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Feasibility of montmorillonite-assisted adsorption process for the effective treatment of organo-pesticides

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ABSTRACT

Over the years, the emergence of pesticides practice has prevailed to be the most intricate environmental turmoil amongst the scientific community. Specifically, pesticides constitute an accumulative, persistent and detrimental impact towards the survival of flora, fauna and environmental matrix. This has inspired a developing research with a variety of treatment technologies. Adsorption is recognized as the most efficient and promising approach, due to the ease of operation, simplicity of design, insensitivity to the toxic substances and superior capability for removing a broad range of pollutants. Its diverse applications, however, are retarded by the high cost of adsorbents and difficulties associated with regeneration. Montmorillonite and its derivatives, a unique group of under-utilized clay-based minerals has been proposed to be a suitable candidate for the treatment of contaminated wastewater. It plays a key role as the natural scavenger of pesticides, due to the abundantly availability, large specific surface area and high adsorptive and ion exchange properties. This paper describes the origin, physical, chemical and physicochemical properties of natural montmorillonite. The preparation procedure, reusability, commercial product and economical evaluation are highlighted. The specific classification, environmental and health implication of organo-pesticide are discussed. The revolution of montmorillonite-assisted adsorption process for the remediation of organo-pesticide was summarized. Additionally, the characterizations, surface chemistry and mechanism investigation are outlined.

Keywords: Adsorption; Clay; Modification; Montmorillonite; Pesticide

1. Introduction

In 1950, the world population was reported at 2.5 billion, whereas in 2000, the number has risen to 6.1 billion. By 2050, the growth rate is predicted to be further strengthened, implying a steady growth rate of 1.5 billion per year [1]. Simultaneously, a growing interest about the pesticide practice for pest resistance and hygienic control to fulfil the pressing food demand is increasing amongst the researchers and manufacturers [2]. The excessive use of pesticides is a matter of environmental concern because these

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Table 1
Technical advantages and disadvantages of the existing pesticides treatment technologies [1]

Treatment	Advantages	Disadvantages
Fenton process	Rapid decomposition of organic and inorganic pesticides (High removal rates) Ability to remove a broad range of pesticides (biodegradable and nonbiodegradable) Ease of handling Low operational cost	Production of residual sludge Require large usage of chemical reagents Mismanagement could lead to accumulation of ion particles or free radicals
Biological treatment	Capable to treat a variety of pesticides that cannot be treated by chemical or membrane technologies	Require large surface areas for implantation of treatment and biomass separation units Hampered by the presence of bio-refractory organics (humic substance or surfactants) Limited suitability to treat stabilized pesticide (fewer biodegradables) due to the recalcitrant characteristics of its organic carbon Low digestion rates (days or weeks) Require suitable cultured condition and constantly fed bacteria
Advanced oxidation	Particularly useful for cleaning biologically toxic or nondegradable pesticides. Nonselective pathway allows treatment of multiple pesticides in a single step Accelerate pesticides removal via solar, UV–vis-rays or ultrasonic radiation	Deteriorated by potentiality of chlorine oxidation, resulting in the formation of chlorine or hypochlorite Poor economic acceptability for large-scaling processes Extra energy sources (solar, UV-vis-rays or ultrasonic) are involved
Membrane technologies	Operated without phase changes or chemical conditioning. Only low energy consumption (pressure) is needed	Subjected to the fouling effect by a wide spectrum of constituents (resulting in short lifetime of membranes and decrease of process productivity) Huge generation volume of concentrate (which is unusable and require further treatments)
Ion exchanged	Exhausted resins are regenerable. Low operational cost Low energy consumption	Different resins are fabricated to selectively remove preferable types of pesticides Improper to treat chlorinated pesticides The presence of micro-organisms can reduce the exchanged capacity (irreversibility) leading to a reduction in the treated water quality Disposal of the treated pesticides is usually a problem to the loaded waste treatment systems (after the regeneration step)

chemicals are mobile in soil and readily migrate into the water table to compromise the water quality and human health [3]. Additionally, a greater amount of the applied pesticides have not fully reached to their intended targets due to their degradation, volatilisation and leaching effects, which would likely to be found in the surface or ground water [4].

Over the years, a developing technology for water pollution control has accelerated a dramatic progress in the scientific community (Table 1) [1]. However, the selection of the treatment process is a complex task with considerations of the availability of space, reliability of equipment, secondary waste generation and high operating costs. Furthermore, their wide-scale applications are restricted due to the high substantial financial input, which has overridden the cost of waste management. Amongst all, adsorption is considered to be a better treatment technology due to the ease of operation, simplicity of design and wider capability to remove a broad range of pollutants [5]. Activated carbon is recognized as an effective adsorbent, mainly ascribed to its high surface area, pore structure, special surface reactivity and thermal stability [6,7]. Nevertheless, it is restricted by the cost of adsorbent and difficulties associated with regeneration [8]. Therefore, the suitability of low-cost and renewable adsorbents, particularly clay-based derivatives has drawn great attention for the remediation of toxic pollutants [9]. Of major interest, montmorillonite has been proposed to be a good candidate [10], evidence from the intercalation of water pollutants by the modification of *d*(0 0 1) reflection [11–16].

More importantly, physical, chemical and physiochemical modifications of the natural montmorillonite have permitted the adsorption of both ionic and nonionic forms of pesticide, to inspire wider water treatment applications. This paper attempts to describe the origin, distinct physicochemical properties and potential applications of natural montmorillonite. The present work is aimed at providing up-to-date information on the environmental implications of organo-pesticides, and the feasibility of montmorillonite for the effective remediation of organo-pesticides. The physical and chemical characterizations, surface chemistry and mechanism studies have been outlined to familiarize the knowledge deficiencies regarding organo-pesticides treatment via montmorillonite-assisted adsorption process.

2. Montmorillonite: the origin, physical, chemical and physicochemical properties

Since the ancient Egyptians times, montmorillonite has been well known for its healing properties. It was firstly found in 1847 by Montmorillon in the Vienne prefecture of France, 50 years before the discovery of

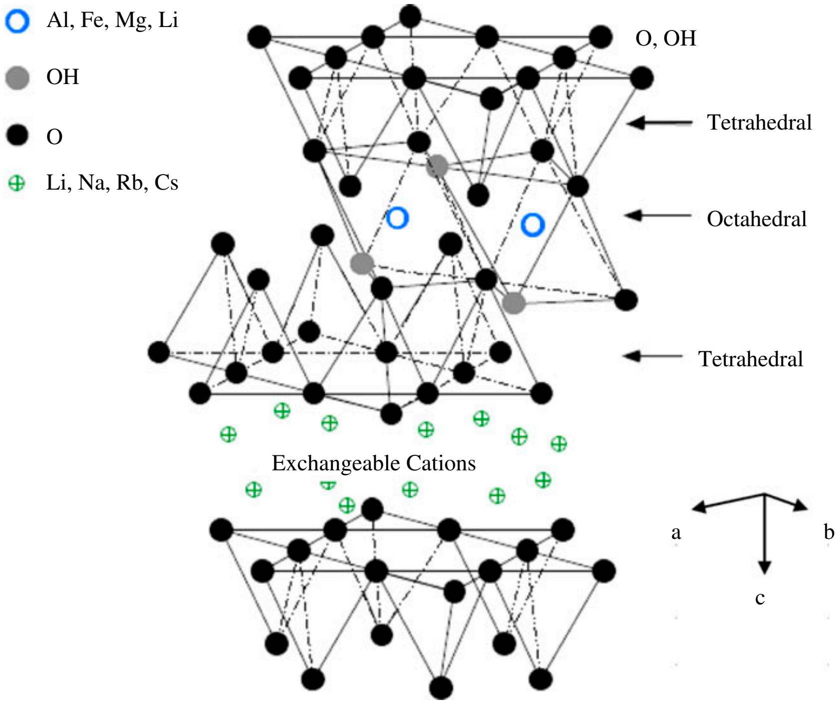


Fig. 1. The molecular structure of montmorillonite [18].

bentonite in the USA [17]. Montmorillonite is a type of smectites, the most famous 2:1 type layer-lattice clay minerals. The structural feature of montmorillonite, (Fig. 1) was earlier proposed by Marshall [18]. It is composed of units made up of two silica tetrahedral sheets with a central lumina octahedral sheet. The tetrahedral and octahedral sheets combine in such a way that the tips of the tetrahedral of each silica sheet form a common layer. The atoms of these layers, which are common to both sheets become oxygen instead of hydroxyl. It is thus referred to three-layered clay mineral with T-O-T layers, making up the structural unit. The silica-alumina-silica units are continuous in the *"a"* and *"b"* crystallographic directions, and are stacked one above the other in the *"c"* direction. In the stacking of these units, oxygen layers of each unit are adjacent between one another with the neighbouring units. This forms weak bonding and excellent cleavage between the units.

The outstanding feature of this clay structure is that water and other polar molecules could enter between the layers, and allow the lattice to expand in the *"c"* direction. The *"c"* axis of montmorillonite may vary with the presence of cations within the silicate layers, with a minimum value of 9.6 Å. In industry, montmorillonite is commonly the main constituent of bentonite. These clays show a 2:1 layer type structure, where an octahedral aluminate sheet is sandwiched between the two tetrahedral silicate layers. The layers are continuous in the length (*"c"* direction) and width directions (*"a"* and *"b"* directions), where the weak bonds between the layers would allow water and other molecules to intercalate into the interlamellar space with an expansion. In other words, the 2:1 layered silicate montmorillonite swells when it contacts with water and shrinks when it is dry.

The diversity of montmorillonite is derived primarily from its unique structure (Table 2) [19]. It appears in varieties of colours due to the presence of trace elements within the molecular structure. The moisture content of montmorillonite might deviate even up to 30-fold, due to the swelling effects of hydration. Montmorillonite forms multiple layers of crystalline structure in the natural environment, with approximately 0.9–1.2 nm of interlayer spacing. The thickness is about 1 nm, with an aspect ratio of 100–1,500 and surface area of 580–750 m^2/g. McEwan [20] and Grim [21] have provided an in-depth historical perspective in the determination and establishment of montmorillonite structure. The ideal structure (½ unit cell) of montmorillonite is:

$$(\mathrm{Al}_{2-x}\mathrm{Mg}_x)(\mathrm{Si}_{4-y}\mathrm{Al}_y)\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{M}^+_{x+y}\cdot n\mathrm{H_2O} \tag{1}$$

Table 2
The properties of montmorillonite clay mineral [19]

Characteristics	Properties
Layer structure	2:1
Colour	Tan, olive green, grey or white
Cation substitution	Octahedral and tetrahedral substitutions
Layer charge	High (0.7–1.70 mol sites/kg)
Base exchange	High (80–150 cmol [p^+]/kg)
Morphology	Thin flakes and laths
Surface area	Very high (580–750 m^2/g)
Adsorption capacity	High
Viscosity	Very high

and the molecular formula of montmorillonite is proposed as:

$$(\mathrm{Si}_{7.8}\mathrm{Al}_{0.2})^{\mathrm{IV}}(\mathrm{Al}_{3.4}\mathrm{Mg}_{0.6})^{\mathrm{VI}}\mathrm{O}_{20}(\mathrm{OH})_4 \tag{2}$$

The theoretical composition of montmorillonite without the interlayer constituents is 66.7% of SiO_2, 28.3% of Al_2O_3 and 5% of H_2O. This empirical formula allows the substitution of Si^{4+} by Al^{3+} in the tetrahedral layer, and Al^{3+} by Mg^{2+} in the octahedral layer. The net layer charge of montmorillonite is calculated by:

$$\begin{aligned}&[7.8(+4)]+[0.2(+3)]+[3.4(+3)]+[0.6(+2)]+[20(-2)]\\&\quad+[4(-1)]\\&\quad=-0.8\ \text{charge/unit cell.}\end{aligned} \tag{3}$$

Montmorillonite is a clay mineral with substantial isomorphic substitution. The resulting negative net charge is balanced by exchangeable cations adsorbed between the unit layers and around their edges. The kinetic of cation exchange is fast, and cations such as Na^+ and Ca^+ would form outer-sphere surface complexes, which could be easily substituted by varying the cationic compositions. From the process, adsorbate ions are bounded to the clay surface by sharing one or several ligands (generally oxygen) as isolated complexes, and precipitation might occur if the system equilibrium is disturbed (solution pH or adsorbate concentration) [22]. Besides, the interlayer swelling phenomenon might occur when montmorillonite is exposed to water, and it depends mainly on the valences and atomic radii of the exchangeable cations. Al and Si atoms which exposed to the crystallite edges would be partially hydrolyzed to silanol (SiOH) and aluminol (AlOH) groups, and these unsaturated edge sites are more reactive than the saturated basal sites [23,24]. These properties have enabled the viable use of montmorillonite to react as scavengers for a variety of applications, including adsorbents, rheological control agents, paints, inks, polishes, chromatography, catalysis, fixation of pollutants, grease, cosmetics, personal care products and oil well driffling fluids [25,26].

3. Montmorillonite

3.1. Modification technique

Organophilization of montmorillonite (Table 3) [27–34] is the intercalation of organic molecules or insertion of a guest species within the interlayer space of 2:1 layered silicates. This intercalation is of paramount importance as it changes or modifies the particular characteristics (Table 4) [35] of layered silicates. It alters the surface chemistry of clay mineral through the ion exchange of organic cations and it increases the basal spacing between the clay layers. The fundamental principle of intercalation process is driven by the unique interactions between the organic or inorganic cations within the clay mineral including adsorption, ion exchange, binding of inorganic or organic anions (mainly at the edges), grafting of organic compounds, acid activation, pillaring by different types of poly-(hydroxo metal) cations, intraparticle and interparticle polymerization, dehydroxylation and calcination, delamination and reaggregation of smectites, lyophilisation and ultrasound or plasma treatment [36]. Of major interest, the most preferential modification techniques of montmorillonite are the cation exchange, solid state reaction, pillaring process and acid activation.

3.1.1. Cation exchange

Cation exchange is defined as the interlayer cations exchange of clay minerals by quarternary alkylammonium cations in the aqueous solution. During the reaction, the surfactant molecules are predominantly adsorbed in the interlayer spaces through cation exchange at low surfactant loading levels and as the loading increases, it is subjected to both cation exchange and hydrophobic binding [37,38]. This hydrophobic binding, the mutual attraction between the alkyl chains of surfactant molecules would be the dominant mechanism as the cation exchange capacity (CEC) has been exceeded, resulting in a higher positive charge on the clay particles. The list of names, common abbreviations and structures of some organic surfactants that has commonly used for the preparation of organo-montmorillonite for the environmental remediation of pesticides are shown in Table 5 [33,35,39–41]. Generally, these interactions could be structured into three different interactions, cation exchange, electrostatic attraction force, physisorption and translocation of surfactant molecules within the interlayer spaces [26].

3.1.2. Solid state reaction

The intercalation of organic molecules by solid-state reaction without the use of chemical solvents is an environmental friendly process. During the reaction, the intercalation of neutral compounds is not necessarily accompanied by cation movement between the silicate layers (outer-surface complex). The cation remain in contact with a silicate layer, the oxygen atoms which occupy the coordination sites of the cation [42]. Majority of the solid-state reactions are based on the ion–dipole interaction. Upon the interaction, organic molecules with polar groups are attached to the interlayer cations, and the negative part of the molecules would be attracted to the cations, and water molecules are displaced from the interlayer cations [43].

3.1.3. Pillaring

The pillaring process is generally presented as a way of increasing the accessibility of the clay layers, and it stabilizes “oxide” particles of nanometre dimension to prevent aggregation. The surface groups that are exposed to these ultradispersed “oxides” play a key role to enhance the promising adsorptive and catalytic properties of the pillared clays [44]. In pillared clays, the two-dimensional silicate layers of thickness of about 1 nm are kept apart by ceramic oxides with a dimension of nano- to subnano-metre sizes [45]. A pillared clay is distinguished from an ordinary intercalate by virtue of intracrystalline porosity made possible by the lateral separation of the intercalated guest molecules. They undergo calcination at a moderately high temperature of approximately 773 K to transform the polyoxocations to metal oxidic particles cross-linked to the clay lamellae, with the formation of a stable porous structure [46].

Clays pillared with metal oxides (Fig. 2) [47] are of great importance mainly due to their great thermal stability, high surface area and intrinsic catalytic activity. They are usually prepared by cations exchange in the interlayer region of swelling clays with bulky alkylammonium ions, polynuclear complex ions bearing

Table 3
Organophilization of montmorillonite [27–34]

Preparation procedure	Modification agents	Remarks	Pesticide application	Refs.
Pillared	$Fe(NO_3)_3 \cdot 9H_2O$ salt	1 M of pillaring solution Fe(III) was prepared by dissolution of $Fe(NO_3)_3 \cdot 9H_2O$ salt at room temperature with the vigorous stirring with a 2 M solution of KOH, until reaching a ratio of $OH^-/Fe = 2$. The pH was controlled to attain a value lower than 1.8 for 4 h. A deionized water dispersion of 1 wt.% of montmorillonite was mixed with the pillaring solution with a Fe/montmorillonite ratio of 60 mmol Fe/g montmorillonite. The mixture was allowed to react at room temperature for 12 h, and it was obtained by centrifugation, and washed by successive redispersions in deionized water followed by centrifugation until the conductivity value lower than 10 μS was attained. The product was air-dried, and heated at 300°C for 2 h	Picloram	[27]
Cation exchange	Hexadecyltrimethylammonium Phenyltrimethylammonium	10 g of Arizona montmorillonite, SAz-1 was treated with 100 mL of an ethanol–water solution containing alkylammonium (chloride salt) equal to the cation exchange capacity of 120 $cmol_c/kg$. The suspensions were shaken for 24 h, centrifuged, washed with distilled water and lyophilized	Hexazinone	[28]
Cation exchange	Cetyltrimethylammonium, (CTMA)	The CTMA-clay complex was prepared by the slow addition of 500 mL of 0.1 M aqueous solution of CTMA bromide to a 1,000 mL suspension (0.001 g/mL) of Na-montmorillonite. The prepared complex was rinsed with distilled water and ethanol to remove possible excess CTMA-Br, and dried at 60°C	Fenamiphos	[29]
Cation exchange (inorganic modification)	NaCl, KCl, $MgCl_2$, or $FeCl_3$	The original clays Wyoming montmorillonite (SWy-2) and Arizona montmorillonite (SAz-1) were saturated with Na^+, K^+, $Mg^{2+,}$ and Fe^{3+} by treating 10 g of clay with 100 mL of a 1 M solution of NaCl, KCl, $MgCl_2$, or $FeCl_3$, respectively. The resulting homoionic clays were washed with distilled water until it is Cl-free and then lyophilized	Hexazinone	[30]
Cation exchange (organic cation)	Octadecylammonium (ODA), dioctadecyldimethylammonium (DODDMA), phenyltrimethylammonium (PTMA), and hexadecyltrimethylammonium (HDTMA)	10 g of Wyoming montmorillonite (SWy-2) and Arizona montmorillonite (SAz-1) was treated with 100 mL of an ethanol/water (50:50) solution containing an amount of alkylammonium (chloride salt) equal to the CEC of the clay. The suspensions were shaken for 24 h, centrifuged, washed with distilled water until Cl-free, and then lyophilized	Hexazinone	[30]
Acid activation	Sulphuric acid, H_2SO_4	20 g of Na-montmorillonite was refluxed in 200 mL of 0.25 M H_2SO_4 for 3 h. The resulting acidic activated clay was centrifuged and washed several times until it was free of SO_4^{2-}, with the pH of the washing of 6.8. The sample was dried at 378 K in air until weight was constant	8-quinolinecarboxylic acid	[31]
Acid activation followed by cation exchange	Sulphuric acid and solid ammonium acetate salt	Montmorillonite (Org-H-M) was prepared by the addition of 5 mmol of solid ammonium acetate salt to 1 L of a 1% (w/v) aqueous dispersion of acid-activated montmorillonite under stirring for 24 h. The Org-H-M was separated by centrifugation (4 g, 30 min) and the sediments were washed three times with distilled water and dried for further used		

(*Continued*)

Table 3 (*Continued*)

Preparation procedure	Modification agents	Remarks	Pesticide application	Refs.
Pillared	Phenyltrimethylammonium bromide (PTMAB)	The pillaring solution was prepared by the slow mixing of 1.95 g PTMAB with 100 ml of deionized water. 10 g of Na momtmorillonite was dispersed in 490 mL of deionized water, and the suspension was stirred for 3–4 h with ageing for 12 h. The pillaring solution was added drop wise and the mixing process lasted for 2 h under stirring. The filtered product was dried at 80˚C in an oven, and sieved	Benzene hexachloride, dichlorodiphenyltrichloroethane, Aldrin and quintozene	[32]
Cation exchange	Tetradecyltrimethyl ammonium bromide (TTAB), dodecyltrimethylammonium bromide (DTAB) and Cetylpyridinium chloride (CPC)	The <2 μm clay fraction were obtained by wet sedimentation and subsequently saturated with Ca^{2+} cations by washing the clay repeatedly with $CaCl_2$ solution (0.1 mol/L). The HDTMA bromide was dissolved in warm distilled water and the clay suspensions containing 25 g of smectite was treated by adding HDTMA bromide solution (0.03 mol/L) in an amount just equal to the CEC of 900 $mmol_c$/kg. The mixtures were agitated overnight at room temperature and washed with distilled water repeatedly until it is free of bromide ions. These HDTMA organoclays were subsequently quick-frozen freeze-dried, and srored in bottles	Malathion and butachlor	[33]
Cation exchange	Hexadecyltrimethylammonium (HDTMA)	10 g of sodium-rich Wyoming montorillonite or calcium-rich Arizona montmorillonite was treated with 100 ml of an ethanol/water (50:50) solution containing an amount of alkylammonium (chloride salt) equal to the CEC of the mineral clay. The suspensions were shaken for 24 h, centrifuged, washed with distilled water and lyophilized	Aminocyclopyrachlor	[34]
	Hexadimethrine (Hexadim) Spermine (Sper)	The amount of organic cation (chloride or bromide salt) corresponding to 100% of CEC of sodium-rich Wyoming montorillonite (CEC = 764 mmol/kg) or calcium-rich Arizona montmorillonite (CEC = 1,200 mmol/kg) was dissolved in 50 mL of 1 mmol HNO_3 and added to 1 g of clay mineral. The suspensions were shaken for 24 h, centrifuged, washed and freeze-dried		
	Fe^{3+}	10 g of original clay mineral was treated with 100 mL of 1 mol $FeCl_3$ solution and the resulting clay was washed with distilled water until it is Cl-free		

Table 4
The impact of organo-modification on clay minerals [35]

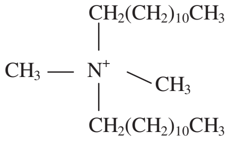
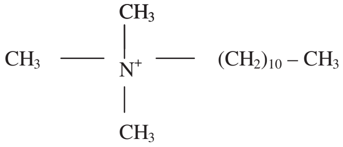
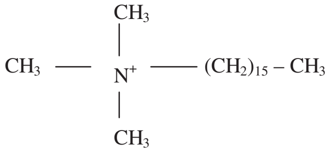
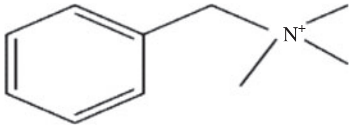
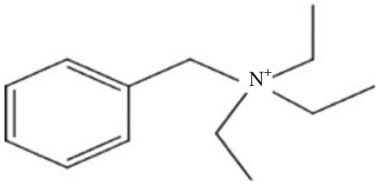
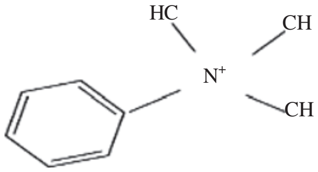
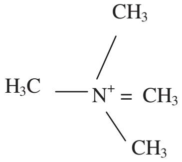
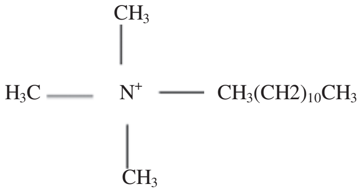
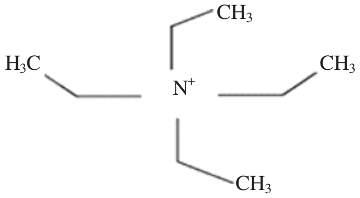
Effect	Description
Basal spacing	Basal spacings of different models corresponding to lateral monolayer, lateral bilayer, pseudotrilayer, paraffin-type monolayer and paraffin-type bilayer arrangements may coexist at the intermediate stages depending on the heterogeneity of charge on various layers. These arrangement models can be explained in terms of the CEC of montmorillonite. However, some authors have emphasized interlayer cation density (ξ) and alkyl chain length in the surfactant molecules as the responsible factors giving rise to various arrangement models
Morphological structure	At low surfactant concentrations, the intercalation of surfactant is usually random and the increase in surfactant packing density results in the regular stacking of surfactant–montmorillonite galleries
Surface area and pore structure	The smaller ions create large numbers of micropores as they are isolated from each other in the interlamellar space. Further, the coexistence of micropores and mesopores resulted in a larger surface fractal dimension, and the hydrated ions induced shrinkage of inter lamellar cavities. On the contrary, the larger cations produce a dense packing in the interlamellar cavity resulting in a sharp decrease in BET surface area and a sharp increase in average pore size. This was attributed to hydrophobic bonding by conglomeration of large alkyl groups associated with the presence of long-chained surfactants in the interlayers of the organoclay
Thermal properties	Na-montmorillonite shows two decomposition regions when it is subjected to the temperatures up to 1,000℃, with release of free (absorbed) water at 100 to 400℃, and dehydroxylation of the aluminosilicate lattice between 500 and 1,000℃. On the other hand, organically modified montmorillonite shows four distinct decomposition zones: (a) free water release below 200℃, (b) decomposition of organic substances between 200 and 500℃, (c) dehydroxylation from 500 to 800℃ and (d) release of organic carbon between 800 and 1,000℃ in some yet unknown way
Coloidal stability	The adsorbent is most effective as long as it exists in a suspended condition. But the adsorption of amphiphilic substances would gradually change the surface properties from hydrophilic to hydrophobic, thereby accelerating the coagulation rate in the aqueous medium. This has been attributed to an increase in surfactant loadings in the organoclays, leading to a decrease in their colloidal stability and faster growth of the aggregates
Surface charge behaviour	The charge properties of organoclays depend mostly on the organic surfactant loadings. At low-surfactant concentrations, the surface charge of organotreated clay particles remains negative in the entire pH range, irrespective of the pH-dependent charge inversion when the concentration exceeds the mineral CEC. The surface charge becomes positive with an increased value at low pH values, while for pH > ~6–7, the particle charge gets reduced
Sorption properties	The intercalation not only changes them from hydrophilic to hydrophobic, but also greatly increases the basal spacing of the interlayers. The increased basal spacing together with the hydrophobic nature of the surface makes organoclays effective materials for immobilizing organic and inorganic contaminants in soil and water environments

inorganic ligands (hydroxo ligand and chloro ligand), or/and large metal complex ions bearing organic ligands. These newly intercalated species are capable to prevent the collapse of the interlayer spaces and prop open the layers as pillars, with the formation of interlayer space. During the heating stage, inorganic species would be converted to metal oxide clusters, generating a highly stable minerals with a well developed porosity.

3.1.4. Acid activation

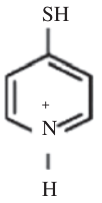
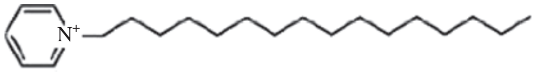
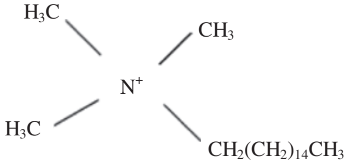
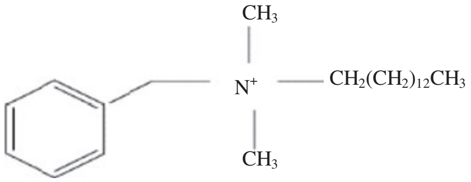
Acid treatment of clay minerals at high concentration and temperature is an important control over mineral weathering and genesis [48]. It can replace exchangeable cations with H^+ ions, with Al^{3+} and other cations escaping out of its tetrahedral and octahedral sites, leaving the SiO_4 groups largely in intacted [49]. This modification would increase the specific surface area and acidity [50]. Along with the elimination of mineral impurities and partial dissolution of external layers, the degree of changes would depend on the clay minerals and the overall chemical composition, type of cations which present between the interlayer space, acid concentration and type, the process, temperature and treatment time [51]. Amongst all, the depopulation and treatment time of

Table 5
List of surfactants specifically applied for the modification of montmorillonite [33,35,39–41]

Name	Abbreviation	Structure
Didodecyldimethylammonium	$DODMA^+$	
Octadecyltrimethylamminium	$ODTMA^+$	 $CH_3 - \overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{N^+}} - (CH_2)_{10} - CH_3$
Hexadecyltrimethylammonium	$HDTMA^+$	 $CH_3 - \overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{N^+}} - (CH_2)_{15} - CH_3$
Benzyltrimethylammonium	$BTMA^+$	
Benzyltriethylammonium	$BTEA^+$	
Trimethylphenylammonium	$TMPA^+$	
Tetramethylammonium	TMA^+	
Dodecyltrimethylammonium	$DTMA^+$	 $H_3C - \overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{N^+}} - CH_3(CH2)_{10}CH_3$
Tetraethylammonium	TEA^+	

(*Continued*)

Table 5 (*Continued*)

Name	Abbreviation	Structure
4-Mercaptopyridinium	4-MP	
Cetylpyridinium	CP	
Hexadecylpyridinium	HDPY	
Cetyltrimethylammonium	$CTMA^+$	
Benzyldimethyltetradecylammonium	$BDTDA^+$	

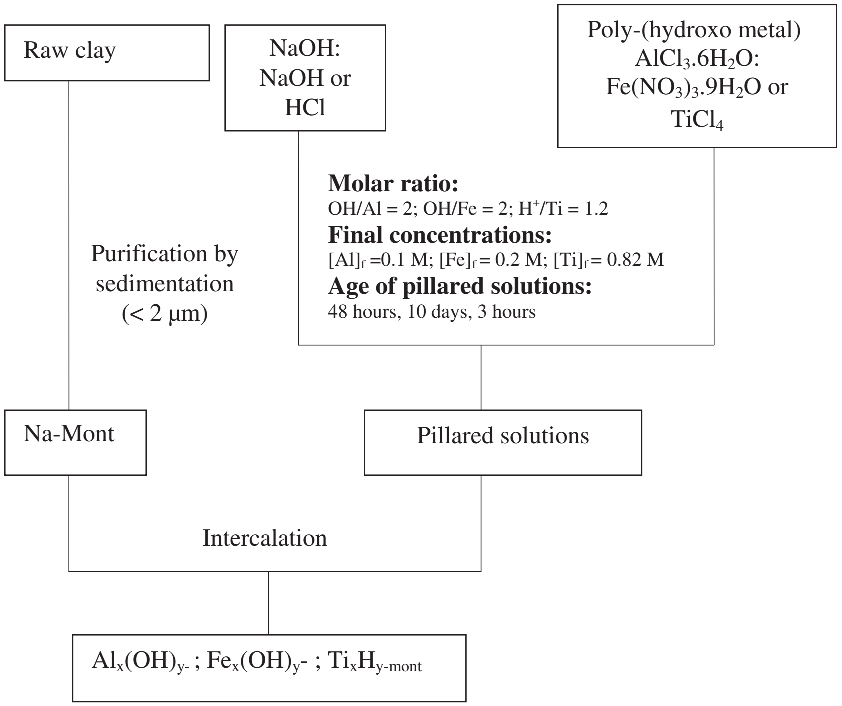


Fig. 2. Typical procedure for preparation of pillaring clay [47].

the octahedral layer of montmorillonite has been reported as the leading factor to determine the levels of structural decomposition and individual resistance to acid attack of the clay minerals [52].

3.2. Regenerative potential

A primary concern of clay adsorbents is the reusability after they serve their purposes. During the sorption process, these organoclays actually remove or relocalize the water contaminants from the liquid phase into the solid phase, but do not essentially decompose them into the harmless forms. Once the maximum adsorption capacity had been achieved, it would lose its holding property. An economically viable and environmentally sustainable option is adsorption of contaminants subsequent by degradation on these organoclay surface. The total replacement of the spent adsorbent requires the additional costs of infrastructure, time, labour and technical support. There is also a risk of redispersal of contaminants from spent organoclay at the dumping site which would be governed by the hydrological condition: pH, redox condition, temperature, ionic strength and dissolved organic matter [35].

The regenerative process could be achieved by imparting thermal treatment, chemical desorption or biological activity to the exhausted clay minerals. The major practical disadvantages of thermal treatment are the decomposition of nontarget surfactant molecules at the elevated temperature range, and the generation of secondary pollutants. Whereas, biological treatment involves the microbial degradation of water pollutants to allow the reusability of the spent organo-montmorillonite [53]. The micro-organisms that thrive well on the clay surface are capable of mineralizing of the adsorbted contaminants completely into CO_2 and water as the carbon and energy source.

The concept of regeneration could also be achieved by the alteration of chemical properties such as pesticide formulations. Most pesticide formulations in the current use deliver the bulk of the active ingredient in an immediately available form, and readily to be released to the natural environment [54]. These formulations may result in great pesticide losses after the application, before these acting molecules have diffused into the soil aggregates and reached to the adsorption sites [55]. Table 6 [28,30,56–58] summarized previous researches on the design of new pesticide formulations in relation to the montmorillonite clay adsorbents. Increased attention has been directed to the reduction of pesticide transport through the

Table 6
Previous researches on the design of new pesticide formulation in relation to the clay adsorbents [28,30,56–58]

Montmorillonite	Modifier	Pesticide	Remarks	Refs.
Arizona montmorillonite	Hexadecyltrimethylammonium	Hexazinone	The initial release ranged from 25 to 90% and 50 to 90% for the final release of herbicide present in the formulations	[28]
	Phenyltrimethylammonium		Released the herbicide instantaneously	
Arizona montmorillonite	Fe^{3+} Hexadecyltrimethylammonium	Hexazinone	Displayed slow release properties in water and soil/water suspensions, reduced herbicide leaching in soil columns and maintained herbicidal activity	[30]
Montmorillonite	Polydiallyldimethylammonium-chloride (PDADMAC)	Imazapyr	25–40% released of imazapyr	[56]
Montmorillonite	Wheat gluten	Ethofumesate	The release mechanism would be rather governed by pesticide/montmorillonite interactions than montmorillonite/polymer matrix in the case of a hydrophobic pesticide such as ethofumesate, and a hydrophilic matrix such as wheat gluten	[57]
Wyoming montmorillonite	Fe^{3+} Octadecylammonium, ODA Hexadecyltrimethylammonium, HDTMA	Picloram	Yielded a slow release of 65, 10 and 9% of the complex Fe^{3+}, ODA and HDTMA, respectively	[58]

development controlled-release (CR) formulations, in which only part of the active ingredient is in an immediately available form. In these formulations, the bulk of the herbicide is trapped or adsorbed in an inert support, and it would be gradually released over time [58]. The unique beneficial effects related to the use of CR formulations include reduction in the amount of chemicals required for pest control, lower the risk of environmental pollution, savings in manpower and energy requirement, higher safety precautions for the pesticide applicators and a general decrease in the nontargeted effects [59].

3.3. Commercial montmorillonite

Today, a wide range of organoclays has been applied for the wide scale production of polymer nanocomposite. Table 7 [60] outline the major applications and typical examples of some commercial organoclay, while Table 8 [61–79] provides a list of organo-montmorillonite that has been commonly used for the commercial production of polymer nanocomposites. In particular, Southern Clay and Nanocor are the major producers for polymer nanocomposites, while Laviosa Chemica Mineraria, Southern Clay Products and Elementis Specialities are the main producers of quaternary ammonium salts derived organoclays and montmorillonite. Nanofil®, organoclay based on the intercalation of quaternary ammonium salts in montmorillonite is the primary product of Süd-Chemie. Another new Nanofil® generation, Nanofil® SE 3000 and Nanofil® SE 3010 are currently under the patenting process. These new grades of clays would enable safe handling and highly recommended for all common polymer systems without the requirement of compatibilizers.

Similarly, another popular montmorillonite product, modified with primary amine and quaternary ammonium salts containing silane has been offered by Nanocor. One of them is Imperm®, a family of superior gas barrier resins useful in extending the package shelf life. It is prepared by the dispersion of the organoclay into the polyamide (meta-xylylene adipamide, tradename MXD6) to form a nanocomposite with significantly enhanced barrier, but remain the similar characteristics to the polyamide itself. NanoMax™, a series of nanomer-polyolefin resin masterbatches, which contain 40–60 wt.% of Nanomer®, is the first organoclay that features a convenient pellet form. These masterbatches are produced through melt compounding based on the patented technologies (US 6,462,122 and 6,632,868).

3.4. Economical evaluation

Presently, there are three principle types of adsorbents that have been developed as efficient adsorbents for the environmental remediation, namely natural organic sorbents, natural inorganic sorbents and synthetic sorbents [35]. The first group includes peat moss, straw, sawdust, milkweed floss, cotton fibres and a series of cellulose-based products. The major advantages of these group of adsorbents is the low reusability and difficulties associated with regeneration. Synthetic adsorbents are featured by the highly manufacturing cost and low biodegradability, while the natural inorganic adsorbents are deteriorated by the high hydrophilicity, which imparts the low adsorbing capability to the water pollutants. This inherent drawback has been overcome by the organic modification to enhance the efficiency, durability and reusability. Table 9 [60] summarizes an economical evaluation of common adsorbents applied for the effective treatment of water contaminants. Amongst all, clays appear to be the most cost-effective adsorbents due to the wide availability from readily natural sources with high suitability and tremendous potential to be developed for wide scale applications.

4. Organo-pesticide: classification, environmental and human impact

Pesticide is featured by its unique chemical properties. It is developed to mimic or substitute for specific

Table 7
The major applications and typical examples of some commercial organoclays [60]

Supplier	Region	Commercial lines	Application
Southern Clay	USA	Cloisite®	Polymer nanocomposites
		Garamite®	Polymer resin (epoxies, polyesters and vinyl esters)
		Claytone®	Rheology modifiers
Nanocor	USA	Nanomer®	Polymer nanocomposites
Süd-Chemie	Germany	Nanofil®	Polymer nanocomposites
Laviosa Chemica Mineraria	Italy	Dellite®	Polymer nanocomposites
Bentec (from Laviosa group)	Italy	Viscogel®	Rheology modifiers
Elementis Specialities	–	Bentone® Nanoclays	Polymer nanocomposites

Table 8
List of organo-montmorillonite that has been commonly applied for the commercial production of polymer nanocomposites [61–79]

Type/commercial lines	Modification agent	Route of preparation	Application	Refs.
Sodium montmorillonite Kunipia F (Kunimine Industries)	Octadecylammonium chloride	Cation exchange in aqueous solution	Polypropylene nanocomposite	[61]
Sodium montmorillonite cloisite (Southern Clay)	Octadecylamine	Ion–dipole technique (solid state reaction)	Polypropylene nanocomposite	[62]
Sodium montmorillonite Cloisite (Southern Clay)	Crown ethers, cryptand	Ion exchange	Polystyrene nanocomposite	[63]
Montmorillonite K-10 (Aldrich Co.)	Dodecylammonium chloride	Cation exchange in aqueous solution	Epoxy nanocomposites	[64]
Sodium montmorillonite (Tolsa S.A., Spain)	Octadecylammonium chloride	Cation exchange in aqueous solution	Natural rubber nanocomposite	[65]
Sodium montmorillonite (Wyoming—USA)	Dioctadecyl dimethylammonium chloride	Cation exchange	Epoxy nanocomposite	[66]
Sodium montmorillonite Kunipia F (CO-OP Chemical Co., Japan)	Hexadecylamine salt	Cation exchange in aqueous solution	PLA nanocomposite	[67]
Montmorillonite (Keyan Company)	Hexadecyl trimethylammonium Bromide, Octadecylammonium bromide	(1) Cation exchange (2 salts) (2) Solubilization of hexadecyl trimethylammonium in alcohol, wetting of montmorillonite in alcohol and mixing of the them into a blender at high speed and drying. (3) Mixing of hexadecyl trimethylammonium bromide and montmorillonite in a mortar (solid state reaction)	Polypropylene nanocomposite	[68]
Sodium montmorillonite Cloisite (Southern Clay)	Alkyl-imidazolium salts	Cation exchange in water/ethanol (50/50, v/v)	Study of thermal stability to apply in polymeric nanocomposites	[69]
Sodium montmorillonite Kunipia F (Kunimine Industries Co.)	Octadecylamine	Cation exchange	Polypropylene nanocomposites	[70]
Sodium montmorillonite (Nanocor)	Maleic anhydride (MA), Pentaerythritol, Decacylammonium chloride, Dodecylammonium			[71]

(*Continued*)

Table 8 (*Continued*)

Type/commercial lines	Modification agent	Route of preparation	Application	Refs.
	chloride, Tetradecylammonium chloride, Octadecylammonium chloride	(1) MA—dissolution and stirring in anhydrous acetone (2) Pentaerythritol—aqueous solution (proceeding similar to cation exchange) (3) Ammonium salts—cation exchange in aqueous solution	Polyethylene terephthalate nanocomposite	
Calcium montmorillonite (Nanjing Tangshan Clay Factory, China)	Octadecylammonium chloride	Cation exchange in aqueous solution	Polyamide-6 nanocomposite	[72]
Sodium montmorillonite Kunipia F (Kunimine Industries)	Octadecylammonium chloride Bis (2-hydroxyethyl)laurylammonium chloride, diethyl [2-(methacryloyoxyl) ethyl]ammonium chloride bis(2-hydroxyethyl)lauryl (vinylbenzyl) ammonium chloride	Cation exchange in aqueous solution	Vinylester resin nanocomposite	[73]
Sodium montmorillonite (Industrial Tech. Res. Institute)	(4-carboxybutyl)-triphenylphosphonium bromide	Cation exchange	Polyimide nanocomposite	[74]
Sodium montmorillonite (Kunimine Industries Co.)	Octadecylammonium chloride Maleic anhydride	Cation exchange in aqueous solution+co-intercalation of maleic anydride	Polypropylene nanocomposite	[75,76]
Sodium montmorillonite (Zhangjiakou Qinghe Chemical Factory, Hebei China)	Octadecyl trimethylammonium chloride	Cation exchange in aqueous solution	Polypropylene nanocomposite	[77]
Sodium montmorillonite (Wyoming—USA)	Cetyl pyridinium chloride monohydrate	Cation exchange	Polypropylene nanocomposite	[78]
Sodium montmorillonite Cloisite (Southern Clay)	Ammonium salt based on triethylaminte and copolymer of vinylbenzyl chloride and lauryl acrylate	Dispersion of montmorillonite in a solution of THF	Polyethylene and polypropylene nanocomposites	[79]

Table 9
Economical evaluation of clays and other adsorbents [60]

Types of adsorbents	Price (US \$/kg)$^{-1}$
Clay	0.04–0.12
Commercial activated carbon	20.00–22.00
Spheroidal cellulose	1.07
Lignin	0.06
Chitosan	15.43
Zeolite	0.03–15.43
Clinoptilolite	0.03–0.12
Chabazite	0.03–0.12
Peat	0.023
Coconut shell charcoal (CSC)	0.34
Nitric acid oxidized CSC	0.34
Nitric acid oxidized CAC	1.37
Sphagnum moss peat	0.02
Filtrasorb-400	20–22
Perlite	1.50

molecules to the targeted pests [80]. More precisely, it is a mixture of chemical substances, selectively applied against a specific group of pests or microbes in the agricultural field. The classification of pesticide is categorized according to its targeted organisms or to the physiological chemical classes (Fig. 3) [80]. Pesticide is bio-accumulative, toxic, persistent in the ecosystems and continue to be detected in the surface water even after 20 years of its usage [81–83].

The long-term presence and carcinogenic effect of pesticides in the natural environment have attracted critical concern amongst the environmental practitioners. Pesticides have been reported to interfere with the transmission of light through water, retard photosynthetic activities and inhibit the growth of biota terrestrial ecosystems (synthesis of caratenoid, aromatic and branched chain amino acids). Deeper studies have found its potential to damage the quality of the irrigation channels and impede the propagation of algae, resulting in food chains and ecological imbalance [84,85]. These impacts are getting more transparent when the transportation of pesticides is not restricted or controlled, which in turn to be degraded into more toxic substances or nonstable radicals.

In particular, inappropriate application of pesticides has been linked with adverse effects on the nontargeted organisms (reduction of beneficial species

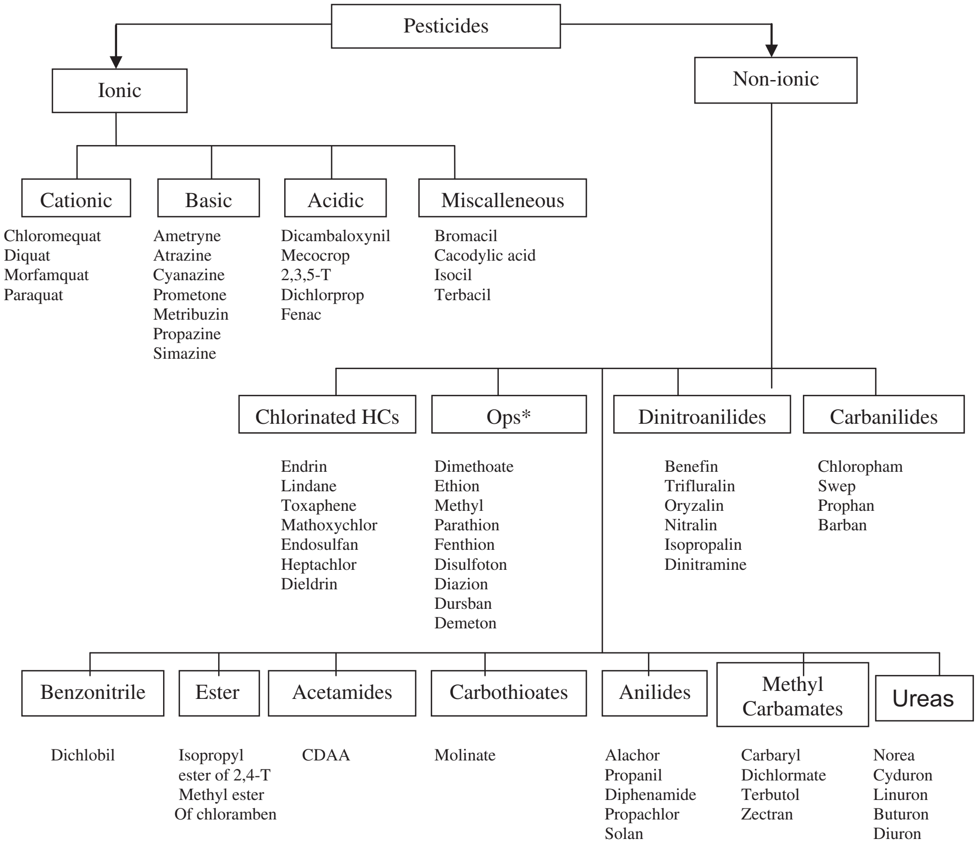


Fig. 3. The classification of pesticides on the basis of the significant physicochenmical properties and behaviour in water and soil [80].

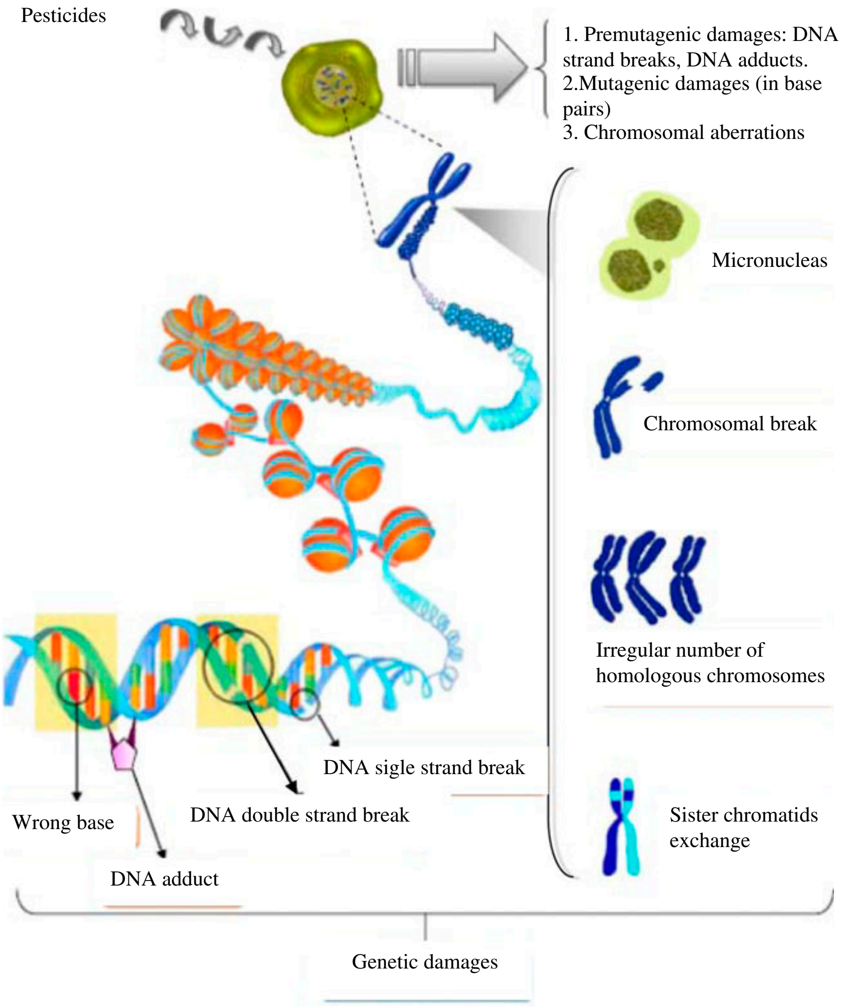


Fig. 4. A schematic model for the induction of genetic damages by the exposure to pesticides [87].

population), water contamination from the mobile pesticides, air pollution from the volatile pesticides, injury on nontargeted plants from herbicide drift and injury to rotational crops from volatile herbicides residues due to improper time, rates and frequencies of usage or unfavourable environmental conditions for the practice of pesticides applications [86]. In addition to the environmental implications, long-term exposure to organo-pesticides might induce genetic damages (Fig. 4) [87] and epigenetic modifications (Fig. 5) [87], to cause reproductive and developmental disorders, cancer, diabetes, neurodegenerative (parkinson or alzheimer), respiratory (asthma), cardiovascular (atherosclerosis) and renal (kidney failure) diseases [87]. To govern the long-term effects of pesticides towards the natural environment, flora, fauna and human body, the emission (Fig. 6) [80] to the natural environment, specifically governed by the rain water wash off, degradation, sorption, desorption, leaching, free runoff or plant uptake should be restricted and a possible eco-friendly solution is montmorillonite-assisted adsorption process, which has proven the capability to retain water pollutant within its unique molecular structure.

5. Revolution of montmorillonite-assisted adsorption process for the remediation of organo-pesticide

Since 1920s, the introduction of X-ray diffraction [88] has inspired a growing exploration on montmorillonite and its derivatives, as documented by Smith in 1934 [40]. Despite its wide popularity for the treatment of effluent waste streams, the affinity towards hydrophobic organic pollutants is deteriorated by the hydrophilic aluminosilicate structure on the natural surface. This has stimulated a developing research to

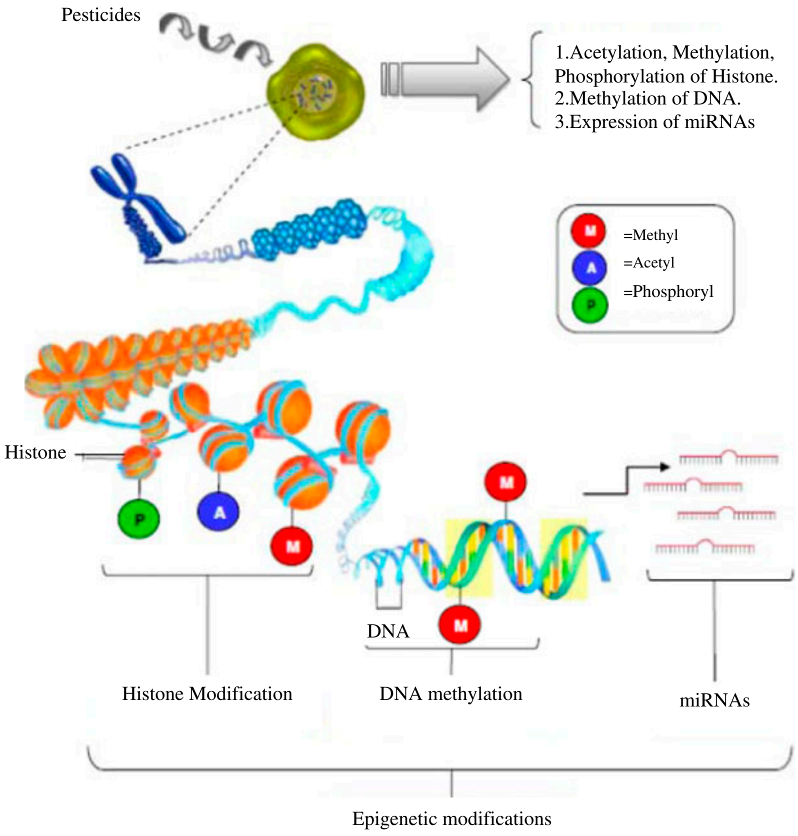


Fig. 5. A schematic model for the induction of epigenetic modification by the exposure to pesticides [87].

integrate inorganic cations for surface modifications or functionalizations to enhance the adsorption capabilities towards hydrophobic pollutants [89,90]. According to Brixie and Boyd [91], organoclays showed strong immobilization effects towards nonionic organic chemicals with low water solubility. Therefore, organoclays have been proposed to be a controlled-release formulation to reduce the leaching of pesticides into the ground water tables [92]. In a study conducted by Rodríguez-Cruz et al. [93] the viable role of octadecyltrimethylammonium bromide (ODTMA) modified organoclays (montmorillonite, kaolinite and palygorskite) to control the immobilization of organic pesticides (linuron, atrazine and metalaxyl) into the water body has been measured. Result indicated that the mobility of the pesticides was reduced drastically by the treatment of ODTMA modified organoclay, with the complete removal of linuron and lower leaching kinetics for the less hydrophobic pesticides (atrazine and metalaxyl). In the study, the retardation factors, R for the leaching process increased in the range of 3.59–69.5 (linuron), 1.5–2.08 (atrazine) and 1–1.32 (metalaxyl) as the organic barriers were intercalated into the natural soil, and ODTMA modification has detected its feasibility to enhance the hydrophobicity and affinity for the organic pesticides.

Meanwhile, the affinities of hexazinone onto hexadecyltrimethylammonium exchanged Arizona montmorillonite (HDTMA-SA) and phenyltrimethylammonium-exchanged Arizona montmorillonite (PTMA-SA) have been examined by Celis et al. [28]. HDTMA-SA showed a lower water released property to retard the leaching effect with the initial and final release, ranged between 25–90%, and 50–90%, respectively. The greater affinity for hexazinone was attributed to the availability of interlamellar space within the organo-montmorillonite. Accordingly, modifications with long-alkyl chain cationic surfactant via ion exchange process could affect the molecular structure of natural montmorillonite, which in turn improve the adsorption mechanism of the nonionic organic compounds.

The efficiency of three organo-modified montmorillonites [modified with octadecyllamine(ODA-M), dimethyl- diaalkylamine (DMDA-M), and octadecylamine and aminopropyltriethyoxysilane (ODAAPS-M)] to remove organic pollutants from the pesticide

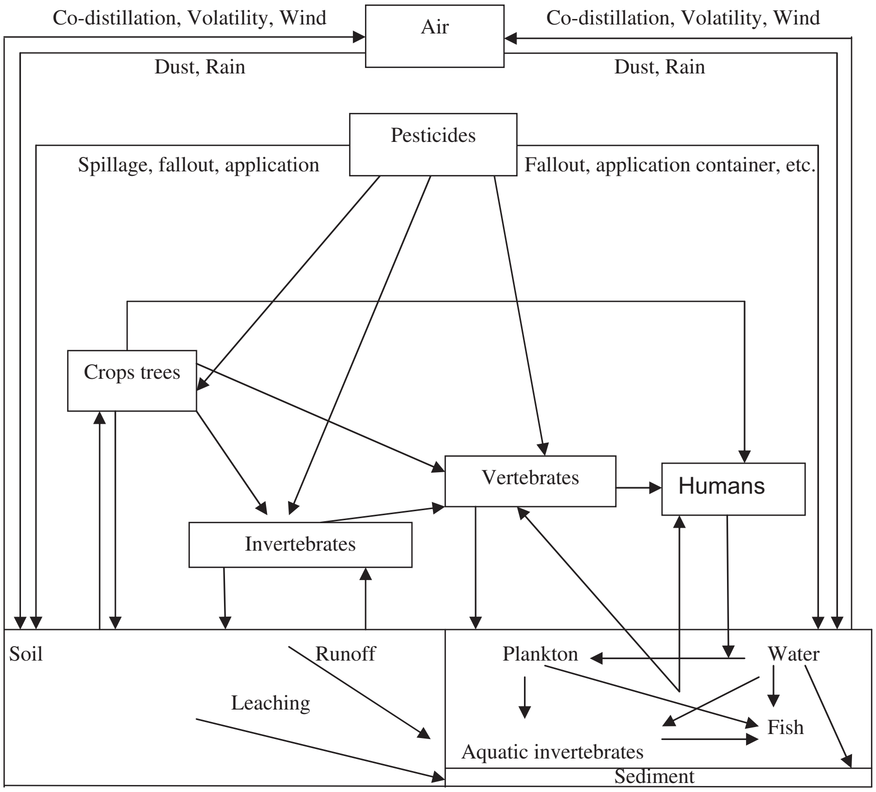


Fig. 6. The transportation of pesticides in the natural environment [80].

mixtures, namely alachlor, metalachlor, chlorpyriphos, fibronil, α-endosulfan, β-endosulfan, *p,p´*-DDE and endosulfan sulphate have been investigated by Saha et al. [94]. The performance for the adsorptive removal of mixed pesticides followed the order ODAAPS-M > DMDA-M > ODA-M, which the tendency of these pesticides to be removed was in according with the sequence *p,p´*-DDT (0.42–0.52 mg/g) > *p,p´*-DDE (0.33–0.38 mg/g) > chlorpyriphos (0.29–0.35 mg/g) > α-endosulfan (0.32–0.34 mg/g) > β-endosulfan (0.26–0.28 mg/g) > endosulfan sulphate (0.24–0.26 mg/g) > fibronil (0.20–0.27 mg/g) > alachlor (0.18–0.19 mg/g) > metalachlor (0.17–0.19 mg/g). The findings concluded that the adsorption performance was affected not only by the physicochemical behaviour of the individual pesticides, but also by the modifications of organo-montmorillonite. The short-chain organo-montmorillonite is sensitive to the competition of accompanying compounds and background interface, while long-chain organo-montmorillonite is less governed by the competitive effect. In particular, the cationic surfactants or quaternary ammonium salts with long hydrocarbon chains are of special high interest due to the reactivity provided by the surfactant to specific hydrophobic compounds on the organoclays [95–97].

Additionally, modification with cationic gemini surfactants are more efficient to expand the interlayer space within the montmorillonite [98], and the arrangements could be proposed on the *d*(0 0 1) basal spacing. The thickness of the montmorillonite was 9.6 Å, while the height of alkyl chain lying parallel to the clay layer ranged between 4 to 4.5 Å. The basal spacing of montmorillonite intercalated with 5.6 mol/g of surfactant was 15.7 and 16.7 Å, suggesting the coexistence of monolayer and bilayer arrangement of the intercalated surfactants. Carrizosa et al. [99] have further investigated the adsorption–desorption of dicamba, a highly mobile and leachable herbicides onto two smectites (SAz and SWy) treated with different amounts of alkylammonium cations, octadecyl-(C18), hexadecyltrimethy (HDT)- and dioctadecyldimethy (DOD)-ammonium. The adsorption capacity of dicamba increased parallel with the changes of surface charges of alkylammonium and bulky organic cations, mainly attributed to the hydrophobic and polar interactions responsible for the adsorption of dicamba onto organoclays.

Table 10
Recent researches on the pesticides treatment via montmorillonite-assisted adsorption process [12,31,33,41,100–106]

Montmorillonite	Modifications	Pesticide	Adsorption capacity (mg/g)	Ref.
Montmorillonite	–	Carbaryl	3.70	[12]
Sodium montmorillonite, (Na-M)	–	8-quinolinecarboxylic acid (8-QCA)	65.4	[31]
Acidic montmorillonite, (H-M)	–		67.6	
Organo-acidic montmorillonite, (Org-H-M)	–		75.9	
Montmorillonite	–	Malathion	7.95	[33]
	Tetradecyltrimethyl ammonium bromide (TTAB)		12.60	
	Dodecyltrimethylammonium bromide (DTAB)			
	Cetylpyridinium chloride (CPC)		10.50	
	–			
	Tetradecyltrimethyl ammonium bromide, (TTA-M)		14.20	
		Butachlor	8.88	
			16.30	
Ca-Arizona Montmorillonite, SAz-1	–	Aminocyclopyrachlor	–	[41]
	Hexadecyltrimethylammonium		53%	
	Hexadimethrine		36%	
	Spermine		3.0%	
Na-Wyoming montmorillonite, SWy-2	–		–	
	Hexadecyltrimethylammonium		2.2%	
	Hexadimethrine		1.8%	
	Spermine		6.1%	
	Fe^{3+}		86%	
Na^+ montmorillonite	Methyl, tallow, bis-2-hydroxylethyl (MT2EtOH)	Chlorpyrifos	6.63	
		Penconazole	6.33	
	Dimethyl, dihydrogenatedtallow (2M2HT)	Chlorpyrifos	8.32	[100]
		Penconazole	3.47	
Montmorillonite	–	Aldrin	14.26	[101]
Organo-montmorillonite	Stearyl-dimethybenzylammonium cations (SDBA)	Fenitrothion	8.32×10^{-2}	[102]
Na^+-Montmorillonite	–	Phosmet	1.040×10^{-3}	[103]
Ca^+-Montmorillonite	–	Phosmet	1.648×10^{-3}	
K^+-Montmorillonite	–	Phosdrin	1.882×10^{-3}	
Na^+-Montmorillonite	–	Phosdrin	3.548×10^{-3}	
Ca^+-Montmorillonite	–	Phosdrin	2.150×10^{-3}	
Montmorillonite	–	2,4-D	0.90 μg/kg	[104]
	–	Dimethoate	0.96 μg/kg	
Montmorillonite	Hexadecyltrimethyammonium	2,4-D	158.73	[105]
	Dioctadecyldimethylammonium	2,4-D	161.29	
Montmorillonite	Dodecyltrimethylammonium, DDTMA	Imazaquin	0.2369	[106]

(*Continued*)

Table 10 (*Continued*)

Montmorillonite	Modifications	Pesticide	Adsorption capacity (mg/g)	Ref.
	Hexadecyltrimethyammonium, HDTMA	Imazaquin	5.7143	
	Didodecyldimethylammonium, DDDMA	Imazaquin	10.977	
	Dodecyltrimethylammonium, DDTMA	Atrazine	0.3388	
	Hexadecyltrimethyammonium, HDTMA	Atrazine	0.0846	
	Didodecyldimethylammonium, DDDMA	Atrazine	1.1101	

Table 10 summarizes the novel implications of montmorillonite and its derivatives for the adsorptive treatment of organo-pesticides [12,31,33,41,100–106]. Chen et al. [12] have examined the adsorption of carbaryl onto montmorillonite, kaolinite and goethite. Result revealed that the adsorption capacity of carbaryl onto montmorillonite, kaolinite and goethite was 3.7, 1.6, and 2.1 mg/g, respectively, and the extend of adsorption depended primarily on the concentration of adsorbate, pH, temperature, adsorbent dosage, chemical modification [107], salinity content [108], the intercalation of organic cations [94], concentration of organic compounds [109], polarisation of the exchangeable cations [110] and specific interactions between the clay minerals [111].

Cabrera et al. [41] have investigated the ability of two montmorillonite (Ca-Arizona montmorillonite, SAz-1 and Na-Wyoming montmorillonite, SWy-2) and their derivatives [modified with inorganic Fe^{3+}, soil constituents (ferrihydrite, and humic acid) and organic cations (hexadecyltrimethylammonium (HDTMA), hexadimethrine and spermine) for the adsorptive treatment of aminocyclopyrachlor. Introduction of inorganic cations, Hexadim and HDTMA into SAz-1 improved the adsorptive removal of aminocyclopyrachlor to 36 and 53%, indicating the influence of chain length and surface charge density to the sorption behaviour. Meanwhile, the greater affinity (86%) of SWy-2 by Fe^{3+} substitution was due to the protonation of N ortho ring and formation of carboxyl group.

Celis et al. [112] have further synthesized montmorillonite-chitosan bio-nanocomposite by modification of wyoming montmorillonite, (SWy-2) and sodium-saturated SWy-2 for the adsorption of cylopyralid from the aqueous solution. Result revealed that the removal of clopyralid increased from 15 to 55% by increasing the amount of chitosan from 7 to 43.6%. In contrast, the effect of solution pH on the adsorption process was almost negligible, indicating the absence of polarization effect [113]. On the other hand, Ozcan et al. [101] in an attempt to remove selected organochlorine pesticides, reported that the adsorption behaviour of aldrin onto montmorillonite was strongly affected by solution pH, with complete removal at pH 1. The adsorption mechanism could be explained by the formation of complexes, resulting from the interaction between oxygen atoms on the montmorillonite surface with the water molecule in the acidic medium. The formation of positive charge is shown as follows:

$$-MO + H - OH \xleftrightarrow{H^{+}} M - OH_2^{+} + OH^{-} \qquad (4)$$

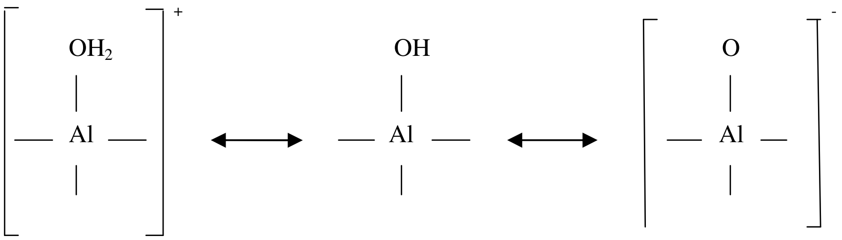


Fig. 7. The resonance structure of the edges charge in montmorillonite [21].

Moreover, the electronegativity of chlorine atoms (aldrin) could create negative inductive effects with the residual particle negative charge (*d*−), and positive charge (*d*+) of the *p*-cloud aromatic rings. Consequently, the adsorption of aldrin may occur via electrostatic force between the negative dipole charge of chlorine with the $M–OH_2^+$ groups of montmorillonite surface, and negative dipole charges of chlorine with the exchangeable surface cations. Increasing the ionic strength showed a higher adsorption capability, mainly ascribed to the changes in double layer thickness [114], which in turn lower the hydrophobicity and enhance the charge–dipole interactions. Specifically, the adsorption process is governed by the permanent negative charge from isomorphous substitution within the montmorillonite structure, and reversible surface edge around the silica-alumina units (Fig. 7) [21]. Therefore, at $pH < PZC_e$, the $-OH_2^+$ groups around the surface would be neutralized, with a lower charge-dipole interaction and adsorption capacity.

In addition, the adsorption of the hydrophobic molecules could be affected by the salinity of the aqueous solutions. El-Nahhal and Lagaly [108] have examined the effect of salts on the adsorption of linuron onto the chemical modified montmorillonite. The affinity of linuron increased from 0.418 to 4.828 mg/g by substitution of Ca^{2+} ions with hexadecylpyridium and hexadecyl tributylphosphonium. However, the adsorption capacity of linuron decreased from 4.83 to 0.70 mg/g, by increasing the salt concentration from 0 to 80 g/L, following the order $NaClO_4 \approx KClO_4 < NaCl < NaBr < RbCl < CsCl$. For a deeper explanation, the alkyl chains of the alkylammonium montmorillonite form a perfect van der Waals interactions bonded to the surface oxygen atoms of silicate layer [115], and this interaction is mutually strong when these alkyl chains are contacted directly with the silicate surface. In other words, the interlayer adsorption (intercalation) of water or any neutral solvents onto the montmorillonite surface requires the transformation of alkyl chains from parallel into the paraffin-type arrangement. Consequently, due to the clustering of water molecules within the alkyl chains [116], the alkyl chain arrangement would be disturbed by the penetration of salts into the interlayer space to retard the adsorption of hydrophobic molecules.

Whereas, montmorillonite with low organic carbon content demonstrated a lower capability to restrict the mobility of pesticides. As a result, organic amendments have been proposed to be a good enrichment to further improve the structural stability and adsorption performance of the natural montmorillonite. In a study conducted by Torrets and Jayasundera [117], the adsorption of three nonionic pesticides, alachor, metalachor and linuron onto pure sodium montmorillonite, SWy-1 and organic carbon (OC)-coated SWy-1 were evaluated. The alachlor uptake decreased proportional to the degree of surface coating of OC, suggesting that the surface adsorption sites have been partially blocked by the OC-coated complexes [118]. The interaction was driven by the hydrogen bonding between the carbonyl group of alachlor herbicides, carboxyl and hydroxyl functionalities on the organic surfaces, and charge transfer between the aromatic nuclei [119].

On the contrary, OC-coated Na-montmorillonite showed a different behaviour, and the Freundlich sorption coefficient (K_F) for metalachor increased from 1.63×10^{-3} to 9.78×10^{-3} $(dm^3/g)^n$. The findings illustrated the higher affinity of organic matrices to metalachlor, mainly governed by the hydrophobic interactions. A similar phenomenon has been reported by Hengpraprom et al. [120] in an investigation to examine the adsorption performance of α-endosulfan onto montmorillonite in the presence of humic acid and natural organic matters. Result revealed that the adsorption capacity of α-endosulfan onto montmorillonite was approximately 1.7 times greater than the montmorillonite-only system, indicating the important role of the humic substances to further enhance the adsorption capability of montmorillonite, to influent the availability of pesticides in the natural ecosystems.

6. Characterization, surface chemistry and mechanism study

The structural properties of montmorillonite are highly depended on the molecular structure, chemical properties, physicochemical behaviour and the modification of organic surfactants. The essential analysis and characterizations offer an additional insight view on the natural properties, strategic design, preparational conditions or modifications for different applications [39,121]. Fig. 8 illustrates the morphological studies of the natural montmorillonite and its intercalated derivatives (sodium montmorillonite, MMT-Na and Wyoming montmorillonite, SWy-2) [27,98,112]. Typically, the textural structure of the natural occurring montmorillonite, could be found as equalized, covered by small and well distributed particles (Fig. 8(a) and (b)). In contrast, surface modifications led to the formation of agglomerations as shown in Fig. 8(c) and (d). Marco-Brown et al. [27,122] have proposed montmorillonite as a clay mineral with face-to-edges contacted between the particles, with randomized orientation, and no formation of domains (group of particles) or clusters (group of domains that act as a unit) along the surface (Fig. 8(e)). The modification by the pillaring process identified the pore spaces and particles with the range size between 200 and 400 nm, and co-aggregated iron oxide to disperse randomly at different directions (Fig. 8(f)). These structural modifications remain unchanged even after the adsorption of pesticides [98].

Fig. 9 displays Fourier transformed infra-red (FTIR) spectrum of the acidic montmorillonite (H-M), organo acidic montmorillonite (Org-H-M), 8-quinolinecarboxylic (8-QCA) and the herbicide 8-QCA intercalated Org-H-M [31]. The broad bands at 3,625, 3,380, 1,008, 798 and 515 cm^{-1} are corresponded to the (OH), (Si–O), (Al(Mg–O–)) and (Si–O–(Mg)Al) derivatives [123–125]. The intensities at 3,380 and 1,631 cm^{-1} identified the presence of water content, suggesting hydration and interlayer inorganic cations exchange process. The spectrum of Org-H-M showed two N-H bonding vibrations at 1,443 and 2,920–2,840 cm^{-1}, where the spectrum of Org-H-M/8-QCA demonstrated the peak between 1,615 and 1,659 cm^{-1}, probably assigned to stretching of C=N bonds.

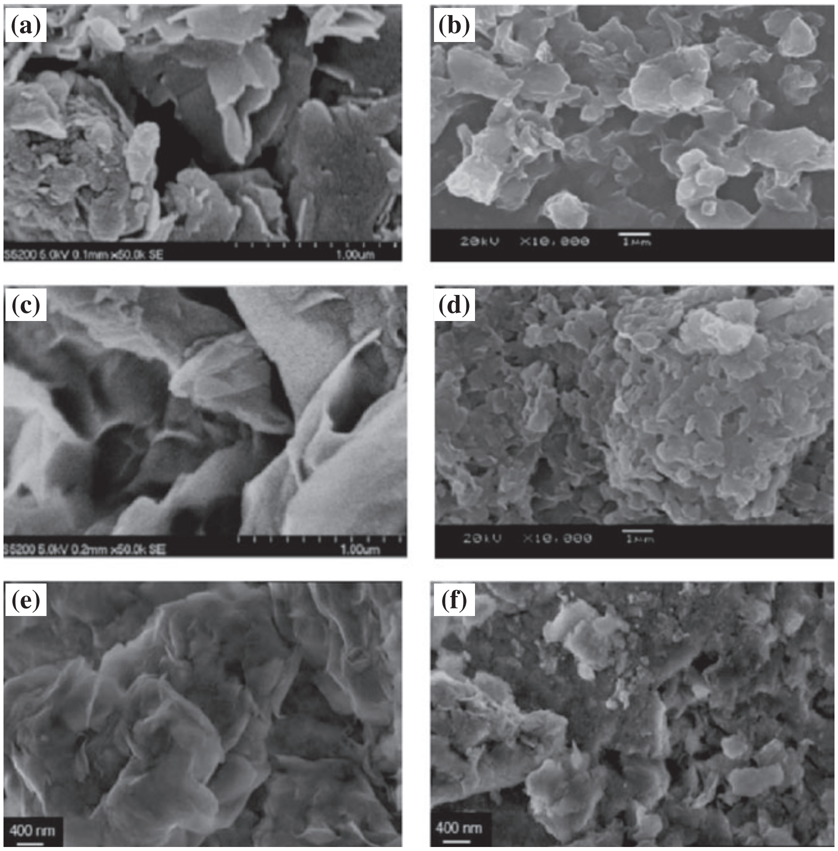


Fig. 8. Scanning electron micrographs (SEM) of (a) Wyoming montmorillonite, (b) sodium montmorillonite, (c) Wyoming montmorillonite chitosan bionanocomposite, (d) sodium montmorillonite intercalated with gemini surfactant, (e) natural montmorillonite and (f) iron oxide pillared montmorillonite [98,112,122].

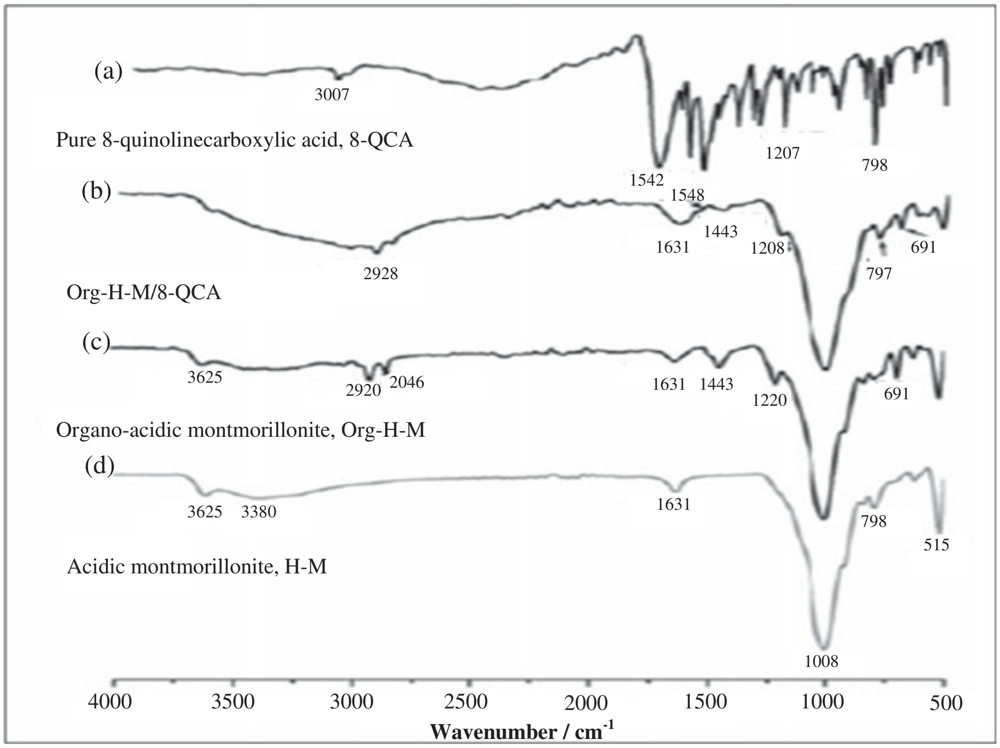


Fig. 9. FTIR spectrum of the (a) pure 8-QCA herbicide, (b) Org-H-M/8-QCA (c) organo-acidic montmorillonite and (d) acidic-montmorillonite [31].

Amarasinghe et al. [126] have further explained the changes of H–O–H vibration in the interlayer of Na-montmorillonite, and the effect of organic fluids with different dielectric constants on the clay structure. Regardless of the polarity of the solvent, the shift in the interlayer of montmorillonite occurred almost immediately after the mixing process. The FTIR result concluded that montmorillonite-organic fluid interaction was nonbonded in general. The alteration of Si–O stretching and H–O–H vibration with low and nonpolar solvents tended to return close to the original positions and intensities quickly. During the interaction of high polar solvents, the alteration of Si–O stretching was intense, permanent, and did not return to the original intensities during the experiment.

Fig. 10 shows transmission electron microscopy (TEM) images of the sodium-montmorillonite (Fig. 10(a)), and acidic montmorillonite (Fig. 10(b)) [31]. Although both samples illustrated a lamilar structure, clear difference could be observed in the morphological surfaces with respect to organo-acidic montmorillonite (Fig. 10(c)). Specifically, acidic-montmorillonite showed a largely exfoliated morphology, indicating a combination mesoporous and microporous structure. The hysteresis loop with slit-shaped pores, narrow necks and wide bodies could be associated with capillary condensation of liquid nitrogen in mesopores. The hysteresis phenomenon was more prominent after acidic activation due to the structural deformation, with the transformation of laminar to a delaminated structure [127]. The results were supported by enhancement of specific surface area from 32 to 140 m^2/g and 161 m^2/g for acidic montmorillonite and organo-acidic montmorillonite [31].

Table 11 summarizes the enhancement of basal spacing with the modification of intercalating agents [30,31,33,40,41,117,128,129]. The interlayer arrangement of organic molecules within the montmorillonite texture was extensively investigated by Lagaly and Weiss [130]. They reported that the short chain alkyl ammonium ions lay flat on the montmorillonite surface as monolayer or bilayers. However, the critical chain length, longer chain alkyl ammonium ions were presumed to acquire pseudo-trimolecular structure to transform into the paraffin arrangement [131]. In the paraffin-type structures, the angles between the chains axes and silicate layer increase by increasing the surface charge. Therefore, the increase in basal spacing with the chain length of cation varies with the charge density [130]. The interlayer chitosan-montmorillonite

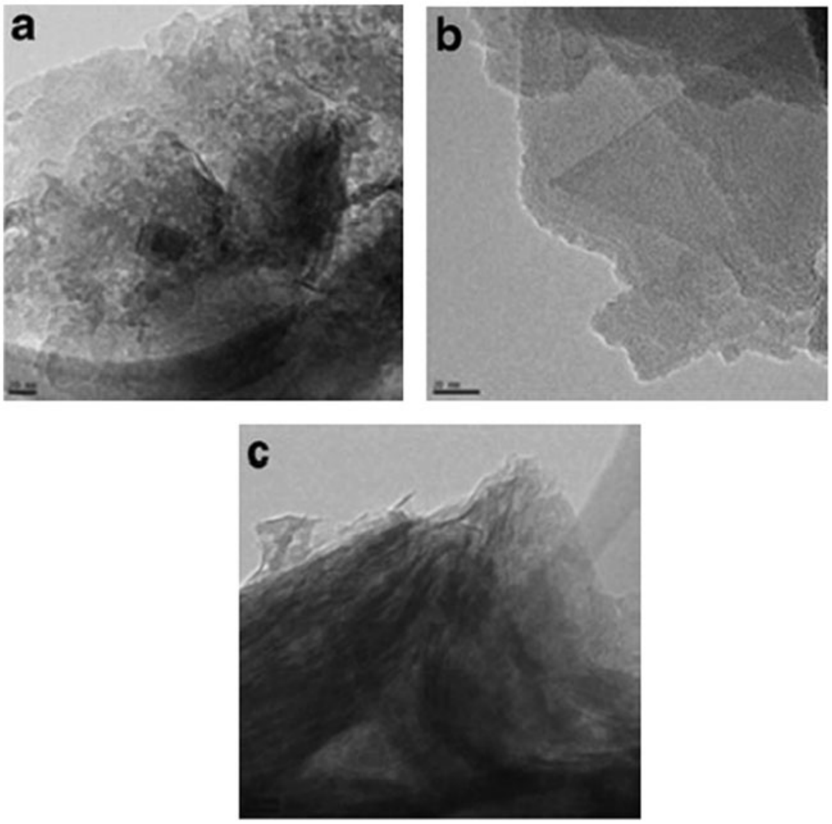


Fig. 10. TEM images of (a) sodium montmorillonite, (b) acidic montmorillonite and (c) organo-acidic montmorillonite [31].

was examined using infrared spectroscopy, as shown in Fig. 11 [132]. The inter-chitosan layers were bonded by electrostatic interactions between the $-NH_3^+$ groups of chitosan with the surface charges of montmorillonite, and the innerlayer adsorption was promoted by the establishment of hydrogen bondings to increase the basal spacing from 1.20 to 2.09 nm.

Table 12 exhibits the changes of basal spacing of homionic montmorillonite with respect to the treatment of organophosphorus pesticides [103]. When montmorillonite is contacted with the pesticides, the changes in the basal spacing were related to the difference of polarizing power and organization or aggregation of intercalated organic molecules onto the organoclays. Accordingly, the homionic montmorillonite which saturated with high polarizing power (Cu^{2+}, Ni^{2+} and Mg^{2+}) would form complexes with high spacing pesticides rather than with a complex radical. When the polarizing power decreases, the tendency for the formation of two-layer complex is greater. Whereas, the montmorillonite that saturated with cations of lower polarizing power (K^+ and Ba^{2+}) would form multiple complexes with the pesticides of smaller molecular size (monolayer). The finding is in agreement with the lower availability of space, the nature of pesticides, and polarity of these monovalent cations.

Fig. 12 demonstrates thermogravimetric analysis for montmorillonite with different CEC and alkyl chain length. Two types of anchorages were found on the long-chain surfactant molecules of the organo-montmorillonite [121]. A significant amount of organics was weakly bonded to the montmorillonite surfaces via van der Waals forces with intercalated alkyl chains, and the other part was strongly confined within the interlayer space. The peaks in the lower-temperature region were defined as desorption peaks, and the high-temperature region was known as the main decomposition peaks. The analysis demonstrated that excess adsorption was guided by the two dominating factors, chain length of the cation and CEC of the montmorillonite.

The decomposition of surfactant-modified montmorillonite takes place in four steps: water desorption, dehydration, surfactant desorption and dehydroxylation of the organoclay. In a study conducted by Zhou et al. [98] on the modification of montmorillonite surfaces using gemini surfactant,

Table 11
Porosity structures of the natural montmorillonite and its derivatives [30,31,33,40,41,117,128,129]

Adsorbent	Modification/treatment	Pore diameter (nm/Å)	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Refs.
Wyoming montmorillonite	K$^+$	1.1	–	–	[30]
	Na$^+$	1.3	–	–	
	Mg^{2+}	1.5	–	–	
	Fe^{3+}	1.2	–	–	
	Octadecylammonium	1.7	–	–	
	Dioctadecyldimethylammonium	3.3	–	–	
	Phenyltrimethylammonium	1.5	–	–	
	Hexadecyltrimethylammonium	1.8	–	–	
Arizona montmorillonite	Octadecylammonium	3.7	–	–	
	Dioctadecyldimethylammonium	4.0	–	–	
	Phenyltrimethylammonium	1.5	–	–	
	Hexadecyltrimethylammonium	2.4	–	–	
Na-montmorillonite	–	3.6	32	0.16	[31]
Acidic-montmorillonite	–	–	140	0.69	
Organo-acidic montmorillonite	–	–	161	0.70	
Montmorillonite	–	–	80		[33]
	Tetradecyltrimethyl ammonium bromide (TTAB)	–	91.30	–	
Montmorillonite	–	13.4	750	–	[40]
	Octadecyltrimethylammonium bromide (ODTMA)	22.0	–	–	
Calcium-rich Arizona montmorillonite	–	15	–	–	[41]
	Hexadecyltrimethylammonium	24	–	–	
	Hexadimethrine	14.2	–	–	
	Spermine	13	–	–	
Sodium-rich Wyoming montmorillonite	–	15	–	–	
	Hexadecyltrimethylammonium	18	–	–	
	Hexadimethrine	14	–	–	
	Spermine	13	–	–	
	Fe^{3+}	12	–	–	
Na-montmorillonite	–	–	31.8	–	[117]
Ca-montmorillonite	–	–	97.42	–	
Na-montmorillonite (110℃)	–	9.71	–	–	[128]
	3-chloroanaline	10.79	–	–	
	3,4-dichloranaline	10.52	–	–	
	2,4,6-trichloroanaline	10.71	–	–	
Ca^{2+}-montmorillonite	–	–	66	–	[129]

sodium montmorillonite showed a peak at 55℃ corresponded to the volatilization of the free water, and a sharp peak at 618℃ identical to the structural water, resulting from the dehydroxylation of montmorillonite units. In comparison with the sodium montmorillonite, organic montmorillonite showed a lower mass loss at 55℃, implying lower free water content in the modified montmorillonite. A possible explanation on the phenomenon is the presence of surfactants, which is lowering the surface energy of the inorganic material and convert the hydrophilic silicate to the organophilic surface. In addition, differential thermal analysis (DTA) results show that there are four major peaks on the organic montmorillonite within the temperature range of 160–500℃. In contrast, sodium montmorillonite did not undergo dramatic thermally induced changes in that temperature range, and the weight loss should be attributed

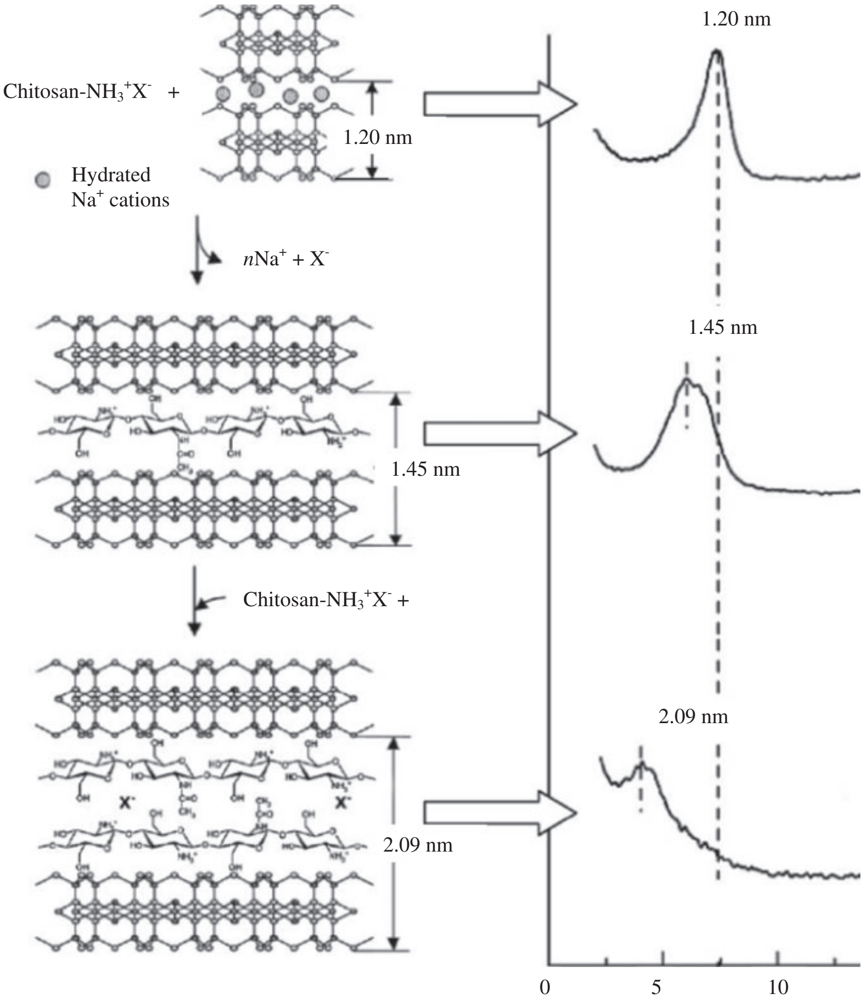


Fig. 11. Intercalation of chitosan layers into montmorillonite and the corresponding XRD patterns for (a) sodium montmorillonite and nano-biocomposite prepared from chitosan/sodium-montmorillonite at the ratio (b) 0.5/1 and (c) 10/1 [132].

to the decomposition of surfactants, that vary with different molecular environment.

Whereas, Ni et al. [133] have synthesized gemini surfactant molecules by refluxing bis-(2-bromoethyl) ether with N-alkyl-N, N-dimethylamine in isopropanol, and the modified clay was subjected to thermal analysis. There were two different interlayer arrangements of gemini surfactants within the montmorillonites surface. The weight loss for gemine surfactant intercalated montmorillonite was different from the cetyltetraethyl ammonium bromide (CTAB) modified montmorillonite. The intensities of gemini modified montmorillonite at 210–330 and 350–480˚C were higher than montmorillonite-CTAB, mainly due to the big size of gemini surfactant molecule, which was more difficult to be attached to the interlayer structure and strong electrostatic interaction of polar head groups within the external surface. Meanwhile, increasing alkyl chain length showed a stronger intensity at the surface peak around 210–330˚C, and it turned weaker at 350–480˚C.

The thermal analysis of montmorillonite-aminotriazole interactions was conducted by Morillo et al. [134] as shown in Fig. 13. Result illustrated that aminotriazole was adsorbed in the interlamellar space of montmorillonite as cation, with a shift of dehydroxylation peak to the lower-temperature region. The finding indicated the protective role of montmorillonite to delay the decomposition step and catalyse the final decomposition of aminotriazole at a lower temperature. Meanwhile, Zhu et al. [135] have compared the NMR shifts of cetyltrimethy ammonium bromide in bulk state and in the intercalated situation of montmorillonites via ^{13}C NMR analysis. The ^{13}C resonance of long chain intercalates was found to be sensitive to the difference of conformation and packing with their chemical structures, and the five carbon resonance of

Table 12
Changes of basal spacings (*d* 0 0 1) of homioinic montmorillonite treated with organophosphorus pesticides [103]

	Interlayer cation						
Pesticides	Na^+	K^+	Ba^{2+}	Ca^{2+}	Mg^{2+}	Cu^{2+}	Ni^{2+}
Dichlorvos	29.42	25.22	25.22	26.72	26.75	26.75	26.75
Phosdrin	20.06	16.05	16.05 20.06	20.06	20.06	20.06	20.06
Bidrin	16.35 20.06	15.77	16.35	16.35 20.06	20.06	20.06	20.06
Phosphamidon	16.35	15.77	15.77	16.35 20.06	20.06	20.06	20.06
Ciodrin	16.05	14.97	15.23	16.35	16.35	16.35	16.35
Monochrotophos	16.35	15.78	16.35	20.06	20.06	20.06	20.06
Metasystox	16.33 20.06	16.05	16.05	20.06	20.06	20.06	20.06
Sumithion	14.01	14.01	16.05	16.05	16.05	16.05	16.05
Diazinon	–	13.06	14.02	15.35	15.35	17.66	17.66
Zinophos	16.05	14.97	17.66	17.66	17.66	17.66	17.66
Dimethoate	15.77	15.77	16.05	16.35	16.35	16.35	16.35
Phosmet	14.24	13.38	16.05	16.05	16.05	14.15 16.05	16.05
Azinphosmethyl	14.72	13.10	16.05	16.05	16.05	16.05	16.05
Malathaion	15.77	14.72	16.05	16.35	16.35	16.35	16.35
Methyltrithion	14.97	14.97	16.05	16.05	16.05	16.05	16.05

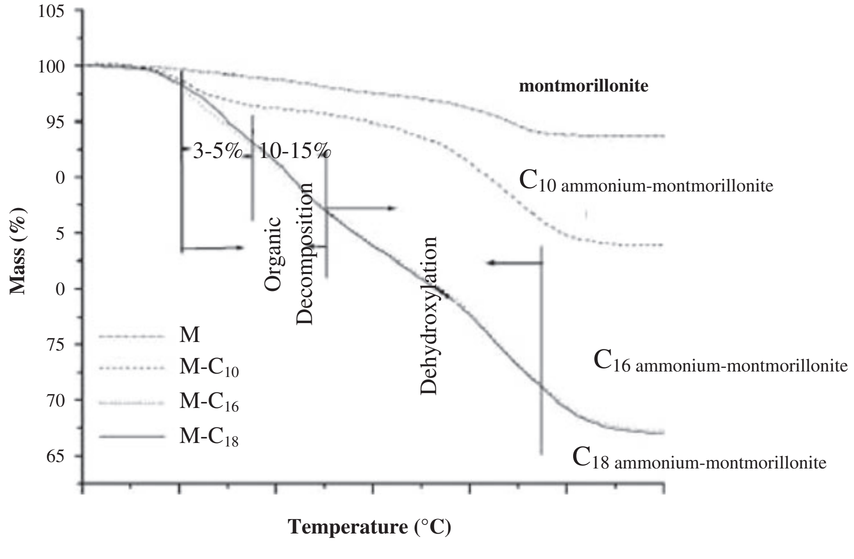


Fig. 12. Thermogravimetry (TG) plots of ammonium salt-intercalated montmorillonite with different (C_{10}, C_{116}, C_{18}) chain length [121].

crystalline cetyltrimethyl ammonium bromide was detected at C_{16} (16.8 ppm), C_{15} (24.9 ppm), $C_{2–14}$ (32.9 ppm), C_1 (64.5 ppm) and C_N (55.1 ppm). The shift in the intercalated montmorillonites was related to the local environment of the interlayer space. Results indicated the 1–3 ppm upfield chemical shift for the end-methyl (δC_{16}) and methylene (δC_{15}, $\delta C_{2–14}$) of the intercalated surfactant molecule, with freer conformational situation. For these hybrids, the conformational freedom decreased with increasing the surfactant concentration, and 2 ppm downfield shift was shown for the C_1 carbon atom with higher

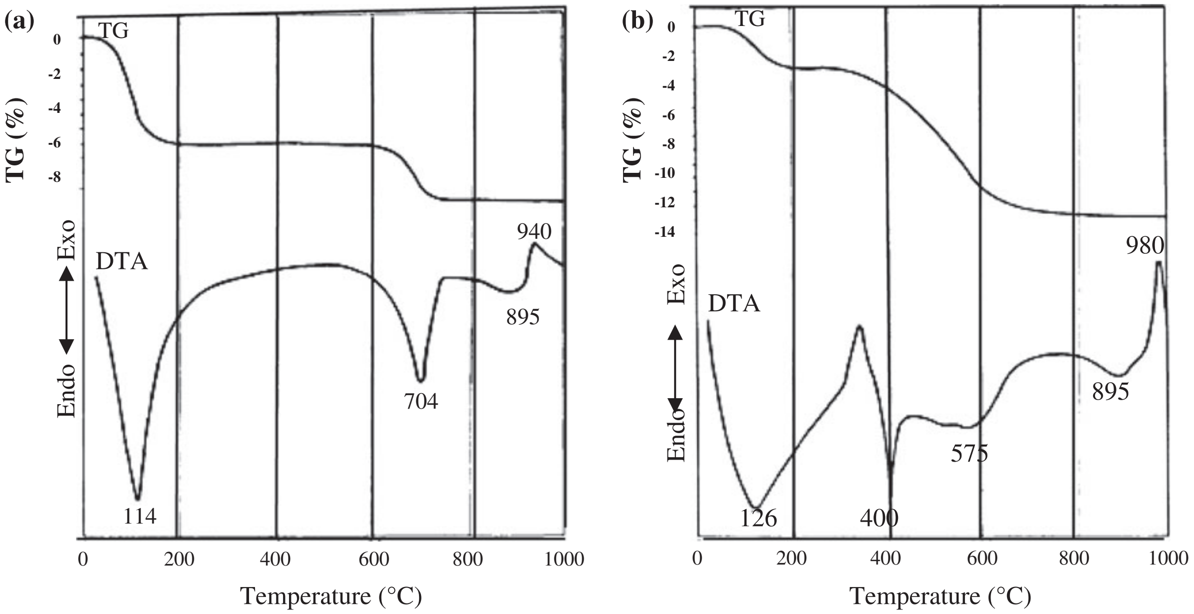


Fig. 13. DTA and thermogravimetry (TG) (%) curves of (a) wyoming montmorillonite and (b) wyoming montmorillonite-aminotriazole complex [134].

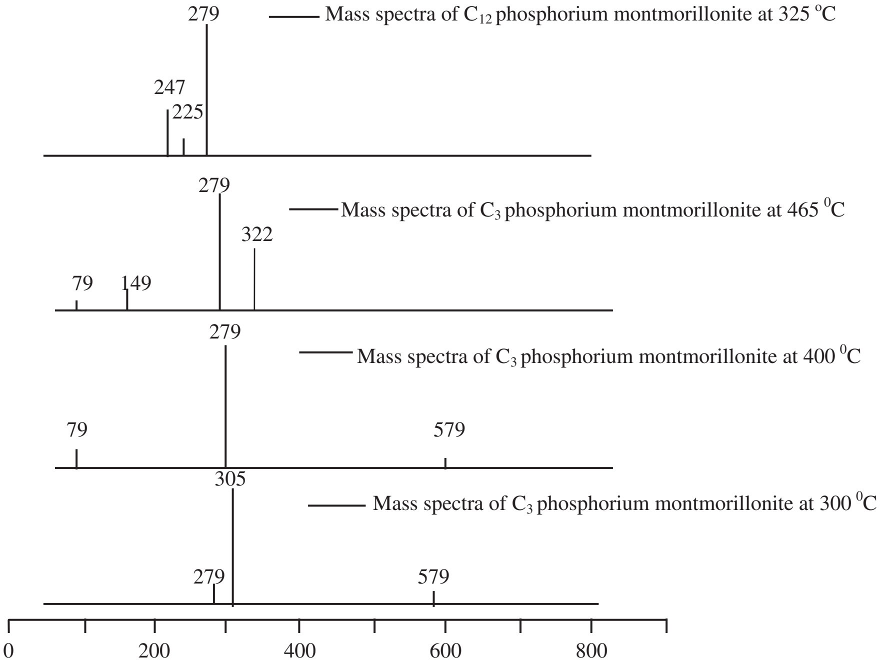


Fig. 14 Fragments of alkyltriphenyl phosphonium montmorillonite evolved during heat treatment [121].

surfactant content. This study demonstrated the mobility difference of carbon atoms in the intercalated alkyl chain. Fig. 14 illustrated the mass spectral analysis of the fragments of alkyltriphenyl phosphonium montmrillonite [121]. The thermal degradation pathway was deduced from the activation energy and isothermal analysis. The mass spectra plots revealed the presence of different phosphonium cations at different temperature region that could be regenerated via heat treatment.

7. Conclusion

For decades, pesticide practice has been widely implemented for algae, micro-organism, pests, insects and nematodes control. The wide-scale application has raised global concern about its potential risk towards biological ecosystems and the natural environment. Montmorillonite, a low-cost clay-based adsorbent, naturally with its hydrophilic characteristics have emerged to be a new solution to control the mobility and emission of pesticides in the groundwater tables. Specifically, montmorillonite and its modified derivatives are found capable to remove anionic contaminants, hydrophobic or nonpolar organic pollutants through the interlayer (quaternary ammonium cations) exchange process. Additionally, modifications with cationic surfactants could improve the swelling properties, surface hydrophobicity and basal spacing, which in turn enhances the adsorption capabilities of various organic chemicals. This has governed the transportation, transformation and biological degradation of pesticides in subsurface groundwater and reduced its infiltration to the natural environment.

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References

[1] K.Y. Foo, B.H. Hameed, Detoxification of pesticide waste via activated carbon adsorption process, J. Hazard. Mater. 175 (2010) 1–11.

[2] N.A. Laoufi, F. Bentahar, Pesticide removal from water suspension by UV/TiO_2 process: A parametric study, Desalin. Water Treat. 52 (2014) 3804–3818.

[3] E. Wołejko, B. Łozowicka, P. Kaczyński, Pesticide residues in berries fruits and juices and the potential risk for consumers, Desalin. Water Treat. 52 (2014) 3804–3818.

[4] S. Etteieb, A. Kawachi, F. Elayni, J. Han, J. Tarhouni, H. Isoda, Environmental risk assessment of groundwater quality and treated wastewater reuse on aquifer recharge: A case study in Korba, Tunisia, Desalin. Water Treat. 52 (2014) 2032–2038.

[5] K.Y. Foo, B.H. Hameed, An overview of dye removal via activated carbon adsorption process, Desalin. Water Treat. 19 (2010) 255–274.

[6] K.Y. Foo, B.H. Hameed, Potential of jackfruit peel as precursor for activated carbon prepared by microwave induced NaOH activation, Bioresour. Technol. 112 (2012) 143–150.

[7] K.Y. Foo, B.H. Hameed, Preparation and characterization of activated carbon from sunflower seed oil residue via microwave assisted K_2CO_3 activation, Bioresour. Technol. 102 (2011) 9794–9799.

[8] M.-C. Lu, M.L. Agripa, M.-W. Wan, M.L.P. Dalida, Removal of oxidized sulfur compounds using different types of activated carbon, aluminum oxide, and chitosan-coated bentonite, Desalin. Water Treat. 52 (2014) 873–879.

[9] A. Vanaamudan, N. Pathan, P. Pamidimukkala, Adsorption of Reactive Blue 21 from aqueous solutions onto clay, activated clay, and modified clay, Desalin. Water Treat. 52 (2014) 1589–1599.

[10] I. Feddal, A. Ramdani, S. Taleb, E.M. Gaigneaux, N. Batis, N. Ghaffour, Adsorption capacity of methylene blue, an organic pollutant, by montmorillonite clay, Desalin. Water Treat. 52 (2014) 2654–2661.

[11] M.E. Aydin, S. Ozcan, F. Beduk, Removal of lindane and dieldrin from aqueous solutions by montmorillonite and bentonite and optimization of parameters, Fresenius Environ. Bull. 18 (2009) 911–916.

[12] H. Chen, X. He, X. Rong, W. Chen, P. Cai, W. Liang, S. Li, Q. Huang, Adsorption and biodegradation of carbaryl on montmorillonite, kaolinite and goethite, Appl. Clay Sci. 46 (2009) 102–108.

[13] A. Olad, F. Farshi Azhar, A study on the adsorption of chromium(VI) from aqueous solutions on the alginate-montmorillonite/polyaniline nanocomposite, Desalin. Water Treat. 52 (2014) 2548–2559.

[14] S. Sen Kavurmaci, M. Bekbolet, Specific UV–vis absorbance changes of humic acid in the presence of clay particles during photocatalytic oxidation, Desalin. Water Treat. 52 (2014) 1903–1910.

[15] M. Eloussaief, S. Bouaziz, N. Kallel, M. Benzina, Valorization of El Haria clay in the removal of arsenic from aqueous solution, Desalin. Water Treat. 52 (2014) 2220–2224.

[16] G.A. Khoury, T.C. Gehris, L. Tribe, R.M. Torres Sánchez, M. Dos Santos Afonso, Glyphosate adsorption on montmorillonite: An experimental and theoretical study of surface complexes, Appl. Clay Sci. 50 (2010) 167–175.

[17] M. Abehsera, The Living Earth-the Miracle of Clay, Swann House Publishing Co., Brooklyn, New York, 1974.

[18] C.E. Marshall, Layer lattices and the base-exchange clays, Z. Krist. 91 (1935) 433–449.

[19] H.H. Murray, Traditional and new applications for kaolin, smectite, and palygorskite: A general overview, Appl. Clay Sci. 17 (2000) 207–221.

[20] D.M.C. McEwan, Interstratified clay minerals, in: G. Brown (Ed.), The X-ray Identification and Crystal Structure of Clay Minerals, Mineralogical Society, London, 1961, pp. 143–207.

[21] R.E. Grim, Clay Mineralogy, McGraw-Hill Book Company Inc, New York, NY, 1953.

[22] R. Dähn, A.M. Scheidegger, A. Manceau, E. Curti, B. Baeyens, M.H. Bradbury, D. Chateigner, The uptake on montmorillonite: A powder and polarized extended X-Ray absorption fine structure (EXAFS) study, J. Colloid Interface Sci. 249 (2002) 8–21.

[23] C. Hennig, T. Reich, R. Dahn, A. Scheidegger, Structure of uranium sorption complexes at montmorillonite edge sites, Radiochim. Acta 90 (2002) 653–658.

[24] E.J. Elzinga, D.L. Sparks, Nickel sorption mechanisms in a pyrophyllite–montmorillonite mixture, J. Colloid Interface Sci. 213 (1999) 506–512.

[25] G.W. Beall, M. Goss, Self-assembly of organic molecules on montmorillonite, Appl. Clay Sci. 27 (2004) 179–186.

[26] Y. Xi, Z. Ding, H. He, R.L. Frost, Infrared spectroscopy of organoclays synthesized with the surfactant octadecyltrimethylammonium bromide, Spectrochim. Acta, Part A 61 (2005) 515–525.

[27] J.L. Marco-Brown, C.M. Barbosa-Lema, R.M. Torres Sánchez, R.C. Mercader, M. dos Santos Afonso, Adsorption of picloram herbicide on iron oxide pillared montmorillonite, Appl. Clay Sci. 58 (2012) 25–33.

[28] R. Celis, G. Facenda, M.C. Hermosin, J. Cornejo, Assessing factors influencing the release of hexazinone from clay-based formulations, Int. J. Environ. Anal. Chem. 85 (2005) 1153–1164.

[29] N. Singh, M. Megharaj, W.P. Gates, G.J. Churchman, J. Anderson, R.S. Kookana, R. Naidu, Z. Chen, P.G. Slade, N. Sethunathan, Bioavailability of an organophosphorus pesticide, fenamiphos, sorbed on an organo clay, J. Agric. Food Chem. 51 (2003) 2653–2658.

[30] R. Celis, M.C. Hermosín, M.J. Carrizosa, J. Cornejo, Inorganic and organic clays as carriers for controlled release of the herbicide hexazinone, J. Agric. Food Chem. 50 (2002) 2324–2330.

[31] M. Mekhloufi, A. Zehhaf, A. Benyoucef, C. Quijada, E. Morallon, Removal of 8-quinolinecarboxylic acid pesticide from aqueous solution by adsorption on activated montmorillonites, Environ. Monit. Assess. 185 (2013) 10365–10375.

[32] X.S. Wang, H.B. Ma, G.B. Li, J.B. He, P. Na, Removal of pesticides by organic montmorillonite composites, Adv. Mater. Res. 875–877 (2014) 262–266.

[33] O.R. Pal, A.K. Vanjara, Removal of malathion and butachlor from aqueous solution by clays and organoclays, Sep. Purif. Technol. 24 (2001) 167–172.

[34] A. Cabrera, C. Trigo, L. Cox, R. Celis, M.C. Hermosin, J. Cornejo, W.C. Koskinen, Sorption of the herbicide aminocyclopyrachlor by cation-modified clay minerals, Eur. J. Soil Sci. 63 (2012) 694–700.

[35] B. Sarkar, Y. Xi, M. Megharaj, G.S.R. Krishnamurti, M. Bowman, H. Rose, R. Naidu, Bioreactive organoclay: A new technology for environmental remediation, Crit. Rev. Environ. Sci. Technol. 42 (2012) 435–488.

[36] F. Bergaya, G. Lagaly, Surface modification of clay minerals, Appl. Clay Sci. 19 (2001) 1–3.

[37] E. Tombácz, M. Szekeres, Colloidal behavior of aqueous montmorillonite suspensions: The specific role of pH in the presence of indifferent electrolytes, Appl. Clay Sci. 27 (2004) 75–94.

[38] Y. Xi, Q. Zhou, R.L. Frost, H. He, Thermal stability of octadecyltrimethylammonium bromide modified montmorillonite organoclay, J. Colloid Interface Sci. 311 (2007) 347–353.

[39] Y. Park, G.A. Ayoko, R.L. Frost, Application of organoclays for the adsorption of recalcitrant organic molecules from aqueous media, J. Colloid Interface Sci. 354 (2011) 292–305.

[40] C.R. Smith, Base exchange reactions of bentonite and salts of organic bases, J. Am. Chem. Soc. 56 (1934) 1561–1563.

[41] A. Cabrera, C. Trigo, L. Cox, R. Celis, J. Cornejo, A comparative study of the use of organoclay-based formulations and organic amendment to reduce the leaching of the herbicide MCPA in soil, Clean—Soil, Air, Water 36 (2008) 990–995.

[42] F. Bergaya, B.K.G. Theng, G. Lagaly, Handbook of Clay Science, first ed., Elsevier, United Kingdom, UK, 2006.

[43] L.B. de Paiva, A.R. Morales, F.R. Valenzuela Díaz, Organoclays: Properties, preparation and applications, Appl. Clay Sci. 42 (2008) 8–24.

[44] M.A. Vicente, J.-F. Lambert, Synthesis of Pt pillared clay nanocomposite catalysts from $[Pt^{II}(NH_3)_4]Cl_2$ precursor, Phys. Chem. Chem. Phys. 3 (2001) 4843–4852.

[45] H.Y. Zhu, S. Yamanaka, Molecular recognition by Na-loaded alumina pillared clay, J. Chem. Soc., Faraday Trans. 93 (1997) 477–480.

[46] A. Gil, L.M. Gandía, M.A. Vicente, Recent advances in the synthesis and catalytic applications of pillared clays, Catal. Rev. Sci. Eng. 42 (2000) 145–212.

[47] O. Bouras, J.-C. Bollinger, M. Baudu, H. Khalaf, Adsorption of diuron and its degradation products from aqueous solution by surfactant-modified pillared clays, Appl. Clay Sci. 37 (2007) 240–250.

[48] A.G. Norman, Advances in Agronomy, Academic Press Inc, New York, NY, 1953.

[49] C.R. Theocharis, K.J. s'Jacob and A.C. Gray, Enhancement of Lewis acidity in layer aluminosilicates. Treatment with acetic acid, J. Chem. Soc., Faraday Trans. 1 F, 84 (1988) 1509–1515.

[50] J. Ravichandran, B. Sivasankar, Properties and catalytic activity of acid-modified montmorillonite and vermiculite, Clays Clay Miner. 45 (1997) 854–858.

[51] M. Önal, Y. Sarikaya, T. Alemdaroğlu, İ. Bozdoğan, Isolation and characterization of a smectite as a micro-mesoporous material from a bentonite, Turk. J. Chem. 27 (2003) 683–694.

[52] C. Breen, J. Madejová, P. Komadel, Correlation of catalytic activity with infra-red, ^{29}Si MAS NMR and acidity data for HCl-treated fine fractions of montmorillonites, Appl. Clay Sci. 10 (1995) 219–230.

[53] B. Witthuhn, P. Klauth, T. Pernyeszi, H. Vereecken, E. Klumpp, Organoclays for aquifer bioremediation: Adsorption of chlorobenzene on organoclays and its degradation by RHODOCOCCUS B528, Water Air Soil Pollut. Focus 6 (2006) 317–329.

[54] R.M. Johnson, A.B. Pepperman, Release of atrazine and alachlor from clay-oxamide controlled-release formulations, Pestic. Sci. 53 (1998) 233–240.

[55] Z. Gerstl, A. Nasser, U. Mingelgrin, Controlled release of pesticides into soils from clay−polymer

formulations, J. Agric. Food Chem. 46 (1998) 3797–3802.

[56] A. Radian, Y.G. Mishael, Characterizing and designing polycation−clay nanocomposites as a basis for imazapyr controlled release formulations, Environ. Sci. Technol. 42 (2008) 1511–1516.

[57] A. Chevillard, H. Angellier-Coussy, V. Guillard, N. Gontard, E. Gastaldi, Controlling pesticide release via structuring agropolymer and nanoclays based materials, J. Hazard. Mater. 205–206 (2012) 32–39.

[58] R. Celis, C. Hermosín, L. Cornejo, J. Carrizosa, J. Cornejo, Clay-herbicide complexes to retard picloram leaching in soil, Int. J. Environ. Anal. Chem. 82 (2010) 503–517.

[59] R. Celis, M.C. HermosÍn, L. Cox, J. Cornejo, Sorption of 2,4-dichlorophenoxyacetic acid by model particles simulating naturally occurring soil colloids, Environ. Sci. Technol. 33 (1999) 1200–1206.

[60] K.G. Bhattacharyya, S.S. Gupta, Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review, Adv. Colloid Interface Sci. 140 (2008) 114–131.

[61] N. Hasegawa, H. Okamoto, M. Kato, A. Usuki, Preparation and mechanical properties of polypropylene-clay hybrids based on modified polypropylene and organophilic clay, J. Appl. Polym. Sci. 78 (2000) 1918–1922.

[62] D. Merinska, Z. Malac, M. Pospisil, Z. Weiss, M. Chmielova, P. Capkova, J. Simonik, Polymer/clay nanocomposites based on MMT/ODA intercalates, Compos. Interface 9 (2002) 529–540.

[63] H. Yao, J. Zhu, C.A. Wilkie, A.B. Morgan, Crown ether-modified clays and their polystyrene nanocomposites, Polym. Eng. Sci. 42 (2002) 1808–1814.

[64] S.-J. Park, D.I. Seo, J.-R. Lee, Surface modification of montmorillonite on surface acid–base characteristics of clay and thermal stability of epoxy/clay nanocomposites, J. Colloid Interface Sci. 251 (2002) 160–165.

[65] M. Arroyo, M.A. López-Manchado, B. Herrero, Organo-montmorillonite as substitute of carbon black in natural rubber compounds, Polymer 44 (2003) 2447–2453.

[66] R. Bongiovanni, R. Monchietto, M. Sangermano, G. Malucelli, A. Priola, Epoxy Coatings, via Cationic UV-curing, Containing Nanodispersed Phyllosilicates, Pisa, Italy, Annais of XVI Convegno Italiano di Scienza e Tecnologia delle Macromolecole, 2003, pp. 245–246.

[67] J.-H. Chang, Y.V. An, D. Cho, E.P. Giannelis, Poly (lactic acid) nanocomposites: Comparison of their properties with montmorillonite and synthetic mica (II), Polymer 44 (2003) 3715–3720.

[68] Y. Tang, Y. Hu, L. Song, R. Zong, Z. Gui, Z. Chen, Preparation and thermal stability of polypropylene/montmorillonite nanocomposites, Polym. Degrad. Stab. 82 (2003) 127–131.

[69] W.H. Awad, J.W. Gilman, M. Nyden, R.H. Harris Jr, T.E. Sutto, J. Callahan, P.C. Trulove, H.C. DeLong, D.M. Fox, Thermal degradation studies of alkyl-imidazolium salts and their application in nanocomposites, Thermochim. Acta 409 (2004) 3–11.

[70] J.H. Kim, C.M. Koo, Y.S. Choi, K.H. Wang, I.J. Chung, Preparation and characterization of polypropylene/layered silicate nanocomposites using an antioxidant, Polymer 45 (2004) 7719–7727.

[71] A. Sánchez-Solís, I. Romero-Ibarra, M.R. Estrada, F. Calderas, O. Manero, Mechanical and rheological studies on polyethylene terephthalate-montmorillonite nanocomposites, Polym. Eng. Sci. 44 (2004) 1094–1102.

[72] W. Shishan, J. Dingjun, O. Xiaodong, W. Fen, S. Jian, The structure and properties of PA6/MMT nanocomposites prepared by melt compounding, Polym. Eng. Sci. 44 (2004) 2070–2074.

[73] Y. Someya, M. Shibata, Morphology, thermal, and mechanical properties of vinylester resin nanocomposites with various organo-modified montmorillonites, Polym. Eng. Sci. 44 (2004) 2041–2046.

[74] Y.-H. Yu, J.-M. Yeh, S.-J. Liou, Y.-P. Chang, Organo-soluble polyimide (TBAPP–OPDA)/clay nanocomposite materials with advanced anticorrosive properties prepared from solution dispersion technique, Acta Mater. 52 (2004) 475–486.

[75] Y.-Q. Zhang, J.-H. Lee, J.M. Rhee, K.Y. Rhee, Polypropylene-clay nanocomposites prepared by in situ grafting–intercalating in melt, Compos. Sci. Technol. 64 (2004) 1373–1389.

[76] Y.-Q. Zhang, J.-H. Lee, H.-J. Jang, C.-W. Nah, Preparing PP/clay nanocomposites using a swelling agent, Composites: Part B 35 (2004) 133–138.

[77] H. Qin, S. Zhang, C. Zhao, G. Hu, M. Yang, Flame retardant mechanism of polymer/clay nanocomposites based on polypropylene, Polymer 46 (2005) 8386–8395.

[78] L. Százdi, B. Pukánszky Jr, E. Földes, B. Pukánszky, Possible mechanism of interaction among the components in MAPP modified layered silicate PP nanocomposites, Polymer 46 (2005) 801–810.

[79] J. Zhang, D.D. Jiang, C.A. Wilkie, Polyethylene and polypropylene nanocomposites based upon an oligomerically modified clay, Thermochim. Acta 430 (2005) 107–113.

[80] M. Gavrilescu, Fate of pesticides in the environment and its bioremediation, Eng. Life Sci. 5 (2005) 497–526.

[81] G.M. Klečka, D.L. Rick, M.E. Witt, K. Ritalahti, T.L. Marsh, Natural biological attenuation of phenoxy herbicides in groundwater: Dow Agrosciences Paritutu site, New Zealand, Biorem. J. 5 (2001) 79–92.

[82] J. Foght, T. April, K. Biggar, J. Aislabie, Bioremediation of DDT-contaminated soils: A Review, Biorem. J. 5 (2001) 225–246.

[83] R.C. Kuhad, A.K. Johri, A. Singh, O.P. Ward, Bioremediation of pesticide-contaminated soils, Appl. Biorem. Phytorem. 1 (2004) 35–54.

[84] P. Neve, Challenges for herbicide resistance evolution and management: 50 years after Harper, Weed Res. 47 (2007) 365–369.

[85] J. Dich, S.H. Zahm, A. Hanberg, H.-O. Adami, Pesticides and cancer, Cancer Causes Control 8 (1997) 420–443.

[86] I. Eleftherohorinos, Weed Science: Weeds, Herbicides, Environment, and Methods for Weed Management, AgroTypos, Athens, Greece, 2008.

[87] S. Mostafalou, M. Abdollahi, Pesticides and human chronic diseases: Evidences, mechanisms, and

perspectives, Toxicol. Appl. Pharmacol. 268 (2013) 157–177.

[88] D. MěřínskÁ, Z. MalÁč, M. Pospíšil, Z. Weiss, M. ChmielovÁ, P. ČapkovÁ, J. Šimoník, Polymer/clay nanocomposites on MMT/ODTA intercalates, Compos. Interfaces 9 (2002) 529–540.

[89] A. Mansri, S. Belkaid, New hydrophobic hybrid inorganic and organic particles based on poly(n-hexadecyl-4-vinylpyridinium bromide) adsorption on micron-sized bentonite, Desalin. Water Treat. 54 (2015) 405–411. doi:10.1080/19443994.2014.883191.

[90] M. Cruz-Guzmán, R. Celis, M.C. Hermosín, J. Cornejo, Adsorption of the herbicide simazine by montmorillonite modified with natural organic cations, Environ. Sci. Technol. 38 (2004) 180–186.

[91] J.M. Brixie, S.A. Boyd, Treatment of contaminated soils with organoclays to reduce leachable pentachlorophenol, J. Environ. Qual. 23 (1994) 1283–1290.

[92] M.J. Carrizosa, M.J. Calderón, M.C. Hermosín, J. Cornejo, Organosmectites as sorbent and carrier of the herbicide bentazone, Sci. Total Environ. 247 (2000) 285–293.

[93] M.S. Rodríguez-Cruz, M.J. Sánchez-Martín, M.S. Andrades, M. Sánchez-Camazano, Modification of clay barriers with a cationic surfactant to improve the retention of pesticides in soils, J. Hazard. Mater. 139 (2007) 363–372.

[94] A. Saha, T.P. Ahammed Shabeer, V.T. Gajbhiye, S. Gupta, R. Kumar, Removal of mixed pesticides from aqueous solutions using organoclays: Evaluation of equilibrium and kinetic model, Bull. Environ. Contam. Toxicol. 91 (2013) 111–116.

[95] S. Xu, G. Sheng, S.A. Boyd, Use of Organoclays in Pollution Abatement, Adv. Agron, USA, 1997.

[96] S.-M. Koh, J.B. Dixon, Preparation and application of organo-minerals as sorbents of phenol, benzene and toluene, Appl. Clay Sci. 18 (2001) 111–122.

[97] M.J. Sanchez-Martin, M.S. Rodriguez-Cruz, M.S. Andrades, M. Sanchez-Camazano, Efficiency of different clay minerals modified with a cationic surfactant in the adsorption of pesticides: Influence of clay type and pesticide hydrophobicity, Appl. Clay Sci. 31 (2006) 216–228.

[98] L. Zhou, H. Chen, X. Jiang, F. Lu, Y. Zhou, W. Yin, X. Ji, Modification of montmorillonite surfaces using a novel class of cationic gemini surfactants, J. Colloid Interface Sci. 332 (2009) 16–21.

[99] M.J. Carrizosa, W.C. Koskinen, M.C. Hermosin, J. Cornejo, Dicamba adsorption–desorption on organoclays, Appl. Clay Sci. 18 (2001) 223–231.

[100] N.A. Suciu, E. Capri, Adsorption of chlorpyrifos, penconazole and metalaxyl from aqueous solution by modified clays, J. Environ. Sci. Health., Part B 44 (2009) 525–532.

[101] S. Ozcan, A. Tor, M.E. Aydin, An investigation on the sorption behaviour of montmorillonite for selected organochlorine pesticides from water, Environ. Technol. 33 (2012) 1239–1245.

[102] D. Kovacević, J. Lemić, M. Damjanović, R. Petronijević, Đ. Janaćković, T. Stanić, Fenitrothion adsorption–desorption on organo-minerals, Appl. Clay Sci. 52 (2011) 109–114.

[103] M. Sánchez Camazano, M.J. Sanchez Martin, Factors influencing interactions of organophosphorus pesticides with montmorillonite, Geoderma 29 (1983) 107–118.

[104] M. Al Kuisi, Adsorption of dimethoate and 2,4-D on Jordan Valley soils and their environmental impacts, Environ. Geol. 42 (2002) 666–671.

[105] D.Bhardwaj, P.Sharma, M.Sharma, R.Tomar, Surfactant modified tectosilicates and phyllosilicates for 2,4-D removal and slow release formulation, RSC Adv. 4 (2014) 4504–4514.

[106] Y. Park, Z. Sun, G.A. Ayoko, R.L. Frost, Removal of herbicides from aqueous solutions by modified forms of montmorillonite, J. Colloid Interface Sci. 415 (2014) 127–132.

[107] J. Zolgharnein, A. Shahmoradi, J. Ghasemi, Pesticides removal using conventional and low-cost adsorbents: A Review, Clean—Soil, Air, Water 39 (2011) 1105–1119.

[108] Y.Z. El-Nahhal, G. Lagaly, Salt effects on the adsorption of a pesticide on modified bentonites, Colloid Polym. Sci. 283 (2005) 968–974.

[109] G. Sheng, C.T. Johnston, B.J. Teppen, S.A. Boyd, Potential contributions of smectite clays and organic matter to pesticide retention in soils, J. Agric. Food. Chem. 49 (2001) 2899–2907.

[110] B.L. Sawhney, S.S. Singh, Sorption of atrazine by Al- and Ca-saturated smectite, Clays Clay Miner. 45 (1997) 333–338.

[111] P. Benoit, E. Barriuso, V. Bergheaud, V. Etiévant, Binding capacities of different soil size fractions in the formation of herbicide-bound residues, Agronomie 20 (2000) 505–512.

[112] R. Celis, M. Adelino, M. Hermosín, J. Cornejo, Montmorillonite–chitosan bionanocomposites as adsorbents of the herbicide clopyralid in aqueous solution and soil/water suspensions, J. Hazard. Mater. 209–210 (2012) 67–76.

[113] V.M. Boddu, K. Abburi, J.L. Talbott, E.D. Smith, R. Haasch, Removal of arsenic(III) and arsenic(V) from aqueous medium using chitosan-coated biosorbent, Water Res. 42 (2008) 633–642.

[114] X. Peng, J. Wang, B. Fan, Z. Luan, Sorption of endrin to montmorillonite and kaolinite clays, J. Hazard. Mater. 168 (2009) 210–214.

[115] G. Lagaly, R. Malberg, Disaggregation of alkylammonium montmorillonites in organic solvents, Colloids Surf. 49 (1990) 11–27.

[116] G. Lagaly, R. Witter, H. Sander, Water on hydrophobic surfaces, in: R.H. Ottewill, C.H. Ronchester, A.L. Smith (Eds.), Adsorption from Solution, Academic Press, London 1983, pp. 65–77.

[117] A. Torrents, S. Jayasundera, The sorption of nonionic pesticides onto clays and the influence of natural organic carbon, Chemosphere 35 (1997) 1549–1565.

[118] E.M. Thurman, Organic Geochemistry of Natural Waters, Martinus Nijhoff/Dr W Junk Publishers, Dordrecht, The Netherlands, 1997.

[119] G. Chesters, G.V. Simsiman, J. Levy, B.J. Alhajjar, R.N. Fathulla, J.M. Harkin, Environmental fate of alachlor and metolachlor, Rev. Environ. Contam. Toxicol. 110 (1989) 1–74.

[120] S. Hengpraprom, C.M. Lee, J.T. Coates, Sorption of humic acids and α-endosulfan by clay minerals, Environ. Toxicol. Chem. 25 (2006) 11–17.

[121] S. Ganguly, K. Dana, T.K. Mukhopadhyay, T. Parya, S. Ghatak, Organophilic nano clay: A comprehensive review, Trans. Indian Ceram. Soc. 70 (2011) 189–206.

[122] J.L. Marco-Brown, M.M. Areco, R.M. Torres Sánchez, M. dos Santos Afonso, Adsorption of picloram herbicide on montmorillonite: Kinetic and equilibrium studies, Colloids Surf., A 449 (2014) 121–128.

[123] J.B. Dixon, S.B. Weed, Minerals in Soil Environment, Soil Science Society of America Book Series, Berkeley, 1997.

[124] G.M. do Nascimento, V.R.L. Constantino, R. Landers, M.L. Temperini, Aniline polymerization into montmorillonite clay: A spectroscopic investigation of the intercalated conducting polymer, Macromolecules 37 (2004) 9373–9385.

[125] D. Lee, K. Char, S.W. Lee, Y.W. Park, Structural changes of polyaniline/montmorillonite nanocomposites and their effects on physical properties, J. Mater. Chem. 13 (2003) 2942–2947.

[126] P.M. Amarasinghe, K.S. Katti, D.R. Katti, Insight into role of clay-fluid molecular interactions on permeability and consolidation behavior of Na-montmorillonite swelling clay, J. Geotech. Geoenviron. Eng. 138 (2011) 138–146.

[127] J. Temuujin, T. Jadambaa, G. Burmaa, Sh Erdenechimeg, J. Amarsanaa, K.J.D. MacKenzie, Characterisation of acid activated montmorillonite clay from Tuulant (Mongolia), Ceram. Int. 30 (2004) 251–255.

[128] S. Angioi, S. Polati, M. Roz, C. Rinaudo, V. Gianotti, M.C. Gennaro, Sorption studies of chloroanilines on kaolinite and montmorillonite, Environ. Pollut. 134 (2005) 35–43.

[129] U. Herwig, E. Klumpp, H.-D. Narres, M.J. Schwuger, Physicochemical interactions between atrazine and clay minerals, Appl. Clay Sci. 18 (2001) 211–222.

[130] G. Lagaly, A. Weiss, Proceedings of the International Clay Conference on Determination of The Layer Charge in Mica-Type Layer Silicates, Tokyo, Israel University Press, Jurusalem, 1969.

[131] A.G. Lagaly, Charge Characteristics of 2:1 Clay Mineral, Boulder, Colorado, 1994.

[132] F. Chivrac, E. Pollet, L. Avérous, Progress in nano-biocomposites based on polysaccharides and nanoclays, Mater. Sci. Eng. R: Rep. 67 (2009) 1–17.

[133] R. Ni, Y. Huang, C. Yao, Thermogravimetric analysis of organoclays intercalated with the gemini surfactants, J. Therm. Anal. Calorim. 96 (2009) 943–947.

[134] E. Morillo, J.L. Pérez-Rodríguez, C. Real, P.J. Sánchez-Soto, Thermal analysis of montmorillonite-aminotriazole interactions, J. Therm. Anal. Calorim. 44 (1995) 313–327.

[135] J. Zhu, H. He, L. Zhu, X. Wen, F. Deng, Characterization of organic phases in the interlayer of montmorillonite using FTIR and ^{13}C NMR, J. Colloid Interface Sci. 286 (2005) 239–244.