



Fabrication of Ag/TiO₂ Cotton Fabric to Enhance Photocatalytic Degradation of Anionic Dye

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 09-08-2020

Revised: 10-10-2020

Accepted: 01-11-2020

Key Words:

Ag/TiO₂
Photocatalysis
Anionic dye
Degradation

ABSTRACT

Ag/TiO₂ composite fabric was prepared by coprecipitation with TiCl₄ as a titanium source and AgNO₃ as a silver source. The samples were characterized by scanning electron microscope (SEM), thermogravimetric analyzer (TG) and Fourier transform infrared spectrometer (FTIR). The photocatalytic activity of synthetic fabrics was measured by the degradation of anion dyes under ultraviolet light. The effects of silver loading concentration, fabric area, initial concentration, and photocatalytic time on photocatalytic activity were investigated. The experimental results showed that the degradation rate of Ag/TiO₂ composite fabric on anion dyes could reach 70.76% in 50 minutes, indicating that the prepared Ag/TiO₂ composite fabrics had high photocatalytic activity.

INTRODUCTION

The rapid development of the printing and dyeing industry has brought us a wealth of printing and dyeing products as well as pollution problems (Holkar et al. 2016, Anastasi et al. 2011). The research of efficient and economical sewage treatment technology has become a research hotspot. Traditional water treatment methods mainly include physicochemical methods and biological methods (Banks et al. 2020). However, these methods have several disadvantages such as low degradation efficiency and unsatisfactory effect, and cannot meet the increasingly strict wastewater discharge standards, which pose a serious threat to the water environment.

Photocatalytic technology, as a new green environmental protection technology, can oxidize and decompose organic molecules into carbon dioxide, water, and some inorganic small molecules under light irradiation (Lu & Zhao 2018). Because of its excellent photoactivity, chemical and thermal stability, and the ability to degrade toxic organic pollutants in water, TiO₂ has become one of the most promising environmental remediation materials (Riegel & Bolton 1995, Farbod & Khademalrasool 2011, Kaneco et al. 2006). It was widely used in wastewater treatment, organic degradation, air treatment, and other fields. However, the practical application of TiO₂ has been extremely limited. The wide bandgap (e.g.

= 3.2 eV) reduces the utilization rate of sunlight (Zhao et al. 2020, Habibi-Yang & Feizpoor 2019). Meanwhile, the recombination of electrons and holes that generate on the TiO₂ is unfavorable to the efficiency of the TiO₂ photocatalysts (Ma et al. 2020).

To overcome these shortcomings, a large number of studies have concentrated on the improvement of the photocatalytic efficiency and visible light utilization of TiO₂. At present, various strategies including noble metal deposition (Benz et al. 2020), semiconductor composite (Lv et al. 2014), metal or non-metal doping (Khan et al. 2017, Li et al. 2018), and load modification (Zhao et al. 2012) have been explored. Among them, noble metal (Pt, Ag, Au) deposition of TiO₂ significantly improves the electron capture efficiency, which is one of the most effective ways to improve its photocatalytic activities. Due to the large Fermi level between nano TiO₂ and noble metal, it is thermodynamically possible to transfer electrons brought by TiO₂ conduction to metallic particles, resulting in the formation of electron accumulation center on the surface of noble metal. This is a kind of photoelectron trap, which achieves a good separation of electrons and holes and greatly improves the photocatalytic activity of TiO₂ (Kulkarni et al. 2015). In this work, Ag was selected as the deposited noble metal. Considering the properties of easy doping, high electrical conductivity, and good light absorption ability, it is

one of the most suitable materials for industrial applications. What's more, there is a synergy between Ag and TiO₂ at room temperature. Working as an electron receiver, Ag helps to reduce the recombination rate of electron-hole pairs. Ag/TiO₂ materials can receive light energy in both ultraviolet and visible light, optimizing the utilization of solar energy. A large number of studies have shown that silver deposition can effectively improve the photocatalytic of TiO₂ (Zheng et al. 2019, Rana et al. 2016).

MATERIALS AND METHODS

Materials and Reagents

The titanium tetrachloride (TiCl₄, 99.5%), nitric acid (HNO₃, 65-68%), and absolute ethanol were purchased from Aladdin Industrial Corporation. The silver nitrate (AgNO₃) was obtained from Shanghai Fine Chemical Research Institute.

Preparation of Ag/TiO₂ Cotton Fabric

Add 2 g of TiCl₄ into 10 mL absolute ethanol, and mark it as solution A. Add AgNO₃ (0%, 2%, 5%, 8%, 10%, 15%) into 40 mL absolute ethanol and altering the pH level to 2, marking it as solution B. Soak the washed cotton cloth into B solution. Lastly, add solution A to B at a slow rate of about 2 sec per drop while constantly stirring the solution. After stirring for about 2 hours, wash the fabric with distilled water and dry it in the oven (60°C, 15 mins).

Characterization of Ag/TiO₂ Cotton Fabric

FTIR was used to detect the chemical groups of unmodified and Ag/TiO₂ cotton fabric in the wavelength range of 500-4000 cm⁻¹. We use TG to analyze the thermal performance and decomposition kinetics. The microstructure and morphology of the prepared fabric were analyzed by SEM.

Photocatalytic Activity of Ag/TiO₂ Cotton Fabric

The photocatalytic activity of Ag/TiO₂ fabric was evaluated by testing the degradation of anionic dye solution as a model pollutant by using UV light. The photocatalytic activity of the Ag/TiO₂ fabric area varies from 15 cm² to 35 cm². The effect of initial concentration on the photocatalytic activity of the dye solution varies from 5 mg.L⁻¹ to 25 mg.L⁻¹. The distance of the UV lamp was kept 15 cm above the dye solution. We use the ultraviolet-visible spectrophotometer to measure the absorbance of the solution every 5 minutes.

RESULTS AND DISCUSSION

Morphology of the Fabric

The morphology of the non-modified, pure TiO₂ and 15% Ag/TiO₂ fabric is shown in Fig. 1. The surface of the pure TiO₂ and 15% Ag/TiO₂ composite fabric looked uneven with particles attached, indicating that TiO₂ and Ag were successfully supported on the fabric. The surface agglomeration of

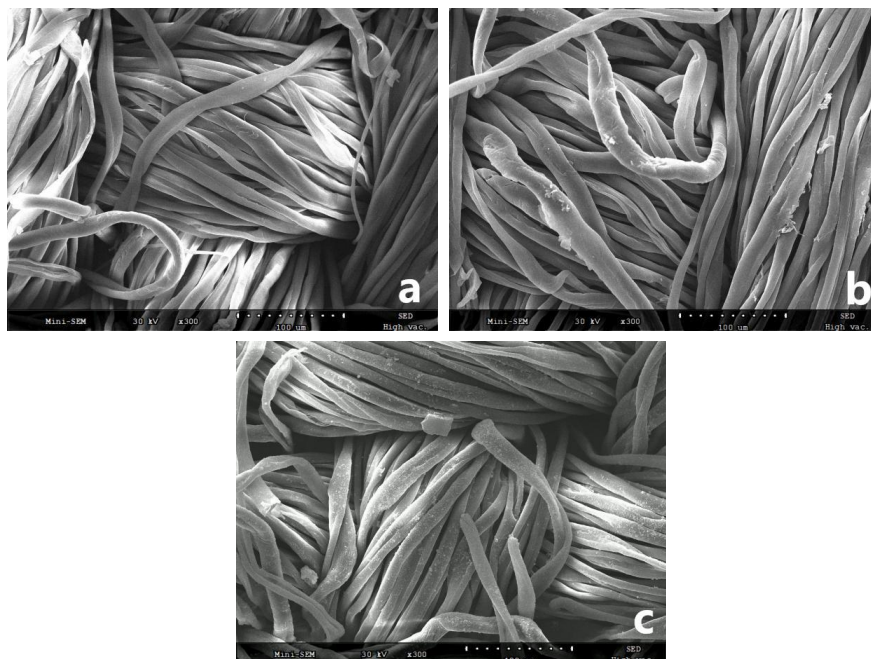


Fig. 1: The morphology of the non-modified (a), pure TiO₂ (b), 15% Ag/TiO₂ (c) fabric.

pure TiO₂ fabric is obvious, which may be because TiO₂ is attracted and then agglomerated by polar groups of cotton fabric. The surface of the Ag/TiO₂ composite fabric also has some pellets. However, compared with pure TiO₂, doping Ag reduced the particle agglomeration and the dispersion degree is higher.

Chemical Structure

In Fig. 2, no new absorption peak appeared in the infrared spectra of a, indicating that Ag-doped would not affect Ti-O bond, O-O bond and Ti-Ti bond in the TiO₂ structure. 3338 cm⁻¹ is the stretching vibration peak of O-H on the fabric surface, which confirmed the strong interaction of water molecules on the surface of TiO₂. The peak at 1644 cm⁻¹ is caused by the bending vibration of O-H and is due to the absorption of water molecules. The peaks in the range of 526-664 cm⁻¹ are caused by the stretching vibration and variable angle vibration of Ti-O. It indicated that Ag/TiO₂ indeed existed on the surface of the fabric. The peak near 2901 cm⁻¹ is C-H stretching vibration, and the peak at 1167, 1108, and 1050 cm⁻¹ is -C-O-C stretching vibration, which is in line with the characteristic peak of the infrared spectrum of cotton fiber.

Thermo Gravimetric Analysis

Fig. 3 shows the thermogravimetric characterizations of non-modified cotton and 15% Ag/TiO₂ fabric. The results show that the decomposition of 15% Ag/TiO₂ fabric is earlier

than unmodified fabric. At room temperature of 275°C, there is dehydration of physically adsorbed water and evaporation of waxes and other small molecules. Between 275°C and 355°C, both of them had a large mass loss, which is caused by the decomposition of fibrous macromolecules of organic matter. It is obvious that the residual value of the weight of unmodified cotton is lower than that of 15% Ag/TiO₂ fabric, which proved that the thermal stability of the modified fabric is improved.

Factors Influencing the Photocatalytic Activity

Effect of Doped Silver Content on Photocatalytic Degradation

Fig. 4 shows that under the same irradiation time, the photocatalytic efficiency of Ag/TiO₂ composite fabric with different silver loads is improved to different degrees compared with pure TiO₂ fabric. At the same time, Ag increases the content of hydroxyl and O₂, promoting the redox reaction. However, the composite of Ag and TiO₂ has a saturation value. The photocatalytic activity of the fabric peaked when the silver load was 5%. This may be because too much silver forms excessive contact sites. Ag itself constantly accepted electrons, however, it could not transmit electrons to O₂, and its ability to accept holes was constantly enhanced, leading to the combination of electrons and holes captured by Ag (Parastar et al. 2013). Other studies have shown that excessive Ag will cover the surface of TiO₂, resulting in the decrease

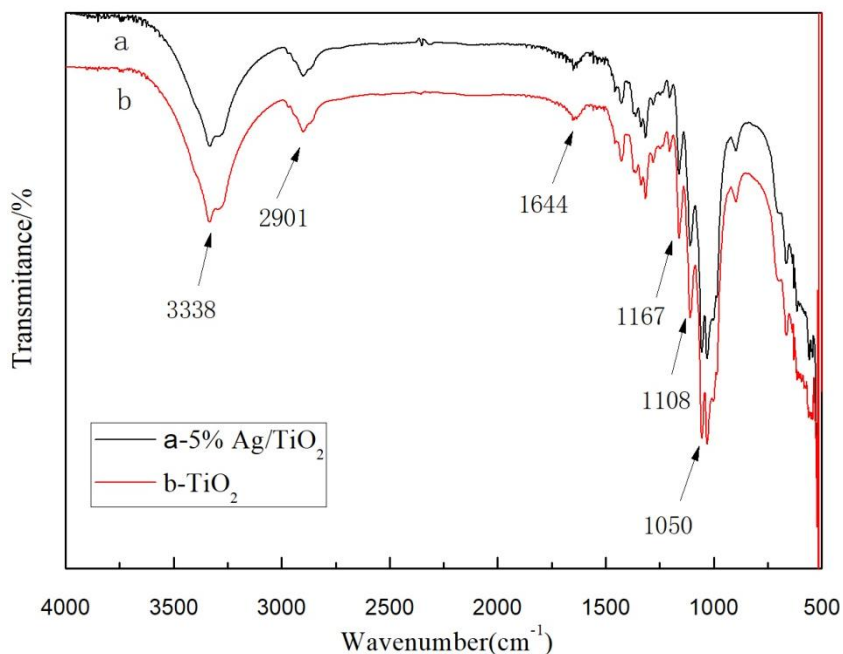


Fig. 2: FTIR spectra of pure TiO₂ and 5% Ag/TiO₂ fabric.

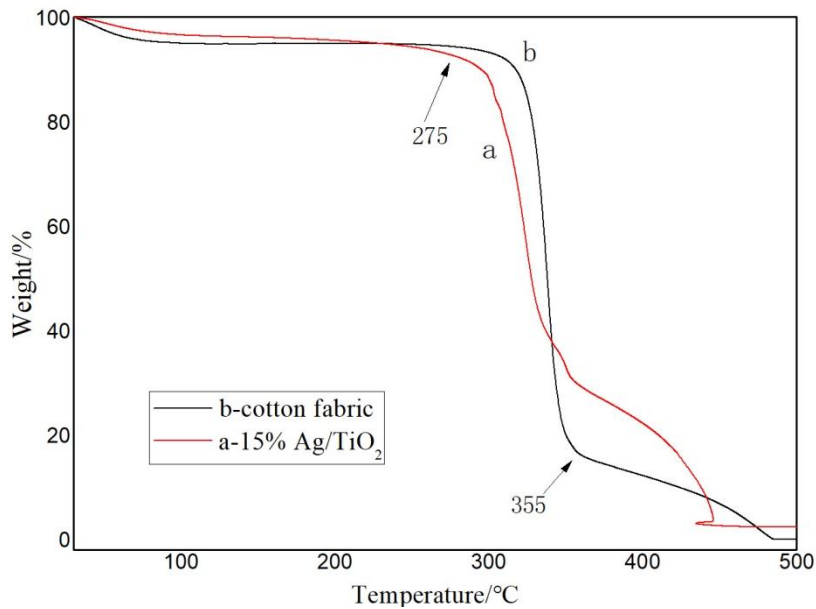


Fig. 3: Thermogravimetric characterizations of 15% Ag/TiO₂ cotton fabric (a) and cotton fabric (b).

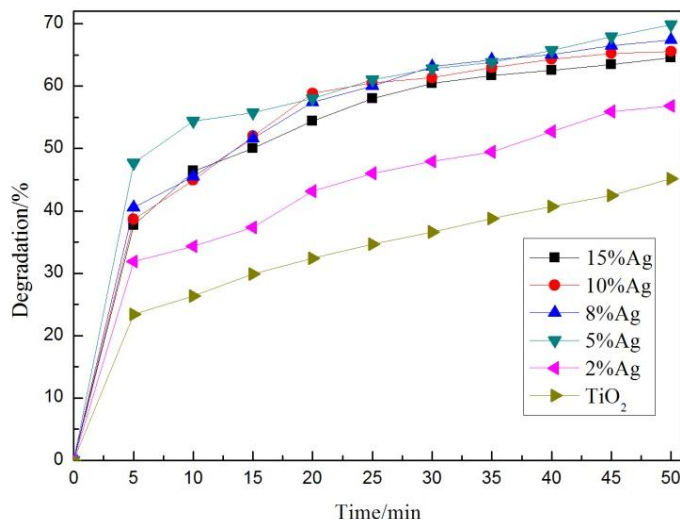


Fig. 4: Effect of doped silver content on photocatalytic degradation.

of hole concentration (Suwarnkar et al. 2014).

Effect of Initial Concentration of Dye on Photocatalytic Degradation

In Fig. 5, the influence of initial dye concentration on photocatalytic degradation is shown. As shown in this figure, when the dye concentration is lower than 15 mg.L⁻¹, the degradation rate increase with an increase in the initial concentration. This may be because the degradation process conformed to the first-order reaction kinetics in a certain range of dye

concentration. Dye molecules competitively adsorbed on the catalyst surface which accounted for the increase of reaction rate and degradation rate. When the concentration is higher than 15 mg.L⁻¹, the initial degradation rate slows down, and the final degradation rate decreases. Excessive dye molecules adsorbed on TiO₂, preventing the reaction of dye molecules with free radicals and electron holes.

Effect of Fabric Area on Photocatalytic Degradation

The effect of fabric area on anionic dye degradation under

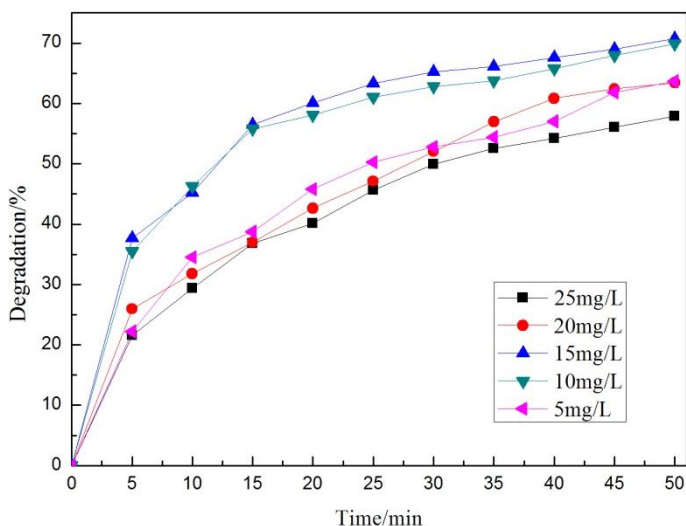


Fig. 5: Effect of initial concentration on photocatalytic degradation.

UV irradiation is shown in Fig. 6. When the fabric area is below 25 cm², the initial degradation rate increased rapidly with the increase of fabric area, and the degradation rate was also improved. The increase of fabric area was equivalent to the increase in the amount of catalyst and catalytic active centers. The result is the opposite when the fabric area is larger than 25 cm². This may be because when the fabric area is too large, the light transmittance is affected, the light absorption and the O₂ contact of the lower layer are reduced, resulting in the decrease of photocatalytic activity.

Effect of Irradiation Time on Photocatalytic Degradation

Fig. 7 shows the degradation of dye at different irradiation

times. With the increase of illumination time, the degradation degree of anionic dyes increased. And the degradation rate of 5% Ag/TiO₂ composite fabric was higher than that of pure TiO₂ fabric, indicating that Ag was an effective catalyst. When the UV light lasted for more than 50 minutes, the degradation rate of the two fabrics no longer significantly increased, indicating the photocatalytic reaction basically approached equilibrium.

Catalytic Mechanism Analysis

The possible catalytic mechanism is shown in Fig. 8. When Ag/TiO₂ is exposed to ultraviolet light ($h\nu > 3.2$ eV), electrons are stimulated and transfer from the valence band (VB) to the conduction band (CB), leaving holes in the valence

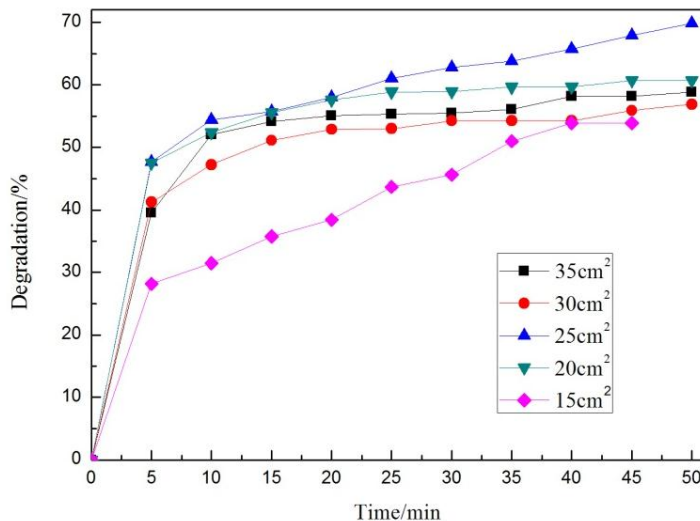


Fig. 6: Effect of fabric area on photocatalytic degradation.

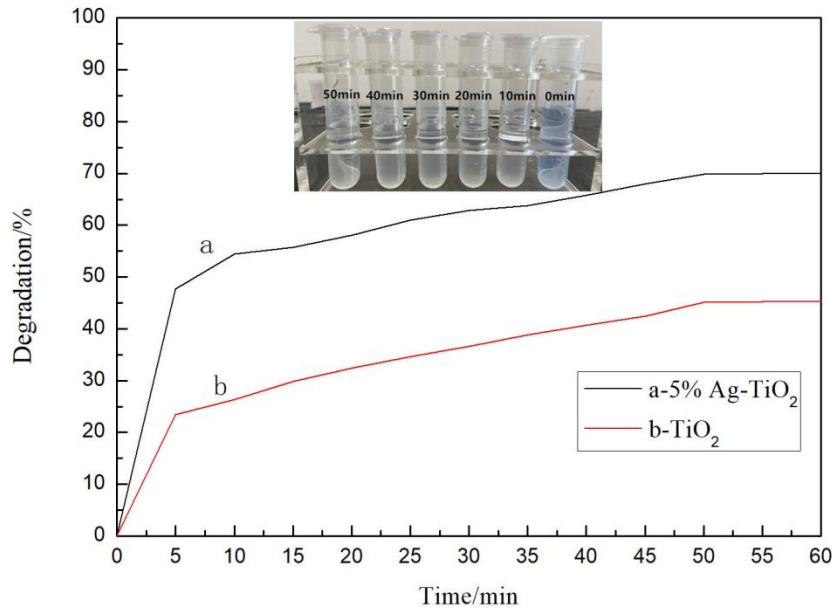


Fig. 7: Effect of irradiation time on photocatalytic degradation.

band. The silver then acts as an electron receiver, capturing electrons from TiO_2 and storing them on its surface. Ag can effectively attract and conduct electrons, and effectively prevent electrons from recombining with holes. The adsorbed oxygen molecules on the silver are quickly captured by electrons, reduced to form superoxide radical (O_2^-), and further react with H^+ to form hydroxyl radical ($\cdot\text{OH}$). On the other hand, the holes of Ag^+ can react with H_2O to form $\cdot\text{OH}$. The e^- and h^+ get more chances to react with O_2 and H_2O . $\cdot\text{OH}$ and O_2^- have high oxidation capacity, which can oxidize and degrade organic molecules to H_2O and CO_2 . The degradation reactions are shown in the following equations.

CONCLUSIONS

These experiments studied the photocatalytic degradation of anionic dye with Ag-doped TiO_2 cotton fabric (produced by coprecipitation method) under UV irradiation. The effects of Ag-doped, initial concentration, fabric area, and irradiation time were investigated. The experiments confirmed that Ag/ TiO_2 was successfully doped on cotton fabric and the photocatalytic property of the modified fabric was improved. In this study, results showed that the optimal silver content doped on TiO_2 was 5%, the fabric area was 25 cm^2 , the initial concentration was $15 \text{ mg}\cdot\text{L}^{-1}$, and the optimal irradiation time

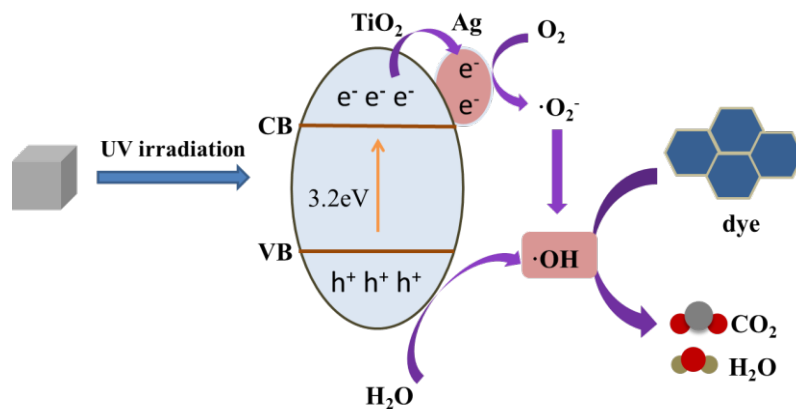


Fig. 8: Catalytic mechanism of Ag/ TiO_2 .

was 50 mins. Under the best conditions, the degradation rate could reach 70.76%.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (Grant No. 51703130), and the International Science and Technology Cooperation Project of Shaoxing University (Grant No. 2019LGGH1004).

REFERENCES

- Anastasi, A., Parato, B., Spina, F., Tigini, V., Prigione, V. and Varse, G.C. 2011. Decolourisation and detoxification in the fungal treatment of textile wastewaters from dyeing processes. *N. Biotechnol.*, 29(1): 38-45.
- Banks, D., Jun, B.M., Heo, J., Her, N., Park, C.M. and Yoon, Y. 2020. Selected advanced water treatment technologies for perfluoroalkyl and polyfluoroalkyl substances: A review. *Sep. Purif. Technol.*, 231: 115929
- Benz, D., Felter, K.M., Köser, J., Thöming, J., Mul, G. and Grozema, F.C. 2020. Assessing the role of Pt clusters on TiO₂ (P25) on the photocatalytic degradation of Acid Blue 9 and Rhodamine B. *J. Phys. Chem.*, 124(15): 8269-8278.
- Farbod, M. and Khademalrasool, M. 2011. Synthesis of TiO₂ nanoparticles by a combined sol-gel ball milling method and investigation of nanoparticle size effect on their photocatalytic activities. *Powder Technol.*, 214(3): 344-348.
- Habibi-Yangjeh, A. and Feizpoor, S. 2019. Combination of NiWO₄ and polyaniline with TiO₂: Fabrication of ternary photocatalysts with highly visible-light-induced photocatalytic performances. *J. Iran. Chem. Soc.*, 17(2): 351-365.
- Holkar, C.R., Jadhav, A.J., Pinjari, D.V., Mahamuni, N.M. and Pandit A.B. 2016. A critical review on textile wastewater treatments: possible approaches. *J Environ. Manag.*, 182: 351-366.
- Kaneco, S., Katsumata, H., Suzuki, T. and Ohta, K. 2006. Titanium dioxide mediated photocatalytic degradation of dibutyl phthalate in aqueous solution-kinetics, mineralization, and reaction mechanism. *Chem. Eng. J.*, 125(1): 59-66.
- Khan, M.I., Bhatti, K.A., Qindeel, R., Fazale, A., Naeemur, R. and Alonizan, N. 2017. Sol-gel deposition and characterization of multilayer 2% Cu doped TiO₂ nanostructured thin films. *J. Mater. Sci. - Mater. Elect.*, 28(13): 9471-9477.
- Kulkarni, R.M., Malladi, R.S., Hanagadakar, M.S., Doddamani, M.R. and Bhat, U.K. 2015. Ag-TiO₂ nanoparticles for photocatalytic degradation of lomefloxacin. *Desal. Water Treat.*, 57(34): 16111-16118.
- Li, X., Wu, Y., Shen, Y., Sun, Y., Yang, Y. and Xie, A. 2018. A novel bifunctional Ni-doped TiO₂ inverse opal with enhanced SERS performance and excellent photocatalytic activity. *Appl. Surf. Sci.*, 427: 739-744.
- Lu, Y. and Zhao, P., 2018. Preparation of ZnO Nano-photocatalysts and their performance on photocatalytic degradation of coking wastewater. *Nat. Environ. Pollut. Technol.*, 17(3): 953-956.
- Lv, J., Su, L., Wang, H., Liu, L., Xu, G. and Wang, D. 2014. Enhanced visible-light photocatalytic activity of TiO₂ nanotube arrays modified with CdSe nanoparticles by electrodeposition method. *Surf. Coat. Technol.*, 242: 20-28.
- Ma, H., Zheng, W., Yan, X., Li, S., Zhang, K. and Liu, G. 2020. Polydopamine-induced fabrication of Ag-TiO₂ hollow nanospheres and their application in visible-light photocatalysis. *Coll. Surf. A- Physicochem. Eng. Asp.*, 586.
- Parastar, S., Nasser, S., Borji, S.H., Fazlzadeh, M., Mahvi, A.H. and Javadi, A.H. 2013. Application of Ag-doped TiO₂ nanoparticle prepared by photodeposition method for nitrate photocatalytic removal from aqueous solutions. *Desal. Water Treat.*, 51(37-39): 7137-7144.
- Rana, M., Hao, B., Mu, L., Chen, L. and Ma, P.C. 2016. Development of multi-functional cotton fabrics with Ag/AgBr-TiO₂ nanocomposite coating. *Comp. Sci. Technol.*, 122: 104-112.
- Riegel, G. and Bolton, J.R. 1995. Photocatalytic efficiency variability in TiO₂ particles. *J. Phys. Chem.*, 99(12): 4215-4224.
- Suwarnkar, M.B., Dhabbe, R.S., Kadam, A.N. and Garadkar, K.M. 2014. Enhanced photocatalytic activity of Ag-doped TiO₂ nanoparticles synthesized by a microwave-assisted method. *Ceramics International*, 40(4): 5489-5496.
- Zhao, H., Su, F., Fan, X., Yu, H., Wu, D. and Quan, X. 2012. Graphene-TiO₂ composite photocatalyst with enhanced photocatalytic performance. *Chinese J. Catal.*, 33(4-6): 777-782.
- Zhao, L.N., Jia, Y.H., You, H., Wang, S.T. and Fu, L. 2020. Photocatalytic performance and application outlook of 3D TiO₂/titanium mesh modified by GO-Ag joined-deposition. *Catal. Today*, 340: 106-114.
- Zheng, X., Zhang, D., Gao, Y., Wu, Y., Liu, Q. and Zhu, X. 2019. Syntheses and characterization of cubic Ag/TiO₂ nanocomposites for the photocatalytic degradation of methyl orange in aqueous solutions. *Inorg. Chem. Comm.*, 110.