



Increasing photoactivity of titanium dioxide immobilized on glass plate with optimization of heat attachment method parameters

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ABSTRACT

In the present work the optimization of heat attachment method for increasing photoactivity of immobilized TiO₂ on glass plate was investigated. Results show that sonication time, TiO₂ suspension dosage, immobilization temperature, solvent type and immobilization replications are very effective on the photoactivity of immobilized TiO₂ on glass plate on the removal of C.I. Acid Red 88 (AR88) and optimizing these parameters increases the photoactivity of immobilized catalyst. In other step, the effect of operational parameters such as light intensity and initial concentration of AR88 on the removal of AR88 was investigated with four times immobilized TiO₂ on glass plate. Results show that removal rate decreases with increasing initial concentration of AR88 but increases with increasing UV-light intensity.

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1. Introduction

Dyes and pigments are widely used in the textile industries [1] and approximately 10,000 dyes, are presently used in textile industry. Azo dyes are among the most widely used commercial dyes [2]. The release of these dyes into the environment without treatment will cause severe ecological problems to the nature. The textile wastewaters are very colourful and have high chemical oxygen demand (COD). Azo dyes and their derived products are known to present serious carcinogenic effect [1]. The majority of azo dyes are resistant to cost-effective biological treatment. Coagulation, adsorption on activated carbon and electrocoagulation [3] merely transfer the pollutant from wastewater to solid phase and cause secondary pollution. Reverse osmosis can also be used for the treatment of textile wastewater, but its cost is high. Hence, it is necessary to develop destructive methods leading to complete mineralization of these dyes. Semiconductors such as TiO₂, ZnO, Fe₂O₃, CdS and ZnS due to their electronic structure (lie a filled valence band and an empty conduction band) can act as sensitizers for light-induced redox processes [4]. In conventional photocatalytic processes, TiO₂ powder was used as a photocatalyst for destruction of organic and inorganic compounds. However, two major problems are involved using suspended particles: the scattering of UV

light by particles and difficulty of recycling the photocatalyst. Thus, TiO₂ was immobilized on solid supports to solve these problems [5–8]. Over the last two decades the interest on systems based on supported TiO₂ as a photocatalyst for water treatment has grown considerably. A variety of supporting materials, coating methods and reactor arrangement are important subjects to investigate [9].

In this work optimization of effective parameters in the heat attachment method such as sonication time, furnace temperature, slurry dosage of TiO₂ and solvent type on immobilization of TiO₂ (Degussa P25) on glass plate was investigated and then photoactivity of immobilized TiO₂ on glass plate at different conditions was tested for decolorization of C.I. Acid Red 88 (AR88) as a model compound from monoazo textile dyes.

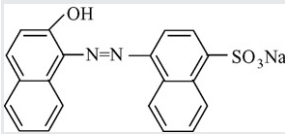
2. Experimental

2.1. Materials

AR88 a monoazo anionic dye was obtained from ACROS. Its chemical structure and other characteristics are listed in Table 1. Titanium dioxide was Degussa P25 and it constitutes approximately 80% anatase and 20% rutile. It had a BET surface area of $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$ and average particle diameter of 21 nm, containing 99.5% TiO₂. HF, NaOH, EtOH were purchased from Merck (Germany). Solutions were prepared by dissolving appropriate amount of the dye in double distilled water ($0.42 \mu\text{s cm}^{-1}$) before each experiment.

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Table 1
Structure and characteristics of C.I. Acid Red 88 (AR88)

Structure	Class	Ionization	Solubility in water	M_w (g mol ⁻¹)	λ_{max} (nm)	C.I. number
	Azo	Acid	Soluble	400.8	505	15620

2.2. Photoreactor

All experiments were carried out in a batch photoreactor. The radiation source was a UV lamp (15 W, UV-C, $\lambda_{max} = 254$ nm, manufactured by Philips, Holland), which was placed in front of a quartz tube reactor. The light intensity was measured by Lux-UV-IR meter (Leybold Co.). The immobilized TiO₂ on glass plate was placed inside quartz tube reactor vertically (Fig. 1). 100 mL of AR88 solutions was poured into the quartz tube reactor.

2.3. Immobilization of TiO₂-P25 on glass plate

To prepare the immobilized TiO₂-P25 on glass plate (1.4 cm × 19 cm) heat attachment method was used [10]. Suspension of commercial Degussa P25 TiO₂ was prepared in distilled water, pH was adjusted to about 3 [11] and was sonicated in ultrasonic bath (T/460 H, Windaus) under frequency of 35 kHz. 100 mL of suspension was carefully poured on the glass plate and allowed to dry out at 90 °C for a few hours. After drying, the plate was placed in furnace for 3 h and washed with distilled water for the removal of weakly attached TiO₂-P25 particles (Fig. 2). During the heating, as a result of reaction between OH groups from the catalyst surface and the support one molecule of water is lost and one oxygen bridge is created, thus the adherence of the catalyst to the support increases [11]. Before deposition, the glass surface was treated using dilute acid solution of HF and washed in a solution of NaOH (0.01 M) in order to increase the number of OH groups [12].

2.4. Procedure

For investigation of the effect of various parameters such as sonication time, TiO₂ suspension dosage, furnace temperature, solvent type and immobilization replications on the photoactivity of immobilized TiO₂ on glass plate, various immobilized TiO₂ on glass plates

were prepared under different conditions. The TiO₂ loaded glass plate was inserted in quartz tube reactor containing dye solution with known concentration (20 mg L⁻¹). For saturation of solution with oxygen it was continuously purged with oxygen 30 min before irradiation and also during irradiation. The flow rate of oxygen was kept at 0.4 mL min⁻¹. Photocatalytic decolorization of AR88 was analyzed with a UV–vis spectrophotometer (Ultrospec 2000, Biotech Pharamcia, England) at 505 nm. A calibration plot based on Beer–Lambert's law was established by relating the absorbance to the concentration. The changes in the absorption spectra of AR88 at different irradiation times were recorded on a double-beam UV–vis spectrophotometer (Shimadzu UV 1700) at the wavelength range of 190–700 nm.

2.5. Chemical oxygen demand

The closed reflux-colorimetric method was used to determine COD values. Each time the appropriate amount of sample was introduced into commercially available digestion solution (WTW, Germany) and the mixture was then incubated for 120 min at 150 °C in a COD thermoreactor (model CR 3000, WTW, Germany). COD concentration was measured colorimetrically using a Photolab spectral (WTW, Germany).

3. Results and discussion

3.1. Influence of optimization of heat attachment method parameters on immobilization and photoactivity of TiO₂ supported on glass plate

3.1.1. The effect of sonication time

For optimization of sonication time effect on photoactivity of immobilized TiO₂ on glass plate, three glass plates with 2 g L⁻¹ of TiO₂ slurry dosage in the furnace temperature of 400 °C were

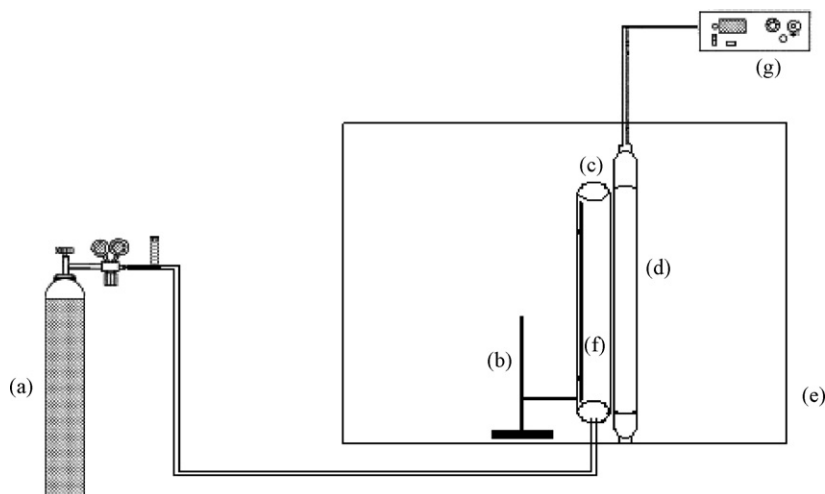


Fig. 1. Scheme of the photocatalytic reactor: (a) O₂ cylinder, (b) clamp, (c) quartz tube reactor, (d) UV lamp, (e) shield, (f) immobilized TiO₂ on glass plate and (g) source.

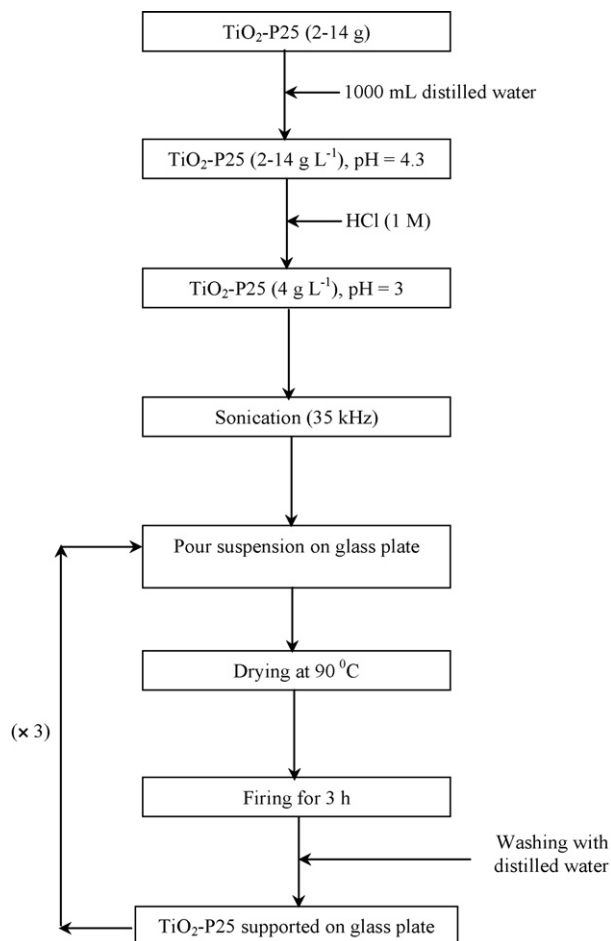


Fig. 2. Scheme of the heat attachment method for immobilization of TiO₂ on glass plate.

prepared at various sonication times. The photoactivity of immobilized TiO₂ on glass plate was tested in the removal of AR88. Fig. 3 shows the semi-logarithmic graphs of the concentration of AR88 for different supported TiO₂ on glass plates prepared at various sonication times, which yield straight lines that show the dye removal process could be perfectly fitted by pseudo-first-order kinetic. Fig. 4 shows that k_{ap} increased with increasing sonica-

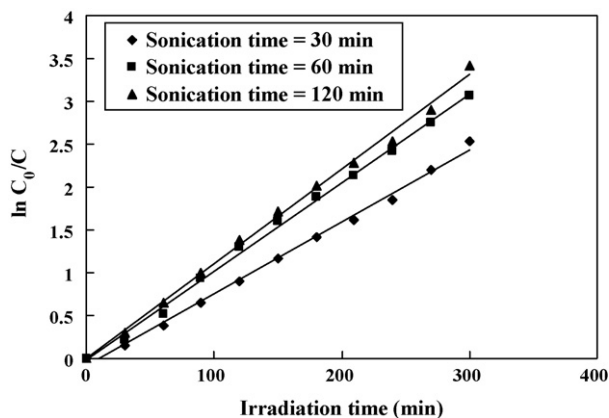


Fig. 3. The semi-logarithmic plot of AR88 concentration vs. irradiation time on immobilized TiO₂ on glass plates prepared at different sonication time. $[AR88]_0 = 20 \text{ mg L}^{-1}$, $I_0 = 37 \text{ W m}^{-2}$.

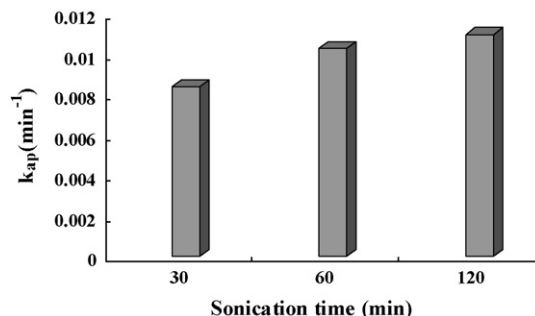


Fig. 4. Pseudo-first-order degradation rate constant of AR88 vs. sonication time. For experimental details refer to Fig. 3.

tion time, because when TiO₂ slurry was subjected to sonication, mechanical dispersion and de-agglomeration occurred and resulting to TiO₂ particles dispersed in all volume of liquid and inhibited the precipitation of them. Mechanical deagglomeration of TiO₂ in water in the effect of sonication was shown with Lorimer et al. [13]. A powder sample made up in water consisting initially of agglomerates (volume mean diameter ca. 19 μm) was rapidly broken apart to provide a limiting size of 1.6 μm particles. Furthermore, the sonicated sample showed no sign of re-agglomeration even after being allowed to stand for a period of 24 h. Increasing time from 60 to 120 min had no significant effect on the activity which showed that sonication time had an optimum of 60 min.

3.1.2. The effect of annealing temperature

For investigating the effect of furnace temperature on the photoactivity of immobilized TiO₂ on glass plate, two glass plates with 2 g L⁻¹ and two glass plates with 4 g L⁻¹ of TiO₂ slurry, at sonication time of 60 min were prepared under different furnace temperatures of 400 and 500 °C. Results show that k_{ap} enhanced from 0.012 to 0.017 min⁻¹ for 4 g L⁻¹ of TiO₂ slurry and from 0.01 to 0.015 min⁻¹ for 2 g L⁻¹ of TiO₂ slurry after increasing furnace temperature from 400 to 500 °C, respectively. The better photocatalytic activity of Degussa P25 could be explained on the basis of the fact that P25 being composed of small nano-crystallites of rutile dispersed within anatase. The smaller band gap of rutile “catches” the photons, generating electron/hole pairs. The electron transfer, from the rutile 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 [12]. As shown in XRD patterns (Fig. 5a and b) with increasing temperature from 400 to 500 °C, the anatase content decreased from 77 to 71% and the rutile content increases from 23 to 29%. The variation of anatase/rutile ratio could be responsible for increasing activity of immobilized TiO₂ on glass plate at photocatalytic degradation of AR88.

3.1.3. The effect of solvent type

For investigation of solvent type effect on photoactivity of immobilized TiO₂ on glass plate, three glass plates with 4 g L⁻¹ of TiO₂ slurry, at sonication time of 60 min in the furnace temperature of 500 °C were prepared using water, ethanol and butanol as solvents. The pseudo-first-order rate constants (k_{ap}) were 0.017, 0.019 and 0.012 min⁻¹ for water, ethanol and butanol, respectively. The positive influence of EtOH on photoactivity of immobilized TiO₂ on glass plate can be related to further volatility and easier evaporation of EtOH than water in experiment conditions. Similar results were obtained with Haarstrick et al., [14], which used 2-isopropanol instead of water as suspension matrix in the coating of quartz sand with TiO₂. Authors reported good

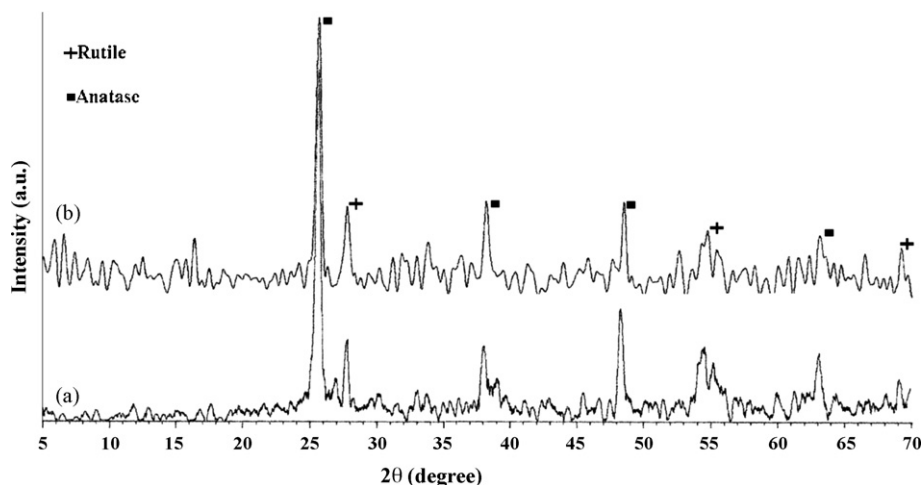


Fig. 5. XRD patterns of immobilized TiO₂ on glass plates at different furnace temperature. (a) 400 °C and (b) 500 °C.

mechanical stability and an acceptable photoactivity for the coating they obtained. They related selection of 2-isopropanol instead of water and high photoactivity of immobilized system to the higher volatility of this alcohol compared with that of water which facilitate the evaporation and drying operations. Using EtOH instead of water as a solvent in preparing slurry did not considerably increase k_{ap} ; therefore we used water as a solvent in other experiments.

3.1.4. The effect of immobilization numbers

For investigation of immobilization numbers on photoactivity of immobilized TiO₂ on glass plate, one glass plate with 4 g L⁻¹ of TiO₂ slurry in water as solvent at sonication time of 60 min in the furnace temperature of 500 °C was prepared and another glass plate was prepared at the same condition but immobilization was repeated for four times. Fig. 6 shows that increasing immobilization numbers from one to four times cause an increase of k_{ap} from 0.017 to 0.025 min⁻¹. This result indicated that loaded TiO₂-P25 on the surface of the glass plate was enhanced with increasing immobilization numbers. Fig. 7a and b shows scanning electron microscope (SEM) picture of TiO₂-P25 immobilized on the glass plates at two different resolutions that indicate first coat does not cover the entire surface but additional coats lead to complete coverage.

3.1.5. The effect of TiO₂ suspension dosage

For optimization effect of TiO₂ suspension dosage on the photoactivity of immobilized TiO₂ on glass plate, different glass plates

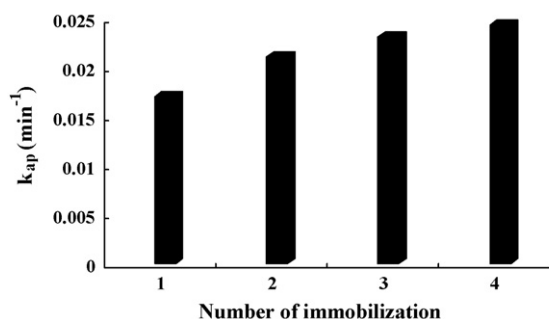


Fig. 6. The effect of immobilization numbers on photocatalytic activity of immobilized TiO₂ on glass plate. [AR88]₀ = 20 mg L⁻¹, I_0 = 37 W m⁻².

at sonication time of 60 min in the furnace temperature of 400 °C were prepared with different TiO₂ slurry dosages. Fig. 8 shows the plot of k_{ap} versus TiO₂ slurry dosage. As can be seen from this figure, increasing in TiO₂ slurry dosage obviously increased photoactivity of immobilized TiO₂ on glass plate. This is due to the enhancement of loaded TiO₂ at higher TiO₂ slurry dosage. Increasing TiO₂ slurry dosage up to 14 g L⁻¹ caused a decrease in photoactivity of immobilized TiO₂ on glass plate. This is due to the agglomeration of TiO₂ particles when high dosage of TiO₂ particles is used.

3.1.6. Adhesion test

Many studies neglect to check the photocatalyst adherence to the support. However, this adherence is of paramount importance, because if it is not strong enough, some of the photocatalyst grains will return to the liquid, where they can eventually act as a suspended catalyst. Absorption spectrum of aqueous colloidal TiO₂ suspension was shown as a sharp absorption band in the UV range [15].

For adhesion test, double-distilled water was poured into the photoreactor, which contains four numbers immobilized TiO₂ on glass plate and the absorbance of remaining water was measured at 334 nm to determine if any TiO₂ was present. Results showed that there were not any absorbances at 334 nm in samples which was withdrawn at 30 min intervals which confirm TiO₂ particles are strictly immobilized on glass plate.

3.1.7. Recycle test of immobilized TiO₂ on glass plate and comparison with slurry system

For investigation of durability of immobilized TiO₂ after a long period of operation, immobilized TiO₂ after 40th time's operation was compared to new immobilized TiO₂. Results show that the photocatalytic activity of immobilized TiO₂ on glass plate did not decrease considerable after 40th time's operation. This indicates that immobilized TiO₂ is not deactivated during reactions and can be reused. The removal percent for first and 40th time's operation after 90 min of irradiation were 93 and 89%, respectively. Also a comparison between immobilized and slurry system was done; results show that the slurry TiO₂-P25, was more effective than the supported TiO₂ particles in the removal of AR88. The limited photocatalytic efficiency of the immobilized system can be related to the fact that the immobilization process reduces the active surface area available for adsorption and catalysis. Since, in the slurry systems the catalyst must be removed with a solid-liquid separation stage

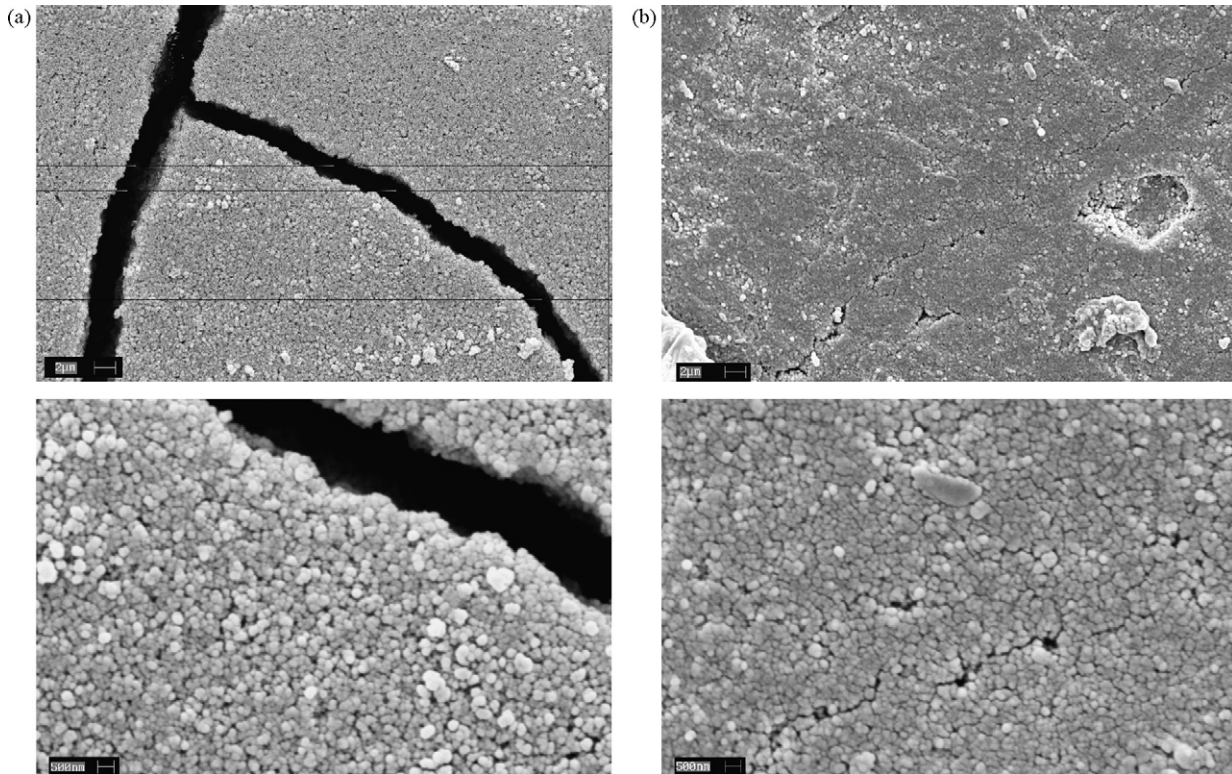


Fig. 7. SEM micrographs of immobilized TiO₂ on glass plates with two resolution (a) one number immobilization and (b) four numbers immobilization.

which adds to the overall capital and running costs of the plant. In order to make the environmental application of TiO₂ photocatalysis more practical, immobilization of TiO₂ on a certain substrate is required.

3.2. Influence of UV/TiO₂ operational parameters on the removal of AR88 with four numbers coated TiO₂ on glass plate

3.2.1. Influence of UV light intensity and initial concentration of AR88

Influence of the UV light intensity and initial concentration of AR88 on the photoactivity of four numbers immobilized TiO₂ on glass plate in the removal of AR88 was shown in Fig. 9. Results showed that light intensities used in this research approximately were in the low range because k_{ap} was linearly enhanced with increasing light intensity, and also with increasing AR88 initial con-

centration k_{ap} was considerably decreased because with increasing initial concentration of AR88 more and more organic substances are adsorbed on the surface of TiO₂, therefore the generation of hydroxyl radicals will be reduced since there are only a fewer active sites for adsorption of hydroxyl ions and generation of hydroxyl radicals. Furthermore, as the concentration of dye solution increases, the photons get intercepted before they can reach the catalyst surface, hence the absorption of photons by the catalyst decreases, and consequently the degradation percent is reduced [9].

3.2.2. Spectral changes of AR88 and COD measurements

The changes in absorption spectra of AR88 and COD measurements during photocatalysis degradation using four numbers immobilized TiO₂ on glass plate are shown in Figs. 10 and 11. The

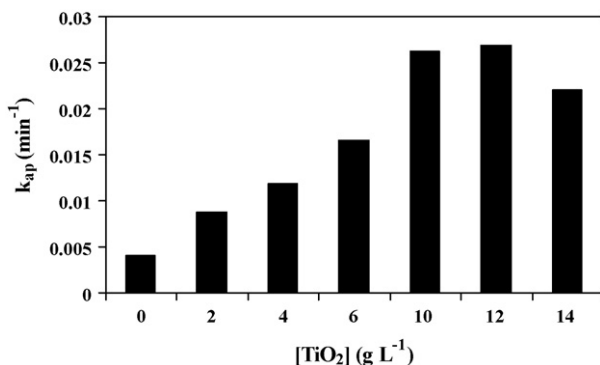


Fig. 8. Pseudo-first-order degradation rate constant of AR88 as a function of TiO₂ slurry dosage at preparation of immobilized TiO₂ on glass plate. [AR88]₀ = 20 mg L⁻¹, I_0 = 37 W m⁻².

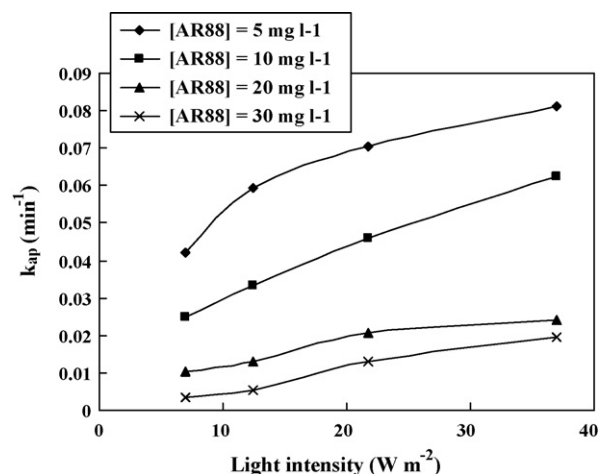


Fig. 9. k_{ap} vs. light intensity at different initial AR88 concentrations.

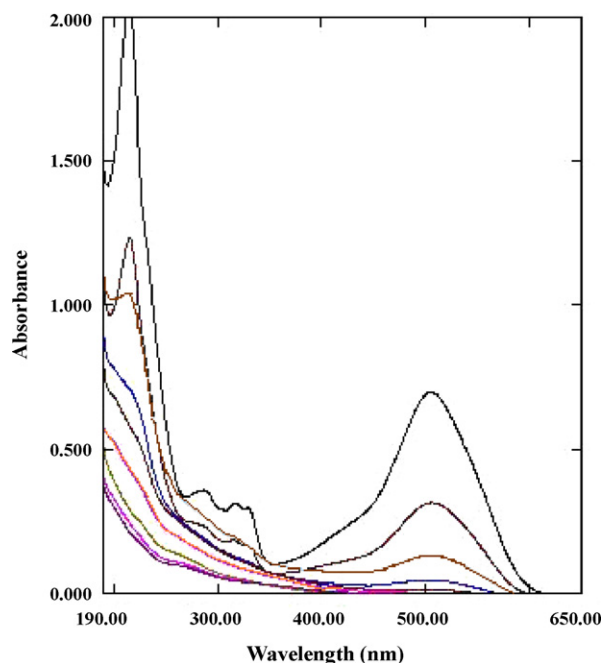


Fig. 10. UV-vis spectral changes of AR88, recorded during the dye degradation at 20 min irradiation intervals. $[AR88]_0 = 20 \text{ mg L}^{-1}$, $I_0 = 37 \text{ W m}^{-2}$.

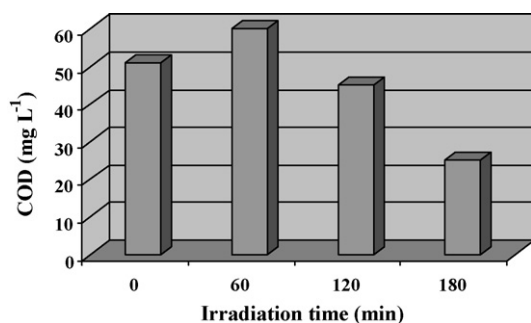


Fig. 11. COD changes vs. irradiation time for photocatalytic degradation of AR88. $[AR88]_0 = 20 \text{ mg L}^{-1}$, $I_0 = 37 \text{ W m}^{-2}$.

decrease of absorption of AR88 at 505 nm indicates the decolorization of azo dye. Nitrogen double band ($-\text{N}=\text{N}-$) of the azo dye is the most active site for oxidative attack. As shown in Fig. 10 the absorption of the visible band at 505 nm decreased with prolonging irradiation time. Absorbance at 254 nm, initially decreased at first 20 min of irradiation from 0.43 to 0.32 cm^{-1} , then increased to 0.39 cm^{-1} and finally decreased; these trends suggest that in the first period a poly aromatic rings in AR88 start to degrade, creating monosubstituted aromatics [16].

The COD results are in agreement with this trend. As can be seen from Fig. 11 COD increased in the first 60 min of irradiation time which was attributed to the decomposition of the AR88 to smaller compounds that are more easily oxidized than AR88. Finally, almost 50% of COD was removed after 180 min of irradiation. Result of blank experiment with distilled water shows an increase in COD

at 60 min of irradiation is not as a result of desorption of intermediates products from catalyst surface to solution, which confirms above hypothesis.

4. Conclusions

Results indicate that with optimization of operational parameters such as sonication time, TiO_2 slurry dosage, furnace temperature and solvent type, photoactivity of TiO_2 supported on glass plate considerably increases. With increasing TiO_2 slurry dosage, sonication time and furnace temperature photoactivity of immobilized TiO_2 on glass plate was enhanced significantly. Also using EtOH instead of water and numbers of immobilizations can be effective in the photoactivity of immobilized TiO_2 on glass plate. Increasing light intensity and decreasing AR88 initial concentration cause photoactivity of immobilized TiO_2 on glass plate to increase.

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