou *et al.* 2009, Pino and Encines 2012, Benabbou *et al.* 2007). For example, Djokić *et al.* (2012) have studied the degradation of BY28 using P160-TiO₂ based catalyst. Gözmen *et al.* (2009) have used pure TiO₂ (99.9%) purchased from Aldrich as the catalyst for the degradation of BY28. However, no information is available about photocatalytic decomposition of BY28 using Degussa P25 as the catalyst. The aim of the present study is to investigate photocatalytic decomposition and removal of BY28 in the presence of Degussa P25 irradiated by the UV-A light. All experiments carried out in a commercial photocatalytic reactor. The effect of various oxidation conditions such as initial dye concentration and irradiation time was studied.

2. Materials and methods

2.1 Materials

BY28 was supplied by Alptekin Boya ve Kimyevi Maddeler A.Ş. with commercial names Astrazone Goldgelb GL-E and used without any purification. BY28 is a cationic azo dye which can be also called azomethine dye ($-\text{CH}=\text{N}^-$) or hydrazone dye ($=\text{N}-\text{N}(\text{H}, \text{R})-$). The characteristic and structure of BY28 are summarized in Fig. 1. The stock solution of BY28 dye was prepared in 1000 mgL⁻¹ concentration with deionized water. Degussa P25, titanium dioxide, which was used as photocatalyst was purchased from Evonik.

2.2 Experimental procedure

All experiments were carried out in a commercial photocatalytic reactor which has five UV-A lamps, each one having 8 W light power (Fig. 2). These UV lamps which emit their maxima radiation at 365 nm were selected because of familiarity to sun light (Ultraviolet A spans 315 to 400 nm; Visible light spans 380 to 780 nm). The reactor stands at the distance of 12.5 cm from UV lamps. In irradiation experiments, the effects of initial dye concentration and irradiation time were investigated with 25 mL of aqueous solution of BY 28 dye and 0.25 g Degussa P25. Investigated initial dye concentrations were 50, 75 and 100 mgL⁻¹ for BY28 dye. In all of the experiments, dye solutions were illuminated at its own pH values which were about 5.2, and the system was stirred during the irradiation experiments at 20°C. After filtration of solid phase, the content of BY28 in

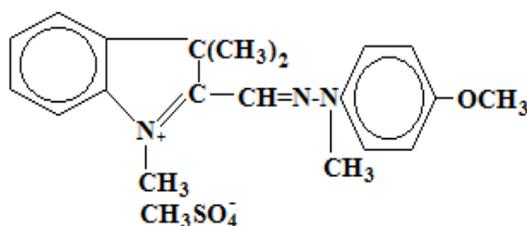


Fig. 1 Molecular structure of BY28 (MW: 433 gmol⁻¹)

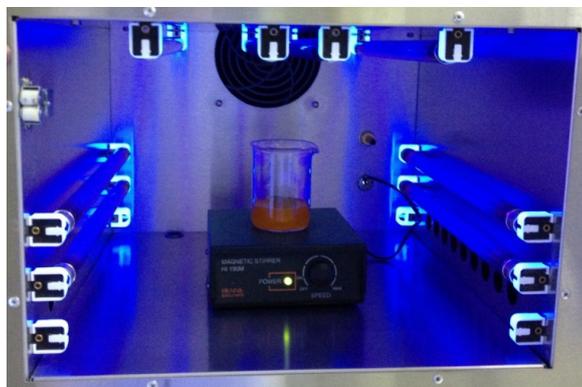


Fig. 2 Photocatalytic reactor used for photocatalytic oxidation experiments

the liquid phase was determined in terms of total organic carbon (TOC). In order to determine the effect of photocatalysts on the color removal in water, absorbance values of each experiment were measured at 438 nm. Before irradiation experiments, the suspensions stirred in the dark to see the effect of adsorption equilibrium.

2.3 Analytical methods

UV-vis Perkin Elmer Lambda 35 spectrophotometer was used for analysis of the studied dyes. The concentrations of the model dye wastewater at initial and after photocatalytic irradiation were characterized by the analyses of TOC contents. TOC analyses were performed by total organic carbon analyzer (Hach-Lange IL550 TOC-TN), which is based on combustion catalytic oxidation method, using a highly sensitive multi-channel non-dispersive infrared detector (NDIR). Standard solutions for the calibration were prepared by using potassium hydrogen phthalate (Acros, purity 99.5%). All the reagents were pure for analytical use. In order to provide precise data, the samples were analyzed in triplicate, and the averages are reported as results. The removal efficiency of dye was given as C_i/C_0 where, C_0 and C_i (mg/L) are the initial and remaining dye concentration at given time t . The chemical oxygen demand (COD) of the dye solution was determined by silver-catalyzed oxidation with potassium dichromate / sulfuric acid at 148°C during a two hour period. X-ray diffraction (XRD) experiments were conducted in a Panalytical™ X'Pert PRO using the setting of 40 mA and 40 kV at a 2θ range between 0-90 and 2-70 with a scan speed of 5° min⁻¹. The diffraction peaks of anatase and rutile phases were identified with XRD database patterns JCPDS-00-021-1272 and JCPDS-00-021-1276, respectively.

3. Results and discussion

3.1 Material characteristics

Degussa P25 used in the experiments was characterized using XRD, Fourier transform infrared spectroscopy (FTIR) and zeta potential measurements. Titanium dioxide catalyst (Degussa P25) with purity ca. 99% was used as without further modification. It is mostly in the anatase form

(80% anatase and 20% rutile) with a reactive surface (BET) area of $55 \pm 15 \text{ m}^2/\text{g}$ and a mean particle size of 30 nm. The bonding characteristics of functional groups in TiO₂ (Degussa P25) were identified by FTIR spectroscopy as shown in Fig. 3. A broad band at 3360 cm^{-1} is the primary O-H stretching of the hydroxyl functional group. The band around 1630 cm^{-1} is attributed to the bending vibration H-OH groups for Degussa P25. These groups are the most basic and photoactive ones, and are accepted defects on the catalyst structure. The band due to the presence of Ti-O-Ti and Ti-O-H network appears as a broad band below 1000 cm^{-1} and 800 cm^{-1} (Zhang *et al.* 2002).

The zeta potential of Degussa as a function of pH is shown in Fig. 4. The measured isoelectric point was approximately 6.3. Particles had a positive zeta potential when pH was lower than 6.3, while the zeta potential was negative when pH was higher than 6.3. Therefore, all experiments were carried out at constant pH value of 6.3. The crystal phases of Degussa P25 were analyzed by means of X-ray diffraction, as shown in Fig. 5. For Degussa P25, the peaks at 25.3° and 27.4° are the characteristic reflection for anatase and rutile, respectively. Beside the peak at 25.3 , the peaks at 37.8 , 48.0 , 53.9 , 54.9 , 62.7 , 68.7 , 69.7 and 75.1 corresponds to diffraction peaks of anatase phase.

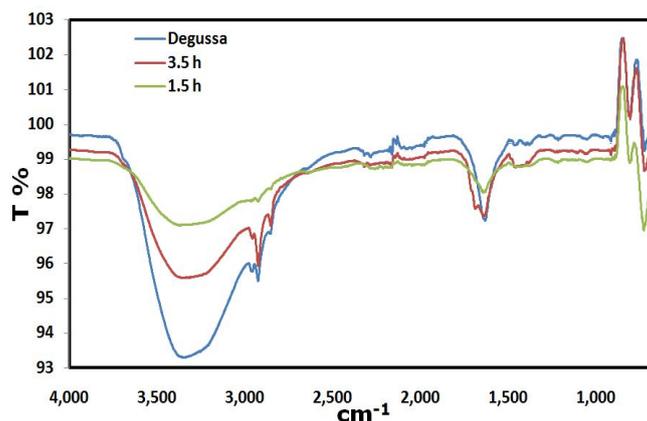


Fig. 3 FT-IR Spectra of Degussa P25, Degussa adsorbed BY28 for 50 mgL^{-1} solution after irradiation times of 1.5 h and 3.5 h, respectively

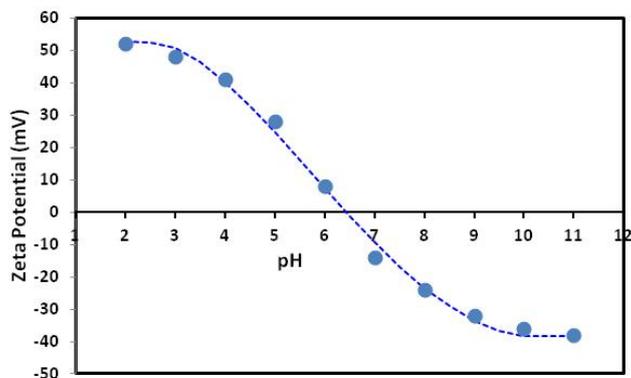


Fig. 4 Zeta potential curve of Degussa P25

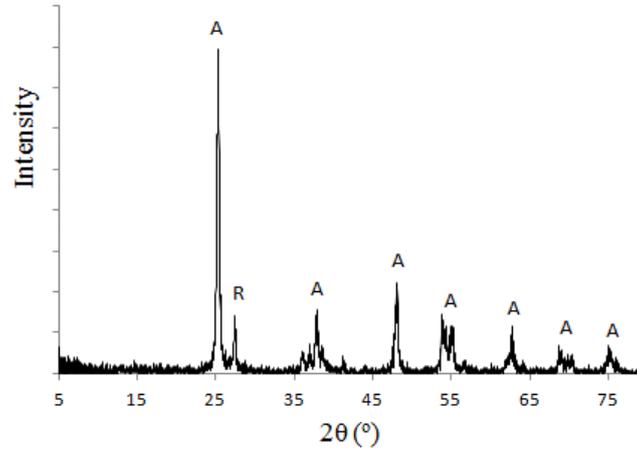


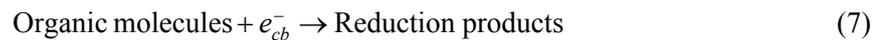
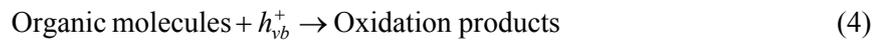
Fig. 5 XRD Pattern of Degussa P25 (A: Anatase phase; R: Rutile phase)

3.2 Photocatalytic degradation of BY28

Photocatalytic reactions on semiconductors are initiated by the absorption of a photon with energy greater than the semiconductor bandgap. This energy ($h\nu$) is 3.2 eV for the anatase TiO_2 and promotes an electron from the valence band (vb) to the conduction band (cb), with the consequent formation of an electron (e_{cb}^-)–hole (h_{vb}^+) pair (Eq. (1))



The photogenerated valance band holes (h_{vb}^+) and conduction band electrons (e_{cb}^-) can induce the reduction of electron acceptor species and the oxidation of electron donor species, respectively, both adsorbed on the semiconductor surface (Eqs. (2)-(7)).



The organic load of the wastewater is oxidized with hydroxyl and perhydroxyl radicals formed as described above equations (Silva *et al.* 2007). However, this oxidation process occurs on the surface as long as the photons are adsorbed to the catalyst surface. In order to confirm this

circumstance, BY 28 solutions with the appropriate amount of catalyst was stirred for 15, 30, 45 and 60 min in the dark to see achieving maximum adsorption of dye onto the semiconductor surface. As seen in Fig. 6, a negligible amount of the dyes was removed from solution based on TOC when it was stirred without UV light. On the other hand, there was no decolourization. These results show that the dye molecules adsorb to the catalyst surface, however, they don't react with oxygen because of no irradiation or hydroxyl and perhydroxyl radicals.

In Fig. 7, removal of BY28 from its aqueous solution by the Degussa P25 was plotted against irradiation time of UV rays after saturation of adsorption in dark. The photocatalytic degradation at low initial BY28 concentrations was faster than those its high concentrations. The highest TOC removal efficiency, which was 100% degradation rate, was obtained at 50 mgL⁻¹ BY28 aqueous solution after 2.5 h of irradiation time. However, as the dye concentration increased to 75 mgL⁻¹ and 100 mgL⁻¹, 96.5 and 66.60 % of TOC removals were obtained after 3.5 h of illumination time, respectively. The results indicate that the photocatalytic degradation of the Degussa P25 depends on the dye concentration remarkably. The photocatalytic activity reduces with increasing the dye concentration. Similar trend was also confirmed with the UV-vis absorbance results as seen in Fig. 8. The highest degradation efficiency was obtained at the dye solution of 50 mgL⁻¹ for the

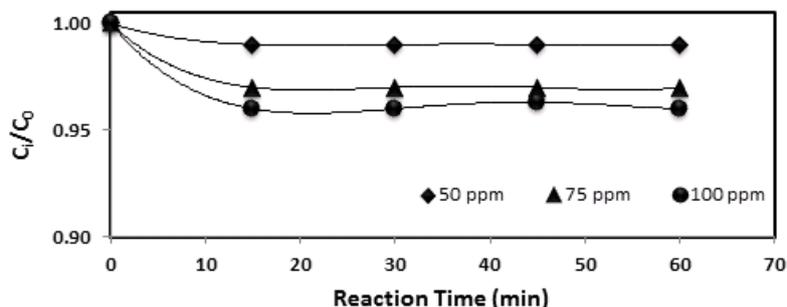


Fig. 6 Removal of BY28 solution in the dark medium

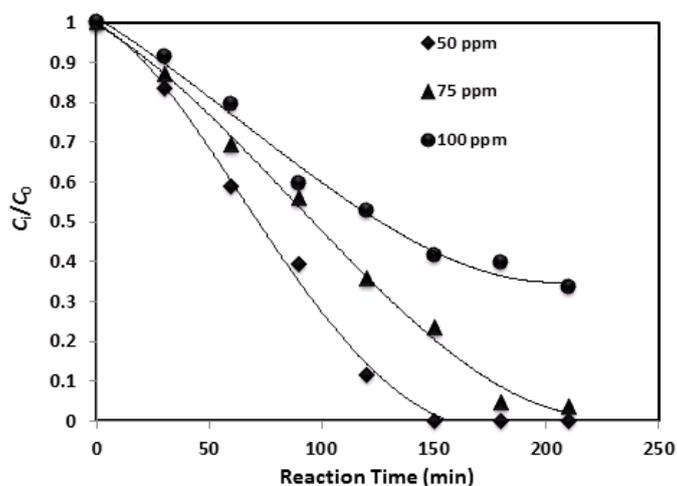


Fig. 7 Degradation of BY28 as a function of irradiation time and initial dye concentration by TOC measurement

irradiation time of 120 min according to UV-vis measurement. For BY28 aqueous solution of 75 and 100 mgL⁻¹, it was observed that the dye removal was completed at the irradiation times of 150 and 180 min, respectively. Fig. 9 shows the color removal visually. A whole color removal was obtained at short irradiation times for low BY28 concentrations compared with those for the increased dye concentrations.

The TOC removal efficiencies of 50 ppm BY28 after 1.5 and 3.5 h irradiation were measured as 58% and 100%, respectively. In order to confirm the degradation of adsorbed dye molecule, FTIR spectra of the Degussa P25 with adsorbed dye molecules after irradiation times of 1.5 and 3.5 h were taken and shown in Fig 3. Spectrum of 1.5 h irradiation shows that how fresh catalyst properties can be changed the existence of dye molecules with respect to time on the surface (Velmurugan *et al.* 2012). At the spectrum of 1.5 h, disappearance of the peak at 2900 cm⁻¹ indicates that the dye molecules adsorbed onto the catalyst surface hide the characteristic properties of the catalyst. The spectrum of catalyst at the irradiation time of 3.5 h indirectly shows that the dye was removed.

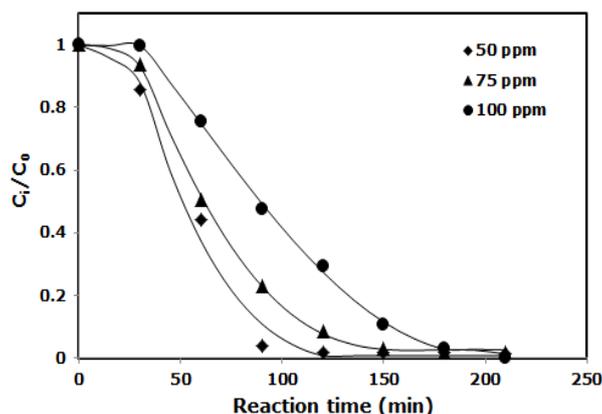


Fig. 8 Degradation of BY28 as a function of irradiation time and initial dye concentration by UV-vis spectrometer measurement

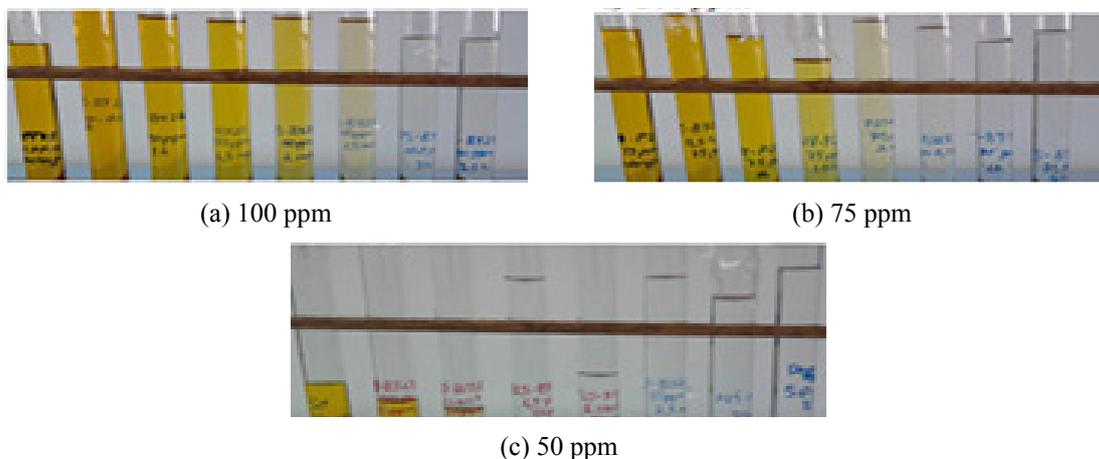


Fig. 9 Visual picture of the dye solutions for increasing irradiation times

According to water pollution control regulations in Turkey, acceptable COD limits for textile industry are up to 200 mgL⁻¹. To evaluate the degradation characteristics of Degussa P25, the change of COD values with time for BY28 solution of 100 mgL⁻¹ was investigated. As can be seen from Fig. 10, initial COD value was decreased to under limitations in an irradiation time of 160 min.

3.3 Photodegradation kinetics of BY28

As seen Fig. 7, the initial concentration of BY28 has a negative effect on the degradation rate. As the dye concentration increase, reactant in solution absorbs UV light much more. Because of decreasing irradiation intensity on the catalyst surface, the photocatalyst activity of the Degussa P25 decrease. Therefore, the degradation rate decreases with increasing initial dye concentration. Owing to the degradation curves in Fig. 7 are fitted by an exponential decay model, a pseudo-first-order homogeneous reaction model can be taken in consideration for describing the kinetic behavior with respect to the concentration of BY28 in the bulk solution (C)

$$-\frac{dC}{dt} = k_{obs} C \quad (8)$$

Integration of Eq. (8) according to the initial concentrations of BY28 in the bulk solution gives the equation described below

$$\ln\left(\frac{C_0}{C}\right) = k_{obs} t \quad (9)$$

where k_{obs} is the observed pseudo-first-order rate constant which is affected by dyestuff concentration. A plot of $\ln(C_0 / C)$ versus t for all the experiments with different initial bulk concentration of BY28 is shown in Fig. 11. The values of k_{obs} can be calculated as $9.5 \cdot 10^{-3} \text{ min}^{-1}$ for 50 ppm, $6.4 \cdot 10^{-3} \text{ min}^{-1}$ for 75 ppm and $5.3 \cdot 10^{-3} \text{ min}^{-1}$ for 100 ppm from the slope of the linear curve in the plot, respectively. As a function of the initial dye concentration, the observed pseudo-first-order rate constant decreases. Although different types of TiO₂ (P160) as catalyst are

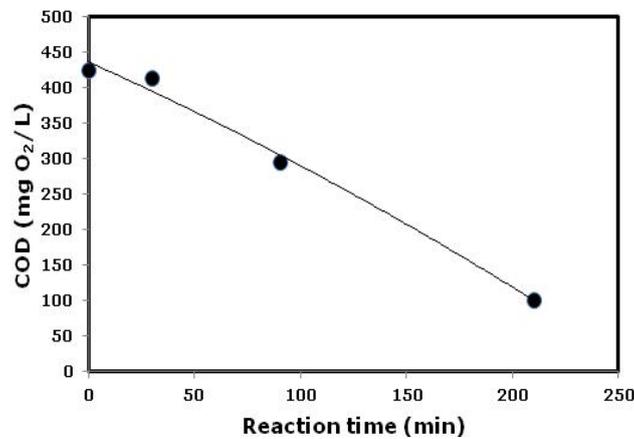


Fig. 10 COD change of BY28 as a function of irradiation time

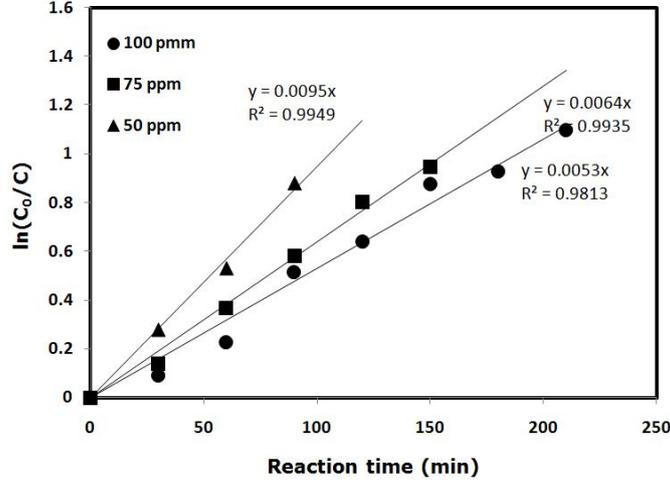


Fig. 11 Linear plots of Eq. (9) for each initial concentration of BY28

used, Djokić *et al.* (2012) have found that the observed pseudo-first-order rate constants are in the range of $6.5 \cdot 10^{-2}$ and $2.85 \cdot 10^{-2} \text{ min}^{-1}$ with increasing BY28 concentration from 30 to 60 mgL^{-1} .

The Langmuir-Hinshelwood model was used to analyze the photooxidation kinetics of dye. The titania surface is assumed to possess both acidic and basic sites. The basic sites of surface sites are hypothesized to adsorb the dye molecules and their degradation products, while acidic sites adsorb hydroxyl and perhydroxyl radicals formed by the photocatalytic reactions on the TiO_2 . In this hypothesis, the reaction rate for second order surface decomposition of the dye BY28 may be written in terms of Langmuir-Hinshelwood kinetics as

$$-\frac{dC_{dye}}{dt} = k' \Theta_{OH} \Theta_{dye} \quad (10)$$

where k' is the surface second order rate constant, Θ_{OH} is the fractional site coverage by hydroxyl and perhydroxyl radicals, and Θ_{dye} is the fraction of sites covered by the dye BY28. Θ_{OH} and Θ_{dye} can be written in the following way

$$\Theta_{OH} = \frac{K_{OH} C_{OH}}{1 + K_{OH} C_{OH}} \quad (11)$$

$$\Theta_{dye} = \frac{K_{dye} C_{dye}}{1 + K_{dye} C_{dye} + \sum_i K_i C_i} \quad (12)$$

where K_{OH} , K_{dye} and K_i are equilibrium adsorption constants and C_i refers to the various intermediate products of BY28 degradation. Eq. (12) contains several unknown factors, but can be modified by making the following assumption

$$K_{dye} C_{dye} + \sum_i K_i C_i = K_{dye} C_0 \quad (13)$$

where C_0 is the initial concentration of BY28. The assumption is that the adsorption coefficients for all organic molecules present in the reacting mixture are effectively equal. Substitution of Eq. (13) into Eq. (12) produces the expression

$$-\frac{dC_{dye}}{dt} = k' \frac{K_{OH}C_{OH}}{1 + K_{OH}C_{OH}} \frac{K_{dye}C_{dye}}{1 + K_{dye}C_0} \quad (14)$$

Owing to the irradiation intensity was constant, the hydroxyl and perhydroxyl radical concentrations was assumed to remain constant for all the photocatalytic runs, the fractional site covered by hydroxyl radicals and perhydroxyl radical was also constant

$$k' \frac{K_{OH}C_{OH}}{1 + K_{OH}C_{OH}} = \text{constant} = k_c \quad (15)$$

Therefore, Eq. (14) can be written as

$$-\frac{dC_{dye}}{dt} = k_c \frac{K_{dye}C_{dye}}{1 + K_{dye}C_0} = k_{obs}C_{dye} \quad (16)$$

that is a first-order kinetic equation with respect to dye concentration. The relationship between k_{obs} and C_0 can be expressed as a linear Eq. (17).

$$-\frac{1}{k_{obs}} = \frac{1}{k_c K_{dye}} + \frac{C_0}{k_c} \quad (17)$$

Fig. 12 shows the plot of $1/k_{obs}$ versus C_0 . By means of a least square best fitting procedure, the values of the adsorption equilibrium constant, K_{dye} , and the second order rate constant, k_c . The values were found as $K_{dye} = 6.689 \cdot 10^{-2} \text{ L mg}^{-1}$ and $k_c = 0.599 \text{ mg L}^{-1} \text{ min}^{-1}$. However, these values were found as $K_{dye} = 6.126 \text{ L mg}^{-1}$ and $k_c = 0.272 \text{ mg L}^{-1} \text{ min}^{-1}$ for increasing BY28 concentration from 30 to 60 mgL^{-1} by Djokić *et al.* (2012). Reason of different values may be because of

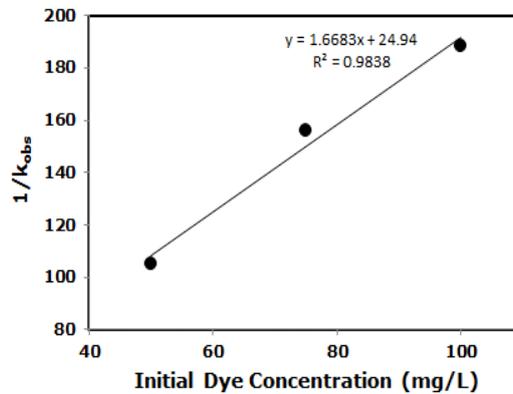


Fig. 12 Linear plots of Eq. (17) for each initial concentration of BY28

structural dissimilarity between P25-TiO₂ used in this study and P160-TiO₂ used by Djokić *et al.* (2012).

4. Conclusions

Degussa 25 shows photocatalytic activity for the degradation of many refractory organics, since it has higher anatase phase compared with other commercial TiO₂ products. In order to demonstrate the effects on the textile dyeing effluents, the degradation of Basic Yellow 28 dye as a model wastewater by Degussa P25 was investigated in a batch system at different initial dye concentrations and treatment times. It was observed that the Degussa P25 has a high catalytic capacity for the degradation of BY28 dye under UV irradiation and obtained that efficiencies between 66% and 100% based on TOC measurements. At high concentrations of BY28, lower efficiency of the photocatalytic process may result from the inhibition of the by-products during the parent compound transformation. After all, photocatalyst has high efficiency on the colour parameter, and can be used to treat diluted dye wastewater. It was determined that the photodegradation followed to a pseudo-first-order kinetic model modified with the Langmuir-Hinshelwood mechanism. Using all experimental data, the adsorption equilibrium constant and the rate constant of the surface reaction were calculated as $K_{dye} = 6.689 \cdot 10^{-2} \text{ L mg}^{-1}$ and $k_c = 0.599 \text{ mg L}^{-1} \text{ min}^{-1}$, respectively.

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