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Effects of zeolites X and Y on the degradation of malathion in water

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Abstract: The inclusion of both zeolites X and zeolite Y significantly affected the dissipation of malathion in water. In the fresh water, malathion degradation followed a pseudo-first order kinetics with concomitant half-life dropping from 8.76 hours in fresh water to 4.44 and 6.65 hours up on the introduction of faujasite X and Y, respectively. Zeolite X had higher degradation efficiency as compared to the Y type. In pure fresh water, Malathion mainly hydrolyzed to form malathion monocarboxylic and dicarboxylic acids as the only degradation products. However, in the presence of zeolites X and Y, in addition to the degradation products obtained in the fresh water, dimethyldithiophosphate was also formed. Notably, all the degradation products obtained are environmentally benign compared to the parent malathion. Eventually, both the adsorption on the zeolite framework and zeolite catalyzed degradation processes contributed to the overall dissipation behavior of the malathion and its degradation products.

Keywords: Degradation Kinetics, Faujasite X And Y, Fresh Water, Half Life, Malathion

1. Introduction

Malathion (S- 1, 2- bis (ethoxycarbonyl) ethyl O, O-dimethylphosphorodithioate - C₁₀H₁₉O₆PS₂) belongs to the organophosphate class of pesticides [1]. Human exposure to malathion may result in nausea, vomiting, stomach cramps, diarrhea, blurred vision, confusion, sweating, muscle twitching, irregular heartbeat and eventually convulsions and fatality [1]. Malathion usually adsorbs on soils and through surface runoff and leaching, it finds its way into rivers and lakes whose waters, in most cases, the surrounding population rely on for their domestic use [2]. Malathion degradation in water is pH dependent, with faster decomposition at higher pH [3]. Hydrolysis is the main route of decomposition in alkaline aerobic conditions though biodegradation may also play a role [4]. Metabolites resulting from hydrolysis include malaoxon, malathion alpha and beta monoacid, diethyl fumarate, diethyl thiomalate, O, O-dimethylphosphorodithioic acid, diethylthiomalate, and O, O-dimethylphosphorothionic acid [3], while breakdown con-

stituents of biodegradation include beta monocarboxylic acid, dicarboxylic acid, and diethyl thiomalate [4]. Although the current water treatment methods are less efficient in getting rid of pesticides and their degradation products, some recent developments incorporate zeolites among water purifiers as a means to removing cations and some organics [5, 6].

Faujasite X (NaX or X) and Faujasite Y (NaY or Y) zeolites can be effective alternatives for mopping up malathion from waters due to their abilities to adsorb and catalyze degradation of organophosphates [7, 8]. Although zeolite X and Y have similar topographical structure, they differ in their pore diameter (7.3Å for X and 7.4Å for Y) and Si/Al ratio (1.00-2.50 for X and more than 2.50 for Y) making their chemistry also somewhat different [9]. Ref. [8], reported that zeolites degrade malathion faster though the kinetics of such zeolitic action, the nature of reaction products, and the toxicity or otherwise of the degradation products have not been documented. The current study, therefore, investigated the possible effects when low Si/Al (X) compared to a high Si/Al (Y) zeolites were used to decontami-

nate fresh water off malathion.

2. Materials and Methods

2.1. Chemicals

The n-hexane, dichloromethane and diethyl ether solvents used were supplied by Kobian Ltd, Nairobi, Kenya, and were all of Analytical Reagent (AR) grade. Analytical grade anhydrous Na₂SO₄, and NaCl both 99% pure, Purified Reagent (PR) grade Florisil, activated charcoal PR grade and Whatman No. 1 filter papers were also obtained from Kobian Ltd. Analytical standard malathion and both zeolite X and zeolite Y were obtained from Sigma-Aldrich Inc, St. Louis, USA.

2.2. Water Sampling

Forty (40) litres of Lake Victoria water was collected from Asembo Bay (0°10'S, 34°25'E), 100 m offshore and about 30 cm from the surface. The initial pH of the water was measured using an Everscale pH-03(Shanghai, China) and thereafter the water was filtered into a pre-cleaned 20 L plastic container using Whatman No 1 filter paper to remove any suspended particles. The lake water used was first stored in the dark at room temperature for about two weeks before use.

2.3. Degradation Experiments

All the set-ups were laboratory based in a water bath at 27 ± 1 °C. In the setup, one litre of water sample in a pre-cleaned 2 L glass jar was spiked with malathion pre-dissolved in 2 mls of acetone so as to make 5, 10 and 20 ppm malathion concentrations and then 1.0 g of activated zeolite X added in each case. Another similar set of malathion solutions but without any zeolites was also separately prepared as a control for this set up. A blank was prepared by taking 1 L of water sample into a 2 L glass jar and adding 1.0 g activated zeolite X. After every 1, 2, 4, 6, 12, 24, 48, 96, 192, 384 and 768 hours, 40 mL from each set up was transferred to a clean amber bottle and kept at 4 °C before analysis. The same procedure was repeated for zeolite Y incorporated samples. At the end of the study duration, the solid zeolite cakes of both the zeolites X and Y treatments and the blank set-ups were dried by pressing the cake in between Whatman No. 1 filter papers. The dried cakes were then considered ready for X-ray diffraction (XRD) and Fourier Transform Infra Red (FT-IR) characterization.

2.4. Extraction and Clean Up

The 40 ml of the extracted samples were transferred into a 100 ml separating funnel and 2 grams of NaCl(s) was added to each sample to facilitate extraction of the malathion. 20 mL of dichloromethane was then added to the mixture and the mixture shaken for about 5 minutes, with periodical venting to release pressure [10]. The mixture was allowed to stand for ca. 10 minutes to afford a clear separation between

the aqueous and the organic layers. The aqueous layer was then drained into a second separation funnel and the organic layer transferred into a clean 100 ml Erlenmeyer flask. The aqueous phase was then twice extracted with fresh solvents. The extracts were first combined then dehydrated by 10 g anhydrous Na₂SO₄. To remove the clumped Na₂SO₄ crystals from the extracts, vacuum filtration was performed. The dried sample was then concentrated by rotary evaporation at 40 °C to a 10 mL final volume.

Then cleaning up in an n-hexane washed glass column (2 cm i.d) packed with 20 g Florisil followed. Earlier, 2 g of the anhydrous Na₂SO₄ and 1 g of activated charcoal were also added at the top of the column to remove any pigmentation. The elution was sequentially done with 50 ml of n-hexane, followed by 200 ml of 6 % diethyl ether in n-hexane, 200 ml of 15 % diethyl ether in n-hexane and finally by 200 ml of 50 % diethyl ether in n-hexane and the fractions collected (www.caslab.com/EPA-Method-3620c, accessed on March 18th 2012). The third fraction was concentrated to dryness in a rotary evaporator in a water bath temperature at 40 °C. Three milliliters of HPLC grade n-hexane was used to re-constitute the analyte before analysis and quantification.

2.5. Analysis

Varian Chrompack CP-3800 Gas chromatograph (GC) acquired from Palo Alto, CA, USA with Nitrogen-Phosphorus Detector (NPD) was used for the analysis. The capillary column was a DB-210 of length 30 m, id 0.25 mm and 0.25 µm film. The carrier and make up gas was nitrogen with a 2 ml/min and 30 ml/min flow rates respectively. Hydrogen at 8 ml/min and air at 80 ml/min were employed in a splitless mode for the detector. 2.0 µL of the sample was injected at a temperature of 270 °C. The oven temperature was kept at 120 °C with a hold time of 1 minute, then from 120 °C to 205 °C at a rate of 25 °C/min with a hold time of 1 minute and finally from 205 °C to 250 °C at a rate of 1 °C/min with a hold time of 1 minute. The detector was maintained at 300 °C. The detection limit calculated as the standard deviation of triplicate analyses with a 95% confidence level was 0.01 ppm for malathion. The recovery for malathion was 73.6 ± 4.7 %. The malathion peak was characterized by comparing the retention times and area count with those of the external standard while the degradation products were identified and confirmed using GC-Mass spectroscopy (GC-MS).

The Gas Chromatography –Mass spectrophotometer (GC-MS) (Agilent 6890 GC and 5975 MS, EI) from Agilent technologies, Santa Clara CA, USA was used for the analysis. The capillary column was a VF5 ms of length 30 m, i.d 320 µm and 0.25 µm film. The carrier gas was helium with flow rate 1.2 ml/min in splitless mode with sample injection volume of 2 µl. The injector temperature was maintained at 250 °C. The oven temp was programmed as: 60 °C, hold time 0 min then to 165 °C at 15 °C hold time 0 min then to 280 °C at 2 °C hold time 1 min. MS detector temperature was 280 °C, that of Quadrupole was 150 °C and source temperature of 230 °C. The GC-MS was operated in a SIM/SCAN

Mode and the following were the SIM ions: (Target) 127, (Q1)173, (Q2)158.

The X-ray diffraction (XRD) data was collected at room temperature on a Scintag XDS 2000 powder diffractometer using Cu α radiation of $\lambda = 1.5418 \text{ \AA}$ with a solid state detector. The instrument settings were 40 KV, 30 mA, step size of 0.02° (2θ) and a scan rate of $2\theta/\text{min}$ for $5^\circ \leq 2\theta \leq 50^\circ$. The FT-IR measurements were done on the Bruker Equinox 55 spectrometer from Madison, WI, USA with a nominal resolution of 2 cm^{-1} . The spectrometer was purged with nitrogen gas for 30 minutes before and after pellet insertion, after which the spectrum was recorded over the $4000 - 400 \text{ cm}^{-1}$ range. A total of 128 scans were collected for each sample spectrum.

3. Results and Discussions

3.1. Effects of Zeolites on Degradation Rate of Malathion

Lower malathion concentrations of 5 and 10 ppm were first investigated but the pesticide residual amounts in water with time especially after exposure to zeolites were minimal and could not enable time dependent study of this nature to be performed. Consequently, only the results for 20 ppm malathion concentration are reported herein. A gain, the data reported here are corrected for losses occasioned by volatilization, evaporation and adherence to container walls.

Over the period of study, the pH of water before the treatments with zeolite was 7.8 ± 0.5 , while that after zeolite X treatments was 8.1 ± 0.6 and after zeolite Y treatments was 8.0 ± 0.5 . On average, the changes in the pH of water both before and after zeolite addition and in the course of reaction were statistically insignificant. Significantly, differences in malathion dissipation existed in the waters treated with the zeolites compared to those in untreated waters (Table 1). The initial dissipation of malathion in water without zeolite could be attributed to photolysis and the transformation of malathion to its degradation products which are majorly acids. Ref. [11] had also noted this phenomenon where the malathion concentration continued dropping as the transformation proceeded. In the long term, the rate of degradation continued to significantly slow down and was almost stagnated by the 20th hour of study.

In Table 1, the lower Si/Al zeolite X showed slightly higher percentage removal of malathion with time as compared to the higher Si/Al zeolite Y. This increased dissipation rate is attributable to the catalytic action and/or adsorption of the zeolites.

A first-order kinetics was obtained for the dissipation of the malathion in all the three media of water alone, when exposed to Y and when exposed to X with half-lives of 8.76, 6.65, and 4.44 hours, respectively. Ref. [12], reported a half-life of 2 days at 28°C and a pH of 8.2, while ref. [4] reported a half-life of 2 days but under unspecified conditions thus underscores that the differences in the half-lives could be attributed to the different climatic conditions since the literature data cited above were acquired in the temperate

regions while the current study was in the tropics [13]. The reduction in half-life in the presence of zeolites is in agreement with past studies which indicated that zeolites are capable of enhancing the degradation of organophosphates [7]. The enhanced degradation of malathion by zeolites is attributable to zeolitic catalysis since the zeolites are imbued with higher amounts of both exchangeable cations and cavity dielectric charge which would contribute in the reaping a part of the molecule [9]. Since Faujasite X has more exchangeable cations in its cavities than Faujasite Y [14] its reaction is therefore expected to be faster than the Y type as observed in this study.

Table 1. Amount of malathion residue in water alone, water treated with zeolite X and water treated with zeolite Y. Where n.d = means non-detectable concentration level. All the concentrations are expressed as (ppm \pm S.D) where n=3

Time (hrs)	Malathion in Water alone (ppm)	Malathion in X + Water treatment (ppm)	Malathion in Y + Water treatment (ppm)
1	5.18 \pm 0.04	2.78 \pm 0.08	5.13 \pm 0.04
2	4.21 \pm 0.05	2.13 \pm 0.10	3.08 \pm 0.05
4	2.93 \pm 0.11	1.42 \pm 0.09	1.74 \pm 0.11
6	1.99 \pm 0.06	0.95 \pm 0.11	1.36 \pm 0.06
12	1.18 \pm 0.03	0.56 \pm 0.11	0.95 \pm 0.03
24	0.58 \pm 0.01	0.27 \pm 0.03	0.38 \pm 0.01
48	0.24 \pm 0.02	n.d	n.d
96	0.10 \pm 0.02	n.d	n.d

3.2. Degradation Products of Malathion in Fresh Water

Fig. 1 shows the degradation trend of the malathion and the accumulation of its degradation products in fresh water. Under ordinary aquatic conditions, the hydrolysis breakdown sequence for the malathion (Mal.) follows both parallel and consecutive reaction mechanism resulting in malathion monocarboxylic acid (MMCA), malathion dicarboxylic acid (MDCA), Fumaric acid (FA), diethyl mercaptosuccinate (0,0- Dimethyl S- [1,2- bis (ethoxy- carbonyl) ethyl] dithiophosphate) (DEMS), O, O- dimethylphosphorothiolate (DEPT), and, O, O- dimethylphosphorodithionate (DMPDT) as degradation products. In some cases, a more toxic malaoxon is also a product [15]. Here, the only degradation products of malathion found in the fresh water (Fig. 1) were the malathion monocarboxylic (MMCA) and malathion dicarboxylic (MDCA) acids. This is in agreement with the reports by ref. [16] who similarly obtained the same products.

Typical of mechanisms for consecutive reactions, the accumulation trend of the products as shown in Fig. 1 indicates an equal production rates for both the MMCA and MDCA up to the 50th hour thereafter the MMCA concentration peaked over that of MDCA. The 50th hr coincided with the point when the degradation rate of malathion is, to the best approximation, zero. Such a trend where the daughter

(MDCA) becomes more prominent after the depletion of the reactants (Mal.) is consistent with a consecutive reaction [17].

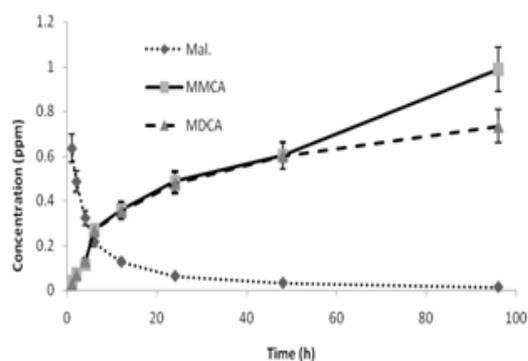


Fig. 1. Degradation trend of malathion and accumulation its degradation products in water.

However in the presence of the zeolites X and Y, in addition to the MMCA and MDCA that were obtained in fresh water, Dimethyldithiophosphonate (DMDTP) was detected. The trend of degradation of the malathion in the presence of zeolite Y is presented in Fig. 2.

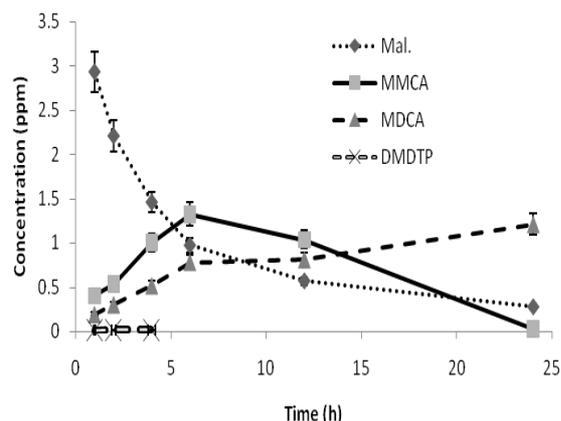


Fig. 2. Distribution of malathion and its degradation products in the presence of zeolite Y.

Here, the DMDTP was in minimal amounts and could only be detected up to the 5th hour. In addition, the zeolite Y afforded an increasing concentration of MMCA up to the 6th hour followed by a gradual decrease till the end of study period (Fig. 2).

Somewhat similar degradation pattern to that for Y was also observed for X treatment (Fig. 3). Unlike in water alone, the quantity of the MMCA product increased up to the 6th hour, there after it decreased to maintain a constant amount from the 15th hour to the end of the study duration. Such an increase followed by a decrease in the concentration of MMCA is expected since it is a sequential hydrolysis of malathion that leads to formation of MMCA after which the MMCA degrades further to MDCA. Meaning that the increase from the start to the sixth hour then a decrease in the concentration of MMCA is attributable to the sorption-desorption by the zeolites [7] followed by the sequential

formation of the MDCA.

A gain, as opposed to the type of products in the water alone, both Zeolite X and Y treatments afforded the DMDTP as an additional product however the amounts were minimal (Fig. 2, and Fig. 3). Conversely, the failure to detect DMDTP in water alone could be attributed to the paucity of dissolved water-bound cations that could stabilize the DMDTP as possibly happened for Zeolite-Na-DMDTP. The Na⁺ ions stabilizing the DMDTP could have been availed from the NaX and NaY zeolites used.

The degradation products (MMCA, MDCA and DMDTP) realized for Y (Fig. 2) and for X (Fig. 3) from the zeolite treatments had much lower toxicity levels than malathion itself and other degradation products of malathion in an aqueous medium [18]. It is worthy to note that malaoxon; a common and more toxic product of malathion degradation in most aqueous environments [3], was not detected in this work.

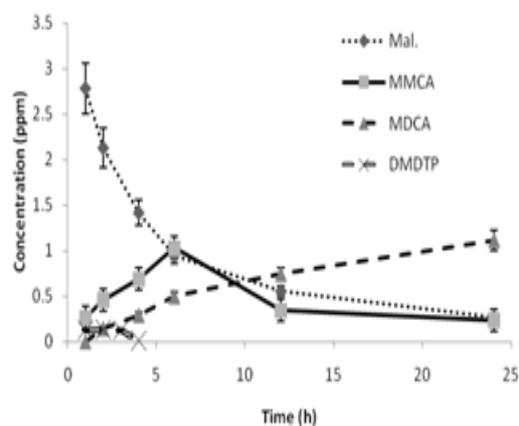


Fig. 3. Distribution of malathion and its degradation products in presence of zeolite X.

Statistically, there were several statistically significant differences between the effects of zeolites X and zeolite Y on the dissipation behaviour of malathion and its products (Table 2). Similarly, there were also significant changes in the degradation rates with time and the degradation patterns were also statistically different save for that of DMDTP in which the interaction was not significant.

Table 2 indicates that water treated with the zeolites made malathion dissipate faster than in the untreated. In comparison, zeolite X is more efficient in enhancing the degradation of malathion than zeolite Y. Such a difference is expected since the number of exchangeable univalent cations vary from about 10-12 per cage for zeolite X to as low as 6 for high silica zeolite Y [14]. Consequently, as compared to zeolite Y, zeolite X acquires a larger framework electronic charge for more effective catalysis and adsorption resulting to a faster dissipation rate for the pesticide than in zeolite Y. This observation concurs with previous studies which reported that zeolites X had higher degradation efficiency when compared to Y [19]. In effect, lower Si/Al zeolites would favour faster rates of malathion degradation.

Table 2. Variation of malathion and its degradation products with zeolite type and reaction time. Where NS = not significant.

Products	Treatments	Time(hr)						Mean for zeolite
		1	2	4	6	12	24	
Mal. (ppm)	Zeolite X	2.784	2.130	1.418	0.949	0.558	0.271	1.352
	Zeolite Y	2.932	2.207	1.458	0.970	0.567	0.274	1.401
	Mean time	2.858	2.169	1.438	0.960	0.563	0.272	
	CV%				2.570			
	LSD $p \leq 0.05$				0.052			0.149
	Interaction				0.074			
MMCA (ppm)	Zeolite X	0.270	0.459	0.691	1.030	0.346	0.238	0.506
	Zeolite Y	0.402	0.532	1.003	1.325	1.037	0.021	0.720
	Mean time	0.336	0.496	0.847	1.178	0.691	0.130	
	CV%				6.790			
	LSD $p \leq 0.05$				0.062			0.176
	Interaction				0.087			
MDCA (ppm)	Zeolite X	0.244	0.267	0.496	0.741	1.113	1.454	0.719
	Zeolite Y	0.193	0.303	0.518	0.781	0.810	1.208	0.635
	Mean time	0.218	0.285	0.507	0.761	0.962	1.331	
	CV%				11.200			
	LSD $p \leq 0.05$				0.112			0.322
	Interaction				0.159			
DMDTP (ppm)	Zeolite X	0.134	0.141	0.132	0.034	0.000	0.000	0.073
	Zeolite Y	0.013	0.014	0.015	0.000	0.000	0.000	0.007
	Mean time	0.074	0.077	0.073	0.017	0.000	0.000	
	CV%				4.110			
	LSD $p \leq 0.05$				0.045			0.128
	Interaction				NS			

To monitor framework changes within the zeolites such as any migrations by the exchangeable cations that could corroborate a cation-aided catalysis, XRD analysis was performed. Typical of XRD diffractograms for Faujasite framework, intensity changes for the $9.9^\circ (2\theta)$ and $11.6^\circ (2\theta)$ diffractograms depict cationic migrations [20]. In this set-up, such a migration would signify the participation of the framework Na^+ ions in the degradation mechanism. After normalising the peak intensities for the two graphs (X0 – unreacted X, and X20 – exposed to 20 ppm malathion) and setting the relative intensity of the strongest peak to 1.00 arbitrary units (a.u.) (ca. $6.0^\circ (2\theta)$), the corresponding relative intensities for the other peaks were similarly calculated and are as shown in Fig. 4.

From Fig. 4, the exposure of zeolite X to malathion had significant effect on the relative intensities of the diffracto-

grams at ca. $9.9^\circ (2\theta)$ changing from ca. 0.63 to 0.27 a.u. Simultaneously, the relative intensity of that at $11.6^\circ (2\theta)$ minimally increased from ca. 0.20 to 0.22. Similar exposure of the Zeolite Y to malathion resulted in a similar though minimal effect on the relative intensities of the diffractograms at $9.9^\circ (2\theta)$ from 0.23 to 0.21, while that at $11.6^\circ (2\theta)$ the intensity substantially increased from 0.16 to 0.22 (Fig. not shown). Such intensity changes corroborate cationic migrations from one site to another within the framework [20]. The changes depicted in Fig. 4 are therefore consistent with the involvement of Na^+ ions in the mechanism of this degradation. Due to the observed relatively high changes in the diffractograms intensities for X treatments, the XRD analysis therefore implies zeolite X has better catalytic and/or adsorption properties than Y. In addition, the difference in the amount of exchangeable Na^+ ion concentration

between the X and the Y treatments explains the observed differences in the DMDTP concentrations between X (Fig.2) and Y (Fig. 3) values. Therefore, it is understandable when X treatments had a higher concentration of the DMDTP compared to Y treatments.

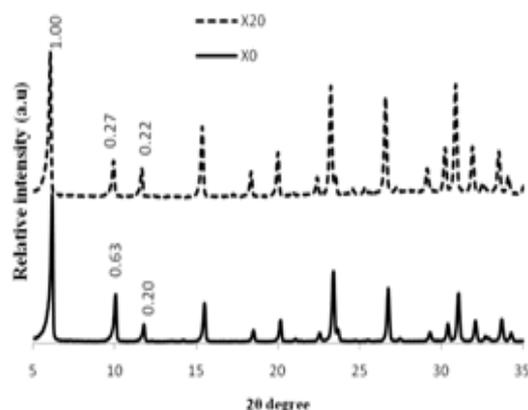


Fig. 4. XRD spectra for zeolite X in malathion. Where X0= zeolite X with 0 ppm malathion, X20 = zeolite X with 20 ppm Malathion.

To ascertain whether some amounts of the malathion and its degradation products were adsorbed in the zeolite matrix, a FT-IR characterization was performed. In IR, any changes in mass of the vibrating components, either through attachments or dissociations would result in a blue or red shift, respectively [20].

The Single-Four-Ring (S4R) which in a free zeolite X vibrates at ca. 764 cm^{-1} was shifted to ca. 742 cm^{-1} up on exposure to the malathion. A similar, though moderate shifting from ca. 770 cm^{-1} to 755 cm^{-1} was observed for the zeolite Y. A part from the above listed vibrational band shiftings, no any other changes were noted for the remaining finger-print bands. Assuming other factors are constant, such shifting imply an increase in the mass of vibrating framework which is consistent with the adsorption of some malathion or its degradation products on to the zeolite matrix. The attachment implies that apart from catalytic degradation of the pesticide, adsorption was also a major player in the decrease in concentration of the malathion in zeolite treatments. However, this work could not quantify how much of the malathion or its degradation products were adsorbed.

4. Concluding Remarks

The lower malathion concentrations of 5 and 10 ppm were totally adsorbed by both zeolite X and Y. Thus for zeolites to be used in drinking water purification, knowing the adsorption capacity and the Si/Al ratio of the individual zeolite is important. Faujasite zeolites were found to enhance the degradation of malathion, at 20 ppm, in water with the X type being faster than the Y type. Both the adsorption and catalytic activities significantly contributed in the dissipation processes of the malathion. The amount of exchange-

able Na^+ ions in the zeolite framework dictated the rate of and the nature of the product formed during the dissipation. Malathion degradation in fresh water and in the presence of zeolites produces the malathion monocarboxylic, malathion dicarboxylic acid and dimethyldithiophosphate as the degradation products. The more toxic maloxon was not produced during the malathion degradation when zeolite is used.

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