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14. ABSTRACT

This report results from a contract tasking American University of Sharjah as follows: To achieve the goals of the project, three major tasks will be performed:

Task #1: The development of nanoclusters embedded in zeolites as potential photocatalysts.

Task #2: Identify conditions for optimum synthesis of nano-sized tungsten oxide (WO₃) based materials. We will investigate synthetic sol-gel strategies for incorporating mixed metal into the WO₃ framework.

Task #3: Surface analysis and catalytic studies.

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“Synthesis of metal nanoclusters doped in porous materials as photocatalysts”

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1. Summary

The prepared nanoclusters of silver doped into the mordenite host show strong luminescence emission that depends on the excitation wavelength. These variations in the emission modes are due to the site selective luminescence where various luminophores might be excited upon selecting the proper excitation wavelength. The selected material was found to have strong affinity to absorb/adsorb quinalphos pesticide which is widely used for the protection of several vegetable and fruit crops. The silver nanoclusters in zeolites enhance the photodecomposition rates of the pollutants when compared to the pollutant's behavior in the absence of silver doped zeolites. HPLC and GC-MS techniques were used to follow the kinetic data and to identify the photodecomposition products, respectively. The presence of the Ag-mordenite catalyst not only adsorbs the quinalphos from the solution, but it also reduces the toxic effect of the pesticide as determined in this study.

2. Introduction

Pesticides are widely used for the control of agricultural pests and as insecticides for various purposes. In the last few decades, pesticides have been reported to seriously affect non-targeted individuals due to their use in large quantities, leading to a variety of neuropathological disorders and disturb the biochemical processes [1]. Most pesticides may cause neurotoxicity due to their ability to cross the blood–brain barrier and exert central nervous system toxicity [2].

Quinalphos (O,O-diethyl, O-2 quinoxalinyyl phosphorothioate) is used on vegetables, fruits, cotton, groundnuts, cereals and rice. It is rapidly metabolized in plants, animals and soil and it is converted into 2-hydroxyquinoxaline, O,O-diethyl phosphorothioate and O,O-diethyl phosphate [3]. It is a colorless crystalline solid with broad spectrum contact and stomach organophosphorus insecticide and acaricide (see structure 1). The pure compound is stable at 208°C for 1 yr. The formulations are stable for 2 yr. In addition, quinalphos is highly acutely toxic to mammals, with oral LD50 values ranging from 14 to 137 mg/kg in rats [3,4]. Therefore, due to the high stability, toxicity and its wide usability, we tempted in this work to provide materials that decontaminate water resources from quinalphos pesticide. As presented in my previous report (Mid-report), I was successful in preparing various catalysts with different surface properties to tune the catalytic activities toward organic pollutants such as pesticides.

For example, monoclinic tungsten oxide (m-WO₃) powders and films has generated significant interest because of their photocatalytic applications [5-9], photochromic behavior [10,11], and their use in semiconducting metal oxide (SMO) based sensors for the detection of gaseous adsorbates [12-15]. Since, the commercial m-WO₃ particles are considered as poor materials with 1-5 micron diameter with surface areas of 1-2 m²/g. So we were able to modify receipies to fabricate tungsten oxide based materials with high surface area. In addition, zeolites are aluminosilicates with well-defined pore and channel structures. Because of their porosity and surface properties we were able to modify these materials by doping an active sites based on metal nanoclusters such as silver ions.

This final report focuses on applying the materials that were prepared and characterized during phase 1 of this project (see Mid-report) for the photodecomposition and adsorption properties of the studied pollutants.

3. Methods, Assumptions, and Procedures

3.1. Preparation of silver clusters doped into mordenite: Silver clusters were doped in mordenite via cation exchange process of Na-Mordenite with Tollen's solution (Mixture of silver nitrate solution in minimum amount of ammonia) for 12 hours at 70 °C. The product was filtered, washed five times with distilled deionized water (ddH₂O), and dried at 375 K for two hours. Before spectroscopic measurements were taken, silver doped in zeolite sample was pretreated as follows: degassed at room temperature for one hour, calcined at 450 K in the presence of 20 torr of O₂ for one hour, and finally degassed at 450 K for 2 hours.

The silver loadings were analyzed using an ICP Perkin-Elmer Optima with a rf power of 1300 W. The samples were digested as follows: 10 mg of the Ag-zeolite was mixed with 200 μL of 48% hydrofluoric acid and 200 μL 9M sulfuric acid. The sample was then diluted to a total volume of 10 mL using ddH₂O. The metal free zeolite was used as a blank. A standard solution of 200 mgL⁻¹ silver was used to obtain a calibration curve.

3.2. Irradiation of pollutant molecules: A 60 ppm stock solution of quinalphos pesticide was prepared in a 10:90 v:v% methanol:water mixture. All solutions were prepared immediately before beginning the irradiation experiments and diluted accordingly to obtain the correct solution concentrations in the photochemical reactions. All irradiations were performed using UV lamp which emits a narrow band of irradiation at 302 nm (model midrange UV lamps from VWR Scientific, Inc). . The relative intensity of the lamp is 1300 μW/cm² at 3 inches.

Each sample was irradiated in quartz test tubes that have an inside diameter of 12.5 mm, a length of 10 mm, and 1 mm wall thickness. Only one test tube was irradiated at a time. The quinalphos solutions were prepared and exposed to UV light at a distance of 3.0 inches, where a maximum output of the lamp was reached. A test tube rack was set flat on the bench in such a way that if a tube was inserted into the rack, light from the lamp would shine directly onto it. A rectangular holder covered with aluminum foil to help bounce light back from the lamp.

3.3. HPLC and GC-MS analysis: HPLC was used to quantify the irradiated samples from the photolysis experiments. Samples were analyzed on Agilent 1100 series High Performance Liquid Chromatograph equipped with an operating software Chemstation for LC 3D with diode-array detector. Separations were made on a Zorbax Eclipse XDB-C8 column, 150 mm x 4.6 mm, 5 μ particle size. Flow rate was 1 mL/min for all experiments. The mobile phase used was 60% methanol, 40% of 0.1 M KH_2PO_4 buffer solution at pH = 3.0. The detector was set to monitor 234 nm.

GC-MS measurements were made on a Varian CP-3800 Gas Chromatograph with a Varian Saturn 2000 GC/MS/MS serving as the detector. A 30 m x 0.25 mm ID DB-5 MS column from J&W Scientific was used. Components of various samples were separated using the following parameters: injector temperature set at 373K, and detector temperature set at 593K. The initial oven temperature of 373K was held for 3 minutes. Then the temperature was ramped to 373K at a rate of 20°C/min and held constant for 3 minutes. Finally, the temperature was ramped to 553K at the rate of 20°C/min and held constant for 3 min. Helium was used as the carrier gas with a flow rate of 1 mL/min. Samples were filtered through a Gelman 2mm Acrodisc® syringe filter to remove any particles that may obstruct the column.

3.4. Toxicity testing protocols.

Fruit Fly (*Drosophila melanogaster*). The flies used in this experiment were taken from the laboratory reared or cultured wild type *Drosophila*. They were cultured on a medium containing a mixture of starch, sugar, yeast, agar powder in certain proportions. The cooked molten media were dispensed in culture milk bottles and were sterilized by autoclaving before the addition of Quinalphous and/or zeolite of desired concentrations before the media solidified. Ten flies were transferred on each bottle of medium containing a specified concentration of the substances tested. Rate of mortality were observed in relation to the dose or concentration of the test substances.

4. Results and discussion.

4.1. Emission spectroscopy (same as in Report 1). A sample of silver nanocluster doped in mordenite zeolite was prepared and ICP analysis showed that the silver loading was 2.5 wt%. The prepared sample shows rich luminescence properties that depend on the excitation wavelength and temperature. Figure 1 shows the emission spectra of the Ag-mordenite zeolite sample recorded at 77 K and at the indicated excitation wavelengths. Two major luminescence bands with maxima at 415 and 520 nm were observed upon excitation at the wavelengths indicated in the figure. Since the luminescence of d^{10} systems has a demonstrated sensitivity toward metal-metal interactions, different emission bands are expected to occur from various silver centers in the zeolite framework [16-18]. The large dependence of the emission properties of silver nanoclusters doped in mordenite on the excitation wavelength explains the formation of silver nanoclusters with various sizes in the zeolite framework where each emission band is associated with a different excitation peak.

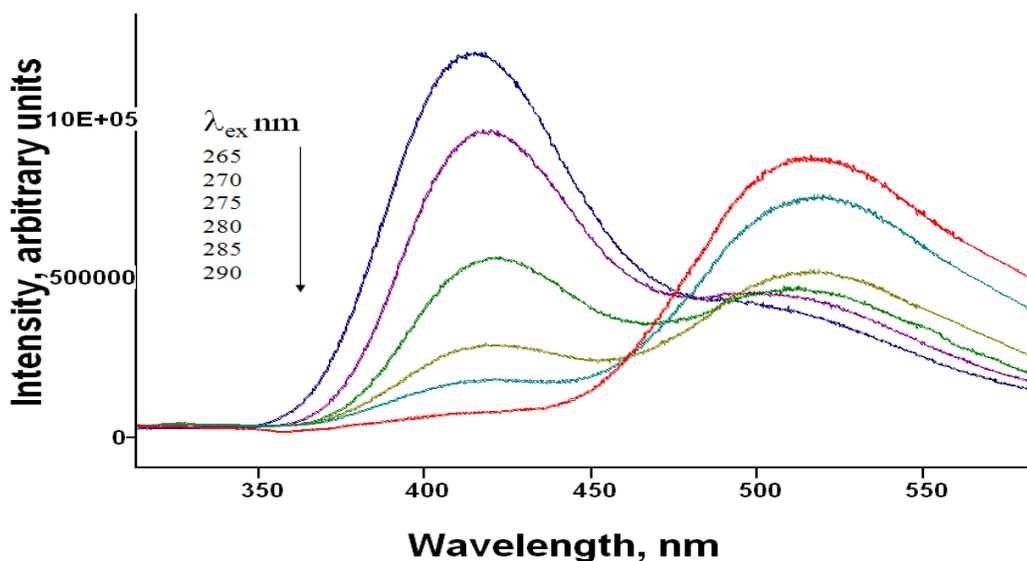


Figure 1. Emission spectra of Ag-Mordenite monitored at 77K and at various excitation wavelengths.

4.2. Catalytic properties of the prepared materials toward quinalphos pesticide.

The aim of this work is to test the catalytic properties of various materials prepared in phase 1 toward the photodecomposition of pesticides namely quinalphos. The choice of quinalphos stems from its wide spread use on vegetables, fruits, cotton, groundnuts, cereals and rice. The molecular structure of Quinalphos is illustrated in Figure 2.

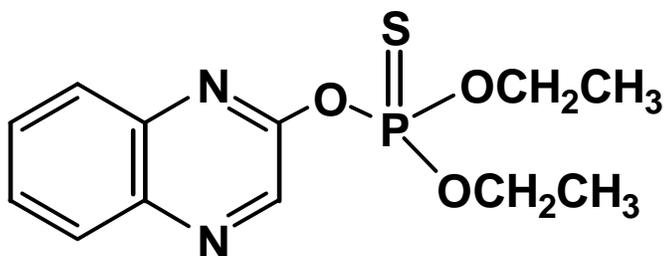


Figure 2. Chemical structure for Quinalphos pesticide.

Several catalysts were tested for the decomposition of quinalphos pesticide. For example, the WO_3 based samples were found to be inactive upon irradiation. This was due to the fact that the active surface sites of the WO_3 - based materials are fully saturated with water that is adsorbed on the surface. Therefore, the presence of water reduces the activity of these compounds. In contrast, the results obtained on silver doped mordenite catalyst are interesting and will be explained in this report.

Figure 3 shows the emission spectra of a 60 ppm solution of quinalphos recorded upon the exposure to 302 nm UV light for different times. As shown in Figure 3, quinalphos shows a weak emission band at 435 nm upon excitation at 290 nm. Upon irradiation, a new emission mode at 380 nm was observed. As shown in Figure 3, the 380 nm band's intensity increases with the irradiation time.

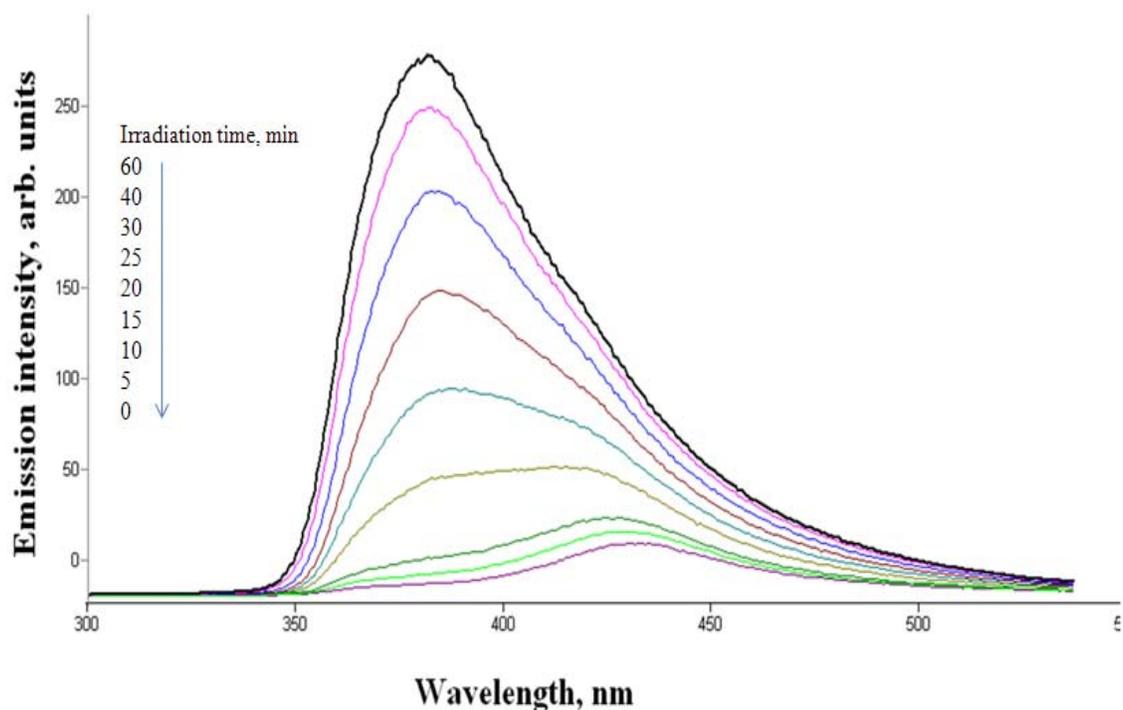


Figure 3. Emission spectra of 60 ppm quinalphos aqueous solution irradiated for various times.

This result suggests that irradiating the quinalphos solution gives products that are fluorescent. GC-MS analysis for the irradiated products, suggest the formation of 2-quinoxalinol. To support this conclusion, we have purchased a pure sample of 2-quinoxalinol. Figure 4, shows the emission spectra of three solutions of quinalphos, 2-quinoxalinol, and the irradiated product for 60 minutes. As shown in Figure 4, both the irradiated quinalphos and the standard solution of 2-quinoxalinol give the same emission mode, as expected.

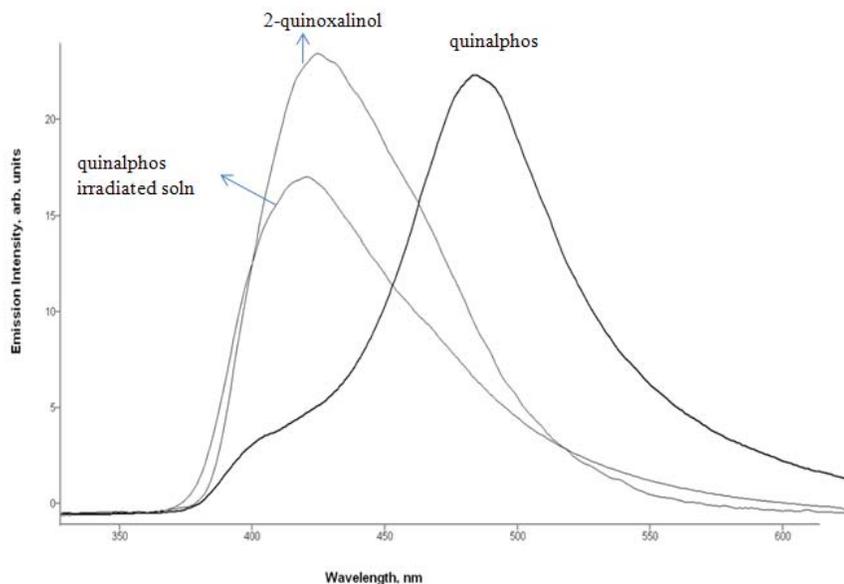


Figure 4: Emission spectra of quinalphos , irradiated quinalphos for 60 minutes, and 2-quinoxalinol solutions recorded at $\lambda_{exc} = 300$ nm

Since the emission intensity of quinalphos is weak, we used the HPLC technique to follow and analyze the kinetic data for the irradiation experiments. Prior to the kinetic experiments, we used HPLC to identify a pure quinalphos solution. Figure 5 shows the HPLC chromatogram for 60 ppm solution of quinalphos. As shown in Figure 5 two bands were observed which indicates the presence of a hydrolyzed product (appears after 2.75 minutes) along with quinalphos (appears after 4.76 minutes). Interestingly, the quinalphos mode (at 4.76 minutes) disappeared upon mixing of 5 mL of 60 ppm quinalphos with a 10 mg sample of the catalyst. This result is exciting since, the quinalphos pesticide was fully adsorbed on the catalyst. To test the adsorption capacity, 1.0 mL of 2000 ppm quinalphos solution was mixed with various amount of the Ag-Mordenite catalyst. The HPLC results are shown in Figure 6. As shown in Figure 6, only quinalphos is being adsorbed on the catalyst since the intensity of the band appears at 4.76 minutes is reduced while the band's intensity for the 2.75 min product is fixed. The adsorption capacity of the catalyst was determined and is illustrated in Figure 7.

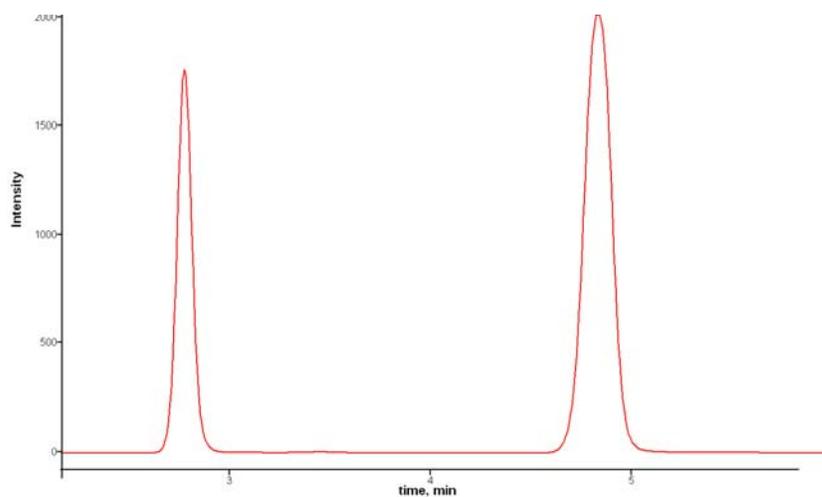


Figure 5. HPLC chromatogram for 60 ppm quinalphos solution.

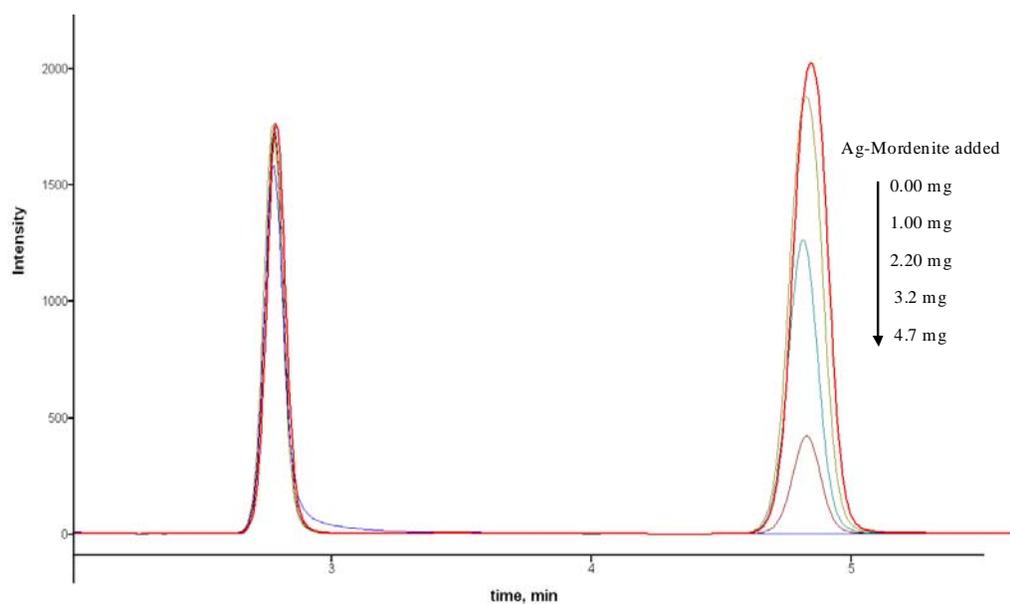


figure 6. HPLC chromatograms for quinalphos added top various amount of Ag-Mordenite. **F**

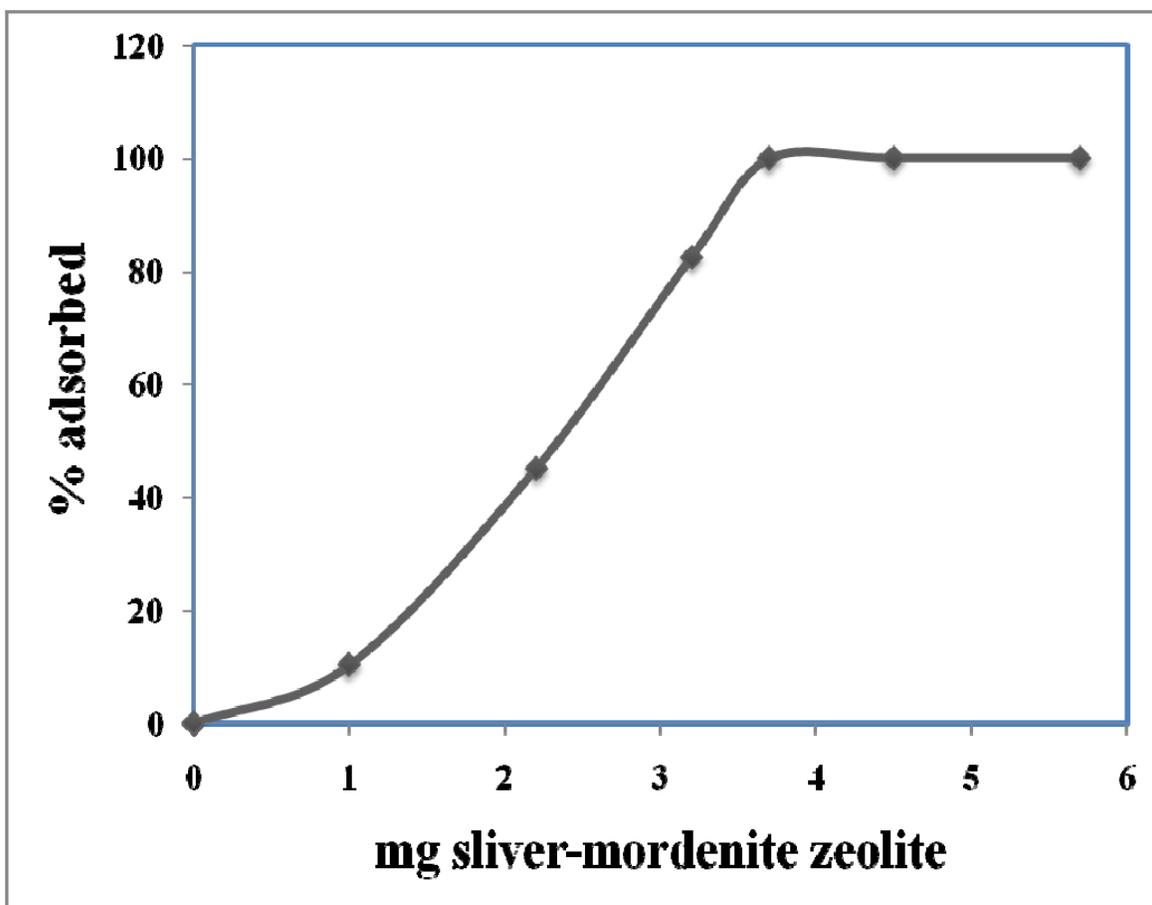


Figure 7: Adsorption profile of quinalphos over Ag-Mordenite catalyst.

Since, the Ag-mordenite material has a strong capacity to adsorb quinalphos, it is difficult to monitor the decomposition kinetics for this pesticide. However, we tested the catalytic properties of Ag-mordenite toward the hydrolyzed product 2-quinoxalol. Figure 8 shows a plot of $\ln [2\text{-quinoxalinol}]$ vs irradiation time in the presence and the absence of the catalyst. It is clearly shown that the presence of the zeolite catalyst enhances the photodecomposition of the studied sample (2-quinoxalinol). The photodecomposition products of irradiated quinalphos in the presence and the absence of the catalyst were also analyzed using GC-MS. Irradiated quinalphos solution for 24 hours gave only one product, 2-quinoxi. Whereas, the irradiated solution in the presence of the catalyst gave the products shown in Figure 9.

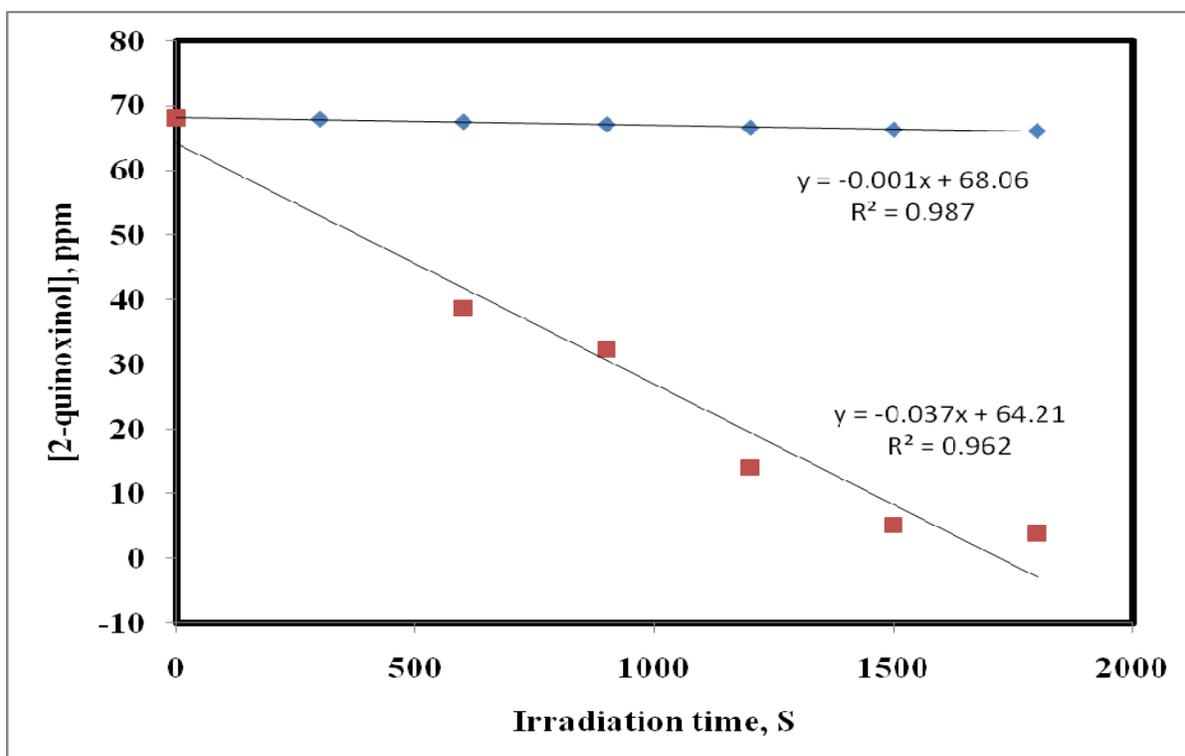


Figure 8. Kinetic data for 2-quinoxalinol irradiated in the presence and the absence of the catalyst

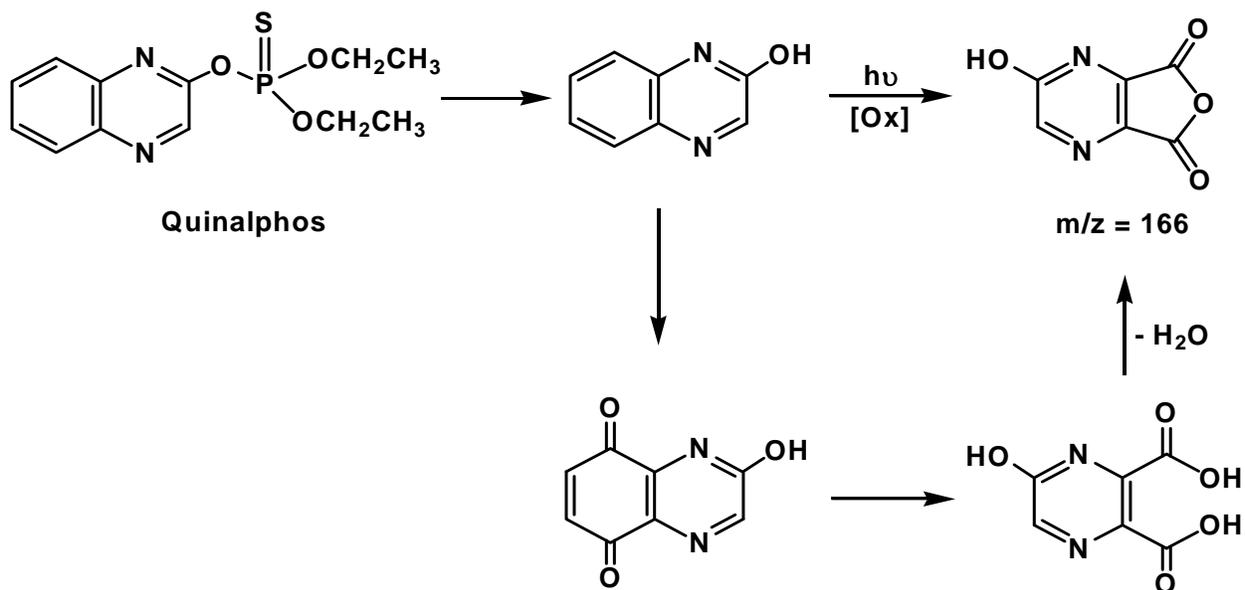


Figure 9. Schematic diagram represents the photodecomposition products of quinalphos over Ag-Mordenite catalyst.

4.3. Toxicity testing.

Fruit Fly (*Drosophila melanogaster*) were cultured on a medium containing a mixture of starch, sugar, yeast, agar powder in certain proportions. The cooked molten media were dispensed in culture milk bottles and were sterilized by autoclaving before the addition of quinalphos and/or zeolite of desired concentrations before the media solidified. Ten flies were transferred on each bottle of medium containing a specified concentration of the substances tested. The rate of mortality was observed in relation to the dose or concentration of the test substances. Figure 10 shows the effect of quinalphos and quinalphos-adsorbed on zeolite that were mixed with their sterilized food on the Fruit fly population. As shown in Figure 10, in the presence of the sterilized food, the population was constant at 100%. Whereas, all flies were died after 60 minutes in the presence of quinalphos alone. Interestingly, the adsorbed quinalphos on zeolite reduces the toxic effect by 50% where the flies population became zero after 150 minutes. Beside the population counts, the flies activity was found to be reduced when quinalphos was only presented in the food, while they were significantly active in the quinalphos-zeolite medium.

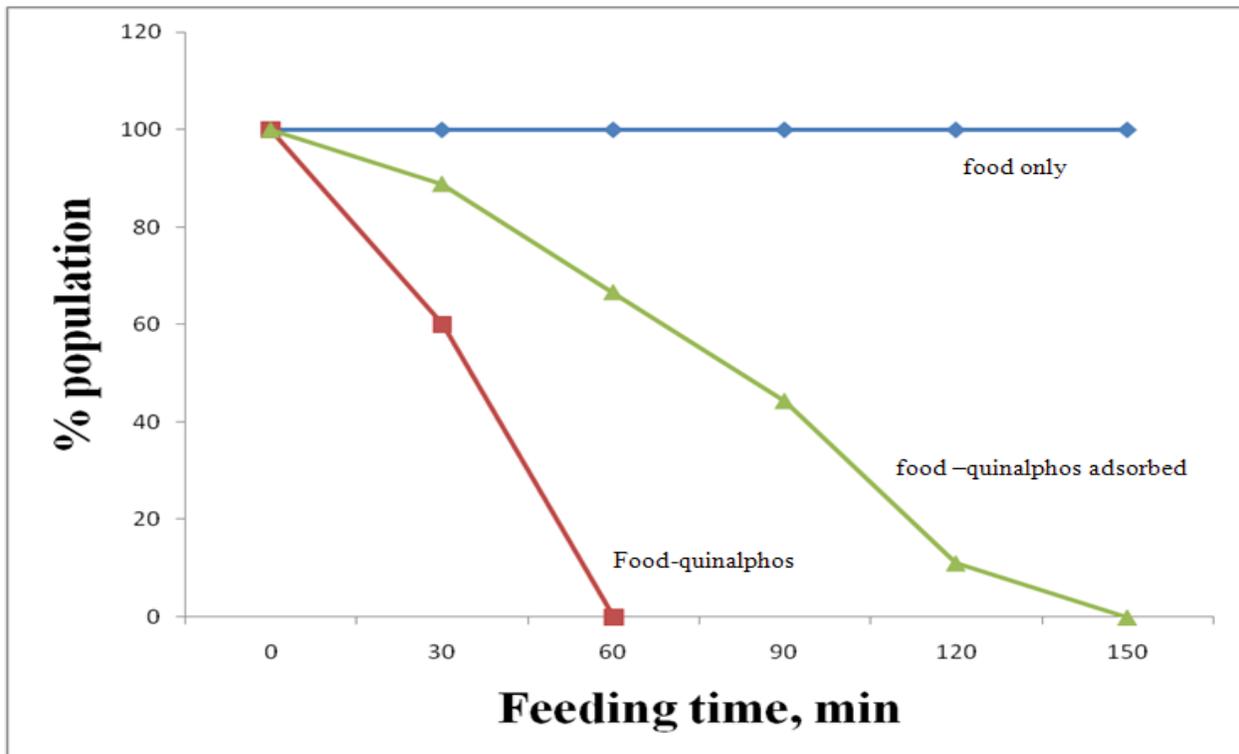


Figure 10. The toxic effect of quinalphos and quinalphos- surface on the tested flies.

5. Conclusions:

Silver clusters doped into the mordenite framework were prepared and characterized. The materials were found to be a good adsorbate for quinalphos pesticide. In addition, the toxicity of quinalphos was lowered upon its adsorption on the catalyst. The photodecomposition of quinalphos in the absence of the catalyst leads to the formation of 2-quinoxalinol while the presence of the catalyst provide further decomposition products. No catalytic properties were found on nano-WO₃-based materials. This is mainly due to the presence of water which strongly binds to the active sites on the surface.

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