

Effect of particles size on adsorption isotherm of chlorantraniliprole, dinotefuran, bispyribac-sodium, and metribuzin into sandy loam soil

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ABSTRACT

The efficiency of different sorbents (bulk soil, sand, silt, clay and humic acid-HA) for chlorantraniliprole (CAP), dinotefuran (DNF), bispyribac-sodium (BPS), and metribuzin (MBZ) adsorption was described and compared. The adsorption of CAP, DNF, BPS and MBZ were significantly greater on clay and HA fractions than the bulk soils. Also, the tested pesticides sorption was greater on HA fraction compared to clay fraction except in the case of BPS. The mass unit of bulk soil adsorbed of CAP, DNF, BPS and MBZ approximately 15, 20, 10 and 5 % of the same of HA and 40, 60, 95 and 35 % of that of clay fraction, respectively. The actual amounts adsorbed on bulk soil ranged from (88.63 to 93.93 %) of the calculated amounts adsorbed on all soil components indicating high efficiency of the tested soils to adsorb tested pesticides. All adsorption data fitted well to the linear Freundlich equation. The adsorption of tested pesticides in soil and their different constituents is S-type according to $1/n$ (except some cases).

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1. Introduction

Particle size is an important factor into sorption.^{1,2} Particle size provides a means of coupling the effects of physical and chemical properties of sediments on sorption and transport. When sediment chemical and physical characteristics are integrated into a geochemical, geological and hydrological framework, they can yield insight into the sorption and transport of nonionic organic compounds in aquifers.^{2,3,4} Clays are the main components of the mineral fraction of soils. They are effective natural adsorbents due to their small particle sizes, lamellar structures, and negatively charged surfaces, which make them good cation adsorbents with large reactive surface areas for ion exchange or electrostatic attraction.^{2,5} One limitation in predicting behavior of organic contaminants is an incomplete understanding of the effect of heterogeneity in geochemical properties of sediments on the sorption. A negative correlation between hydraulic conductivity and distribution coefficient enhances solute spreading. Although the importance of heterogeneity in sorption parameters on transport, sediment geochemical properties at the grain scale was demonstrated that influence spatial variation in sorption of nonionic organic compounds are poorly understood.^{2,6} The powdered activated carbon can provide greater binding capacity for toxins than granular carbon commonly used in detoxifying columns. The rate of adsorption of activated carbon and zeolites depends inversely on particle size. In addition, the adsorption properties of activated carbon depend on their shape, internal surface area and pore size distribution. Sorption of tetrachlorobenzene and pentachlorobenzene increase with decreasing sediment particle-size.³ The effect of particle size on the paraquat adsorption and measurements of the pore properties of the clay adsorbents with three different particle sizes were carried out. The effect of the particle size of

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the clay adsorbent on the adsorption kinetics was found to be of considerable significance; namely, the rate constant (k) of paraquat, bispyribac-sodium (BPS) and metribuzin (MBZ) sorption by the clay adsorbent decreased with increasing particle size.^{2,5}

The fate and behavior of pesticide in soil depends on different factors including soil type and organic matter (OM) content.^{7,8} Aqueous ecosystems and soil solutions contain various dissolved and suspended organic compounds such as humic substances, metal oxides and flocculated clay particles. These fractions contain the main reaction sites and functional groups responsible for pesticides retention in soil solution and water-sediment colloidal systems. The humic acid (HA) fraction is a complex heterogeneous mixture of organic compounds consisting of different aliphatic and aromatic molecules active in the adsorption process through their carboxylic and phenolic groups. The clay fraction is known to have a larger active surface area than other soil constituents.^{1,2}

Adsorption and desorption characteristics of endosulfan in four Indian soils were studied.⁹ Maximum adsorption took place in clay soil followed by composted soil and red soil. Adsorptions of alpha and beta endosulfan were negligible in sand. OM and crystal lattice of the clay soil played a significant role in adsorption and desorption of endosulfan. The effect of the solid and dissolved OM fractions, mineral composition and ionic strength of the soil solution on the sorption behavior of pesticides was studied. The sorption behavior of atrazine, isoproturon and paraquat was dominated by the solid state soil components and the presence of dissolved OM had little effect. The sorption of 2,4-D was slightly affected by the soluble OM in the soil. However, this effect may be due to competition for adsorption sites between the pesticide and the soluble OM rather than due to a positive interaction between the pesticide and the soluble fraction of soil OM. The major factor governing the sorption of these pesticides is the solid state organic fraction with the clay mineral content also making a significant contribution. The dissolved organic carbon (OC) fraction of the total OC in the soil and the ionic strength of the soil solution appears to have no effect on the sorption transport characteristics of these pesticides.^{10,11} Herbicides generally become more persistent as soil OM and clay contents increase, presumably due to greater adsorption. Imazaquin adsorbed in greater amounts and dissipated more slowly in a silty clay with 2.3% OM than in a silt loam with 1.4% OM. Imazaquin degradation in soil occurs primarily through microbial activity, and soil type affects the rate of imazaquin degradation by microorganisms under laboratory conditions.¹² The OC was the main factor affecting phenylurea herbicides sorption. The carbofuran adsorption capacity was significantly higher in soil with high OM.¹³

The adsorption of the s-triazines by soils is affected by clay and OM content.^{14,15,16} MBZ sorption and mobility were significantly correlated with each other and both parameters were significantly associated with clay content, OM, and water content.^{17,18,19,20} Several investigators have reported increased MBZ adsorption with increased OM. There was no correlation between the Freundlich adsorption constant (K_f) and OM. There was significant negative correlation between sand content and adsorption while a significant positive correlation between clay content and adsorption was found. Increased soil mobility of MBZ has been reported with increased sand content and decreased clay and OM content.²¹ The adsorption of atrazine on clay loam soil was reversible and desorption was nearly complete. Atrazine adsorption on the HA increased as pH decreases and temperature increased, and there was very little desorption of atrazine from the HA.^{15,22}

2. Materials and Methods

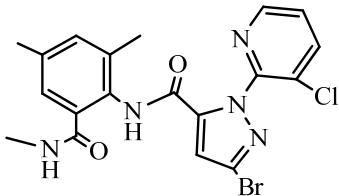
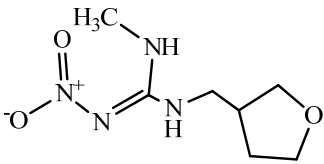
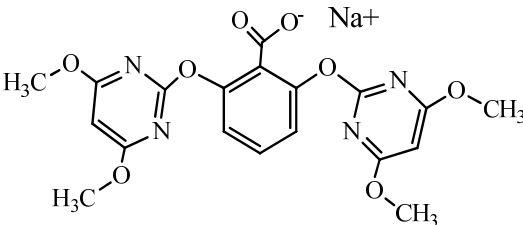
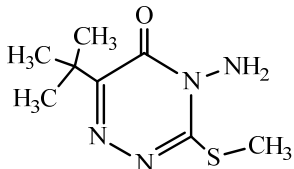
2.1. Pesticides

The physiochemical characteristics of chlorantraniliprole (CAP), dinotefuran (DNF), bispyribac-sodium (BPS), and metribuzin (MBZ) are summarized in Table 1.

2.2. Soil

Soil was air-dried, ground and passed through a 2-mm sieve prior to use. The soil texture was determined by the hydrometer method. Soil pH was measured in the presence of 0.01 M calcium chloride (CaCl_2) at 1:2, w/w, soil:solution slurry. The OM content and OC content were determined by dichromate oxidation according to the Walkley-Black method.^{18,23,24} Soil analysis showed that the texture is sandy loam (14% clay, 11% silt, 75% sand), water-holding capacity 36 mL, EC 2.34 m mhos/cm, pH 8.19, OM 1.32%, and total carbonate 41%.

Table 1. Physiochemical characteristics of tested pesticides

Characteristics	CAP	DNF	BPS	MBZ
IUPAC name	3-Bromo-N-[4-chloro-2-methyl-6-(methylcarbamoyl) phenyl]-1-(3-chloro-2-pyridine-2-yl)-1H-pyrazole-5-carboxamide	(RS)-1-methyl-2-nitro-3-(tetrahydro-3-furylmethyl) guanidine	Sodium 2,6-bis[(4,6-dimethoxypyrimidin-2-yl)oxy] benzoate	4-amino-6-terbutyl-3-methylsulfanyl-1,2,4-triazin-5-one
Class	Anthranilic diamide	Neo-nicotinoid	Pyrimidinyloxybenzoic acid	Triazinone
Structure				
Technical (%)	95.3	90.0	95.0	97.0
Type	Insecticide	Insecticide	Herbicide	Herbicide
Formulations	Coragen 20% SC	20% Starkle SG	10% SC, 40% SC, 20% WP	Sencor 70% WP
Uses	In fruit, vegetables, cotton, grapes, potatoes, rice and landscaped areas. It is used against moths, beetles, caterpillars, etc.	In fruit, vegetables and paddy rice. It can be applied to foliage, soil, nursery boxes and to paddy water by spray, drench, broadcast and 'pricking-in-hole' treatment. It is used against sucking insects.	Control of grasses, sedges and broad-leaved weeds, especially <i>Echinochloa spp.</i> , in direct-seeded rice and weeds in non-crop situations.	For pre and post-emergence control of many grasses and broad-leaved weeds in soya beans, potatoes, tomatoes, sugar cane, and cereals.

2.3. Soil component fractionation

The HA fraction was extracted from soils with 0.5 M NaOH as described by (El-Aswad et al. and Fouad et al.),^{1,2} and by following the International Humic Substances Society (IHSS) standards (Fig. 1). The clay, silt and sand fractions of the soils were obtained by a wet sedimentation method using a substance sodium hexametaphosphate as shown in Fig. 2.^{1,2}

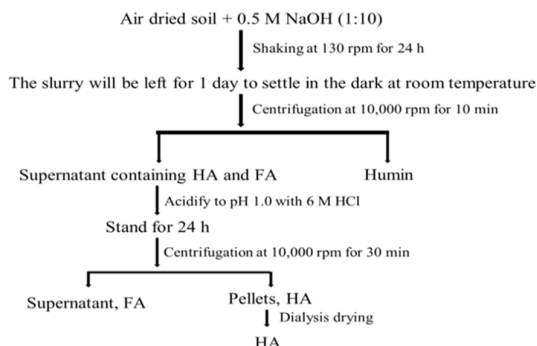


Fig. 1. Schematic diagram of extraction of HA from soil

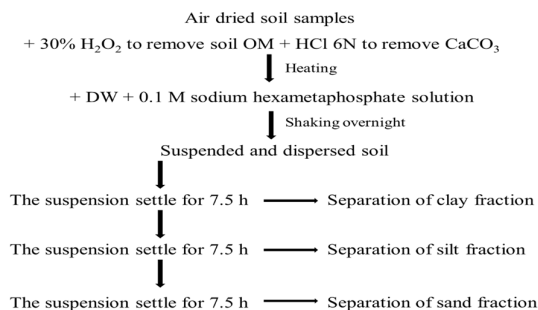


Fig. 2. Schematic diagram of extraction of clay, silt and sand fractions from soil according to wet sedimentation method.

2.4. Adsorption isotherm of tested pesticides

Adsorption isotherms by soil and its clay and HA fractions was quantified using the batch equilibration technique. Experiments were carried out in duplicate with a sorbent mass to pesticide solution ratio of 1:5 for the bulk soil and a 1:20 ratio for both clay and HA fractions. Initial pesticide concentrations in 1-50 mg/L range were prepared in 0.01 M CaCl₂. The pesticide solutions were equilibrated with soil, clay or HA fraction in 25-mL polypropylene centrifuge tubes. The tubes were shaken mechanically at 150 rpm at room temperature for a time to achieve equilibrium based on its kinetics study and centrifuged at 4000 rpm for 15 min. The pesticide concentration in supernatants was determined by a spectrophotometer at the proper λ_{max} . Control samples (no pesticide) containing only adsorbent substances and 0.01 M CaCl₂ were included in each series of experiments. Blanks containing pesticide solution with no adsorbents indicated that sorption onto the reaction tube was insignificant. The amount of pesticide sorbed, C_s , by solid phase after equilibrium was calculated,

$$C_s = (C_i - C_e) \times \frac{V}{M_s}$$

where C_s is the concentration or amount of pesticide sorbed per mass unit of adsorbent ($\mu\text{g/g}$), C_i is the initial concentration of pesticide ($\mu\text{g/mL}$), C_e is the equilibrium concentration of the pesticide per mass unit of solution ($\mu\text{g/mL}$), V is the volume of added solution (mL) and M_s is the weight of the adsorbent sample (g). The sorption partition coefficient, $Kd_{ads} = (C_s/C_e)_{ads}$.^{22,25}

2.5. Freundlich equation

The empirical formula of the Freundlich equation can be written as;

$$q_e = K_F C_e^{1/n}$$

where K_F is a constant indicative of the adsorbent ($\text{mg}^{1-(1/n)} \text{L}^{-1/n} \text{g}^{-1}$) and $1/n$ is a constant indicative of the intensity of the adsorption. The maximum adsorption capacity ($q_m \text{ mg g}^{-1}$) could be theoretically determined, $K_F = \frac{q_m}{C_o^{1/n}}$, it is necessary to operate with constant initial concentration (C_o); thus $\log q_m$ is the extrapolated value of $\log q$ for $C = C_o$.^{22,25}

3. Results

3.1. Adsorption of tested pesticides on bulk soil and their clay and HA fractions

Fig. 3 indicated that the sorption of CAP, DNF, BPS and MBZ were significantly greater on clay and HA fractions than the bulk soils. Also, the tested pesticides sorption was greater on HA fraction compared to clay fraction except in the case of BPS. The obtained results were confirmed by calculating the adsorption mean. The average adsorption were 63.5, 155.4 and 424.7 $\mu\text{g CAP/g}$ sorbent; 124.5, 204.4 and 572.5 $\mu\text{g DNF/g}$ sorbent; 84.2, 88.5 and 940.1 $\mu\text{g BPS/g}$ sorbent and 50.4, 142.6 and 943.3 $\mu\text{g MBZ/g}$ sorbent for bulk soil and its clay and HA fractions, respectively. The data were perfectly fitted according to the linear Freundlich equation. The sorption and Freundlich parameters were summarized in Table 2. The K_F values of CAP were only 0.011 and 0.403 for bulk soil and clay fraction whereas 78.864 for HA. The Kd values of CAP,

calculated by $K_d = C_s/C_e$, where C_s is the concentration of sorbed CAP ($\mu\text{g/g}$) and C_e is the equilibrium concentration of CAP per mass unit of solution ($\mu\text{g/mL}$). Data of K_F and K_d indicate that the HA fraction has (> 10 times) and the clay fraction has (> 5 times) more capacity for CAP sorption than that of bulk soil. For insecticide DNF, the Freundlich exponent $1/n$ value was >1 for soil and their components clay and HA fractions, indicating that the adsorption isotherm of DNF in these sorbents is S-type. Isotherms show that DNF adsorption on the three sorbents for each soil increases with increasing the initial concentration within the tested range. The adsorption of BPS on the bulk soil, clay fraction and HA fraction increases with increasing the initial concentration of the herbicide. Showed that no significant differences were obtained in the adsorbed BPS on bulk soil and clay fraction, while the significant differences were obtained between the adsorption process of BPS on HA fraction and other adsorbents, clay fraction and bulk soil. Also, the K_F values and K_d values indicated that the sorption capacity of BPS was more on HA fraction followed by bulk soil than that on clay fraction of soil. K_d values of BPS were 130.0, 4.4 and 9.2 for HA, clay fraction and bulk soil, respectively. Having the highest MBZ adsorption capacity, HA fraction extracted from soil adsorbed the highest amount of MBZ compared with clay fraction and Bulk soil. High significant differences were obtained between the adsorption of MBZ on HA fraction and other sorbents clay fraction and bulk soil, while low significant differences were detected between the adsorption of MBZ on clay fraction and soil bulk (Fig. 3). Values of $1/n$ for all adsorbents were more than 1, indicating the adsorption of MBZ in soil and their constituents clay and HA fractions is S-type.

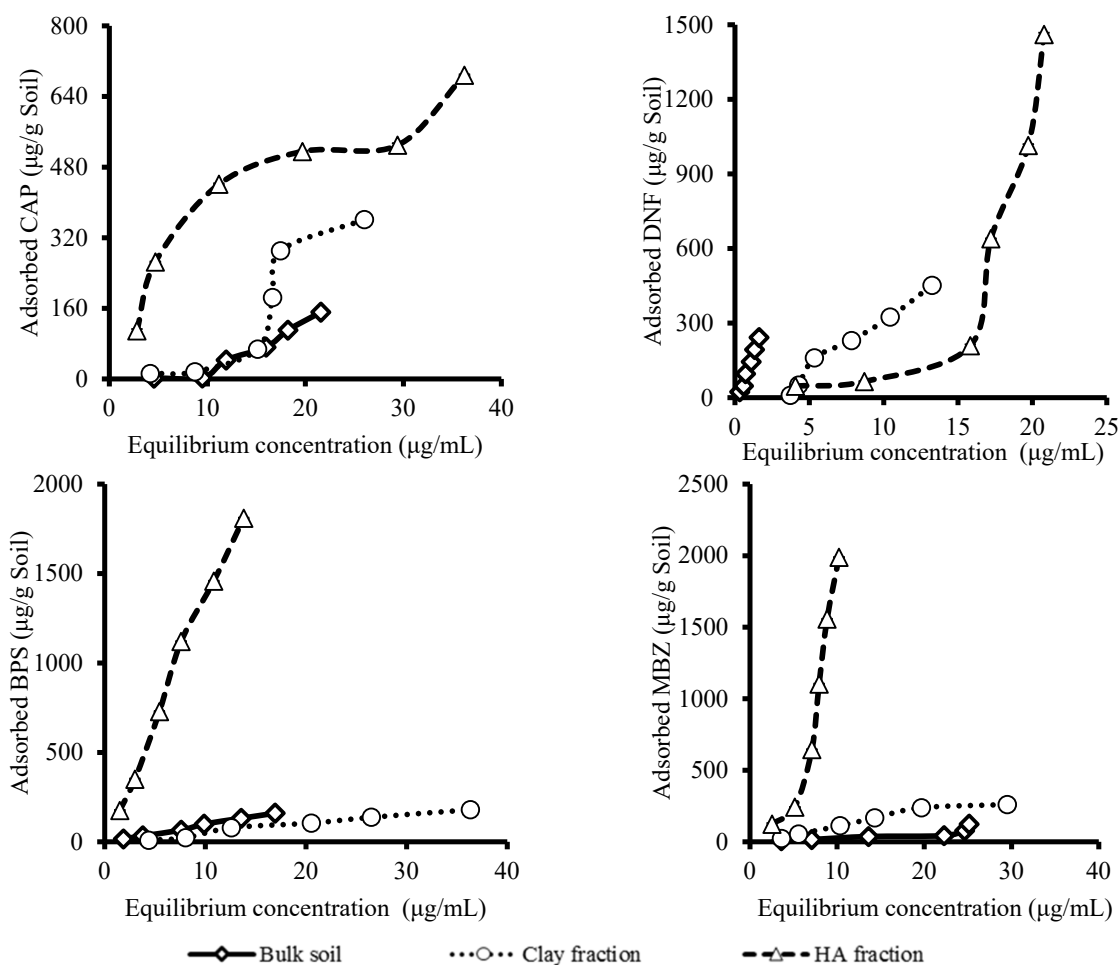
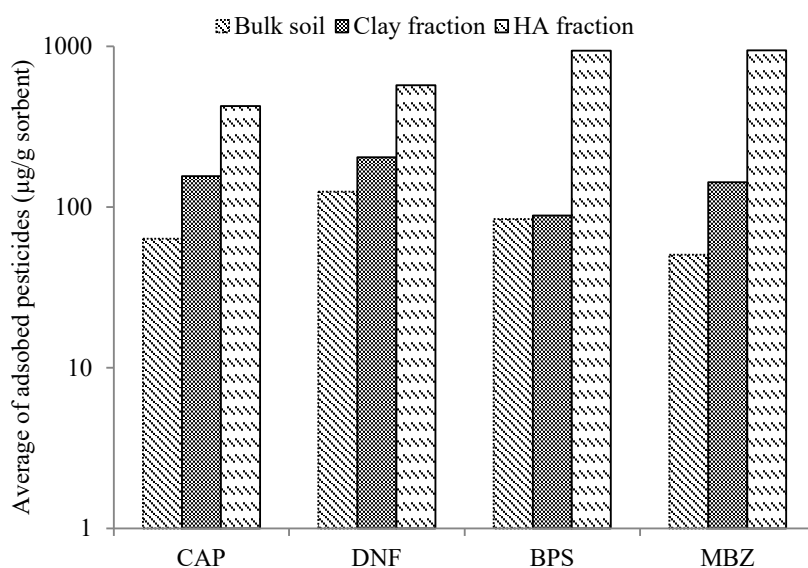


Fig. 3. Adsorption of tested pesticides in sandy loam soil and their clay and HA fractions (error bars represent one standard error of the mean).

The average of pesticide adsorption ($\mu\text{g/g}$ sorbent) was calculated, and the data are shown in **Fig. 4**. It was exhibited that the sorptive capacity of HA fraction extracted from soil was the highest one followed by that of clay fraction. Soil constituents are often associated and coagulated in aggregates and their individual contribution in various reactions is poorly understood and cannot be distinguished unless separated. One of the specific goals of this study is to extract clay and HA fractions and calculate their separate and specific contributions to tested pesticides on actual tested bulk soils. It is necessary to determine the relative contribution of soil clay minerals and OM constituents, to improve prediction of the sorption process. Obviously, as described earlier, HA fraction has more capacity than clay fraction and the soil itself.

Table 2. Freundlich and adsorption parameters of tested pesticides sorption on bulk soil and their HA, clay, silt and sand fractions.

Soil fractions	Bulk soil	HA	Clay	Silt	Sand
Parameter	CAP				
K_F	0.011	78.864	0.403	1.691	0.665
$1/n$	3.098	0.616	2.082	1.527	1.674
R^2	0.824	0.887	0.849	0.883	0.897
Kd	3.600	33.000	8.500	6.900	4.200
Parameter	DNF				
K_F	125.780	1.550	0.898	2.986	1.623
$1/n$	1.410	2.067	2.554	1.807	1.530
R^2	0.977	0.819	0.792	0.877	0.936
Kd	119.200	31.800	23.100	18.300	6.100
Parameter	BPS				
K_F	8.225	113.110	1.194	0.198	0.287
$1/n$	1.056	1.080	1.459	1.629	1.482
R^2	0.998	0.995	0.951	0.978	0.989
Kd	9.200	130.000	4.400	1.300	1.200
Parameter	MBZ				
K_F	1.299	13.397	6.348	7.624	7.877
$1/n$	1.277	2.084	1.178	0.981	0.918
R^2	0.927	0.925	0.958	0.869	0.984
Kd	2.800	116.000	9.900	7.600	6.600

**Fig. 4.** Average of adsorbed tested pesticides ($\mu\text{g/g}$ sorbent) on bulk soils and their clay and HA fractions.

Also, the mass unit of bulk soil adsorbed of CAP, DNF, BPS and MBZ approximately 15, 20, 10 and 5 % of the same of HA and 40, 60, 95 and 35 % of that of clay fraction, respectively. To estimate the contribution of clay and OM, it can be separately and simply calculated according to the following equation;

$$C_{S \text{ soil}} = f_{\text{clay}} C_{S \text{ clay}} + f_{\text{OM}} C_{S \text{ OM}} + f_{\text{others}} C_{S \text{ others}}$$

where $C_{S \text{ soil}}$ is the total amount of a tested pesticide that could be adsorbed on all fractions of soil, $f_{\text{clay}} = 0.14 \text{ g clay/g soil}$, $f_{\text{OM}} = 0.0132 \text{ g OM/g soil}$ and $f_{\text{others}} = (1 - f_{\text{clay}} - f_{\text{OM}}) \text{ g/g soil}$. **Table 3** shows the measured amounts of adsorbed tested pesticides on soil and their clay and HA fractions. Based on these actual amounts adsorbed on clay ($C_{S \text{ clay}}$) and OM ($C_{S \text{ OM}}$) fractions multiplied by their practically determined fraction in soil, their specific contribution was estimated, assuming the independency and full accessibility of their sites for pesticide binding. Using the fraction contribution and its assumptions, the 0.14 g fraction of clay per mass unit of soil could have adsorbed 21.75, 28.62, 12.39 and 19.97 and the 0.0132 g fraction of OM per mass unit of bulk soil could have contributed 5.61, 7.56, 12.41 and 12.45 CAP, DNF, BPS and MBZ, respectively.

Table 3. Actual adsorbed amounts of tested pesticides on bulk soil and their clay and HA fractions and the specific contribution to soil-sorbed pesticides.

Parameters		CAP	DNF	BPS	MBZ
Actual adsorbed amounts	$C_{s \text{ soil}}$ ($\mu\text{g/g soil}$)	63.51	124.45	84.15	50.43
	$C_{s \text{ clay}}$ ($\mu\text{g/g clay}$)	155.36	204.40	88.50	142.63
	$C_{s \text{ om}}$ ($\mu\text{g/g HA}$)	424.75	572.51	940.10	943.31
Calculated potential contribution	Clay fraction ($\mu\text{g/g soil}$)	21.75	28.62	12.39	19.97
	HA fraction ($\mu\text{g/g soil}$)	5.61	7.56	12.41	12.45
	Total $C_{s \text{ soil}}$ ($\mu\text{g/g soil}$)	70.05	140.42	94.89	53.69
contribution	Clay fraction (%)	31.05	20.38	13.06	37.19
	HA fraction (%)	8.00	5.38	13.08	23.19
Actual adsorbed on bulk soil (%)		90.66	88.63	88.68	93.93

Data as the mean of adsorption values corresponding to initial concentrations from 5 to 50 $\mu\text{g/ml}$

Calculated potential contribution of clay = actually adsorbed onto clay ($C_{s \text{ clay}}$) multiplied by its fraction (F_{clay}) in bulk soil

Calculated potential contribution of OM = actually adsorbed onto HA ($C_{s \text{ om}}$) multiplied by its fraction (F_{om}) in bulk soil

For soil B: $F_{\text{clay}} = 0.14$ clay/g soil, $F_{\text{om}} = 0.0132$ OM/g soil

% of clay contribution = $[(C_{s \text{ clay}} / \text{total potentially adsorption on both clay and OM}) * 100]$

% of OM contribution = $[(C_{s \text{ om}} / \text{total potentially adsorption on both clay and OM}) * 100]$

Total $C_{s \text{ soil}}$ ($\mu\text{g/g soil}$) = clay contribution + HA contribution + others contribution

2. Effect of sorbent particle-size on tested pesticide sorption

After removing the OM content chemically and removing the coarse fraction ($> 500 \mu\text{m}$) physically, samples of soil were separated in three fractions depending on their size by physical treatments [$50 \mu\text{m} < \phi < 500 \mu\text{m}$ (sand); $2 \mu\text{m} < \phi < 50 \mu\text{m}$ (silt); $\phi < 2 \mu\text{m}$ (clay)]. The adsorption capacities and affinities of different fractions; clay, silt and sand to tested pesticides; CAP, DNF, BPS and MBZ were investigated.

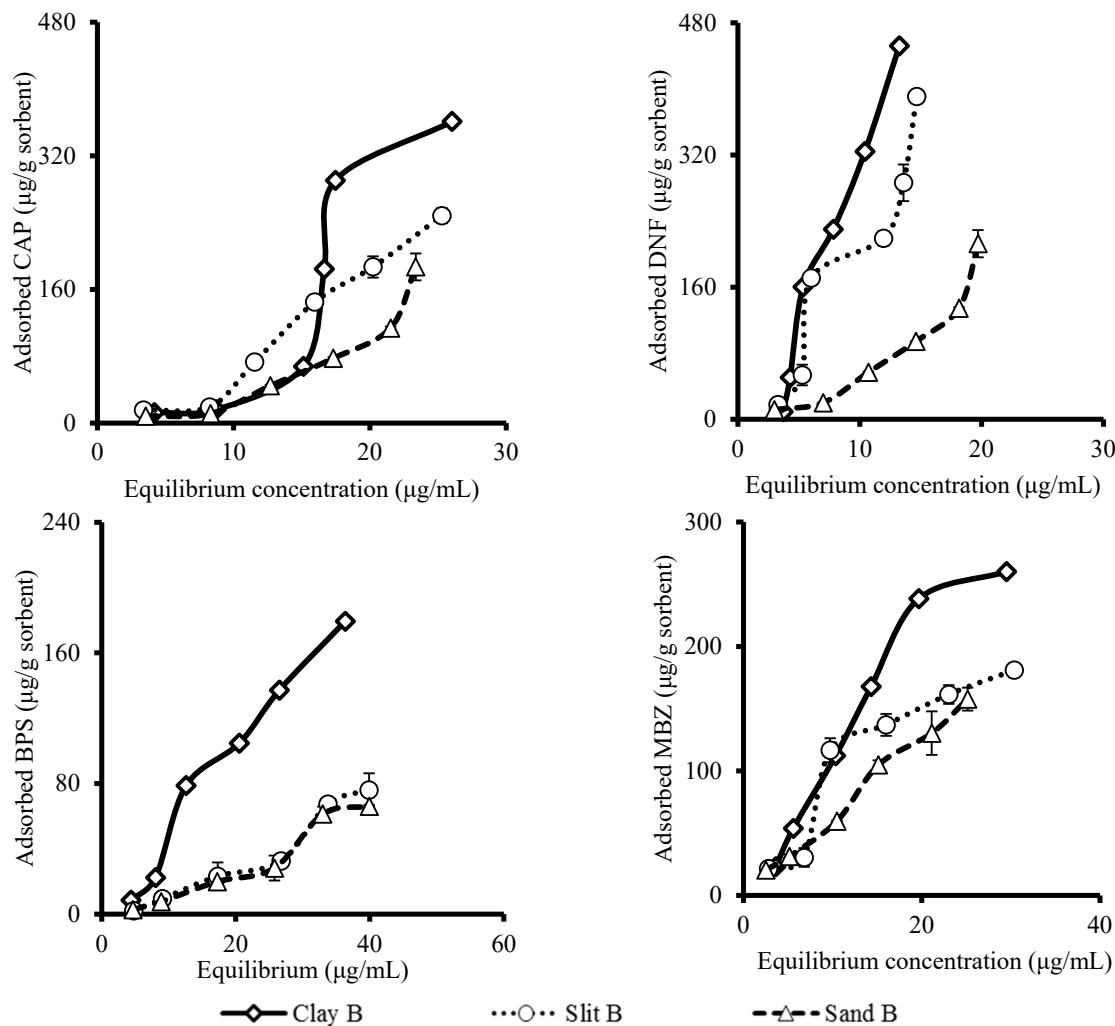


Fig. 5. Adsorption of tested pesticides in clay, silt and sand fractions of sandy loam soil (error bars represent one standard error of the mean).

The results presented in **Fig. 5** showed in general that the adsorption amounts of the tested pesticides were greater in clay fraction while minimal in sand fraction. The significant differences were recorded among different sorbent fractions for CAP sorption in the case of soil. Also, the adsorption of DNF on clay fractions was higher statistically than those on silt and sand fractions. BPS sorption on clay fraction was higher than that on sand fraction while, almost the adsorptions of BPS on silt and sand fractions were equal. In addition, significant differences were obtained among the sorption of MBZ on different sorbents except at low concentration.

All adsorption data fitted well to the Freundlich equation. The Freundlich adsorption parameters and partition Coefficient values of the pesticides are summarized in **Table 2**. The K_F values increase with decreasing particle size particularly in the case of adsorption of CAP and DNF on silt and sand fractions. Comparison of the adsorption's behavior of different pesticides on the basis of their K_d values clearly suggest an inverse relationship of K_d and adsorbent particle size. The slope ($1/n$) values for CAP, DNF, BPS and MBZ adsorption on clay, silt and sand fractions isolated from sandy loam soil, except some cases, were greater than 1.

4. Discussions

The efficiency of different sorbents (soil, clay and HA) for tested pesticides adsorption was described and compared. The fact that the soil OM is a significant site for the binding of pesticides and is the predominant factor influencing the retention of non-ionic pesticides in soils has been extensively documented.^{26,27,28} The soil OM is constituted of humic substances, which are mostly composed of humic and fulvic acids.^{1,2} Humic compounds have aliphatic moieties and the aromaticity of HA ranges from 20 to 70%.²⁹ These acids have many intrinsic chemical properties that significantly augment their interaction with organic pesticides.²⁶ Also, as a result of holes in the humic structures, organic chemicals of appropriate sizes may be trapped in the humic substances.^{1,2,30} On the other hand, an increase in the soil clay content is often observed to increase pesticide retention by soil. Clay minerals may be grouped into two broad categories; swelling and non-swelling clays.^{1,2,31,32} Thus, though organic compounds are able to bind to clay minerals in either category, the clay type will clearly affect pesticide retention. The adsorption patterns represent the S-type phase increases.³³ Clay fraction shows more affinity to adsorb DNF than HA fraction. El-Aswad and Hedeia found that isotherms of aldicarb adsorption coefficient on the OM and clay fractions of soil were S-type.³⁴ Hedia and El-Aswad found that the adsorption of spinosad on soil and its constituent's clay and HA fractions followed the S-type.³⁵ OM is a versatile sorbent and polar and even ionic molecules' soil sorption can show some correlation with OM content.^{1,2} However, for more polar salutes, surfaces of other materials in soils can become important sorbents, particularly in soils where the OM fraction is low.¹⁰ Therefore, it is expected that soil and sediments with higher OM and clay are more capable of pollutant sequestration than soils with less clay and OM.³⁶

Fouad et al reported that in some cases, mineral fractions may contribute more than soil OM to the retention of certain neutral pesticides.² However, OM and clay minerals are generally considered as the two important soil components in the retention of soil-applied pesticides.^{1,2} Thus, the OM is a critical factor controlling the sorption process. Collectively, the total possible contribution of both clay and HA fractions together indicated that the other soil fractions (f_{others}) have minimal contributions in pesticide adsorption. Fushiwaki and Urano found that their organic chemicals were adsorbed on inorganic matter in soil.³⁷ The actual amounts adsorbed on bulk soil ranged from 88.63 % to 93.93 % of the calculated amounts adsorbed on all soil components indicated that high efficiency of tested soil to adsorb tested pesticides. The korickhoff model assumes that all sites of soil constituents are independently active and accessible. Obviously, the results indicated that some of the active sites on the clay-HA complexes within other soil comments might be blocked by other constituents and did not actively participate in pesticide adsorption. Although the capacity and affinity of HA toward most pesticides sorption is much larger than that of clay, the role of clay fraction should not be ignored as the major contributor for pesticide adsorption due to its higher fraction (f_{clay}) than OM fraction (f_{OM}) in tested soil. Data showed that the clay fraction contributed about 30 to 12 % to the different pesticides. The lowest contribution was for BPS adsorption by both clay fractions. The HA fraction was responsible for 13-5 % within the actual soils. Based on these findings and in alignment with others,³⁸ this study emphasizes the major role of clay minerals in pesticide sorption due to its higher ratio to OM content. Spark and Swift stated that in soils that have a low OM content, the sorption of pesticides is instead often related to the active components of the inorganic fraction, predominantly the clay size fraction.¹⁰

It was clearly indicated that at lower concentration of herbicides; atrazine and MBZ, particle size had no effect on herbicides sorption. However, at higher concentrations the effect of particle size is clearly visible. At higher herbicide concentrations 150 - 250 μm fraction exhibited higher sorption for atrazine, while in case of MBZ it was the < 150 μm fraction, which showed maximum adsorption. Also, Najm et al, reported that the efficiency of adsorption of powdered activated carbon for many pesticides including MBZ can be significantly improved by using smaller-size powdered adsorbent. A decrease in the particle radius, resulted in higher adsorption capacity. This trend agrees with the finding by Fouad et al.² Also, Gao et al, stated that a positive correlation between pentachlorophenol sorption and sediment particle-size and noted that the distribution exhibited a bimodal behavior; both the smaller particles (clay, fine silt) as well as the larger particles (fine sand) showed the most effective sorption of pesticides.⁴⁰ In addition, the sorption of chlorobenzenes increase with decreasing sediment particle size.³ Moreover, the rate and extent of lambda-cyhalothrin adsorption decreased by increasing the particle size of adsorbent. This behavior can be attributed to the diffusion in the internal pores of the particles.⁴¹ Also, it can be explained from the relation between the effective specific surface area of the adsorbent particles

and the particles size, the fine-size fractions are usually characterized by higher specific surface areas.³³ The results indicated that the clay and silt fractions adsorbing considerable amounts of tested pesticides, but the adsorptive strength of the fine sand fraction is low. This was attributed to the larger surface area of clay and silt for sorbing pesticides compared with other fractions. Similar results are known from other investigations.^{37,40} Therefore, surface area is a key indicator of the adsorptive power of adsorbent.⁴²

The isotherms are of the S-type according to the classification by GH.⁴³ The S-shaped isotherm for adsorption to α -alumina has been found for the adsorption of benzoic acid and for the adsorption of 2,4-D on ferrihydrite.^{44,45} According to our results, it was very interested to state that the adsorption tested pesticide capacities of clay fraction followed by silt fraction are always higher than that of sand fraction. Minkina et al, reported that the clay and silt fractions are the most dynamic and active soil components.⁴⁶ The clay fraction mainly contains secondary clay minerals, coagels of iron aluminum oxide and silicic acid, amorphous compounds and organic and organomineral compounds clays are effective natural adsorbents due to their small particle sizes, lamellar structures and negatively charged surfaces.⁴⁷ Consequently, it was found that quartz and calcite play a smaller role than clay minerals for adsorption of atrazine isoproturon, 2,4-D and bentazone.⁴⁸ Therefore, the magnitude of the adsorption depends on the type of pesticide, the type of clay mineral and the specific surface of the mineral. On the other hand, although basic relations between particle size and sorption have been established in laboratory studies, the relation between sorption, particle size and transport in aquifers is not as clear.⁴⁹ However, the effect of increasing nonionic organic compounds sorption with decreasing particle size also significantly reduce rates of transport through zones of fine sand and silt compared to zones of coarser sediment.³ Therefore, the relation between particle size, sorption and hydraulic conductivity is a critical consideration in understanding organic-solute transport.

5. Conclusion

The absorption of CAP, DNF, BPS and MBZ were significantly greater on HA fraction followed by clay fraction than the bulk soil. The mass unit of bulk soil adsorbed of CAP, DNF, BPS and MBZ approximately 15, 20, 10 and 5 % of the same of HA and 40, 60, 95 and 35 % of that of clay fraction, respectively. The 0.14 g fraction of clay per mass unit of soil could have absorbed 21.75, 28.62, 12.39 and 19.97 μg and the 0.0132 g fraction of OM per mass unit of bulk soil could have contributed 5.61, 7.56, 12.41 and 12.45 μg of CAP, DNF, BPS and MBZ, respectively. The total possible contribution of both clay and HA fractions together indicated that the other soil fractions (f_{others}) have minimal contributions in pesticide adsorption. The capacity and affinity of HA toward most the tested pesticides sorption is much larger than that of clay, the role of clay fraction should not be ignored as the major contributor for pesticide adsorption due to its higher fraction (f_{clay}) than OM fraction (f_{OM}) in sandy loam soil. The clay fraction contributed about 31 to 13 % and the HA fraction was responsible for 23-5 % within the actual soils to the different pesticides. The adsorption amounts of all tested pesticides were significantly greater on clay fraction followed by silt fraction than on sand fraction in the case of soil. The KF and Kd values increase with decreasing particle size particularly in the case of adsorption of CAP, DNF and MBZ, indicating the adsorption process was more easily adsorbed on clay fraction. The S-shaped isotherms illustrate that the more pesticide is already adsorbed on the clay, silt and sand fractions, the easier it is for additional molecules to become fixed. The adsorption capacity of sandy loam soil fractions was the highest for CAP whereas the lowest for BPS.

References

1. El-Aswad A. F., Aly M. I., Fouad M. R., and Badawy M. E. I. (2019) Adsorption and thermodynamic parameters of chlorantraniliprole and dinotefuran on clay loam soil with difference in particle size and pH. *J. Environ. Sci. Health B*, 54 (6) 475-488.
2. Fouad M. R., El-Aswad A. F., Aly M. I., and Badawy M. E. I. (2023) Sorption characteristics and thermodynamic parameters of bispyribac-sodium and metribuzin on alluvial soil with difference in particle size and pH value. *Curr. Chem. Lett.*, 12 (3) 545-556.
3. Barber L. B., Thurman E. M., and Runnells D. D. (1992). Geochemical heterogeneity in a sand and gravel aquifer: Effect of sediment mineralogy and particle size on the sorption of chlorobenzenes. *J. Contam. Hydrol.*, 9 (1-2) 35-54.
4. Ahmed A. A., Mohamed S. K., and Abdel-Raheem Sh. A. A. (2022) Assessment of the technological quality characters and chemical composition for some Egyptian Faba bean germplasm. *Curr. Chem. Lett.*, 11 (4) 359-370.
5. Tsai W., Lai C., and Hsien K. (2003) The effects of pH and salinity on kinetics of paraquat sorption onto activated clay. *Colloids Surf. A Physicochem. Eng. Asp.*, 224 (1-3) 99-105.
6. Fouad M. R. (2023) Effect of peat, compost, and charcoal on transport of fipronil in clay loam soil and sandy clay loam soil. *Curr. Chem. Lett.*, 12 (2) 281-288.
7. Aly M. I., Fouad M. R., Abou-Elnasr H. S., and El-Aswad A. F. (2021) Comparison of Dissipation Kinetics and Residual Behaviour for Fenitrothion Insecticide and Thiobencarb Herbicide in Clay Soil. *Alex. J. Agric. Sci.*, 66 (1) 1-11.
8. Fouad M. R. (2023) Effect of Soil Amendments on Leaching of Thiamethoxam in Alluvial and Calcareous Soil. *Basrah J. Agric. Sci.*, 36 (1) 164-172.
9. Kumar M., and Philip L. (2006) Adsorption and desorption characteristics of hydrophobic pesticide endosulfan in four Indian soils. *Chemosphere*, 62 (7) 1064-1077.
10. Spark K., and Swift R. (2002) Effect of soil composition and dissolved organic matter on pesticide sorption. *Sci. Total. Environ.*, 298 (1-3)147-161.

11. Fouad M. R., Badawy M. E. I., El-Aswad A. F., and Aly M. I. (2023) Experimental modeling design to study the effect of different soil treatments on the dissipation of metribuzin herbicide with effect on dehydrogenase activity. *Curr. Chem. Lett.*, 12 (2) 383-396.
12. Loux M. M., and Reese K. D. (1992) Effect of soil pH on adsorption and persistence of imazaquin. *Weed Sci.*, 40 (3) 490-496.
13. Chirukuri R., and Atmakuru R. (2015) Sorption characteristics and persistence of herbicide bispyribac sodium in different global soils. *Chemosphere*, 138: 932-939.
14. Fouad M. R., and El-Aswad A. F. (2018) Competitive and non-competitive adsorption of atrazine and diuron on alluvial soil. *Alex. Sci. Exch. J.*, 39 (July-September) 527-533.
15. McGlamery M. D., and Slife F. (1966) The adsorption and desorption of atrazine as affected by pH, temperature, and concentration. *Weeds*, 14 (3) 237-239.
16. Fouad M. R., Shamsan A. Q. S., and Abdel-Raheem Sh. A. A. (2023) Toxicity of atrazine and metribuzin herbicides on earthworms (*Aporrectodea caliginosa*) by filter paper contact and soil mixing techniques. *Curr. Chem. Lett.*, 12 (1) 185–192.
17. Savage K. (1976) Adsorption and mobility of metribuzin in soil. *Weed Sci.*, 24 (5) 525-528.
18. El-Aswad A. F., Fouad M. R., Badawy M. E. I., and Aly M. I. (2022) Effect of Calcium Carbonate Content on Potential Pesticide Adsorption and Desorption in Calcareous Soil. *Commun. Soil Sci. Plant Anal.*, 1-9.
19. Shamsan A. Q. S., Fouad M. R., Yacoob W. A. R. M., Abdul-Malik M. A., and Abdel-Raheem Sh. A. A. (2023) Performance of a variety of treatment processes to purify wastewater in the food industry. *Curr. Chem. Lett.*, 12 (2) 431–438.
20. Fouad M. R. (2023) Effect of temperature and soil type on the adsorption and desorption isotherms of thiamethoxam using the Freundlich equation. *Egypt. J. Chem.*, 66 (7) 197-207.
21. Peek D. C., and Appleby A. P. (1989) Phytotoxicity, adsorption, and mobility of metribuzin and its ethylthio analog as influenced by soil properties. *Weed Sci.*, 37 (3) 419-423.
22. Fouad M. R. (2023) Physical characteristics and Freundlich model of adsorption and desorption isotherm for fipronil in six types of Egyptian soil. *Curr. Chem. Lett.*, 12 (1) 207-216.
23. Badawy M. E. I., El-Aswad A. F., Aly M. I., and Fouad M. R. (2017) Effect of different soil treatments on dissipation of chlorantraniliprole and dehydrogenase activity using experimental modeling design. *Int. J. Adv. Res. Chem. Sci.*, 4 (12) 7-23.
24. Fouad M. R. (2021) Study on toxicity effect of bispyribac-sodium herbicide on earthworms by filter paper and soil mixing method. *Int. J. Environ. Agric. Res.*, 7 (4) 755-766.
25. Fouad M. R. (2023) Validation of adsorption-desorption kinetic models for fipronil and thiamethoxam agrichemicals on three types of Egyptian soils. *Egypt. J. Chem.*, 66 (4) 219-222.
26. Barraclough D., Kearney T., and Croxford A. (2005) Bound residues: environmental solution or future problem?. *Environ. Pollut.*, 133 (1) 85-90.
27. Abd El-Aal M., Mogharbel R. T., Ibrahim A., Almutlaq N., Zoromba M. S., Al-Hossainy A. F., and Ibrahim S. M. (2021) Synthesis, characterization, and photosensitizer applications for dye-based on ZrO₂-acriflavine nanocomposite thin film [ZrO₂+ ACF]^C. *J. Mol. Struct.*, 1250 131827.
28. Fouad M. R., Abou-Elnasr H., Aly M. I., and El-Aswad A. F. (2021) Degradation Kinetics and Half-Lives of Fenitrothion and Thiobencarb in The New Reclaimed Calcareous Soil of Egypt Using GC-MS. *J. Adv. Agric. Res.*, 26 (1) 9-19.
29. Fuehr F. (1987) What is the fate of the herbicide residues in the soil? *Rheinische Monatschrift fuer Gemuese Obst Zierpflanzen* (Germany, FR).
30. El-Aal M. A., and Seto T. (2021) Spark discharge deposition of au/cu nanoparticles for surface-enhanced Raman scattering. *Surf. Interface Anal.*, 53 (9) 824-828.
31. Pu X., and Cutright T. J. (2006) Sorption-desorption behavior of PCP on soil organic matter and clay minerals. *Chemosphere*, 64 (6) 972-983.
32. Mohamed S. K., Mague J. T., Akkurt M., Alfayomy A. M., Abou Seri S. M., Abdel-Raheem Sh. A. A., and Abdul-Malik M. A. (2022) Crystal structure and Hirshfeld surface analysis of ethyl (3E)-5-(4-chlorophenyl)-3-[[4-(4-chlorophenyl)formamido]imino]-7-methyl-2H,3H,5H-[1,3]thiazolo[3,2-a]pyrimidine-6-carboxylate. *Acta Cryst.*, 78 (8) 846-850.
33. Delle Site A. (2001) Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. *J. Phys. Chem. Ref. Data.*, 30 (1) 187-439.
34. El-Aswad A. F.; Hedeia R. M. (2002) Fate and behavior of aldicarb under Egyptian soil conditions. National Sym. on Problem of Land degradation in Egypt and Africa. Institute of African Research, Studies Department of natural resources, Cairo University, March 23-24, P. 57-68.
35. Hedia R. M., and El-Aswad (2016) Spinosaad Adsorption on Humic and Clay Constituents of Lacustrine Egyptian Soils and It's Leaching Potential. *Alex. Sci. Exch. J.*, 37 (3) 457-466.
36. Koskinen W. C., Cox L., and Yen P. (2001) Changes in sorption/bioavailability of imidacloprid metabolites in soil with incubation time. *Biology and Fertility of Soils*, 33: 546-550.
37. Fushiwaki Y., and Urano K. (2001) Adsorption of pesticides and their biodegraded products on clay minerals and soils. *J. Health Sci.*, 47 (4) 429-432.

38. Kandil M. M., El-Aswad A. F., and Koskinen W. C. (2015) Sorption–desorption of imidacloprid onto a lacustrine Egyptian soil and its clay and humic acid fractions. *J. Environ. Sci. Health B*, 50 (7) 473-483.
39. Najm I. N., Snoeyink V. L., Suidan M. T., Lee C. H., and Richard Y. (1990) Effect of particle size and background natural organics on the adsorption efficiency of PAC. *J. Am. Water Works Assoc.*, 82 (1): 65-72.
40. Gao J., Maguhn J., Spitzauer P., and Kettrup A. (1998) Sorption of pesticides in the sediment of the Teufelsweiher pond (Southern Germany). I: Equilibrium assessments, effect of organic carbon content and pH. *Water Res.* 32 (5) 1662-1672.
41. Al-Qudah A. A., Mitchell C. A., Biagioni P. A., and Hussey D. L. (2007) Effect of composite shade, increment thickness and curing light on temperature rise during photocuring. *J. Dent.*, 35 (3) 238-245.
42. Yang Y., Chun Y., Sheng G., and Huang M. (2004) pH-dependence of pesticide adsorption by wheat-residue-derived black carbon. *Langmuir*, 20 (16) 6736-6741.
43. CH G. (1960) Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurements of specific surface areas of solids. *J. Chem. Soc.*, 786: 3973-3993.
44. Madsen L., and Blokhuis A. M. (1994) Adsorption of Benzoic Acid on α -Alumina and γ -Boehmite. *J. Colloid Interface Sci.*, 166 (1) 259-262.
45. Celis R., and Koskinen W. C. (1999) Characterization of pesticide desorption from soil by the isotopic exchange technique. *Soil Sci. Soc. Am. J.*, 63 (6) 1659-1666.
46. Minkina T. M., Pinskii D. L., Mandzheva S. S., Antonenko E. M., and Sushkova, S. N. (2011) Effect of the particle-size distribution on the adsorption of copper, lead, and zinc by Chernozemic soils of Rostov oblast. *Eurasian Soil Sci.*, 44: 1193-1200.
47. Draoui K., Denoyel R., Chgoura M., and Rouquerol J. (1999) Adsorption of paraquat on minerals: a thermodynamic study. *J. Therm. Anal. Calorim.*, 58 (3) 597-606.
48. Clausen L., and Fabricius I. (2001) Atrazine, isotoproturon, mecoprop, 2, 4-D, and bentazone adsorption onto iron oxides. *J. Environ. Qual.*, 30 (3) 858-869.
49. Freeze R. A.; Cherry J. A. (1979) *Groundwater*, 604 pp. Prentice-Hall, Englewood Cliffs, NJ.



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