Photocatalytic oxidation of perchloroethylene by TiO_2 coated on glass-bead

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Abstract

Chlorinated volatile organic compounds (VOCs), such as perchloroethylene (PCE), are widely used as industrial solvents in the dry cleaning, degreasing of metals, and plastics industries. In this study, the photocatalytic removal of perchloroethylene was investigated by a filled glass-bead reactor. Also, the effect of relative humidity, residence time, concentration and ultraviolet light on the photocatalytic removal process was investigated. The photocatalytic effect of ultraviolet light and photocatalyst TiO_2 was compared, with reaction conditions, 1 min, 3000 ppm concentration and relative humidity of 30%, and the photocatalyst TiO_2 had a higher removal capacity than ultraviolet light.

Introduction

Volatile organic compounds (VOCs) are one of the causes of air pollution. Organic compounds are compounds that contain carbon and hydrogen. The majority of organic compounds that are used are human made. Some of these compounds are liquid and solid, and they require an additional level of warming to create steam. These organic materials are stable compounds. Another group of organic compounds is unstable and the other is known as volatile organic compounds. Any combination of steam (gas) at ambient temperature (25C°) (atmospheric pressure) or evaporating rapidly under standard conditions is known as volatile organic compounds, some of which are hazardous if inhaled excessively [1, 2].

The elimination of chlorinated organic pollutants by controlling the source of contamination, increasing the air exchange rate and using air purifiers are among the commonly used methods for controlling air pollution. It is difficult to control the source of contamination in many places, and increasing the exchange of air may cause more pollution to the surrounding environment. Normal cleaners also use absorbent materials such as activated Carbon or filters that do not eliminate contaminants, but only transfer to another phase (they merely collect them). And common practices such as absorption processes or air vacuum that only transfer pollutants between phases. Despite significant innovations and advances in the development of methods for the elimination of pollutants in recent years, it remains a challenge for researchers. Therefore, it is important to find an appropriate way to solve these problems. A lot of research has been done by researchers and scientists to find complete and acceptable solutions to these problems. A significant amount of these studies has been devoted to testing the capability of semiconductor bodies using the appropriate light to oxidize toxic organic compounds. Is. In this process, a semiconductor object acts as a chemical catalyst. This method is known as optical catalytic oxidation (photocatalyst). In this study, we compared the photocatalytic activity by ultraviolet light and the Tio_2 catalyst (sol-gel synthesized) on chloride escape pollutants in the gas phase by a glass beads-filled photoreactor [3].

Perchlorotylene, with the name of abbreviation of perchlorotylene with molecular weight and density, was 165/8 g/mol and 6/1 g/ mL, melting point and boiling point were -19 °C and 121/1 °C, vapor pressure 18/5mmHg at 25 °C and solubility It is 150 mg / L at 20 °C. Perchlorotylene is used as a solvent, a detergent in detergent and as a fat removing agent widely used in laundries, metal and textile industries. The most important health effects of perchlorotylene on human exposure to the central nervous system, affect the kidneys and lungs in acute and chronic contact. It can also increase the risk of cancer, esophagus, pancreas, and cancers of the lungs, kidneys, cervix. The International Agency for Cancer Research (IAEA) has identified this compound as a category of priority and carcinogenic type 2 contaminants. The maximum permitted concentration of chlorine hydrocarbons (staphyte concentration according to the law of safe drinking water as human and environmental protection) is equal to zero according to the EPA standard of 5 µg / L and the maximum target concentration. The WHO guidelines are 0.04 mg /L [4].

In the study of chloroethylene studies, the catalysts mentioned in Fig. 1 have been used to destroy this pollutant [1, 2, 5-12]:

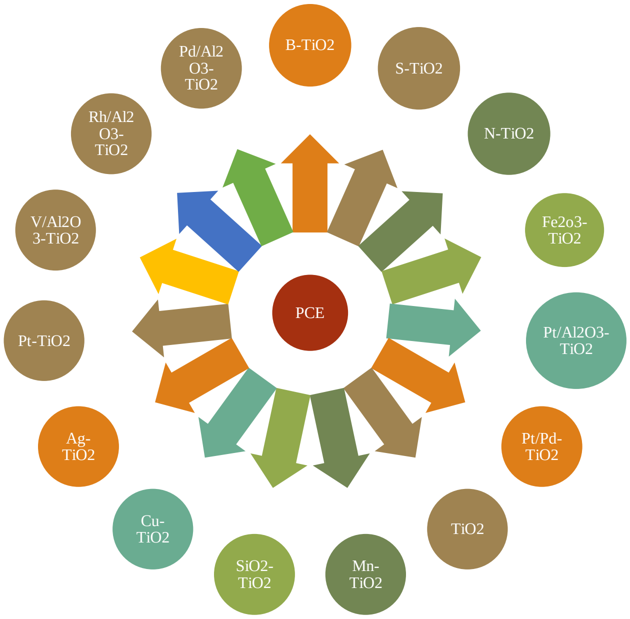


Fig. 1. Examined catalysts for PCE degradation

Method

Chemical materials

Tetra-butyl ortho-titanate (TBT), ethyl alcohol, diluted water, hydrochloric acid.

Synthesis method

Transparent glass beads with a diameter of 5-6 mL (transparent glass balls) were used to insert the photocatalyst inside the reactor, and to increase the contact surface of the pollutant with photocatalyst. Glass beads were roughened mechanically by sand blasting and sanding powder, so that more photocatalyst would sit on its surface. A mechanical stirrer was used to rinse, and in a 10 L container, 1 to 2 sand blasts and mash glass were added and 50 g of corrugated powder was added and applied to the mixture to the appropriate water level (about 10 centimeters higher than the mixture). The mixture was placed under mechanical stirrer for an hour and rotated carefully every 20 minutes, until it was cooled down. After one hour, the glass was removed from the sand and powder and washed with water. To clean the glasses completely, 700 g (sufficient to fill the reactor to a specified height) were separated and disintegrated twice with water and washed with acetone twice to prepare for coating [13, 14].

The synthesis of TiO_2 by sol-gel method, 50 mM tetra-butyl ortho-titanate, was slowly added dropwise to 90 ml of ethanol and 20 ml of deionized water in a 250 ml flask, and then 4 ml of 1 M mol /L of chloride was added slowly. The material was blended at 25 ° C and at a rate of 500 rpm for 3 hours. After 3 hours, the ready glass was prepared in a mixture of TiO_2 synthesized and resting for 10 minutes. Then, remove the liquid mixture from the glasses, and the synthesized liquid with the glasses, which were coated on the catalyst, was placed in an oven at 110 °C to dry. Dried powder and glasses were placed in oven at a temperature of 350 ° with a temperature gradient of 1 °/min for 5 hours to complete the calcination process.

Photocatalysis process

The photocatalyst system shown in the Fig. 2, a Pyrex cylindrical reactor with a height of 40 cm and an inner diameter of 7 cm was designed and built inside a coil-shaped coil with an outer diameter of 4.2 to fit the light source [15]. In order to keep the reaction temperature constant and to completely remove the products from the reactor, a thermocouple cylindrical thermal jacket fitted with a temperature setting of 30 to 130 ° C was fitted around the reactor. For a light source, an 8 wat (UVC /8W/T5) lamp was considered to provide adequate light for the reaction. Then, the tank was filled with glass bulbs up to a height of 30 cm, which, after being placed in the reactor, ultimately filled Effective reactor reached 200 ml. To supply feed to the reactor, i.e., the air contaminated with perchlorotylene, air is passed through an impinge containing PCE, and the moisture needed to conduct the catalytic reaction is also fed through an impeder containing water, which after mixing in The tank enters the reactor. The concentration of the PCE input through the routers installed before the gas bottles is adjusted by varying the amount of dilution of the contaminated stream and the inlet flow to the reactor is also routed to the reactor's input. We will continue to look at the operational images of the system. GC-Mass was used to measure PCE concentration in the inlet and outlet flow.

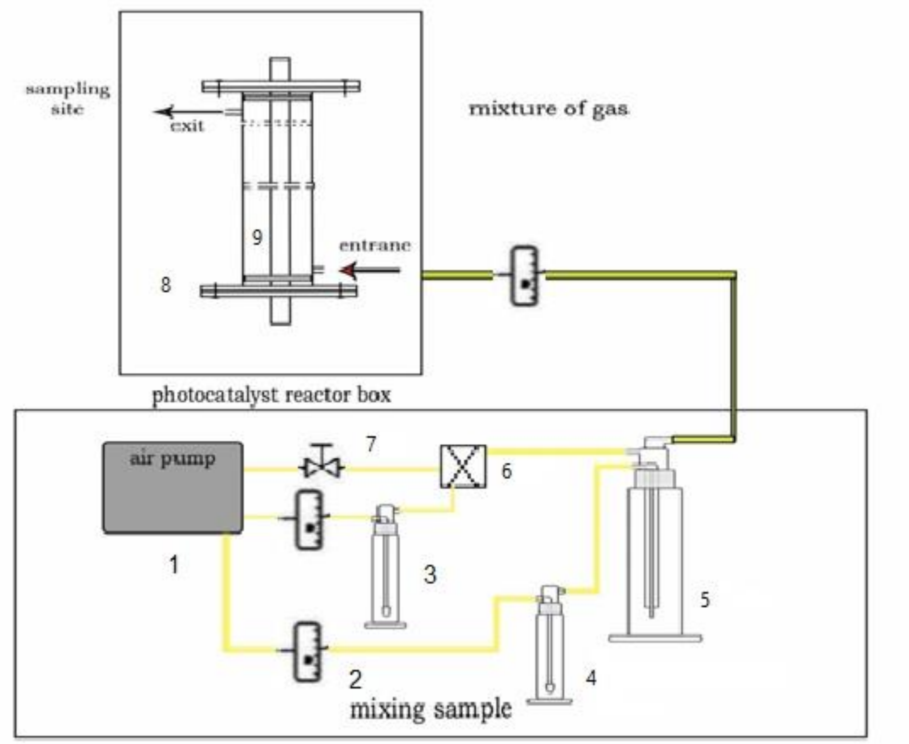


Fig. 2. Schematic of photocatalytic system .1) Air reservoir; 2. Rotamer; 3. Impinger containing water. 4) impinger containing Perchloroethylene. 5) Mixing chamber. 6) Tee. 7) Tap. 8) Reactor. 9) Light source

Results & Discussion

In the X-ray diffraction spectrum, and to a certain extent, the composition of the synthesized nanoparticles has been confirmed, which is consistent with the anatase according to the JCPDS card number 21- 1272 (Fig. 3).

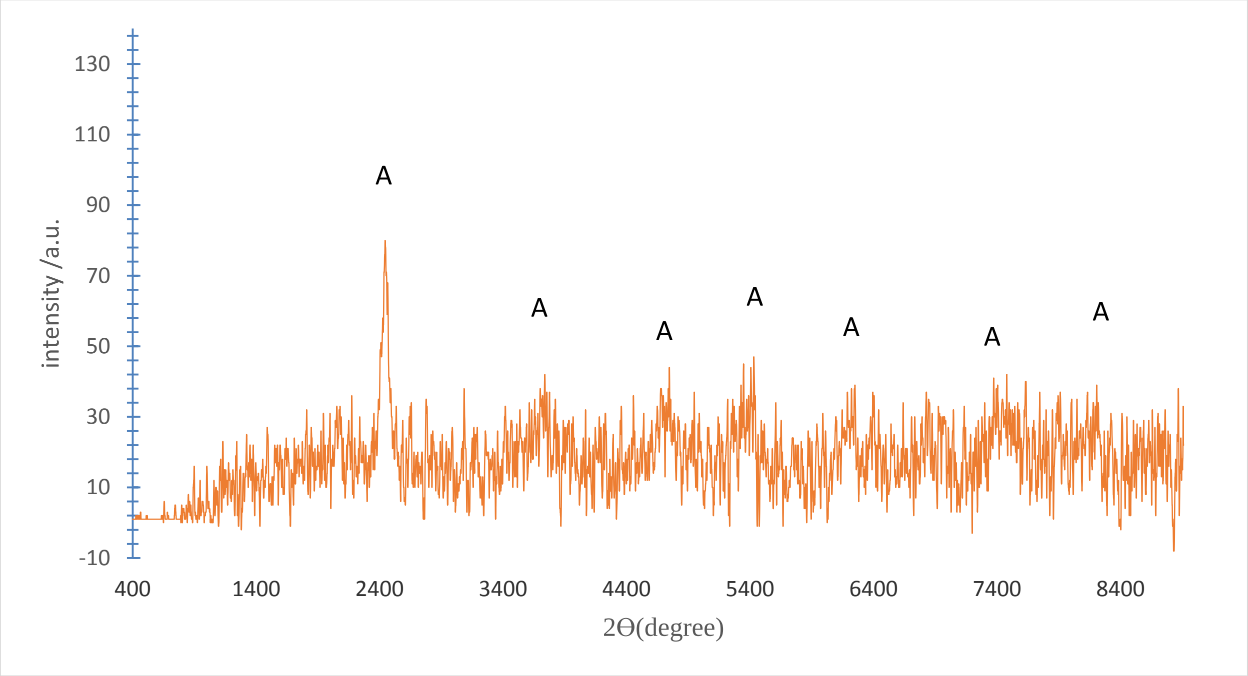


Fig. 3. X-ray diffraction pattern of TiO_2 nanoparticles

At FT-IR spectrum of TiO_2 in Fig. 4, peaks range from 400 to 800 cm^{-1} in the spectrum, indicating a Ti-O-Ti bond. Also, the peaks from 2400 to 3700 cm^{-1} correspond to the OH-band tensile bond and the 1620 cm^{-1} correspond to OH bond bend.

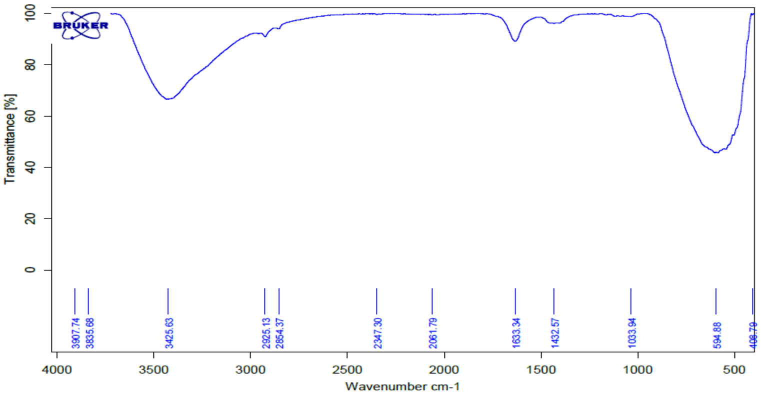


Fig. 4. FT-IR Spectrum of TiO_2 nanoparticles

In the study of SEM image of synthesized nano powders (Fig. 5), monolithic TiO_2 nanoparticles have been observed at 500 nm and 200 nm spacing and particle sizes of 14-28 nm have been confirmed.

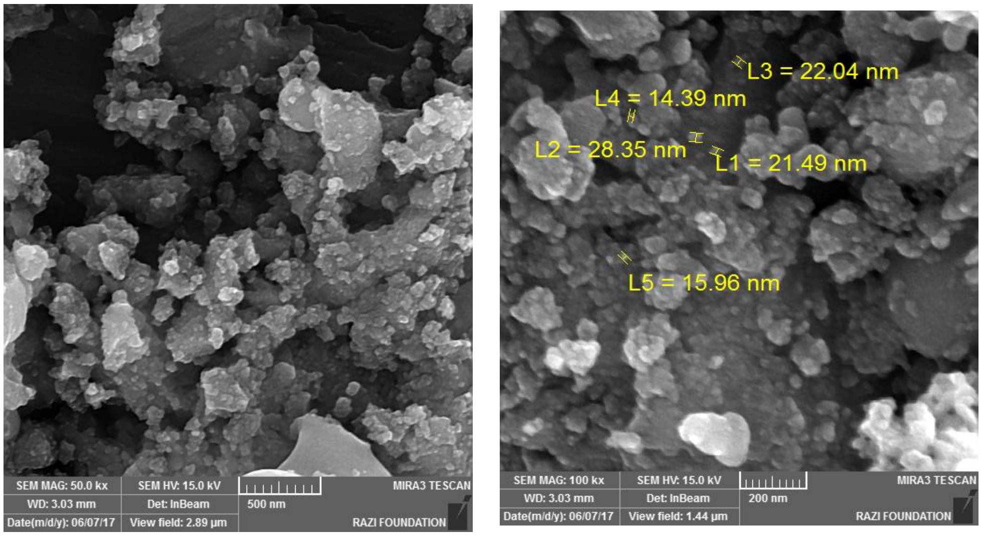


Fig. 5. SEM images of TiO_2 nanoparticles in the scale of 500 and 200 nm

We first filled the system with glassless balls without catalyst to detect the effect of UV light on the reaction. Concentration of 3000 ppm and relative humidity of 30%, and after ensuring the constant concentration of the concentrations before and after the system, we set the temperature of the thermal jacket to a temperature of 30 degrees to equalize the temperature inside the reactor from the accumulation and condensation of gas materials In the inner part of the reactor, when we assured that the reaction conditions were fixed in the reactor, we lit the lamp and sampled the system at different times and examined the GC-Mass device. The graph of the photocatalytic reaction was plotted as the output concentration in time (Fig. 6).

Table 1. Table of time and concentration of UV light

TIME(MIN)	DENSITY(PPM)	EFFICIENCY
0	3252	0
2	477	85.32292
10	187	94.24
20	328	89.90216
45	70	97.85307
60	98	96.98196
70	61	98.11608
120	30	99.07203

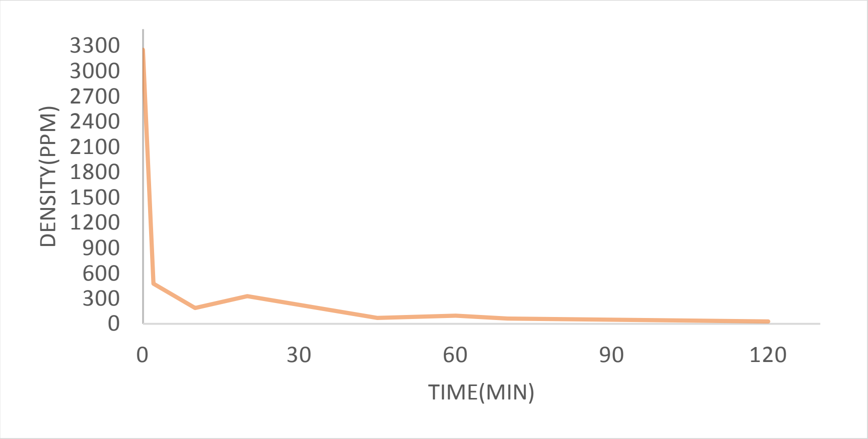
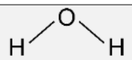
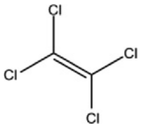
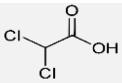
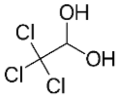
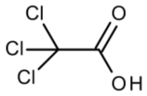


Fig. 6. Output concentration graph in terms of ultraviolet light

With increasing time, perchloroethylene concentrations have decreased. But this reduction is not due to the completeness of the reaction. According to the observations, after a long time after turning on the lamp, a large volume of crystals inside the outlet tube, the sample container and the inside of the system, as well as the concentrated sample collected from the system and injected into the GC-Mass system We find compounds that are the result of a simple breakdown of perchloroethylene bonds. And the main products of the reaction, namely chloride, water and carbon dioxide, were very small at the margins of the products, with other spices taken from a thick sample of the products shown in the Fig. 7. According to the GC-Mass survey, the observed peaks are related to the following products. The products offered by the GC device included perchlorotylene, water, low levels of carbon tetrachloride and trichloroacetic acid. The long peak observed was n-Hexane, which we used as solvent. In Table 2, the list of compounds observed by the GC-Mass machine is visible along with the composition structure.

Table 2. Products obtained from photocatalytic decomposition of perchlorethylene with ultraviolet light

COMPOUND NAME	CHEMICAL STRUCTURE	COMPOUNDS PERCENT
H_2O		
C_2Cl_4		
dichloro acetic acid		
trichloro dihidrat(		
trichloro acetic acid		

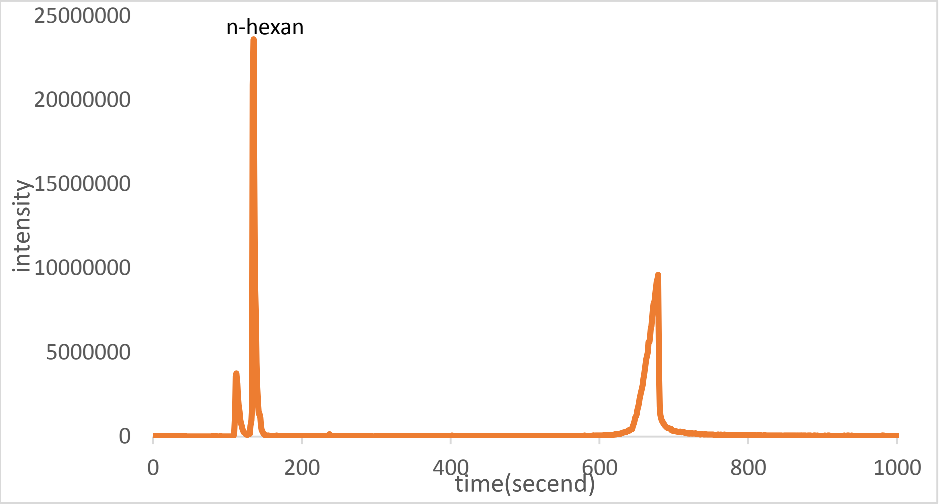


Fig. 7. Product range of UV light without photocatalyst

After finishing the work, they removed the beads and cleaned the system thoroughly with deionized water and filled with beads covered withTiO_2 catalyst. With opening air in the system, the ratio of 30% relative humidity and 3000 ppm perchloroethylene with a flow of 200 ml / min (equivalent to 1 minute) was established. After passing time and ensuring the uniform concentration of the input into the system and the concentration of the output from the system, the thermal jacket was turned on to maintain the temperature of the system and turned on the temperature of 30 degrees to equalize the internal temperature of the accumulation and condensation of gas materials in Prevent the internal part of the system. When we made sure that the reaction conditions were fixed in the system, we lit the lamp and sampled the system at different times and examined the GC-Mass device. The graph of the photocatalytic reaction was plotted as the output concentration in time.

With increasing time, perchlorotylene concentrations have decreased. According to observations made on the system's monitoring, we encountered crystals after the lamp was turned on. With excessive accumulation of reaction-induced crystals, turn off the lamp and, after collecting a large amount of crystals inside the outlet tube and collecting the sample, and dissolving them with a normal hexane solvent, a concentrated sample is collected. We injected the system into a GC-Mass device and came across compounds that are the result of a simple breakdown of perchlorotylene bonds. And the main reaction products, namely chloride acid, were water at the peak of the products.

Table 3. Table of time and concentration for UV light and TiO_2 catalyst

TIME(MIN)	**DENSITY(PPM)**	**EFFICIENCY**
0	3715.91	0
2	528.84	85.76
10	229.91	93.81
20	305.62	91.77
30	103.97	97.20
40	59.93	98.38
60	45.93	98.76
90	15.06	99.5
120	65.49	98.2
150	3.35	99.90
220	1.44	99.96
240	23.38	99.37
280	3.08	٩٩,٩١

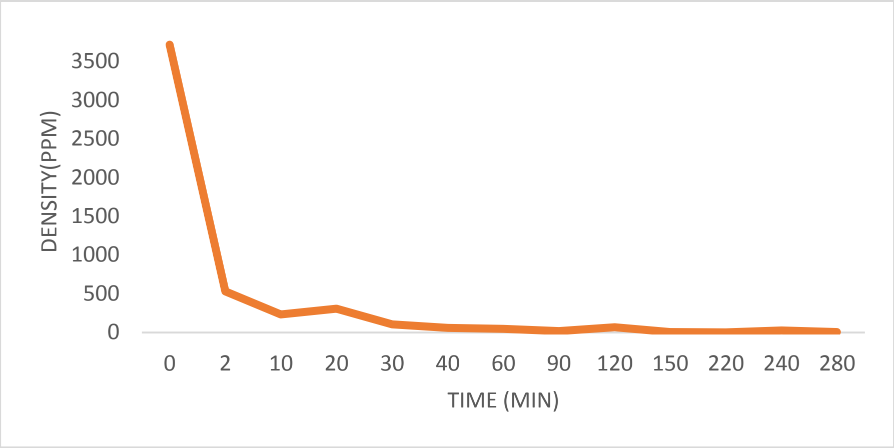


Fig. 8. Timing of the output concentration according to time with TiO_2 catalyst

The spectrum taken from a thick sample of products is shown in Fig. 9. According to the GC-Mass survey, the observed peaks are related to the following products. As shown in the diagram, the product type is different with no catalyst. Products offered by GC include percholorethylene, water, chloride-acid, a very small amount of phosgene, hexaclorothane, small amounts of carbenetrachloride and small quantities of trichloroacetic acid. The observed peak of the observed n-hexane has been used as solvent. Table 4 shows the list of compounds observed by the GC-Mass device along with the composition structure.

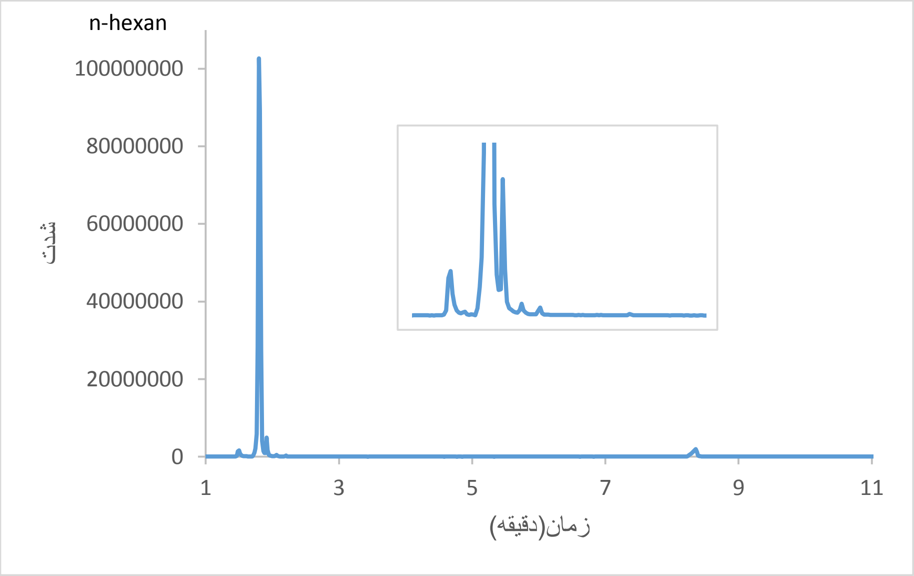
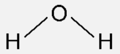
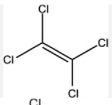
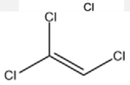
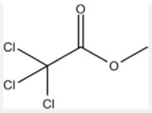
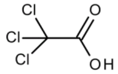


Fig. 9. Product spectrum of UV light with TiO_2 catalyst

COMPOUND NAME	CHEMICAL STRUCTURE	COMPOUNDS PERCENT
H_2O		
HCl	H−Cl	
C_2Cl_4		
Trichloroacetyl chloride		
Methyl trichloroacetate		
trichloro acetic acid		

Conclusion

The TiO_2 catalyst and ultraviolet light alone have been shown to break down the perchlorotylene bonds and changes in the compounds exited from the system, but, according to the percholorethylene degradation mechanism, no high levels of chloridric acid were observed. The TiO_2 catalyst had higher oxidation capacity than ultraviolet light and the compounds obtained in its products differed from those obtained in ultraviolet light

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