Investigating the Effect of UV Radiation Changes and Bed Temperature in Photocatalytic Destruction of Toluene in a Circular Fluid Bed Reactor

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ABSTRACT
Increase the system efficiency in photocatalytic systems is necessary for economic aspects. In this study, for photocatalytic destruction of toluene in a circular fluid bed or substrate reactor, the effect of UV radiation changes and bed temperature was investigated. The Efficiency of the photocatalytic system was studied in various conditions of relative humidity variables, UV intensity and bed temperature. This study showed by increasing the photocatalyst loading percentage of more than 20%wt., there is no significant change in the efficiency of toluene degradation. In a steady state of all other parameters, when the intensity of the UV radiation rises from 5 w/m^2 to 17 w/m^2, Toluene degradation efficiency also has an increasing trend. Also, we found that with increasing temperature, the efficiency of photocatalytic oxidation of toluene is increasing. The independent effect of each of the variables on the efficiency of toluene removal are interdependent and mutually influential, and in order to have the appropriate efficiency, all variables should be examined together in the appropriate conditions.

Keywords: Photocatalytic System, Toluene, UV Radiation, Temperature, Fluidized Bed Reactor

INTRODUCTION
Organic compounds escape arrived into the atmosphere from various sources, such as petrochemicals, refineries, oil refineries, natural gas processing plants, and automobile outputs [1]. Control and reduction of these compounds are important for maintaining human health and protecting the environment [2, 3]. Volatile organic compounds are divided into various groups such as ketones, alcohols, phenols, aromatic hydrocarbons, and aldehydes. Toluene is one of the aromatic compounds which is used in various industries as intermediates. Therefore, it is essential to use methods to control the contamination of volatile organic gases, especially toluene. So far, physical, chemical, and biological methods have been used to control volatile organic compounds [4]. One of the newest methods used is photocatalytic oxidation [5]. This method is based on the oxidation of volatile organic compounds and their conversion into low-risk products such as carbon dioxide and water [6], this is done by active radicals such as hydroxyl. Among the photocatalyst used in the studies, the photocatalytic oxidation process of titanium dioxide has become more prominent in terms of its specific characteristics, such as cheaper safety and chemical stability. Crystal anatase titanium dioxide has more photocatalytic activity, so in photocatalytic reactions, this crystalline form is used more [7]. The energy difference between the capacity layer and the crystalline anatase conduction layer is 3.2 electron volts. Thus, the UV waves with 388 nm or fewer wavelengths can activate the crystal anatase. Therefore, the UV radiation usage is an important factor in the photocatalytic oxidation reaction. Of course, the amount of beam utilization can also be partly related to the design and structure of the reactor. The fluid bed reactor is considered as one of the most effective schemes in terms of contact between reactants [8]. The strengths of this reactor can also be seen in the restriction's absence on mass and heat transfer. Therefore, the use of these reactors has received a lot of attention in the photocatalytic oxidation process of air pollutants [9]. In the forthcoming study, toluene photocatalytic degradation is investigated in a fluid bed reactor. The catalyst used in fixed bed reactors is fixed and non-moving in its place, while in the fluid bed reactor, the photocatalyst bed particles are easily fluidized and movable inside the reactor due to its small size, lightness and release. In the fluid bed reactors, relatively high gas flows can enter the reactor and provide effective contact between ultraviolet light photons, solid catalyst and reactive gases. For this purpose, Titanium Dioxide particles have been used on silica gel particles as photocatalyst. And the effects of parameters are studied, such as UV radiation intensity, reactor column temperature,

photocatalyst loading percentage and relative humidity on the photocatalytic oxidation of toluene.

MATERIALS AND METHODS

As shown in Fig. 1, the reactor is a circular fluid bed reactor. Which consists of a central cylinder made of quartz glass with an inner diameter of 40 mm and a height of 100 cm. A UV Lamp with a beam intensity of 5 w/m^2, a wavelength of 254 nm in the center of the cylinder and four UV-light intensive wavelengths of 3 w/m^2, a wavelength of 253 nm has been for better illumination around the central cylinder. In order to have a uniform flow into the reactor from a porous air distributor at the beginning of the bed inlet and a standard blow, the pump is used to provide a positive pressure for the required air. The method of required concentration of toluene as well as relative humidity is provided by passing air from impinger containing toluene and water. In this study, the toluene initial concentrations from 100 to 1000 ppm and the relative humidity logged in the system from 10 to 70 percent were investigated.

The efficiency of toluene removal is also calculated according to the following formula.

$$Toluene\ Conversion\ (\%) = \frac{(C_{in} - C_{out})}{C_{in}} \times 100$$

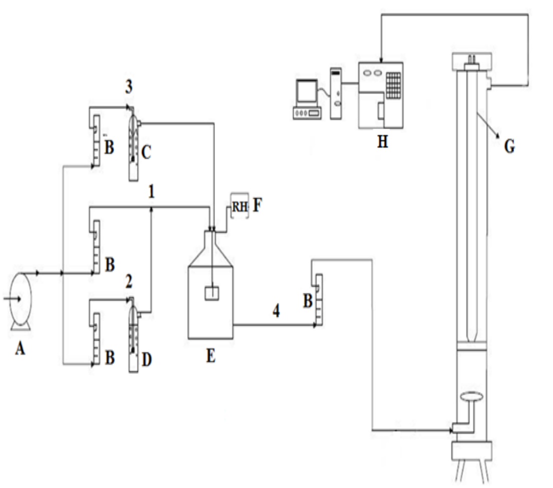

Fig. 1: Schematic diagram of the fluid bed reactor along with a system for providing the pollutant-specific concentration and relative humidity. Air Blower (A), Rotameter (B), Water Impinger (C), Toluene Impinger (D), Mixing Enclosure (E), Moisture Sensor (F), Fluid Bed Reactor (G), Gas Chromatography (H)

The photocatalyst used in this study is the titanium dioxide p-25 particles manufactured by the Degussa Corporation, coated with silica gel particles of 10 to 100 micrometers. Immersion has also been used to perform the coating process. The catalyst was placed in an electric furnace at $200^{\circ C}$ for 2 hours to allow the catalyst to be calcinated. The survey of Photocatalyst after coating was studied by scanning electronic microscopy (SEM).

RESULTS

According to Fig. 2, it is shown that titanium dioxide particles are deposited on silica gel particles ideally.

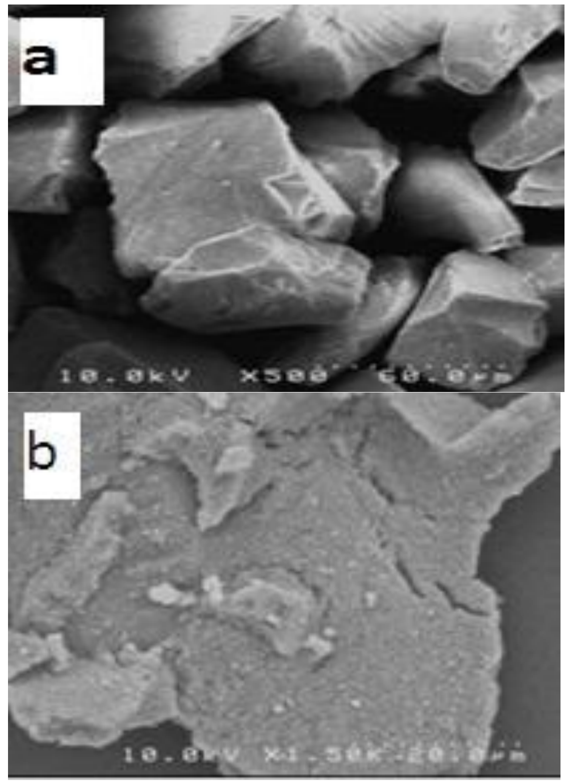

Fig. 2: Micrograph prepared by a scanning electron microscope from the silica gel bed (a) and catalyst TiO_2/SiO_2 (b)

As shown in Fig. 3, under the same conditions of relative humidity, the intensity of the UV-light in the same concentrations of toluene, when the loading percentage of the photocatalyst is 20%wt., Toluene degradation efficiency is more than photocatalytic with lower wt.%. It is also clear that by increasing the photocatalyst loading percentage of more than 20%wt., there is no significant change in the efficiency of toluene degradation. This means that up to 20%wt., the UV intensity is the optimal mode for activating the photocatalyst. However, by increasing the photocatalyst loading percentage to more than 20%wt., although is increase the %wt. of the photocatalyst. However, due to the constant intensity of UV radiation, it should not be expected that there would be a significant increase in the rate of toluene degradation.

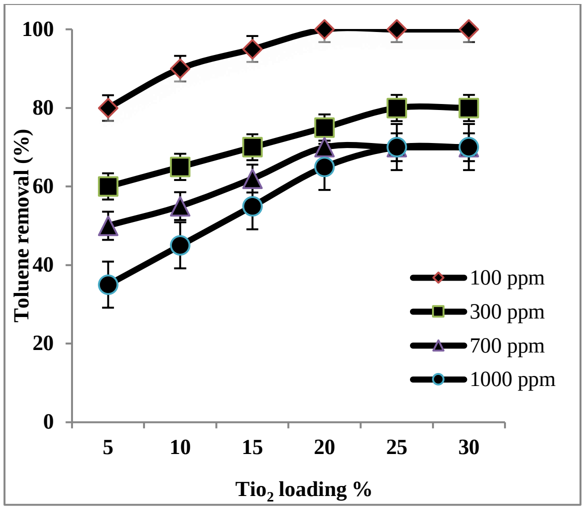

Fig. 3: Toluene photocatalytic oxidation efficiency using TiO_2 / SiO_2 catalyst (catalyst; 5 to 30 wt.%, toluene concentration; 100 to 1000 ppm, apparent gas velocity; 2 l/m, humidity; 45%).

As shown in Fig. 4, in a steady state of relative humidity, the photocatalyst loading percentage and the toluene initial concentration, when the intensity of the UV radiation rises from 5 w/m^2 to 17 w/m^2, Toluene degradation efficiency also has an increasing trend. We know that active hydroxyl is one of the main oxidizing agents in the photocatalytic oxidation process [6]. But according to equation 1, Ozone is another oxidizing agent that can be used to improve the photocatalytic oxidation process [10]. Ozone is an oxidizing agent that cannot directly affect the photocatalytic oxidation of toluene, but when it is adjacent to the photocatalyst-P25 (TiO_2), it can be converted to oxidants such as active oxygen and is effective in the oxidation process of toluene (Equation 2) [11]. The wavelength and intensity of UV radiation are factors that influence the amount of Ozone produced in the photocatalytic oxidation process. Therefore, it can be said that increasing the intensity of UV radiation can be effective in improving the photocatalytic oxidation process of toluene.

$$\mathbf{H_2O + hv \rightarrow H^* + OH^*}$$
$$\mathbf{O^* + H_2O \rightarrow 2\,OH^*}$$
$$\mathbf{O^* + O_2 \rightarrow O_3} \quad \text{Equation (1)}$$
$$\mathbf{O_3 + {}^* \rightarrow O_2 + O^*}$$
$$\mathbf{O^* + O_3 \rightarrow O_2 + O_2}$$
$$\mathbf{O_2^* \rightarrow O_2 + {}^*} \quad \text{Equation (2)}$$

According to Fig. 5, it is shown that the photocatalytic degradation efficiency of toluene at lower temperatures (less than 60$^{\circ C}$) is much lower than the higher temperatures. This shows that with increasing temperature, the efficiency of photocatalytic oxidation of toluene is increasing. The temperature increase is effective both indirectly and directly to the photocatalytic oxidation process. The direct effect of temperature on the photocatalytic oxidation process means that increase the conversion percentage due to temperature rise in the range of 60 to 130$^{\circ C}$ suggests that toluene is still highly absorbent in the surface of the catalysts. In other words, rapid desaturation of reaction products from the level of catalysts and providing empty sites to attract toluene would increase the conversion rate [12]. However, the indirect effect of temperature on photocatalyst oxidation appears when ozone is present as an oxidizing agent in the process. This means that when ozone is present as a process oxidizer, it can increase the efficiency of the photocatalytic oxidation process at higher temperatures [13].

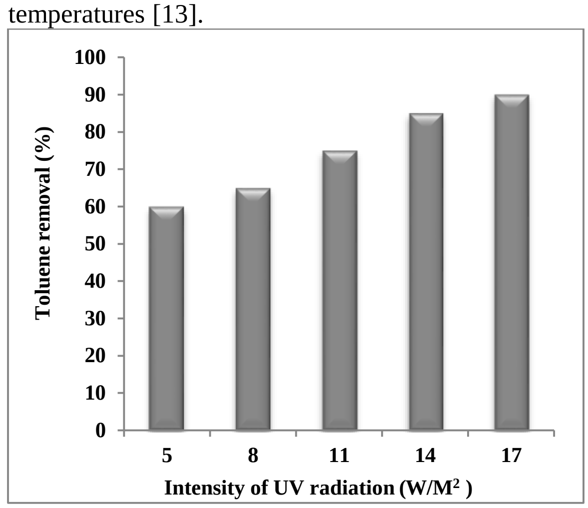

Fig. 4: Effect of UV Lamp intensity on toluene removal efficiency (300ppm toluene concentration - 45% relative humidity)

Therefore, it can be concluded that the photocatalytic oxidation process of toluene has higher efficiencies at higher temperatures.

According to Fig. 6, it is shown that relative humidity is one of the factors affecting the rate of photocatalytic oxidation of toluene. In low moisture content (10%), the efficiency of toluene degradation is lower and with increasing relative humidity (45%), the efficiency of the photocatalytic oxidation process increases. The reason for this is that according to the equation 3, the presence of moisture in the vicinity of an oxidizing agent, such as Ozone, leads to the formation of activated hydroxyl that can play an important role in the photocatalytic oxidation process [14]. However, with increasing relative humidity (more than 45%) it is shown that the reaction rate does not increase, but because of the water-friendliness of the photocatalyst particles, the photocatalytic oxidation process is reduced [15].

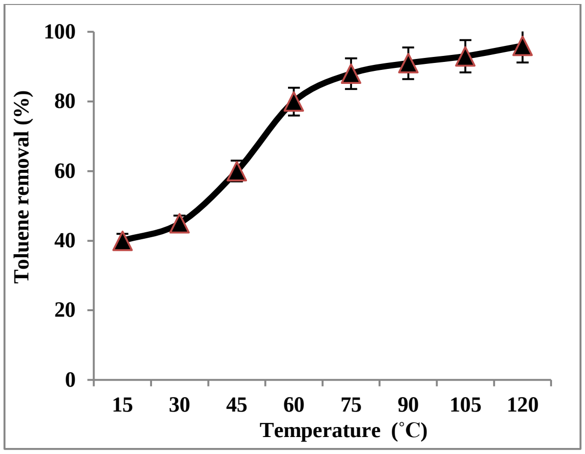

Fig. 5: Effect of reactor column temperature on toluene removal efficiency (300 ppm toluene concentration - relative humidity 45% - intensity of UV radiation 17 w / m²)

$$3e^- + 3h^+ + 2H_2O + O_2 \rightarrow 4OH^*$$

$$O_3 \rightarrow O^* + O_2$$

$$O_3 + H_2O \rightarrow 2\,OH^* + O_2 \quad \text{Equation (3)}$$

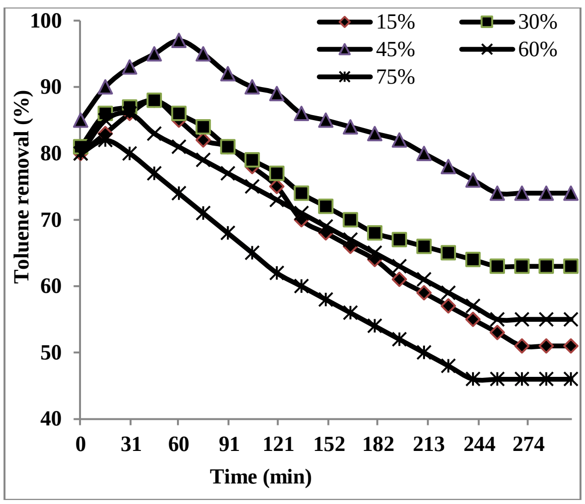

Fig. 6: Effect of relative humidity on toluene removal efficiency (toluene concentration of 300 ppm and UV intensity of 17 w/m²)

DISCUSSION

Photocatalytic oxidation is a modern and efficient way to control the release of fugitive organic gases, which enter the environment from various industrial and non-industrial activities. Various studies have been conducted to make this process workable, most of them seek to find ways in which they can efficiently increase the efficiency of this process. In this study, it was tried to improve the efficiency of the process by studying the effects of variables such as percentage of photocatalyst loading, relative humidity, UV radiation intensity and reactor column temperature on the photocatalytic oxidation process of toluene. In examining the percentages effective in photocatalyst loading, it was found that for certain constituents of toluene, and with constant moisture and intensity of UV radiation, the percentage of photocatalyst loading increased. This trend was seen to increase from 5wt% to 20wt% of photocatalyst loading. But in loads of more than 20%, the only increase in catalytic mass alone was not effective in improving the reaction rate. This means that the photocatalyst loading up to 20wt%, the intensity of the UV lamp had an optimal mode for activating the photocatalyst. However, by increasing the percentage of photocatalyst loading to more than 20wt%, although the weight percentage of the photocatalyst is increased, however, because of the constant intensity of the beam, there should be no significant increase in the efficiency of the toluene degradation [16]. Therefore, in order to increase the reaction rate in weight percentages of more than 20%, it is necessary to increase the rate of photocatalyst exposure to UV radiation. In the study of the effect of irradiation radiation intensity, it was determined that the intensity and the appropriate wavelength of the irradiation radiation, directly and indirectly, affect the increase of the photocatalytic oxidation reaction rate. The direct effect of increasing the radiating radiation intensity means that, with increasing photocatalyst mass and increasing the number of active sites, when the radiation intensity reaches the level that covers all active photocatalyst sites, the photocatalyst oxidation reaction rate increases [12]. However, the indirect effect of UV wave intensity with suitable wavelength (UV-C) on the rate of photocatalytic oxidation process means that, by providing an effective radiation beam, in addition to common oxidizing agents such as active hydroxyl, the presence of Ozone oxides such as Ozone can be used to improve process rates [9]. Although ozone cannot directly contribute to the oxidation of toluene, ozone, in the presence of photocatalyst such (TiO_2- P25) can be converted to oxidants such as active oxygen and has an effective role in improving the photocatalytic oxidation of toluene(11). Therefore, an increase in UV wave intensity with suitable wavelength (UV-C), it can be considered as one of the most influential factors in increasing the photocatalytic oxidation of toluene [17].

In the study of the temperature effect, it was found that the temperature increase also has a direct and indirect effect on the photocatalytic oxidation process. Investigating the direct effect of temperature on the photocatalytic oxidation process shows that the conversion rate also increases as temperature rises.

This effect is quite clear in the range of 60 to 130$^{\circ C}$, causes toluene to be highly absorbed into the catalysts. In other words, rapid deactivation of reaction products from the catalytic level and the provision of vacant sites for the addition of toluene leads to an increase in its conversion rate [12]. However, the indirect effect of temperature on photocatalyst oxidation appears when Ozone is present as an oxidizing agent in the process. This means that when Ozone is present as an oxidizing agent at a higher temperature, it can increase the efficiency of the photocatalyst oxidation process. One of the most effective parameters for increasing oxidizing power such as ozone is the proper temperature. This means that at low temperatures, even if we have a good ozone concentration, but because the temperature is low, there will be no change in the incremental rate of photocatalyst oxidation [13]. In the study of the effect of UV radiation intensity and temperature, since the increase in the intensity of the appropriate wavelength (UV-C) causes higher ozone production, But ozone needs to be exposed at high temperatures to influence the rate of photocatalytic oxidation process, so in order to take advantage of the presence of an oxidizing agent such as Ozone, in addition to increasing the intensity of the UV radiation, it should provide the appropriate temperature to cause the photocatalytic oxidation reaction rate. Another variable that influences the photocatalytic oxidation reaction rate is relative humidity. As it was mentioned, in lower moisture content (10%), the efficiency of toluene degradation is lower and with increasing relative humidity (45%), the efficiency of the photocatalytic oxidation process increases. The reason for this is that according to the relations No. 3, the presence of moisture in the vicinity of an oxidizing agent, such as ozone, leads to the formation of activated hydroxyl that can play an important role in the photocatalytic oxidation process [18]. However, with higher relative humidity (more than 45%), it is evident that not only the reaction rate will not increase, but also the photocatalytic oxidation process will decrease. Therefore, the 45% moisture content is an optimal level for the photocatalytic oxidation of toluene. Therefore, by increasing the amount of moisture, the competitive absorption of water and toluene molecules into photocatalyst occurs, and photocatalyst active sites are saturated with water molecules and prevent the oxidation of toluene [19].

CONCLUSION

In this study, we tried to increase the efficiency of this process by examining the effects of variables such as photocatalyst loading, relative humidity, and UV radiation intensity and reactor column temperature on the photocatalytic oxidation process of toluene. In addition to the independent influence of each of these variables on the photocatalytic reaction of toluene, it was found that these variables themselves are affected by each, and for proper efficiency, all of these variables should be considered together in appropriate conditions.

ETHICAL ISSUES

Ethical issues including plagiarism double publication and/or submission, redundancy, etc. have been completely observed by the authors.

COMPETING OF INTEREST

The authors have declared that no competing interest exists.

AUTHORS' CONTRIBUTIONS

All authors equally participated in drafting, revising and approving of the manuscript.

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REFERENCES

[1] Kampa M, Castanas E. Environmental Pollution Human health effects of air pollution, Environmental Pollution J. 2008; 151(2): 362-67.

[2] Zuo S, Liu F, Tong J, Qi C. Complete oxidation of benzene with cobalt oxide and ceria using the mesoporous support SBA-16, Applied Catalysis A: General J. 2013; 467 (2): 1-6.

[3] Golhosseini SM, Kakooei H, Shahtaheri SJ, RezazadehAzari M, Azam K, Distribution of Total Volatile Organic Compounds at taxi drivers in Tehran., Iranian Journal of Health, Safety & Environment. 2015; 2(2): 250-56.

[4] Parmar GR, Rao N, Technology. Emerging Control Technologies for Volatile Organic Compounds. Critical Reviews in Environmental Science and Technology, 2008;, 39(1): 41-78.

[5] Kuo H, Wu C, Hsu RJ. Continuous reduction of toluene vapours from the contaminated gas stream in a fluidised bed photoreactor. Powder Technology J. 2009; 195(1): 50-56.

[6] Zhao J, Yang XB, Photocatalytic oxidation for indoor air purification: a literature review, Building and environment, 2003; 38(5): 645-54.

[7] Kisch H. Semiconductor photocatalysis—mechanistic and synthetic aspects. Angewandte International Edition Chemie. 2013; 52(3): 812-47.

[8] Jafari R, Sotudeh-Gharebagh R, Mostoufi N. Modular simulation of fluidized bed reactors. Chemical Engineering Technology, 2004; 27(2): 123-29.

[9] Lim M, Zhou Y, Wang L, Rudolph V, Lu G. Development and potential of new generation photocatalytic systems for air pollution abatement: an overview, Asia pacific of Chemical Engineering, 2009; 4(4): 387-02.

[10] Alapi T, Dombi A. Direct VUV photolysis of chlorinated methanes and their mixtures in an oxygen stream using an ozone producing low-pressure mercury vapour lamp. Chemosphere, 2007; 67(4): 693-01.
[11] Li W, Gibbs G, Oyama S. Mechanism of ozone decomposition on a manganese oxide catalyst. 1. In situ Raman spectroscopy and ab initio molecular orbital calculations. Journal of the American Chemical Society, 1998; 120(35): 9041-46.
[12] Mo J, Zhang Y, Xu Q, Lamson JJ, Zhao R. Photocatalytic purification of volatile organic compounds in indoor air: a literature review. Atmospheric Environment, 2009; 43(14): 2229-46.
[13] Reza S,Hassan Z, Samaneh S. Comparison of the Performance of AOP Method Using O_3/H_2O_2 in the Presence of TiO_2 and ZrO_2 Nano Particles Stabilized on Pumice for the Removal of Pentachlorophenol from Aquatic Solution: Kinetic Studies. Iranian Journal of Health, Safety & Environment, 2018; 5(3):1082-90.
[14] Huang H. Removal of air pollutants by photocatalysis with ozone in a continuous-flow reactor. Environmental Engineering Science, 2010; 27(8): 651-56.
[15] Huang Y, SaiHang S, Lu Y, Niu R, Xu L, Cao J, Lee S. Removal of Indoor Volatile Organic Compounds via Photocatalytic Oxidation: A Short Review and Prospect, Molecules 2016, 21(1): 56-60.
[16] Li Y, Wu CY. Role of moisture in adsorption, photocatalytic oxidation, and reemission of elemental mercury on a SiO_2-TiO_2 nanocomposite, Environmental science & technology. 2006; 40(20): 6444-48.
[17] Herrmann JM. Titania-based true heterogeneous photocatalysis. Environmental science and pollution research international, 2012; 19(9): 3655-65.
[18] Huang H, Ye X, Huang H, Hu P, Zhang L, Leung D. Photocatalytic oxidation of gaseous benzene under 185 nm UV irradiation. International Journal of Photoenergy. 2013; 2: doi.10.1155/2013/890240.
[19] Ebrahimi H, Shahna FG, Bahrami A, Jaleh B, Abedi KAD. Photocatalytic degradation of volatile chlorinated organic compounds with ozone addition, Archives of Environmental Protection. 2017; 43(1): 65-72.
[20] Dong K, Lee S Chul Ki *et al.* Photocatalytic oxidation of microcystin-LR in a fluidized bed reactor having TiO_2-coated activated carbon. Separation and Purification Technology, 2004; 34(1): 59-66.
[21] Víctor M, Rut R.D, Soraya R.R, María J. Titanium dioxide nanoparticle coating in fluidized bed via supercritical anti-solvent process (SAS), Chemical Engineering Journal. 2015; 279(1): 425-32.
[22] Gary A, Leekea T, Rachel B, Jonathan P.K. Application of nano-particle coatings to carrier particles using an integrated fluidized bed supercritical fluid precipitation process, The Journal of Supercritical Fluids. 2014; 91: 7-14.