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THE OXIDATION OF AROMATIC HYDROCARBONS VAPORING WASTE AIR STREAMS USING VUV ADVANCED OXIDATION PROCESS

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ABSTRACT:

Introduction: The vacuum UV (VUV) system is a novel chemical-less advanced oxidation processes (AOP) used to decompose different class of organic contaminants. The present study aimed at investigating the efficiency of VUV process to degrade toluene as a model of aromatic hydrocarbons from the gas stream in a bench-scale photo-reactor.

Materials and methods: The effect of various parameters including radiation flux, relative humidity, toluene concentration, and ozone dosage were investigated on toluene degradation in the VUV process.

Results: The results showed that increasing the relative humidity up to 45% could considerably accelerate the oxidation of toluene as compared with the dry air stream in the process. Complete destruction of toluene was reached at radiation fluxes of 0.366 and 0.732 mJ/cm^2 for 5 and 15 ppm of toluene, respectively. Dosing ozone into the VUV photo-reactor at the dosages of 20, 40 and 60 µg/s led to improve the toluene degradation from 65.6% to 100%. The removal of toluene in the VUV process under the selected optimum conditions followed a pseudo-first order reaction model with the degradation rate values of 5.99 mg/L.min.

Conclusions: It was found that VUV process might be a novel and emerging AOP, which can efficiently perform for decomposition of aromatic hydrocarbons in contaminated air stream.

INTRODUCTION

Volatile organic compounds such as toluene, benzene and formaldehyde are released to environment due to their consumption in paint, adhesive, cleaner and plastic polymer productions in industrial process [1].These compounds can create sick building syndrome for indoor residents and staffs in occupational ambient, even contact with some of these compounds can increase the risk of cancer in people exposed [2]. In addition to individual and public health risks caused by exposure to harmful VOCs in occupational ambient, they are also playing an important role in outdoor air pollution. It was confirmed which

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these compounds are able to create dark particles in atmosphere due to photochemical smog. It is also well documented that VOCs are a threat to atmospheric ecosystems and human life [2, 3].

Due to the health and environmental effects of VOCs, their removals from waste air streams are encouraged. Adsorption on porous material [4, 5], liquid absorption [6, 7], catalytic combustion [8], and advanced oxidation processes [9], heterogeneous catalytic [10], and photo-catalytic oxidation [2, 3, 11] have been studied for their removal. There are some limitations behind the above-mentioned process. For example, adsorptions of VOCs on porous materials transfer them from air streams on to solid surfaces in concentrated form, while the contaminant is also in environment [12, 13]. Other proposed processes also lead to the generation of by-products which can be hazardous [9, 14].

In order to overcome the deficiency of the proposed processes, some studies are being conducted for VOCs removal. Due to the high reaction rates and simplicity of operation, AOPs could be considered as an efficient technique. Vacuum ultraviolet (VUV) radiation is one of the newly developed processes for removal and destruction of various contaminants from polluted air and water. VUV radiation at wavelength of 185 nm causes to generate highly oxidizing ozone through Eqs. (1), (2) and (3) [15-17]. Ozone can directly react with VOCs and destruct them. In addition, presence of water molecules in environment leads to generation of hydroxyl radical which is a non-selective highly oxidizing agent (Eqs.(4) and (5)) [18-20].

$$O_2 + hv\ (\lambda < 243) \rightarrow O\left({}^1D\right) + O\left({}^3P\right) \quad (1)$$

$$O\left({}^1D\right) + M \rightarrow O\left({}^3P\right) + M \quad (2)$$

$$O\left({}^3P\right) + O_2 + M \rightarrow O_3 + M \quad (3)$$

$$H_2O + hv\ (\lambda = 185\ nm) \rightarrow HO^{\bullet} + H^{\bullet} \quad (4)$$

$$\Phi = 0.33$$

$$H_2O + hv\ (\lambda = 185\ nm) \rightarrow HO^{\bullet} + H^{+} + e^{-} \quad (5)$$

$$\Phi = 0.045$$

Although oxidation of VOCs by photo-catalytic process with VUV as UV radiation source has been investigated, to our knowledge, there has never been any comprehensive study to enhance VUV radiation for VOC destruction. In order to investigate the effect of VUV radiation on VOC removal from waste air streams, toluene was selected as a model contaminant. Toluene is one of the commonly used solvents in industrial processes. Therefore, presence of toluene in indoor and outdoor environments is inevitable. That's why American Society of Heating, Refrigeration, and Air-Conditioning Engineers (ASHRAE) referred to toluene as one of the eight criteria by indoor air pollution [9].

Therefore, present study was aimed to investigate the efficacy of VUV advanced process for destruction of toluene from waste air streams. In this study effect of toluene concentration, radiation fluence, the relative humidity of the air stream and injection of ozone to the photo-reactor were investigated. Finally the mechanism of toluene degradation was identified.

MATERIALS AND METHODS

Experimental setup

Experimental setup for this study is shown in Fig.1. Air and nitrogen gases were used as toluene carrier and were supplied by air and nitrogen cylinders. Carrier gases were divided into three different pathways to create different concentrations of toluene and relative humidity and a bypass stream to adjust the flow of polluted air stream entering the photo-reactor. Various concentrations of toluene was created by injecting liquid toluene (Merck with purity of 99/99%) using a syringe pump (Fresenius Vial PILOT A_2) to the flow of clean air/nitrogen stream. A 500 mL impinger was used to provide desired relative humidity. All three streams containing toluene and humidity along with bypass clean stream were entered into the mixing chamber (5 L) equipped with a mixing fan. Afterward, polluted air stream at desired toluene concentration and relative humidity were injected to the VUV photo-reactor.

VUV photo-reactor was a tubular glass (internal diameter of 30 mm and height of 380 mm) with two ports at the bottom and one port at top of the photo-reactor. This photo-reactor was equipped with a quartz shield (internal diameter of 25 mm) and a low-pressure mercury UV lamp (5.7 W Heraeus Co.). UV light detector (Boston Electronic Co.) was used to measure the UV radiation. Fluence of radiation emitting at 1 cm from surface of the used lamp at 254 and 185 nm (flux was <10%) were 56 and 5 $\mu W/cm^2$, respectively. Radiation fluence of the VUV lamp was varied by changing the air flow rate which leads to the change in toluene retention time in the photo-reactor. A sintered glass filter with pore diameter of 100 µm at 2 cm above the entrance was embeds ded. Input for ozone injection is located at 1 cm above the sintered glass filter. Flow rate of ozone generator (ARDA, Model AEGCOG-2A) in all the experiments was set to be 60 mL/min.

Analytical methods

Toluene inlet and outlet of photo-reactor measured online by Phocheck analyzer (Ion Science Ltd). The device is equipped with PID detector and at the same time performs sampling and measurement. Of course, in order to verify the results of the device for each variable number of samples also were monitored by gas chromatography (GC-FID) and the outcome of which was similar to that of direct reading. Removal of toluene TR (%) was calculated as follow equation:

$$TR = (Ti - T0) \times 100/Ti$$

Where T_i and T_0 are inlet and outlet concentration respectively. As well as to reduce error caused by light radiation changes all the trials took place 30 m after the light VUV bulb. Humidity and temperature of polluted air flows was measured online by the digital hygro-thermometer (SIBATA TH-2). Dose of ozone injection to the photo-reactor was determined using the methodology presented in standard method [25].

RESULTS AND DISCUSSION

Effect of the humidity at varying radiation fluence

Based on the previous studies, it has been reported that humidity is one of the key elements for the oxidation of VOCs by AOPs [20]. Therefore,

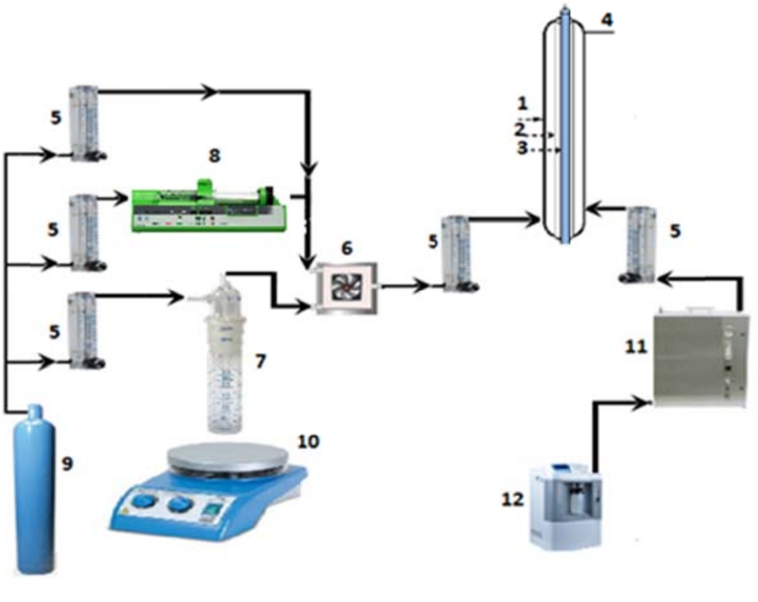

Fig.1. Schematic of setup for VUV experiments

(1. photo-reactor, 2. sleeve, 3. VUV lamp, 4. outlet, 5. flow meter, 6. mixing chamber, 7. impinger, 8. syringe pump, 9. air/nitrogen cylinder, 10. heater, 11. ozone generator, 12. oxygen supplier)

different relative humidity (RH) of toluene-laden air stream was investigated. Fig.2 is representing the effect of RH in toluene degradation at different radiation fluence. As shown in the figure there is a considerable increase in the toluene removal in the presence of humidity. However, the toluene removal efficiency did not show any changes when the RH was above 45%. Therefore, 45% RH was selected as optimum relative humidity.

As presented in the figure, removal efficiency reached to almost 75% when there was no humidity (radiation fluence of 0.732 mJ/cm^2), degradation at this level is attained by photo-degradation and oxidation by the generation of ozone in the photo-reactor Eqs.(1), (2) and (3). Increasing the RH to 45% led to complete destruction of toluene. This increase in removal efficiency could be attributed to the generation of highly oxidizing agents such as hydroxyl radical. Therefore, hydroxyl radical-based reactions along with ozone oxidation and photo-degradation are the toluene degradation pathways. Also, humidity can enhance the generation of hydroxyl radicals to decompose more contaminant at the same radiation fluence. According to a research, the degradation of dichloromethane was studied by VUV radiation, and it was found that the highest removal efficiency reached at the humidity of 80% [21]. Higher radiation fluence of VUV is attained at higher retention time. As shown in the figure, the higher exposure time of toluene to the VUV radiation leads to the increase in toluene removal efficiency.

Effect of toluene concentration

The effect of toluene concentration (5-75 ppm) on the removal efficiency was investigated at optimum RH at varying radiation fluence. As shown in Fig.3, the removal of toluene decreased with the increase of inlet concentration at a constant fluence. This is due to the reduction of toluene to oxidize agent ratio; therefore, higher retention times are required for toluene degradation at higher inlet concentrations.

Effect of the ozone presence

In order to enhance the efficacy of the VUV radiation for toluene degradation, external ozone at concentrations of 20-60 µg/s was injected to the photo-reactor. Fig.4 is illustrating the results of ozone presence for degradation of toluene. As it is seen in the figure, presence of the ozone in the photo-reactor has a considerable effect on the oxidation of toluene. As shown in Eqs. (1),

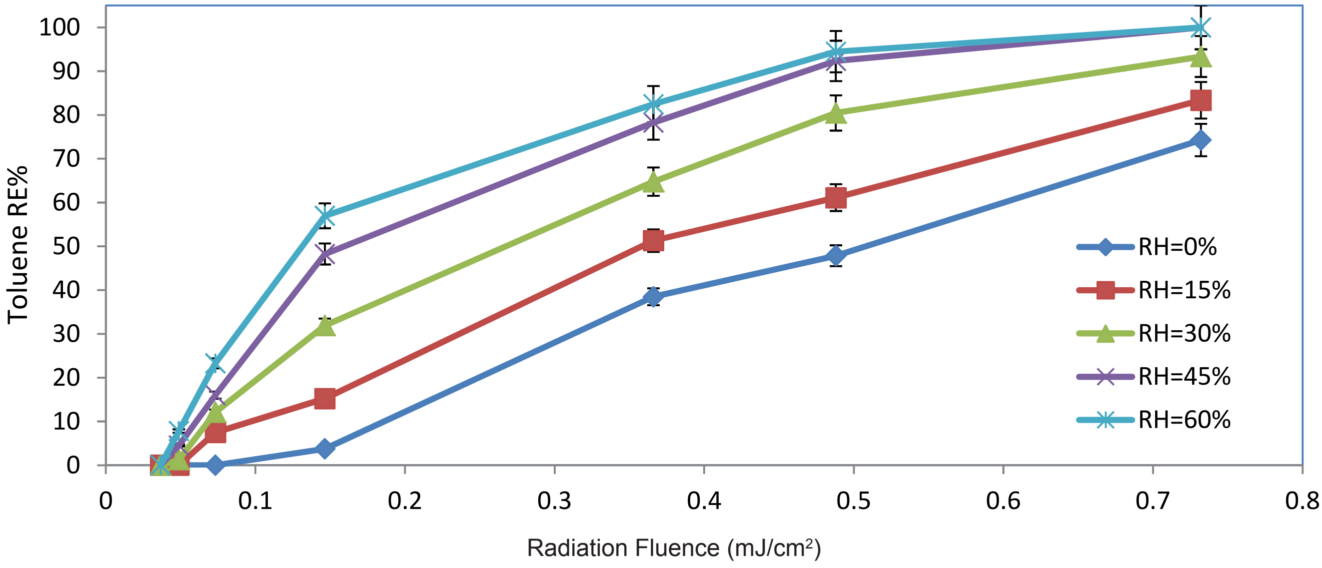

Fig.2. Toluene removal under different humidity
(Toluene initial concentration=15 ppm)

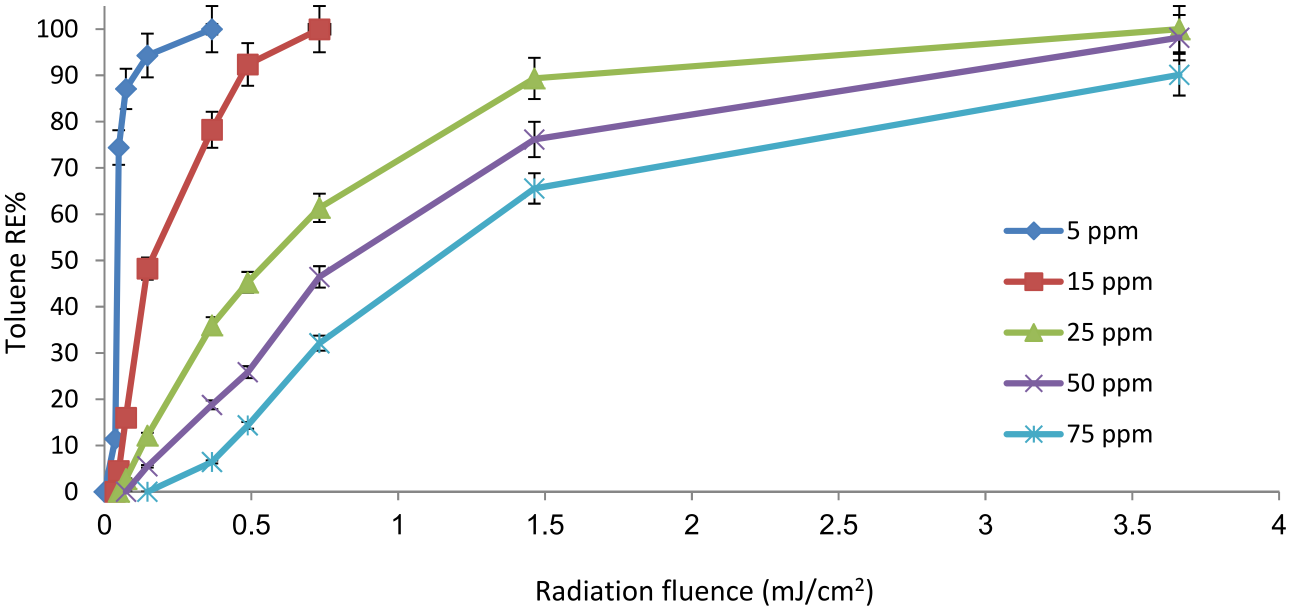

Fig.3. Destruction of different concentrations of toluene by VUV radiation (RH=45%)

(2) and (3), ozone is generated by VUV radiation. However, intrusion of external ozone is able to increase the removal efficiency. Ozone is a strong oxidizing agent which can react directly with toluene and also it could be a precursor to the generation of other oxidizing agents such as hydroxyl radical. Ozone molecule's radiation by VUV light leads to the generation of hydrogen peroxide and subsequently hydroxyl radical is generated as the results of hydrogen peroxide radiation (Eqs. (6) and (7)) [22].

$$H_2O + O_3 \rightarrow H_2O_2 + O_2 \quad (6)$$

$$H_2O_2 + h\nu\ (\lambda = 185\ nm) \rightarrow 2HO^{\bullet} \quad (7)$$

Therefore addition of ozone to the photo-reactor is able to increase generation of hydroxyl radical and enhance the performance of the VUV radiation.

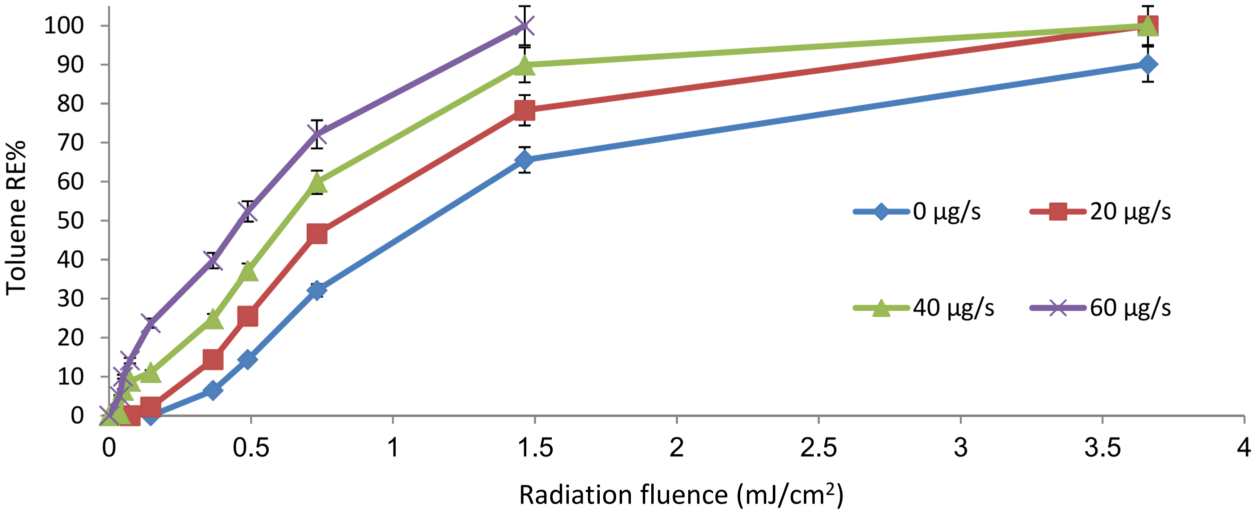

Fig.4. Presence of different ozone dose on oxidation of toluene in the VUV radiation
(Toluene initial concentration=75 ppm, RH=45%)

Oxidation mechanism

In order to understand the degradation mechanisms of toluene in the photo-rector, different experiment were conducted to inhibit the oxidizing agents generation. As previously mentioned intrusion of humidity and water vapor to the photo-reactor is leading to generation of hydroxyl radical. Fig.5 is representing the results of this experiment. There is almost 75% reduction in the removal efficiency when there is no humidity in the photo-reactor. Considering the effect parameters for toluene oxidation reactions presented in Eqs.(4-7) have been inhibited in the absence of water molecules. Therefore, generation of oxidizing agents such as hydroxyl radical and hydrogen peroxide are inhibited. Therefore, it can be concluded that ozone and direct photo-degradation of toluene are the only degrading agents in the process.

In the next experiment, inert nitrogen gas was injected to the photo-reactor instead of air. By this action almost degradation degree of toluene decreased by half. Abstraction of oxygen molecules from reactions taking place in toluene degradation ceases the generation of ozone and the related reactions. At this experiment, Eqs.(4), (5) and (7) could be the main degradation pathways. The next was aimed to see the effect of photo-degradation of toluene in the absence of both oxygen and water molecules. The results show that there is only 21% removal efficiency at this case which is reached due to the photo-degradation of toluene molecules by VUV radiation. Table 1 contains the energy bonds of toluene molecule. On the other hand, VUV radiation at 185 nm produces 6.7 eV energy which is higher than of toluene molecule's bonds. That's why VUV radiation is able to oxidize toluene in the absence other oxidizing agents.

Kinetic for toluene removal

In order to conduct a better understanding about the rate of reactions, kinetic of toluene degradation has been investigated based on pseudo-first order kinetic (Eq.(8)).

$$\ln(C_t - C_0) = -k_1 t \tag{8}$$

Where C_0 and C_t are the toluene concentration (ppm) at the beginning and at time *t* after the reaction started, respectively, and k_1 (min^{-1}) is the

Table 1. Energy bonds of in the toluene molecule

Bound	Energy (ev)
C-H in the methyl	3.7
C-H in the aromatic ring	4.3
C-C in the methyl	4.4
C-C in the aromatic ring	5 – 5.3
C=C in the aromatic ring	5.5

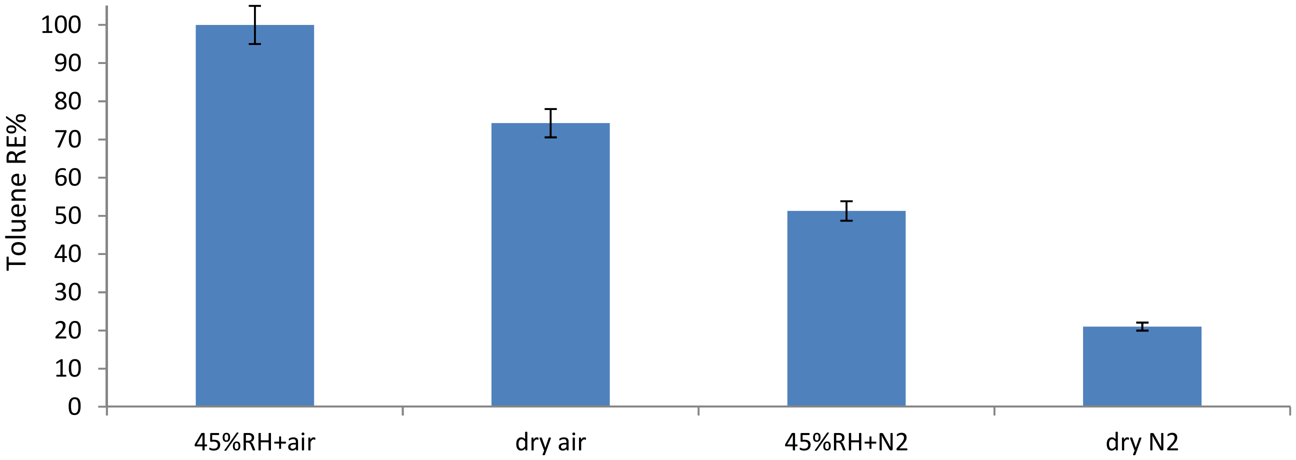

Fig.5. Oxidation mechanism of toluene
(Initial concentration of toluene=15 ppm, fluence=0.732 mJ/cm^2)

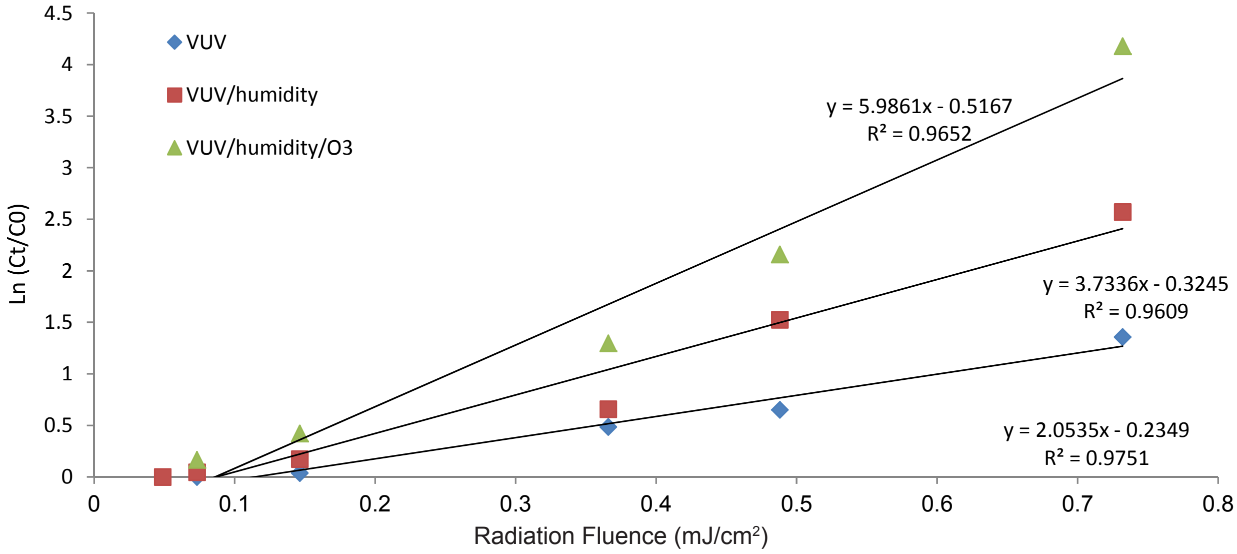

Fig.6. Kinetic of toluene removal in the VUV, VUV/humidity, VUV/humidity/ozone, (initial concentration of toluene 15 ppm, humidity 45%, dose of ozone 60 µg/s).

pseudo-first order kinetic rate constant.

Comparing rate constants of the different processes, it is clear that rate constant of toluene removal is increased by 1.81 times when humidity is present in the photo-reactor. External ozone addition to the photo-reactor has also led to an increase of 2.91 times. Therefore, in the presence of ozone and humidity toluene removal efficiency is reached in mush less time. In a study, it was investigated the oxidation of dichloromethane (DCM) by VUV radiation. They found that oxidation of DCM by VUV radiation followed second-order kinetic model. They also have reported that rate constant of DCM has increased from 0.069 at RH of 2% to 0.251 at RH of 80% [23].

CONCLUSIONS

In this study VUV advanced oxidation process was applied for toluene removal. By addition of humidity and ozone to the process, reaction time for toluene removal decreased substantially. Also, it was confirmed that removal of toluene was achieved by direct photolysis and reaction with hydroxyl radical generated by oxygen and ozone molecule photolysis and water molecule hemolysis. Results of our study showed that VUV advanced oxidation process can be considered as a high-performance and environmental friendly treatment for volatile organic compounds treatment.

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COMPETING INTERESTS

We have read and understood JAPH policy on declaration of interests and declare that we have no competing interests.

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ETHICAL CONSIDERATIONS

The manuscript is the original work of the authors, who agree to submit it to Journal of Air Pollution and Health. It is confirmed that this manuscript has not been submitted/published earlier elsewhere.

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