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Photodegradation of reactive red 222 using TiO₂ nanostructured thin films prepared by modified sol-gel method

ABSTRACT

F. Oshani^{1,2}
S. Rasouli^{2,*}
R. Marandi¹
M. Keramati Farhoud²

¹Department of Engineering,
Islamic Azad University, North
Branch, Tehran, Iran.

²Department of Nanomaterials
and Nanotechnology, Institute
for Color Science and
Technology.

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In this paper, a modified sol-gel method using peroxotitanic acid sol (PTA) was applied for the preparation of TiO₂ nanostructured thin films on glass plates. The peroxotitanic acid sol was synthesized using titanium isopropoxide, isopropylalcohol, H₂O and hydrogen peroxide. TiO₂ films were then calcined at 500°C and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD results showed that increasing the number of coated layers would lead to the formation of anatase phase at high level. Addition of Polyethylene Glycol (PEG) on the PTA sol could cause uniform coating without any cracks. The photocatalytic performance of the obtained films was investigated by the photodegradation measurements of Reactive Red 222 (RR222) in a batch reactor. For further investigations the effect of some parameters such as initial RR222 concentration, pH value, hydrogen peroxide addition and temperature on the photocatalytic performance of TiO₂ thin films was studied as the important factors. Kinetic study results of this reaction represented that it obeys of was pseudo-first-order model. The degradation of RR22 was enhanced by the addition of optimum amount of hydrogen peroxide. This is due to the increasing amount of the radical hydroxyls.

Keywords: Modified sol-gel; Photocatalyst; PTA; TiO₂; RR222.

INTRODUCTION

One of the upgrowing treatment technologies for the remediation of textile industry wastewater is advanced oxidation process (AOP). This process involves the generation of highly active hydroxyl radicals in order to complete mineralization the water contaminants. AOP process is consisted of the combination of oxidants and irradiation. Heterogeneous photocatalysis process by employing semiconductor and light source has been considering a promising process which leading to total destruction of nonbiodegradable pollutants [1-3].

* Corresponding author:
Sousan Rasouli
Department of Nanomaterials
and Nanotechnology, Institute for
Color Science and Technology.
Tel +98 21229 52272
Fax +98 21229 47537
Email rasouli@icrc.ac.ir

Among them, heterogeneous photocatalysis employs semiconductor catalysts such as TiO₂, ZnO, Fe₂O₃, CdS and ZnS. The rutile phase has a tetragonal structure that is stable at high temperatures and the brookite phase has an orthorhombic form. Among the three types of TiO₂, the anatase form appears to be the most photoactive and the most practical form for widespread environmental applications such as water purification, wastewater treatment and air pollution control.

These catalysts have demonstrated their efficiency in demolishing a wide variety of dyes wastewater. TiO₂ (in the anatase form) is believed to be the most beneficial species owing to its excellent photocatalytic activity, high stability and non-toxicity [4-6]. However there are various problems remained unsolved such as separation and filtration of TiO₂ nanoparticles from solution and effective utilization of photons in the photodegradation process [7, 8]. It seems to be that immobilizing of TiO₂ nanoparticles on the surface of solid template would solve the problems. A number of methods have been employed for the preparation of TiO₂ thin films such as, sol-gel, sputtering and chemical vapor deposition. The sol-gel method is the most widely used [9].

In this paper, a modified sol-gel method using peroxotitanic acid sol (PTA) was employed for the preparation of nanostructured TiO₂ thin film on the glass plate. This method has various advantageous aspects compared with other sol-gel methods. The PTA is neutral and stable solution which can be easily coated onto vast variety of materials even pure metals [10].

The performance of the immobilized photocatalytic reactor was tested for the degradation of RR222 dye in aqueous steam.

EXPERIMENTAL

Preparation of nanostructured TiO₂ thin films

In the preparation of TiO₂ sol, 5ml of Titanium tetra iso-propoxide (Ti (OC₃H₇)₄, Merck) and 10 ml of Iso-Propanol (Merck) were mixed and then hydrolyzed with certain amount of deionized water. The precipitation of titanium hydroxide was washed thoroughly to remove excess alcohol. The precipitate was then dissolved in 20 ml of aqueous

hydrogen peroxide (30%, Merck) to obtain a transparent orange sol of titanium peroxy complex. During dissolution certain content of distilled water was added to this solution to avoid immediate dense gel formation. 0.3 gr of 10% Poly Ethylene Glycol (PEG, Merck, M_w=4000) solution was added. This titanium peroxide sol was allowed to stand 4-5 hours to form a viscous sol.

Before deposition of thin film, two glass plates (4.5× 39.5×0.2Cm) were cleaned and dried. For deposition of nanostructured TiO₂ thin films, the glass plates were dipped in the viscous titanium peroxy complex with a rate of 1mm s⁻¹ and pulled out with a same rate. A thin film were formed then were dried at 100°C for 1 hour in electric oven. These films were calcined for 2 hours at 500°C. For three layers thin films, this deposition was repeated for 3 cycles.

TiO₂ film characterization

A PW 1800 (Philips, Germany) Diffractometer was used for X-ray diffraction (XRD) analysis. Morphology and size analysis was performed using LEO 1455VP (Oxford, UK) Scanning Electron Microscope (SEM).

Photocatalytic degradation of RR222 on TiO₂ thin films

The photocatalytic activity of the TiO₂ thin films was measured in a batch rectangular reactor with the capacity of 2 liter and a UV lamp (15 watt, Philips) which has been located in the center of the reactor. RR222 (RR222) was purchased from Indofix Company (Indian). Figure 1 shows chemical structure of RR222.

The TiO₂ thin films were put in the reactor. The degradation of RR222 under UV light irradiation was determined by measuring absorption spectra using a Lambda25 UV-vis spectrophotometer. The degradation efficiency of TiO₂ thin films were calculated by the equation 1.

$$d(\%) = \frac{[dye]_o - [dye]}{[dye]_o} \times 100 \quad (1)$$

Where, $[dye]_0$ and $[dye]$ are the concentration of RR222 before and after degradation, respectively.

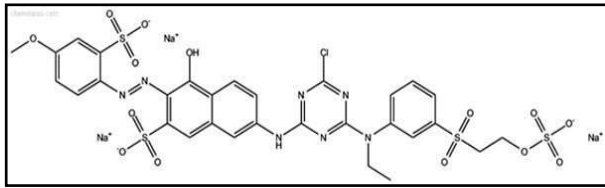


Fig. 1. Chemical structure of RR222

RESULTS AND DISCUSSION

TiO₂ film characterization

Figure 2 shows the XRD patterns of TiO₂ and films. According to JCPDS (01-083-2243), anatase phase, were observed in the XRD patterns of the TiO₂ films. From XRD pattern, high amounts of anatase crystalline were obtained. This may be attributed to the high content of titanium dioxide with several coating cycles resulting in the obvious peak of anatase [11].

The average crystallite size of the anatase phase of films was calculated from the Scherrer equation (equation 2) [12].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

Where λ is the wavelength of incident X-ray, β is the half width of diffracted peak, θ is diffracted angle.

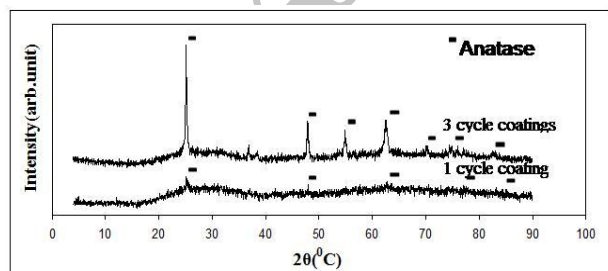


Fig. 2. XRD patterns of 1 and 3 cycles coating of TiO₂ films

Figure 3(A-B) shows the SEM images of TiO₂ thin films which were prepared under

different conditions, 1 dip coating without using PEG and 3 dip coating by the utilization of PEG respectively. The results show that in the absence of PEG the surface of TiO₂ thin films becomes non-uniform and cracks is created at many places, whereas the film prepared by the addition of PEG has a uniform and without cracks surface.

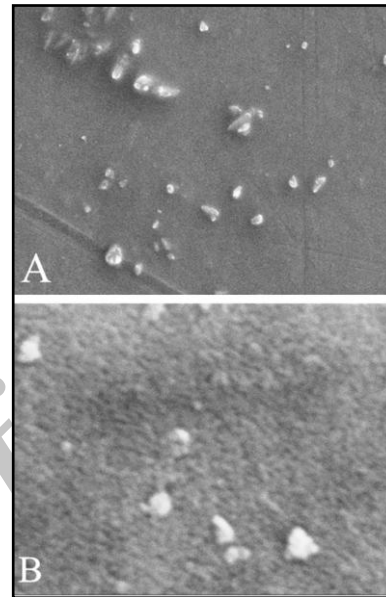


Fig. 3. SEM images of the TiO₂ thin film (A) 1 cycle coating without using PEG, (B) 3 cycle coating with using 0.3 gr PEG 10%.

Figure 4 shows the TEM images of TiO₂ powder prepared from a modified peroxotitanic acid sol which is scratched from the surface of the film. Images represent that the samples are consisted of fine TiO₂ crystals which is crystallized well.

Photocatalytic Activity of thin films

Figure 5 shows the photocatalytic activity of TiO₂ thin films by measuring the photodegradation efficiency of RR222 in 120 min. In the presence of TiO₂ thin film under UV irradiation 35% of RR222 was degraded, where TiO₂ film without the presence of UV irradiation showed only 14% of dye destruction. The RR222 degradation efficiency measurement was also performed under UV irradiation in the absence of TiO₂ thin film, the result was negligible (1%). The results are in well agreement with the presence of

UV irradiation and TiO₂ thin films in achieving the efficient photodegradation content of RR222.

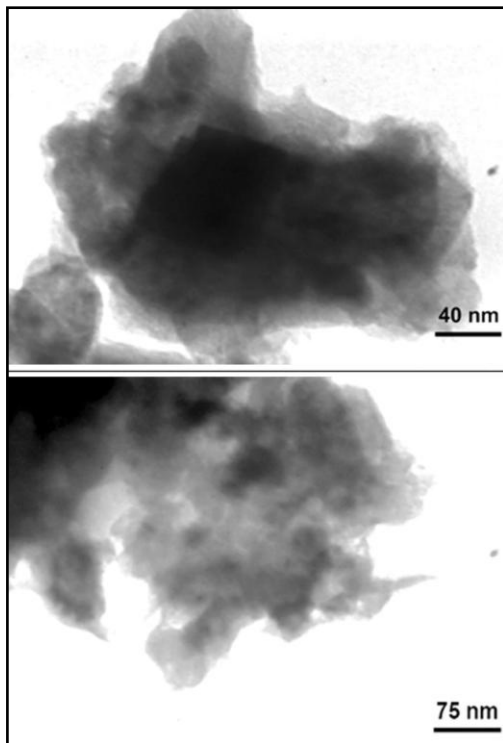


Fig. 4. TEM images of TiO₂ thin films

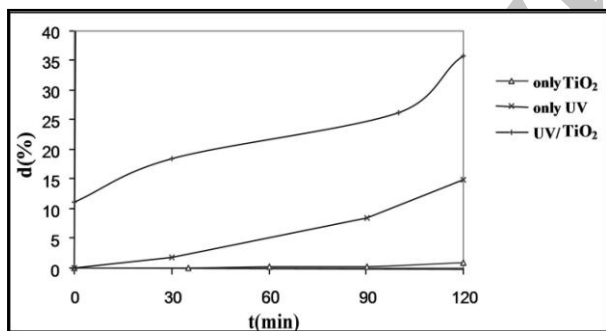


Fig. 5. Effect of TiO₂ film and UV light on degradation of RR222. [dye]₀=20ppm, pH=8

Effect of Hydrogen peroxide concentration

The effect of hydrogen peroxide (H₂O₂) was studied from H=20-60. H is explained by the equation 3.

$$H = \frac{[H_2O_2]_o}{[dye]_o} \quad (3)$$

Which [H₂O₂] and [dye] are known as the initial concentrations of hydrogen peroxide and RR222?

Figure 6 shows that in the range of H=20-50 the degradation efficiency of RR222 is at maximum content, but then decreased at H=60. As a result, H=20 is the optimum point.

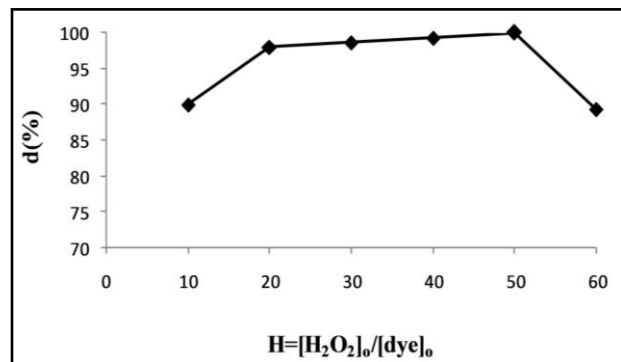
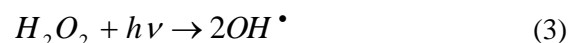
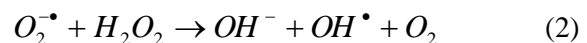
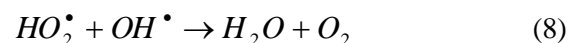
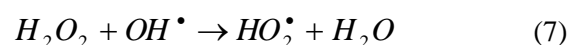


Fig. 6. Effect of hydrogen peroxide concentration on the photodegradation of RR222

These observations were due to the increase in the hydroxyl radical concentration and the reaction rate by the addition of hydrogen peroxide. At H=10-20 hydrogen peroxide prevents the electron-hole from recombining according to equation 4, and it could act as an alternative electron acceptor to oxygen (equation 5), because it is a better electron acceptor than molecular oxygen. Also, hydrogen peroxide could split photolytically to produce hydroxyl radical directly (equation 6).



But at high concentrations (H=50), H₂O₂ is a powerful OH[•] scavenger (equation 7 and 8). Therefore the reaction rate is decreased [13].



Effect of pH

In the photocatalytic process, pH is one of the most important operating parameters that affect the charge on the catalyst. Figure 7 shows the effect of pH=3-8 (from acidic to basic) on the photodegradation of RR222 at 120min. According to the point of zero charge of TiO₂ catalyst, its surface charge is positive in acidic solution and negative in basic solution, respectively. The RR222 is an anionic species, the adsorption of RR222 on the surface of TiO₂ is better, since the RR222 is cationic. The results in Figure 7, show that the degradation efficiency of RR222 in pH=3 is the highest [14].

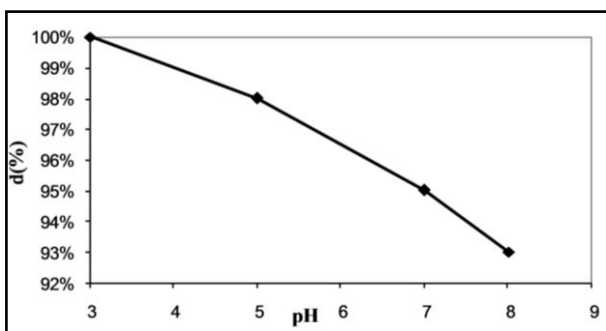


Fig. 7. Effect of pH on the degradation of RR222, [dye]₀=20ppm and H=20

Effect of Temperature

Figure 8 represents the temperature variation effect (20-40°C) on the photodegradation of RR222. The photodegradation of RR222 was found to be less temperature dependent. This was due to Arrhenius rule ($K=Ae^{-E/RT}$), when temperature is increased, K value is increased. Therefore, optimum temperature is 40°C.

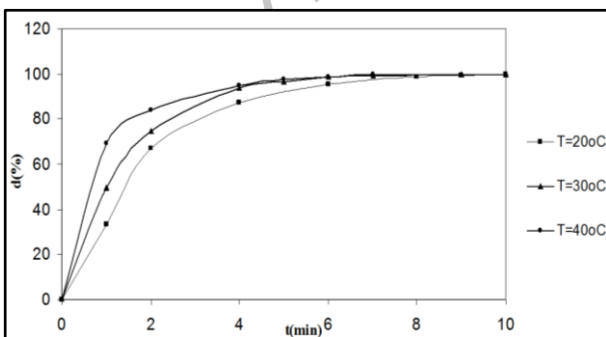


Fig. 8. Effect of temperature on the degradation of RR222, pH=3, [dye]₀=20ppm and H=20

Effect of initial RR222 dye concentration

Figure 9 shows the effect of initial dye concentration here RR222 at photodegradation efficiency of TiO₂ thin films. It is revealed in Figure.9, that the rate of RR222 photodegradation was increased at lower concentration (20ppm). This was due to large amount of adsorbed dye inhibited the reaction of dye molecules with radical hydroxyl. By increasing the RR222 concentration, the content of adsorbed dye molecules on the surface of photocatalyst would increase so the photocatalytic activity of photocatalyst would also decrease because the photons reached to the photocatalyst surface would decrease [13].

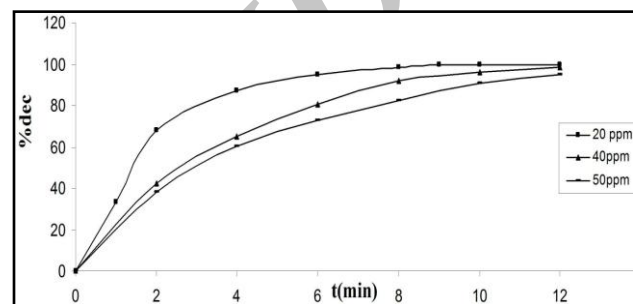


Fig. 9. Photocatalytic degradation of RR222 at different initial dye concentration, pH=3, T=20°C and H=20

RR222 Photodegradation Kinetics

Generally, the photodegradation rate of chemical compounds on semiconductor surfaces follows the Langmuir-Hinshelwood model.

$$r = -\frac{dC}{dt} = k_r \theta_x = \frac{k_r KC}{1 + KC} \quad (9)$$

The photocatalytic reaction rate (r) is proportional to the fraction of surface coverage by the organic substrate (θ_x), k_r is the reaction rate constant, C is the concentration of dye and K is the Langmuir adsorption constant: When the RR222 concentration is low, an apparent first-order rate constant could be expressed where $K'(\text{min}^{-1})=k_r K$ [15]:

$$-\ln\left(\frac{C}{C_0}\right) = k_r K t = K' t \quad (10)$$

According to Figure 10, the plot of $-\ln(C/C_0)$ versus time for RR222 is linear. Therefore, the photodegradation reaction follows pseudo-first-order and the apparent reaction rate constant was 0.0043min^{-1} .

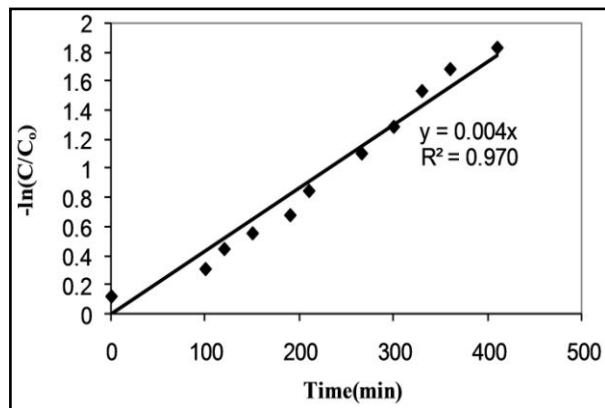


Fig. 10. The kinetic data for photocatalytic degradation of RR222 in the presence of TiO_2 thin film

CONCLUSIONS

This study is focused on the synthesis of TiO_2 thin film photocatalyst using modified sol-gel technique. The immobilization of TiO_2 photocatalyst on glass plates was done by using dip coating. SEM results revealed the uniform and without any cracks surface of TiO_2 thin film attached on the glass plate after 3 cycles coating and applying PEG as a surfactant. TEM images show the fine crystallized TiO_2 particles. XRD analysis showed the presence of anatase crystalline phase of TiO_2 after calcination process at temperature of 500°C .

The results of RR222 degradation showed that both UV light and TiO_2 film were needed to reach to an acceptable degradation rate. The result indicated that the degradation of RR222 was affected by variations of initial concentration of RR222, pH and temperature. Optimum concentration of hydrogen peroxide was also measured according to the photodegradation process of RR222. The RR222 photodecomposition kinetic measurements represented that TiO_2 thin film photocatalytic activity of RR222 obeys pseudo-first-order kinetic model.

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