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Photocatalytic Decoloration of Methyl Orange by TiO_2 in Slurry

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Abstract

The problem of water depollution is gaining importance, especially as regulatory standards concerning drinking water are increasingly strict. The different industries (textile industries) generate chemically stable pollutants such as methyl orange which make their degradation difficult. It is therefore necessary to find new, more effective techniques for the treatment of these discharges. Among the different solutions proposed to deal with this problem, we find advanced oxidation processes (POAs) which are clean and promising technologies in the field of wastewater depollution. In this regard, heterogeneous photocatalysis was used in an aqueous suspension of titanium oxide (TiO_2) using a ultraviolet (UV) lamp as artificial radiation. The objective of this work is to study the influence of some operating parameters such as: the catalyst mass, the initial pollutant concentration, the volume of the solution and the pH of the solution, were examined. The results obtained showed that this photocatalyst made it possible to degrade 99.85% of the initial concentration of methyl orange (10 ppm), after 240 min of irradiation with an optimal mass of 0.50 g of TiO_2 for a volume of 200 mL of methyl orange solution at pH = 3.0.

Keywords

Depollution, Methyl Orange, TiO_2, Slurry

1. Introduction

Water, the source of life, represents the essential raw material for our planet. Consumption of this resource has increased considerably in recent decades due to population growth, industrialization, the intensification of agriculture and changes in consumption patterns. In return, a sharp increase in the volumes of urban, agricultural, and industrial wastewater discharges has accompanied this development [1] [2]. Unfortunately, the medium for discharge of all these types of wastewaters is frequently the environment and particularly watercourses. The increase in anthropogenic activities and textile industries constitute a source of water pollution [3] [4]. This pollution by chemicals is a real health problem for humans and their environment. Simple and inexpensive solutions are therefore strongly required. Among them, we have advanced oxidation processes [5]-[7] which have already shown their potential in the treatment of persistent pollutants [8]. They are essentially based on the production of HO° hydroxyl radicals which are very powerful oxidants able of oxidizing and mineralizing all kinds of organic pollutants [9] [10]. One of these oxidation processes is heterogeneous photocatalysis [11] which is based on the excitation by light (natural or artificial) of a semi-conductor (photocatalyst) such as titanium dioxide (TiO_2) [12] [13] which generates radical oxidants on its surface. Methyl orange is taken as the target molecule in this work because it has been the subject of studies [14]-[16]. It is used in several sectors of activity such as chemistry, pharmacology, medicine, biology and especially in the textile industry. The abusive use of this substance has harmful consequences on human health (acute inhalation toxicity) and the environment (fauna and flora). This work aims to treat water contaminated by methyl orange with titanium dioxide in suspension under UV radiation. To do this, we have studied the influence of certain physicochemical parameters such as the pH of the solution to be treated, the initial concentration of methyl orange, the volume of the solution and the quantity of TiO_2.

2. Material and Methods

2.1. Reactants

All reagents used in this study have not previously undergone purification. Azo dye methyl orange (orange acid 52) or helianthin ($C_{14}H_{14}N_3NaO_3S$; 99%) (**Figure 1**) was supplied by the company SHARLAU. Its peak absorption wavelength is $\lambda_{max} = 465$ nm [16]. Sodium hydroxide (0.1 N) and hydrochloric acid (0.1 N) respectively supplied by the SHARLAU and CARLOERBA companies were used to adjust the pH of the solution using a HANNA Instruments brand pH-meter. Crystalline powder titanium dioxide (TiO_2 P25; average size 20 nm, purity 97%, surface area 50 $m^2 \cdot g^{-1}$ and 80% anatase, 20% rutile) was supplied by the company SHARLAU. Distilled water was used to prepare the solutions.

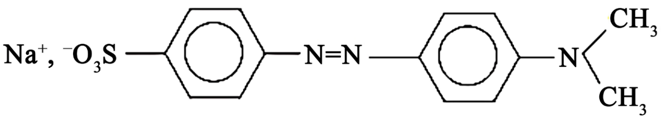

Figure 1. Structure formula of methyl orange.

2.2. Photocatalytic Device

All experiments were carried out at room temperature in a glass beaker containing the solution of methyl orange (from 10 to 30 mg·L^{-1}) and titanium dioxide (from 0.3 to 1.0 g) in slurry. The solutions, whose volumes varied from 300 to 900 mL with pH ranging from 3.0 to 11.0, were irradiated under four "WAN YUE, 20 W" fluorescent type UV-A lamps positioned horizontally 40 cm above the housing. Magnetic stirring is triggered by a magnetic bar throughout the photochemical reactions to ensure the homogeneity of the irradiated solutions in the reactor. The device is enclosed in a black enclosure to allow proper irradiation of the reaction medium (**Figure 2**).

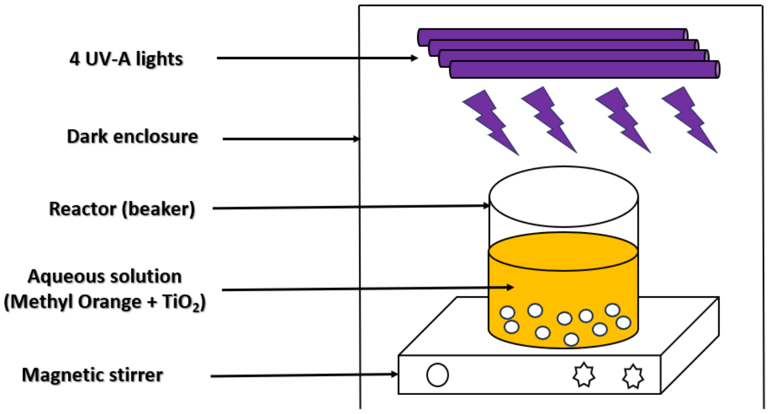

Figure 2. Simplified schematic of the photocatalytic device.

2.3. Photocatalytic Tests

The adsorption phase in the dark is carried out for 30 minutes to reach the state of equilibrium between the dye molecules and the TiO_2 photocatalyst in suspension. After this phase, the lamps are turned on and the timer is started. It is the instant t = 0 min. At regular time intervals, 5 mL of the solution is taken with a syringe, then filtered using a 0.2 μm millipore filter to separate the liquid and solid phases. The samples are analyzed using a WFJ-762 UV-visible spectrophotometer (λ_{max} = 465 nm). The influence of parameters such as the mass of TiO_2, the initial concentration of methyl orange, the volume of the solution and its pH were highlighted. Considering that the degradation follows a pseudo-first order kinetics, the apparent kinetic constant k_{app} was calculated according to the following equations:

$$r = -\frac{dC}{dt} = k_{app}C \tag{1}$$

$$k_{app}t = \ln\left(\frac{C_o}{C}\right) \tag{2}$$

with r: reaction rate; C: residual concentration of the pollutant; C_o: initial concentration of the pollutant; k_{app}: apparent kinetic constant and t: UV irradiation time.

The rate of removal of the dye by photocatalytic decolorization was calculated using the following equation:

$$T(\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{3}$$

with T(%): rate of removal of the dye; C_0: initial concentration of the dye; C_t: concentration of the dye at time t.

3. Results and Discussion

3.1. Influence of TiO_2 Dosage

To determine the optimal quantity of photocatalyst for which the reaction speed is the greatest, we studied the effect of its mass in a volume of 300 mL of solution containing the dye. This operating parameter is important because the quantity of the photocatalyst depends on the geometric shape of the static flow reactor. The results showed that the discoloration of methyl orange increases with increasing TiO_2 concentration from 0.30 g (1.0 g·L^{-1}) up to 0.50 g (1.6 g·L^{-1}) and then decreases (**Figure 3**). This observation can be explained by the availability of active sites on the TiO_2 surface and the possibility of penetration of UV light over the entire surface of the photocatalyst in the solution. This causes an increase in the number of $OH^{\bullet}$ radicals which can participate in the degradation of methyl orange [17]. On the other hand, beyond 0.5 g (1.6 g·L^{-1}) of TiO_2, the solution becomes cloudy, and a screening effect occurs, thus preventing the diffusion of UV light in the solution. This causes a reduction in the efficiency of the photocatalytic degradation process of the pollutant. The optimal value for which the dye bleaching rate is maximum is 0.50 g (1.6 g·L^{-1}) of TiO_2. This value makes it possible to achieve a degradation rate of around 98.73% and an apparent speed constant of 0.0117 min^{-1} (**Table 1**) after four (4) hours of UV-A irradiation. In a static luminous flux photoreactor, Guettaï and Air Amar studied the influence of the quantity of TiO_2 P25 (from 0.2 to 1.6 g·L^{-1}) in the presence of methyl orange. The authors showed that at 0.8 g·L^{-1}, the reaction speed was the greatest [18].

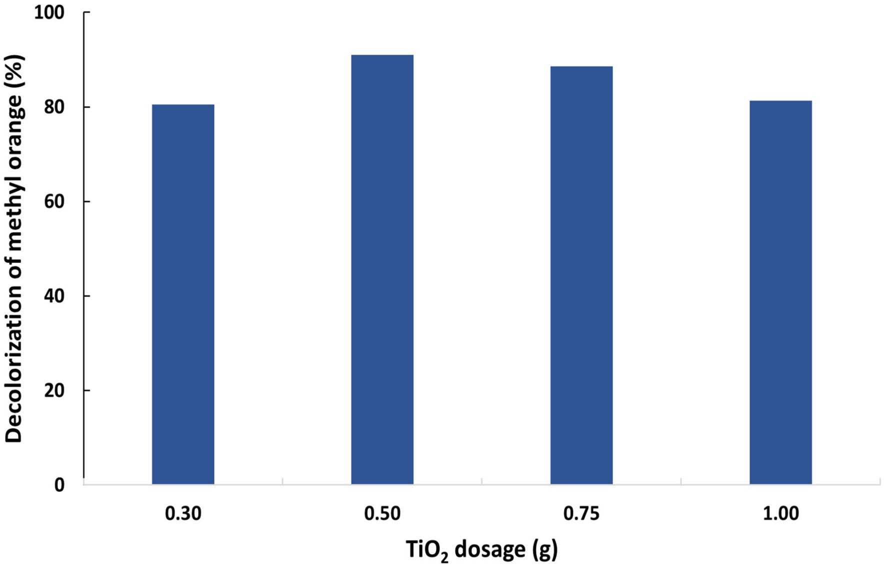

Figure 3. Influence of the TiO_2 dosage: 0.30; 0.50; 0.75 and 1.00 g; C_o = 10 mg·L^{-1}; pH = 6.4; V = 300 mL; UV-A irradiation; batch mode.

Table 1. Values of apparent rate constants (k_{app}), half-life times ($t_{1/2}$) and decolorization rate of methyl orange with different dosages of TiO_2.

TiO_2 dosage (g)	k_{app} (min^{-1})/R^2	$t_{1/2}$ (min)	Decolorization of Methyl orange (T%)
0.30	0.0034/0.975	204	63.80
0.50	0.0117/0.952	59	98.73
0.75	0.0076/0.956	91	91.11
1.00	0.0046/0.971	151	73.86

3.2. Influence of the Methyl Orange's Initial Concentration

The concentration of dyes in industrial liquid waste varies with the seasons and modes of use. To this end, we carried out a series of methyl orange degradation tests, considering the optimal operating conditions. The influence of the initial concentration of methyl orange on its photodegradation was studied for a TiO_2 mass of 0.50 g. **Figure 4** shows that the discoloration of methyl orange decreases as its concentration increases from 10 to 30 mg·L^{-1}. In other words, the degradation of methyl orange is faster at lower concentrations [19]. Beyond this concentration, the degradation kinetics are greatly reduced. The latter has generally been interpreted in terms of the increasing importance of the screening effect of the molecules of the pollutant making the photons unavailable for the TiO_2 or by a strong adsorption of the dye which then covers a considerable part of the active sites thus reducing the speed of formation of hydroxide radicals [20]. **Table 2** shows that the apparent rate constants k_{app} and the dye decolorization rate decrease after four (4) hours of treatment, respectively from 0.0110 min^{-1} to 0.0026 min^{-1} and 97.5% to 48.00% when the dye concentration increases [21].

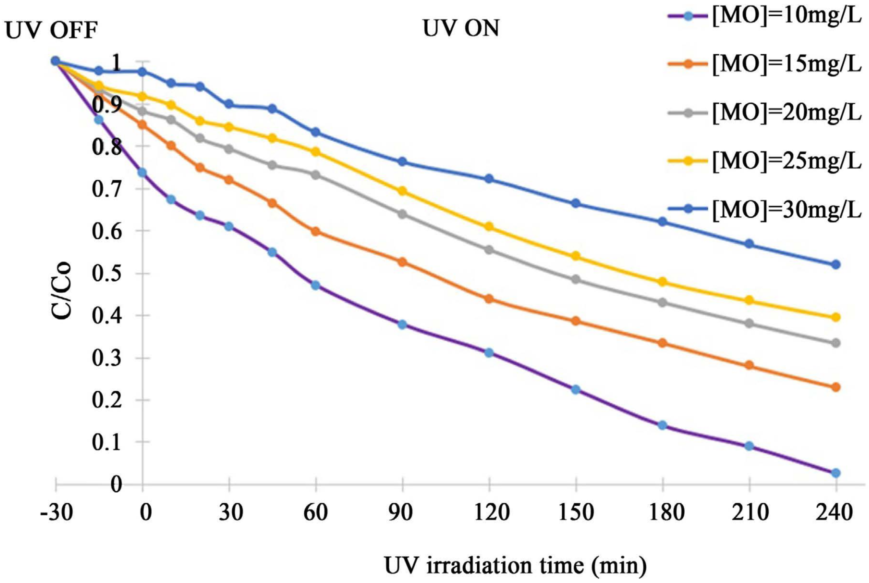

Figure 4. Influence of the methyl orange's initial concentration: 10; 15; 20; 25; 30 mg/L; m (TiO_2) = 0.50 g, pH = 6.4, V = 300 mL; UV irradiation; batch mode.

Table 2. Values of apparent rate constants (k_{app}), half-life times ($t_{1/2}$) and decolorization rate of methyl orange with different initial concentrations of the dye.

C_o (mg/L)	k_{app} (min^{-1})/R^2	$t_{1/2}$ (min)	Decolorization of Methyl orange (T%)
10	0.0110/0.956	63	97.50
15	0.0053/0.969	131	76.00
20	0.0040/0.966	173	66.00
25	0.0035/0.988	198	56.00
30	0.0026/0.990	266	48.00

3.3. Influence the Solution's Volume

With a view to developing a water depollution system on a larger scale, it is necessary to evaluate our process with larger volumes of effluent to see its influence on the transfer of matter. The experiments carried out correspond to volumes of 300 mL, 500 mL, 700 mL and 900 mL. **Figure 5** shows that volume has an influence on the degradation of the pollutant methyl orange. We note that an increase in volume contributes to reducing the rate of degradation of the pollutant with the optimal mass of the catalyst. This is explained by an increase in the quantity of methyl orange molecules around the TiO_2. These molecules form a screen to incident UV light. This results in a reduction in the production of radicals in the reaction medium. According to **Table 3**, the best degradation rate of 82.48% is obtained with a low volume (300 mL). During the photodegradation of Paraquat by N, S-doped TiO_2, Zahedi and co-workers have varied the volume of the solution from 600 mL to 150 mL and they arrived at the same conclusions as us. The authors showed that the degradation rate of Paraquat decreased from 92.38% to 25.00% when the volume increased after 8 h of visible irradiation in recirculation in the photocatalytic system [22].

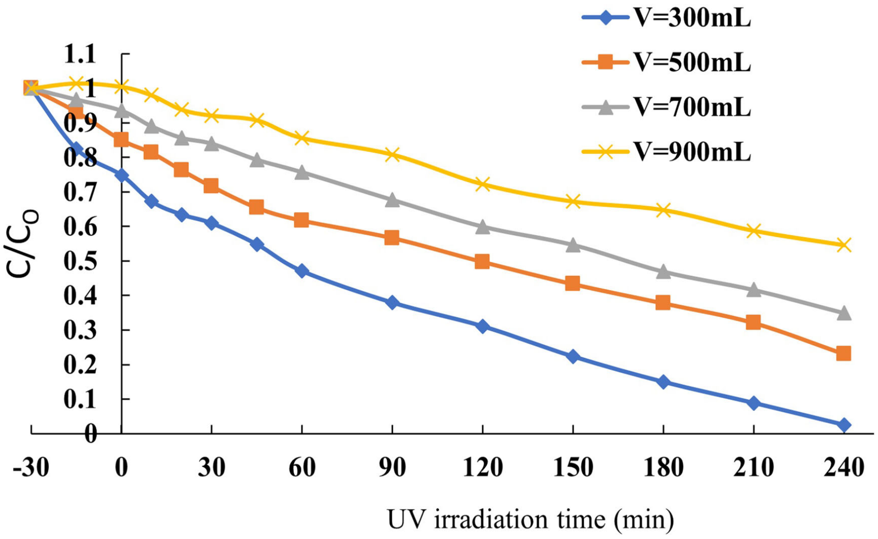

Figure 5. Influence of the volume of the solution: 300; 500; 700 and 900 mL; m (TiO_2) = 0.5 g; C_o = 10 mg/L; pH = 6.4; UV irradiation; batch mode.

Table 3. Values of apparent rate constants (k_{app}), half-life times ($t_{1/2}$) and decolorization rate of methyl orange with different initial volumes of the dye.

Volume (mL)	k_{app} (min^{-1})/R^2	$t_{1/2}$ (min)	Decolorization of Methyl orange (T%)
300	0.0106/0.95	65	82.48
500	0.0049/0.97	141	76.91
700	0.0039/0.99	178	65.03
900	0.0026/0.98	266	45.40

3.4. Influence of pH

The effect of pH on the removal of methyl orange was examined in five pH media: 3.0; 5.0; 6.4; 9.0 and 11.0. The results obtained (**Figure 6**) show that at pH = 3.0 the disappearance of methyl orange is faster. This result can be explained by the force of attraction between the dye and the surface charge of the photocatalyst increasing the probability of encounter with the photocatalyst. In a basic medium (pH = 9.0; 11.0), we observe a drop-in photocatalytic activity, this is due to repulsive interactions between the dye and the surface charge of the photocatalyst thus reducing the probability of encounter with the photocatalyst [23]. The apparent rate constant decreases from 0.0171 to 0.0034 min^{-1} as the pH increases from 3.0 to 11.0 (**Table 4**). Optimal photodegradation is found at pH = 3.0 during 240 min of UV irradiation [24]. In alkaline solution, the methyl orange molecules are negatively charged, and their adsorption is also expected to be affected by an increase in the density of TiO_2 groups on the semiconductor surface. Thus, due to coulombic repulsion, the dye is scarcely adsorbed. At high pH values the hydroxyl radicals are so rapidly scavenged that they do not have the opportunity to react with dyes. For the above reasons the photocatalytic activity of anionic dyes (mainly sulphonated dyes) reached a maximum in acidic conditions followed by a decrease in basic conditions [18].

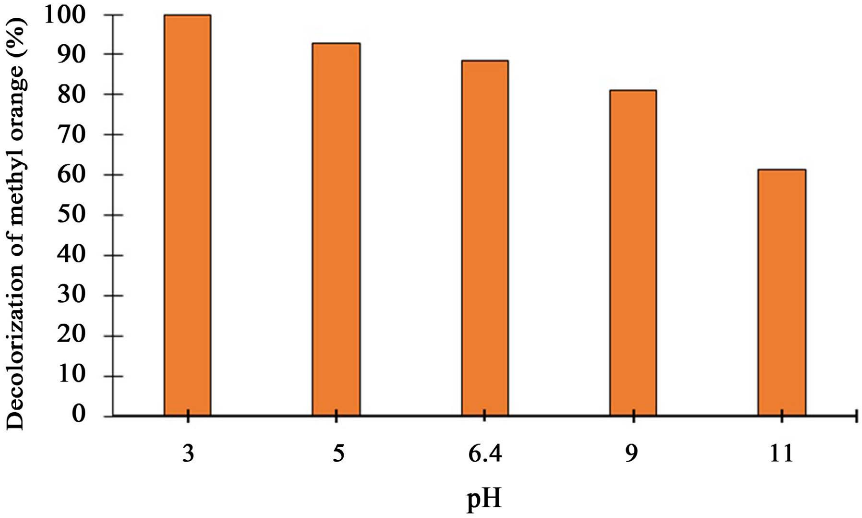

Figure 6. Influence du pH: 3.0; 5.0; 6.4; 09; 11.0; m (TiO_2) = 0.50 g; C_o = 10 mg/L; V= 300 mL; Irradiation UV; batch mode.

Table 4. Values of apparent rate constants (k_{app}), half-life times ($t_{1/2}$) and decolorization rate of methyl orange with different initial pH of the dye.

pH	k_{app} (min^{-1})/R^2	$t_{1/2}$ (min)	Decolorization of Methyl orange (T%)
3.0	0.0171/0.92	41	99.85
5.0	0.0083/0.97	82	92.79
6.4	0.0071/0.89	98	88.50
9.0	0.0055/0.98	126	81.17
11.0	0.0034/0.99	203	61.00

4. Conclusion

This study falls within the general framework of wastewater decontamination. Its objective was to study the degradation by heterogeneous photocatalysis (TiO_2/UV) of methyl orange, which is a synthetic dye present in effluents from textile industries. The degradation of the dye is carried out by the oxidizing action of hydroxyl radicals (OH°) produced in the medium to be treated. These radicals are capable of degrading almost all persistent organic pollutants because of their very high oxidizing power, their reactivity, and their non-selectivity towards organic substances. To carry out this work, we used the suspended TiO_2 photocatalyst and an artificial UV irradiation source by varying some physicochemical parameters. The results showed that the adsorption phenomenon of methyl orange (without irradiation) took place on the TiO_2 catalyst before photodegradation. The investigated experimental parameters significantly affect the photocatalytic decolorization of methyl orange. Thus, working under optimal experimental conditions: m (TiO_2) = 0.5 g (1.67 g. L^{-1}); pH = 3.0; [MO]o = 10 mg. L^{-1} and V = 300 mL, we recorded an oxidation of methyl orange of 99.85% during four (4) hours of treatment. The kinetic study allowed us to determine the apparent rate constant which is 0.0171 min^{-1}, or a half-reaction time $t_{1/2}$ = 41 min. This work could be continued by immobilizing TiO_2 onto supports at lower cost to treat liquid effluents from the textile industries.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] El-Mekkawi, D.M., Abdelwahab, N.A., Mohamed, W.A.A., Taha, N.A. and Abdel-Mottaleb, M.S.A. (2020) Solar Photocatalytic Treatment of Industrial Wastewater Utilizing Recycled Polymeric Disposals as TiO_2 Supports. *Journal of Cleaner Production*, **249**, Article ID: 119430. https://doi.org/10.1016/j.jclepro.2019.119430

[2] Perrich, J.R. (2018) Activated Carbon Adsorption for Wastewater Treatment. CRC Press.

[3] Gandini, D., Comninellis, C., Tahar, N.B. and Savall, A. (1998) Électrodépollution: Traitement électrochimique des eaux résiduaires chargées en matières organiques toxiques. *Actualité Chimique*, **10**, 68-73.

[4] Kouamé, N.A., Robert, D., Keller, V., Keller, N., Pham, C. and Nguyen, P. (2012)

TiO_2/β-sic Foam-Structured Photoreactor for Continuous Wastewater Treatment. *Environmental Science and Pollution Research*, **19**, 3727-3734. https://doi.org/10.1007/s11356-011-0719-6

[5] Zhang, T., Liu, Y., Rao, Y., Li, X., Yuan, D., Tang, S., et al. (2020) Enhanced Photocatalytic Activity of TiO_2 with Acetylene Black and Persulfate for Degradation of Tetracycline Hydrochloride under Visible Light. *Chemical Engineering Journal*, **384**, Article ID: 123350. https://doi.org/10.1016/j.cej.2019.123350

[6] Zazou, H. (2015) Dégradation de pesticides dans l'eau par les procédés d'oxydation avancée (POA). Paris Est.

[7] Deng, Y. and Zhao, R. (2015) Advanced Oxidation Processes (AOPs) in Wastewater Treatment. *Current Pollution Reports*, **1**, 167-176. https://doi.org/10.1007/s40726-015-0015-z

[8] Wang, T., Wang, Y., Liao, C., Cai, Y. and Jiang, G. (2009) Perspectives on the Inclusion of Perfluorooctane Sulfonate into the Stockholm Convention on Persistent Organic Pollutants. *Environmental Science & Technology*, **43**, 5171-5175. https://doi.org/10.1021/es900464a

[9] Asghar, A., Abdul Raman, A.A. and Wan Daud, W.M.A. (2015) Advanced Oxidation Processes for *In-Situ* Production of Hydrogen Peroxide/Hydroxyl Radical for Textile Wastewater Treatment: A Review. *Journal of Cleaner Production*, **87**, 826-838. https://doi.org/10.1016/j.jclepro.2014.09.010

[10] Ismail, L., Rifai, A., Ferronato, C., Fine, L., Jaber, F. and Chovelon, J. (2016) Towards a Better Understanding of the Reactive Species Involved in the Photocatalytic Degradation of Sulfaclozine. *Applied Catalysis B*: *Environmental*, **185**, 88-99. https://doi.org/10.1016/j.apcatb.2015.12.008

[11] Ibhadon, A. and Fitzpatrick, P. (2013) Heterogeneous Photocatalysis: Recent Advances and Applications. *Catalysts*, **3**, 189-218. https://doi.org/10.3390/catal3010189

[12] Christian M'Bra, I., Keller, N., Trokourey, A. and Robert, D. (2023) Photocatalytic Efficiency of Suspended and Immobilized TiO_2 P25 for Removing Myclobutanil, Penconazole and Their Commercial Formulations. *Photocatalysis*: *Research and Potential*, **1**, 1-10. https://doi.org/10.35534/prp.2023.10004

[13] Armaković, S.J., Uzelac, M.M. and Armaković, S. (2021) Application of TiO_2 Nanomaterials for Water Purification Based on Photocatalysis. *Book of Abstracts*, 7.

[14] Ramutshatsha-Makhwedzha, D., Mavhungu, A., Moropeng, M.L. and Mbaya, R. (2022) Activated Carbon Derived from Waste Orange and Lemon Peels for the Adsorption of Methyl Orange and Methylene Blue Dyes from Wastewater. *Heliyon*, **8**, e09930. https://doi.org/10.1016/j.heliyon.2022.e09930

[15] Gong, B., Wu, P., Yang, J., Peng, X., Deng, H. and Yin, G. (2021) Electrochemical and Photocatalytic Properties of Ru-Doped TiO_2 Nanostructures for Degradation of Methyl Orange Dye. *International Journal of Electrochemical Science*, **16**, Article ID: 21023. https://doi.org/10.20964/2021.02.18

[16] Oladipo, G.O., Akinlabi, A.K., Alayande, S.O., Msagati, T.A.M., Nyoni, H.H. and Ogunyinka, O.O. (2019) Synthesis, Characterization, and Photocatalytic Activity of Silver and Zinc Co-Doped TiO_2 Nanoparticle for Photodegradation of Methyl Orange Dye in Aqueous Solution. *Canadian Journal of Chemistry*, **97**, 642-650. https://doi.org/10.1139/cjc-2018-0308

[17] Daneshvar, N., Rasoulifard, M.H., Khataee, A.R. and Hosseinzadeh, F. (2007) Removal of C.I. Acid Orange 7 from Aqueous Solution by UV Irradiation in the Presence of ZnO Nanopowder. *Journal of Hazardous Materials*, **143**, 95-101. https://doi.org/10.1016/j.jhazmat.2006.08.072

[18] Guettaï, N. and Ait Amar, H. (2005) Photocatalytic Oxidation of Methyl Orange in Presence of Titanium Dioxide in Aqueous Suspension. Part I: Parametric Study. *Desalination*, **185**, 427-437. https://doi.org/10.1016/j.desal.2005.04.048

[19] Barka, N., Assabbane, A., Nounah, A., Albourine, A. and Ait-Ichou, Y. (2008) Dégradation Photocatalytique de Deux Colorants Séparés et en Mélange Binaire par TiO_2-Supporté. *Sciences & Technologie A*, No. 7, 9-16.

[20] Al-Qaradawi, S. and Salman, S.R. (2002) Photocatalytic Degradation of Methyl Orange as a Model Compound. *Journal of Photochemistry and Photobiology A*: *Chemistry*, **148**, 161-168. https://doi.org/10.1016/s1010-6030(02)00086-2

[21] M'Bra, I.C., Robert, D., Keller, N., Drogui, P. and Trokourey, A. (2020) Photocatalytic Degradation of Myclobutanil and Its Commercial Formulation with TiO_2 P25 in Slurry and TiO_2/β-Sic Foams. *Journal of Nanoscience and Nanotechnology*, **20**, 5938-5943. https://doi.org/10.1166/jnn.2020.18547

[22] Zahedi, F., Behpour, M., Ghoreishi, S.M. and Khalilian, H. (2015) Photocatalytic Degradation of Paraquat Herbicide in the Presence TiO_2 Nanostructure Thin Films under Visible and Sun Light Irradiation Using Continuous Flow Photoreactor. *Solar Energy*, **120**, 287-295. https://doi.org/10.1016/j.solener.2015.07.010

[23] Bouanimba, N., Laid, N., Zouaghi, R. and Sehili, T. (2015) Effect of Ph and Inorganic Salts on the Photocatalytic Decolorization of Methyl Orange in the Presence of TiO_2 P25 and PC500. *Desalination and Water Treatment*, **53**, 951-963. https://doi.org/10.1080/19443994.2013.848667

[24] Yang, H., Zhang, K., Shi, R., Li, X., Dong, X. and Yu, Y. (2006) Sol-Gel Synthesis of TiO_2 Nanoparticles and Photocatalytic Degradation of Methyl Orange in Aqueous TiO_2 Suspensions. *Journal of Alloys and Compounds*, **413**, 302-306. https://doi.org/10.1016/j.jallcom.2005.06.061