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Alleviation of Pesticide Residue in Surface Water

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Abstract

Reduction of environmental pollution incurred from pesticide use is very important. Zeolite is a natural mineral capable of removing certain chemical contaminants from water. This study was carried out to test the effect of zeolite treatment on pesticide residue alleviation in surface water. Ten surface water samples were treated with natural zeolite by filtering through. An EPA method was used to extract pesticide residue from the water samples and the surfactant used to modify the net charge on the zeolite was hexadecyltrimethylammonium chloride (HDTMA-Cl). Gas chromatography-mass spectrometry was used to analyze water samples. Alleviation was achieved in all the 10 water samples that were filtered through zeolite. The highest removal of pesticides from water with zeolite included 100% of bifenthrin in sample CLC, atrazine in BPH, CDG and LBT; metolachlor in CLC, LBT, BCH, TRH2 and BPI; acetolachlor in BBH and BCH; azoxystrobin in BBH; desethylatrazine in BCH and BPI; metribuzin in BCH, TRH2 and BPI; and both clomazone and bromacil in sample BDC. A minimum reduction of 10.9% was found for metolachlor in sample BRH. Further reduction of pesticide residues up to 50% was recorded in the SMZ treatment as the concentrations of 4 out of 8 pesticide residues were reduced. This study confirms the potential of both the natural zeolite-Clinoptilolite, and SMZ of alleviating pesticide residues in water.

Keywords

EPA (United States Environmental Protection Agency),
Gas Chromatography, Mass Spectrometry, Zeolite,
Hexadecyltrimethylammonium Chloride (HDTMA-Cl),
Surface-Modified-Zeolite (SMZ), Bifenthrin, Metolachlor, Metribuzin,
Acetolachlor, Azoxystrobin, Desethylatrazine, Clomazone, Bromacil,
Atrazine, Clinoptilolite, Alleviation

1. Introduction

A clean environment is required for maintaining good health and agricultural sustainability. Regular use of pesticides in modern day agriculture demands the need to devise a means of removing or reducing possible pesticide residues from our environment. Waters that are available in the environment where pesticides are used are of high risk of harboring pesticide residues. Leaching enhances environmental pollution as chemicals drain from the treated region to non-targeted environments. Therefore, surface waters have the potential of getting contaminated when irrigation water that has passed over pesticide-treated environment leaches into the surface waters [1]. Storms could sometime result in spontaneous flow of contaminated water into surface water [2]. Another source of pollution is drift that occurs if a pesticide spray misses its targets having been deflected by wind or resulting from human error, thereby, landing on a non-targeted area. When the level of the pesticide contamination reaches a critical level in food, ground waters, lakes, rivers or ponds, it becomes an issue that could lead to illness or death in the organisms that depend on them.

Due to its unique attributes, zeolite is a mineral with the potential of removing chemical contaminants from water as earlier published [3] [4]. Some of the past efforts made in removing pesticide residues in water include the use of clay [3] [5], activated carbon [6] [7] and ozonization [6]. Use of clay is limited by its adsorption capacity due to its shrink-swell behavior and zeolites are free of such flaws [8]. Saturation of carbon filters resulting in cost of replacement; and a decrease in the efficiency of activated carbon with increased organic contaminants are limitations in the use of activated carbon [9]. Formation of byproducts like peroxides, ozonides, organobromine and bromate is associated with the use of ozonization [9]. A natural zeolite like clipnotilolite is high in cation exchange capacity due to its net negative charge on the outer surface [10] [11] [12]. When a natural zeolite is fortified with an overall positive charge using a surfactant, its affinity for cation changes for anion and it entraps negatively charged organic ions such as chromate and hydrophobic organic ions [13] [14]. Clinoptilolite has high affinity for chromate and selenium and organic hydrophobics [15] and also for Pb^{2+} [16] when modified by hexadecyltrimethylammonium bromide (HDTMA-Br). These unique attributes of a zeolite are both utilized in this study as we seek to alleviate pesticide residues in surface waters across Louisiana. This article reports the evaluation of natural zeolite, and HDTMA-Cl surface-modified-zeolite on pesticide residue alleviation in surface water.

2. Materials and Methods

2.1. Water Sample Storage and Preparation

Ten surface water samples were collected from different locations in Louisiana. These were sourced from the pool of samples from the Pesticide Laboratory of the Agricultural Chemistry department, Louisiana State University through the Louisiana State Department of Agriculture and Forestry (LDAF). Water samples and their sources were as listed in Table 1. Each sample was labeled after its

Table 1. Water samples

Water	Source
BPH	Bayou Pierre, Hwy 1 S of Powha (*WM-S-A-01)
CLC	Chatlin Lake Canal, Hwy 457 T2N (WM-S-A-04)
CDG	Coulee Des Grues, hwy 115-SW (WM-S-A-05)
BCH	Big Creek Hwy 80 at Holly Ridge (WM-S-M-03)
LBT	Lake Bruin T12N R12E S29 (WM-S-M-06)
TRH2	Tensas River Hwy 15 at Clayon (WM-S-M-07)
BPI	Bayou Portage I-10 at Henderson (WM-S-O-07)
BDC	Bayou De Cannes, Hwy 98 2 MI, W (WM-S-C-03)
BBH	Black Bayou, Hwy 530 2 MI. E. of Foley AL 36535 (WM-S-S-01)
BRH	Boeuf River, Hwy 2 T2 IN R8E S25 Eunice LA (WM-S-M-01)

*WM = Water monitoring.

source by abbreviating the name of the source. For instance, sample BPH was obtained from Bayou Pierre, Hwy 1 S of Powha. All water samples were stored at 4˚C until each was analyzed.

2.2. Pesticide Residue Extraction in Fresh Surface Water

The method used for pesticide residue extraction in surface water is same as earlier described [17]. Analyte samples, positive and negative controls were prepared in 2 replicates in vials and analyzed.

2.3. Water Filtration through Natural Zeolite-Clinoptilolite

Ten water samples—BPH, CLC, CDG, BBH, BRH, BCH, LBT, TRH, BPI, and BDC, were selected from the original pool of 35 samples of surface water studied for detection of pesticide residues. The criterion used in selecting those 10 samples was the water samples that had the most pesticide residues based on the results from a similar study [17]. As shown in **Figure 1**, each of the 3 compartments of the water filtration system used to filter surface water samples from top to bottom contained 20 g each, of gravel, sand and Zeolite. A funnel was placed on the topmost column and filtration was initiated. The filtrate was collected into a 1 liter amber color bottle as shown in **Figure 1(b)**. For each water sample, a total of 1000 ml was filtered per 20 g of zeolite after which the filtration system was dismantled, cleaned by hot wash in soap, rinsed in running potable water three times and allowed to dry before re-assembled and re-used. Fresh zeolite was used for each sample.

2.4. Preparation of HDTMA-Cl (Hexadecyltrimethylammonium Chloride)-Surface-Modified Zeolite

As earlier described [18], 0.056 M surfactant (HDTMA-Cl) was prepared to treat the natural zeolite. On a weighing balance, 1.43 g HDTMA-Cl was measured and poured into a 125 ml beaker containing 70 ml of milliQ water. With a gentle
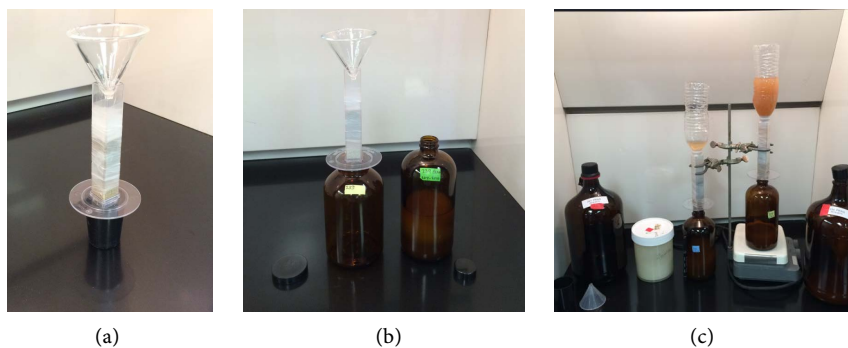
Figure 1. (a) Water filtration system. ((b) & (c)) Surface water filtration through zeolite and HDTMA-Cl SMZ.

swirl until all surfactant dissolved, solution was poured into 100 ml graduated cylinder and milliQ water added up to 80.5 ml final volume. Twenty gram of natural zeolite was dispersed in the 80.5 ml of 0.056 M surfactant for 2 hours. The supernatant was drained away after 2 hours and the surface-modified zeolite (SMZ) was spread out on a clean aluminum foil to air dry overnight.

2.5. Water Filtration through HDTMA-Cl-Surface-Modified Zeolite

The water sample BRH was selected based on its highest volume of pesticide residue content. The filtration system for SMZ consisted of 3 columns in layers. The upper layer was empty followed by a middle layer of natural zeolite and base layer of HDTMA-Cl-SMZ.

2.6. Pesticide Residue Extractions in Both Zeolite-Filtered, and SMZ-Filtered Waters

As listed in Table 2, ten zeolite-filtered water samples were extracted for pesticide residues. The same extraction method used in pesticide residue extraction in fresh surface water as earlier stated was repeated for both sets of samples-10 zeolite-filtered samples and 1 SMZ-filtered sample. In each case, the same volume of 1000 ml of water was ran through the natural zeolite and the SMZ accordingly. Sample vials for the GC-MS were prepared and analyzed.

2.7. Gas Chromatography-Mass Spectrometry

GC-MS analysis was the same as earlier described [17]. On column concentration of the samples were calculated. Spiking rate was computed and the efficiency of the methodology was confirmed through the value of the spike recovery. On column concentration expected from a spike was calculated and it provided a clue to where matrix standard needed to be in order to use it to calculate the recovery rate. The amount of sample represented in the liquid injected onto column was calculated. Parameters obtained regarding the quantitation and retention time are as outlined in Table 3.

2.8. Statistical Analysis

Statistical analytical system (SAS) was employed to run paired student T-test in

Table 2. Effect of zeolite treatment on pesticide residue (ppb) in surface water.

Sample	pH	Origin	Reduction	Pesti Resid	Before	After	% Reduction
BPH	7.7	2	2	Atrazine	0.2	ND	100
				Metolachlor	0.16	0.12	25
CLC	7.7	4	4	Atrazine	6.48	0.06	99.1
				Desethatz	0.74	0.55	25.7
				Metolachlor	1.08	ND	100
				Bifenthrin	0.02	0	100
CDG	7.2	2	2	Atrazine	0.68	ND	100
				Metolachlor	0.84	0.73	13.1
BBH	7.2	4	4	Atrazine	1.78	1.26	29.2
				Metolachlor	1.16	1.01	12.9
				Acetolachlor	0.06	ND	100
				Azoxystrobin	0.02	ND	100
BRH	7.3	8	8	Atrazine	6.2	0.64	89.7
				Clomazone	2.4	1.54	35.8
				Desethatz	0.62	0.38	38.7
				Metribuzin	0.34	0.17	50
				Metolachlor	17.2	15.32	10.9
				Propanil	0.08	0.03	62.5
				Metalaxyl	0.08	0.06	25
				Dimethenamid	0.16	0.12	25
LBT	7.7	5	3	Desethatz	0.22	0.17	22.7
				Atrazine	0.6	ND	100
				Metolachlor	0.36	ND	100
				Glyphosate	ND	ND	ND
				AMPA	ND	ND	ND
BCH	7.1	6	5	Atrazine	6.24	1.4	77.6
				Desethatz	0.54	ND	100
				Acetolachlor	0.28	ND	100
				Metribuzin	0.36	ND	100
				Metolachlor	3.9	ND	100
				Clomazone	0.04	ND	ND
TRH2	7.2	6	5	Atrazine	0.38	0.16	57.9
				Desethatz	0.26	0.06	76.9
				Metribuzin	0.3	ND	100
				Metolachlor	3.4	ND	100
				Clomazone	0.18	ND	ND
				Azoxystrobin	0.06	0.02	66.7
BPI	7.2	7	6	Atrazine	0.72	0.22	69.4
				Desthatz	0.2	ND	100
				Metribuzin	0.28	ND	100
				Metolachlor	0.74	ND	100

Continued

				Metalaxyl	0.12	0.1	16.7
				Clomazone	0.04	ND	ND
				Azoxystrobin	0.06	0.04	33.3
BDC	6.8	5	2	Clomazone	0.3	ND	100
				Bromacil	0.42	ND	100
				Metalaxyl	0.04	ND	ND
				Metolachlor	0.06	ND	ND
				Propiconazole	0.12	ND	ND

Origin = original pesticide residue in surface water; Reduction = reduced amount of pesticide residue in surface water; Pesti resid = pesticide residue; Desethatz = Desethylatrazine; before = pesticide residue (ppb) in water sample before filtration through zeolite; 1st and 2nd = First and second pesticide residue quantitation reading after filtration through zeolite; PR = pesticide residue; ND = non-detected.

Table 3. Retention time and quantitation ion for target compounds and their degradation products.

Compund	t_R (min)	Q_{ion} (m/z)	Compound	t_R (min)	Q_{ion} (m/z)
Acetochlor	6.87	223	Hexazinone	9.01	171
Alachlor	6.95	188	Malathion	7.2	173
Atrazine	6.5	200	MB45950fm	7.29	420
Azoxystrobin	11.51	344	MB46136fm	7.8	383
Bifenthrin	8.57	181	MB46513,Fip. met.	6.76	388
Bromacil	7.5	207	Metalaxyl	7.1	249
Captan	7.8	79	Methyl Parathion	7.16	263
Captan deg.	5.67	79	Metolachlor	7.22	162
Carbofuran	6.65	164	Metribuzin	7.18	198
Carbofuran deg.	4.08	164	Molinate (Ordram)	5.57	126
Chlorpyrifos	7.26	197	Norflurazon	8.76	303
Clomazone	6.53	125	Pendameth	7.5	252
Cyanazine	7.57	225	Prometone	6.34	225
Cyfluthrin 1	9.69	206	Propicon1	8.56	259
Cyfluthrin 3	9.76	206	Propicon2	8.59	259
Cypermet1	9.88	181	Prometryn	7.05	241
Cypermet2	9.95	181	Propanil	7.1	161
Desethylatrazine	6.24	172	Tebupirimiphos	6.42	261
DesIsopropylatz	6.28	173	Tefluthrin	6.17	177
Diazinon	6.4	137	Terbacil	6.93	161
Dimethenamid	6.91	154	Terbufos	6.4	231
Eptam	4.24	128	Thimet	6.17	75
Esfenvalera1	10.36	167	Trifluralin	5.6	306
Esfenvalerate	10.45	167	λ-cyhalot1	8.91	181
Etridiazole	5.04	183	λ-cyhalot	8.99	197
Fipronil	7.35	367			

λ = lambda; DesIsopropylAtz = desisopropylatrazine; MB46136fm = MB46136, Fip. met.; MB45950 = MB45950, Fip. met. Pendameth = Pendamethalin; Propicon2 = Propiconazole 2; Propicon1 = Propiconazole 1; λ-cyhalot1 = Lambda-cyhalothrin 1; λ-cyhalot = Lambda-cyhalothrin; Cypermethrin 1 = Cypermet1; Cypermethrin 2 = Cypermet2; Esfenvalerate 1 = Esfenvalera1.

order to compare the concentration of pesticide residues in the water samples before and after zeolite treatments. The alpha value was set at P = 0.05. That is, when the calculated P-value is less than 0.05 then a statistical difference can be declared.

3. Results

3.1. Role of Natural Zeolite in Pesticide Alleviation

Reduction in pesticide residues was observed in the 10 zeolite-filtered surface waters analyzed (Table 2).

As shown in Table 2, reduction in pesticide residue levels following zeolite filtration ranged from the minimum of 10.9% to a maximum of 100%. Minimum reduction was recorded in metolachlor in sample BRH, while the maximum were in atrazine in samples BPH, CDG and LBT; metolachlor in samples CLC, LBT, BCH, TRH2 and BPI; bifenthrin in sample CLC; acetolachlor in BBH and BCH; azoxystrobin in BBH; desethylatrazine in BCH and BPI; metribuzin in BCH, TRH2 and BPI; and both clomazone and bromacil in sample BDC. A high reduction rate of 99.1% was found in atrazine in the same sample CLC. Atrazine was also alleviated in sample BRH up to 89.7%. Moderately high rates of reductions were also found in atrazine at the rate of 77.6% in sample BCH; 57.9% in sample TRH2; and 69.4% in sample BPI. Reductions recorded in sample BRH included 50% metribuzin and 62.5% propanil; and in sample TRH2 was 66.7% azoxystrobin.

Statistics of the means comparison for the pesticide residues found before and after filtering water through natural zeolite using a paired student t-test is as shown in Table 4 at $P_{critical}$ = 0.05. The difference between the atrazine levels before and after filtration of water sample through natural zeolite was highly significant in CLC and was significant in BRH and BCH. Difference between the atrazine levels was not significant in samples BBH and TRH2. Second analysis of BPI atrazine was not detected and therefore paired t-test not applicable. No statistical difference was found between the desethylatrazine levels before and after zeolite treatment in samples CLC and BRH and LBT. No significant difference was found before and after treatment with zeolite for the pesticide levels in metolachlor in samples BPH, CDG and BBH. There was no statistical difference between desethylatrazine levels before and after zeolite treatment in CLC, BRH and LBT.

3.2. Role of Surfactant-Modified-Zeolite (SMZ) in Pesticide Alleviation

As summarized in Table 5, following SMZ treatment of sample BRH, 6 pesticides were detected out of 8. Propanil and dimethenamid were undetected after SMZ treatment.

Greater reduction of pesticide residues was recorded (Table 6) in the sample BRH that was filtered through the surfactant-modified-zeolite (SMZ). A 50% reduction was observed as 4 out of the 8 residues found were reduced following

Table 4. Paired t-test comparison of pesticide residue means before and after zeolite treatment.

Sample	PR	Before	After	Means ± SD	Pr > |t|	Sig.
BPH	Metolachlor	0.16	0.12	0.04 ± 0.03	0.3	NS
CLC	Atrazine	6.48	0.06	6.42 ± 0.00	0.0001	***
	Desethatz	0.74	0.55	0.10 ± 0.14	0.5	NS
CDG	Metolachlor	0.84	0.73	0.11 ± 0.01	0.06	NS
BBH	Atrazine	1.78	1.26	0.52 ± 0.11	0.1	NS
	Metolachlor	1.16	1.01	0.15 ± 0.0.13	0.34	NS
BRH	Atrazine	6.2	0.64	5.56 ± 0.31	0.03	*
	Desethatz	0.62	0.38	0.10 ± 0.50	0.83	NS
LBT	Desethatz	0.22	0.17	0.13 ± 0.01	0.05	NS
BCH	Atrazine	6.24	1.4	4.84 ± 1.84	0.01	**
TRH2	Atrazine	0.38	0.16	0.29 ± 0.04	0.07	NS
BPI	Atrazine	0.72	ND	NA	NA	NA
BDC	Metolachlor	0.06	ND	NA	NA	NA

Sig. = Significance; NS = no significant difference found among the pesticide residue levels recorded before and after treatment with natural zeolite clinoptilolite; * & *** = significant difference and highly significant difference respectively found among the pesticide residue levels recorded before and after treatment with natural zeolite clinoptilolite; SD = standard deviation; SE = standard error; PR = pesticide residue; df (degree of freedom) = 1; Pr > \|t\| = calculated P value by SAS; Alpha = 0.05 (critical P value); NA = not applicable.

Table 5. Effect of surfactant-modified-zeolite (SMZ) on pesticide residue in surface water.

Sample	Pesticide Residue (ppb)			
		Before	After	Mean ± SD
			1st	2nd	
BRH	Atrazine	6.2	0.34	0.28	0.31 ± 0.04
	Clomazone	2.4	1.12	0.84	0.98 ± 0.20
	Desethylatrazine	0.62	0.5	0.34	0.42 ± 0.01
	Metribuzin	0.34	0.24	0.22	0.23 ± 0.01
	Metolachlor	17.2	10.16	7.82	8.99 ± 1.66
	Metalaxyl	0.08	0.04	0.04	0.04 ± 0.00
	Propanil	0.08	ND	ND	NA
	Dimethenamid	0.16	ND	ND	NA

SD = standard deviation; ND = not detected.

Table 6. Percentage reduction of the pesticide residue (ppb) in surface water filtered through SMZ.

Sample	PR	BZ	AZ	ASMZ	% Zeolite reduction	% SMZ reduction
BRH	Atrazine	6.2	0.64	0.31	89.7	95
	Clomazone	2.4	1.54	0.98	35.8	59.2
	Desethylatrazine	0.62	0.38	0.42	38.7	32.3
	Metribuzin	0.34	0.17	0.23	50	32.4
	Metolachlor	17.2	15.32	8.99	10.9	47.7
	Metalaxyl	0.08	0.06	0.04	25	50

BZ = before zeolite treatment; AZ = after zeolite treatment; ASMZ = after surface-modified-zeolite; SMZ = surface-modified-zeolite; PR = pesticide residue.

filtration through SMZ. The 4 compounds that were reduced by SMZ compared to filtration through natural zeolite included atrazine @ 95% compared to 89.7% reduction with natural zeolite (NZ); 59.2% clomazone compared with 35.8% with NZ; 47.7% metolachlor compared with 10.9% with NZ and 50% metalaxyl compared with 25% with NZ.

As outlined in Table 7, paired t-test means comparison of pesticide residue before and after SMZ treatment was conducted. A significant difference (P_{calc} = 0.003) was found in atrazine between the pesticide level recorded before and after the SMZ treatment of sample BRH. A highly significant difference (P_{calc} < 0.0001) was similarly found in metalaxyl levels before and after SMZ treatment. In pesticide levels recorded for clomazone, desethylatrazine, metribuzin and metolachlor, there was no statistical difference found among them.

Further paired t-test comparison of pesticide levels was conducted between the levels recorded after treatment with natural zeolite and the levels recorded after treatment with surfactant-modified-zeolite. The outcome of this as outlined in Table 8 showed a statistical difference in metalaxyl, and the difference ob-

Table 7. Paired t-test comparison of pesticide residue means before and after SMZ treatment.

Sample	PR	Mean ± SD	Pr > |t|	Sig.
BRH	Atrazine	5.89 ± 0.04	0.003	***
	Clomazone	1.42 ± 0.20	0.06	NS
	Desethatz	0.20 ± 0.11	0.24	NS
	Metribuzin	0.11 ± 0.01	0.06	NS
	Metolachlor	8.21 ± 1.66	0.09	NS
	Metalaxyl	0.04 ± 0.00	<0.0001	***

*Sig. = Significance; NS = no significant difference found among the pesticide residue levels recorded before and after treatment with Hexa decyl trimethyl chloride surfactant-modified-zeolite clinoptilolite; ** = very significant difference found between the pesticide residue levels recorded before and after treatment with HDTM-Cl SMZ; SD = standard deviation; SE = standard error; PR = pesticide residue; df (degree of freedom) = 1; Pr > \|t\| = calculated p value by SAS; Alpha = 0.05 (critical p value).

Table 8. Paired t-test comparison of levels of PR (ppb) of zeolite-treated and SMZ-treated sample.

Sample	PR	Mean ± SD	Pr > |t|	Sig
BRH	Atrazine	0.33 ± 0.04	0.06	NS
	Clomazone	0.56 ± 0.20	0.16	NS
	Desethatz	neg0.04 ± 0.11	0.71	NS
	Metribuzin	neg0.06 ± 0.01	0.11	NS
	Metolachlor	6.33 ± 1.66	0.12	NS
	Metalaxyl	0.02 ± 0.00	<0.0001	***

Sig. = Significance; NS = no significant difference found among the pesticide residue levels recorded between zeolite treated and SMZ treated sample BRH; *** = highly suignificant difference found among the pesticide residue levels recorded between zeolite treated and SMZ treated sample BRH; SD = standard deviation; SE = standard error; PR = pesticide residue; df = degree of freedom; Pr > \|t\| = calculated p value by SAS; Alpha = 0.05 (critical p value).

served was highly significant ($P_{calc} < 0.0001$). No statistical difference between treatment was observed for atrazine, clomazone, desethylatrazine, metribuzin and metolachlor. However, negative mean value and t value computed for desethylatrazine and metribuzin showed a negative trend because the levels recorded after filtration through the SMZ was higher than the levels after filtration through the natural zeolite. As outlined in Table 6, after filtration through natural zeolite desethylatrazine level was reduced from original 0.62 ppb to 0.38 ppb compared to 0.42 ppb for SMZ. After filtration through zeolite, metribuzin level was reduced from 0.34 to 0.17 compared to 0.23 ppb recorded after filtration through SMZ.

4. Discussions

As obtained in this study, adsorption of metalaxyl using zeolite has been earlier reported [4]. Reduction in atrazine recorded in this study is similar to two reports earlier published [3], [19], even though they used SDBAC (stearyldimethylbenzylammoniumchloride) as surfactant to modify the zeolite and HDTMA-Cl (hexadecyltrimethylammonium chloride) was used in this study as modifying surfactant. Further reduction of atrazine, clomazone, metolachlor and metalaxyl after filtration through SMZ conforms to the theoretical principle of effect of exchanging CEC (cation exchange capacity) property of clinoptilolite with an anion exchange capacity, thereby enhancing its ability to retain negatively charged organic ions that ordinarily would have escaped. Differences recorded in the pH (ranging from 6.8 through 7.7) of the surface water samples may have impacted the cation exchange capacity of the zeolite. This finding is in agreement with the result of a similar study [20] where they confirmed that the success of clinoptilolite in removing organic contaminations is a function of pH, temperature, contact duration, and initial concentrations of humic acid and ammonia. Pesticide residues were alleviated in all the samples whose pH ranged between 7.1 through 7.7, while the low pH 6.8 in sample BDC might be responsible for those pesticide residues that were non-detected. Similar to the assertion [20] that the optimum temperature at which zeolite could reduce organic contaminants in water is about room temperature which was the reason while sample waters were always allowed to acclimatize to room temperature after retrieved from cold storage. Findings in this study may also imply that water samples need to be above neutral pH in order for the zeolite to work at its optimum as earlier suggested [21] that sample water needs to be about the pH of natural water (pH 7.0) for the detection of residues to be at its best. High atrazine level of 6.2 ppb originally detected in the BRH sample which was reduced to 0.64 ppb when treated with zeolite, and further reduced to 0.31 ppb when treated with SMZ confirmed the adsorption capacities of the natural zeolite (clinoptilolite) and HDTMA-Cl SMZ as a potential remedy to the concentrations of this herbicide in surface water. Some residues were not detected in the water samples and this could be due to their low concentration probably tending toward infinitesimal amount as GC-MS detection limits were surpassed. It could also mean that they have been totally removed from the sample by the SMZ treatment. As op-

posed to the expected event that enhanced reduction be observed when filtered through SMZ, a reversed trend observed in desethylatrazine and metribuzin may imply that they have greater affinity for natural zeolite than for zeolite modified by HDTMA-Cl surfactant. Great affinities of clinoptilolite zeolite for ammonium ion [22] and that of SMZ for chromate and selenite [15] are an indication that any trace amount of NH_4^+, chromate or selenate in any of the 10 samples studied in this section may have been reduced. However, lack of measurement of these ions limited us from any information regarding this aspect. Part of future work would be to examine water for metal contaminants like arsenic [23] [24]; Fe and Mn [25]; Cd and Pb [26]; Pb^{2+} [16], and the cation NH_4^+.

5. Conclusion

Results obtained in the reduction of atrazine, metolachlor, bifenthrin, clomazone, desethylatrzine, metribuzin, propanil and metalaxyl are good to build upon as modern scientists aspire to provide a permanent solution to pesticide residues in surface water. This could be a basis for a large scale pesticide reduction in other forms of water like ground water and potable water as time goes on. Development of an industrial scale filtration system that could utilize zeolite as water filtration medium will be required in order to put the results obtained in this study into the effective use that will impact communities, national and international boundaries. Simplicity of this method with its low cost filtration system, coupled with the fact that it is free of any form of health risk will enhance its practical use and eventually lead to a global adoption of this methodology.

Acknowledgements

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