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Fe DOPED TiO_2 THIN FILMS COATED ON GLASS FIBER TO INHIBIT BACTERIAL OF *E. COLI* PREPARED BY SOL-GEL METHOD

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Fe doped TiO_2 thin films coatings on glass fiber have been prepared by the sol-gel method and calcined at 500 °C for 2 h with a heating rate of 10 °C/min. The thin films were characterized by XRD, SEM, AFM, photocatalytic activity was determined by means of degradation of methylene blue (MB) solution and antibacterial activity was evaluated by the inactivation of *Escherichia coli* (*E. coli*) bacteria. The antibacterial activity against *E. coli*, has been studied applying the so called antibacterial drop test. The bactericidal activity for the above bacteria cells was estimated by relative number of bacteria survived calculated from the number of viable cells which form colonies on the nutrient agar plates. The results show that the thin films exhibited a high antibacterial activity, which was enhanced with the increase of Fe dopant concentration. With the highest dopant concentration investigated in this experiment (TiO_2 doped Fe with 5 mol% condition) the thin films show antibacterial activity of 97.78% under UV irradiation for 40 min.

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Keywords: Fe doped TiO_2 thin films, Inhibit bacterial of E. coli, Photocatalytic activity, Sol-gel method

1. Introduction

In recent years, titanium dioxide (TiO_2) is used in wide application in photocatalyst, self-cleaning surfaces, solar cells, water and air purification, gas sensing and optical coating [1-3] because of its unique properties such as good photocatalytic activity, chemical stability, non toxic nature, large band gap and low cost [4-6]. TiO_2 has three different crystal structures: anatase, rutile and brookite [7-9]. Two crystal structure of TiO_2, anatase and rutile are usually used in photocatalyst. The structure of anatase and rutile showed a higher photocatalytic activity [10-11]. The photocatalytic agent TiO_2, known for its chemical stability and optical competency, has been used extensively for killing different groups of microorganisms including bacteria, fungi and viruses, because it has high photoreactivity, broad-spectrum antibiosis and chemical stability [12-14]. The photocatalytic activity of TiO_2 nanoparticles depends not only on the properties of the TiO_2 material itself, but also on the modification of TiO_2 with metal or metal oxide. Previous studies reported that the addition of Fe in TiO_2 enhances its photocatalytic efficiency [15-18]. However, Fe nanoparticles have prospective applications including biosensing, biodiagnostics, optical fibers, and antimicrobial and photocatalytic uses. Fe ions are known to cause denaturation of proteins present in bacterial cell walls and slow down bacterial growth [16, 19-20].

The sol-gel method is considered as an effective approach for the prepared of immobilized TiO_2 thin films because good homogeneity, low processing temperature and low cost [21-23]. In the present experiments, we report on the synthesis and characterization of Fe doped TiO_2 thin films coated on glass fiber prepared by using a sol-gel method. The samples have been characterized using XRD, SEM and AFM technique. Phase, morphology, photocatalytic activity of

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degradation of methylene blue (MB) and antibacterial of *Escherichia coli* (*E. coli*) properties of the samples were investigated.

2. Experimental

2.1 Raw materials

Titanium (IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$, TTIP, Aldaich chemistry, 97%), iron (III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$, Fluka Sigma-Aldrich, 97%), nitric acid (HNO_3, Fluka Sigma-Aldrich, 97%) were used as starting materials and ethanol (CH_3CH_2OH, Merck, 36.5-38.0%) was used as solvent.

2.2 Sample preparation

Fe doped TiO_2 thin films coated on glass fiber were prepared via sol-gel method. Firstly, $Fe(NO_3)_3.9H_2O$ with fixed at 0, 1, 3 and 5 mol% of TiO_2 and TTIP with fixed at 10 ml were mixed into 150 ml of CH_3CH_2OH, and the mixture was vigorously stirred at room temperature for 15 min. The pH of mixed solution was adjusted to about 3-4 by 3 ml of 2 M HNO_3. Finally, it was vigorously stirred at room temperature for 45 min until clear sol was formed. The thin films were deposited on glass fiber by dip-coating process at room temperature with the drawing speed of dip-coater at about 1.25 mm/s. The coated samples were dried at room temperature for 24 h and calcined at the temperatures of 500 °C for 2 h with a heating rate of 10 °C/min. For this work the Fe doped TiO_2 thin films containing 0, 1, 3 and 5 mol% were designated as TP, T1Fe, T3Fe and T5Fe, respectively.

2.3 Characterization

The morphology of the Fe doped TiO_2 thin films were characterized by scanning electron microscope (SEM) (Quanta 400). Surface roughness of thin films was measured by atomic force microscope (AFM) for an area of 1x1 μm^2. The phase composition was characterized using an x-ray diffractometer (XRD) (Phillips X'pert MPD, Cu-K). The crystallite size was calculated by the Scherer equation, Eq. (1) [24].

$$D = k\lambda/\beta cos\theta_B \quad (1)$$

Where D is the average crystallite size, k is equal to 0.9, a shape factor for spherical particles, λ is the X-ray wavelength (λ = 0.154 nm), θ is the Bragg angle and $\beta = B–b$, the line broadening. B is the full width of the diffraction line at half of the maximum intensity and b = 0.042 is the instrumental broadening.

2.4 Photocatalytic activity test

The photocatalytic activity was evaluated by the degradation of MB under UV irradiation using eleven 50 W of black light lamps. Fe doped TiO_2 thin films with an diameter of 2.50 cm was soaked in a 10 ml of MB with a concentration of 1×10^{-6} M and kept in a dark chamber for 1 h, after that kept in a chamber under UV irradiation for 0, 1, 2, 3, 4, 5 and 6 h. After photo-treatment for a certain time, the concentration of treated solution was measured by UV-vis. The ratio of remained concentration to initial concentration of MB calculated by C/C_0 [25-26] was plotted against irradiation time in order to observe the photocatalytic degradation and the percentage degradation of the MB molecules was calculated by Eq. (2) [24-26].

$$M = 100(C_0-C)/C_0 \quad (2)$$

Where M is the percentage degradation of the MB molecules, C_0 is the concentration of MB aqueous solution at the beginning (1×10^{-6} M) and C is the concentration of MB aqueous solution after exposure to a light source.

2.5 Antibacterial activity test

The antibacterial activity of Fe doped TiO_2 thin films against the bacteria *E. coli* were prepared by used 1 ml of 10^3 CFU/ml concentration of *E. coli* dropped on thin films (diameter of 2.50 cm) that placed in Petri dish plate and then exposed to either UV irradiation (eleven 50 W of black light lamps) for 0, 20, 40 and 60 min. Then, 0.1 ml of mixture suspension was sampled and spread on Macconkey Agar plate and incubated at 37°C for 24 h. After incubation, the number of viable colonies of *E. coli* on each Macconkey Agar plate was observed and disinfection efficiency of each test was calculated in comparison to that of the initial or control (N/N_0) [26-27]. Percentage bacterial reduction or *E. coli* kill percentage was calculated according to the following equation, Eq. (3) [24, 26-27].

$$E = 100(N_0-N)/N_0 \qquad (3)$$

Where E is the percentage bacterial reduction or *E. coli* kill percentage, N_0 and N are the average number of live bacterial cells per milliliter in the flask of the initial or control and thin films finishing agent or treated fabrics, respectively.

3. Results and discussion

3.1 Characterization

Figure 1 shows the XRD pattern of Fe doped TiO_2 powders, heated at 500°C for 2 h in air. All samples have shown similar peaks with the highest peak at 25.26° which was indicated as 100% anatase phase. Fe compound phase can’t be verified in these XRD peaks due to a very small amount of Fe doping. The crystallite size of Fe doped TiO_2 with 0, 1, 3 and 5 mol% Fe were 20.7, 16.9, 16.6 and 13.8 nm, respectively. This result shows the Fe doping in range of 1-5 mol% exhibits nearly the same crystallite size of anatase phase. The morphology of glass fiber and Fe doped TiO_2 thin films observed by SEM with the 5,000 magnifications are shown in **Figure 2**. All samples of thin films have surfaces are dense of thin films. **Figure 3** show the surfaces roughness of glass fiber and Fe doped TiO_2 thin films are 0.691, 0.733, 1.061, 1.209 and 3.279 nm for glass fiber, 0, 1, 3 and 5 mol% of Fe doping, respectively. It was found that the surfaces roughness increases when doping Fe in TiO_2 thin films and surfaces roughness increases with an increase in Fe doping due to the contribution of Fe effect.

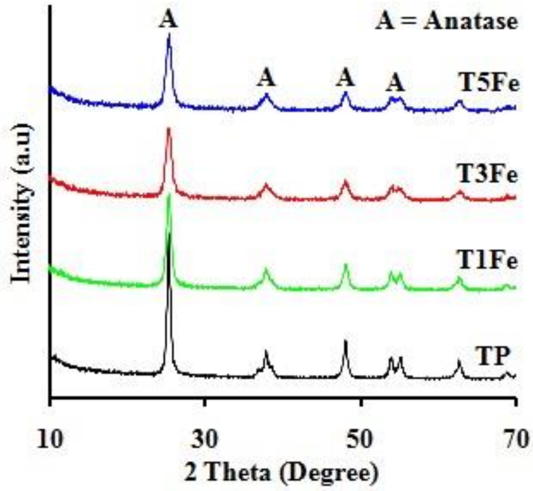

Fig. 1. XRD pattern of Fe doped TiO_2 powders

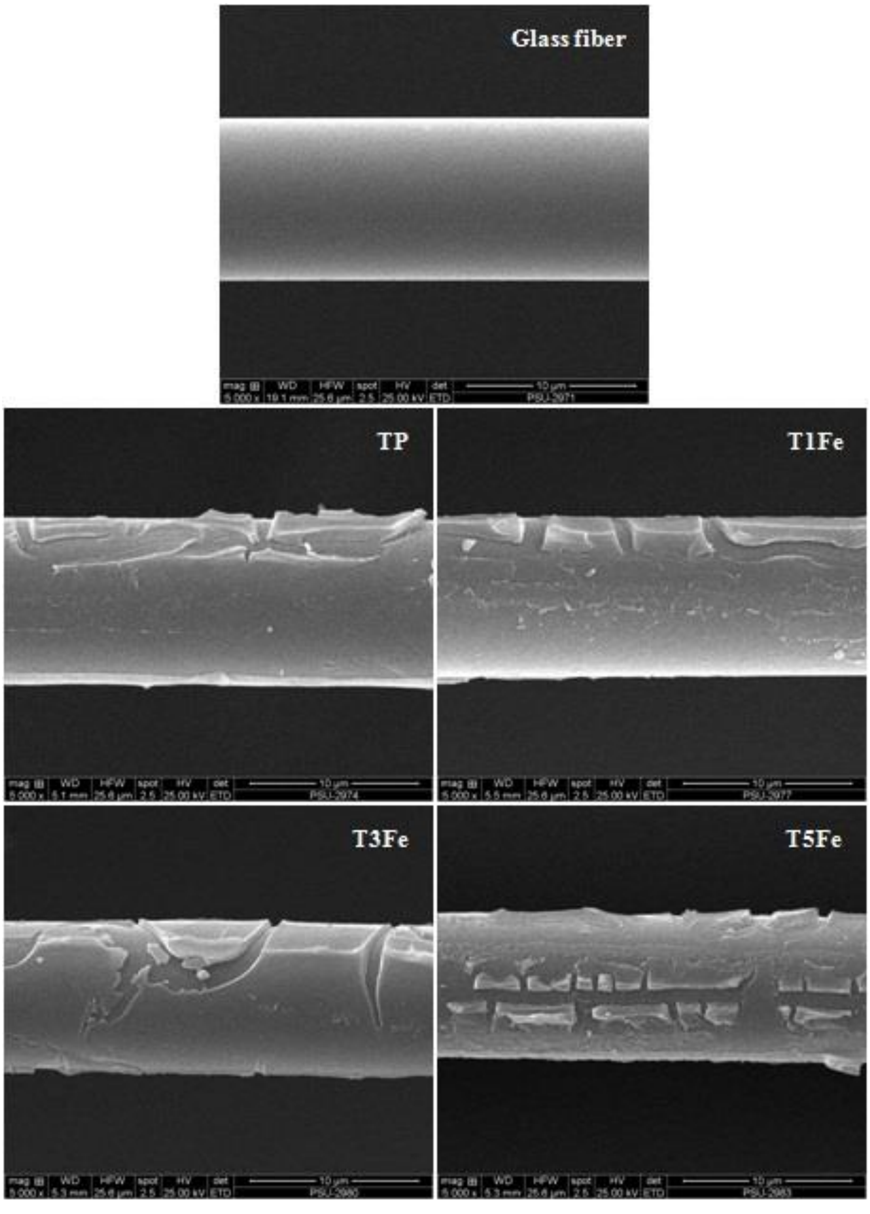

Fig. 2. SEM image of glass fiber and Fe doped TiO_2 thin films with the 5,000 magnifications

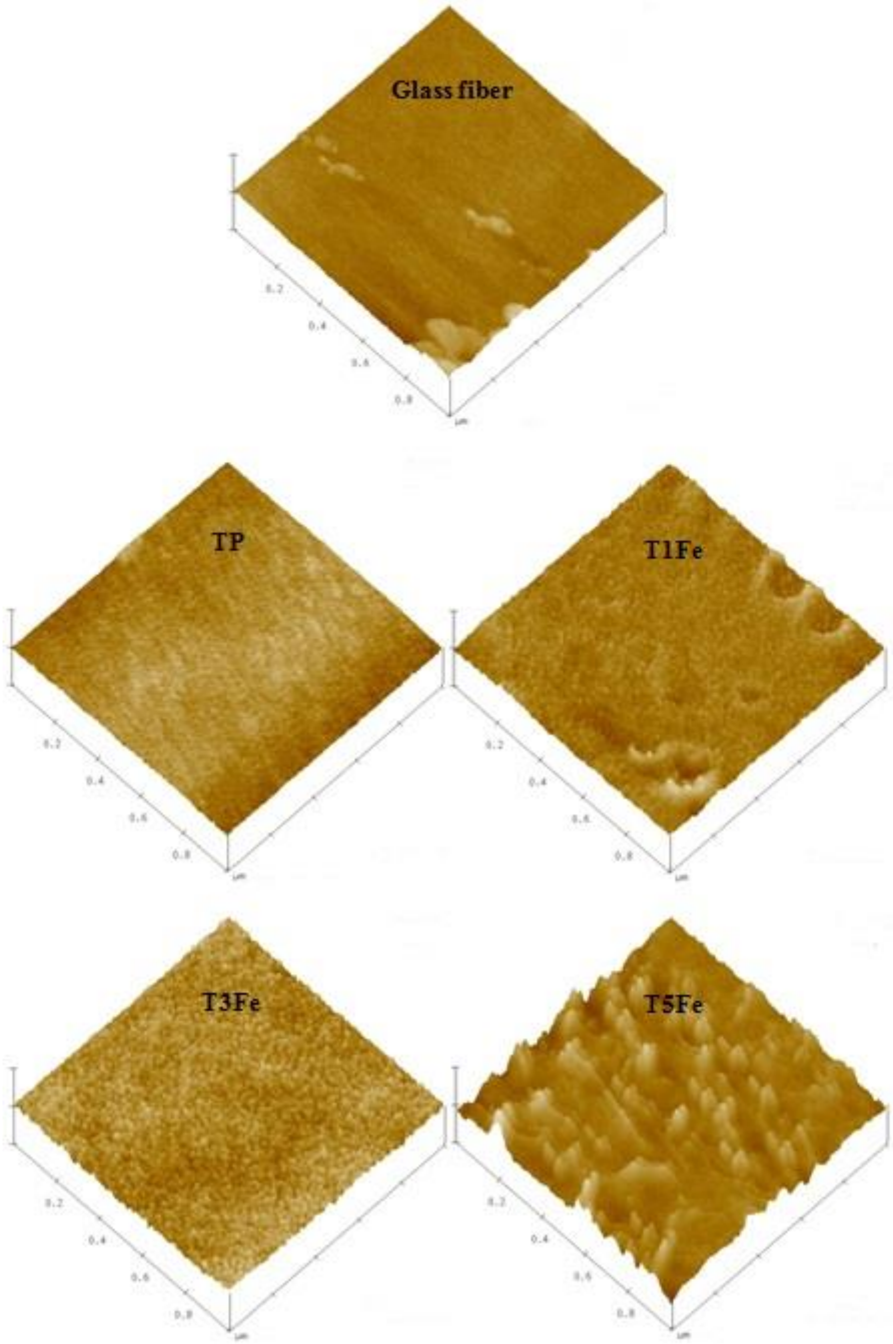

Fig. 3. AFM image of glass fiber and Fe doped TiO_2 thin films

3.2 Photocatalytic activity

The photocatalytic degradation of MB by using Fe doped TiO_2 thin films under UV irradiation is show in **Figure 4**. It was apparent that Fe added in TiO_2 has significantly effect on photocatalytic reaction under UV irradiation compared with undoped Fe (TP). For TiO_2 doped with Fe thin films, it was found that the photocatalytic activity increases with increases Fe doping due to a small of crystallite size and high surfaces roughness. The MB degradation percentage of thin films under UV irradiation is shown in **Figure 5**. It was found that MB degradation percentage of thin films under UV irradiation for 6 h are 44.49, 50.64, 57.43 and 75.08% for 0, 1, 3 and 5 mol% of Fe doping, respectively. It was found that TiO_2 doped Fe with 5 mol% (T5Fe) thin films show the best photocatalytic activity under UV irradiation.

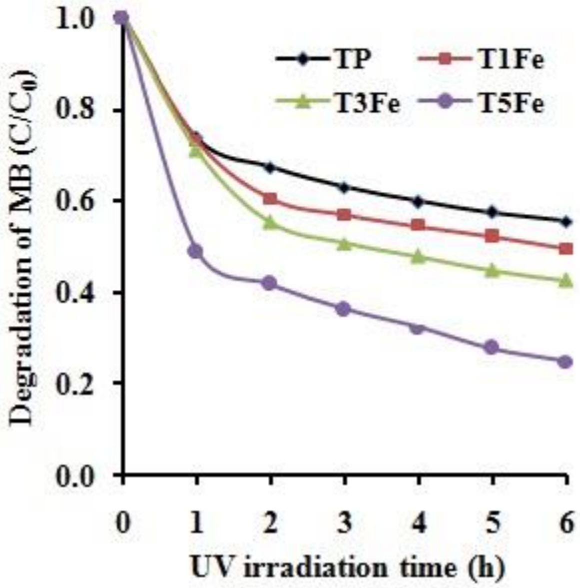

Fig. 4. The photocatalytic activity of Fe doped TiO_2 thin films

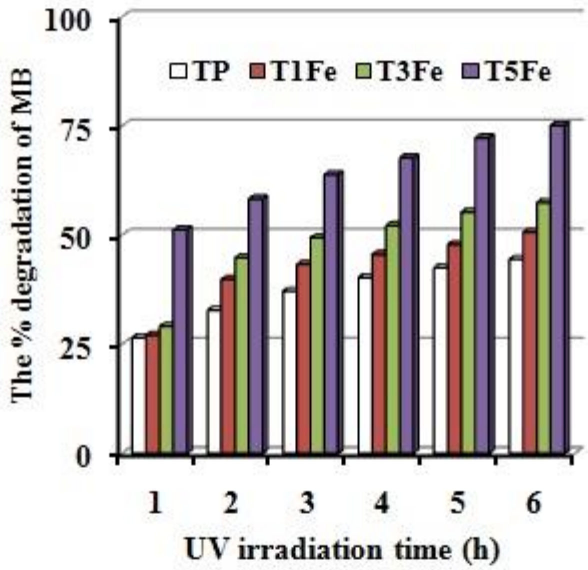

Fig. 5. The MB degradation percentage of Fe doped TiO_2 thin films

3.3 Antibacterial activity

The antibacterial activity of Fe dope TiO_2 thin films were investigated against *E. coli* bacteria under UV irradiation, as presented in **Figure 6** and **Figure 7**. For **Figure 6** displays the *E. coli* survival rate (N/N_0) after testing with UV irradiation on Fe dope TiO_2 thin films. The result shows that the *E. coli* survivals decrease with UV irradiation time. The *E. coli* survival rate of Fe dope TiO_2 thin films under UV irradiation for 60 min are 0.31, 0.24, 0.11 and 0.02 for TiO_2 doped Fe with 0, 1, 3 and 5 mol% thin films respectively. It also indicates that the TiO_2 doped Fe with 5 mol% thin films exhibit higher antibacterial activity compared to TiO_2 doped Fe with 0, 1 and 3 mol% thin films, respectively. The *E. coli* kill percentage of Fe dope TiO_2 thin films under UV irradiation is shown in **Figure 7**. It is seen that the percentage bacterial reduction or *E. coli* kill percentage increased at the presence of Fe doped TiO_2 thin films. The pure TiO_2 (un-dope Fe, TP) thin films showed a weak *E. coli* kill percentage under UV irradiation while introducing Fe to TiO_2

matrix led to increase in *E. coli* kill percentage. By increasing the Fe concentration in TiO_2 matrix antibacterial activity enhances remarkably. The *E. coli* kill percentage of Fe dope TiO_2 thin films under UV irradiation for 60 min are 68.89, 75.56, 88.89 and 97.78% for TiO_2 doped Fe with 0, 1, 3 and 5 mol% thin films, respectively. It was found that 5 mol% Fe doped TiO_2 thin films show the best antibacterial activity under UV irradiation. **Figure 8** shows an image of the *E. coli* cell wall and membrane damages of TiO_2 doped Fe with 5 mol% thin films treated under UV irradiation for 60 min. The photo of viable bacterial colonies (red spots) on synthesized Fe doped TiO_2 thin films treated with UV irradiation for 0, 20, 40 and 60 min are illustrated in **Figure 9**. It is very obvious that the cell walls and cell membranes were damaged when microbial cells came into contact with Fe doped TiO_2 thin films being activated by UV irradiation. In this sense, the photo-generated hydroxyl (OH°) and super oxygen (O_2^-) radicals acted as powerful oxidizing agents which react with peptidoglycan (poly-*N*-acetylglucosamine and *N*-acetylmuramic acid) of bacterial cell wall [28].

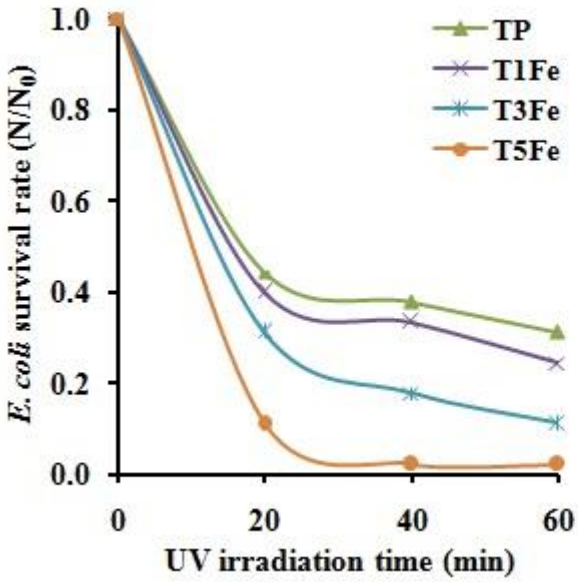

Fig. 6. The antibacterial activity of Fe doped TiO_2 thin films

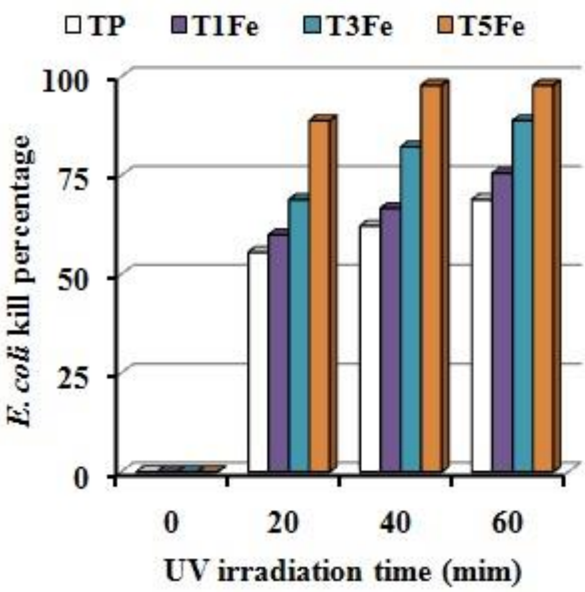

Fig. 7. The antibacterial activity of Fe doped TiO_2 thin films

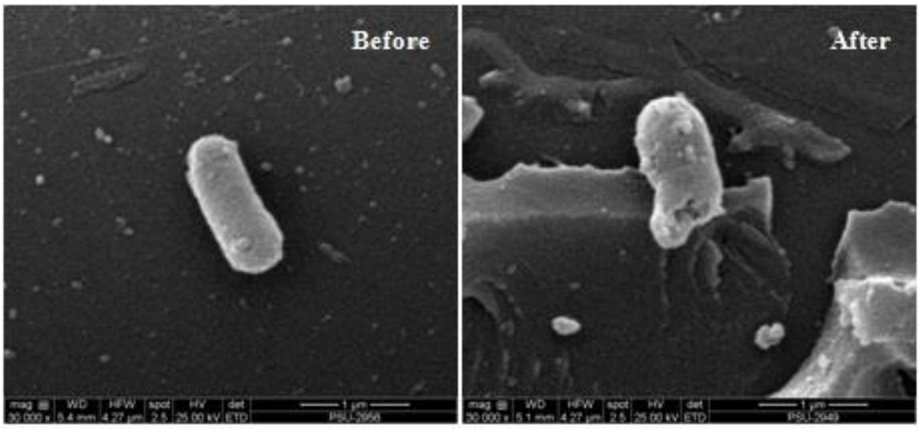

Fig. 8. SEM image of the E. coli cell wall and membrane damages of TiO_2 doped Fe with 5 mol% thin films before and treated with UV irradiation for 60 min

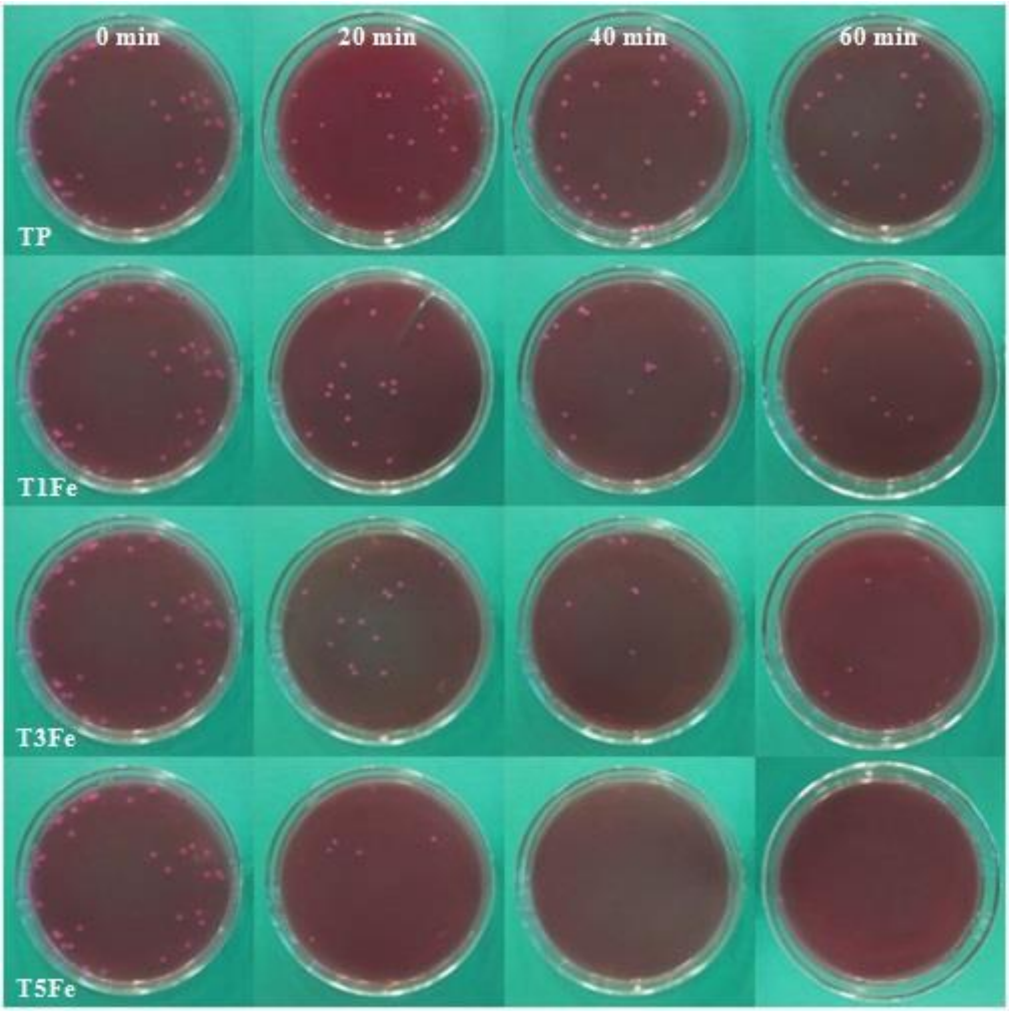

Fig. 9. Photo of viable E. coli colonies (red spots) on synthesized Fe doped TiO_2 thin films

4. Conclusion

In this work, Fe doped TiO_2 thin films were prepared by sol-gel method and dipped coating on glass fiber and calcined at 500 °C for 2 h with a heating rate of 10 °C/min. The thin films were characterized by XRD, SEM, AFM, photocatalytic activity was determined by means of degradation of MB solution and antibacterial activity was evaluated by the inactivation of *E. coli* bacteria. It was found that Fe affects to phase, morphology, photocatalytic activity and antibacterial of *E. coli* properties. It can be note that TiO_2 doped Fe with 5 mol% thin films have highest photocatalytic activity (75.08%, for 1 h) and antibacterial of *E. coli* properties (97.78% for 40 min).

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