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Mixed silver–zinc encapsulated zeolite-Y powders toward the photodegradation of aqueous fenoxycarb solutions

Sofian M. Kanan[a,*], Ahmed Malkawi[b]

[a]*Department of Chemistry, American University of Sharjah, P. O. Box 26666, Sharjah, UAE, Tel. +971-6-515-2409, email: skanan@aus.edu*
[b]*Department of Chemistry, Northwest Missouri State University, 800 University Drive, Maryville, MO 64468, USA, Tel. +1-660-562-1295, email: amalkaw@nwmissouri.edu*

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ABSTRACT

Mixed silver–zinc doped in zeolite Y was prepared via cation exchange process. Two samples with various silver and zinc contents were prepared as well as two samples modified with microwave treatment before the calcination process. The prepared samples behave as good adsorbents towards fenoxicarb where up to 30% of the pesticide was removed from solutions upon mixing for one minute. In addition, all of the modified materials tend to enhance the photo-degradation of fenoxicarb when irradiated at 254 nm UV light. The study indicates that Ag-ZnY1 (10.7% Ag and 10.32% Zn) provides the best catalytic activity towards the degradation of fenoxycarb where the rate constant was 0.041 min^{-1} compared to the observed rate constant of 0.0162 min^{-1} for the similar test without a catalyst. In addition, both microwave samples provide an enhancement in the photo-degradation by 1.6–1.7 times compared to the zeolite-free samples. The data showed that silver played the major role in the observed catalytic activity. For example, the rate constant of the Ag-ZnY1M sample (1.8% Ag and 0.20% Zn) was 0.0283 min^{-1} while the reaction proceeds with a rate constant of 0.0270 min^{-1} when Ag-ZnY2M (0.90% Ag and 0.30% Zn) catalyst was used. GC-MS analysis of the irradiated solution of fenoxycarb for 60 min showed the formation of 4-(2-aminoethoxy)phenol ethane as the major product.

Keywords: Zeolite; Fenoxycarb; Silver; Zinc; Pesticide; Luminescence; Photo-catalysts

1. Introduction

Pesticides are chemical agents that are meant to kill, incapacitate, or repel pests. They are often employed to protect crops and food-stores and to reduce the spread of disease [1]. While pesticides are desired to be selective towards a particular organism, this level of selectivity is rarely seen [2]. Often, pesticides affect other species, reducing biodiversity and eventually causing a decline in the habitat where they are employed [3,4]. Moreover, pesticides can contaminate water and soil, leading to their uptake by both plants and animals [5]. Consumption of pesticide-contaminated products can lead to a variety of adverse health effects, ranging from simple irritation to cancer [6]. As such, several methods of eliminating or containing the effects of pesticides have been developed. Methods for the removal of organic pollutants from water include physical (adsorption or settling), biological and chemical treatment [7–13]. However, photo-catalytic degradation (decomposition via exposure to light) is one of the more efficient methods of pesticide and organic pollutants removal. As Hupka et al. explains, “photo-catalytic degradation is ideal in bodies of water where the pesticide concentration is too high for biological treatment” [14]. In addition, Al Hattab noted that a disadvantage of using adsorbents to remove pesticides is that they do not actually destroy the pesticide and must consequently be disposed of after use [7].

The degradation process can be further catalyzed by the introduction of silver-doped zeolites. The zeolites

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*Corresponding author.

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adsorb the pesticide, bringing it into contact with silver which catalyzes its decomposition under UV radiation [15–17]. Silver-doped zeolites have been proven to effectively catalyze the breakdown of different types of pesticides [15,18,19]. Zeolites are alumino-silicates that possess micro-porous structures. They are employed in a variety of fields as adsorbents, molecular sieves (i.e.: they are selective towards molecules via size exclusion), ion exchangers and catalysts [20–23]. Numerous studies have been published by the authors involving zeolite assisted photo-catalysis of organic pollutants, for example, carbamate-based pesticides [24–33]. The zeolites in these studies are used as adsorbents for the various pollutants as well as acting as supports for metal-based photo-catalysts that can degrade the pollutants [17,25]. Different zeolites are distinguished typically by their Al/Si ratio, micro-structure and pore diameter. Due to their porosity and high surface area, zeolites have the ability to capture molecules and ions onto their surface [29,31–34]. This property has allowed researchers to use zeolites in separation and purification processes, where a particular component of a mixture may be removed, and as the base for metal as photo-catalysts [29,31,32,34]. With regards to the adsorption of metals ions, this occurs due to the negative charge present in the zeolite as a result of AlO_4^- being included in the framework structure. Silver and gold doped into zeolites have been identified as active photo-catalytic materials in aqueous solutions. This photo-catalytic activity is due to their tendency to aggregate and form nanoclusters within the pores of a zeolite and on its surface as well [31]. Silver is also chemically stable and can operate as a photo-catalyst under low UV conditions. Faujasite Y is typically chosen as the base for metal encapsulation due to its large pore sizes with high surface area, which allow the clustering of the metal ions to occur [35].

Fenoxycarb (ethyl N-[2-(4-phenoxyphenoxy)ethyl] carbamate) is a non-neurotoxic carbamate insect growth regulator (Fig. 1). Its primary mode of action is mimicking insect juvenile hormones, thus preventing the targeted insect from reaching maturity. Fenoxycarb has a relatively low solubility in water (6.0 mg/L), and shows a tendency to adhere to soil, meaning that it is less likely to contaminate ground water. However, when present in water, it shows considerable resistance to hydrolysis. As noted by Sullivan, the half-life of fenoxycarb in aqueous media with pH of 5, 7 and 9 are 1406, 3136 and 4101 d, respectively [36]. It is, however, susceptible to photolysis; fenoxycarb decomposes in 18–23 d when exposed to UV radiation.

Fenoxycarb is generally nontoxic to mammals and has been shown to have minor immediate effects if consumed by humans in small amounts. There is little information on the long term effects of exposure to fenoxycarb. However, Oda et al. reported that fenoxycarb may cause neonatal defects [37]. Furthermore, fenoxycarb is notably toxic to various species of fish. The LC_{50} ranges from 0.6 ppm (48 h) for Daphnia to 1.6 ppm (96 h) for Rainbow Trout [35]. In the present work, various samples of Zn-Ag coupled system supported onto Y-zeolite were prepared as substrates for testing the possibility of increased photo-catalytic activities. To follow the activity of the obtained systems, they were used in photo-degradation of aqueous fenoxycarb. Effects of the zeolite-metal composition and the microwave treatment were investigated for their effectiveness in degrading aqueous samples of fenoxycarb.

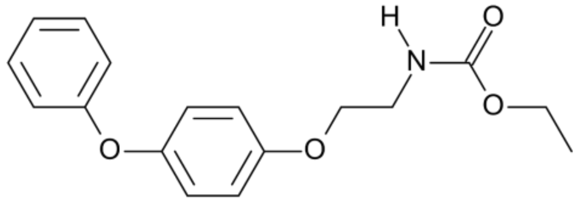

Fig. 1. The molecular structure of fenoxycarb.

2. Experimentation

2.1. Chemicals

Fenoxycarb (Ethyl N-[2-(4-phenoxyphenoxy)ethyl] carbamate) crystals under normal conditions having a 99.6% purity was purchased from Chem Service Inc. Quinalphos solutions were prepared at room temperature in 5:95 V:V% methanol : water (de-ionized). All solvents were purchased from Sigma-Aldrich Chemical Company and were HPLC grade. Analytical-grade standard aqueous solutions of 100 mg/L silver and 100 mg/L zinc were purchased from Sigma-Aldrich Chemical Company. Silver nitrate (ACS reagent, 99.0%) and ammonium hydroxide (30% aqueous solution) were purchased from Fischer Scientific. Zeolite Y was received from Zeolyst International. All chemicals were used as received without further purification.

2.2. Sample preparation

2.2.1. Preparation of Ag-ZnY1 and Ag-ZnY2 samples

Two solutions containing both silver and zinc were prepared. In preparing solution 1, 1 mmole of silver nitrate in 10 mL ammonia and 1.0 mmole of zinc acetate were dissolved in deionized water. Solution 2 was prepared by dissolving 10.0 mmoles of silver nitrate and 1.0 mmole of zinc acetate. Two samples containing approximately 5.0 g of zeolite Y were transferred to separate conical flasks with solution 1 and solution 2 being gradually added. The resulting solutions were stirred for 48 h at 75°C. Afterwards, each solution was divided into two portions. One portion was filtered and the powders were collected and dried at 100°C for 24 h. Subsequently, the samples were annealed under nitrogen atmosphere at 300°C for 24 h.

2.2.2. Preparation of Ag-ZnY1M and AgY2M

The stored portions that were taken from the above solutions were digested with 5.0 mL of nitric acid followed by microwave digestion that was done using QLAB 6000 from Questron Technologies Corp. The temperature of the vessels reached 190°C and was held at this temperature for 30 min. The mixture was then filtered and the zeolites were collected and dried for 24 h at 100°C before being annealed under nitrogen atmosphere at 300°C for 24 h.

2.3. Instrumentation

The photo-decomposition of fenoxycarb with time was monitored via a Cary Eclipse fluorescence spectrophotometer. The SEM images were taken using the casting method from a suspension of the zeolites in methanol. The images were taken using a Tescan VEGA III LMU scanning electron microscope (Oxford Instrument EDS); the range of accelerating voltage was 0.2–30 kV.

The lamp (VWR Scientific, Inc.) uses black-light bulbs to emit UV radiation at either 254 nm or 302 nm. It contains two 4-watt tubes that emit shortwave (254 nm) and medium wave (302 nm) UV radiation.

The silver and zinc loadings were analyzed using ICP Perkin-Elmer Optima with 1,300 W rf power. The samples were digested as follows: 0.250 g of the zeolite was mixed with 9.0 mL of 1.0 M nitric acid. Two standard solutions of 100 mg/L silver and 100 mg/L zinc were used to obtain a calibration curve. Nitrogen adsorption/desorption isotherm was used to determine the surface area of the modified samples.

Gas Chromatography-Mass Spectrometry (GC-MS) measurements were made on a GC-2010 Plus and GCMS-QP2010 Ultra Shimadzu. The Mass detector is Electron Ionization Quadropole MS. A 30 m × 0.25 mm ID Factor Four VF-5 MS column was used. Components of various samples were separated using the following parameters: injector temperature set at 150°C, and detector temperature set at 320°C. The initial oven temperature of 80°C was held for 3 min before the temperature was ramped to 150°C at a rate of 20°C/min and held constant at this temperature for 3 min. Finally, the temperature was ramped to 300°C at the rate of 20°C/min and held constant at 300°C for 3 min.

2.4. Irradiation of pollutant molecules

Stock solutions (30.0 ppm) of the pesticide fenoxycarb were prepared in a 10:90 V:V% methanol:water mixture. All solutions were prepared immediately prior to the irradiation experiments and diluted accordingly to obtain the correct solution concentrations need for the photo-chemical reactions. All irradiations were performed using UV lamp, which emits a narrow band of irradiation at 254 nm (model short range UV lamps from VWR Scientific, Inc.) with a relative intensity of 1300 µW/cm^2 at a distance of 3 inch. Each sample was irradiated in quartz test tubes with an inside diameter of 12.5 mm, a length of 10 cm, and 1 mm wall thickness. Only one test tube was irradiated at a time. All solutions were prepared and exposed to UV light at a distance of 3.0 inch, where a maximum output of the lamp was reached. The same procedure was followed for the fenoxycarb solutions containing 50.0 mg of the zeolite catalysts Ag-ZnY1, Ag-ZnY2, Ag-ZnY1M, and Ag-ZnY2M.

3. Results and discussion

Images of SEM for all samples were captured with various magnifications. Fig. 2 shows an example of the SEM image for Ag-ZnY1 sample as well as a depicted EDX elemental analysis profile. For every zeolite test sample, at least 3 sampling sites were depicted for the EDS surface analysis with the average metal contents is recorded in Table 1. It is primarily seen that the microwave digestion reduces the silver and zinc loadings in both samples. The analysis also shows that Ag-ZnY1 has the highest metal content overall. To determine the exact metal loading in bulk samples, ICP analysis was also conducted. As shown in Table 1, the metal content mostly corroborates that microwave digestion lowers the metal loading in the zeolite samples. However, both Ag-ZnY1M and Ag-ZnY2M held a very small amount of silver and zinc.

The BET surface area of the four catalysts was also determined using a Quantachrome Autosorb iQ and grade 5 (99.999%) nitrogen gas with all results recorded in Table 2. The results show that the digested samples are with lowest surface area when compared to the analogue samples without digestion. SEM images showed that the microwave digestion changes the surface morphology of the doped zeolite samples where the pores of the zeolite being reduced, which explains the reduction in the surface area and likelihood of adsorption in addition to the random distribution of the loaded metals of the samples. The highest surface area was recorded for Ag-ZnY2 while Ag-ZnY2M displayed the lowest area.

Fig. 3 shows the emission spectra of a 30.0 ppm fenoxycarb solution recorded at λ_{ex} = 272 nm before (labeled as t = 0) and after the exposure to 254 nm UV light for several

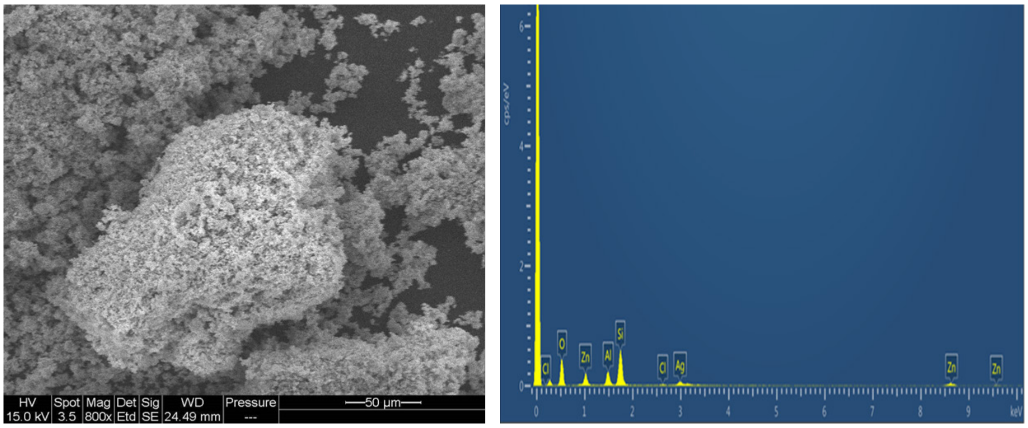

Fig. 2. SEM image for Ag-ZnY1 catalyst and the EDS analysis profile for depicted area.

Table 1
The silver and zinc contents of the prepared samples as obtained from SEM-EDS and ICP analysis (presented in paranthesis)

Catalyst	Silver content (% w/w)	Zinc content (% w/w)
Ag-ZnY1	11.7 (10.7)	14.32 (10.32)
Ag-ZnY2	4.1 (4.6)	8.4 (8.5)
Ag-ZnY1M	None (1.8)	None (0.2)
0.0014Ag-ZnY2M	None (0.9)	2.0 (0.3)

Table 2
The results of the BET surface area analysis of zeolite-silver-zinc samples.

Catalyst	Rate Constant (min^{-1})	Surface area (m^2/g)
None	0.0162	–
Ag-ZnY1	0.0409	303.643
Ag-ZnY2	0.0233	545.921
Ag-ZnY1M	0.0283	254.924
Ag-ZnY2M	0.0270	250.106

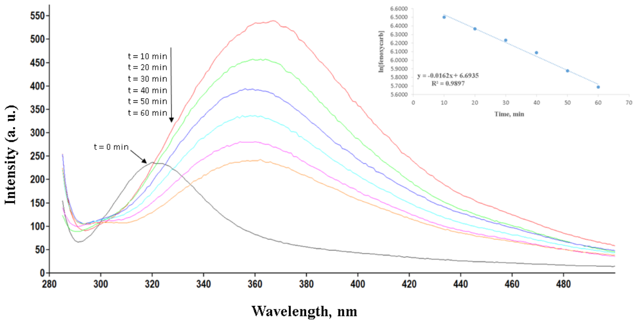

Fig. 3. Time course emission spectra of fenoxycarb without catalyst irradiated with 254 nm UV light and recorded at λ_{ex} = 272 nm. The insert shows the plot of Ln [fenoxycarb] as function of the irradiation times.

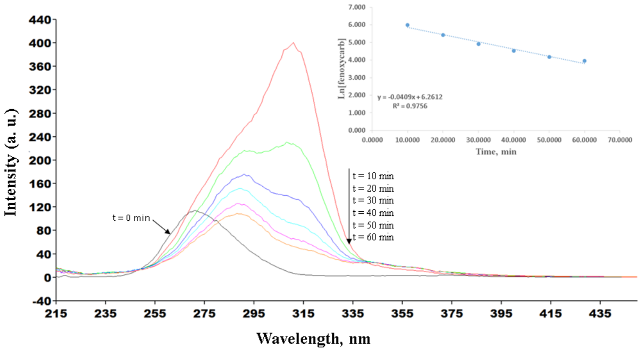

Fig. 4. Time course emission spectra of fenoxycarb in the presence of Ag-ZnY1 recorded at Δλ-50 nm for solutions before and after irradiation with 254 nm UV light. The insert shows the plot of Ln [fenoxycarb] as function of the irradiation times.

periods of time. As shown in Fig. 3, the emission of fenoxycarb shows a major broad peak observed at 320 nm. By irradiating the solution with 254 nm UV light, the observed luminescence band perceived a redshift with a great increase in the emission intensity. This increase in intensity is due to exciting the free electrons on the carbamate nitrogen and oxygen atoms. This reduces the photo-induced electron transfer process that opens the emission process upon irradiation. The observed emission bands endured a gradual decrease in their intensity with further irradiation. The insert in Fig. 3 represents a plot of Ln [fenoxycarb] versus irradiation time, which indicates a pseudo-first order process with a rate constant of 0.0162 min^{-1}.

Synchronous scan luminescence spectra (SSLS) is a selective technique for the analysis of fluorescing mixtures since it involves scanning both the excitation and emission mono-chromators with a constant difference over the spectrum range [33,38]. The photo-degradation of fenoxycarb was also investigated in the presence of the modified Ag-Zn zeolite samples. Fig. 4 shows the SSLS of fenoxycarb exposed to Ag-ZnY1 surface Δλ = 30 nm. As shown in Fig. 4, fenoxycarb possess a band with maximum emission at 321 nm. This mode was broadened and shifted upon irradiation for 10 min. Analysis of the results also indicated that the degradation process followed a pseudo-first order profile. In addition, the SSLS of the pesticide exposed to Ag-ZnY1M samples presented in Fig. 5 shows a similar trend as the irradiated fenoxycarb without catalyst and with the intensity between the two observed modes being reversed. This indicates that oxygen and nitrogen show different behavior on the metal surface. It has been reported that silver tends to make excimers with nitrogen atoms; therefore, the band observed at 290 nm occurs as a result of the photo-induced electron transfer through the nitrogen carbamate moiety to the conjugated system within the pesticide [Ag-N exciplex]. Interestingly, the photo-catalytic behavior of fenoxycarb in the presence of the AgY shows a gradual reduction in the peak intensities without any shift in the SSLS upon irradiation [33]. When the carbamate fenoxycarb reacts with silver(I) clusters in their excited electronic state, strong bonding occur that forms a strong bond between the two. This new fenoxycarb-Ag bond causes a weakening and eventual dissociation of the intramolecular fenoxycarb bonds [18]. Since $Ag^+$and Zn^{+2} ions are with un-reactive closed shell d^{10} ions in their ground state but can be excited to reactive, open shells d^9s^1 or d^9p^1 state, the binding is stronger with these free ions upon excitation, which results in the fast degradation process. Table 2 summarizes the rate constants of the fenoxycarb degradation under 254 nm in the presence (and in the absence) of the four catalysts. It is worth mentioning that the modified samples show a good affinity to absorb/adsorb up to 30% of the initial fenoxycarb directly upon mixing due to their high porosity and thus high surface area. It is clearly noticed that the presence of Ag-Zn doped zeolite have significantly enhanced the photo-degradation of fenoxycarb. The best activity was observed for Ag-ZnY1 when the initial pesticide went through 90% degradation of the initially irradiated sample.

Fig. 6 shows the decomposition products of fenoxycarb. The products were identified upon the degrada-

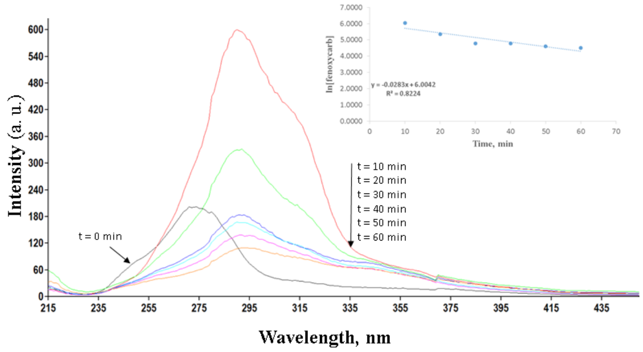

Fig. 5. Time course synchronous spectra of fenoxycarb in the presence of Ag-ZnY1M catalyst recorded at Δλ-50 nm before and after irradiation with 254 nm UV. The insert shows the plot of Ln [fenoxycarb] as function of the irradiation times.

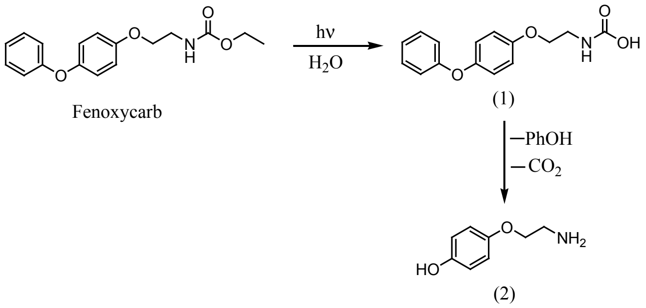

Fig. 6. The observed photo-degradation products obtained after irradiating fenoxycarb for 60 min at 254 nm.

tion of fenoxycarb after irradiation for 60 min using Gas Chromatography-Mass Spectrometry (GC-MS). Three GC bands appeared after 8.11, 18.7, and 20.3 min. The Mass spectrum of the 20.3 min peak indicates the presence of the fenoxycarb whereas, the Mass analysis for the 18.7 peak indicates the formation of N-[2-(4-phenoxy-phenoxy)ethyl] carbamic acid (1) (273 amu) resulting from the hydrolysis of the ester functional group in fenoxycarb. The peak observed after 8.11 min with 153 amu indicates the formation of 4-(2-aminoethoxy)phenol (compound 2), which produced after decarboxylation of the carbamic acid derivative (compound 1).

4. Conclusion

In this study, we have developed a novel highly active mixed-metal Ag-Zn catalyst for the photo-degradation of the pesticide fenoxycarb. This catalyst is prepared by doping Ag and Zinc nanoparticles into Y zeolite and then digested by microwave treatment. Silver-Zinc metal ions incorporated into the zeolite Y framework has once again proven capable of reducing the level of pesticide in an aqueous solution where up to 30% of the pesticide were absorbed/adsorbed by the modified materials. Interestingly, the presence of the maximum amount of silver loaded on the zeolite decomposes fenoxycarb by 90% after UV irradiation for one hour into one product 4-(2-aminoethoxy)phenol. Future work will focus on examining the relationship between silver and zinc cluster structure and the catalytic activity in the presence of dissolved organic carbon to mimic the conditions of natural water systems.

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