Photocatalytic Oxidation of Carbofuran Pesticide Using Zinc Oxide

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In recent years, the application of ultraviolet irradiation and zinc oxide (UV/ZnO) process water and wastewater treatment has gained removal activity of the persistence organic compounds. The degradation of carbofuran pesticide was investigated under ultraviolet irradiation and zinc oxide (UV/ZnO) process. Likewise, the effect of the operational parameters such as reaction volume, initial concentration of catalyst, initial carbofuran concentration, light intensity and pH were studied. In this study the (UV/ZnO) process at different initial concentrations (50-250 mg/L), 5 different initial pH and 5 different initial concentration of catalyst was investigated. Analyses were performed by gas chromatography mass spectroscopy. Results showed that the carbofuran initial concentration of 50 mg/L, ZnO concentration of 300 mg/L, pH of 8, light intensity of 125 watts and reaction volume of 150 mL, were the optimum condition for degradation of carbofuran by UV /ZnO system. This study demonstrated that carbofuran could be effectively degraded by ultrasonic irradiation.

Keywords: Carbofuran, Ultraviolet irradiation, Zinc oxide.

INTRODUCTION

Carbofuran ($C_{12}H_{15}NO_3$) is a well-known carbamate insecticide used to prevent insect activity in soybeans, sugar cane, potatoes, corn, rice, alfalfa, grapes tobacco, maize and vegetables¹. This insecticide is directly sprayed onto soil and vegetation immediately after emergence. It is an inhibitor of acetylcholinesterase and highly toxic to fish and mammals. This organophosphorus insecticide is highly soluble in water (350 mg L^{-1}) therefore, it is subject to leaching through the soil profile². Pesticides are toxic to living systems being carcinogenic, sometimes non-biodegradable and are often detected in surface and ground waters. The maximum concentration of carbofuran recommended by the World Health Organization (WHO) and USEPA in drinking water are 3 and $40 \mu\text{g/L}$, respectively³. Therefore the removal of carbofuran from drinking water is essential and the development of effective and inexpensive techniques for their removal from water has generated increased research interests in recent year. Advanced oxidation processes (AOPs) are commonly used to organic priority pollutants and non-biodegradable pollutants change them into carbon dioxide by producing OH radicals. Several type of AOPs have been effectively used in the treatment of water and wastewater containing pesticides. The combination of ultrasound (US) and ultraviolet irradiation⁴, $\text{UV}/\text{H}_2\text{O}_2$ ⁵, UV/TiO_2 ⁶, ultrasound/ferrioxalate/UV⁷ and UV/O_3 ⁸. The enhancement reached in the oxidation rate by the presence of the free

hydroxyl radicals in the AOPs. The applicability of the above techniques is limited some times by the economic considerations or by the strict operating conditions. The combination of oxidants with a photocatalyst has the capability of oxidizing several highly persistent compounds. Many researchers reported that Advanced oxidation processes (AOPs) was capable of degrading various pesticides such as Doong and Chang⁹ have reported the oxidation of several pesticides with the combined $\text{H}_2\text{O}_2/\text{TiO}_2/\text{UV}$ system and Dehghani and fadaei¹⁰ have reported the oxidation of organophosphorous pesticides with UV/ZnO system. Other reported the oxidation of pesticides with (AOPs), methyl parathion and dichlorvos, monocrotophos and methyl parathion¹¹⁻¹³. Several catalysts have been used and among them ZnO is one of the most effective¹⁴. Titanium dioxide is also frequently used. The biggest advantage of ZnO in comparison to TiO_2 is that it absorbs over a larger portion of the UV spectrum and the corresponding threshold wavelength of ZnO is 400 nm ¹⁵. The aim of this work was to study the removal of carbofuran by means of photocatalytic oxidation. The effect of parameters such as reaction volume, initial concentration of catalyst, initial carbofuran concentration, light intensity and pH were studied.

EXPERIMENTAL

Zinc oxide catalyst was procured from Fluka. The diameter specific surface area and band gap energy of ZnO were 14 nm,

10 m² g⁻¹ and 2.92 eV, respectively. The tested compounds in this study carbofuran (from Supellco), NaOH, HNO₃ were obtained Merck Co. (Germany). The concentration of carbofuran in samples was 50, 10, 150, 200, 250 mg L⁻¹ and used the 30 % insecticides. The samples were adjusted in reactor in 5 time of remaining 30, 60, 90, 120, 150 min. The pH of the samples solution carbofuran were 2, 4, 6, 8, 10 and reaction temperature is 25 ± 1 °C. For the photodegradation of carbofuran, a solution containing known concentration of the pesticides and ZnO nanopowder was prepared and it was allowed to equilibrate for 0.5 h in the darkness, then 50 mL of the prepared suspension was transferred to a Pyrex reactor. The samples were adjusted in reactor in 5 reaction volume remaining 150, 300, 450, 600, 750 mL. Irradiation was carried out with a 125 W medium pressure mercury lamp (Philips, Holland), which was above the batch photo reactor. The intensity of light in samples was 75, 100, 125 Watts. The distance between solution and UV source was constant, 3.75 cm in all experiments. The pH of the reaction of HNO₃ or NaOH and then the pH values were measured with pH meter (Sartorius, Germany). After that, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained by magnetic stirrer (IKA, Werke, Germany) to keep the suspension homogeneous and the suspension was sampled after an appropriate illumination time. Temperature 25 ± 1 °C by circulating water in a double jacket cooling array. For the extraction of diazinon and malathion was used techniques (DLLME) dispersive liquid-liquid microextraction¹⁶. A 5 mL of sample (water + analyte) mixed with 500 mL extraction solution (2 mL internal standard: chlorpyrifos 1000 mg L⁻¹, 10 mL chloroform with 100 mL acetone). The mixture was then centrifuged for 5 min at 3500 rpm. After this process, the upper layer of aqueous phase was collected by pipette. The droplets were sedimented at the bottom of the conical test tube and 1 mL injected in to GC/MS. Analyses were performed by gas chromatography mass spectroscopy (GC-MS). For identification, 1 mL samples were injected into the GC-MS (Varian CP-3800 GC with MS trap detector Varian Saturn 2200, run in EI mode). Injector temperature was 270 °C and analysis was done using a capillary column (Varian DB-5 column; 30 m 250 µm I.D., film thickness 0.25 µm). The method started at 150 °C, which was held for 2 min, then ramped to 120 °C at a rate of 25 °C/min, followed by an increase to 270 °C (held for 2 min) the method used a split, split ratio 1:10 Helium (99.999 %) was used as carrier gas at 1 mL/min. Data were analyzed using T-test, ANOVA one way test using SPSS software.

RESULTS AND DISCUSSION

The changes of removal percentage of carbofuran with pH value is shown in Fig. 1. It was observed that pesticide was significantly influenced by pH value of the solution and the highest removal efficiency was achieved at pH 8. About 96.3 % degradation of carbofuran was observed at pH 8. The results indicated that degree of removal percentage increases with increase in pH from 2 to 8 and then decreases. The effect of pH on the UV/ZnO reaction is commonly attributed to the surface charge of zinc oxide. The point of zero charge (pzc) of ZnO is about 9. Therefore, ZnO surface is mostly positively

charged below those pHs and negatively charged above those degree. Electrostatic attraction or repulsion between pesticide and zinc oxide happen and consequently, the carbofuran removal percentage can be improved or inhibited¹⁷. The lower rate of degradation at pH 2 may be attributed to acid corrosion of ZnO, while the lower rate at pH 10 may be due to photo-corrosion¹⁸. Therefore, the UV/ZnO process can be effectively carried out under initial pH of around 8. Solution's pH has a complex effect on photocatalytic oxidation rates. For weakly acidic pollutants, reaction rates increase at lower pH. On the other hand, pesticides which are hydrolyzed under alkaline conditions may show an increase of reaction rate with increase of pH. Finally, the presence of ionic species could affect the degradation process *via* adsorption of the pesticides, absorption of UV light and reaction with hydroxyl radicals¹⁹. Therefore, the pH of the solution can play a key role in the adsorption and photocatalytic oxidation of pesticide.

Fig. 1. Comparison of removal percentage for UV/ZnO process at different pH of carbofuran

Effects of ZnO amount: Effect of catalyst amount is the concentration of carbofuran shown in Fig. 2. The highest removal percentage was observed when 300 mg L⁻¹ of catalyst was used. The decrease at higher loading beyond the optimum dosage is owing to decrease in the light penetration. Additional,

Fig. 2. Comparisons of removal percentage in UV/ZnO system of carbofuran at different catalyst dose. [carbofuran]₀ = 50 mg L⁻¹, pH = 8

at higher catalyst loading, it is difficult to maintain the suspension homogeneous due to particles agglomeration, which decreases the number of active sites²⁰. The use of excessive amounts of catalyst may reduce the amount of energy being transferred into the medium due to the opacity offered by the catalyst particles. For economic removal of pesticides from the water and wastewater, the optimum amount of catalyst is necessary to be determined for efficient removal since reaction rate has been found to be dependent on the catalyst loadings²¹.

Effect of initial concentration carbofuran: The effect of initial concentration of carbofuran on the removal percentage was studied by several different the initial concentration over a wide range from 50 to 250 mg L⁻¹. The results are illustrated in Fig. 3. The photocatalytic degradation of carbofuran was shown to decrease from 92.6 to 16.5 % as the initial concentration increases from 50 to 250 mg/L. The value of photodegradation decreased with increasing of initial concentration of carbofuran²². For this reason the available OH radicals are inadequate for pesticide degradation at higher concentrations. Consequently the pesticide degradation rate decreases as the concentration increases²³. In addition, an increase in the initial concentration of carbofuran can lead to the generation of intermediate products. Many studies have shown that the initial pesticide concentration has a significant effect on the photocatalytic removal rates. High concentrations can cause deactivation of the catalyst, which require in certain cases dilution of the highly concentrated solutions to again high efficiency removals²⁴.

Fig. 3. Effect of initial concentration on photodegradation of carbofuran

Effect of reaction volume: The effect of reaction volume of carbofuran on the removal percentage shown in Fig. 4. It is seen that the degradation under UV/ZnO increased with decreasing reaction volume. The effect of volume change is less significant in UV/ZnO irradiation. This improvement in the photocatalytic degradation is attributed to the decrease in the thickness of the irradiated region which minimises the reduction of the UV intensity through the solution²⁵.

Effect of light intensity: The effect of light intensity on the photodegradation of the carbofuran was studied in the range of 75 to 125 Watts. shown in Fig. 5. It is seen that the degradation under UV/ZnO increased with increasing light intensity.

Fig. 4. Influence of reaction volume on removal percentage of carbofuran

With increase light intensity, the rate electron-hole pair formation at the ZnO surface increases and consequently so does its ability to oxidize pesticide²⁶. Light intensity distribution within the reactor consistently determines the overall pesticide change and degradation efficiency²⁷. Therefore, the rate of photocatalytic removal increases when more radiation fall on the ZnO surface and hence more hydroxyl radicals are produced²⁸.

Fig. 5. Effect of light intensity on the removal of carbofuran in presence of ZnO

Conclusion

In this study, the synergistic effects of UV and ZnO for the degradation of carbofuran with different factors were investigated. The major factors affecting UV/ZnO process are: initial pesticide load, amount of catalyst, reaction volume, UV irradiation time, temperature, pH, light intensity and presence of scavengers.

So far, UV/ZnO process has been extensively used for water and wastewater treatment. The key advantages of this process are the operation at ambient conditions, the lack of mass transfer limitations when nanoparticles are used as photocatalysts and the possible use of solar irradiation. In UV/ZnO process most of the produced holes and conduction band electrons. However, several topics such as the relatively high operational cost of these processes due to the use of costly chemicals and the increased energy consumption, as well as the formation of unknown intermediates which in some cases

could be more toxic than the parent compounds remain unsolved. Moreover, all these methods are susceptible to scavenging of hydroxyl radicals by non-target substances, while they are not suitable for certain categories of toxic compounds which resist attack by hydroxyl radicals.

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