Adsorption of Pesticides onto Clay Minerals

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Adsorption of pesticides onto natural clay mineral relies on the use of adsorbents with minimal treatment beyond their preparation to provide a narrow size distribution and homoionic form by exchanging the naturally occurring interlamellar cations (in the case of smectites) by some alkaline (Na^+ or K^+) or alkaline earth (Ca^{2+}or Mg^{2+}) cation. Additional modifications include organophilization, intercalation with metal polycations and pillaring. The adsorption capacity and strength of pesticides onto homoionic, organophilic and intercalated/pillared clay minerals depend on the chemical nature of the pesticide, surface area, and pore volume. Electrostatic interactions, hydrogen and coordinative bonds, surface complexations, and hydrophobic associations are the main interactions between pesticides and clay minerals.

montmorillonite vermiculite bentonite organoclays pesticides modified clay minerals

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1. Introduction

The so-called Green Revolution dramatically increased agricultural productivity from the middle of the twentieth century to the present [1]. However, this increase relied heavily on chemical fertilizers and a wide range of pesticides, especially herbicides. Consequently, herbicides' contamination of soils, groundwater, and surface water is a concern of prime importance due to the severe effects of these compounds on humans, animals, and the ecosystem's equilibrium [2][3][4][5][6].

Adsorption is among the most efficient technologies to prevent or remediate pollution from pesticides because it relies on low-cost materials such as biomaterials, aluminum, and iron oxides, or oxyhydroxides, zeolites, and clay minerals. Clay minerals exhibit properties such as high superficial area, high adsorption capacity, low cost, and ready availability that are valuable to the development of herbicide formulations with controlled releasing of active components [7][8], cleanup of contaminated soils, groundwater protection [9], and water treatment [10][11][12].

Clay minerals have gained interest because they are abundant in nature and are environmentally compatible. Montmorillonite (Mt), like other smectites, and vermiculite (Vt), have permanent negative charges generated by the isomorphic substitutions of Si^{4+} by Al^{3+} in the tetrahedral sheets and of Al^{3+} by Mg^{2+} in the octahedrons. Cations such as Na^+, Ca^{2+}, and Mg^{2+} in the interlayer keep the electroneutrality. These permanent negative charges interact with cationic herbicides such as paraquat and diquat [13]. Additionally, these interlayer cations are easily exchangeable, for instance, with organic quaternary ammonium salts to produce hydrophobic organoclays suitable for retaining neutral pesticides [14]. Aluminum, Fe 3+ , Cr 3 + , Ti 4+ , Zr 3+ exchange with the interlayer cations and form polynuclear cationic species under hydrolysis, increasing the affinity towards anionic species [15][16]. Alternatively, the suspension of polycations can be first prepared and then exchanged with the interlayer cation [2]. The exchange of the interlayer cation by a polynuclear hydroxyl metal cation is a modification process named intercalating. Calcinating the intercalated clay minerals produces oxide pillars between the layers, increasing the basal spacing d(001), the specific surface area, and the microporosity, enhancing their adsorption capacity and affinity towards a wide variety of organic molecules, including the pesticides [2][17][18][19].

Excellent reviews recently addressed the interactions between organic compounds and clay minerals, aiming to develop controlled released herbicide formulation and water purification [7][9][20]. A straightforward comparison of adsorbent efficiencies towards various compounds is possible only if parameters such a mass to volume ratio, kinetic, adsorption isotherms, and thermodynamic constants derived from adsorption experiments are presented.

2. Natural Homoionic Clay Minerals as Pesticide Adsorbents

Cation exchange, for instance, is the primary retention mechanism for cationic pesticides such as paraquat, diquat, and difenzoquat on natural and modified clays [13][21][22][23][24][25]. For instance, adsorption isotherms of terbutryn (basic), dicamba (anionic), and paraquat on natural and modified clays from Morocco revealed that the natural clay efficiently adsorbed paraquat from aqueous solutions (**Table 1**).

Table 1. Sorbent characterizations and sorption features of pesticides and metabolites onto natural clay minerals.

Clay Mineral	Characterization Techniques	Compounds	Adsorbent Concentration (g L^{-1})/Contact Time (h)	Kinetic Evaluation	Models for Equilibrium Data Treatment	Removal (%) or Adsorption Capacity (Higher Results)	Reference
Mt	CEC, SSA, XRD	AT, 2,4-D, paraquat, metsulfuron methyl, glyphosate	0–8.1/6	No	Langmuir	Paraquat: 457 μmol g^{-1}, Metsulfuron methyl: 56 μmol g^{-1}, 2,4-D: negligible	[26]
Bt, NSC	CEC, SSA, XRD, TG-DTA, organic carbon	Terbutryn, dicamba, paraquat	10/24	No	Langmuir, Freundlich	Paraquat: 100% (Bt), 47% (NSC), Dicamba: 30.6% (Bt), 15.2% (NSC),	[21]

Clay Mineral	Characterization Techniques	Compounds	Adsorbent Concentration (g L^{-1})/Contact Time (h)	Kinetic Evaluation	Models for Equilibrium Data Treatment	Removal (%) or Adsorption Capacity (Higher Results)	Reference
						Terbutryn: 11.3% (Bt), 8.29% (NSC)	
Bt	CEC, SSA, XRD, XRF, TGA, FTIR	Paraquat	2.0/24	No	Langmuir	111 mg g^{-1} (403 µmol g^{-1})	[22]
Mt	SEM, TGA, XRD, SSA, FTIR, elemental analysis, zeta potential	Paraquat	-/6	No	Langmuir	442 µmol g^{-1}	[24]
Bt, Sepiolite, Illite	CEC, SSA, XRD, TGA, organic carbon	Paraquat	2.0/24	No	Freundlich, Langmuir, Dubinin–Radushkevich	48 µmol g^{-1} (sepiolite), 212 µmol g^{-1} (illite), 165 µmol g^{-1} (Bt)	[27]
Mt	SEM, FTIR, SSA, pH_{zpc}	Ametryn	1.0/6	Yes	Freundlich, Langmuir, Temkin,	188.81 mg g^{-1} (831 µmol g^{-1})	[28]
Bt	CEC, XRD, XRF, SSA, FTIR	Decis (deltametrin)	20/4	Yes	Freundlich, Langmuir	36.39–36.74 mg g^{-1} (72.0–72.7 µmol g^{-1})	[29]
Mt, Vt	XRD, SSA, CEC, iron content	AT, DEA, DIA, HAT	10/24	No	Freundlich	AT, DIA, HAT: > 99.5% (Mt), DEA: 64-72% (Mt), HAT: > 90% (Vt), AT, DIA: ≈10% (Vt), DEA: negligible (Vt)	[2]

Clay Mineral	Characterization Techniques	Compounds	Adsorbent Concentration (g L^{-1})/Contact Time (h)	Kinetic Evaluation	Models for Equilibrium Data Treatment	Removal (%) or Adsorption Capacity (Higher Results)	Reference
Mt	pH_{zpc}, FTIR, Mössbauer, XRD, Na, K, Ca, Mg	Glyphosate	6.0/24	No	Freundlich, Langmuir, one/two-sites Sips	85.64 mg g^{-1} (507 µmol g^{-1}) at pH 7.0	[30]
Mt	XRD, XPS, SSA, CEC, SEM, chemical composition	Glyphosate	10/24	No	Langmuir	4.0 ± 0.2 µmol m^{-2} (2.7 × 10^3) µmol g^{-1} at pH 4.0	[31]

CEC: Cation Exchange Capacity, FTIR: Fourier Transform Infrared, pH_{zpc}: pH of zero point of charge, SSA: Specific Surface Area, SEM: Scanning Electron Microscopy, TGA: Thermogravimetric Analysis, TG-DTA: Thermogravimetric-Differential Thermal Analysis, XPS: X-ray Photoelectron Spectroscopy, XRD: X-ray Diffraction, XRF: X-ray Fluorescence, Bt: Bentonite, Mt: Montmorillonite, NSC: Non-swelling clay, Vt: Vermiculite, 2,4-D: 2,4-dichlorophenoxyacetic acid, AT: Atrazine, DEA: Deethylatrazine, DIA: Deisopropylatrazine, HAT: hydroxyatrazine.

3. Organophilic Clay Minerals

Exchange of the inorganic interlayer cations by cationic or zwitterionic surfactants keep apart the aluminosilicate layers, resulting in increased basal spacing and hydrophobicity, thus enhancing the affinity toward neutral organic compounds with poor water solubility or high K_{OW} values [14][32]. Examples of organic cations appear in **Figure 1**, and some relevant applications to removing pesticides from aqueous media are highlighted in **Table 2**. Since log K_{OW} is pH-dependent, proper pH control and reporting are mandatory in adsorption studies, especially for interpreting the adsorption behavior of ionizable pesticides. In their neutral forms, the magnitude of adsorption constants correlates with the K_{OW}. For instance, in organophilic kaolinite and bentonite, the distribution coefficient (K_d) values increased in the order atrazine (log K_{OW} = 2.61) < alachlor (log K_{OW} = 3.52) < trifluralin (log K_{OW} = 5.34) [33]. The size of the alkyl chain of organic cation and the amount incorporated into the clay gallery strongly affect the adsorbent’s hydrophobicity, enabling a fine-tuning in the treatment of the mineral phase to attend to the application needs.

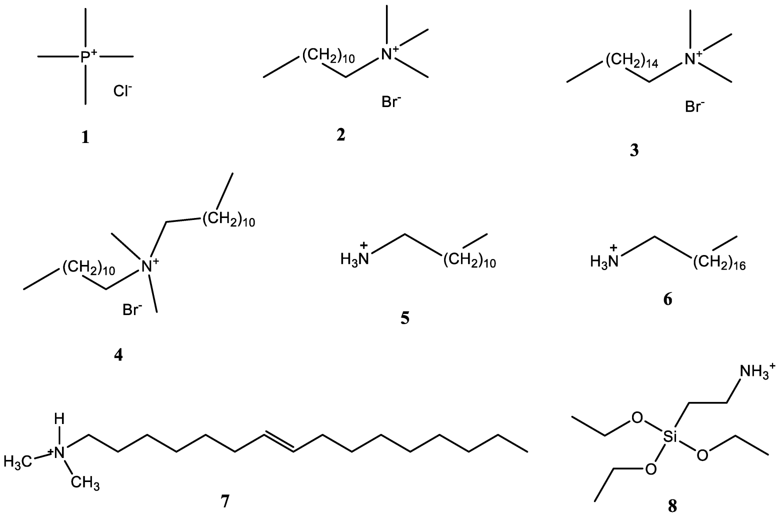

Figure 1. Some examples of organic cations used to produce organoclays: **1**—tetramethyl phosphonium chloride; **2**—dodecyltrimethylammonium bromide (DDTMA), **3**—hexadecyltrimethylammonium bromide (HDTMA), **4**—didodecyltrimethylammonium bromide (DDDTMA), **5**—dodecylamine (DDA), **6**—octadecyl amine (ODA), **7**—C_{14}–C_{18} unsaturated dimethyl dialkyl amine (DDA), **8**—Aminopropyltriethoxysilane (APTES).

Table 2. Sorbent characterizations and sorption features of pesticides and metabolites onto organically modified clay minerals.

Clay Mineral	Characterization of the Adsorbents	Compounds	Adsorbent Concentration (g L^{-1})/Contact Time (h)	Kinetic Evaluation	Models for Equilibrium Data Treatment	Removal (%) or Adsorption Capacities (Higher Results)	Reference
Commercial organophilic Bt	SEM-EDX, SSA, TG-DSC, XRF, FTIR	AT, ametryn, 2,4-D, diuron	5.0/24	Yes	Langmuir, Freundlich, Temkin	AT: 10.5, ametryn: 111, diuron: 202, 2,4-D: 29 µmol g^{-1}	[20]
Bt and NSC modified with ODTMA, TMA, OTMA	CEC, XRD, SSA, TG-DTA, Organic carbon	Terbutryn, dicamba, paraquat	10/24	No	Langmuir, Freundlich	Paraquat: 100% (TMA-Bt), 47% (TMA-NSC), Dicamba: 76.6%, (ODTMA-Bt), 35.5% (ODTMA-NSC), Terbutryn: 95.4% (ODTMA-Bt), 86.5%	[21]

Clay Mineral	Characterization of the Adsorbents	Compounds	Adsorbent Concentration (g L^{-1})/Contact Time (h)	Kinetic Evaluation	Models for Equilibrium Data Treatment	Removal (%) or Adsorption Capacities (Higher Results)	Reference
						(ODTMA-NSC)	
Mt-Alginate	SEM, TGA, XRD, SSA, FTIR, Zeta Potential, elemental, analysis	Paraquat	-/6	No	Langmuir	278 μmol g^{-1}	[24]
Bt, Sepiolite and Illite modified with DDA and NA	CEC, SSA, XRD, TGA, organic carbon	Paraquat	2.0/24	No	Freundlich, Langmuir, Dubinin–Radushkevich	95 μmol g^{-1} (Illite-DDA), 223 μmol g^{-1} (Illite-NA)	[27]
Kt-TMA, Bt-TMA	CEC, SSA, total organic carbon, elemental analysis	AT, alachlor, trifluralin	25/548	No	Freundlich	AT: 69.8% (Bt-TMA), Alachlor: 63.0% (Kt-TMA), Trifluralin: 65.0% (Kt-TMA)	[33]
Vt-HDTMA	XRD, SSA, iron content, elemental analysis	Fulvic Acid	10/24	No	-	74 and 98%	[34]
Mt-DDTMA, Mt-DDDMA, Mt-HDTMA	XRD, XPS, SSA, FTIR, TGA	AT, imazaquin	2.5 and 5.0/12	Yes	Freundlich, Langmuir,	Imazaquin: 35.3 μmol g^{-1} (Mt-DDDMA), AT: 12.1 μmol g^{-1} (Mt-HDTMA)	[35]
Mt-DDDMA	SEM, SSA, FTIR, XRF, XRD,	Fenitrothion	0.4/0.25	No	Freundlich, Langmuir	68.5 ± 1.2 mg g^{-1} (247 ± 4 μmol g^{-1})	[36]
Mt-ODA, Mt-DMDA, Mt-ODAAPS	FTIR, XRD, SEM-EDX	chlorpyriphos, *p*,*p*′-DDT *p*,*p*′-DDE, endosulfan sulphate, α-β-endosulfan,	10/8	Yes	Freundlich	(In μmol g^{-1}) *p*,*p*′-DDT: 1.47, *p*,*p*′-DDE: 1.19, Chlorpyriphos: 1.0, α-	[37]

Clay Mineral	Characterization of the Adsorbents	Compounds	Adsorbent Concentration (g L^{-1})/Contact Time (h)	Kinetic Evaluation	Models for Equilibrium Data Treatment	Removal (%) or Adsorption Capacities (Higher Results)	Reference
	[39]	alachlor, metolachlor, fipronil [41]	[40]			endosulfan: 0.84, β-endosulfan: 0.698, endosulfan sulphate: 0.61, fipronil: 0.62, alachlor: 0.70, metolachlor: 0.67	
Mt-carboxy methyl cellulose-DMDA	XRD, SEM-EDX, FTIR	AT, imidacloprid, thiamethoxam	10/4	No	Freundlich, Langmuir [2][44]	Imidacloprid: 8.82, [41][42][43] thiamethoxam: 5.71, AT: 6.63 µmol g^{-1} [45]	[38]

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the [OH]:[Al^{3+}] ratio, the [Al^{3+}] to clay mineral proportion and the aging temperature have a marked influence on the materials' stability and efficiency [46]. Not only Al^{3+} has been employed in the pillarization, but also other cations, such as Fe^{3+} [2][17][43][45][47][48][49][50][51], Ti^{4+} [47][52][53], Zr^{4+} [44][54], Co^{2+}, Ni^{2+} and Cu^{2+} [55], and Cu^{2+} [56]. These works describe the preparation, characterization, and applications for the adsorption or degradation of different organic compounds since they can support catalysts for photodegradation. Excellent reviews addressed the theory and the preparation procedures [39][46] as well as the removal of organic pollutants from wastewater [39]. The intercalation and pillarization processes produced adsorbent materials for different organic pollutants [2][41][44][56][57][58][59][60] and catalysts or photocatalysts for pollutants degradation/mineralization [40][43][45][53][61]. Among the main applications, the use as adsorbents for pesticides, aiming for water treatment or the preparation of controlled release formulations, deserve highlighting.

TG-DSC: Thermogravimetric-Differential Scanning Calorimetry, Kt: kaolinite, NSC: Non-swelling clay, DDA: dodecylammonium, DDTMA: dodecyltrimethylammonium, (DDDMA) didodecyldimethylammonium, DMDA: dimethyl-dialkylamine, HDTMA: hexadecyltrimethylammonium, NA: nonylammonium, ODA: octadecylamine, ODAAPS: octadecylamine and aminopropyltriethoxysilane, ODTMA: octadecyltrimethylammonium, OTMA: octyltrimethylammonium, TMA: tetramethylammonium. All other abbreviations according to the footnote of **Table 2**.

Table 3. Sorbent characterizations and sorption features of pesticides and metabolites onto intercalated or pillared clay minerals.

Modified Clay Mineral	Characterization of the Adsorbents	Compounds	Adsorbent Concentration (g L^{-1})/Contact Time (h)	Kinetic Evaluations	Model for Equilibrium Data Treatment	Removal (%) or Adsorption Capacity (Higher Results)	Reference
Pillared Mt-Fe	XRD, SSA	AT	10/24	No	Freundlich	62.8-99.1%	[17]
Intercalated Mt-Fe, Vt-Fe	XRD, SSA, CEC, iron content	AT, DEA, DIA, HAT	10/24	No	Freundlich	AT, DEA, DIA, HAT: >94% (Mt-Fe), AT: 3375% (Fe-Vt)	[2]

Modified Clay Mineral	Characterization of the Adsorbents	Compounds	Adsorbent Concentration (g L^{-1})/Contact Time (h)	Kinetic Evaluations	Model for Equilibrium Data Treatment	Removal (%) or Adsorption Capacity (Higher Results)	Reference
Pillared Bt-Al_{13}	XRD, CEC, chemical composition	Thiabendazole	0.6–2.5/24	No	Freundlich, Langmuir	141 µmol g^{-1} (aged 12 h at 60 °C) 318 µmol g^{-1} (aged 12 h at 25 °C)	[41]
Intercalated and pillared Bt-Al_{13}, Bt-Zr	XRD, CEC, SSA, Chemical composition	AT, 3-CA, 3-CP	20/overnight	No	Freundlich, Langmuir	AT: 92–100%, 67.1 µmol g^{-1} (Bt-Al) and 117.6 µmol g^{-1} (Bt-Zr) 3-CA: 14–100%, 3-CP: 10–30%	[44]
Intercalated Mt-Al_{13}, Mt-Fe, Mt-Ti, modified with CTAB	XRD, SSA, DTA, TGA, CEC, FTIR, surface acidity, Zeta-potential	Diuron, DCPMU, DCPU, DCA	0.05–0.5/24	No	Freundlich	Diuron: 15.7, DCPMU: 14.0, DCPU: 6.79, DCA: 6.65 µmol g^{-1}-measured at pH 3.1 and 0.5 g L^{-1} dispersion	[47]
Pillared Mt-Fe	XRD, TG-DTA, SSA, SEM, FTIR, elemental analysis, Mössbauer, Zeta-potential	Picloram	16/48	No	Freundlich, Langmuir	380 µmol g^{-1} at pH 3.0	[49]
Pillared Mt-Fe-Al_{13} modified	FTIR, XRD, XRF, SSA	Imazaquin	1.6/24	No	-	≈65 µmol g^{-1}	[50]

5. Concluding Remarks

Modified Clay Mineral	Characterization of the Adsorbents	Compounds	Adsorbent Concentration (g L^{-1})/Contact Time (h)	Kinetic Evaluations	Model for Equilibrium Data Treatment	Removal (%) or Adsorption Capacity (Higher Results)	Reference
with cyclodextrins							
Pillared Mt-Fe-Al_{13} modified with cyclodextrins	XRD, SSA, FTIR, SEM-EDX	Picloram	1.6/24	No	Freundlich, Langmuir	380 µmol g^{-1}	[51]
Pillared Bt-Al_{30}	SEM, SSA, XRD	heptachlor epoxide, dieldrin, endrin	1.0/5	Yes	Freundlich, Langmuir	Heptachlor epoxide: 0.62, Dieldrin: 0.63, Endrin: 0.62 µmol g^{-1}	[62]

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eviations ally, the experimental conditions should emulate as much as possible those found in the environment. Thus, the influence of ionic strength, pH, temperature, and natural organic matter, among others, on the adsorption parameters should be evaluated for each new clay mineral-based adsorbent proposed.

3-CA: 3-chloroaniline, 3-CP: 3-chlorophenol, DCPMU: 3-(3,4-Dichlorophenyl)-1-methylurea, DCPU: 1-(3,4-Dichlorophenyl) urea DCA: 2,4-Dichloroaniline. All other abbreviations according to the footnote/title of **Table 2**, **Table 3**.

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