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PHOTOCATALYTIC DISINFECTION OF WATER CONTAINING *E. COLI* USING Fe^{3+} DOPED TiO_2 THIN FILMS COATED ON GLASS FIBERS

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Fe^{3+} doped TiO_2 thin films coatings on glass fibers have been prepared by the sol-gel method using Fe^{3+} contents of 0, 1, 3 and 5 mol% and calcined at 500 °C for 2 h with a heating rate of 10 °C/min. The water disinfection efficiency of Fe^{3+} doped TiO_2 thin films was investigated. The water containing *E. coli* with an initial concentration of 10^3 CFU/ml was treated by a photocatalytic reactor filled with 100 g of glass fibers coated with the Fe^{3+} doped TiO_2 thin films for 0-5 circulated cycles. The number of survival bacteria after treatment was evaluated with spared plate techniques. Forthermore, the photocatalytic activity was determined by means of degradation of methylene blue (MB) solution. Finally, the thin films were characterized by XRD, SEM and AFM techniques. The results show that Fe^{3+} doped TiO_2 thin films exhibits greater photocatalytic activity and disinfection efficiency than those of pure TiO_2 (undoped Fe^{3+}). It was found that the bacterials inactivation of the prepared thin films correlates closely to photocatalytic activity preformed by degradation of MB solution. In addition, it was found that 5 mol% of Fe^{3+} doped TiO_2 thin films can kill *E. coli* about 80% within 5 cycled water treatments.

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1. Introduction

Water disinfection is recognized by the WHO as one of the most important challenges for human health protection. The spread of water borne infection is a problem in both developed and underdeveloped countries [1-2]. Particularly, there are concerns about the possible long-term effects of systemic exposure to a certain class of toxins, for instances the release of endotoxin in from *E. coli* upon cell lysis [2-3].

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 [4-6] because of its unique properties such as good photocatalytic activity, chemical stability, non toxic nature, large band gap and low cost [7-9]. 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 [10-12]. 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^{3+} in TiO_2 enhances its photocatalytic efficiency [13-16]. However, Fe^{3+} nanoparticles have prospective applications including biosensing, biodiagnostics, optical fibers, and antimicrobial and photocatalytic uses. $Fe^{3+}$is known to cause denaturation of proteins present in bacterial cell walls and slow down bacterial growth [14, 17-19].

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The aim of this work is to investigate the water containing *E. coli* with an initial concentration of 10^3 CFU/ml was treated by a photocatalytic reactor filled with 100 g of glass fibers coated with the Fe^{3+} doped TiO_2 thin films for 0-5 circulated cycles. The number of survival bacteria after treatment was evaluated with spared plate techniques. Furthermore, the photocatalytic activity was determined by means of degradation of methylene blue (MB) solution was also investigated in order to compare with a result of bacteria inactivation of the prepared films. Finally, the thin films were characterized by XRD, SEM and AFM techniques.

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^{3+} 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^{3+} 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^{3+} 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) [20][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^{3+} doped TiO_2 thin filmswith an diameter of2.50 cmwas 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 [19, 21-23] 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) [19, 21-23].

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

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 Cis the concentration of MB aqueous solution after exposure to a light source.

2.5 Antibacterial activity test

The bacterial strain used was *E. coli* K-12. *E. coli* cells were grown aerobically in 4 ml of tryticase soy broth at 37°C for 24 h. Then the bacterial solution was diluted in saline solution (0.85% NaCl) till the number of *E.coli* in per milliliter solution is in the range of 30-300. The number of viable bacterial in a treated solution can be readily quantified by using spread plate technique in which a sample is appropriately diluted and transferred to an agar plate. After colonies are grown, they are counted and the number of bacterial in the original sample is calculated. It was found that the initial bacterial concentration is an important factor in evaluating the antibacterial efficiency [2]. To obtain a working cell suspension, the stock was serially diluted in saline solution and sampled only 1 ml for adding to the reactor solution (450 ml). The initial bacterial concentration was kept about 10^3 CFU/ml used for all experiments. The detection of *E. coli* cells in the water samples taken from the reactor was carried out by plating appropriate dilutions onto Macconkey agar. The plates were incubated at 37°C for 24 h. The number of viable bacterial was determined by using the spread plate technique after passing through reactor of 0-5 cycleswas observed and disinfection efficiency of each test was calculated in comparison to that of the initial or control (N/N_0) [19, 23]. Percentage bacterial reduction or *E. coli* kill percentage was calculated according to the following equation, Eq. (3) [19, 23]. A photocatalytic reactor is made of Pyrex glass fixed in a dark chamber surrounded by 10 x 6 W of black light lamps. The glass reactor has volume of 500 ml filled with Fe^{3+} doped TiO_2 thin films coated glass fibers 100 g. A flow rate of made up water containing *E. coli* passed through the reactor was kept constant at 90 ml/min

$$E = 100(N_0\text{-}N)/N_0 \quad (3)$$

Where E is the percentage bacterial reduction or *E. coli* kill percentage, $N_0$and Nare 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

Fig 1 shows the XRD pattern of Fe^{3+} 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^{3+} doping. The crystallite size of Fe^{3+} 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^{3+} doping in range of 1-5 mol% exhibits nearly the same crystallite size of anatase phase. The morphology of glass fiber and Fe^{3+} doped TiO_2 thin films observed by SEM with the 3,500 and 2,500 magnifications are shown in Fig. 2. All samples of thin films have surfaces are dense of thin films. Fig. 3 show the surfaces roughness of glass fiber and Fe^{3+} 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^{3+} doping, respectively. It was found that the surfaces roughness increases when doping Fe^{3+} in TiO_2 thin films and surfaces roughness increases with an increase in Fe^{3+} doping due to the contribution of Fe^{3+} effect.

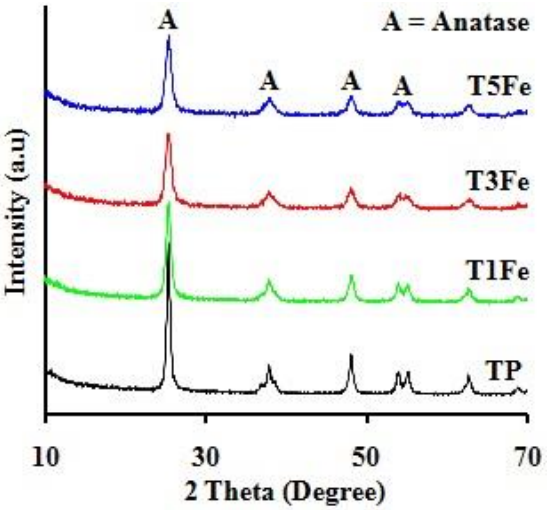

Fig. 1.XRD pattern of Fe^{3+} doped TiO_2 powders

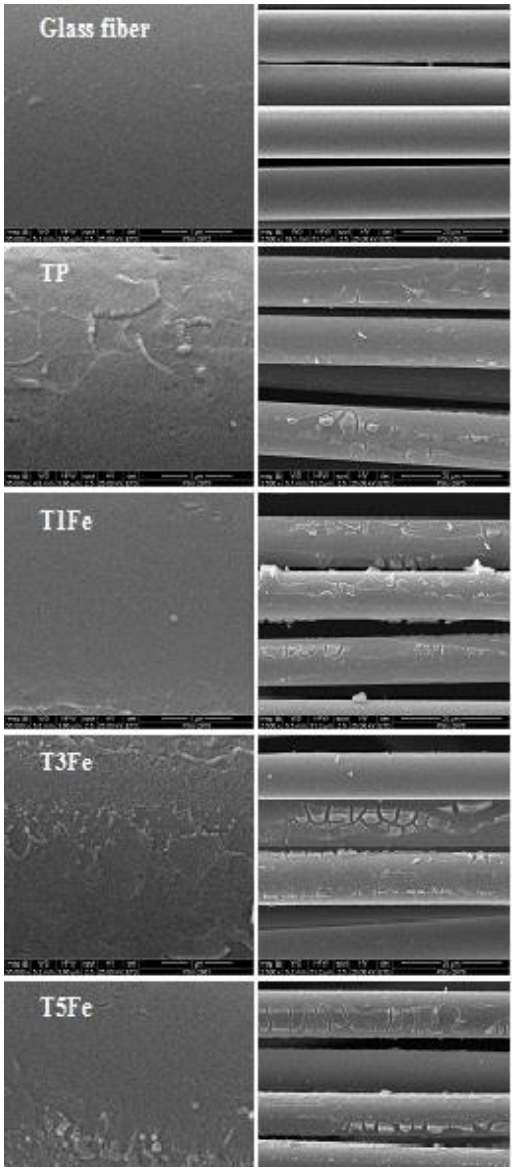

Fig. 2.SEM image (surface and cross section) of glass fiber and Fe^{3+} doped TiO_2 thin films.

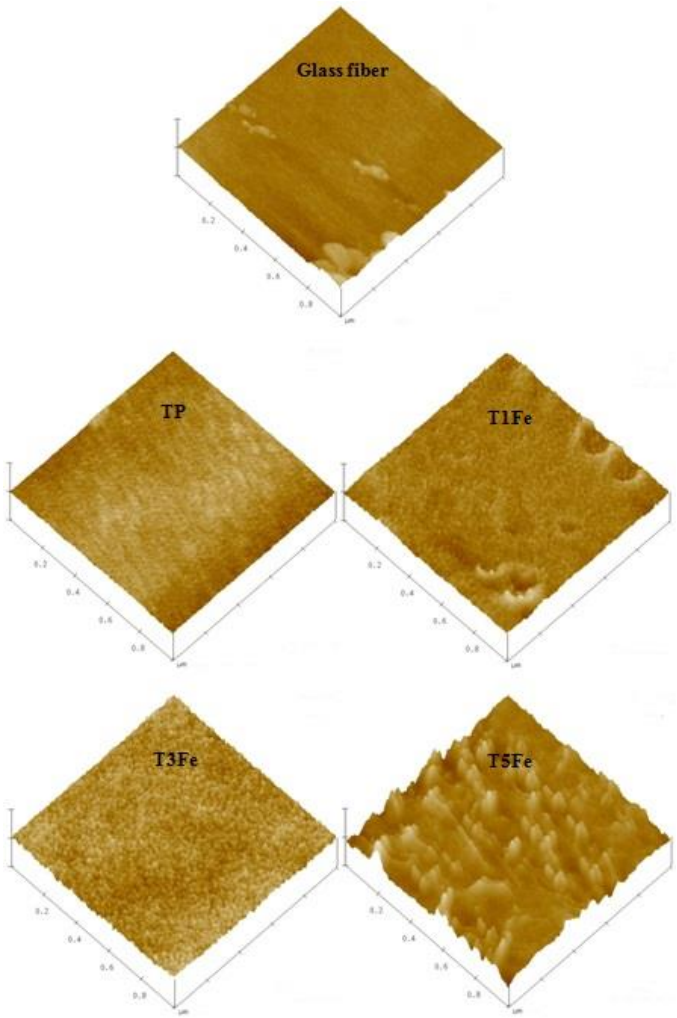

Fig. 3. AFM image of glass fiber and Fe^{3+} doped TiO_2 thin films

3.2 Photocatalytic activity

The photocatalytic degradation of MB by using Fe^{3+} doped TiO_2 thin films under UV irradiation is show in Fig. 4. It was apparent that Fe^{3+} added in TiO_2 has significantly effect on photocatalytic reaction under UV irradiation compared with undoped Fe^{3+} (TP). For TiO_2 doped with Fe^{3+} 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 Fig. 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^{3+} doping, respectively. It was found that TiO_2 doped Fe^{3+} with 5 mol% (T5Fe) thin films show the best photocatalytic activity under UV irradiation.

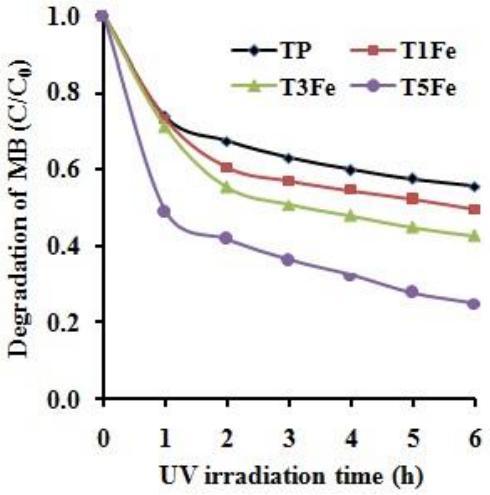

Fig. 4. The photocatalytic activity of MB of Fe^{3+} doped TiO_2 thin films

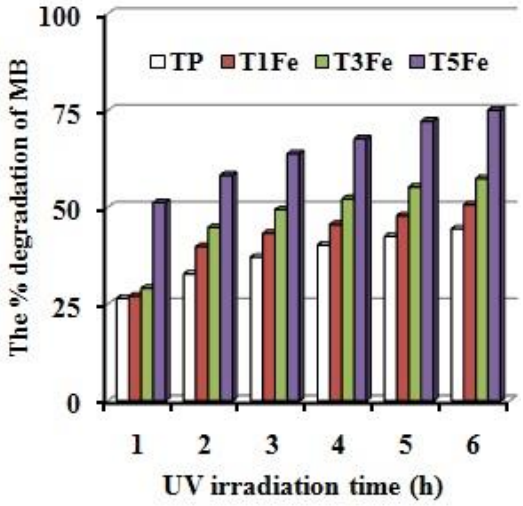

Fig. 5. The MB degradation percentage of Fe^{3+} doped TiO_2 thin films

3.3 Antibacterial activity

The efficiency of *E. coli* photo-inactivation with a UV light was evaluated using distilled water containing the pathogen. The results obtained are given in Fig.6. The survival rating of *E. coli* was determined by counting the number of viable cells in terms of CFU. The *E. coli* bacterial inactivation test was performed by allowing the *E. coli* made-up water flow through 100 g of Fe^{3+} doped TiO_2 thin films packed in reactor surrounded by UV lamps with the flow rate of 90 ml/min for 0-5 circulated cycles. The survival curves of *E. coli* illustrated in Fig. 6 are plotted between N/N_0 ratio and treatment cycle. The result indicated that TiO_2 doped Fe^{3+} with 5 mol% (T5Fe) thin films exhibits higher bactericidal activity against *E. coli* under UV irradiation compared to 3, 1 and 0 mol% of Fe^{3+} doping, respectively.

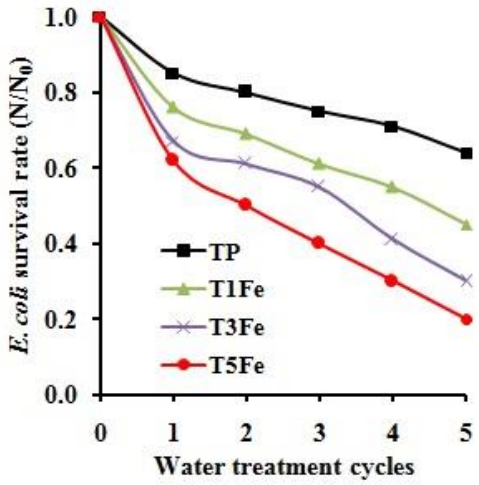

Fig. 6. The antibacterial activity as a function of water treatment cycles for Fe^{3+} doped TiO_2 thin films

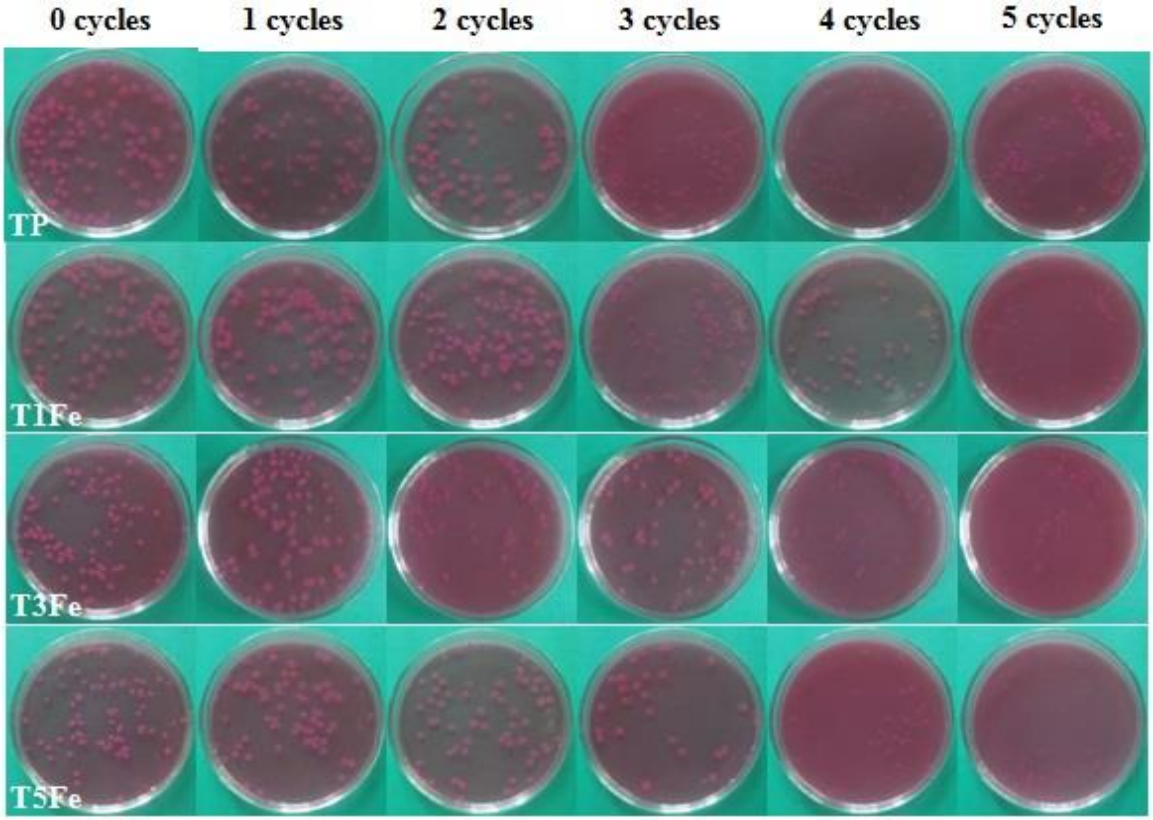

Fig. 7. Growth of E. coli on Macconkey agar plate observed after treatment with Fe^{3+} doped TiO_2 thin films under UV irradiation for 0-5 cycles

Fig. 7 shows the picture of *E. coli* on Macconkey plates observed after treatment for 0-5 cycles of Fe^{3+} doped TiO_2 thin films. From Fig. 6 and Fig. 7, the disinfection efficiency of TiO_2 doped Fe^{3+} with 5 mol% (T5Fe) thin films coated on glass fibers is 80% while those of the TiO_2 doped Fe^{3+} with 3 mol% (T3Fe), TiO_2 doped Fe^{3+} with 1 mol% (T1Fe) and undoped TiO_2 (TP) are 70, 55 and 36%, respectively, after treatment of water containing *E. coli* for 5 cycles. This result well correlates to that of photocatalytic reaction test. It is very obvious that the cell walls and cell membranes were damaged when microbial cells came into contact with Fe^{3+} doped TiO_2 thin

filmsbeing 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 [18].

4. Conclusion

In this work, Fe^{3+} 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 in order to from anatase phase. The quantitative examination of antibacterial activity indicates that the TiO_2 doped Fe with 5 mol%(T5Fe) thin films coated on glass fibers has greater *E. coli* inactivation under UV irradiation than other samples. This result well correlates to that of photocatalytic reaction on MB degradation. Experimental result clearly show that a disinfection efficiency of TiO_2 doped Fe^{3+} with 5 mol%thin films is 80% at a constant water flow rate of 90 ml/min and an initial concentration of *E. coli* about 10^3 CFU/ml. The TiO_2 doped Fe^{3+} with 5 mol%thin films coated on glass fibers are expect to be applied as an antibacterial photocatalyst for a water purification.

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