

ORIGINAL ARTICLE

Adsorption Characteristics of Pesticides in Zeolites

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Abstract

The adsorption characteristics of four pesticides (phosphamidon, fenitrothion, triadimefon, and diniconazole) on natural clinoptilolite (CLL_N) and three synthetic zeolites were investigated. The synthetic zeolites included faujasite (FAU_F) synthesized from coal fly ash; the mixture of FAU and Na-P1 (FAU + Na-P1)_{SF} synthesized using Jeju scoria and coal fly ash at the ratio of 1.5 by weight; and waste fluid catalytic cracking catalyst (FCC_W). The distribution coefficient, K_D and the Freundlich constant, K_F decreased in the following sequence: FCC_W > FAU_F > (FAU + Na-P1)_{SF} > CLL_N among the zeolites and diniconazole > fenitrothion > triadimefon > phosphamidon among the pesticides. The pesticide adsorptivity increased with increasing temperature for FAU_F, (FAU+Na-P1)_{SF} and FCC_W, however, it decreased for CLL_N, regardless of the type of pesticide. The adsorptivity of pesticides was independent of pH for phosphamidon, fenitrothion and triadimefon, whereas it decreased with increasing pH for diniconazole, regardless of zeolite type.

Key words : Adsorption, Natural zeolite, Synthetic zeolites, Pesticides

1. Introduction

The widespread use of synthetic pesticides in golf courses, agriculture and forestry has been critically reviewed by the public due to the adverse effects on both human health and environment (Singh et al., 1990; Chun et al., 2018).

In golf courses, activated carbon and zeolite are paved under the construction. Activated carbon is a strong adsorbent of sprayed pesticides, whereas zeolite is a soil conditioner and can also adsorb pesticides, to some extent. However, the adsorption capacity of zeolites is much lower than that of activated carbon (RIHE-JSGP, 1996).

In the previous studies, several zeolites could

be synthesized using coal fly ash (Lee et al., 2003) and Jeju scoria (Jeon et al., 2004) and the synthesized zeolites showed greater adsorption capabilities for metal ions than the natural zeolites. Hence, these synthesized zeolites can likely substitute natural zeolite (Henmi, 1987).

When pesticides are applied to an adsorbent (such as soil), they come into contact with a variety of adsorbent surfaces to which they may be adsorbed. The adsorption process is a major factor that dictates the behavior of the pesticides as it can influence leaching (desorption), translocation, volatilization, and persistence, (Celis and Koskinen, 1999). The adsorption of pesticides in soil is influenced by the organic matter and clay content of the soil (Singh et al., 1990) as well as the structure, molecular size,

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Table 1. Physical and chemical properties of zeolites used in this study

Zeolite	Properties				
	Channel	Pore diameter (Å)	Specific surface area (m ² /g)	CEC (meq/100 g)	Organic matter (%)
CLI _N ^a	8-ring	2.6×3.7	75	182.2	0.12
	10-ring	3.3×4.6			
		3.0×7.6			
FAU _F ^b			64	136.1	0.19
(FAU+Na-P1) _{SF} ^c	12-ring ^e	7 ~ 8 ^e (entrance) 13 ^e (inside channel)	54	180.8	0.34
FCC _W ^d			150	45.1	0.20

^anatural clinoptilolite; ^bFAU synthesized from coal fly ash; ^cmixture of FAU and Na-P1 synthesized with a ratio of Jeju scoria/coal fly ash at 1.5 by weight; ^dwaste fluid catalytic cracking catalyst; ^echaracteristics for FAU.

Table 2. Chemical composition (wt %) of the zeolites used in this study

Zeolite	SiO ₂	Al ₂ O ₃	Na ₂ O	CaO	Fe ₂ O ₃	Others ^e
CLI _N ^a	68.6	13.3	2.7	2.7	2.1	10.6
FAU _F ^b	38.1	30.1	5.6	4.8	4.9	16.2
(FAU+Na-P1) _{SF} ^c	46.2	14.1	5.8	8.3	13.1	12.4
FCC _W ^d	73.4	25.0	-	-	-	1.6

^anatural clinoptilolite; ^bFAU synthesized from coal fly ash; ^cmixture of FAU and Na-P1 synthesized with a ratio of Jeju scoria/coal fly ash at 1.5 by weight; ^dwaste fluid catalytic cracking catalyst; ^esum of MgO, K₂O, TiO₂, MnO and P₂O₅.

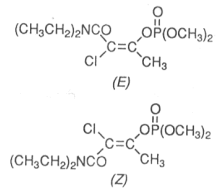
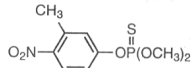
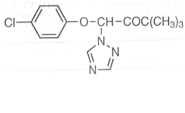
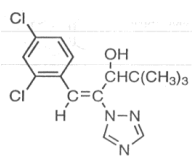
electron charge density, ionizability, hydrophobicity/polarity, geometrical, and topological characteristics of the pesticides (Woodburn et al., 1992; Kah and Brown, 2006), and pH (Oh, 1999) and temperature (Bansal, 1983) of aqueous solutions.

Several studies have focused on the adsorption of pesticides in soils and activated carbon (Futagami et al., 1998). However, studies on the adsorption of pesticides in zeolites are scarce, and their results only suggest that zeolites can adsorb pesticides far less effectively than the activated carbon (RIHE-JSGP, 1996). Although the adsorption and desorption characteristics of triadimefon (triazine pesticide) sprayed in a golf course were briefly investigated using several zeolites, a systematic study was not conducted to include the different pesticides, is the present study aimed to investigate the adsorption characteristics of pesticides in zeolites. Four pesticides phosphamidon, fenitrothion, triadimefon, and

diniconazole, that were sprayed in large amounts in golf courses of Jeju Island, Korea, and were selected as target pesticides. Natural zeolites (paved in golf course) and several synthetic zeolites had been used as adsorbents. The molecular size of the pesticides, the chemical composition, cation exchange capacity (CEC), organic matter content and specific surface area of the zeolites, were measured to determine their adsorption mechanisms in zeolites and/or to compare their adsorptivity. Their adsorptivities were compared using the adsorption isotherms of the pesticides according to the type of zeolite. Model fitting was performed with the experimental data using the Linear and Freundlich adsorption isotherm models. In addition, the effects of pH and temperature on pesticide adsorption were also examined.

2. Materials and Methods

Table 3. Characteristics of pesticides used in this study (Tomlin, 1994)

Pesticide	Phosphamidon	Fenitrothion	Triadimefon	Diniconazole
Chemical Structure				
IUPAC name	2-chloro-3-(diethylamino)-1-methyl-3-oxo-1-propenyldimethyl phosphate	O,O-dimethyl O-(3-methyl-4-nitrophenyl) phosphorothioate	1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone	(E)-(±)-β-[(2,4-dichlorophenyl)methylene]-α-(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol
Molecular weight	299.7	277.2	293.8	326.2
Family	organophosphate insecticides	phenyl organothio-phosphate insecticides	conazole fungicides	conazole fungicides
Water Solubility (mg/L)	1 × 10 ⁶	21 (20°C)	64 (20°C)	4 (25°C)
Molecular size ¹⁾ (minor × major diameter, Å)	6.73 × 11.007	6.37 × 9.77	7.84 × 10.56	6.30 × 10.01
Stability	rapidly hydrolysed by alkalis: DT ₅₀ (calculated) (20°C) 60 d (pH 5), 54 d (pH 7), 12 d (pH 9)	relatively stable to hydrolysis under normal conditions: DT ₅₀ (estimated) 108.8 d (pH 4), 84.3 d (pH 7), 75 d (pH 9) (22°C)	stable to hydrolysis: DT ₅₀ (22°C) > 1 y (pH 3, 6, and 9)	stable to heat, light and moisture

¹⁾Measured in stable conformation of these pesticides using semiempirical AM 1 Hamiltonian computer program.

2.1. Materials

The zeolites used were as follows: (1) natural zeolite (clinoptilolite, CLIN) paved in golf course; (2) the zeolite (faujasite, FAUF) synthesized from coal fly ash (Kam et al., 2002); (3) a mixture of FAU and Na-P1 (FAU + Na-P1)_{SF} synthesized with a ratio of Jeju scoria/coal fly ash at 1.5 by weight (Kam et al., 2002); and (4) waste fluid cracking catalyst (FCC_W: FAU-type zeolite), supplied by company A (Kam et al., 2002)-the zeolite formed by adding the binder component (aluminosilicates, or clay minerals) to ultra-stable Y zeolite (USY) (most of the aluminum components of Y zeolite were removed using steam treatment, and were replaced with silicon components by adding silicon compounds), and discarded after use.

The zeolites were thoroughly washed with

de-ionized water, dried at 105°C, and sieved (200/270 mesh). The chemical composition, organic matter content, CEC, and specific surface area of the zeolites were determined by X-ray fluorescence spectrometry (XRF, Shimadzu model MXF-2100), back titration method (Walkey and Black, 1934), 1 M sodium acetate method (Page, 1985), and classical BET method (Gregg and Sing, 1967), respectively. The physicochemical properties and chemical compositions of the zeolites are summarized in Table 1 and 2, respectively.

All pesticides and solvents used were of analytical grade. The pesticides used in the present study included phosphamidon (purity 93%), fenitrothion (purity 98.9%), triadimefon (purity 99%), and diniconazole (purity 99.8%). All pesticides were obtained from Dr. Ehrenstofer

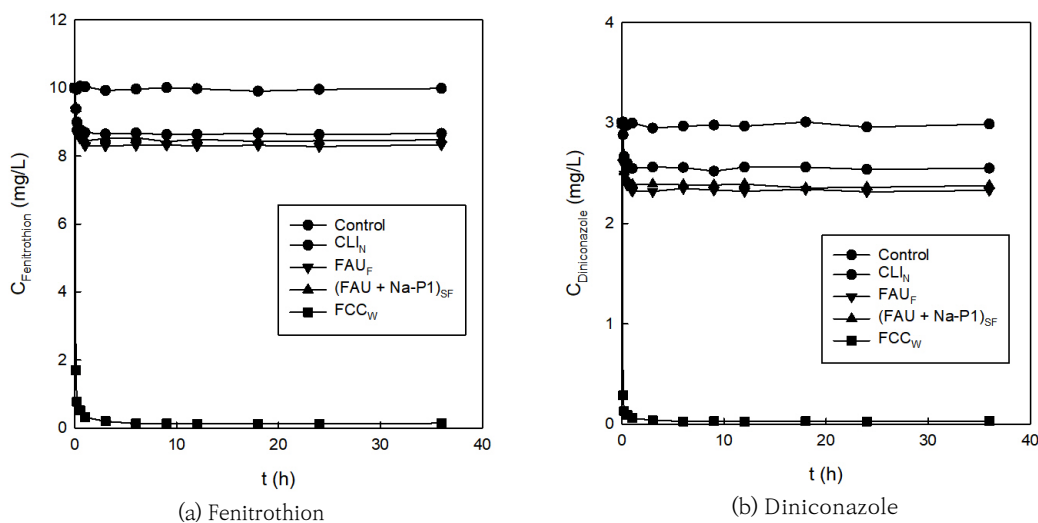


Fig. 1. Effect of shaking time on the adsorption of fenitrothion and diniconazole in several zeolites.

GmbH (Germany) and the properties of the pesticides are listed in Table 3. Stock solutions of these pesticides were prepared at a concentration of 1000 $\mu\text{g}/\text{mL}$ by dissolving them in methanol. Working pesticide solutions were prepared in 0.01 M CaCl_2 at concentrations ranging from 2 to 10 $\mu\text{g}/\text{mL}$ for phosphamidon, fenitrothion, and triadimefon, and from 0.6 to 3.0 $\mu\text{g}/\text{mL}$ for diniconazole by diluting the stock solutions with de-ionized water to facilitate the water solubility of the pesticides.

2.2. Experimental methods

The adsorption experiments of pesticides in zeolites were performed by the batch equilibrium technique using 50 mL borosilicate glass vial with a screw cap. Zeolite sample (0.1 g) were equilibrated with 20 mL of pesticide working solution by shaking in a water bath at 25°C and 220 rpm for 6 h. The samples were prepared in triplicates. After attaining an equilibrium, the suspensions were centrifuged at 4000 rpm for 20 min, and 5 mL of the supernatant was analyzed by gas chromatography after extracting with 5 mL of a mixture of n-hexane:ethyl acetate (1:1). The effects of temperature and pH on the adsorption of

pesticides in zeolites were investigated in the range of 15–45°C and pH 3–10 (adjusted with 0.1 N HNO_3/NaOH). Solutions shaken in glass vials without zeolite served as controls and showed no pesticide loss during the equilibrium periods.

Residue quantification of pesticides was performed by a gas chromatography (Hewlett Packard, HP 5890 Series II equipped with a flame photometric detector (for phosphamidon and fenitrothion) and an electron capture detector (for triadimefon and diniconazole), and HP-1 capillary column (crosslinked methyl silicon gum 10 m x 0.53 μm ID x 0.88 μm thickness)). The operating temperature conditions for gas chromatography were as follows: injection temperature 250°C, detector temperature 250°C, and oven temperature: 165°C for phosphamidon, 170°C for fenitrothion, 200°C for triadimefon, and 220°C for diniconazole.

3. Results and Discussion

The adsorption of pesticides in soils is greatly influenced by the organic matter content of the soils (Singh et al., 1990). In addition the structure, molecular size, electron charge density/ionizability, hydrophobicity/polarity, and

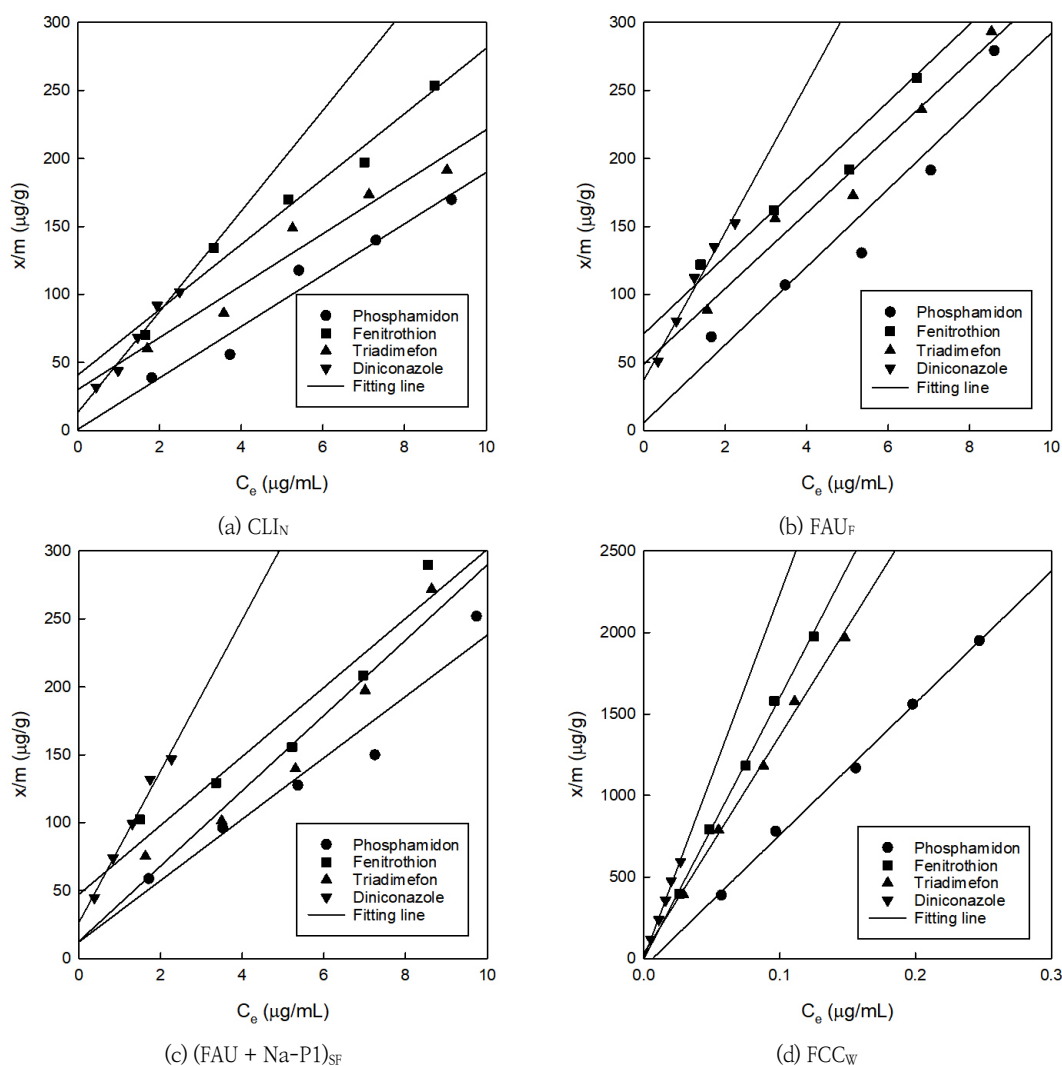


Fig. 2. Linear adsorption isotherms of phosphamidon, fenitrothion, triadimefon and diniconazole in several zeolites.

geometrical and topological characteristics of the pesticide molecule also affect its adsorption (Woodburn et al., 1992). Various factors inherent to adsorbents and adsorbates that influence the adsorption of pesticides have been summarized by Baily and White (1970).

First preliminary adsorption tests of pesticides in all zeolites (including five zeolites (Na-P1, sodalite octahydrate, analcime, nepheline hydrate, and cancrinite) synthesized from Jeju scoria (Jeon et al., 2004) in addition to those

(CLI_N , FAU_F , $(FAU+Na-P1)_{SF}$, and FCC_W) shown in Table 1, were investigated. Batch experiments were conducted with the system containing 10 µg/mL of phosphamidon, fenitrothion, and triadimefon, 3.0 µg/mL of diniconazole, and 0.1 g of each zeolite. The results showed that the pesticides were not adsorbed in zeolites synthesized from Jeju scoria but were adsorbed in zeolites shown in Table 1; this could likely be due to the difference in pore size (Kam et al., 2002). As the organic matter content in zeolites is very

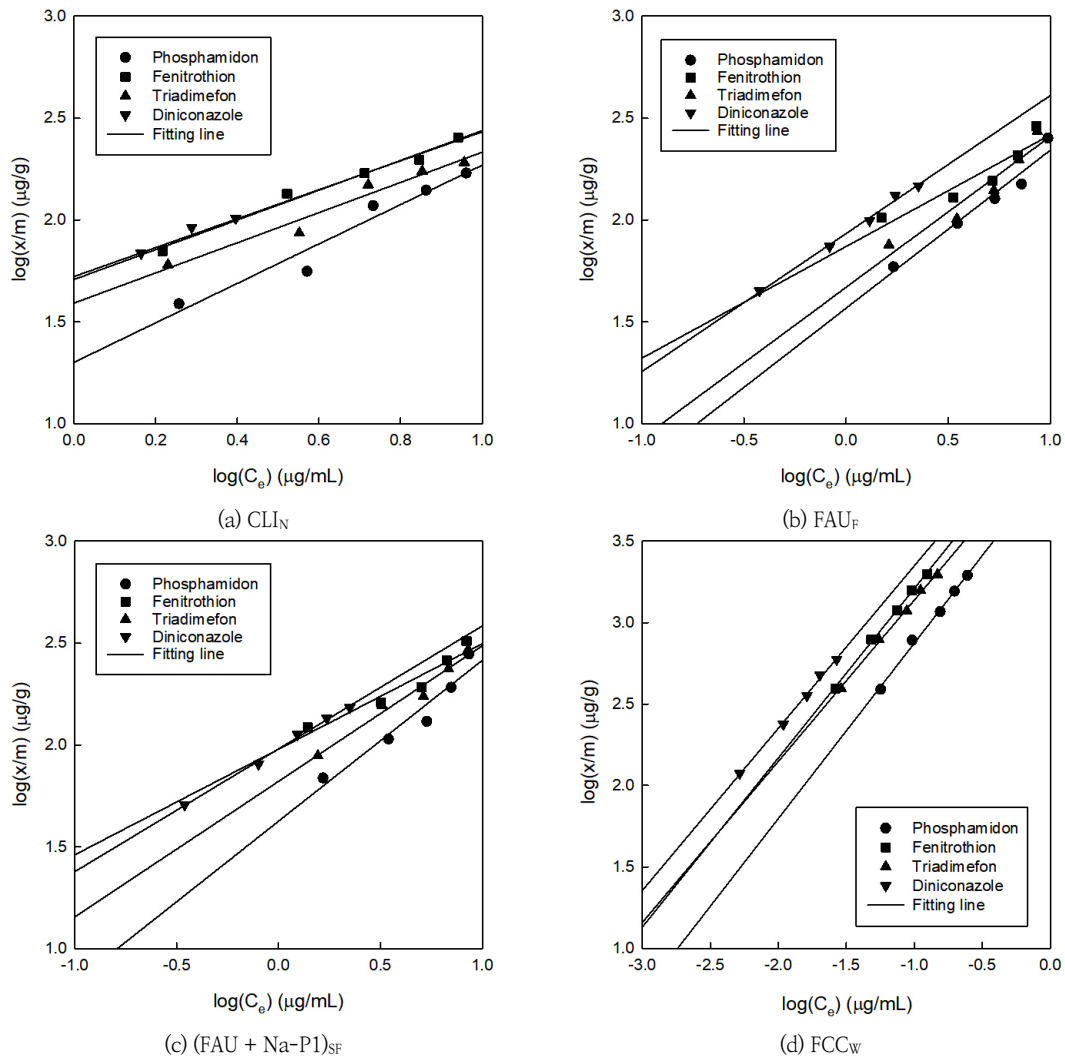


Fig. 3. Freundlich adsorption isotherms of phosphamidon, fenitrothion, triadimefon and diniconazole in several zeolites.

low, it is very difficult for pesticides to be adsorbed on the surfaces of zeolites: thus, they must enter the pores of zeolites: to be adsorbed. However, they can not enter the pores of the former zeolites because their sizes (above 6\AA) are larger than the pores (below 5\AA) of these zeolites, indicating that pesticides can not be adsorbed in these zeolites. In contrast, the latter zeolites, such as CLI_N , FAU_F , $(\text{FAU}+\text{Na-P1})_{\text{SF}}$, and FCC_W , can adsorb pesticides because they have a sufficiently large pore size (approximately

7\AA) for the penetration of pesticides. Therefore, pesticide adsorption studies have been carried out using these zeolites.

3.1. Effect of shaking time

To determine the shaking time necessary to reach pesticides adsorption equilibrium in zeolites, batch kinetic studies were performed by changing the shaking time from 5 min to 36 h, using 0.1 g of zeolite (CLI_N , FAU_F , $(\text{FAU}+\text{Na-P1})_{\text{SF}}$,

and FCC_w) and 20 mL of pesticide solution at 10 µg/mL for phosphamidon, fenitrothion, and triadimefon and 3.0 µg/mL for diniconazole. The results for fenitrothion and diniconazole are shown in Fig. 1; the same results were obtained for phosphamidon and triadimefon. In most previously published studies on pesticide adsorption in soils, a shaking time of 24 h of was necessary to reach pesticide adsorption equilibrium (Celis and Koskinen, 1999; Chun et al., 2018). In the present study, however, the pesticide adsorption kinetics obtained for each zeolite in this study revealed that 6 h was sufficient to reach adsorption equilibrium (Fig. 1). The adsorption equilibria for CLI_N, FAU_F, and (FAU+Na-P1)_{SF} were obtained within 1 h and no change in equilibrium concentration was measured during the next 35 h, regardless of the type of pesticide. For FCC_w, more than 90% of pesticide adsorption occurred within 0.17 h, a slight adsorption took place from 0.17 h to 3 h, and no difference in equilibrium concentration was measured during the next 33 h. Control samples without zeolites, presented no reduction losses of pesticides due to adsorption on glass, or volatilization.

3.2. Adsorption isotherms

Two types of isotherm equation were tested to fit the experimental data for pesticides in the zeolites. Both equations have been extensively used for the adsorption of pesticides in soil.

$$\text{Linear equation : } \frac{x}{m} = K_D C_e \quad (1)$$

Freundlich equation :

$$\log\left(\frac{x}{m}\right) = \log X_F + \frac{1}{n_F} \log C_e \quad (2)$$

where x/m (µg/g) is the amount of solute adsorbed per unit adsorbent at the equilibrium concentration C_e (µg/mL), K_D is the linear distribution or partition constant of the solute between the solvent and the adsorbent, $1/n_F$ is a

measure of the intensity of adsorption reflecting the degree of linearity of adsorption, and K_F is the amount adsorbed per unit equilibrium concentration of solute (i.e., a measure of adsorbent capacity).

Figs. 2 and 3 show the plots applied to the Linear equation (Eq. 1) and the linearized form of the Freundlich equation (Eq. 2), respectively. The estimated model parameters are listed in Table 4.

As shown in Table 4, all the r^2 values were > 0.90 , indicating that the Linear and the Freundlich equations fit the experimental data well. The r^2 values for FCC_w were > 0.99 , which may be due to the fact that FCC_w has many adsorption sites, as it is a pure zeolite, and the concentrations of pesticides are relatively low.

The types of pesticide adsorption isotherms in zeolites can be classified using the values of $1/n_F$ that are shown in Table 4. The values for the FCC_w approach 1, suggesting that these are C-type isotherms. The C-type isotherm represents the constant partition of the solute between the adsorbent surface and the solvent phase whenever new sites on the former become available (Sundaram et al., 1997), whereas the values for CLI_N, FAU_F and (FAU+Na-P1)_{SF}, are lower than 0.9, indicating a convex or L-type isotherms. This type of isotherm may arise due to the minimum competition of the solvent for sites on the adsorbing surface. The slope of the isotherms steadily decreases with an increase in solute concentration because vacant sites become less accessible with the progressive covering of the surface (Bansal, 1983).

This Linear equation may overestimate the quantities of pesticides adsorbed at very low equilibrium concentrations. This was due to the presence of positive or negative intercepts (Fig. 2). A positive intercept indicates the presence of pesticide residues in the original zeolites, while a negative intercept indicates the amount of pesticide adsorbed in an adsorbent that is not in equilibrium between the adsorbent and pesticide solution concentration. As the zeolites had not previously received pesticide applications the

presence of the intercept could only be adjusted owing to the curvilinear fit of the data. Therefore, it may be suggested that the Freundlich equation rather than the simple Linear equation is a better choice for predictive purpose. Nevertheless, K_D values are frequently used to compare adsorptivities of adsorbents and pesticides (Singh et al., 1990). There is a general consensus that the magnitudes of the K_F and K_D values usually indicate the affinity of the chemical to the adsorbent. The higher the values of K_F and K_D are, the lower the potential for the chemical to move through the adsorbent profile (Bosetto et al., 1993).

Table 4 shows the values of K_F and K_D among the zeolites decreased in the following sequences, regardless of the type of pesticide: $FCC_W \rangle FAU_F \rangle (FAU+Na-P1)_{SF} \rangle CLI_N$. In order to compare the pesticide adsorptivity among zeolites, the relative adsorption of pesticides in zeolites was calculated as the ratio of K_D or K_F for FCC_W , FAU_F and $(FAU+Na-P1)_{SF}$ to that for CLI_N which showed the lowest adsorptivity among the zeolites: it was expressed as $R_{D1} = K_D(FCC_W)/K_D(CLI_N)$, $R_{D2} = K_D(FAU_F)/K_D(CLI_N)$, $R_{D3} = K_D[(FAU + Na-P1)_{SF}]/K_D(CLI_N)$, $R_{F1} = K_F(FCC_W)/K_F(CLI_N)$, $R_{F2} = K_F(FAU_F)/K_F(CLI_N)$, and $R_{F3} = K_F[(FAU + Na-P1)_{SF}]/K_F(CLI_N)$.

The values of R_{D1} , R_{D2} , R_{D3} , R_{F1} , R_{F2} and R_{F3} for phosphamidon were 428.2, 1.4, 1.3, 445.9, 2.1, and 1.8, respectively; for fenitrothion were 673.0, 1.2, 1.2, 345.3, 1.9, and 1.5, respectively; for triadimefon, were 698.6, 1.5, 1.5, 344.6, 1.7, and 1.2, respectively; for diniconazole were 575.0, 1.5, 1.1, 403.9, 1.8, and 1.6, respectively. Hence, it was concluded that FCC_W is a much stronger adsorbent, than the other zeolites. This was attributed to the fact that the USY and most polar Al component in the original Y zeolite are converted to a nonpolar Si component, and that the pesticides are also nonpolar. The reason why FAU_F and $(FAU+Na-P1)_{SF}$ exhibit a much lower adsorptivity than FCC_W , may be based on the fact that they are not pure FAU zeolites, and parts of the fly ash or Jeju scoria were converted to FAU. The reason why CLI_N shows the lowest

adsorptivity, even if it has a higher silica content representing nonpolarity (Table 2), may be based on the fact that the middle part of its pore is clogged or most of it has a twin-crystalline structure as it was formed naturally.

The values of K_F and K_D among the pesticides decreased in the following sequences, regardless of the type of zeolite: diniconazole \rangle fenitrothion \rangle triadimefon \rangle phosphamidon. Similar to the zeolites, the relative adsorption was compared among pesticides by calculating the ratio of K_D or K_F for diniconazole, fenitrothion, and triadimefon to that for phosphamidon, which was adsorbed the least in zeolites, that is $R_{D1} = K_D(\text{diniconazole})/K_D(\text{phosphamidon})$, $R_{D2} = K_D(\text{fenitrothion})/K_D(\text{phosphamidon})$, $R_{D3} = K_D(\text{triadimefon})/K_D(\text{phosphamidon})$, $R_{F1} = K_F(\text{diniconazole})/K_F(\text{phosphamidon})$, $R_{F2} = K_F(\text{fenitrothion})/K_F(\text{phosphamidon})$, and $R_{F3} = K_F(\text{triadimefon})/K_F(\text{phosphamidon})$. The values of R_{D1} , R_{D2} , R_{D3} , R_{F1} , R_{F2} and R_{F3} among the pesticides were 1.96, 1.27, 1.01, 2.64, 2.55 and 1.95 for CLI_N , 2.13, 1.11, 1.09, 2.27, 2.26 and 1.57 for FAU_F , 1.68, 1.16, 1.14, 2.37, 2.05 and 1.29 for $(FAU+Na-P1)_{SF}$, and 2.63, 2.00, 1.65, 2.39, 1.97 and 1.51 for FCC_W , respectively. This order was identical to the octanol-water partition coefficients (K_{ow}) (the K_{ow} values for diniconazole, fenitrothion, triadimefon, and phosphamidon were 199953, 2691, 1288, and 6.17, respectively) (Tomlin, 1994), that is pesticides with higher K_{ow} values or lower water solubility were adsorbed the most (Table 3). These results are identical to those of Kim and Feagley (1998), Kam et al. (1999), and Chun et al. (2018), who reported that more pesticides with lower water solubility were adsorbed.

3.3. Effect of temperature

The effect of temperature on the adsorption of pesticides in zeolites was studied for the system containing 10 $\mu\text{g/mL}$ of phosphamidon, fenitrothion and triadimefon, 3.0 $\mu\text{g/mL}$ of diniconazole, and 0.1 g of each zeolite in the temperature range of 15–45°C. The results are

Table 4. The parameters of Linear and Freundlich isotherms for the adsorption of pesticides in several zeolites

Zeolites	Pesticides	Linear		Freundlich		
		K_D	r^2	K_F	$1/n_F$	r^2
CLI _N	phosphamidon	18.89	0.9616	20.0	0.97	0.9458
	fenitrothion	24.01	0.9750	51.0	0.73	0.9836
	triadimefon	19.09	0.9481	39.0	0.74	0.9607
	diniconazole	36.96	0.9727	52.7	0.71	0.9564
FAU _F	phosphamidon	25.64	0.9245	42.2	0.79	0.9258
	fenitrothion	28.45	0.9679	95.3	0.52	0.9250
	triadimefon	27.82	0.9702	66.2	0.67	0.9781
	diniconazole	54.52	0.9787	95.7	0.60	0.9962
(FAU + Na-P1) _{SF}	phosphamidon	24.39	0.9083	36.2	0.80	0.9308
	fenitrothion	28.38	0.9190	74.1	0.55	0.9172
	triadimefon	27.71	0.9496	46.6	0.74	0.9603
	diniconazole	40.96	0.9727	85.7	0.68	0.9945
FCC _w	phosphamidon	8089	0.9970	8917	1.08	0.9941
	fenitrothion	16158	0.9979	17608	1.04	0.9980
	triadimefon	13336	0.9979	13440	0.99	0.9972
	diniconazole	21252	0.9584	21286	0.90	0.9803

shown in Fig. 4. As the temperature increased from 15°C to 45°C, the pesticide adsorptivity increased for FAU_F, (FAU+Na-P1)_{SF} and FCC_w, but decreased for CLI_N regardless of the type of pesticide. This result indicates that the adsorption process is endothermic for FAU_F, (FAU+Na-P1)_{SF} and FCC_w, and exothermic for CLI_N. It is well-documented that an increase in temperature results in a decrease of pesticides adsorption in most soils (Bansal, 1983; Cancela et al., 1990), and that a decrease in adsorption may be attributable to two factors: i) a change in the energy of adsorption or weakening of the van der Waals forces of attraction between the pesticide and the adsorbent and ii) a change in the solubility of pesticides with a change in temperature. However, Bosetto et al.(1993) reported that the adsorption process of alachlor by montmorillonites saturated with several kinds of cations is endothermic or exothermic according to the type of cations, and it must be pointed out that the main contributions to the difference in adsorption pattern are i) the solute adsorption on

the surface of the adsorption pattern, ii) interaction of the adsorbed molecule with the exchangeable cation (exothermic processes), and iii) breaking of the solvent molecules from the adsorbent surface and interlayer expansion (endothermic processes).

It is considered that the difference in pesticide adsorption in zeolites as the temperature increases is caused by the difference in the crystalline structure of zeolites, that is the reason for an increase or decrease in pesticide adsorption with an increase in temperature may be described as follows. As mentioned above, the pesticides should enter the pores to be adsorbed because zeolites have a very low organic matter content. As the natural zeolite (CLI_N) has a straight line-passage structure with the same pore size in an entrance and a channel, and the middle part of its channel is clogged, the pesticide molecules adsorbed at the channel and entrance are easily desorbed by the active pesticide molecular motion with an increase in temperature. This results in decrease in

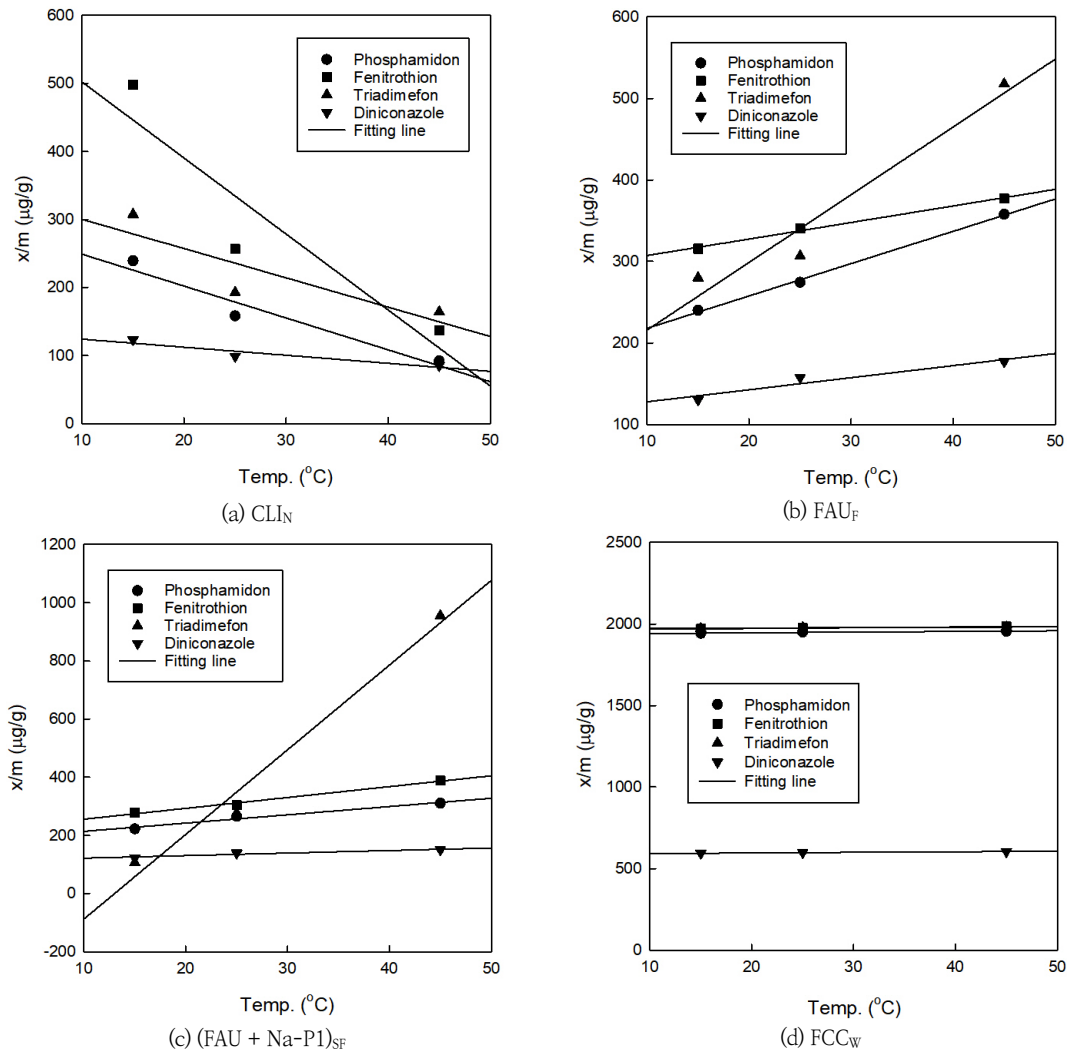


Fig. 4. Effect of temperature on the adsorptivity of phosphamidon, fenitrothion, triadimefon and diniconazole in several zeolites.

pesticides adsorption, whereas the synthetic zeolites (FAU_F , $(\text{FAU} + \text{Na-P1})_{SF}$ and FCC_W) are FAU-type zeolites with a cage structure with narrow entrance (7–8 Å) and interior wide (13 Å) pore sizes (Table 1). Pesticide molecules can easily enter the cage owing to a wider entrance pore size with increasing temperature. Thus it is difficult for the pesticide in a cage to be desorbed through a narrow entrance pore size, even if the molecular motion becomes more

active when the temperature increases in aqueous solutions, indicating an increase in pesticides adsorption capacities with increasing temperature.

3.4. Effect of pH

The effect of pH on the adsorption of pesticides in zeolites was studied for the system containing 10 $\mu\text{g/mL}$ of phosphamidon, fenitrothion and

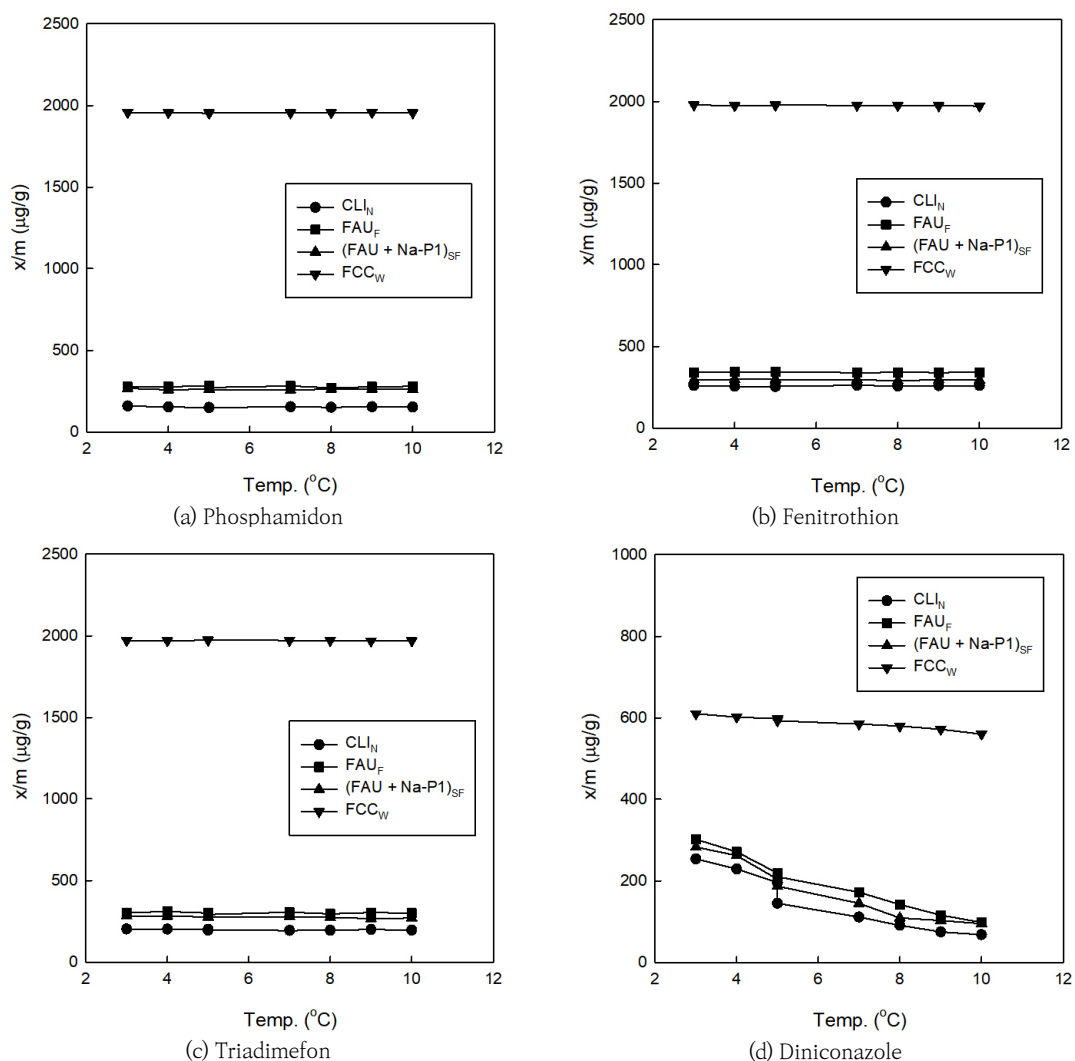


Fig. 5. Effect of pH on the adsorptivity of phosphamidon, fenitrothion, triadimefon and diniconazole in several zeolites.

triadimefon, 3.0 $\mu\text{g/mL}$ of diniconazole, and 0.1 g of each zeolite at pH 3-10 (Fig. 5). The adsorptivity of pesticides was independent of pH for phosphamidon, fenitrothion and triadimefon, whereas it decreased with increasing pH for diniconazole, regardless of zeolite type. The reason for the former, may be caused by the fact that these pesticides are nonpolar and are adsorbed onto zeolites by physical bonding, such as van der Waals force and hydrophobic forces. Similar results have

been reported by Altzman et al. (1972). The same result as the latter is observed for pesticides having a group that can be protonated, that is as the diniconazole has a hydroxyl group that can be protonated with an increase in acidity and protonated diniconazole can be exchanged with the cations in zeolites, its adsorptivity increases with decreasing pH. However, as it may be neutral or deprotonated with increasing pH, its adsorption by ion exchange or physical bonding does not occur,

resulting in the decrease in its adsorption. The reason why the adsorptivity decreases with increasing pH for diniconazole may be based on the fact that this pesticide can be protonated, neutral or deprotonated depending on pH, and the properties of this pesticide formed with pH affect the adsorption in zeolites. The same result was observed for this pesticide in soil (Oh, 1999).

4. Conclusions

The adsorption characteristics of pesticides (phosphamidon, fenitrothion, triadimefon, and diniconazole) on natural zeolite (CLI_N) and several synthetic zeolites (FAU_F, (FAU + Na-P1)_{SF} and FCC_W) were investigated.

The pesticide adsorption kinetics revealed that 6 h was sufficient to reach adsorption equilibrium, regardless of the type of zeolites and pesticides differently from the application of 24 h of shaking in soils.

The Linear and the Freundlich isotherm equations applied to the adsorption of pesticides in zeolites fitted the experimental data well. The distribution coefficient, K_D and the Freundlich constant, K_F, obtained from these two equations to compare the adsorptivity among the adsorbents and the adsorbates, decreased in the following sequence: FCC_W > FAU_F > (FAU + Na-P1)_{SF} > CLI_N among the zeolites, indicating that FCC_W and CLI_N showed the highest and the lowest adsorptivity, respectively; diniconazole > fenitrothion > triadimefon > phosphamidon among the pesticides, indicating that diniconazole and phosphamidon were adsorbed the most and the least in zeolites, respectively, in accordance with their octanol-water partition coefficient (K_{ow}).

As the temperature increased, the adsorptivity of pesticides in zeolites increased for FAU_F, (FAU + Na-P1)_{SF} and FCC_W, but decreased for CLI_N, regardless of the type of pesticide: this may be due to the difference in the crystalline structure of zeolites (i.e., the synthetic zeolites have a cage structure with narrow entrance (7-8Å) and

interior wide (13Å) pore sizes; however, the CLI_N has a straight line-passage structure with the same pore size in the entrance and channel and the clogged channel in the middle part.

The adsorptivity of pesticides in zeolites was independent of pH for phosphamidon, fenitrothion and triadimefon, but for diniconazole, which has a hydroxyl group that can be protonated, neutral, or deprotonated depending on the pH, it decreased as the pH was increased, regardless of the type of zeolites.

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