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ABSTRACT: To prevent the contamination of groundwater and surface water by pesticides, appropriate measures should be taken to treat the contaminated water before discharge. Zeolites seem to be a promising material to adsorb pesticides. This paper deals with the removal of mobile pesticides from water on different types of zeolites. Experiments were performed to understand the adsorption mechanisms of bentazon, clopyralid, imidacloprid, isoproturon and metalaxyl-m on zeolites and to determine the most efficient adsorbent for the purification of water contaminated by these pesticides. More immobile pesticides (imidacloprid, isoproturon and metalaxyl-m) tended to associate with the zeolites, whereas more mobile pesticides (bentazon and clopyralid) partitioned in water. According to the adsorption percentage, zeolite of the types BEA and FAU showed the best results for adsorbing the pesticides. Two different kinetic models, namely, pseudo-first-order and pseudo-second-order models, were used to fit the kinetics data. The experimental data were best described by the pseudo-second-order model. The rate of adsorption was also in line with the mobility of the pesticides. The adsorption isotherms were determined and modelled based on the observed types according to International Union of Pure and Applied Chemistry. The type III isotherm was most frequently observed in this case. The Freundlich model, which describes this type of isotherm, gave a good fit for the adsorption of the pesticides. Different assumptions, that could describe the meaning of these type III isotherms, are discussed in this paper. These assumptions are based on the particle size of the adsorbates, the water adsorption on the zeolites and the modifications of the crystal structures.

INTRODUCTION

Environmental problems associated with the use of pesticides are a matter of concern because pesticides can move through the air and may eventually end up in other parts of the environment, such as in soil or water. It is estimated that only 80% of the applied pesticides reach their targeted areas (Forster 2004). The different pathways by which pesticides spread in the environment are shown in Figure 1. One of the major concerns about the use of these organic compounds in agronomy and horticulture is their ability to leach into groundwater (Colella 2007); especially, the highly mobile pesticides are a matter of current concern (Kalkhoff *et al*. 1998; Kolpin *et al*. 1998).

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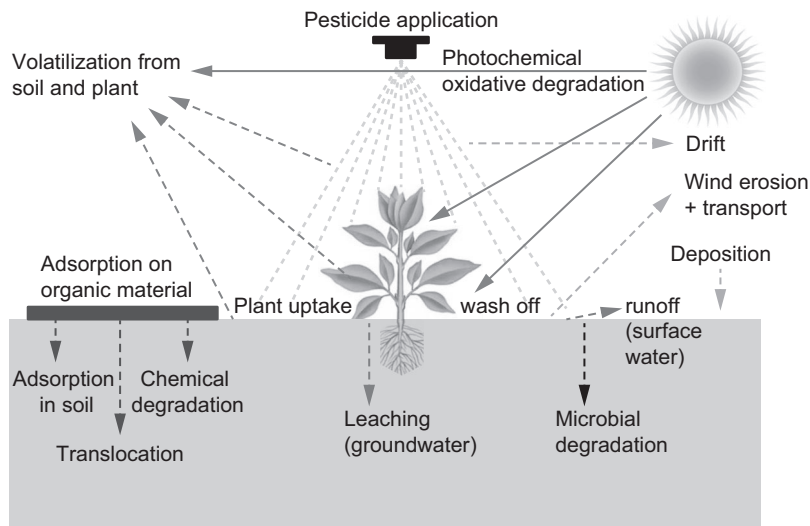
Figure 1. Pathways of pesticide spreads in the environment (based on MIRA 2007).

Several techniques have been developed for the removal of pesticides from water. Adsorption on activated carbon is the most widely used technology for purification of water contaminated by pesticides and other hazardous chemicals (De Wilde *et al.* 2009). There is an increasing interest in the use of natural materials, due to their low cost. One such material is zeolite (Bowman *et al.* 2000; Ranck *et al.* 2005).

Zeolites are a broad range of microporous, crystalline aluminosilicates of natural or synthetic origins. In general, their structure can be considered as an inorganic polymer built from $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral molecules (primary building units), which are linked by the sharing of all oxygen atoms. A pure silica (SiO_2) solid framework is uncharged. When some of the Si^{4+} in the silica framework is replaced by Al^{3+}, the '3+' charge on the aluminium makes the framework negatively charged, which is compensated by the presence of extra-framework cations (counterions), located together with water, to keep the overall framework neutral (Payra and Dutta 2003).

The Si/Al ratio is an important characteristic of zeolites. Differences in the Si/Al ratio can result in variations in location, amount and distribution of negative charge density in the structural frameworks, cages or pores of different diameters, nature or absence of hydration water or other ligands and presence and position of extra-framework cation(s) (Munthali *et al.* 2014). Based on the Si/Al composition, Flanigen (2001) classified zeolites as follows: low silica/hydrophilic zeolites (Si/Al 1–1.5), intermediate silica/intermediate hydrophobic (Si/Al 2–5) and high silica/hydrophobic zeolites (Si/Al > 10). The zeolitic hydrophilic property increases as the aluminium content in the zeolite framework increases and vice versa. The hydrophobic/hydrophilic nature of zeolites also appears to depend on their framework structure (Cekova *et al.* 2006).

The aim of this study was to evaluate the potential of zeolites to adsorb a number of pesticides from aqueous medium. Therefore, the adsorption characteristics including kinetics, isotherms and adsorption energies of five pesticides (bentazon, clopyralid, imidacloprid, isoproturon and metalaxyl-m) with different physicochemical characteristics on several zeolites with different framework structures were investigated.
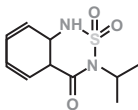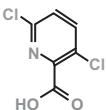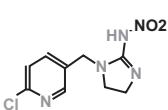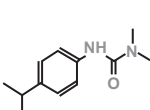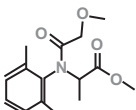
EXPERIMENTAL ANALYSIS
Pesticide Selection (Adsorbates)

The studied pesticides were selected based on their physicochemical characteristics and were divided into five categories based on their mobility (K_{oc}) (Pesticide Properties Database 2014). In addition, the groundwater ubiquity score (GUS) indicator could be used to describe the mobility of the pesticides (Gustafson 1989). A GUS indicator lower than 1.8 indicates an immobile pesticide (De Wilde *et al*. 2008). One or more pesticides were selected from the mobile category to be used in batch adsorption experiments. Clopyralid (Sigma Aldrich) was selected as a strongly mobile pesticide and bentazon (Sigma Aldrich) as a mobile pesticide. Pesticides selected from the moderately mobile category were imidacloprid (Bayer Crop Protection) and isoproturon (Sigma Aldrich). Metalaxyl-M (Syngenta Crop Protection) was selected as a slightly mobile pesticide. The chemical structures of these technical-grade pesticides and their chemical properties are shown in Table 1. The test solutions were prepared by diluting the stock solutions to the desired concentration of 10 mg l^{-1}.

Zeolite Selection (Adsorbents)

Seven commercially available zeolite structures were selected, including zeolite beta (BEA), chabazite (CHA), zeolite Y (FAU), clinoptilolite (HEU), zeolite 4A (LTA), ZSM-5/silicalite-1 (MFI) and mordenite (MOR). The varying arrangement of the structural unit in zeolite frameworks results in the generation of pores and cavities of various dimensions, responsible for the confinement effects during adsorption of molecules. Two quantities of particular interest for characterizing pores are the largest cavity diameter (LCD) and the pore-limiting diameter (PLD). The LCD corresponds to the maximum of the pore-size distribution and the PLD corresponds to the largest characteristic guest

TABLE 1. Pesticide Properties

	Bentazon	Clopyralid	Imidacloprid	Isoproturon	Metalaxyl-M
Molecules					
Purity (%)	97	100	99	99.5	96.6
Size (Å)[a]	<3 × 10 × 5	<3 × 7 × 7	10 × 6 × 5	<3 × 12 × 6	<3 × 12 × 7.6
Chemical formula	$C_{10}H_{12}N_2O_3S$	$C_6H_3Cl_2NO_2$	$C_9H_{10}ClN_5O_2$	$C_{12}H_{18}N_2O$	$C_{15}H_{21}NO_4$
MM (g mol^{-1})	240.3	192.0	255.66	206.28	279.33
S_{water} (20 °C; mg l^{-1})	570	1,43,000	610	70.2	26,000
Log K_{ow} (20 °C; pH 7)	–0.46	–2.63	0.57	2.5	1.71
K_{oc} or K_{foc} (ml g^{-1})	55.3	5.0	225	122	660
GUS	2.59	3.44	3.69	2.61	1.88

[a]All molecular size calculations were performed using the *Gaussian 09* program (Frisch *et al*. 2009).

K_{oc} or K_{foc} = adsorption coefficient; log K_{ow} = octanol–water partition coefficient; MM = molecular weight; S_{water} = water solubility.

TABLE 2. Accessibility of the Different Zeolites

| Material name	Framework type code	Crystal structure	Channel structure	Pore volume ($cm^3\ g^{-1}$)	LCD (Å)	PLD (Å)
Zeolite beta	BEA	Tetragonal	3D	0.416	6.9	6.7
Chabazite	CHA	Rhombohedral	3D	0.434	8.0	4.2
Zeolite Y	FAU	Cubic	3D	0.506	11.9	6.7
Clinoptilolite	HEU	Monoclinic	2D	0.279	6.6	4.3
Zeolite 4A	LTA	Cubic	3D	0.508	11.7	4.9
ZSM-5/Silicalite-1	MFI	Orthorhombic	3D	0.242	7.0	5.0
Mordenite	MOR	Orthorhombic	1D	0.293	6.5	6.5
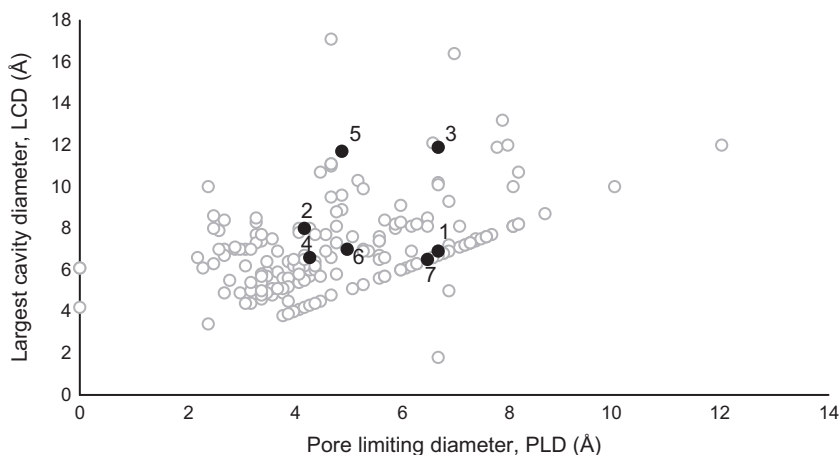
Figure 2. Largest cavity diameter (LCD) plotted against pore limiting diameter (PLD) for structures in the 'Database of zeolite structures', with 1 = BEA; 2 = CHA; 3 = FAU; 4 = HEU; 5 = LTA; 6 = MFI and 7 = MOR (Baerlocher and McCusker 2014; First *et al.* 2014).

molecule size for which there is a non-zero accessible volume (Table 2; Baerlocher and McCusker 2014). These quantities are also plotted in Figure 2. The utility of such a plot is apparent for the consideration of a chemical reaction. A desirable zeolite would require a PLD larger than all species involved and an LCD larger than the transition state structure (First *et al.* 2014).

Zeolite Characterization

The specific surface area of the zeolites was determined using nitrogen adsorption/desorption measurements. The isotherms were recorded on a BELSORP Mini II equipment (Bel Japan Inc., Osaka, Japan) at –196 °C. The samples were pre-treated at 150 °C under vacuum. The results for the different selected zeolites are presented in Table 3. X-ray diffraction was performed with an ARL X'TRA X-ray diffractometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a Cu KR1 tube and a Peltier cooled lithium-drifted silicon solid stage detector. The XRD patterns of the different zeolites showed their characteristic peaks. Finally, the Si/Al ratio of the samples was determined by X-ray fluorescence analysis. This analysis is based on the emission of X-rays by the material when an electron drops down to a vacant level and releases energy. The measurements were performed on an NEX CG (Rigaku) using a Mo–X-ray source.

TABLE 3. Zeolite Properties

FTC		$Si/Al_{practical}$	$S_{BET}\ (m^2\ g^{-1})_{practical}$	Product name
BEA	1	11.84	365	H-BEA-25 (Clariant, Germany)
	2	15.87	413	H-BEA-35 (Clariant, Germany)
	3	49.34	348	CP 811C-300 (Zeolyst, USA)
CHA	4	3.08	8[a]	Siliz MFD CH 200 (Somez, France)
	5	3.12	11[a]	Siliz MFD CH 70 (Somez, France)
FAU	6	15.40	661	CBV 720 (Zeolyst, The Netherlands)
	7	32.91	642	CBV 780 (Zeolyst, The Netherlands)
HEU	8	5.60	21[a]	Slowakije (Zeoliet, Belgium)
	9	5.45	23[a]	Turkije (Zeoliet, Belgium)
	10	5.58	11[a]	Hungary (Terra Humana, Hungary)
LTA	11	1.15	1[a]	Wetstop (FMC, Spain)
	12	1.12	2[a]	Zeolite 4A pH 8 (FMC, Spain)
MFI	13	13.19	8[a]	TZP-302 (Clariant, Germany)
	14	30.19	314	H-MFI-90 (Clariant, Germany)
	15	57.54	198	H-CZP-300 (Clariant, Germany)
	16	17.83	6[a]	NH$_4$-CZP-55 (Clariant, Germany)
	17	–	266	H-CZP-800 (Clariant, Germany)
MOR	18	6.64	16	H-MOR-14 (Clariant, Germany)
	19	10.53	34	H-MOR-20 (Clariant, Germany)

[a]External surface area.

Adsorption Experiments

Adsorption experiments, performed in a batch reactor system, were conducted in three ways, namely, dependent on adsorption (percentage), time (kinetic) and concentration (isotherm). The suspensions (adsorbent and pesticide aqueous solution) were shaken on an orbital shaker at 150 rpm at room temperature (22 °C). The supernatants were then filtered with a syringe filter containing a polyvinylidene difluoride membrane with a pore size of 0.22 μm (Carl Roth, Karlsruhe-Rheinhafen, Germany). The aliquots with bentazone, clopyralid, imidacloprid, isoproturon, linuron and metalaxyl-m were injected into the high-performance liquid chromatography column with photodiode array detector, and the aliquots with bifenthrin and fenpropimorph (after hexane extraction) were injected into the gas chromatography column for pesticide concentration measurements. The amounts adsorbed were determined from the initial and final concentrations of the contaminant solution. All tests were carried out in triplicate and control runs containing the pesticide but without the addition of an adsorbent were also included.

Selection Based on Adsorption Percentage

Adsorption kinetics and isotherms were not determined for all zeolites, but only for those that best adsorbed the pesticides. For these tests, 0.1 ± 0.001 g zeolite was shaken in 100-ml conical flasks with 20 ml of 10 mg l^{-1} solution of the respective pesticide. The adsorption percentage of pesticides on zeolites was calculated as follows:

$$\text{Adsorption (\%)} = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where C_i and C_f are the initial and final pesticide concentrations (mg l^{-1}), respectively.

TABLE 4. Pseudo-First-Order Equation (Lagergren) and Pseudo-Second-Order Equation (Ho)

	Differential equation	Integration: $q_t = 0$, $t = 0$ and $q_t = q_t$, $t = t$	Amount adsorbed (mg g^{-1}) at time t (h)
First-order equation	$dq_t/dt = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$q_t = q_e(1 - e^{-k_1 t})$
Second-order equation	$dq_t/dt = k_2(q_e - q_t)^2$	$1/q_t = 1/q_e^2 + (1/q_e)t$	$q_t = [t/(1/k_2 q_e^2) + t/q_e]$

Adsorption Kinetics

The adsorption kinetic study predicts the rate at which adsorption takes place. An amount of 0.1 ± 0.001 g of the respective zeolite was added to 100 ml of 10 mg l^{-1} solution of the respective pesticide in a 250-ml flat-bottomed flask. The samples were collected after 0, 0.25, 0.50, 1, 3, 6, 24 and 48 hours. The most commonly used kinetic models, that is, the pseudo-first-order equation (Lagergren's equation) and the pseudo-second-order equation (Ho equation), were applied to the obtained experimental data. The equations can be described as shown in Table 4, where k_1 and k_2 are the rate constants of first-order adsorption (hour^{-1}) and second-order adsorption (hour^{-1}), and q_e and q_s are the adsorbed concentration (mg g^{-1}) at equilibrium and at time t (hour).

The adsorbed pesticide concentration was calculated as follows:

$$q_e = \frac{(c_i - c_e)V}{m} \qquad (2)$$

where q_e represents the adsorbed concentration (mg g^{-1}), V the volume of pesticide solution added (l), m the weight of the adsorbent (g) and C_i and C_e are the initial and equilibrium pesticide concentrations (mg l^{-1}), respectively.

Adsorption Isotherms

An adsorption isotherm is a simple description of the performance of an adsorbent for the removal of a given target substance. From this isotherm, the adsorption capacity can be derived, which makes it possible to compare the adsorption capacities of the different adsorbents for pollutants in aqueous solutions. The adsorption isotherms of the pesticides on the zeolites were also measured with the batch equilibration technique. These adsorption isotherms provide information about the surface properties and affinity of the adsorbent. In this experiment, 100 mg zeolite was added to 100 ml of pesticide solution at five different concentrations (50, 100, 250, 500 and 1000 mg l^{-1}). All stock solutions were prepared in distilled water. Adsorption isotherms were obtained by plotting the amount of pesticide adsorbed by the substrate (g kg^{-1}) versus the respective concentration in equilibrium solution (mg l^{-1}). The experimental adsorption isotherms may conveniently be grouped into six classes according to the International Union of Pure and Applied Chemistry (IUPAC) classification (Figure 3). The first five characteristic types were originally proposed by Brunauer and his co-workers as the Brunauer, Deming, Deming and Teller (BDDT) classification (IUPAC 1985).

Type I (Langmuir, Table 5) isotherm is observed during the adsorption on a microporous solid (pore widths < 2 nm). It represents an adsorption process with a low affinity for the adsorbate and the plateau indicates monolayer coverage. This type of behaviour is typical for chemisorption,
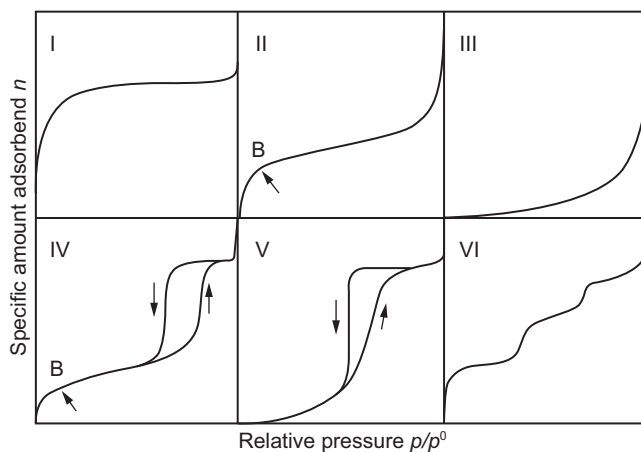
Figure 3. The IUPAC classification for adsorption isotherms (IUPAC 1985).

TABLE 5. Isotherm Equations

	Non-linear form	Linear form
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + (1/n)(\log C_e)$
Langmuir	$q_e = (q_m K_L C_e)/(1 + K_l C_e)$	$1/q_e = (1/q_m K_L)(1/C_e) + (1/q_m)$
BET	$q_e = (q_m K_B C_e C_s)/(C_s - C_e)[C_s + (K_B - 1)C_e]$	$C_e/q_e(C_s - C_e) = 1/q_m K_B + [(K_B -1)/q_m K_B]C_e/C_s$

Note: q_e (mg g^{-1}) is the amount of pesticide adsorbed at equilibrium concentration C_e (mg l^{-1}), q_m (mg g^{-1}) is the maximum adsorption capacity and C_s (mg l^{-1}) is the saturation concentration of the pesticide. K_F (mg g^{-1}) and n are Freundlich constants representing the Freundlich isotherm constant and a constant reflecting the adsorption strength or intensity. K_L (l g^{-1}) represents the Langmuir isotherm constant and K_B (l mg^{-1}) is the BET isotherm constant representing the adsorption intensity.

where the asymptotic approach to a limiting quantity indicates that all of the surface sites are occupied.

Type II (BET, Table 5) isotherms, observed in physical adsorption, are most frequently encountered when adsorption occurs on non-porous or macroporous powders. The inflection point or knee of the isotherm is called 'point B'. This point indicates the stage at which monolayer coverage is complete and multilayer adsorption begins to occur.

Type III (Freundlich, Table 5) isotherms, given by non-porous or macroporous solids, are the characteristic of weak attractive forces. This weakness causes a small uptake in the beginning, but once a molecule has been adsorbed, the adsorbate–adsorbate forces will promote the adsorption of further molecules.

Type IV isotherms occur on mesoporous materials, describing monolayer and multilayer adsorption. The increase in slope indicates an increased uptake of adsorbate as the pores are being filled. The knee, point B, of the type IV isotherm generally occurs near the completion of the first monolayer (i.e. near the onset of multilayer adsorption). A characteristic feature of the type IV isotherm is its hysteresis loop, which is associated with the occurrence of pore condensation. In the simplest case, the initial part of isotherm follows exactly the same path as the corresponding part of type II in a non-porous form.

TABLE 6. Separation Factor Based on the Shape of the Langmuir Isotherm

Value R_L	Type of adsorption
$R_L > 1.0$	Unfavourable
$R_L = 1.0$	Linear
$0 < R_L < 1.0$	Favourable
$R_L = 0$	Irreversible

Type V isotherms are given by microporous or mesoporous solids and show pore condensation and hysteresis. However, in contrast to type IV, the initial part of this adsorption isotherm is very much similar to type III, indicating relatively weak attractive interactions between the adsorbent and the adsorbate.

Type VI isotherms are borderline cases between two or more of the aforementioned types. This stepped isotherm is relatively rare and is associated with layer-by-layer adsorption on a highly uniform surface. The sharpness of the steps is dependent on the system (Rouquerol *et al*. 2014).

The essential features of the Langmuir isotherm may be expressed in terms of the separation factor R_L. Based on the shape of the isotherm of an adsorption system, this dimensionless constant predicts whether the system is favourable or unfavourable (Ghaemi *et al*. 2011). The value of the separation factor can be interpreted as given in Table 6.

$$R_L = \frac{1}{1 + K_L C_i} \tag{3}$$

Hygroscopicity

A measure of the hygroscopicity of a product is a consequence of the magnitude of the increase or decrease in its water content as a function of relative humidity at a certain temperature. The generation of the moisture isotherms will give more information about the hygroscopic effect of zeolites and describe their relationship with water content. These adsorption isotherms were measured with a fully automated vapour adsorption analyzer (Decagon Devices Inc., Pullman, WA, USA).

The double log polynomial model was used to predict the moisture content at a given water activity (Decagon Devices 2015).

$$m = b_3 \chi^3 + b_2 \chi^2 + b_1 \chi + b_0 \tag{4}$$

where m is the moisture in g/100 solids or g/g solids, $\chi = \ln[-\ln(a_w)]$ and $b_0 - b_3$ are empirical constants.

The moisture content value was introduced for calculating weight change at the different a_w values. The water holding capacity (WHC) is the difference between the weight at maximum a_w value and the weight at minimum a_w value divided by the initial weight.

$$WHC = (\text{weight } a_{w,max} - \text{weight } a_{w,min})/\text{weight}_{initial} \tag{5}$$

The temperature used was 25 °C; $a_{w,min} = 0.125$ and $a_{w,max} = 0.900$. The water mass (or weight) is the difference between the weights of the wet and oven-dry samples (24 hours, 105 °C).

RESULTS AND DISCUSSION
Adsorption Percentage

An initial evaluation of the different zeolites was made based on their pesticide adsorption capacity. The adsorption capacity is represented by the adsorption coefficient (K_{oc}) and the octanol–water partition coefficient (K_{ow}) of the pesticides, which is also closely related to the water solubility (S). The logarithmic value (log K_{ow}) is used to describe the hydrophobicity or polarity of a compound. Values of log K_{ow} < 0 are considered as hydrophilic/polar, log K_{ow} between 0.5 and 2.5 as intermediate hydrophobic/polar and log K_{ow} > 3 as hydrophobic/non-polar (Wang and Liu 2007). As described in literature, pesticides that have high solubility in water will remain in water and tend to not adsorb onto non-polar zeolites. This in contrast to non-polar pesticides, which tend to be pushed out of the water (Bansal 2012).

From the adsorption percentages obtained, shown in Table 7, it can be seen that clopyralid did not adsorb onto the zeolites. The high water solubility, low K_{oc} and K_{ow} of clopyralid indicate that this polar pesticide prefers to stay in the aqueous phase. The combination of these properties might explain the fewer adsorption capacity for bentazon and the better adsorption capacity for imidacloprid, isoproturon and metalaxyl-m (Figure 4).

An adsorption trend can be established between the different zeolites. Zeolite beta and zeolite Y had the best adsorption capacity, compared with other zeolites. These results are consistent with the higher values of the surface area (porosity) and PLD for these zeolites. Some nitrogen adsorption and desorption isotherms of the different zeolites (Figure S1, Supplementary Information) are type II isotherms, indicating a non-porous powder, which suggests that the pore openings are too small for nitrogen (0.364 nm) to enter at 77 K (de Lange *et al*. 1995; Jagiello and

TABLE 7. Adsorption Percentage (% ± Standard Deviation) Determined at an Initial Concentration of 10 mg l^{-1}

Adsorption (%)		Bentazone	Clopyralid	Imidacloprid	Isoproturon	Metalaxyl-M
BEA	1	69.56 ± 2.46	9.12 ± 1.20	98.78 ± 0.03	100.00 ± 0.00	42.01 ± 0.79
	2	42.77 ± 2.26	3.55 ± 0.49	98.51 ± 0.02	100.00 ± 0.00	55.19 ± 3.15
	3	50.58 ± 2.17	16.94 ± 1.75	98.02 ± 0.04	100.00 ± 0.00	50.97 ± 1.98
CHA	4	9.90 ± 2.94	3.90 ± 0.33	5.78 ± 1.61	11.07 ± 0.32	0.40 ± 0.78
	5	15.50 ± 2.20	2.72 ± 0.01	8.37 ± 1.31	3.70 ± 0.60	24.06 ± 1.59
FAU	6	63.22 ± 1.63	10.67 ± 1.76	99.75 ± 0.02	100.00 ± 0.00	99.84 ± 0.19
	7	100.00 ± 0.00	10.81 ± 1.53	99.72 ± 0.02	100.00 ± 0.00	99.34 ± 0.14
HEU	8	14.53 ± 3.10	4.24 ± 1.13	10.48 ± 0.93	11.49 ± 1.50	51.48 ± 0.36
	9	14.69 ± 2.76	13.60 ± 1.91	7.47 ± 0.85	7.83 ± 1.77	58.91 ± 1.39
	10	14.01 ± 3.39	9.06 ± 1.23	10.08 ± 0.23	7.06 ± 1.09	42.43 ± 0.80
LTA	11	0.23 ± 0.35	0.00 ± 0.00	44.18 ± 1.02	0.00 ± 0.00	64.56 ± 1.88
	12	1.59 ± 1.63	5.04 ± 0.97	7.26 ± 0.95	0.00 ± 0.00	46.53 ± 6.25
MFI	13	15.93 ± 1.04	2.72 ± 0.47	13.89 ± 0.71	7.21 ± 1.87	29.43 ± 1.62
	14	21.74 ± 2.95	3.87 ± 0.54	21.17 ± 0.80	86.10 ± 0.79	36.87 ± 1.34
	15	7.00 ± 0.96	15.02 ± 1.45	8.46 ± 0.88	18.15 ± 1.46	28.62 ± 1.98
	16	22.16 ± 1.94	0.00 ± 0.00	8.95 ± 0.30	8.74 ± 1.83	27.56 ± 1.52
	17	23.06 ± 2.06	0.00 ± 0.00	8.12 ± 3.69	92.77 ± 0.29	27.04 ± 4.12
MOR	18	24.34 ± 4.88	4.04 ± 0.91	8.17 ± 1.05	9.60 ± 1.89	30.11 ± 2.47
	19	22.05 ± 0.58	12.32 ± 0.70	79.48 ± 0.61	94.71 ± 0.39	31.23 ± 4.30
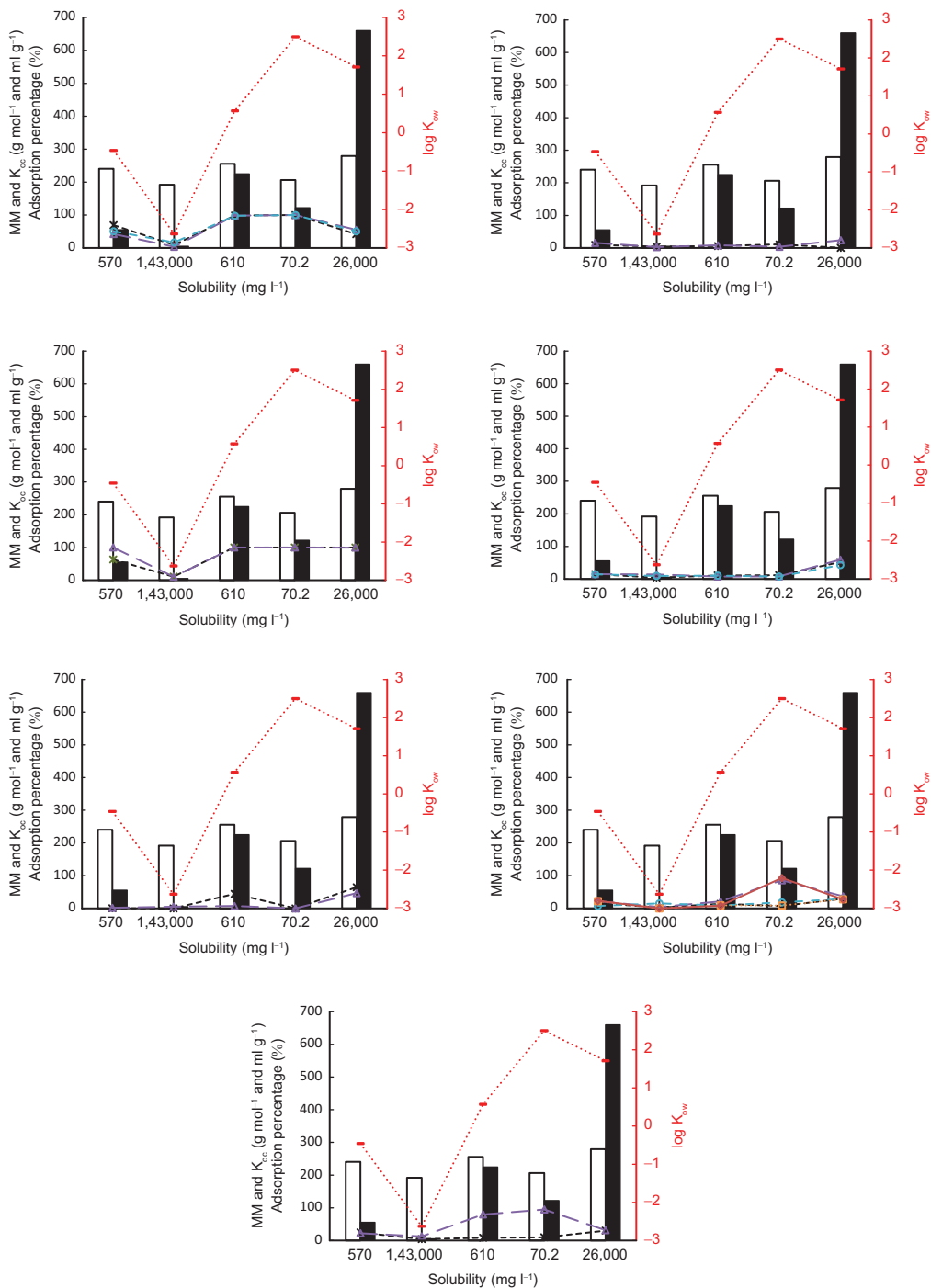
Figure 4. Comparison between the adsorption percentage (lines), the molar mass (open bars), the adsorption coefficient K_{oc} (closed bars), the solubility (asterisks) and the octanol-water coefficient log K_{ow} (marked wi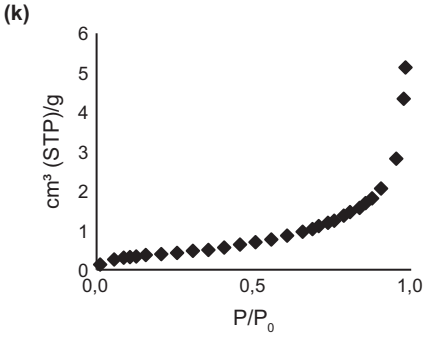th '-') of the different pesticides (bentazon , clopyralid, imidacloprid, isoproturon and metalaxyl-M) onto the different zeolites—BEA, CHA, FAU, HEU, LTA, MFI and MOR .
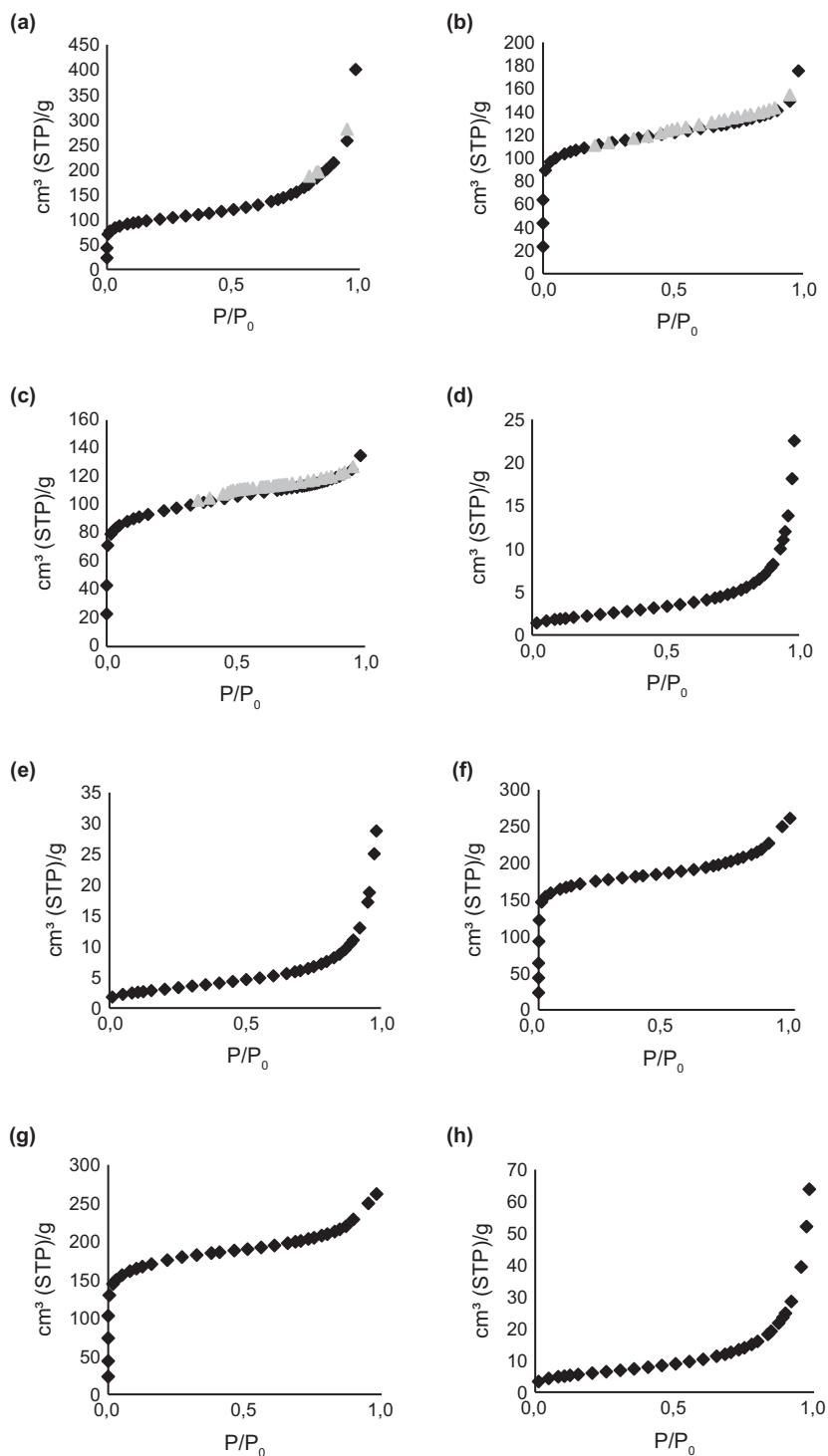
Supplementary Figure 1. Nitrogen adsorption-desorption isotherms. *(continued)*
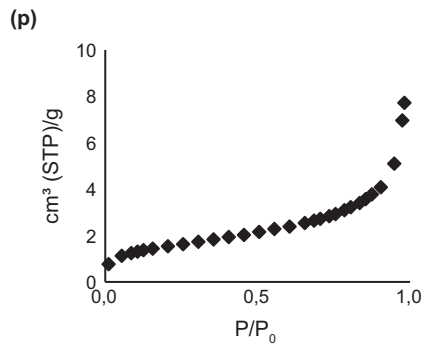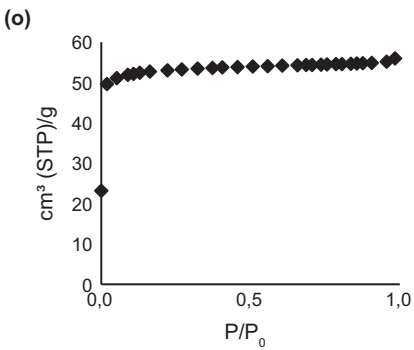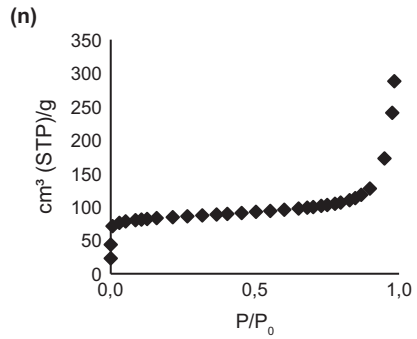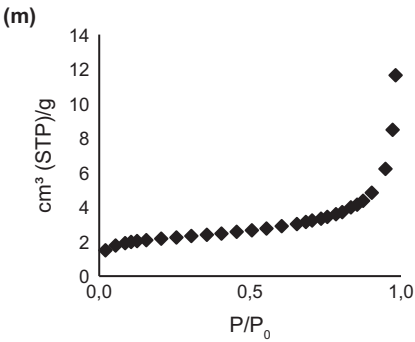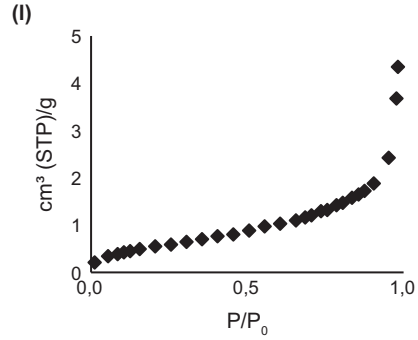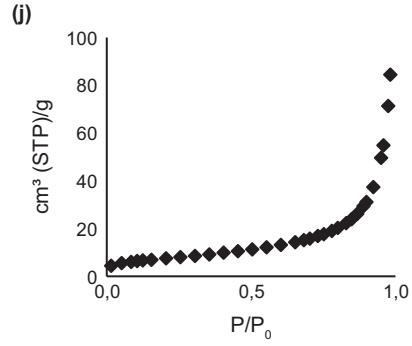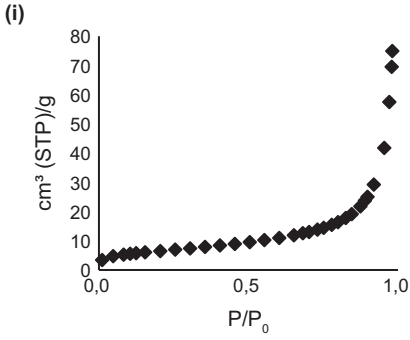
(continued)
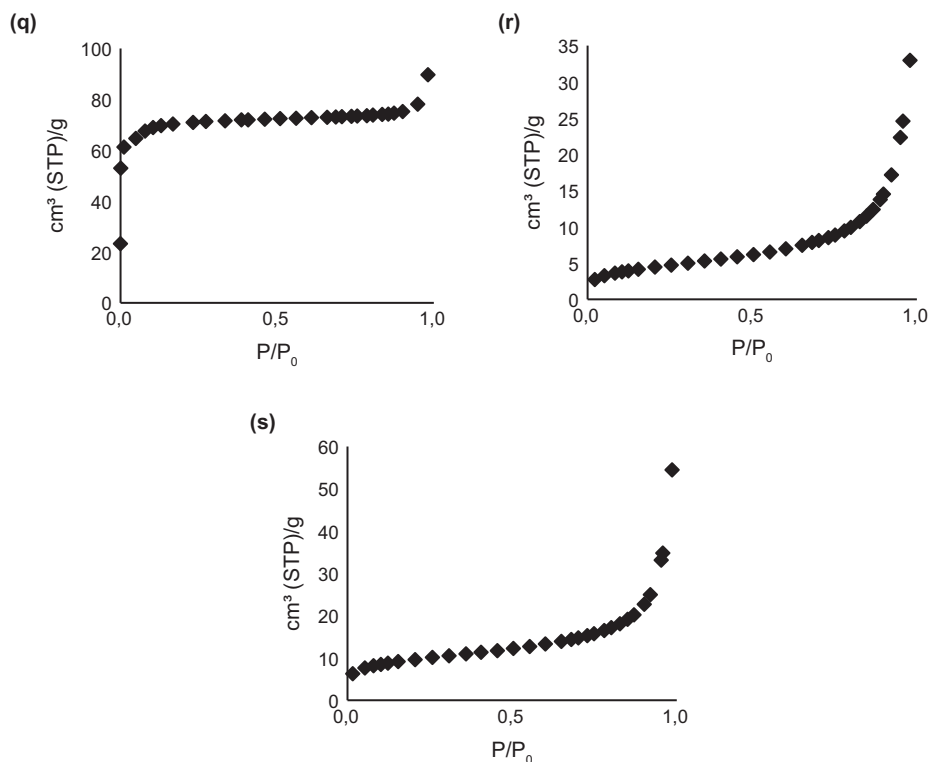
Supplementary Figure 1. *(continued)*

Thommes 2004; Shakarova *et al*. 2014; Valtchev *et al*. 2005). This means that the measured BET surface areas in Table 3 for most zeolites correspond with their external surface area. Rezaei and Wembley (2009) have reported that the external surface area per unit volume is one of the important parameters in this regard and determines the mass transfer in an adsorbent. The higher the external surface area, the better the adsorption of molecules. The large-pore zeolites BEA and FAU, which were able to measure the BET surface area, showed better adsorption results. According to literature sources, the external surface areas of these zeolites are as follows: H-BEA-25, 130 m^2 g^{-1}; H-BEA-35, 41 m^2 g^{-1}; CP 811C-300, not available; CBV 720, 93 m^2 g^{-1}; and CBV 780, 77 m^2 g^{-1} (Kobayashi *et al*. 2015; Wagholika *et al*. 2004). A comparison between the adsorption percentages and the obtained surface areas is shown in Figure 5.

An additional explanation can be given by the hydrophobic properties, depending on the Si/Al ratio, of the zeolites. The zeolitic hydrophobic property decreases as the aluminium content in the zeolite framework decreases and vice versa. These Si/Al values, summarized in Table 3, show that zeolites BEA and FAU are hydrophobic zeolites, and therefore, preferentially adsorb the intermediate and non-polar pesticides (Figure 5). This hydrophobic/hydrophilic nature of zeolites also appears to depend on their framework structure, which explains why the MFI zeolites did not adsorb the pesticides well (Cekova *et al*. 2006). Based on these outcomes, zeolites beta and Y, having the highest adsorption percentages, were selected to determine the kinetic and isotherm adsorption characteristics.
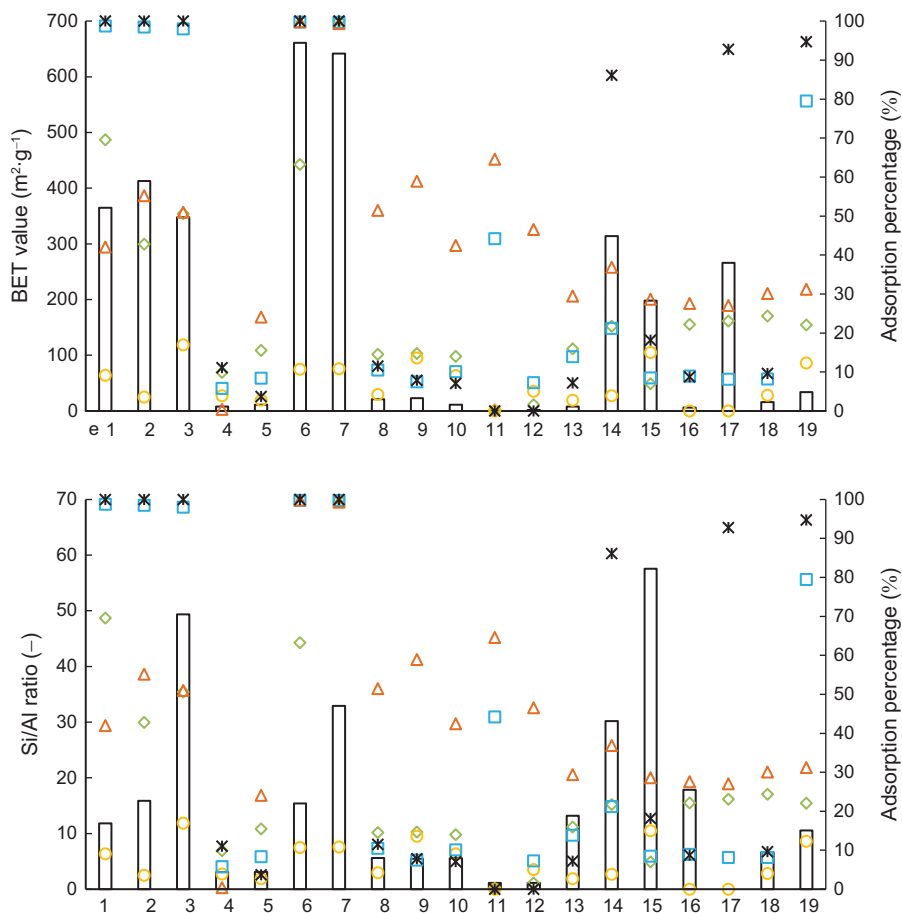
Figure 5. Comparison between the adsorption percentage (points), the specific surface area (open bars, first image) and the Si/Al-ratio (open bars, second image) of the different zeolites (1-19) for the different pesticides. Open diamonds, bentazon; open circles, clopyralid; open squares, imidacloprid; asterisks, isoproturon; open triangles, metalaxyl-M.

Adsorption Kinetics

The adsorption kinetics of the pesticides on zeolite types BEA and FAU are presented in Figure 6. An initial steep increase in the adsorbed pesticide concentration was observed in all cases with 72–100% of the equilibrium concentration adsorbed after 1 hour. (The equilibrium concentrations adsorbed was different for each zeolite and each pesticide. This equilibrium concentration can be derived from Figure 6.) Isoproturon was adsorbed quickly by all zeolites during the first hour of solid–solution contact time, followed by a quick progress towards an apparent equilibrium after 15 and 30 minutes on zeolites BEA and FAU, respectively. Metalaxyl-m was adsorbed best on zeolite FAU, for which the equilibrium was achieved after 15 minutes. Bentazon was less quickly adsorbed on the adsorbents, followed by imidacloprid.

To shed more light on the kinetic process, two kinetic models, which are commonly used to study the kinetics of adsorption, namely, the pseudo-first-order and the pseudo-second-order models, were applied to the experimental data obtained in Figure 6. These results are

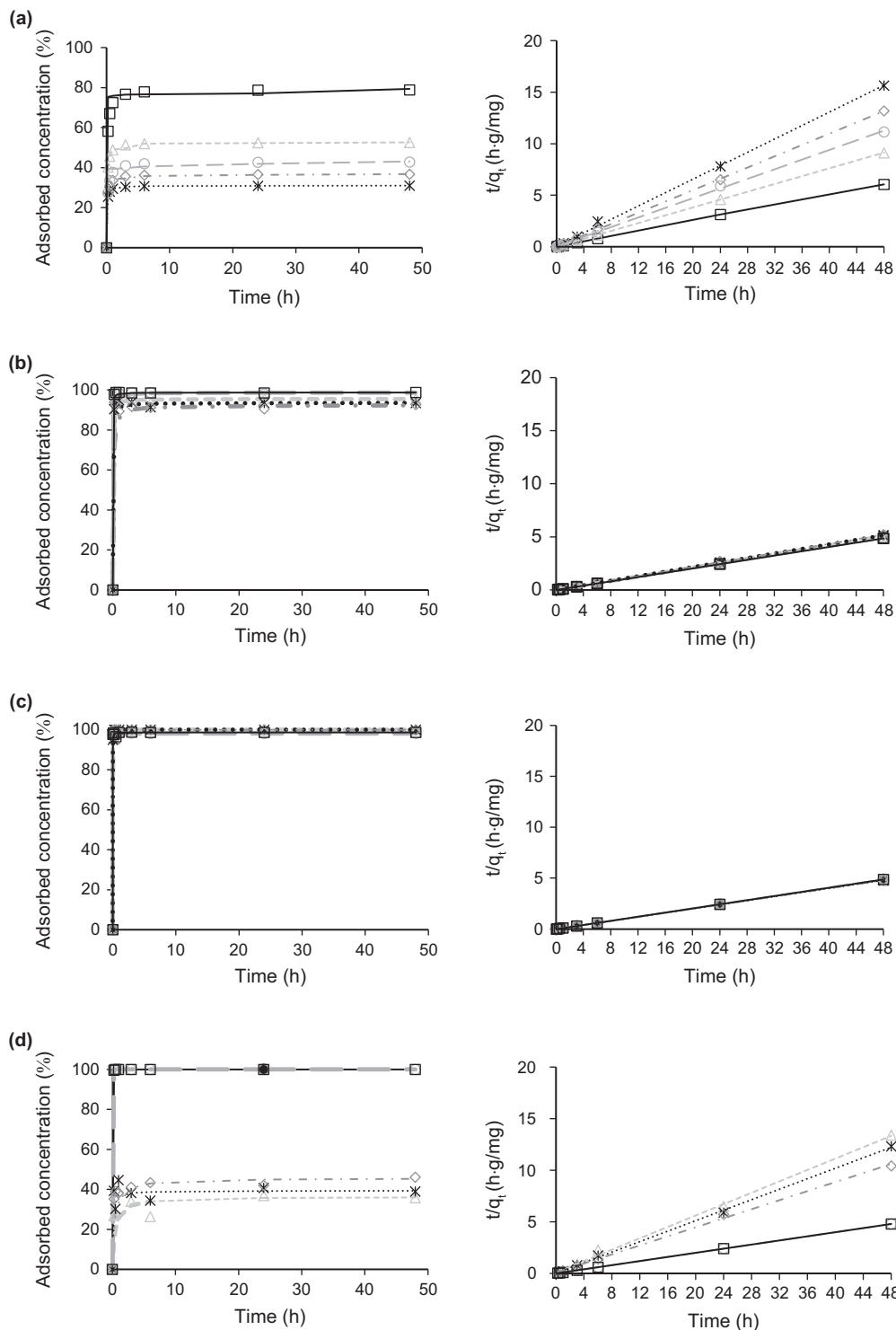**Figure 6.** Experimental (indicated with the geometric symbols) and calculated (indicated with the lines) adsorption kinetics of (a) bentazon, (b) imidacloprid, (c) isoproturon and (d) metalaxyl-m for the different zeolites. Open triangles, zeolite 1; asterisks, zeolite 2; open diamonds, zeolite 3 (all BEA types); open circles, zeolite 6 and open squares, zeolite 7 (all FAU types). Initial pesticide concentration, 10 mg l^{-1}.

TABLE 8. Kinetic Parameters Based on the Pseudo-Second-Order Kinetic Equations

Zeolite	Parameter	Bentazon	Imidacloprid	Isoproturon	Metalaxyl
BEA-1	$q_{e,exp}$ (mg g^{-1})	5.26	9.68	10.00	3.93
	$q_{e,calc}$ (mg g^{-1})	5.28	9.55	10.00	3.63
	k_2 (g mg^{-1} h^{-1})	1.13	6.45	500.00	0.70
	R^2	0.9998	1.000	1.000	0.9977
BEA-2	$q_{e,exp}$ (mg g^{-1})	3.10	9.48	10.00	4.47
	$q_{e,calc}$ (mg g^{-1})	3.08	9.35	10.00	3.93
	k_2 (g mg^{-1} h^{-1})	1.50	4.57	333.33	2.88
	R^2	0.9991	1.000	1.000	0.9992
BEA-3	$q_{e,exp}$ (mg g^{-1})	3.68	9.37	10.00	4.53
	$q_{e,calc}$ (mg g^{-1})	3.65	9.24	10.00	4.56
	k_2 (g mg^{-1} h^{-1})	4.06	1.46	1666.67	0.59
	R^2	0.9999	0.9999	1.000	0.9987
FAU-6	$q_{e,exp}$ (mg g^{-1})	4.31	9.89	9.82	10.00
	$q_{e,calc}$ (mg g^{-1})	4.27	9.87	9.81	10.00
	k_2 (g mg^{-1} h^{-1})	1.41	4.89	25.96	20,000.00
	R^2	0.9992	1.000	1.000	1.000
FAU-7	$q_{e,exp}$ (mg g^{-1})	7.94	9.88	9.87	10.00
	$q_{e,calc}$ (mg g^{-1})	7.89	9.87	9.86	10.00
	k_2 (g mg^{-1} h^{-1})	1.22	4.89	51.41	500.00
	R^2	0.9997	1.000	1.000	1.000

demonstrated in Table 8. The higher values of R^2 and the accuracy to predict $q_{e,calc}$ were used as criteria to define the most suitable model to describe the adsorption kinetics. The R^2 values for the pseudo-first-order model were low for all pesticides, ranging from 0.0029 to 0.6284. Moreover, the $q_{e,calc}$ values did not agree with the $q_{e,exp}$ values. Hence, this model was not applicable to fit the obtained experimental data.

The pseudo-second-order model correlated much better with the experimental data ($R^2 = 0.9991-1.0000$), and the calculated adsorption capacity was also much closer to the experimental value. Table 8 summarizes the kinetic parameters of the pesticides adsorbed at equilibrium using the pseudo-second-order equation. The pseudo-second-order constant k_2 (g mg^{-1} h^{-1}) gives an indication of the adsorption rate. The bigger the k_2 value, the faster the equilibrium has been reached. It can be noted that the k_2 values for isoproturon (BEA and FAU) and metalaxyl-m (FAU) are higher, which is due to the very fast adsorption at 15 and 30 minutes after their initial addition to reach equilibrium. Both isoproturon and metalaxyl-m are non-ionic pesticides, having stronger affinity for the zeolites based on their polarity (Gevao and Jones 2002).

Adsorption Isotherms

Adsorption isotherms are generally important to describe how adsorbates will interact with zeolites and are critical in optimizing the use of zeolites as an adsorber (Juang *et al*. 1996; Teng and Hsieh 1998). Although the adsorption mechanism in aqueous solutions is complicated in nature, the correlation of equilibrium data with a theoretical equation giving a satisfactory description of adsorption often offers a clue to the key mechanistic steps involved in the overall adsorption process (Hsieh and Teng 2000). The different adsorption isotherms obtained in this study are shown in Figure 7. According to IUPAC classification

(a)
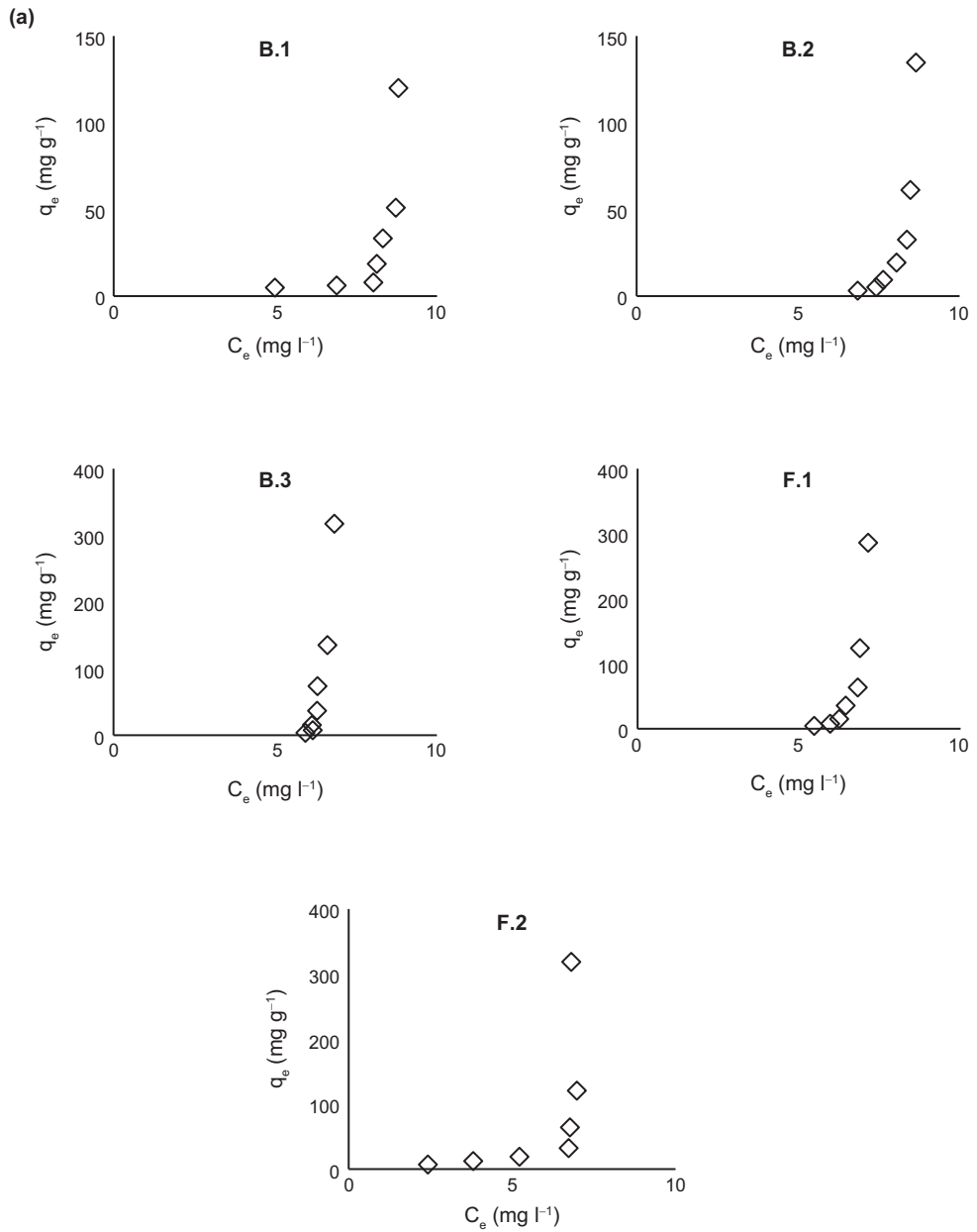
Figure 7. Adsorption isotherms of (a) bentazon, (b) imidacloprid, (c) isoproturon and (d) metalaxyl-m for the different zeolites, BEA [(B.1) = zeolite 1, (B.2) = zeolite 2 and (B.3) = zeolite 3] and FAU [(F.1) = zeolite 6 and (F.2) = zeolite 7]. *(continued)*

(b)

(continued)

(c)
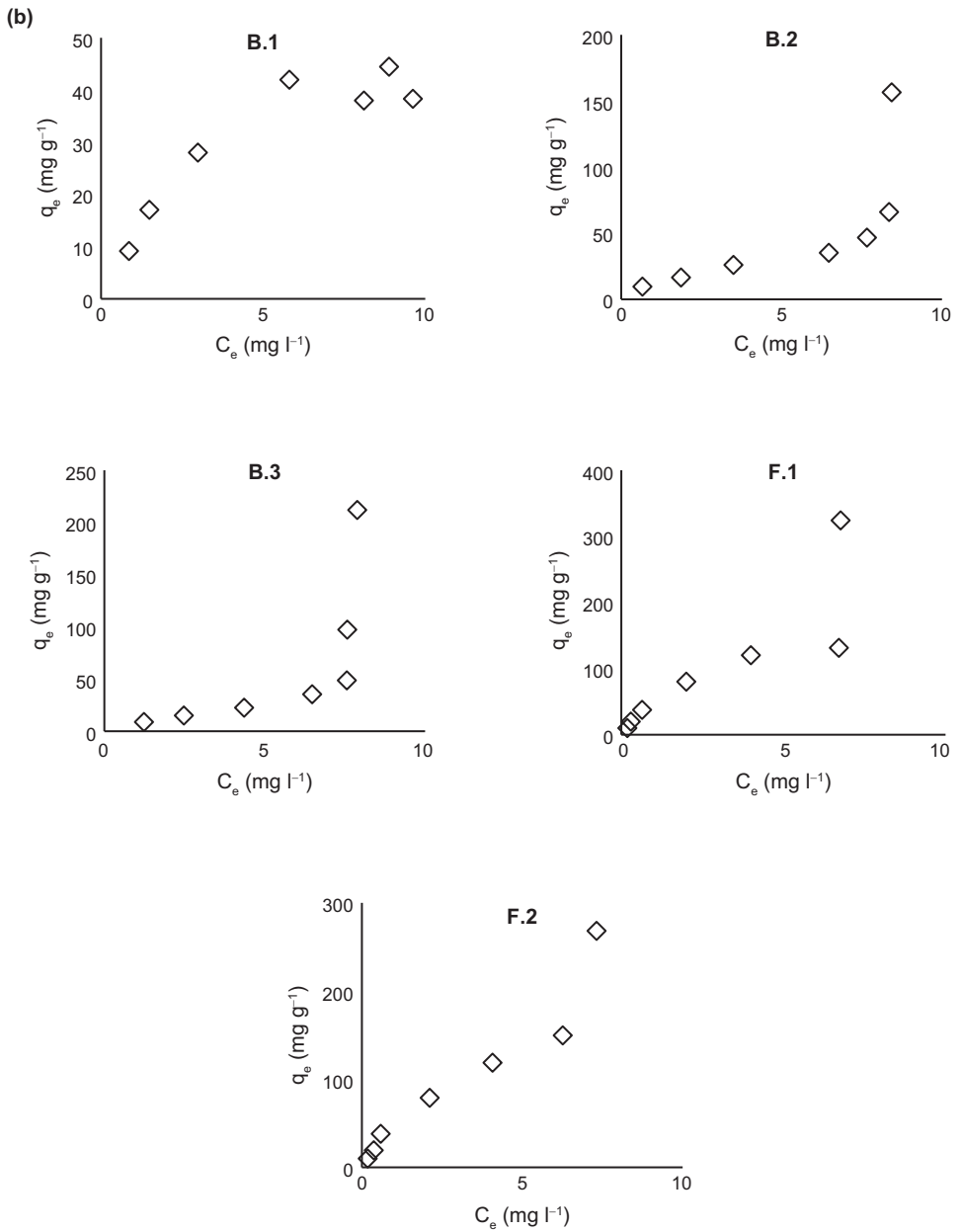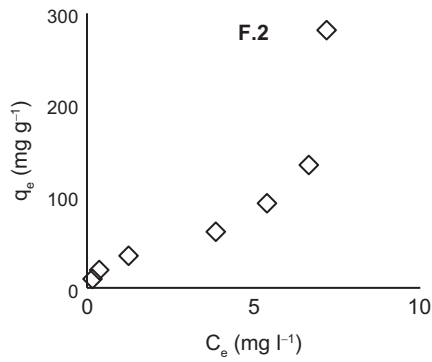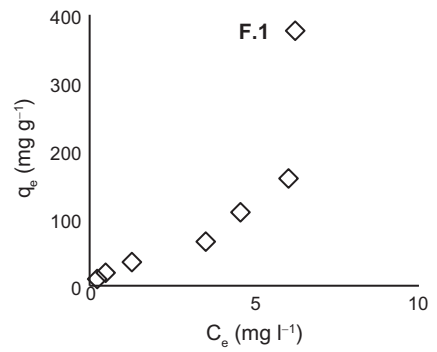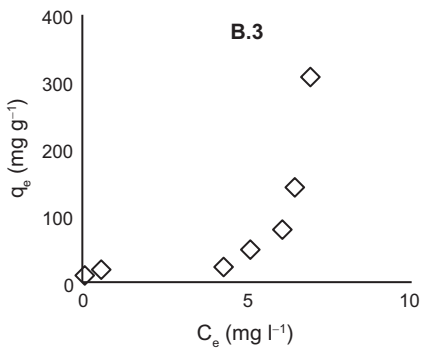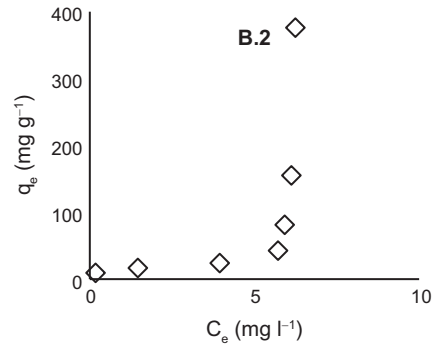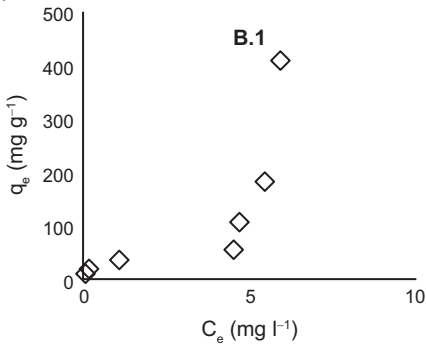
(d)
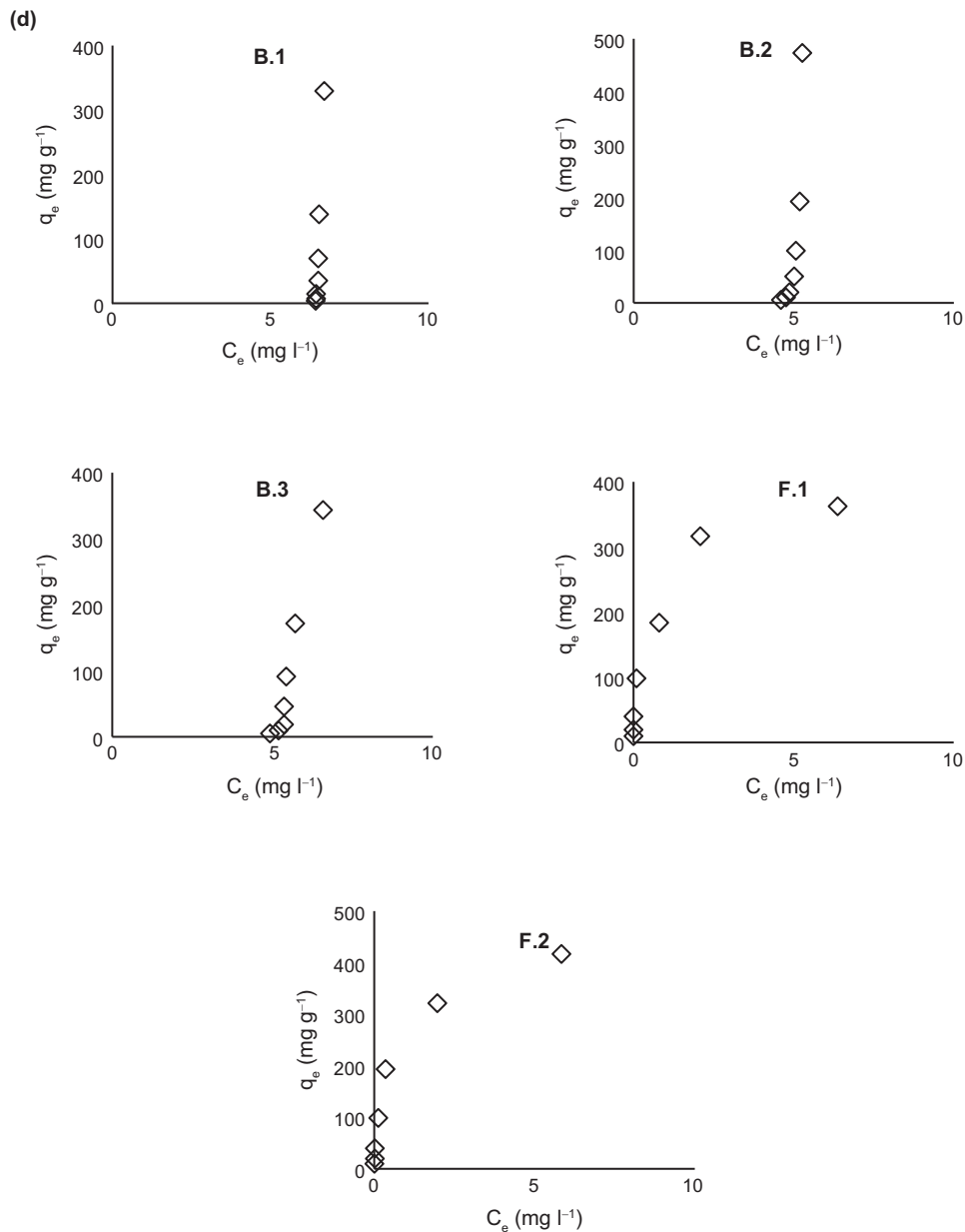
Figure 7 *(continued)*

(1985), these isotherms can be divided into six different types. Based on the results, types I, II and III were observed (Table 9). Although these isotherms shed no light on the mechanism of adsorption, they are useful for comparing results from different sources on a quantitative basis, providing information about the adsorption potential of a material with easily interpretable constants (Dawodu *et al*. 2012).

TABLE 9. Types of Adsorption Isotherm

Zeolite	Bentazon	Imidacloprid	Isoproturon	Metalaxyl
BEA-1	III	I	III	III
BEA-2	III	III	III	III
BEA-3	III	III	III	III
FAU-6	III	II	III	I
FAU-7	III	II	II/III	I

Langmuir Adsorption Isotherms

The Langmuir model is probably the best known and most widely applied adsorption isotherm (Ho *et al*. 2002). The Langmuir equation quantitatively describes the formation of an adsorbate monolayer on the outer surface of a microporous adsorbent containing a finite number of identical binding sites (Dawodu *et al*. 2012; Yousef *et al*. 2011). This type of behaviour is typical for chemisorption. The determination coefficients suggest that the applied Langmuir isotherm appears to produce a reasonable model of the adsorption system and the separation values indicate that the equilibrium adsorption was favourable for imidacloprid and isoproturon onto all zeolites. The negative values in Table 10 observed for K_L and q_m are improbable (Monkiedje and Spiteller 2002). These values, together with a small number of type I isotherms, indicate that the Langmuir model is not suitable to describe the adsorption of the pesticides on the zeolites (Carberry 2001).

BET Adsorption Isotherms

Type II adsorption isotherms show a large deviation from the Langmuir model of adsorption. The big difference between type II (BET) model and Langmuir model is that the BET theory corresponds to multilayer physical adsorption (Bansal and Goyal 2005). This isotherm is most frequently found when adsorption occurs on non-porous powders or powders with diameters exceeding micropores (Bandos *et al*. 2003). Because the pesticides are large molecules, it is more plausible that these molecules did not want to/could not adsorb in the micropores. Instead, they adsorb in the mesopores, forming type II isotherms (Storck *et al*. 1998). As is the case with the Langmuir equation, the determination coefficients suggest that the BET model appears to be a good model to interpret the adsorption behaviour. However, negative values for K_B and q_m were observed in Table 10. The isotherms for imidacloprid seem to fit the experimental data better than those for the other pesticides considered.

Freundlich Adsorption Isotherms

In this case, type III isotherms were the most frequently obtained. This isotherm is seen in systems in which the adsorbate–adsorbent interaction is small compared with the adsorbate–adsorbate reaction. The uptake of the adsorbate is initially slow until surface coverage is sufficient when the interactions between adsorbed and free molecules start to dominate the process (IUPAC 1985). The Freundlich model, which describes this type of isotherm, is found to give a good fit for the adsorption of the pesticides (Table 11). The Freundlich isotherm is the earliest known adsorption isotherm equation and is commonly used to describe the adsorption characteristics for the heterogeneous zeolite surface and considers multilayer adsorption (Boivon *et al*. 2005; Ho *et al*. 2002; Romero *et al*. 2006).

TABLE 10. Isotherm Parameters Based on the Langmuir and BET Equations

Zeolite	Parameter	Bentazon	Imidacloprid	Isoproturon	Metalaxyl
Langmuir isotherm					
BEA-1	K_L (l g^{-1})	−0.076	0.130	3.275	−0.153
	q_m (mg g^{-1})	−7.651	94.340	59.880	−0.079
	R_L	0.808	0.303	0.029	2.133
	R^2	0.6689	0.9801	0.9773	0.6201
BEA-2	K_L (l g^{-1})	−0.119	0.350	2.418	−0.198
	q_m (mg g^{-1})	−0.745	48.780	33.898	−0.584
	R_L	1.230	0.182	0.038	42.553
	R^2	0.9649	0.9699	0.8070	0.9603
BEA-3	K_L (l g^{-1})	−0.158	0.066	5.820	−0.183
	q_m (mg g^{-1})	−0.286	113.636	34.364	−0.567
	R_L	2.385	0.375	0.017	5.850
	R^2	0.9055	0.9854	0.8322	0.9800
FAU-1	K_L (l g^{-1})	−0.147	0.0805	0.414	376.667
	q_m (mg g^{-1})	−1.122	714.286	114.943	88.496
	R_L	1.901	0.357	0.163	3×10^{-04}
	R^2	0.9672	0.9779	0.9946	0.9062
FAU-2	K_L	−0.080	0.100	0.927	380.000
	q_m	−30.864	555.556	78.740	87.719
	R_L	0.832	0.333	0.089	3×10^{-04}
	R^2	0.9694	0.9915	0.9923	0.8993
BET isotherm					
BEA-1	K_B (l g^{-1})	−47.382	166.000	129.000	−3967.750
	q_m (mg g^{-1})	−6.207	60.241	77.519	−0.079
	R^2	0.3417	0.9079	0.7783	0.6185
BEA-2	K_B (l g^{-1})	−66.409	142.000	49.600	−5640.000
	q_m (mg g^{-1})	−0.761	70.423	40.323	−0.591
	R^2	0.953	0.8643	0.7661	0.9557
BEA-3	K_B (l g^{-1})	−89.023	44.500	147.000	−4422.5
	q_m (mg g^{-1})	−0.287	112.360	34.014	−0.565
	R^2	0.8983	0.7045	0.7241	0.9762
FAU-1	K_B (l g^{-1})	−82.867	151.000	16.750	8,83,334.300
	q_m (mg g^{-1})	−1.149	220.751	149.254	188.679
	R^2	0.9532	0.9540	0.7317	0.9901
FAU-2	K_B (l g^{-1})	−49.125	154.333	34.000	1,20,001.000
	q_m (mg g^{-1})	−25.445	215.983	98.039	416.663
	R^2	0.7326	0.9343	0.9023	0.9877

One important characteristic of the Freundlich isotherm is its ability to give an appropriate description of equilibrium data over a restricted range of concentration. According to Kadirvelu and Namasivayam (2000), the value of n between 1 and 10 represents a beneficial adsorption process. The value of n obtained for all pesticides and zeolites lies within this range, which implies that the zeolites have a high affinity for the pesticides in solution. This high affinity is more or less in accordance with their reported K_{oc} values.

TABLE 11. Isotherm Parameters Based on the Freundlich Equation

Zeolite	Parameter	Bentazon	Imidacloprid	Isoproturon	Metalaxyl
Freundlich isotherm					
BEA-1	K_F (mg g^{-1})	0.053	11.858	38.098	3×10^{-134}
	n	0.369	1.530	2.232	0.006
	R^2	0.5323	0.9296	0.9260	0.8681
BEA-2	K_F (mg g^{-1})	2×10^{-10}	11.741	19.436	1×10^{-19}
	n	0.083	1.586	2.121	0.034
	R^2	0.9621	0.9872	0.7520	0.9702
BEA-3	K_F (mg g^{-1})	2×10^{-33}	6.827	24.626	5×10^{-18}
	n	0.023	1.109	2.735	0.039
	R^2	0.8458	0.9764	0.7590	0.7938
FAU-1	K_F (mg g^{-1})	2×10^{-9}	45.092	30.297	202.96
	n	0.080	1.277	1.360	3.080
	R^2	0.9475	0.9785	0.9831	0.9991
FAU-2	K_F (mg g^{-1})	1.355	43.611	31.550	247.172
	n	0.564	1.274	1.717	2.823
	R^2	0.858	0.9730	0.9869	0.9845

In general, non-ionic pesticides are relatively less mobile than ionic pesticides, and consequently their affinity for zeolites is higher (De Wilde *et al*. 2009). This explains why the non-ionic pesticides isoproturon (BEA and FAU) and metalaxyl-m (FAU) have a higher adsorption intensity, compared with the other pesticides. Bentazon had the lowest affinity for the zeolites. Furthermore, the adsorption capacity of the zeolites for the pesticides was highest for the FAU zeolites. This can be explained by their higher specific surface area. The obtained results are in line with the second-order rate constants.

As mentioned earlier, the interpretation of different shapes of isotherms is not an easy task, especially for type III. There is no one simple theory that predicts the exact meaning of isotherms, but different assumptions can be made to explain these isotherms. First, according to literature, type III isotherms may also be the result of very large adsorbate molecules. If these molecules are too large and/or access to the micropores is somehow hindered, adsorption virtually takes place in extra-crystalline pores with surface adsorption being the main adsorption mechanism (Elaiopoulos 2012). As already described for the type II isotherms, this description seems to be applicable by looking at the molecular size of the adsorbates.

Another explanation, given by Zhao *et al*. (2013), is that a type III isotherm is commonly observed in the adsorption of H_2O molecules in crystalline materials. In this case, the adsorption of the pesticides, which were dissolved in water, could be the result of the adsorption of water. To verify this statement, the hygroscopicity of the zeolites was tested. Hygroscopicity is the tendency of a material to adsorb humidity, and thus, a hygroscopic product will have a large water adsorptive capacity. These products may have a porous nature and preferentially adsorb large amounts of water vapour onto specific sites with high binding energy; thus, depressing a_w dramatically for relatively large moisture contents (Decagon Devices 2006).

The WHC is one of the main and most important properties of zeolites (Tzia and Zorpas 2012). The obtained water holding capacities, after drying and wetting all zeolites, are shown in Table 12. These results follow a similar trend as the pesticide adsorption percentages presented in Table 7. Zeolites BEA and FAU are also able to adsorb more water compared with the other zeolites

TABLE 12. Hygroscopic Effect of the Zeolites Based on Their WHC Percentage

Adsorption (%)	% moisture (original)	% weight change (from dry to wet)	% weight change (from wet to dry)	% WHC
BEA-1	5.34	24.52	0.52	24
BEA-2	4.58	16.58	3.37	13.21
BEA-3	8.62	11.66	−2.62	14.28
CHA-4	3.66	1.44	−1.04	2.48
CHA-5	3.90	1.66	−1.30	2.96
FAU-6	10.29	21.74	−6.21	27.95
FAU-7	12.63	18.82	−6.21	28.91
HEU-8	3.35	3.52	−1.47	4.99
HEU-9	5.11	4.22	−2.18	6.40
HEU-10	3.60	3.95	−1.58	5.53
LTA-11	2.19	1.72	−0.27	1.99
LTA-12	6.80	0.99	−1.22	2.21
MFI-13	3.58	2.32	−1.50	3.82
MFI-14	2.57	6.39	−1.75	8.14
MFI-15	6.99	2.56	−2.42	4.98
MFI-16	15.38	1.49	−0.44	1.93
MFI-17	1.42	0.56	0.04	0.52
MOR-18	6.47	2.59	−1.40	3.99
MOR-19	5.81	4.22	−1.19	5.41

(Figure 8). This is in contrast to the hydrophobic properties based on the measured Si/Al ratio. According to Corma (2003), all zeolites containing charges are normally more hydrophilic materials which, depending on the number of charges (extra-framework cations and framework Si/Al ratio), can be more or less selective adsorbents for polar or non-polar molecules. However, pure silica zeolites with no positive charges are highly hydrophobic materials. This is proven by a WHC of 0.52% for the pure silica zeolite 17.

The obtained water adsorption isotherms represented type II instead of type III isotherms, which can be explained in the same way as explained in the "BET Adsorption Isotherms" section. These results were also observed by Halasz *et al.* (2002), who found that less hydrophobic zeolites give rise to a type II isotherm, indicating that water adsorption does not take place in its microchannels. This means that the higher water adsorption of zeolites BEA and FAU can be the result of higher external surface areas. As was also observed by others, the surface area increased with increasing Si/Al ratios of the zeolites (Figure 9; Ali *et al.* 2003; Shanjiao *et al.* 2007). The external surface of zeolites consists of bridging hydroxyls and silanol groups (SiOH), which can form hydrogen bonds with water, making the zeolite hydrophilic (Kühl 1999). These last two statements in turn explain why the hydrophobic properties based on the Si/Al ratio are not applicable here.

Finally, a type III isotherm can be the result of a situation in which previously adsorbed molecules lead to a modification of the adsorbent, which favours further adsorption. Such effects have been reported in studies involving anionic or cationic surfactants as adsorbates (Schwarzenbach *et al.* 2003). However, non-ionic products forming hydrogen bonds with the hydroxyl groups on the solid surface can also cause these modifications. Because the hydrogen bonding is weaker than the electrostatic interaction, the adsorption of the non-ionic product to
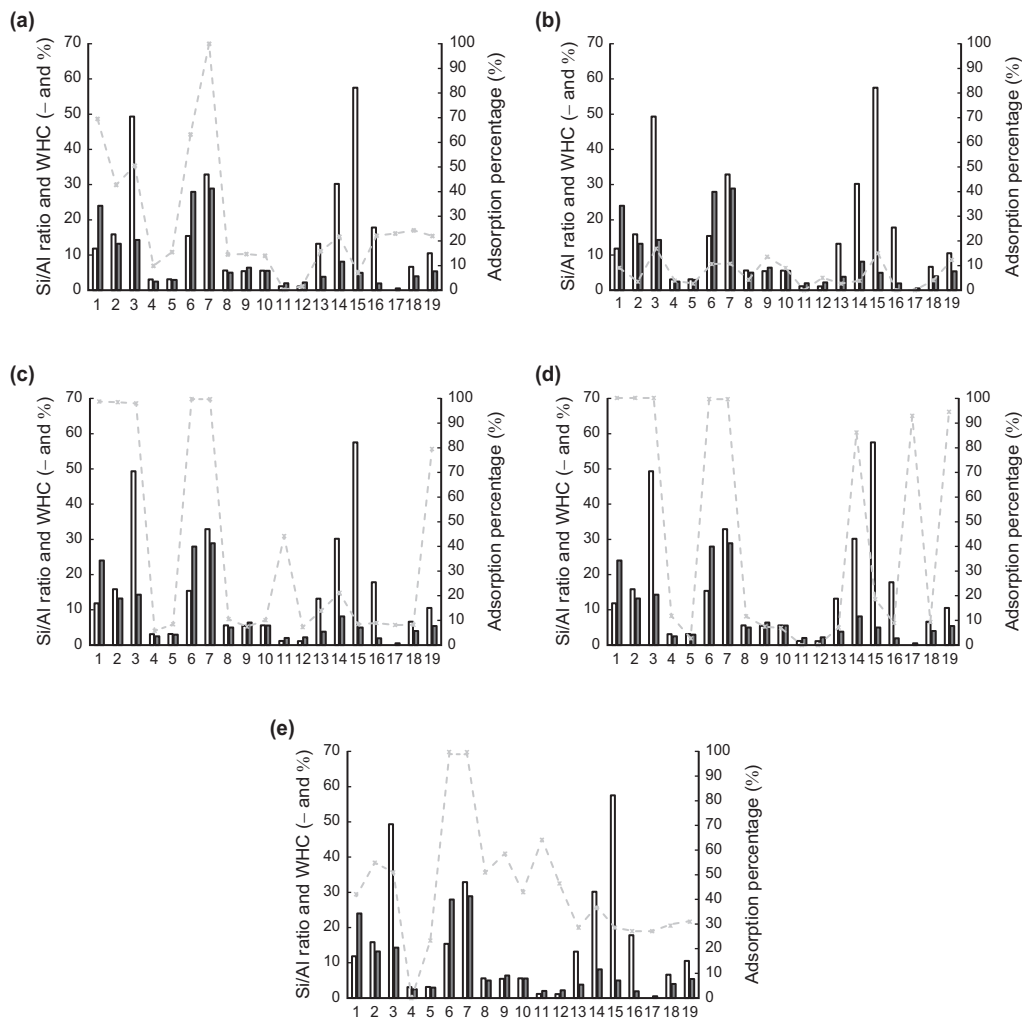
Figure 8. Comparison between the adsorption percentage (asterisks), the Si/Al-ratio (open bars) and the water holding capacity (WHC; closed bars) of the different zeolites (1-19) for the different pesticides: (a) bentazon, (b) clopyralid, (c) imidacloprid, (d) isoproturon and (e) metalaxyl -M.

most solids is less than that of ionic products (Zhang and Somasundaran 2006). To examine whether this type of isotherm is the result of a modification in the crystal structure of the zeolites, XRD patterns of the different zeolites before and after adsorption were compared. Based on the decrease or increase of the relative intensity of the strongest diffraction peak, the zeolite was found to be less crystalline. In other words, this change of intensity is associated with the presence of some defects in the structure (Shanjiao *et al*. 2007). In particular, it will be shown that different types of defects may lead either to the occurrence of transport resistance on a crystal surface or to an enhancement of the adsorption rate due to the existence of cracks on the surface. For molecules with characteristic diameters comparable with the size of the pore
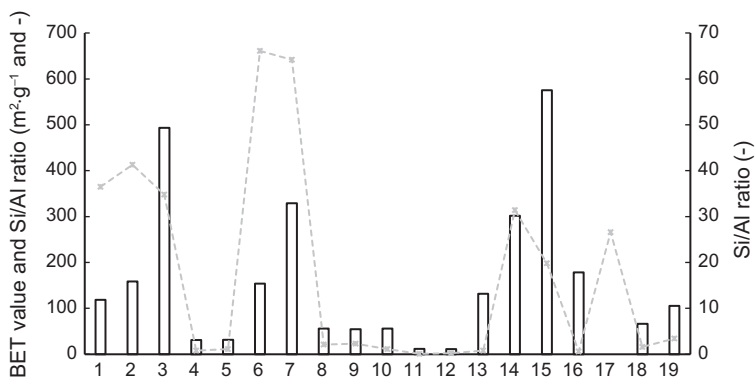
Figure 9. Comparison between the specific surface area (open bars) and the Si/Al-ratio (asterisks) of the different zeolites (1-19).

openings, a small change in the latter could easily cause an order-of-magnitude change in the mass transfer rate (Kortunov *et al*. 2004). However, in case of these large pesticide molecules, the cracks will not be large enough to make a big difference in our results. According to the XRD patterns (Figure S2, Supplementary Information), a change in the intensities can be observed. These little changes are plausible after the adsorption of pesticides, and thus, do not indicate a modification of the structures.

CONCLUSIONS

In this work, it was found that zeolites showed the applicability as adsorbent for treating waters contaminated with pesticides. The adsorption of bentazon, clopyralid, imidacloprid, isoproturon and metalaxyl-m on different zeolites was evaluated in this study. The adsorption of clopyralid was too low onto all zeolites. Subsequently, the adsorption processes of the selected pesticides and zeolites BEA and FAU were found to follow the pseudo-second-order kinetics. The FAU zeolites were able to adsorb the pesticides faster. The mobility of the pesticides also has an influence of the adsorption rate. Isoproturon and metalaxyl-m are both non-ionic pesticides, having stronger affinity for the zeolites based on their polarity.

The equilibrium data were analyzed based on the obtained type of isotherms. In this study, three different types were observed. The type I and II isotherms occurred less frequently compared with the type III isotherms. The Freundlich model, which describes this type of isotherm, was found to give a good fit for the adsorption of the pesticides. Different assumptions could be made to describe the meaning of type III isotherms. First, this isotherm can be the result of the presence of very large adsorbate molecules, which seems applicable taking into account the molecular size of the adsorbents. Subsequently, these isotherms can also be the result of water adsorption. In this case, the adsorption of pesticides, which were dissolved in water, could be the result of the adsorption of water. However, hygroscopic experiments, indicating type II isotherms for the adsorption of water, presented different results in contrast to this statement. This means that the obtained water adsorption was also the result of the higher external surface area of the BEA and FAU zeolites. Finally, adsorbed molecules can lead to modifications of the adsorbent. The XRD patterns of the different zeolites before and after adsorption demonstrate that the observed isotherms are most likely not the result of modifications in the crystal structure of the zeolites.
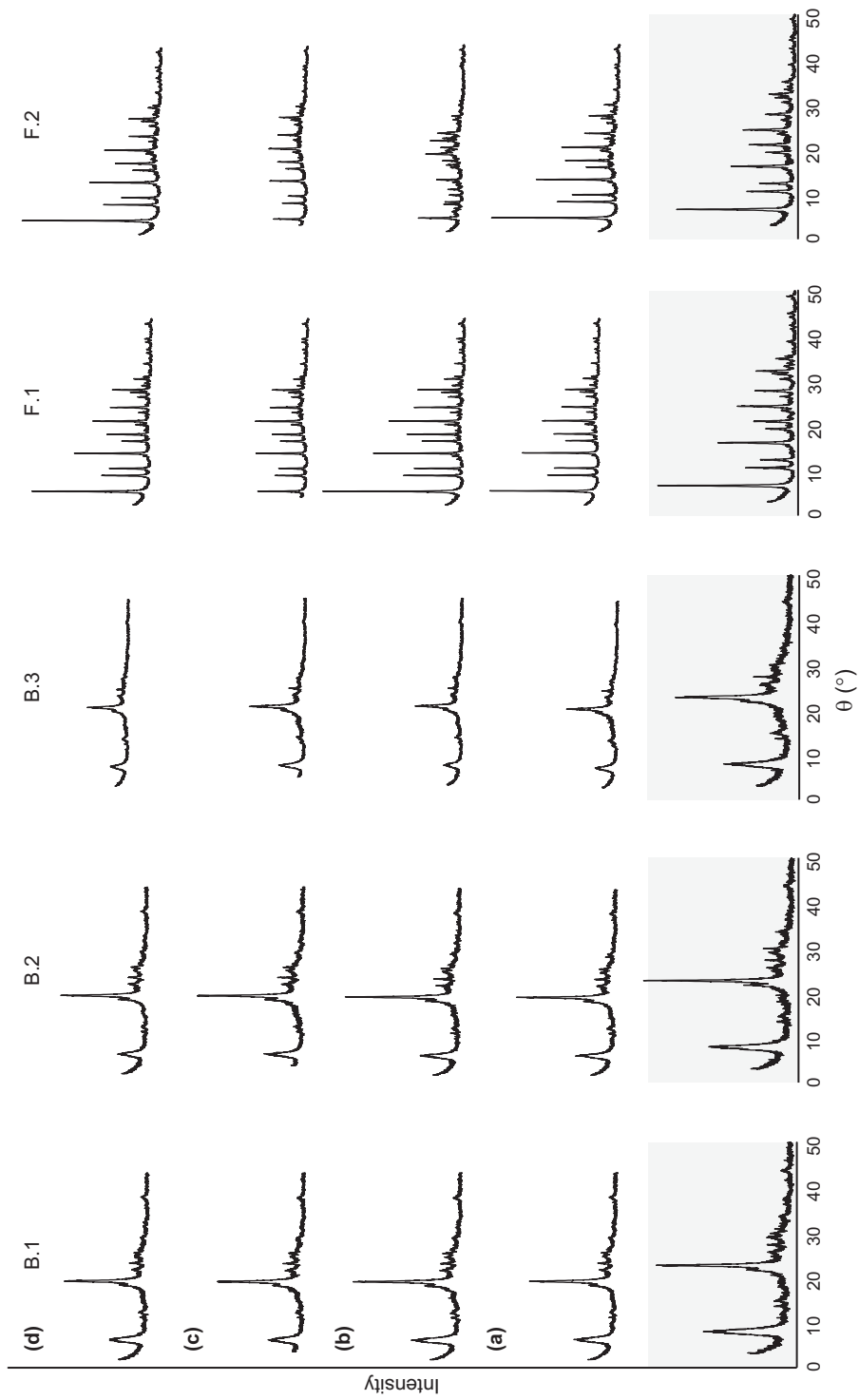
Supplementary Figure 2. XRD patterns of the different zeolites.

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