International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 2 Issue 10, October - 2013

Effects of Zeolite X on Dissipation of Hexazinone from Agricultural Waste Waters in Western Kenya

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Abstract

Dissipation of hexazinone in Zeolite X treated wastewater followed pseudo first-order kinetics giving a calculated half-life of 41 days compared to a half-life of 144 days in untreated wastewater. The herbicide degraded faster (0.0067 h^{-1}) in treated than in non-zeolite-treated wastewater (0.0027 h^{-1}) forming products A, B, C, D and E within the first 12 h. Zeolite X effectively catalyzed the formation of product A compared to the rest. Calculated rate constants for formation of products A, B, D and E were: 8.33×10^{-4} h^{-1}, 5.65×10^{-4} h^{-1}, 5.52×10^{-4} h^{-1} and 1.38×10^{-3} h^{-1} respectively in non-zeolite-treated wastewater; and 3.988×10^{-3} h^{-1}, 4.875×10^{-4} h^{-1}, 4.745×10^{-4} h^{-1} and 2.82×10^{-3} h^{-1} respectively in zeolite-treated wastewater.

Key words: Hexazinone, agricultural wastewater, zeolite X, rate constants.

1. Introduction.

Hexazinone [3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione - $C_{12}H_{20}N_4O_2$], is a broad spectrum herbicide that belongs to the triazine class of pesticides [1]. Hexazinone is used to control weeds in sugarcane plantations [2]. In Kenya, just like in other sugar growing countries, the hexazinone pesticide has been extensively used in sugar plantation. The water used in this study was obtained from one such area; the nucleus estates in Mumias (0°20′ N, 34°29′ E). Literature reports that due to the relative persistence and high mobility of the herbicide in the environment [3,4], hexazinone easily moves off-site during rainy seasons and causes crop injury (i.e. to non-target sugarcane plants) as well as mortality resulting in reduced income since it is a non-selective herbicide [5]. Presence of hexazinone residues in drinking water also causes decreased body weight, decreased appetite, increased white blood cells, decreased liver weight and increased relative brain weight [6]. Current water purification methods do not effectively remove pesticides [7]. Consequently, the purity of drinking water especially in sugar growing regions is in great doubt. Therefore, management practices such as use of zeolites which, when added to wastewater, enhance the degradation of pesticide contaminants are necessary [8]. An attempt has been reported where current water purification practices incorporate the use zeolites as a water purifier [9], but the chemistry of zeolites on the water bound organics especially the pesticides has not been reported. Zeolites are three dimensional alumino-silicate moieties that act as molecular sieves to cationic, anionic and polar organic compounds [9], such as hexazinone [10], thereby eliminating them from the environment. However, kinetic studies on zeolite-facilitated abstraction and degradation of hexazinone have not been documented. This study aimed at investigating the kinetic effects of zeolite X on the dissipation of hexazinone in agricultural wastewater. The data generated would provide vital information for personnel dealing with environmental impact assessment and for future mitigation measures in similar sugarcane growing areas and whenever a major spillage and contamination occurs.

2.0 Materials and Methods.

2.1. Chemicals

Hexazinone was obtained as Velpar (purity 75% active ingredient) from Farmchoice Input & Technical Services Ltd in Kisumu, Kenya and used for the experiments while the pure standard (purity 99% by HPLC) was obtained from Ehrenstorfer, Augsburg, Germany, and was used for GC-NPD and GC-MS analysis. Zeolite X was obtained from Sigma-Aldrich Inc, St. Louis, USA. Dichloromethane DCM (HPLC grade), isooctane (HPLC grade), diethyl ether (analytical grade), anhydrous Na_2SO_4 (analytical grade), Florisil Purified Reagent (PR) grade, and Whatman No. 1 filter papers were obtained from Kobian Ltd, Nairobi, Kenya.

2.2 Experimental

Some 100 dm^3 of agricultural wastewater was collected from Mumias sugarcane nucleus farm canals ($0^o20'$ N, $34^o29'$ E), about 30 cm from the surface. The experiments were done inside a greenhouse in 10-litre concrete-made ponds to simulate batch agricultural wastewater treatment ponds.

The experimental set up was as follows: (1) To 10 dm^3 wastewater in concrete-made pond, 0.13 g of Velpar (purity 75% hexazinone) was added to make 10 ppm of pesticide solution followed by 20 g of activated zeolite X. (2) For controls, 10 dm^3 wastewater in concrete-made pond, 0.13 g of Velpar (purity 75% hexazinone) was added to make 10 ppm of pesticide solution but without zeolite X, (3) To 10 dm^3 wastewater in concrete-made pond, only 20 g of activated zeolite X was added, and, (4) A concrete-made pond contained 10 litres wastewater only (5) To help check the effect of concrete-made walls on adsorption of the pesticide, 1 dm^3 wastewater in glass jug, 0.013 g of Velpar (purity 75% hexazinone) was added to make 10 ppm of pesticide solution followed by 2 g of activated zeolite X. Before the samples were collected from the ponds and glass jug, the solutions were first stirred well by use of glass rods just before sampling. The pH of the wastewater was measured using an Everscale pH-03 (Shanghai, China) prior to and following abstractions in presence and absence of the zeolite. Volumes of 60 mL and 30 mL wastewater samples were collected from the ponds and the glass jug respectively all in triplicate after 1, 2, 4, 6, 12, 24, 48, 96, 168, 504, 840, 1176, and 1512 h.

2.3 Extraction and clean up

Accurately measured 50 mL of wastewater sample (from concrete-made ponds) and 20 mL of tripled-distilled dichloromethane (DCM) were mixed in a 250-mL separating funnel and shaken for 5 minutes while releasing pressure often, it was then allowed to stand for another 5 minutes. The aqueous layer was transferred into a conical flask and the organic layer transferred into another clean 100 mL conical flask. The aqueous layer was transferred into a second separating funnel, followed by 20 mL of the tripled distilled DCM and the process was done two more times (i.e. in triplicate for each wastewater sample) pooling the 60-mL extracts together in the same conical flask. To dry up the extracted sample, one spatula full of anhydrous sodium sulphate was added to the conical flask containing the extract, then shaken and allowed to stand. The DCM extract was filtered in a filter paper (Whatmans No.1) under vacuum in a Buchner funnel to remove clamped crystals of Na_2SO_4 from the extract. To concentrate the dried extracts, the extracts were transferred into a round-bottomed flask and rotar-vaporized below 40 ^oC to a final volume of 10 mL.

A glass column (2 cm i.d.) for sample extract clean-up was packed using slurry method by first putting glass wool at the bottom followed by 20 g anhydrous florisil in 100 mL n-hexane and then anhydrous Na_2SO_4 was placed at the top. The rotary vaporized concentrate was then passed through the column slowly and eluted with 50 mL of diethyl ether. The eluent was then rotar-evaporated to dryness in water bath at below 40 ^oC. Accurately measured 3 mL of HPLC grade DCM was used to reconstitute the analyte before transferring it into a clean dark vial to seclude light before analysis. The amount of the hexazinone residue present was quantitatively determined by GC-NPD, and its degradation products were characterized by GC-MS.

2.4 Analysis of samples

A Varian Chrompack Gas Chromatography (GC) model equipped with a Nitrogen-Phosphorus Detector (NPD) was used for analysis. A DB-210 column of length 30 m, 0.25 mm i.d. and 0.25 μm film thickness was used. Injector temperature, 250°C; detector temperature, 300°C; oven temperature, 80°C with a hold time of 2 min, increased to 120°C at 25°C min^{-1}, held for 5 min, then increased to 250°C at 5°C min^{-1} with a hold time of 10 minutes. Carrier gas was helium with a flow rate of 2.0 mL min^{-1} at 80°C. Make-up gas was nitrogen at 30 mL min^{-1}; plasma gases, air at 90 mL min^{-1} and hydrogen at 6 mL min^{-1}.

A comparison of the retention times with those of the external standard led to the characterization of hexazinone peak. GC-MS was used to identify the degradation products (A, B, C, D and E) followed by their characterization using consensus retention times. GC-MS conditions were as follows. An agilent 5973 mass detector equipped with a 30 m long x 0.25 mm i.d. x 0.25 μm film thickness HP-MS-5 capillary column; helium as carrier gas; oven temperature at 80 ^oC held for 2 min, increased to 200 ^oC at 10 ^oC min^{-1}, held for 4 min, then up to 230 ^oC at 2 ^oC min^{-1}, held for 5 min, and finally increased to 280 ^oC at 4 ^oC min^{-1} with an additional hold time of 5 min. The recovery for hexazinone was 93.4 ± 5.7 %.

3.0 Results.

3.1 Dissipation of malathion

The average daily temperature ranges during the study was between 20 to 24 ^oC. For both set-ups in the glass jug and ponds, no significant changes in the pH amounts were recorded. Thus all the changes discussed here would therefore be attributable to only the adsorptive and catalytic powers of the zeolite. The general trend for both experiments with and without zeolite X reduced very rapidly in the 1st 1 hour then progressively slowly to the end (Tables 1).

Table 1: Residual concentration of hexazinone in water with and without zeolite X

Time (hour)	Hexazinone concentration in ppm	
	Without Zeolite X	With zeolite X
1	0.431 ± 0.038	0.275 ± 0.047
2	0.420 ± 0.017	0.268 ± 0.028
4	0.417 ± 0.025	0.260 ± 0.022
6	0.416 ± 0.040	0.258 ± 0.054
12	0.414 ± 0.026	0.253 ± 0.042
24	0.413 ± 0.020	0.252 ± 0.052
48	0.409 ± 0.018	0.241 ± 0.034
96	0.405 ± 0.015	0.230 ± 0.030
168	0.394 ± 0.011	0.224 ± 0.038
504	0.358 ± 0.038	0.194 ± 0.022
840	0.353 ± 0.015	0.140 ± 0.032
1176	0.322 ± 0.030	0.124 ± 0.026
1512	0.283 ± 0.022	0.086 ± 0.034

SD = Standard Deviation (n = 3)

However the residual values in the two treatments were significantly different throughout the experiments (Table 1 and Figure 1). The significant difference indicated a clear effect of zeolite treatment.

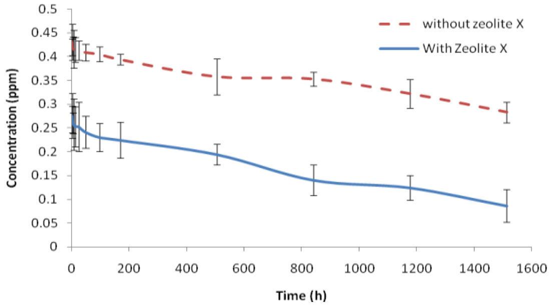


Figure 1: Change in concentration of hexazinone in wastewater spiked with the pesticide without and with Zeolite X.

Since both data for non-zeolite-treated and zeolite-treated wastewater showed pseudo first-order kinetics, the half –life of hexazinone was calculated as given in Table 2.

Table 2. Calculated half-life ($t_{½}$) and rate constants for Hexazinone in wastewater in the absence and presence of zeolite X.

Treatment	Period (h)	Rate constant (k).h^{-1}	Half life $t_{½}$(days)	R^2
Without zeolite X	12	0.0027	10.69	0.555
	24	0.0012	24.06	0.443
	1512	0.0002	144.37	0.974
With zeolite X	12	0.0067	4.31	0.800
	24	0.0032	9.02	0.647
	1512	0.0007	41.25	0.984

Half-life values were calculated for 1st 12 h, 1st 24 h and the entire 1512 h for comparison since organic pesticides dissipate rapidly within a few hours after application followed by slow dissipation and eventually a steady-state. It is worthy to note that $t_{½}$ of first-order reaction is independent of initial concentration. In addition, it is also noted the presence of zeolite had profound influence for entire duration of study.

3.2 Degradation Products

The same degradation products (A, B, C, D and E) were obtained and identified in both non-zeolite-treated and zeolite-treated wastewater samples. For the wastewater without zeolite X (Figure 2), the graph indicates that the average values of the degradation products statistically differed among themselves and also with the amount of residual hexazinone.

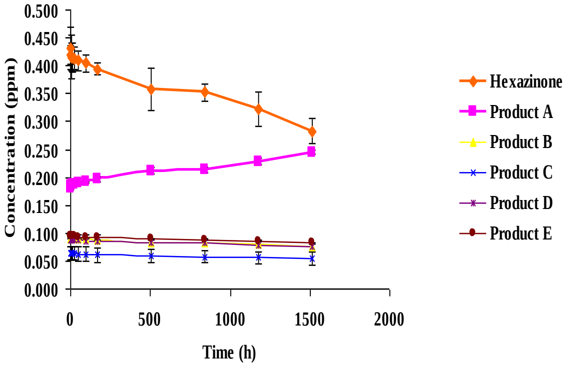


Figure 2: Concentration of products of hexazinone in wastewater without zeolite X with time.

For the wastewater with zeolite (Figure 3), among the products themselves, product A was significantly different than the rest. However, both data for non-zeolite-treated and zeolite-treated wastewaters showed a general trend in terms of gradual decrease in the concentration of the parent compound (hexazinone), a build-up of product A and a somewhat steady-state scenario for the other products.

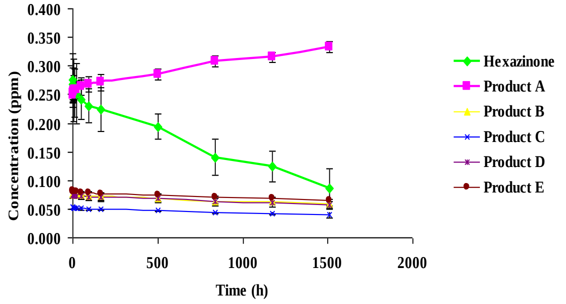


Figure 3: Concentration of products of hexazinone in wastewater with zeolite X with time.

When the amount of residual hexazinone in the glass jug was compared with that of concrete-made pond of similar treatment, the abstraction effect in the concrete-made pond was found to be insignificantly higher. This insignificant difference means that the control having taken care of all other side disappearance routes, the use of concrete-made ponds did not significantly result in different adsorption behavior as compared to normal laboratory glass jug.

4.0 Data Analysis and Discussion.

4.1 Dissipation of malathion

Having taken care of other dissipation related factors through the control treatments, the initial rapid degradation of hexazinone in the wastewater during the 1st 1 hour (Figure 1) could have been due to adsorption and catalysis (for experiment with zeolite). The half-life of hexazinone has been reported to vary greatly and is a function of the physical and chemical properties of the soil and waters [11,12,13]. In this study, hexazinone was found to have a half life of ca. 41 days at pH 8.1± 0.1 when zeolite X was used and of 144 days without the zeolite. Dupont company, in 2007, reported hexazinone hydrolysis half-life of greater than 30 days at pH of 5, 7 and 9 at 25°C in temperate climate zone. Also, Kollman and Segawa (1995) also reported a hydrolysis half-life of greater than 56 days under unspecified conditions [14]. Similarly, Perkins (2002) observed a half-life of 90 – 175 days for the pesticide in water under aerobic conditions [10]. Yang *et al*, (2006) had earlier reported that the catalytic actions of zeolites on organic molecules involve the reaping-apart of the main organic-functional groups [15]. The degradation of hexazinone in the presence of zeolite X led to a lower half life, possibly due to the presence of cation (Na^+) sites which helps in reaping apart the polar hexazinone molecule leading to faster degradation.

4.2 Degradation Products

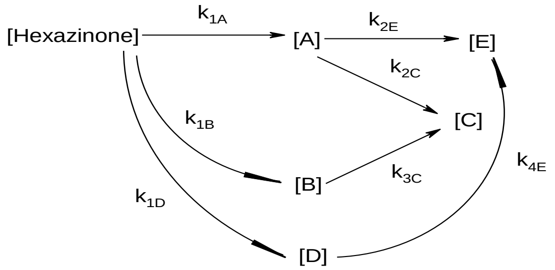
The degradation products of hexazinone identified in this study were: Products A [3-(4-hydroxycyclohexyl)-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione], B [3-cyclohexyl-6-(methylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione], C [3-(4-hydroxycyclohexyl)-6-(methylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione], D [3-cyclohexyl-1-methyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione] and E [3-(4-hydroxycyclohexyl)-1-methyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione]. In a different study involving the use of groundwater, the metabolites of hexazinone detected were C, A1, E, B and D [16].

In Figure 2 for non-zeolite-treated wastewater, product A was formed as a major product whiles the other products B, C, D and E were minor products. According to Ganapathy (1996), metabolites A, B and C are considered major metabolites of hexazinone [17]. The concentration of product A increased gradually as the experiment progressed even though some of it was, possibly, being transformed into the other products [18]. The concentration of products B, C, D and E reduced gradually as they were also probably being converted into the other products or just abstracted into the zeolite framework [15,18].

As in Figure 3 for zeolite-treated wastewater, product A was formed at a higher rate (5.55 $x10^{-5}$ ppm h^{-1}) than in wastewater without zeolite X (4.29 $x10^{-5}$ ppm h^{-1}) (Tables 3 and 4) suggesting that zeolite X acted as a catalyst for formation of product A. The inter-conversions between the products could also occur in a similar manner as in wastewater without zeolite X. Since the mechanisms for the degradation of the pesticide, into its products are already known [2], zeolite X, therefore, played the role of providing a framework for hexazinone degradation where it acted as a catalyst by confining hexazinone molecules in small spaces that caused changes in its structure and reactivity thereby resulting in faster formation of product A [15]. The similarity in the degradation products between the wastewater with and without the zeolite is worthy to note. This similarity corroborates that zeolite X mainly acted as a catalyst in this case and did not offer any different degradation pathway that could generate different degradation products.

4.3 Dissipation rates of hexazinone in wastewater with and without zeolite X.

Based on the products of degradation identified in this study, Scheme 1 represents reaction pathway for degradation of hexazinone into its products in the agricultural wastewater studied.



Scheme 1: Reaction pathway for degradation of hexazinone (Adapted from Ganapathy 1996) [17]. Where [x] is the concentration of species X, and k_i is the pathway rate constant.

The k values for zero order reactions of the products gave the smallest standard deviations (data not provided); therefore, the dissipations of all the degradation products followed overall zero order kinetics. From Scheme 1, hexazinone degradation/dissipation followed both parallel and consecutive types of reactions.[19] Since from the data for with and without zeolite X, the concentration of E was greater than that of C (E > C) (Figures 2 and 3) and that both were terminal (i.e. not changing), there is the possibility that the products E and C were being transformed into other products not detected in the experiment, that the reactions were reversible or that they were being exclusively adsorbed by the zeolite [2,15]. Also given that only A showed appreciable change while the amounts of B, C, D and E were almost constant, then we tacitly assume; $k_{2C} = k_{3C} = k_{4E} \approx 0$, thus, the differential equations describing scheme 1 become:

$$\frac{d[\mathrm{Hexaz}]}{dt} = -\, k' \, [\mathrm{Hexaz}]$$

$$\text{(Where } k' = k_{1A} + k_{1B} + k_{1D}\text{)} \;\ldots\ldots\ldots\ldots \; (1)$$

$$\frac{d[A]}{dt} = k_{1A}[\mathrm{Hexaz}] - k_{2E}[A] \;\ldots\ldots\ldots\ldots\ldots \; (2)$$

$$\frac{d[B]}{dt} = k_{1B}[\mathrm{Hexaz}] \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; (3)$$

$$\frac{d[D]}{dt} = k_{1D}[\mathrm{Hexaz}] \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; (4)$$

Where k_{1A}, k_{1B}, k_{1D}, k_{2E} are rate constants for formation of products A, B, D and E while [Hexaz] the concentration of hexazinone at time t. Considering the parallel reactions of hexazinone that produced A, B and D, the solutions to equations (1), (3) and (4), could be given as follows:

(a) Rates in wastewater without zeolite X

The solution to equation (1)

When equation (1) is integrated it gives;

$$[\mathrm{Hexaz}] = [\mathrm{Hexaz}]_o e^{-k't} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where $[\mathrm{Hexaz}]_o$ is initial concentration of hexazinone. Equation (5) can also be written as

$$\ln[\mathrm{Hexaz}] = -k'\, t + \ln[\mathrm{Hexaz}]_o ,$$

Since pesticide dissipations occur rapidly within the first few hours after commencement of the experiments, the overall rate constant, k', for hexazinone dissipation/degradation in non-zeolite-treated wastewater was considered to be the average of the rate constants during the 1st 12 h and 1st 24 h i.e. 0.0027 h^{-1} and 0.0012 h^{-1} respectively (Table 2).

$$\text{Therefore, } k' = \frac{0.0027 + 0.0012}{2} = 0.00195 \text{ h}^{-1}$$

The solution to equation (3)

Equation (3) can also be written as

$$\frac{d[B]}{dt} = k_{1B}[\mathrm{Hexaz}]_o e^{-k't}$$

Thus the solution takes the form

$$[B] = \frac{k_{1B}}{k'}[\mathrm{Hexaz}]_o(1 - e^{-k't})$$

Given that $[\mathrm{Hexaz}]_o$ = 10 ppm,

(i) at time t = 12 h, k' = 0.0027 h^{-1} (Table 2) and [B] = 0.089 ppm (Table 3).

Substituting in the formula gives

$$0.089 = \frac{k_{1B}}{0.0027}(10)(1 - e^{-0.0324})$$

$$0.089 = 118.15\, k_{1B}$$

$$k_{1B} = \frac{0.089}{118.15} = 7.53\mathrm{x}10^{-4} \text{ h}^{-1} = 0.000753 \text{ h}^{-1}$$

(ii) at time t = 24 h, k' = 0.0012 h^{-1} (Table 2) and [B] = 0.089 ppm (Table 3).

Applying the same formula, k_{1B} = 0.000376 h^{-1}.

Average value of

$$k_{1B} = \frac{0.000753 + 0.000376}{2} = 5.65 \text{ x } 10^{-4} \text{ h}^{-1} = 0.000565 \text{ h}^{-1}$$

The solution to equation (4)

The solution to equation (4) is

$$[D] = \frac{k_{1D}}{k'}[\mathrm{Hexaz}]_o(1 - e^{-k't}) \text{, therefore}$$

(i) At time t = 12 h, k' = 0.0027 h^{-1}, [D] = 0.087 ppm (Table 3), thus

$$0.087 = \frac{k_{1D}}{0.0027}(10)(1 - e^{-0.0324})$$

$$0.087 = 118.15\, k_{1D}$$

$$k_{1D} = \frac{0.087}{118.15} = 7.36\text{x}10^{-4}\ h^{-1} = 0.000736\ h^{-1}$$

(ii) At time t = 24 h, k' = 0.0012 h^{-1}, [D] = 0.087 ppm (Table 3), thus using the same formula, k_{1D} = 0.000368 h^{-1}.

Average value of

$$k_{1D} = \frac{0.000736 + 0.000368}{2} = 5.52 \text{ x } 10^{-4}\ h^{-1} = 0.000552\ h^{-1}$$

The value of k_{1A} in equation (1)

Since $k' = k_{1A} + k_{1B} + k_{1D}$

$$k_{1A} = k' - (k_{1B} + k_{1D})$$

= 0.00195 – (0.000565 + 0.000552) = 8.33 x10^{-4} h^{-1}

The calculated values of k_{1A}, k_{1B} and k_{1D} indicated that $k_{1A} > k_{1B} > k_{1D}$ i.e. 8.33 x10^{-4} > 5.65 x10^{-4} > 5.52 x10^{-4} h^{-1}

This relationship explains the general shape of the graph in Figure 2. The build up of product A showed that its rate constant, k_{1A}, must have been much higher than those of products B and D (i.e. k_{1B} and k_{1D} respectively) whose concentrations showed some steady state scenario.

Considering one of the consecutive reactions that produced product E ([Hexaz]→[A]→[E]), the solution to equation (2) could be given as described below.

The solution to equation (2)

Using the equation (2) given below

$$\frac{d[A]}{dt} = k_{1A}[\text{Hexaz}] - k_{2E}[A]$$

Four values of k_{2E} were calculated at times t = 6 h, 12 h, 24 h and 48 h (using values from Table 3) as; k_{2E} = 0.000965 h^{-1}, 0.000951 h^{-1}, 0.00139 h^{-1} and 0.00136 h^{-1} respectively. Since the calculated k_{2E} values represented two regimes i.e. ≤12 h (slow phase) and ≥24 h (rapid phase), two different average values of k_{2E} were worked out for each of the two phases.

Average value of k_{2E} (slow phase) = 0.000958 h^{-1} = 9.58 x 10^{-4} h^{-1}

Average value of k_{2E} (rapid phase) = 0.00138 h^{-1} = 1.38 x 10^{-3} h^{-1}.

It is worthy to note that product E was formed from product A (Scheme 1). At the initial stages the concentration of E was low, as suggested by k_{2E} value (slow phase), but a build up could have occurred, as suggested by k_{2E} value (rapid phase). The Figure 2 shows that product E was at some steady state. As stated above, product E could have been transformed into other products or just adsorbed into the zeolite framework [15].

(b) Rates in wastewater treated with zeolite X

Solutions to the equations (1), (3), (4) and (2) for the data obtained from wastewater treated with zeolite X were, similarly, determined using the same sequence as in part (a) above.

(i) Solution to equation (1): The overall rate constant, k', for hexazinone dissipation/degradation in zeolite-treated wastewater was also considered to be the average of the rate constants during the 1st 12 h and 1st 24 h i.e. 0.0067 h^{-1} and 0.0032 h^{-1} respectively (Table 2).

$$k' = \frac{0.0067 + 0.0032}{2} = 0.00495\ h^{-1}$$

(ii) Solution to equation (3): Given that $[\text{Hexaz}]_o$ = 10 ppm,

(I) At time t = 12 h, k' = 0.0067 h^{-1} (Table 2) and [B] = 0.075 ppm (Table 4). Substituting in the formula gives;

$$0.075 = \frac{k_{1B}}{0.0067}(10)(1 - e^{-0.0804})$$

0.075 = 115.37 k_{1B}

$$k_{1B} = \frac{0.075}{115.37} = 6.5 \text{ x}10^{-4} = 0.00065\ h^{-1}$$

(II) At time t = 24 h, k' = 0.0032 h^{-1} (Table 2) and [B] = 0.075 ppm (Table 4).

Using the same formula gives, k_{1B} = 0.000325 h^{-1}.

The average value of

$$k_{1B} = \frac{0.00065 + 0.000325}{2} = 4.875 \text{ x}10^{-4} = 0.0004875\ h^{-1}$$

Solution to equation (4): Given that $[\text{Hexaz}]_o$ = 10 ppm, (I) At time t = 12 h, k' = 0.0067 h^{-1}, [D] = 0.073 ppm (Table 4), thus

$$0.073 = \frac{k_{1D}}{0.0067}(10)(1 - e^{-0.0804})$$

0.073 = 115.37 k_{1D}

$$k_{1D} = \frac{0.073}{115.37} = 6.33 \text{ x}10^{-4} = 0.000633\ h^{-1}$$

(II) At time t = 24 h, k' = 0.0032 h^{-1}, [D] = 0.073 ppm (Table 4), thus using the same formula, k_{1D} = 0.000316 h^{-1}. The average value of

$$k_{1D} = \frac{0.000633 + 0.000316}{2} = 4.745 \text{ x}10^{-4} = 0.0004745\ h^{-1}$$

(iv)The value of k_{1A} in equation (1):

$k_{1A} = k' - (k_{1B} + k_{1D})$ = 0.00495 – (0.0004875 + 0.0004745) = 3.988 x10^{-3} h^{-1}

(v) The solution to equation (2) Using the same equation (2) given below

$$\frac{d[A]}{dt} = k_{1A}[\text{Hexaz}] - k_{2E}[A]$$

Four values of k_{2E} were calculated at times t = 6 h, 12 h, 24 h and 48 h (using values from Table 4) as; k_{2E} = 0.00272 h^{-1}, 0.00262 h^{-1}, 0.00308 h^{-1} and 0.00285 h^{-1} respectively.

Table 3: Concentration of Hexazinone degradation products in wastewater without Zeolite X

Time (h)	Concentration in ppm ± SD						
	Hexazinone	Product A	Product B	Product C	Product D	Product E	Total Mass
1	0.431 ± 0.038	0.180±0.002	0.091±0.004	0.064±0.012	0.088±0.012	0.095±0.003	0.949±0.042
2	0.420 ± 0.017	0.184±0.001	0.090±0.004	0.063±0.012	0.088±0.012	0.094±0.003	0.939±0.025
4	0.417 ± 0.025	0.186±0.001	0.090±0.004	0.063±0.012	0.087±0.009	0.094±0.003	0.936±0.030
6	0.416 ± 0.040	0.186±0.001	0.090±0.004	0.063±0.012	0.087±0.009	0.094±0.003	0.935±0.043
12	0.414 ± 0.026	0.187±0.001	0.089±0.003	0.063±0.012	0.087±0.009	0.094±0.003	0.934±0.030
24	0.413 ± 0.020	0.187±0.001	0.089±0.003	0.063±0.012	0.087±0.009	0.094±0.003	0.933±0.025
48	0.409 ± 0.018	0.189±0.002	0.089±0.003	0.062±0.013	0.087±0.009	0.093±0.004	0.929±0.025
96	0.405 ± 0.015	0.191±0.002	0.089±0.003	0.062±0.013	0.086±0.008	0.093±0.004	0.926±0.022
168	0.394 ± 0.011	0.196±0.005	0.088±0.002	0.061±0.013	0.085±0.008	0.092±0.004	0.916±0.020
504	0.358 ± 0.038	0.212±0.006	0.084±0.003	0.059±0.012	0.082±0.009	0.089±0.001	0.884±0.041
840	0.353 ± 0.015	0.214±0.005	0.084±0.003	0.058±0.011	0.082±0.009	0.088±0.001	0.879±0.021
1176	0.322 ± 0.030	0.228±0.006	0.081±0.001	0.056±0.011	0.079±0.010	0.086±0.001	0.852±0.034
1512	0.283 ± 0.022	0.245±0.004	0.077±0.003	0.054±0.012	0.076±0.009	0.082±0.002	0.817±0.027

SD: Standard Deviation (n = 3)

Table 4: Concentration of Hexazinone degradation products in wastewater with Zeolite X

Time (h)	Concentration in ppm ± SD						
	Hexazinone	Product A	Product B	Product C	Product D	Product E	Total mass
1	0.275 ± 0.047	0.249±0.014	0.077±0.008	0.053±0.004	0.075±0.006	0.082±0.003	0.810±0.050
2	0.268 ± 0.028	0.252±0.015	0.076±0.007	0.053±0.004	0.074±0.005	0.081±0.003	0.804±0.033
4	0.260 ± 0.022	0.255±0.014	0.075±0.007	0.052±0.003	0.074±0.005	0.080±0.003	0.797±0.028
6	0.258 ± 0.054	0.256±0.015	0.075±0.007	0.052±0.003	0.073±0.005	0.080±0.003	0.795±0.057
12	0.253 ± 0.042	0.258±0.015	0.075±0.007	0.052±0.003	0.073±0.005	0.080±0.003	0.791±0.046
24	0.252 ± 0.052	0.259±0.015	0.075±0.007	0.052±0.003	0.073±0.005	0.080±0.003	0.789±0.055
48	0.241 ± 0.034	0.264±0.015	0.074±0.007	0.051±0.004	0.072±0.005	0.079±0.003	0.780±0.038
96	0.230 ± 0.030	0.268±0.013	0.073±0.007	0.050±0.003	0.071±0.005	0.078±0.004	0.770±0.034
168	0.224 ± 0.038	0.271±0.014	0.072±0.006	0.050±0.003	0.070±0.006	0.077±0.004	0.765±0.042
504	0.194 ± 0.022	0.285±0.009	0.069±0.007	0.048±0.002	0.068±0.005	0.074±0.008	0.737±0.027
840	0.140 ± 0.032	0.308±0.010	0.064±0.005	0.044±0.002	0.063±0.008	0.070±0.007	0.690±0.036
1176	0.124 ± 0.026	0.315±0.009	0.063±0.005	0.043±0.002	0.062±0.008	0.068±0.007	0.676±0.030
1512	0.086 ± 0.034	0.333±0.009	0.059±0.004	0.040±0.005	0.058±0.009	0.065±0.010	0.641±0.038

SD: Standard Deviation (n = 3)

The calculated k_{2E} values here represented just one regime. Therefore, an average value of k_{2E} was worked out as follows. Average value of

$$k_{2E} = \frac{0.00272 + 0.00262 + 0.00308 + 0.00285}{4}$$

$= 2.82 \times 10^{-3}\ h^{-1}$

For the data without zeolite X, the k_{1A} value was higher than k_{1B} which was in turn higher than k_{1D} ($k_{1A} = 8.33 \times 10^{-4} > k_{1B} = 5.65 \times 10^{-4} > k_{1D} = 5.52 \times 10^{-4}\ h^{-1}$). This indicated that product A was formed as a major product, being consistent to the data in Figure 2. Similarly, for the data with zeolite X, the k_{1A} value was higher than k_{1B} which was in turn higher than k_{1D} ($k_{1A} = 3.988 \times 10^{-3} > k_{1B} = 4.875 \times 10^{-4} > k_{1D} = 4.745 \times 10^{-4}\ h^{-1}$

This showed that zeolite X catalyzed the formation of product A, which was also a major product as supported by data in Figure 3. The k_{2E} values (in both the slow and rapid phases) for data without zeolite X were higher than the k_{1A} value (k_{2E} (slow phase) $= 9.58 \times 10^{-4} > k_{1A} = 8.33 \times 10^{-4}\ h^{-1}$ and k_{2E} (rapid phase) $= 1.38 \times 10^{-3} > k_{1A} = 8.33 \times 10^{-4}\ h^{-1}$), showing that the processes that transformed product E (see above) occurred at a higher rate than the rate at which product A was formed, resulting in steady-state scenario for product E (Figure 2). The k_{2E} value for the data with zeolite X was lower than k_{1A} ($k_{2E} = 2.82 \times 10^{-3} < k_{1A} = 3.988 \times 10^{-3}\ h^{-1}$) implying that product A was formed at a higher rate than the rate at which product E was being transformed (Figure 3). This could be attributed to zeolite X that could have catalyzed the formation of product A.

The overall rate constant, k' value, for the data with zeolite X ($4.95 \times 10^{-3}\ h^{-1}$) was higher than that for data without zeolite X ($1.95 \times 10^{-3}\ h^{-1}$) indicting that zeolite X acted as a catalyst in the degradation/dissipation of hexazinone. The k_{1A} value for the data with zeolite X ($3.988 \times 10^{-3}\ h^{-1}$) was higher than that for data without zeolite X ($8.33 \times 10^{-4}\ h^{-1}$) showing that zeolite X catalyzed the formation of product A. The k_{1B} value for the data with zeolite X ($4.875 \times 10^{-4}\ h^{-1}$) was lower than that for data without zeolite X ($5.65 \times 10^{-4}\ h^{-1}$) implying that zeolite X had a negative effect on the accumulation of product B. Likewise, the k_{1D} value for data with zeolite X ($4.745 \times 10^{-4}\ h^{-1}$) was lower than that for data without zeolite X ($5.52 \times 10^{-4}\ h^{-1}$) showing that zeolite X had a negative effect on the accumulation of metabolite D too.

The above kinetics' were very important in that they helped to explain and thus account for the changes in the amounts of the parent compound and its products as the experiments progressed, though there were no documented data on the same for comparison. Even though losses through volatilization affect kinetics, such losses are minimal especially for products. Besides, hexazinone does not volatilize readily when applied in the field [4].

5.0 Conclusions.

Hexazinone dissipation in the agricultural wastewater treated with and without zeolite X followed pseudo first-order kinetics. Zeolite X enhanced hexazinone degradation in the wastewater affording the calculated half-life to drop from 144 days in untreated to 41 days in zeolite-treated wastewater. Hexazinone degradation in both non-zeolite-treated and zeolite-treated wastewater produced products A, B, C, D and E, with product A forming as a major product in both cases but whose formation was catalyzed by zeolite X. This work highlighted the effects of using zeolite X in treatments of hexazinone contaminated wastewaters. In light of these findings, the overall and synergic environmental effects of hexazinone and its degradation products needs to be investigated especially during water treatments involving zeolites.

6.0 Acknowledgements.

We are grateful to Mr. Richard Chepkui and Dr. Bowa Kwach of Department of Chemistry, Maseno University for helping with data analysis. Exceed partnership network is appreciated for group conference discussions.

7.0 References.

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