



Photocatalytic Decolorization of Methyl Orange by Silica-Supported TiO₂ Composites

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ABSTRACT

Immobilization of TiO₂ on silica gel has been proposed to enable easy separation of the catalyst in aqueous systems after photocatalytic reaction. Our simple synthesizing method reduces production cost, and the photocatalyst could find economical application in wastewater treatment. Silica-supported TiO₂ composites were prepared by molten salt method at 500, 600 and 700 °C for 60 min. The obtained samples were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), diffuse reflectance spectroscopy and X-ray fluorescence. SEM results showed a heterogeneous surface covered with spherical particles. According to XRD findings, the only phase of the prepared TiO₂/SG nanocomposites at all temperatures was pure anatase. The average crystallite size of anatase was roughly 25, 42, 44 and 53 nm for nanocomposites prepared at 550, 600, 700 and 800 °C, respectively. The samples taken at 500 and 600 °C showed a band gap value of 2.98 eV, and for sample synthesized at 700 °C the band gap was 2.95 eV. The decolorization activity has been evaluated by Methyl orange (MO) oxidation in liquid phase. The results showed that the sample obtained at 700 °C had the highest photocatalytic decolorization efficiency activity, and the sample prepared at 500 °C had the lowest. The decolorization activity of photocatalyst prepared at 700 °C did not change during stability experiment.

Keywords: Silica-supported TiO₂; Nanocomposites; Molten salt method; Photocatalyst.

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1. Introduction

Photocatalytic materials are highly efficient in the removal of toxic and non-biodegradable pollutants from the air and municipal or industrial wastewaters [1]. Photocatalytic activity uses light radiation to stimulate semiconductor material, such as TiO₂, on surfaces readied for the oxidation of the pollutant. Although some traditional removal techniques, such as thermal-catalytic incineration, absorption methods and biotechnological abatement methods have been employed, photocatalytic oxidation has greater advantages; for instance, low costs and

toxicity, stability, hydrophilicity, simple operation conditions and availability [2,3,4]. The drawback in using small size photocatalyst particles in the aqueous phase is the cost involved in applying expensive filtration to remove the catalyst after reaction. The separation process requires more effort to become economically workable. One approach involves the use of highly dispersed fine particles in porous material, and another uses a thin film as a support of TiO₂ [5-11]. The most important properties of a suitable support are being chemically inert, presenting a high specific surface

area and its transparency to UV radiation. The literature includes examples of the ways in which immobilized nanoparticles have been focused on siliceous materials as supports; for instance, clays, non-porous silica microspheres and glass, quartz and silica gel [8-11]. Silica gel has been widely used in industry. Additionally, it possesses a moderate hydrophobicity, good light transmission and adsorption of contaminants.

Worldwide, much research has led to supported TiO₂ materials that improve the engineering applications of photocatalytic technologies. Among the published studies are works on flame oxidation of TiCl₄ [12], hydrolysis of TiCl₃ [6], chemical vapor deposition [13-14], oxidation of metallic titanium [15], metal ion implantation [16], post-synthesis hydrolytic restructuring method [5], acid-catalyzed sol-gel process [17], sol-gel [1,6,17-19] and impregnation process [2]. The drawbacks of these approaches are their costly process, and so toxic surfactant or reducing agents are essential. Therefore, they are not easily applicable to large or complex applications. Exploring other sources for nanocomposites is needed in preparation methods. Recently, the molten salt method has been used to synthesize antibacterial nanocomposites such as Ag/SG composite [20] and TiO₂/nano clay [3]. It is known as a method to obtain high purity products. Furthermore, molten reaction provides high diffusivity and prevents any mechanical mixing [16]. At the case of TiO₂ nanocomposites synthesizing, some salts such as LiNO₃ or KNO₃ have been added to titanium powder [15-16]. Although these salts decrease the process temperature to 400 °C, the products need an accurate washing and rutile phase appears, too [16]. To add, these supplementary materials reduce the purity of the product and increase product price. Thus, new methods that reduce the product cost with low environmental impacts remain to be explored.

The aim of this research was to introduce a modified method to load TiO₂ on the surface of silica gel. For this reason, the oxide of titanium and silica gel were heated at 500, 600, 700 and 800 °C. The characteristics of the produced powder are controlled by selection of temperature and heating time. Then, the reacted mass is cooled to room temperature and washed by water to remove the salt. The complex oxide powder is obtained after drying. In contrast with other common methods, expensive equipment and chemical reagents were not utilized. Therefore, minimum processing time, high purity, and inexpensive substrates are the main advantages of our product, which enable it to be produced on an industrial scale.

A series of TiO₂/SG nanocomposites were prepared under different temperatures of molten

salt. Characterizations of TiO₂/SG photocatalysts were reported by SEM, XRD, Micro-EDXRF and UV-Vis DRS. Photoactivity of the catalysts was evaluated using decolorization of Methyl orange (MO) under ultraviolet light irradiation.

2. Experimental

2.1. Preparation of TiO₂/SG nanocomposite

Titanium oxide, silica gel (Kieselgel 60, 0.063-0.200 mm), Methyl orange (MO) were purchased from Merck Co., Inc. (Azma Teb Sahand, Tabriz, Iran). All reagents were used without further refinement. MO is used because it is a typical of cation color and not absorbed by silica gel. Therefore, surface absorption is negligible and photocatalytic properties can be examined. To synthesize composite, 2 g of silica gel were exposed to 2 g of molten TiO₂ at 500, 600, 700 and 800 °C for 60 min. Then, the silica gel was washed three times with distilled water. After dissolution, the nanocomposites were dried in an oven overnight at 25 °C.

2.2. Characterization

XRD patterns of the samples were obtained from an X-ray diffractometer (Philips PW 1050, The Netherlands) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV and 30 mA, 2θ from 0 to 80° with 0.05° steps). The crystallite size was calculated by applying the Scherrer equation (Eq. 1):

$$\text{Crystallite size} = \frac{0.9\lambda}{\beta \cos \theta} \quad (\text{Eq. 1})$$

Where λ is the X-ray wavelength, θ the Bragg angle and β is the full width at half maximum of the reflection.

The microstructure of the samples was observed with a scanning electron microscope (LEO 1430VP, Germany). Absorption spectra of nanocomposites were measured by a UV-Vis diffuse reflectance spectrophotometer (Scinco S4100, Korea) at a wavelength range of 200–700 nm.

Micro-EDXRF analysis was performed using a micro-energy dispersive X-ray fluorescence spectrometer (XMF-104 X-ray Microanalyzer, Unisantia S.A., Switzerland) equipped with a 50 W molybdenum tube and a high resolution two-stage Peltier-cooled Si-PIN detector (Amptek, USA). The samples were placed in definite places, at a constant height from the holder base. The temperature of the experiment was set between 32–34 °C. The voltage and current were 30 kV and 300 μA , respectively. Each micro-EDXRF analysis was performed in 50 s to obtain sufficient counts [4].

2.3. Decolorization experiments

The photocatalytic decolorization activities of the prepared photocatalysts were evaluated using MO as a sample of pollutant. A 4 W UVA

light source was employed (Philips, Netherlands). The catalyst (1 g/L) was dispersed in 500 mL MO solution with an initial concentration of 50 mg/L. The suspension was magnetically stirred in a dark place until it reached adsorption equilibrium. Then, it was exposed to light and the suspension was maintained at room temperature by circulation of water. At given intervals of illumination (30, 60, 120, 180, 240 and 300 min), a small amount of suspension was removed and filtered through 0.45 µm filter. The MO concentration was detected with a spectrophotometer; the detection wavelength was 490 nm.

At low substrate concentration (about 20 ppm), photocatalytic decolorization activity can be evaluated by apparent pseudo-first-order rate constant (Eq. (2)) [17].

$$r = \ln \frac{C_0}{C} = kKt = k't \quad (\text{Eq. 2})$$

where r is the oxidation rate of the reactant (mg/l min),

C_0 is the initial concentration of the reactant (mg/l), C is the concentration of the reactant at time t (mg/l), t is the irradiation time, k the reaction rate constant (min^{-1}), and K the adsorption coefficient of the reactant onto the semiconductor particles (l/mg).

2.4. Stability test

For the stability test, the nanocomposite was exposed to UV (4 W Xenon lamp) for 5 h, without sampling. Afterwards, the solution was filtered, and the nanocomposite was dried at 30 °C for 24 h, and then the photocatalytic activity was measured.

3. Results and discussion

3.1. Characterization of the catalysts

Figure 1 displays SEM images of the composites. The image of silica gel shows a nearly smooth surface. Silica gel coated with TiO_2 presents a surface covered with spherical particles with a heterogeneous distribution. At 500 °C, a small

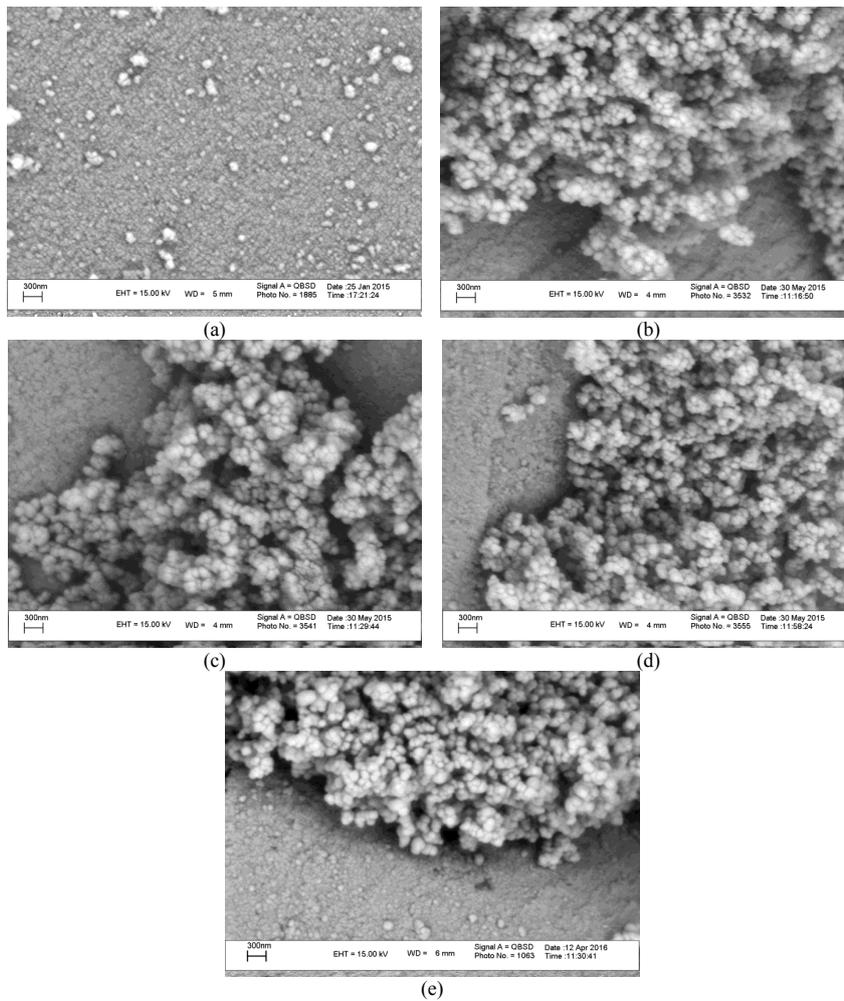


Fig. 1- SEM micrographs of (a) parent silica gel and TiO_2/SG nanocomposites prepared at (b) 500 °C, (c) 600 °C, (d) 700 °C and (e) 800 °C, at a deposition time of 60 min.

fraction of the surface was covered by nanoparticles of TiO_2 . At 700 °C, the covered surface increased. Higher temperature may explain this phenomenon, as it provides higher energy for TiO_2 to move and then attach to the surface.

Figure 2 shows the XRD patterns of TiO_2/SG nanocomposites prepared at different temperatures. The peaks corresponding to the anatase TiO_2 phase appeared at $2\theta = 25.3, 37.9, 48.1, 54.2$ and 62.0° . As observed in Figure 2, the only phase of the prepared TiO_2/SG nanocomposites found at all temperatures was pure anatase. Lack of rutile TiO_2 reflection at $2\theta = 27.4^\circ$ confirmed our claim. Possessing the only observed anatase may be due to the presence of silica gel, which inhibited the phase transformation of TiO_2 from anatase to rutile. However, most studies reported rutile and brookite besides anatase, which has the drawback of photocatalyst activity [16-17]. The simple and fast method in this study successfully synthesized the anatase phase, which is desirable for photocatalyst application. In contrast, nanocomposites produced by common

approaches, which require chemical reagents and longer processing time, may had a rutile phase, too [6]. This consequently reduces the photocatalyst activity. Noticeably, higher temperature resulted in sharper peaks, showing that the average crystallite size was increased with increasing temperature. The average crystallite size of anatase was roughly 25, 42, 44 and 53 nm for nanocomposites prepared at 550, 600, 700 and 800 °C, respectively. Here, the calculated crystallite size of 800 °C was greater than that of 700 °C, which reveals lower photocatalyst activity.

For further evaluation, the XRD patterns of TiO_2/SG and TiO_2 at 700 °C are shown in Figure 3. Interestingly, the graphs are similar in the intensity of peaks and their positions; the only phase is anatase. The crystallite size of TiO_2/SG was 44 nm, and of TiO_2 was 43 nm, which are quite similar. Consequently, the presence of support does not affect crystallinity size and phase.

Figure 4 shows the diffuse reflectance spectra in the UV-visible region for the nanocomposites.

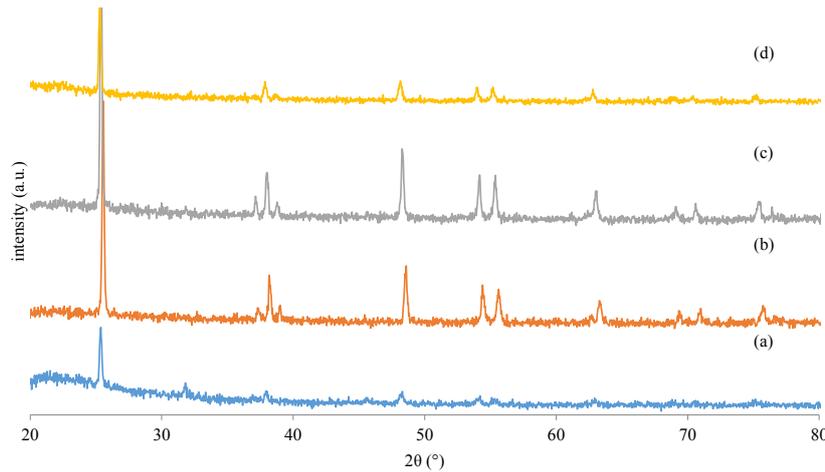


Fig. 2- The XRD patterns of TiO_2/SG nanocomposites prepared at temperatures of (a) 500 °C, (b) 600 °C, (c) 700 °C and (d) 800 °C, with a deposition time of 60 min.

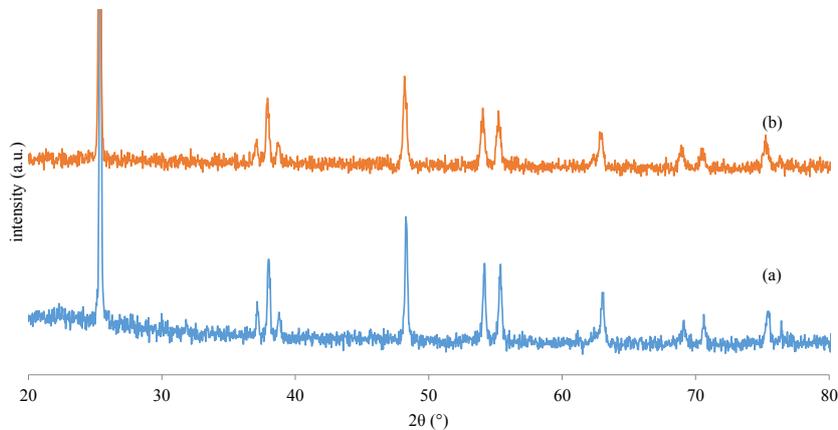


Fig. 3- The XRD patterns of (a) TiO_2 and (b) TiO_2/SG nanocomposites prepared at 700 °C, with a deposition time of 60 min.

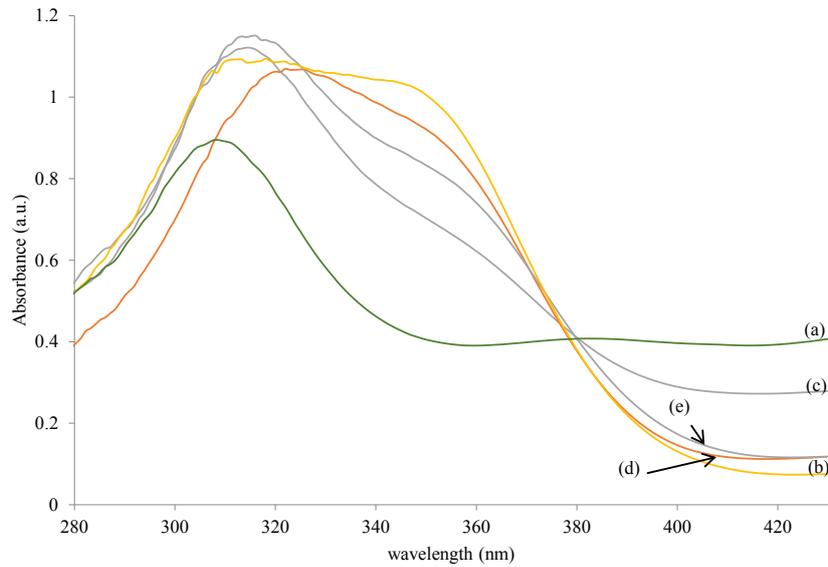


Fig. 4- UV-Vis DRS spectra of (a) silica gel, (b) TiO₂ nanoparticles and (c) TiO₂/SG nanocomposites prepared at temperatures of (d) 500 °C, (e) 600 °C and (f) 700 °C, with a deposition time of 60 min.

It appears that a wide band, centered at 345 nm, was assigned to the electron transfer from O_{2p} to Ti_{3d} corresponding to the valence band, to the conduction band transition of TiO₂ [1]. Clearly, the absorption was increased regularly by raising the molten salt temperature. The band gap energies calculated by UV-Vis DRS spectra with the equation of $E \text{ (eV)} = 1239.95/\lambda \text{ (nm)}$ are shown in Table 1. As compared with pure TiO₂ nanoparticles (band gap value of 3.2 eV), a red shift of the band gap absorption edge was observed in all supported samples; the band gap value of 2.98 eV for samples was obtained at 500 and 600 °C, and of 2.95 eV for the sample synthesized at 700 °C. Researchers reported that by decreasing the crystal size of TiO₂ nanoparticles, band gap increases [18].

It has been reported that the band gap energy changes could be attributed to a mixed effect of the quantum size and the interface interactions due to the support agent [17-18]. The reduction of band gap is one of the most important factors in a photocatalyst system, since an energy source with lower wavelength is preferred to stimulate photocatalyst activity.

The results of micro-XRF are also presented in Figure 5. The spectrum shows a small peak for titanium at about 4.5 keV. This ensures that the nanoparticles shown in the SEM image in Figure 1 are immobilized titanium oxide nanoparticles derived from the molten salt process. In the XRF graphs, the intensity of TiO₂ (I_{Ti}) is proportional to Ti where it was loaded on the substrate [4]. The value of I_{Ti} was obtained from the sharp peak centered at 4.5 keV. In this procedure the intensity of I_{Ti} is zero in the case of silica gel. Referring to

Figs. 5 (a) and (b), it can be concluded that I_{Ti} for samples prepared at 500 °C for 30 and 60 min is 643 eV and 1154 eV, respectively. This value for samples prepared at 600 °C for 30 and 60 min increased to 793 eV and 1217 eV, respectively. At 700 °C, I_{Ti} increased to 1133 eV and 1453 eV for nanocomposites prepared for 30 and 60 min, respectively. These results show that most of the loading of titanium oxide happens in the first 30 min. On the other hand, by increasing time or temperature of molten salt reaction, more titanium oxide nanoparticles formed on the substrate. This result is in agreement with SEM results.

3.2. Photocatalytic decolorization activity

The photocatalytic decolorization activity of the prepared samples has been evaluated using photo-oxidation of Methyl orange as a model reaction (shown in Figure 6). Dark adsorption study of the dye showed that there was some initial adsorption on the surface for both parent silica and nanocomposites. After this initial adsorption, the samples showed little change in absorbance of the dye, even after 24 h. In order to avoid any error due to the adsorption effect, the suspension was initially stirred for 30 min in the dark to reach an adsorption-desorption equilibrium. The results showed that the sample obtained at 700 °C had the highest decolorization activity i.e. 51 %, and the sample prepared at 500 °C had the lowest decolorization activity i.e. 32 %. SEM and XRF revealed that at 700 °C the loaded amount of TiO₂ was greater than in other processes. Clearly, the greater amount of nanoparticles on the surface provided a larger active site for decolorization

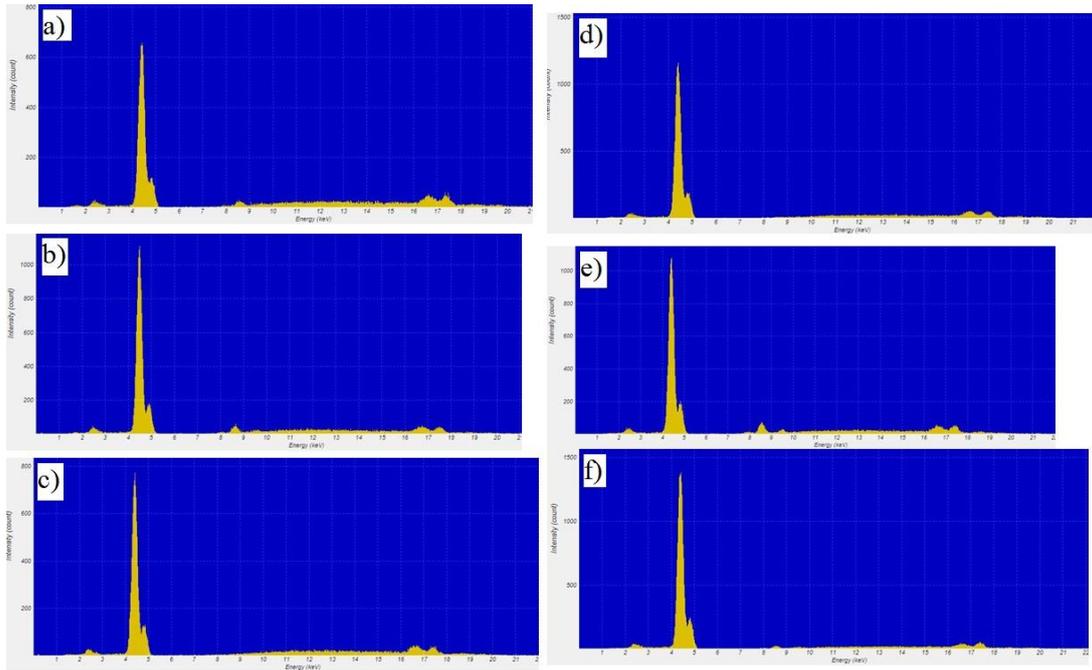


Fig. 5- The micro-EDXRF spectrum of TiO₂/SG nanocomposites prepared at 500 °C with deposition times of (a) 30 and (b) 60 min, at 600 °C with deposition times of (c) 30 and (d) 60 min and at 700 °C with deposition times of (e) 30 and (f) 60 min.

activity. Although increasing the process temperature to 800 °C produced a photocatalyst composite, the activity decreased. This occurred because the larger crystal size of the sample was generated at 800 °C, and reduced the available active surface. The decolorization activity of TiO₂ nanoparticles at 700 °C without support was 62%. Some published works reported that photocatalyst activity decreased after loading on a support [1,7], but this reduction was only 17 % in our study. The reason of this reduction is decreasing the available surface of nanoparticles because of immobilization.

The improved decolorization efficiency of the composites is reflected in the kinetic analysis of the results. Methyl orange degradation follows pseudo first-order kinetics. First-order degradation rate constants were obtained by plotting the natural logarithm of the absorbance against irradiation time for the composites. The values are shown in Figure 7. The values of the rate constant recorded for the composites prepared at temperatures of 500, 600, 700 and 800 °C were 0.012, 0.0013, 0.0023 and 0.017 min⁻¹, respectively.

As discussed previously, the higher

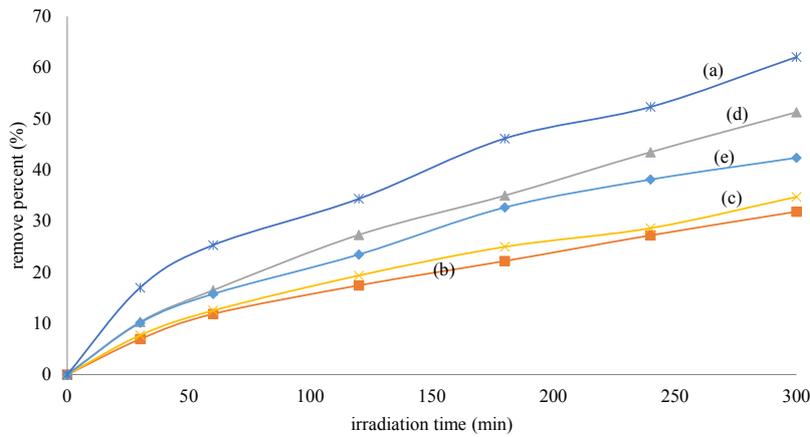


Fig. 6- Photocatalytic activity of (a) TiO₂ nanoparticles and TiO₂/SG nanocomposites prepared at temperatures of (b) 500, (c) 600, (d) 700 and (e) 800 °C, at a deposition time of 60 min.

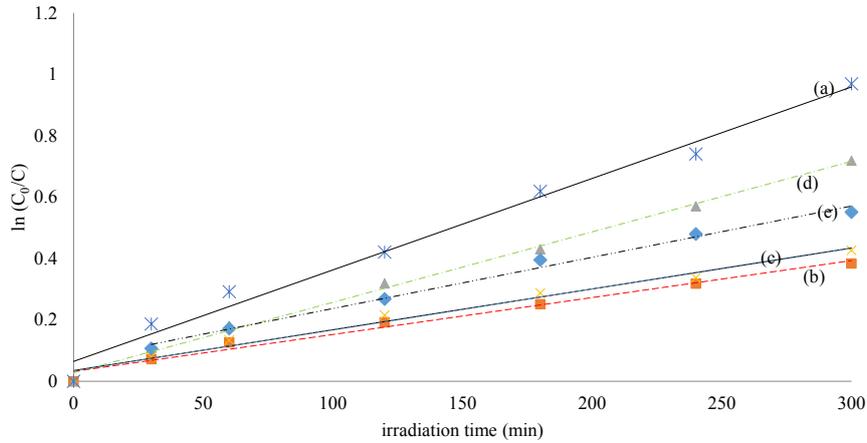


Figure 7. Kinetic analysis of (a) TiO₂ nanoparticles and TiO₂/SG nanocomposites prepared at temperatures of (b) 500, (c) 600, (d) 700, and (e) 800 °C, at a deposition time of 60 min.

photocatalytic decolorization activity of composites prepared at 700 °C results from the increase of the number of TiO₂ nanoparticles forming on the silica gel; since the only sites for photodegradation are surfaces coated by TiO₂ particles. However, the source of UV was only a 4 W lamp. Similar research employed stronger lamps [5]. Although higher watts eliminated more dye, energy consumption increased. However, the elimination at 51% is comparable with other works. For example, Wang et al. (2006) reported $k=0.018$ in experiments with a 20 W lamp and 3 g/l of catalyst [3].

3.3. Stability test

This test was designed to examine the stability of the nanocomposite during the photocatalyst activity. A stronger connection of nanoparticles and support results in high stable nanocomposite, because they remain on the support's surface for

further apply. Figure 8 shows that the activity of the photocatalyst prepared at 700 °C did not change during the stability experiment. This may be explained by a strong connection of nanoparticle with silica base. Photocatalyst decolorization efficiency at reuse utilization is important to knowing its stability. In the surface plasmon resonance (SPR) study, a gold layer on glass slides was used as a converter. Given the weak adhesion of gold and glass, an interlayer of chrome or titanium is usually used to achieve acceptable adhesion [21-23]. In our research, no chemical agent was used, and titanium nanoparticles bound to silica was achieved simply and quickly. This is a key parameter in photocatalyst production, and increases the product's economic efficiency.

4. Conclusion

To achieve a simple, fast and inexpensive method

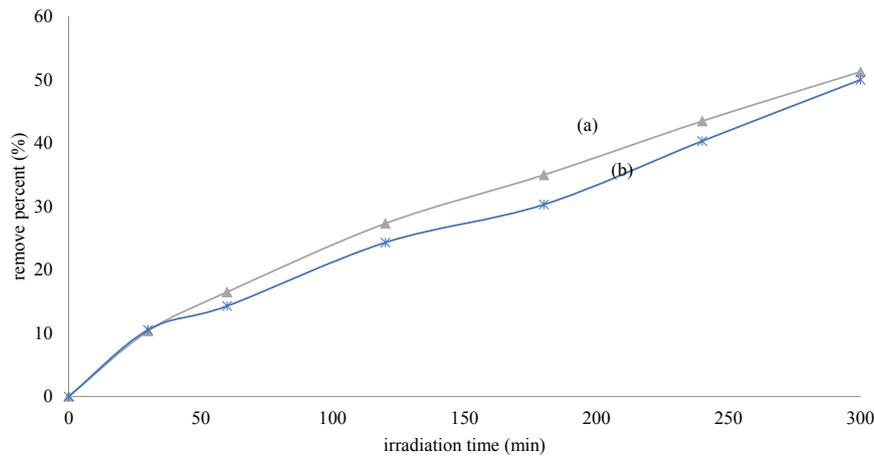


Figure 8. Photocatalytic activity of (a) TiO₂/SG nanocomposites prepared at a temperatures of 700 °C and a deposition time of 60 min and (b) its stability test.

for TiO₂/SG nanocomposite production, the molten salt approach was successfully examined. Not only were the aims of the study achieved, but the nanocomposite contained the only anatase phase. Providing heterogeneous distribution on the surface of silica gel supports photocatalyst activity. A band gap value of 2.98 eV was obtained for samples obtained at 500 and 600 °C, and 2.95 eV for a sample synthesized at 700 °C. So, lower energy is required for stimulation of nanocomposite obtained from 700 °C. Consequently, a lower wavelength for stimulation of the photocatalyst is required. The results showed that the samples obtained at 500 and 700 °C had the lowest and highest photocatalytic decolorization activity, respectively. The activity of the photocatalyst prepared at 700 °C did not change during the stability experiment.

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