

Removal of Residue of Herbicides through Different Types of Modified Clay : A Review

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ABSTRACT

Herbicide is chemical material that consist in solid or liquid or gas form. It is mostly used by farmers. Biological, chemical and physical properties of modified clay (adsorbent) are different from its original form. All reported study of modified clay, montmorillonite was generally preferred and only in few cases other clay minerals like Kaolinite, Illite, Vermiculite have been used for these type of modification. But recent study reported that non expansible layer silicate based on their structure have high or low amount of inorganic cation and saturation of these mineral with organic cation also generate organoclay that have high affinity for hydrophobic compound. Surfactants are long-chain molecules that contain both hydrophilic and hydrophobic moieties, they are found in food as well as in cosmetic and industrial formulations. Modification of clay by use of organic surfactant help in adsorbing hydrophobic and anionic organic compound such as most of herbicide that are not adsorbed by natural clay because of their strongly hydrated nature in aqueous medium due to presence of inorganic cation and confer their surface a hydrophilic character. Thus, they are good adsorbents of ionic or polar compounds. Modified clay is a best opportunity for reduces in losses through various process. At the first sampling time, 10 min, the herbicide concentration in solution was 80% and 60% for WC-AC181-bentazone and SC-AC181-bentazone, respectively, but only 30% and 20% for WC-ADOD2-bentazone and SC-ADOD2-bentazone complexes, respectively.

Key words: Herbicide, Modified clay, Adsorption, Desorption, Surfactant

INTRODUCTION

Since, the green revolution mainly the cultivation ongoing only depended on the various type of chemicals like fertilizers, insecticides and herbicides *etc.* In India 290 registered pesticides are there according to insecticides Act, 1968 under section 9(3) as on

June-6-2018. Pesticide statistics of import of pesticides during 2010-11 to 2016-17 increasing from 53996 M.T. (Tech. grade) to 100238 M.T. respectively (Directorate General of Commercial Intelligence and Statistics-DGCI&S, Kolkata, W.B., Ministry of Commerce).

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Herbicides are mostly used for the control the undesirable plants in the crop such as 2, 4-D (2, 4-Dichlorophenoxy Acetic Acid) and simazine (2, chloro-4, 6-bi-ethylamino-s-triazine) mostly used for broad leaf weeds. That's incorporated to soil or plant as a spray and are interact with soil directly or indirectly. The amount of herbicides worldwide consumed during 1991–2001 was 4400 M.T.. The maximum consumption of herbicides was reported in Punjab followed by U.P., Andhra Pradesh, Maharashtra and W.B.⁷⁰. In recent publication on herbicide use in Indian agriculture, Choudhury *et al.*²⁰, reported that Butachlor (6032 tones) and Glyphosate (6003 tones) were the highest consumed herbicide in India, followed by paraquat (2068 tones), pretilachlor (2418 tones) and pendimethalin (1444 tones) in 2007.

After interaction of herbicides with soil various type of chemical reactions are there be fond of adsorption, desorption and leach down with irrigation water or rainfall that's introduced to groundwater as well as increasing environmental concern. The existence of herbicides and heavy metals in water (surface and ground water) all over the world including India. Tholkappian and Rajendran¹⁰³, establish higher level of pesticide endosulphan in water and other commodities at Kasargod area of Kerala. Kumari *et al.*⁵⁰, monitored the pesticides in rain water in Hisar area and reported the presence of methyl parathion. Singh *et al.*⁸³, analysed Ganga River (Bhagalpur, Bihar) water for organochlorine pesticides and methyl parathion and reported the incidence of organochlorine pesticides endosulphan, lindane and DDT. Shukla *et al.*⁸², reported ground water contamination with organochlorine pesticide at Hyderabad City. These are polluted parts of India mostly. Simazine is relatively persistent and, despite its low water solubility (5 mg L⁻¹), its significance as a nonpoint source of contamination of water was recognized^{113,102,2}.

Clays and modified clays as adsorbents

Clay content in soil mostly plays a major role in upholding of herbicides in soil as well as

groundwater. Clay minerals *i.e.* Montmorillonite, Kaolinite, illite *etc.*, are having dissimilar type of properties like hydrophilic in nature, high CEC, Specific Surface Area, Charge on layers and interlayers, those are responsible for the unlike retention, chemical transport and leaching of herbicides in soil. Among which properties like CEC and ability to swell up in polar medium formulate clay as an unprocessed material for modification through soft chemistry and intercalation methods. Modified clay has large specific surface area, high interlayer space and ability to adsorb both ionic and nonionic substance. Physiochemical properties of the adsorbent are examined by the use of different techniques such as XRD (X-Ray Diffraction), FTIR (Fourier Transform Infrared Spectra), SEM (Scanning Electron Microscopy), DTA (Differential Thermal Analysis)/TGA (Thermogravimetric Analysis) and Zetametry. In this review we have summarized the use of different modified clays for the removal of herbicides from soil system because this is one of the most promising remedy to control or slow release of herbicides.

Herbicide is necessary evil

Herbicide is a chemical compound that is used for the weed or undesirable plants in the crops. Herbicides may be exist in the form of solid or liquid, volatile or non-volatile, soluble or insoluble in nature. These are various type such as selective *i.e.* Simazine, Atrazine, 2, 4-D, MCPA, Butachlor, Alachlor, Fluchloralin, pendimathelin *etc.* and translocative or non-selective *i.e.* Glyphosate, Paraquat and Diquat *etc.* They can apply on plants or soil surface. In the 1940s, farmers did not have much choice for herbicides. The era of herbicide-use started effectively with the import of 2, 4-D during the 1960s. Intended for non-selective weed control, herbicides like lead arsenate or salt were opted. But initially for a long period it was not very much acceptable to common Indian farmers. They used cheap labour to manage weed problems. Due to increasing population pressure, more and more urbanization, labour crisis became major issue

and forceful the farmers to move forward with chemical weed management. Now, 60 herbicides of different modes of action are registered in our country. More than 700 formulations of herbicides are available in the market (Insecticides / Pesticides Registered under section 9(3) of the Insecticides Act, 1968 for use in the Country (as on 20/10/2015), Central Insecticides Board and Registration Committee, Ministry of Agriculture, Government of India).

In India, herbicides are being used on more than 20 million ha, which constitute about 10% of the total cropped area in the country³³. In India, herbicide use has increased up to 30% during the last 10 years in the country. Due to chemical nature of herbicides, excessive and repeated use may pose residue problems, phytotoxicity to crop plants, residual effect on susceptible intercrops or succeeding crops or non targets organisms and ultimately health hazards due to accumulation of herbicide residues in the soil, crop produce and ground water⁹⁶. Many herbicides residues are bound to crop waste and soil particle that are not available to targets and pollute the soil ecosystem in a number of ways. The problem of soil and ground water contamination accelerated in case of highly soluble herbicide because these formulations easily dissolved in soil solution and increase likelihood of leaching and runoff¹³. Out of the total consumption of pesticides, 80% are in the form of insecticides, 15% are herbicides, 1.46% is fungicide and less than 3% are others. In comparison, the worldwide consumption of herbicides is 47.5%, insecticides are 29.5%, and fungicides

17.5% and others account for 5.5% only. Sondhia, 2014 reported that crops in which herbicide application more common - wheat crop (44%), is followed by rice (31%), plantation crop (10%), soybean (4%), and other crops (11%).

Herbicides persistence in the soil is expressed as half-life or time required to degrade fifty percent of the original molecule. However the half-life is not absolute because it depends on the soil type, temperature, and concentration of the herbicide applied. The persistence varies with the nature of a chemical, soil properties and climatic conditions. Heavy rainfall will cause greater leaching and runoff. Sandy soil would have a higher leaching potential than a clay soil due to larger pore spaces and lower CEC^{85,87,89,93}. An herbicide is said to be persistent when it may be found to exist in soil in its original or a closely related but phytotoxic form longer than one crop season after its original application⁸⁶. Ultimate fate of herbicide in soil depends on number of processes such as volatilization, leaching, runoff and degradation by microbes, chemical processes and photodecomposition. In a monitoring study of four herbicides, butachlor residues alone contributed 61% followed by pendimethalin (36%), and fluchloralin (3%). Alachlor was not detected in all the locations. The most often detected herbicides above the prescribed maximum residues limits are 2,4-D, atrazine, cyanazine, carbaryl, simazine, bromacil, diuron, diazinon, prometon, metolachlor, dinoseb, picloram, metribuzin, metsulfuron, glyphosate, metolachlor, propanil, butachlor, pendimethalin, oxyfluorfen etc⁹⁶.

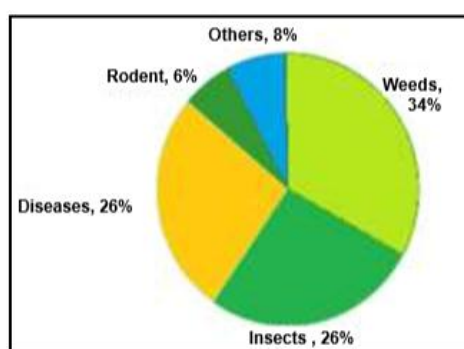


Fig. 1. Losses caused by different pests

Source: Tata Strategic Management Group (2014)

Weeds account for about one-third of the total losses caused by agricultural pests³³. Weeds were reported to cause yield loss of 5% in commercial agriculture, 10% in semi commercial agriculture, 20% in subsistence agriculture¹⁹, and 37–79% in dry land agriculture⁸⁴. A Weed Atlas for major weeds in major crops in 435 districts spread across 19 states of the country was published by DWR³¹. Eight hundred and twenty six weeds species were reported to cause yield losses in India of which 80 and 198 were considered very serious and serious weeds respectively¹⁹. So neglecting the use of herbicide is not possible and it is less laborious and quick method of controlling weeds.

Common herbicides used in India and its cause

2, 4-D

2, 4-D *i.e.* 2, 4-Dichlorophenoxyacetic acid, is an organic compound. It is a systemic herbicide which selectively kills most broadleaf weeds by causing uncontrolled growth in them, but left most of grasses such as cereals, lawn turf, and grassland relatively unaffected. 2, 4-D is one of the oldest pesticides registered in the United States. Its wide agricultural use results also in widespread potential human exposures. Numerous epidemiological studies have connected 2, 4-D to non-Hodgkin's lymphoma (NHL) among farmers^{119,118,40,61,60,28}. Children, especially farm children, may be particularly vulnerable to exposure to 2, 4-D. Children have distinctive exposure patterns and sensitivities to pesticides. In addition, farm children may accompany their parents to work in the fields, further increasing their pesticide exposure.

Simazine-

Simazine is fawn crystalline compound which is sparingly soluble in water. It is a member of the triazine-derivative herbicides, and was widely used as a residual non-selective herbicide, but is now banned in European Union states. About 15 percent of the parent compound remained at one year after initial application and no residues could be detected after 16 months¹⁰⁰. Simazine is more persistent

in soils than atrazine and other triazines such as propazine, ipazine and chlorazine^{5,99}. Under anaerobic conditions, simazine was reported to degrade in loamy sand soil with half times of 8 to 12 weeks by using of ¹⁴C⁵¹. Degradation products included 2-chloro-4, 6-bis(amino)-s-triazine, 2-hydroxy-4,6-bis(ethylamino)-s-triazine and 2-hydroxy-4-ethylamino-6-amino-s-triazine. Monsanto reported an half times for decomposition of simazine was 36 and 234 days in loamy sand and silt loam soils, respectively. Simazine decomposition in soils is affected by moisture content and temperature¹¹². The rate of simazine decomposition in soil is faster in acid than in alkaline soils.

Bentazon -

Bentazon is also known by the trade name Basagran and it is a selective post-emergence herbicide used to control many broadleaf weeds and sedges primarily by contact action in most graminous and many large seeded leguminous crops such as food and feed crops including alfalfa, beans, corn, peanuts, peas, asparagus, cereals, peppers, peppermint, rice and sorghum. It is also used on two terrestrial nonfood crops: ornamental lawns and turf. It has little effect on germinating seeds, and is not used pre-emergence¹¹⁵. Bentazon is a benzothiadiazinone contact herbicide performing as a photosynthetic electron transfer inhibitor, selectivity is based on the propensity of the crop plants to quickly metabolize bentazon to 6-OH- and 8-OH-bentazon and conjugate it with sugar. Since most weeds do not possess this metabolic ability, their photosynthesis is disrupted and the weeds die. Herbicides containing bentazon should be kept away from high heat as it will release toxic sulfur and nitrogen fumes.

Glyphosate

Glyphosate was first introduced in 1974 and is sold under various trade names such as Roundup branded herbicides, Rodeo, and Accord. The major product is a family of herbicides sold under the trade name of Roundup, which dwell of the isopropylamine salt of N-(phosphonomethyl) glycine and a surfactant. The predominant surfactant used is

a polyethoxylated tallow amine (POEA), which is a mixture of polyethoxylated long-chain alkylamines¹⁴. Roundup branded herbicides is sprayed as a liquid with ground and aerial equipment. According to U.S. EPA, glyphosate was the second mainly universally used pesticide in both the agricultural and non-agricultural (home, garden, and commercial) market sectors. In the agricultural market sector, it was estimated that 0.0154 to 0.0172

M.T. and 0.0303 to 0.0331 M.T. of glyphosate were used in 1997 and 1999, respectively. Glyphosate, N-phosphonomethyl glycine (PMG) is a non-selective, post emergent and broad-spectrum herbicide with widely known applications in agriculture⁴¹. Concentrations of glyphosate in groundwater in Europe have been reported rarely but monitoring is still limited¹⁰⁹.

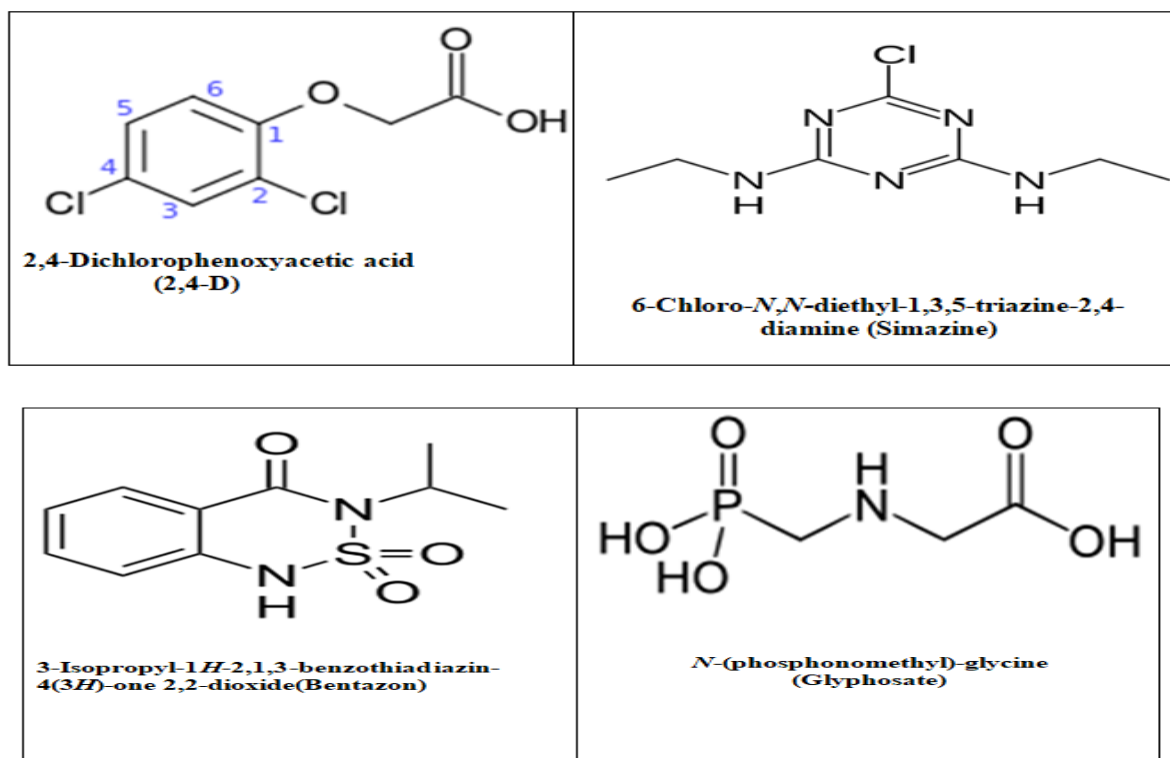


Fig. 2. Structure of some commonly used herbicide

Modified clay

Modification can change the structure of clay to enlarge its specific surface area therefore mounting the adsorption capacity. Chemical composition of clay depends on different properties like its cation exchange capacity, adsorption capacity, charge density and morphology that make significant role in modification of clay⁹⁸. Biological, chemical and physical properties of modified adsorbent are different from its original form⁴⁶. After modification clay surface become more porous and homogenous.

Adsorbent may be mineral, organic or biological origin. One of the best conventional adsorbent, activated carbon has been

extensively used in many applications but at field scale use of it for adsorption of herbicide is not possible. Clay is one of the best materials for adsorption because of abundantly available, less expensive and easy modification etc. Ozcan *et al.*⁶⁶, observed that 0.2 g clay was sufficient for removal of 99% of aldrin from 100 mL of aqueous samples at 10 ppb concentration. Salman *et al.*⁷³, used Bentonite and Kaolinite for removal of formaldehyde, Bentonite was established to be advanced than Kaolinite in adsorption of formaldehyde. The adsorption capacity of different clays NACs were montmorillonite > illite > Kaolinite.

Modification of clay with surfactant-

Surfactants are long-chain molecules that enclose both hydrophilic and hydrophobic moieties; they are created in food⁴⁹ as well as in cosmetic and industrial formulations⁸⁰. Depending on their origin, surfactants are

either biosurfactants or synthetic, and they can be classified as ionic and nonionic according to their hydrophilic moiety¹⁰⁸. Rosen, 2004 creates these structures are continuously forming and disintegrating of surfactant aggregates (Fig. 3)-

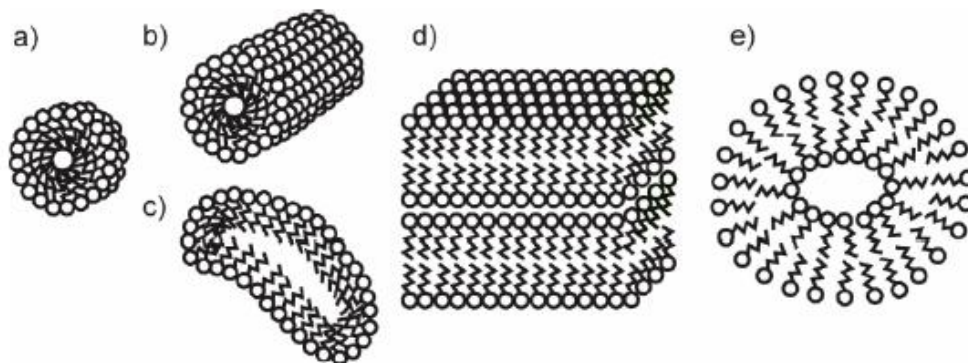


Fig. 3. Surfactant aggregates: (a) spherical micelle; (b) cylindrical micelle; (c) worm-like micelle; (d) lamellar formation; and (e) vesicle

Biosurfactants

Biosurfactants are synthesized by microorganisms, plants, or animals, with a critical micelle concentration (CMC) ranging from 1 to 200 mg/L and a molecular mass ranging from 500 to 1500 Da⁶³. They are classified as glycolipids, lipopeptides, phospholipids, fatty acids, neutral lipids, and polymeric and particulate compounds²⁹. Their hydrophilic moiety comprises carbohydrates, amino acids, cyclic peptides, phosphates, carboxylic acids, or alcohols, with the hydrophobic moiety made up of and long-chain fatty acids^{67,62}. Biosurfactants have been applied for the elimination of copper, zinc, cadmium, and lead from soil and sediments^{63,47}.

Synthetic Surfactants

Synthetic surfactants can be either nonionic or ionic molecules. Nonionic surfactants cannot be ionized in aqueous solution; their hydrophilic moiety contains polyoxyethylene, polyoxypropylene, or polyol groups, and their hydrophobic moiety is comprised of fatty alcohols and saturated or unsaturated fatty acids. Compared to ionic surfactants, nonionic surfactants' lower CMC, higher degree of reduction in surface tension, and relatively

constant properties in the occurrence of salts renders them more suitable to the remediation of soils, although the existence of clays and organic matter may influence their adsorption rate⁶⁷.

Modification of clay by use of organic surfactant -

Modification of clay by use of organic surfactant help in adsorbing hydrophobic and anionic organic compound such as most of herbicide that are not adsorbed by natural clay because of their strongly hydrated nature in aqueous medium due to presence of inorganic cation and confer their surface a hydrophilic character. Thus, they are good adsorbents of ionic or polar compounds^{75,24}. On the other hand Arienzo *et al.*⁴, Sanchez-Martin *et al.*⁷⁶, reported that organic compounds are unable to compete with water for the adsorption sites and are more favorably adsorbed by the organic matter than by the clay minerals. Accordingly, in recent years much attention has been paid to the development of modified clays with improved sorption capacities, such as cation-exchanged organo-clays by cationic surfactants with a high number of carbon atoms. Formation of a hydrophobic organic phase in organo-clay due to alkyl hydrocarbon

chains. This phase acts as a partition medium for hydrophobic organic compounds that is very effective in the adsorption of such compounds from water. The mechanism of the adsorption process is similar to the dissolution of the organic compounds in hexane or octanol^{48,18}. Additionally, several works have shown that the organic phase derived from the organic cations changed in the montmorillonite is more effective than the OM of the soil^{8,54,75}. There are fewer studies that reporting the adsorption of hydrophobic herbicide by use of clay functionalized with organic surfactant. Main aim of this study was preparation of slow – release herbicide^{59,35,36,10,107,53}. and studied about the binding mechanism of pesticides by organo clays^{75,25}.

Interaction of herbicide with clay modified by organic surfactant-

Based on all reported study montmorillonite was generally preferred for these type of modification and only in few cases other clay minerals like Kaolinite, Illite, Vermiculite have been used^{43,81}. Through these modifications use of expansible and non-expansible clay minerals were possible. Non expansible layer silicate based on their structure have high or low amount of inorganic cation and saturation of these mineral with organic cation also generate organoclay that have high affinity for hydrophobic compound⁷⁷. When the hydrophobicity of the

clay was increased, the adsorption of hydrophobic molecules was expected to increase and yield a slower release in aqueous solutions, extending the herbicidal activity for a longer time under field conditions¹¹¹. On the other hand Jaynes and Boyd⁴³, studied that other distinctiveness of these minerals, such as their specific surface area and charge density, affect the organization and distribution of organic cations at the clay surface and may affect the adsorption of hydrophobic compounds by organoclays and also the stability against desorption of these compounds adsorbed by them. Spillner *et al.*⁹⁷, studied that leaching and surface mobility of alachlor herbicide was associated with its water solubility and soil organic matter content. EI-Nahal *et al.*³⁵, found that these modification carried out by adsorbing to clays substituted quaternary ammonium ions $[(CH_3)_3N^+R$ or $(CH_3)_2N^+RR']$, where R and R' are aromatic or alkyl species.

By use of six different minerals like layered expansible and non-expansible clay minerals (montmorillonite, illite, muscovite, and kaolinite) and non-layered clay minerals (sepiolite and palygorskite) modified with the cationic surfactant octadecyl trimethyl ammonium bromide ($C_{18}TAB$) (Fig. 4), Sanchez-Martin *et al.*⁷⁷, studied on adsorption of three herbicide like penconazole, linuron, atrazine.

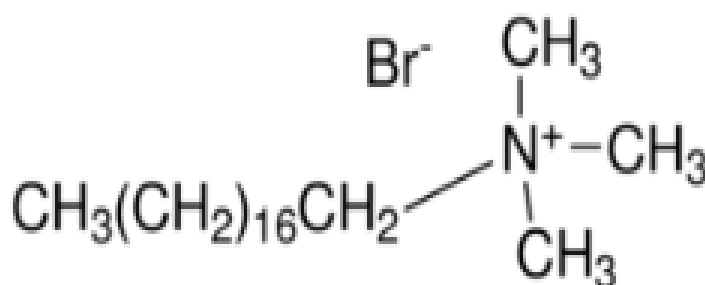


Fig. 4. Structure of octadecyltrimethylammonium bromide ($C_{18}TAB$)

They were found (Table-1) that increases in adsorption capacity due to changes in different characteristics after modification with $C_{18}TAB$ because of distribution of organic cation on

surface of clay silicates. The $C_{18}TAB$ cation did not alter the X-ray diffraction patterns of non-expansible minerals. These characteristic are listed below -

Table 1. Characteristics of natural and organo clays

Sample	CEC ^a (cmol/kg)	OC ^b (%)	OM ^c (%)	Organic cation (cmol/kg)	Surface area (m ² /g)	Charge density ($\mu\text{eq}/\text{m}^2$)	d(001) (Å)
<i>Natural clays</i>							
Montmorillonite	82	0.06	0.10	–	750 ^d	1.09	13.4
Illite	15	1.74	2.99	–	57	2.63	10.0
Kaolinite	6.1	0.10	0.17	–	12	5.08	7.16
Muscovite	21	0.10	0.17	–	105 ^d	2.00	10.0 (12.6) ^e
Sepiolite	5.0	0.08	0.13	–	189	0.27	12.3
Palygorskite	27	0.46	0.79	–	254	1.06	10.6
<i>ODTMA clays</i>							
Montmorillonite	–	20.1	24.9	79.5	–	1.06 ^f	22.0
Illite	–	6.05 ^g	8.33	17.1	–	3.00 ^f	10.0
Kaolinite	–	1.61	2.04	5.99	–	4.99 ^f	7.16
Muscovite	–	5.39 ^h	6.73	20.9	–	1.99 ^f	10.0 (22.0) ^e
Sepiolite	–	1.55	1.96	5.83	–	0.31 ^f	12.3
Palygorskite	–	8.50	10.7	31.7	–	1.25 ^f	10.6

a - Cation exchange capacity, b - Organic carbon, c - Organic matter, d - Total surface area, e - Montmorillonite impurities, f - C₁₈TAB $\mu\text{eq}/\text{m}^2$, g - Total OC content from natural clay and from organic cation, h - Corresponding to saturation of Muscovite and Montmorillonite present as impurities with organic cation.

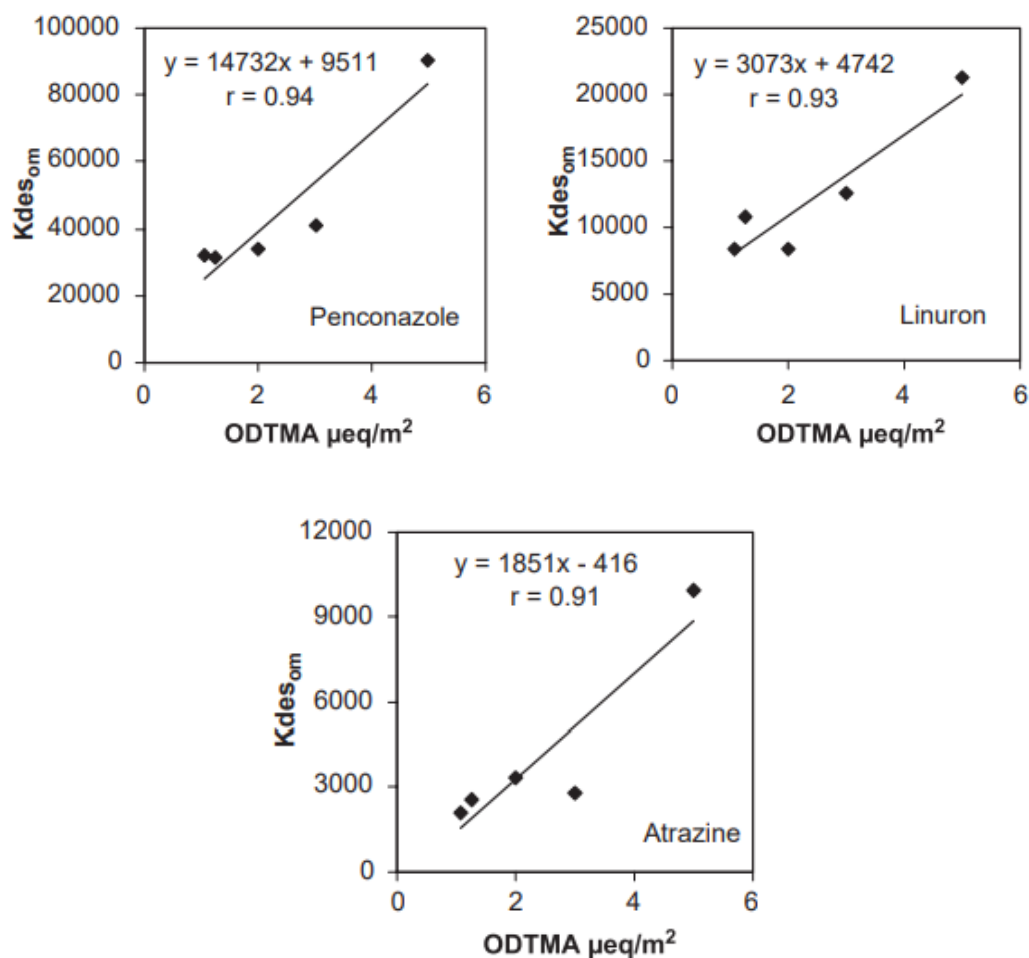


Fig. 5. Relationship between the $K_{des_{om}}$ values for the adsorption of each herbicide by the C₁₈TAB -clays, and the charge density values of organic cation in these clays.

Sanchez-Martin *et al.*⁷⁷, also studied the Correlation coefficient values (r^2) between K and Kdes, (Fig. 5) and organic matter (OM) content of C₁₈TAB-clays indicate a more effective partitioning of the pesticides in the organic phase of C₁₈TAB after desorption. Furthermore in this study they concluded that the efficiency of the C₁₈TAB clays for the adsorption of the pesticides depends on the degree of organic cation saturation; i.e., on the C₁₈TAB content of the clay mineral. However, they found that adsorption capacity of C₁₈TAB as determined by the Kdes_{om} values depends on the charge density of the clay mineral; that was, on the density of the organic cation between the Kdes_{om} (adsorption capacity) values and the charge density of different C₁₈TAB-clays indicated that a higher density of C₁₈TAB in the clay gives rise to the formation of an organic phase more effective for the partition of the pesticides. This correlation explained that the highest Kdes_{om} value obtained was for Kaolinite and the lowest Kdes_{om} value was for montmorillonite in the adsorption of all pesticides by the different organo clays.

Modification with inorganic cation

Modification of clay with inorganic cation helps in generating slow release formulations. These CR (controlled release) formulations help in reducing amount of herbicides required

for weed control, decrease in risk of environment pollution and save manpower by reducing number of applications. Jiang *et al.*⁴⁴, modified the montmorillonite by polymeric aluminium (Al) or ferric (Fe) and/or Al/Fe mixed polymeric species. Modification procedure involved the mixing of the clays with the polymeric metal species for 4 h at 55°C and characterization by X-ray Fluorescence (XRF).

Interaction of inorganically modified clay with herbicide

Celis *et al.*¹³, worked on adsorption of herbicide hexazinone by use of montmorillonite saturated with inorganic cation like Na⁺, K⁺, Mg²⁺, and Fe³⁺ and found that Fe-saturated montmorillonite showed high adsorption compared to others and attributed to protonation of the basic pesticide in the interlayers of the Fe saturated clay mineral followed by retention by a cationic exchange mechanism, as a result of the high surface acidity induced by the interlayer Fe³⁺ ions.

The results of this work showed that hexazinone formulation based on inorganic (Fe-SW) clays display controlled-release properties in water and soil/water suspensions (Fig 6), reduce herbicide leaching in soil columns, and retain herbicidal activity as compared with the currently available commercial hexazinone formulation.

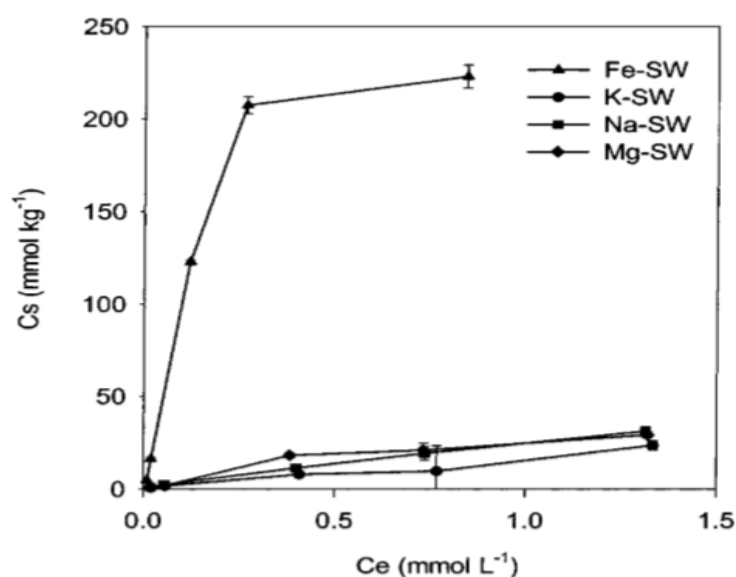


Fig. 6. Hexazinone adsorption isotherms on montmorillonite saturated with different inorganic cations

Celis *et al.*¹³, also prepared three clay-herbicide complexes (4% a.i.): a physical mixture (PM), a weak association complex (WC), and a strong association complex (SC) and reported that decrease in herbicide concentration in leachates without shifting of

the maximum concentration peak can be an artifact due to the amount of herbicide molecules that are irreversibly adsorbed to the clay particles and, therefore, not available for leaching (Fig. 7)

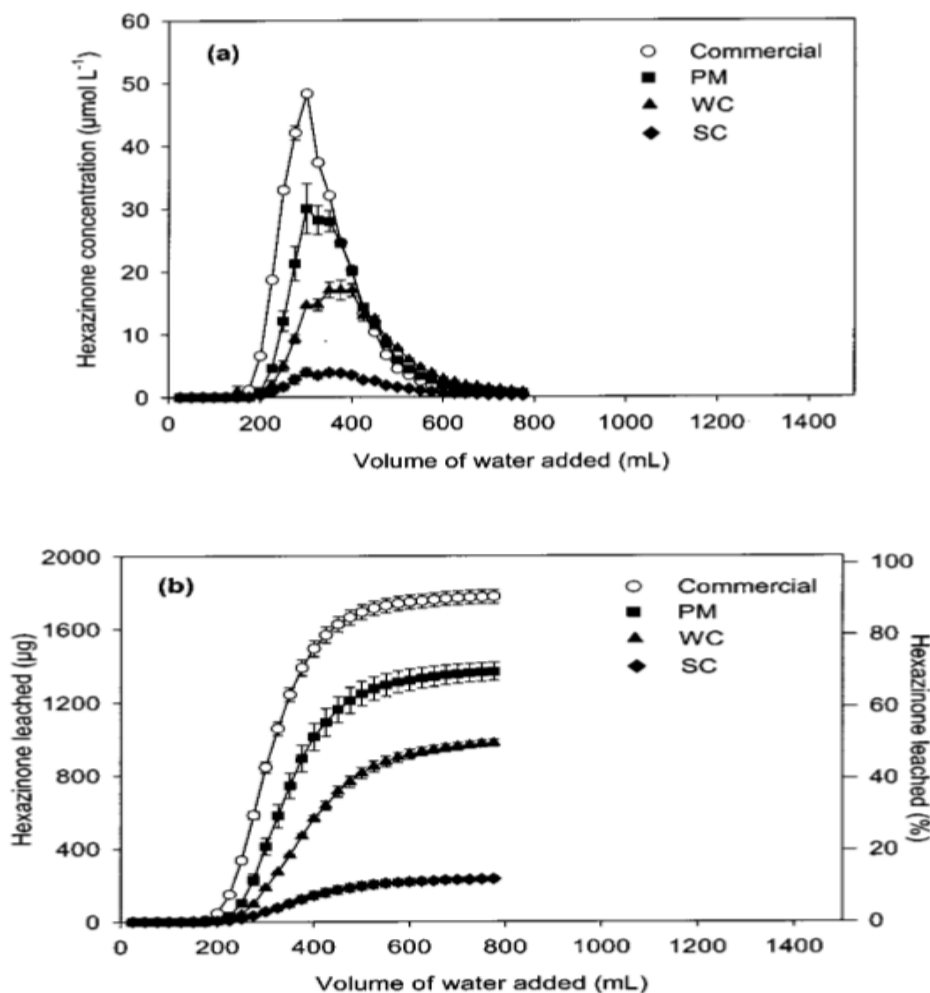


Fig.7. Hexazinone BTCs (Breakthrough curves) after application to soil columns as commercial and Fe-SW formulations: (a) relative BTCs; (b) cumulative BTCs.

Modification of clay by calcinations-

It has been reported as physical method of modification of clay by calcinations at higher temperature¹. The change in structure upon heating is different for different clay and depends on its origin and heating time⁶.

Beragaya *et al.*⁶, also reported that initially in the dehydration stage, removal of adsorbed water and other impurities are removed that attached on clay. These results in weight loss and increase surface area of clay thus enhancing adsorption sites. Further heating corresponds to dehydroxylation. Beragaya *et*

*al.*⁶, Vimonses *et al.*¹¹⁰, concluded that if heating is continued to dehydroxylation the clay structure and surface functional group are altered. Surface modification by calcining montmorillonite with collapsed interlayer space and edge enrichment of aluminium ions or oligomeric hydroxoaluminium cations⁷ change the adsorption processes of organic molecules. Damonte *et al.*²⁷, studied the different parameter like the total and internal specific surface areas and IEP (isoelectric point) values of montmorellinote and its calcined form.

Table 2. Physicochemical parameter of montmorillonite (M) AND its calcined form(C)-

Parameter	M	C
S_{N_2} (m^2/g)	21	31
S_w (m^2/g)	678	237
Internal surface (m^2/g)	657	206
IEP (pH)	2.70	6.97

The internal specific surface = S_w (total specific surface area) – S_{N_2} (external specific surface area).

The decrease of the specific surface area, S_w , with thermal treatment indicated that the collapse of the montmorillonite interlayer spaces which inhibited the entrance of the probe molecule (water). The higher specific surface area (S_{N_2}) of C was assigned to the tumbling of several layers in the edge region by the thermal treatment which liberates aluminium ions or oligomeric hydroxoaluminium cations and creates mesopores⁷. The IEP of M (Table 2) was in

agreement with data found for substances obtained from neighboring localities⁵⁵. The increase of IEP of C was assigned to the liberation of aluminium ions with further remnant surface coating¹⁰⁴. Damonte *et al.*²⁷, also reported that thermal treatment did not alter the surface composition thus no difference in the elemental compositions of major components between M and C (Table 3), indicating that.

Table 3. Elemental surface composition (%) obtained by EDAX for samples M and C-

Sample	Si(%)	Al(%)	Mg(%)	Fe(%)	Ti(%)
M	62.3	18.7	3.2	9.6	1.2
C	60.7	17.3	3.1	9.6	2.8

Interaction of calcined clay with herbicide-

For anionic organic contaminants Calcined clay act as a potential sorbent. An investigation demonstrated that Mg–Al mixed oxide when calcined at 500 °C (HT500)⁷⁹ is capable of adsorbing anions from aqueous solutions through the reconstruction of its layered structure and in its ability to be recycled by recalinations at 500 °C^{106,105}. Pavlovic *et al.*⁶⁸, have been used HT500 as an

adsorbent for adsorption of three acidic herbicide: 2, 4-D, Clopyralid and Picloram. These compounds have a widespread use in the treatment of corn, strawberry, sugar cane, rice¹¹⁶ and are potential pollutants of the environment^{23,32,53}. These herbicides exist mainly as anionic species in soil environments because of their ionizable character, low sorption capacities and high mobility in most environments.

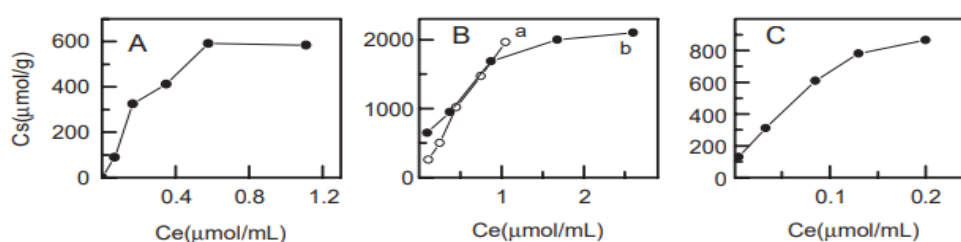


Fig. 8. Adsorption isotherm of pesticides on HT500: (A) 2, 4-D (0.03 g/20 ml, 24 h); (B) Clopyralid (a: 0.03 g/20 ml, 2 h; b: 0.02 g/30 ml, 2 h) and (C) Picloram (0.03 g/20 ml, 3 h

Where-

Ce - adsorbate concentration in the solution at equilibrium ($\mu\text{mol mL}^{-1}$)

Cs-the amount of solute adsorbed in the solid at equilibrium ($\mu\text{mol mL}^{-1}$)

Damonte *et al.*²⁷, also found that thermal analysis of montmorillonite (M) showed the three typical regions were associated to the water-loss (Fig.9) (Reid-Soukup, 2002). The adsorbed water on external surfaces was removed between 80 °C and 150 °C, hydration

water of the interlayer cations was lost at 150 °C - 500 °C and structural water was desorbed >500 °C. The endothermic peak resulting from dehydroxylation was observed at 704 °C⁵⁶, followed by a small exothermic peak at 936 °C due to structure decomposition⁷⁸.

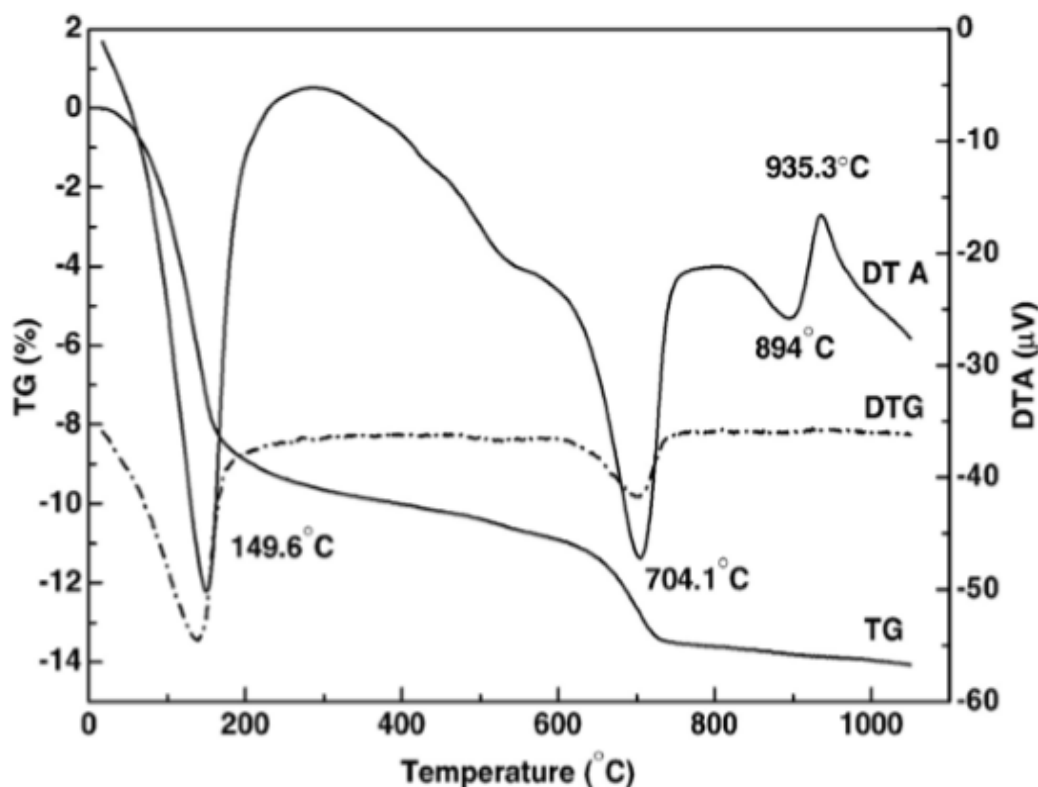


Fig. 9. Thermal analysis for M and C

Pavlovic *et al.*⁶⁸, also studied the Adsorption products by FT-IR spectroscopy to confirm the adsorption of 2, 4-D in the interlayer of the hydrotalcite by the mechanism of reconstruction. The FT-IR spectrum of hydrotalcite (Fig. 10A) displays a wide band at 3480 cm^{-1} attributed to the $\nu_{\text{O-H}}$ vibrations of free and H-bonded hydroxide groups and the low intensity band at 1640 cm^{-1} due to the water-bending mode $\delta_{\text{O-H}}$. The shoulder around 3000 cm^{-1} is attributed to hydrogen bonding between H_2O and the anions present in the interlayer. The stretching-vibration band of carbonate anion is located at 1371 cm^{-1} ¹¹.

FT-IR spectrum of 2, 4-D (Fig. 10C) found bands corresponding to the C=C vibrations of the aromatic ring (1476 cm^{-1} and 1422 cm^{-1}), bands assigned to the antisymmetric and symmetric vibration C–O–C (1315 cm^{-1} and 1089 cm^{-1} , respectively), and bands corresponding to the carboxylic group $\nu_{\text{C=O}}$ at 1735 cm^{-1} and O–H deformation coupled with C–O stretching vibrations at 1231 cm^{-1} . FT-IR spectrum of the adsorption product (Fig 10B) indicates bands related to 2, 4-D is present together with those corresponding to these hydrotalcite.

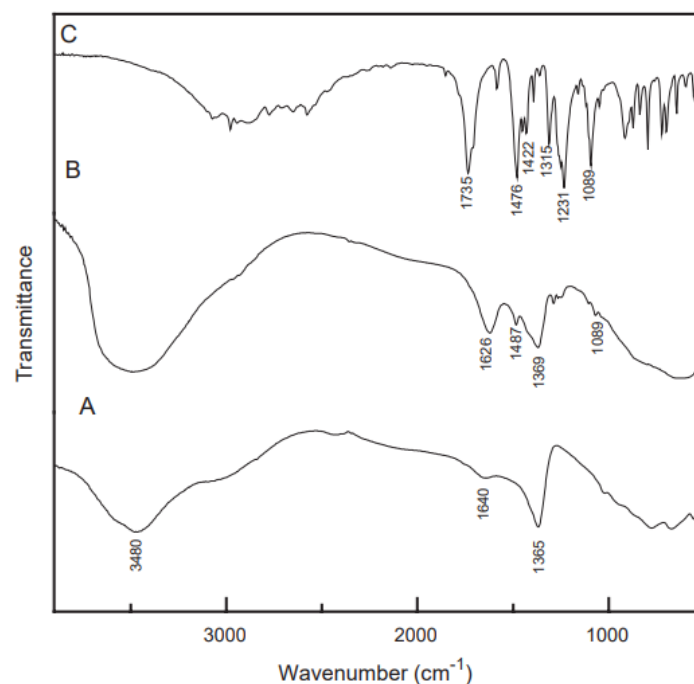


Fig. 10. FTIR- spectra of (A) control sample, (B) HT500-2,4-D product and (C) 2,4-D.

Pillared clay-

Pillared clays (PILCs) are interesting, 2-dimensional microporous materials to be used as adsorbents, clay mostly preferred as raw material due to its low cost, versatile nature and easy to modification. Natural clay exhibit different properties that make it use for many applications in the field of catalysis, adsorption and ion exchange, they have one main disadvantage: their lack of permanent porosity. Due to hydration Smectites swell up, but upon severe dehydration (heating) the layers collapse and the interlayer surface becomes no longer available for chemical processes. To avoid this problem, researchers found a way to prop open the clay layers by the introduction of stable pillars in the interlayer region. By doing so, a high pore volume is created. The pillared interlayered

clay (PILC) maintains its porosity during the hydration or dehydration process due to formation of rigid oxide pillar through calcinations. PILCs exhibit multi-charged centers, large area, high interlayer space and thermal stability. PILC synthesized with oxide pillars of Cr, Zr, Al, Ti, and Fe have been previously used in studies of adsorption of organic compounds^{16,101,120,122}. Among all these adsorbents, aluminium pillared clays (Al-PILCs) have the required technical specifications and the potential for use in environmental applications due to their physical and chemical stability, large surface area and stable colloidal suspension^{57,65,64}. P.Cool & E.F.Vansant, 1998 concluded that ODTMA use as a template on soil particles and it will create large pores (Fig.11)

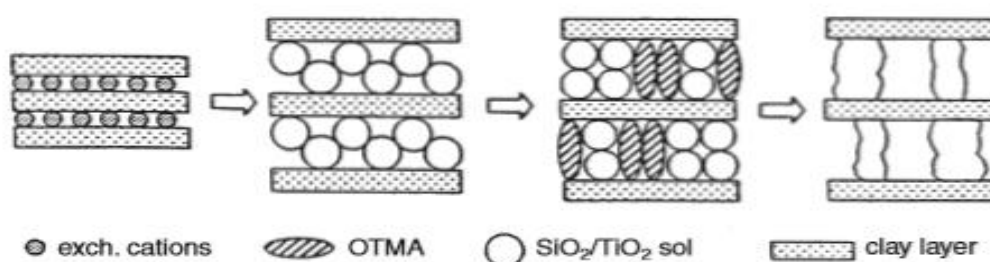


Fig. 11. SiO₂-TiO₂ pillared clay synthesized using OTMA as template

Table 4. Properties of pillared clays intercalated with polyoxycation pillars-

Pillar species	Surface area (m ² /g)	Interlayer free spacing (Å)
Al ₂ O ₃	200–400	7–10
ZrO ₂	200–300	4–14
Cr ₂ O ₃	± 300	± 12
Fe ₂ O ₃	100–300	± 15+ mesopores
TiO ₂	± 300	± 14–18+ mesopores

Interaction of pillared clay and herbicide –

Using of iron oxide pillared montmorillonite Marco-Brown *et al.*⁵⁸, studied adsorption of picloram and found that due to high specific surface area and permanent porosity under similar condition Fe-PMt retain or adsorb 150 times higher picloram (PCM) than raw Mt. The X-ray diffraction pattern (Fig. 12.) of this Mt sample showed a (001) reflection at 1.42 nm (7.3°2θ). Pyrophyllite that did not contain interlayer water has a (001) reflection at 0.92 nm³⁷. The differences between both (001) show the predominance of several hydrated layers on Mt samples³⁸. In another study Burch

and Warburton⁹, Chen *et al.*¹⁷, found that incorporation of Fe oxide in the montmorillonite interlayer resulted in the disappearance of the (001) reflection.

Yuan *et al.*¹¹⁷, found a d-spacing of 7.12 nm(1.2°2θ) for Fe-PILC, obtained with OH and Fe concentration in a ratio of [OH-]/[Fe+3]=2. Some additional work was done to consider the structure of Fe-PILC, especially the specific formation mechanism of delaminated or pillared structure; Clinard *et al.*²¹, indicated that the 7.20 nm peak might be a reflection of a porous structure, rather than being attributed to simple intercalation.

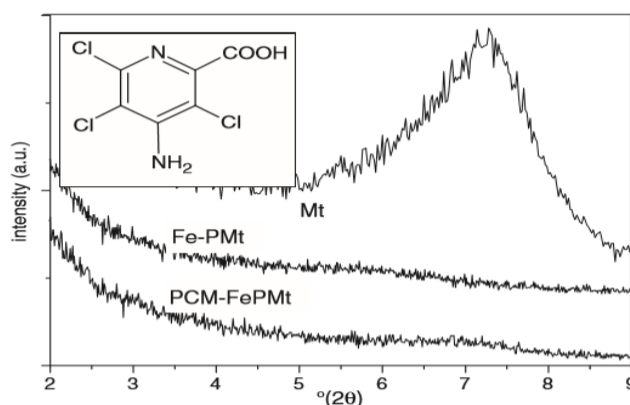


Fig. 12. XRD diffraction patterns of Mt, Fe-PMt and PCM-FeMt

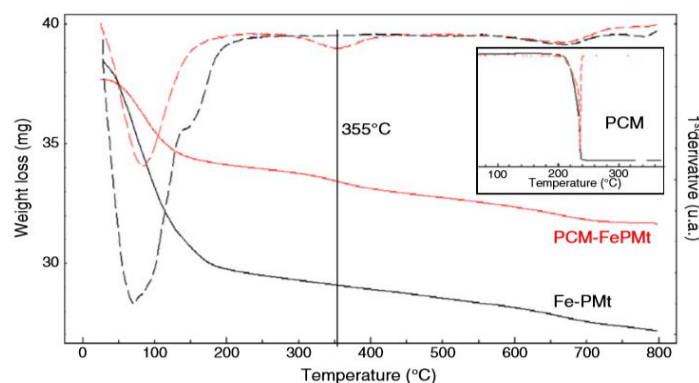


Fig.13. TGA of Fe-PMt and PCM-FePMt. Dashed line corresponds to the first derivative.

Marco-Brown *et al.*⁵⁸, also studied (Fig.13) TGA analysis that showed a strong interaction between PCM and Fe-PMt surface pointed out by the higher decomposition temperature of PCM-FePMt than Fe-PMt samples.

Factors that affecting control the release of herbicide-

Effect of pH on sorption and release of herbicides

Ziekle and Pinnavaia¹²¹, were reported that the amount of adsorbate taken up by the clay was determined at different pH. The time allowed for the attainment of equilibrium was 24 hr. Primary experiments on the uptake of mono- (di- and tri-) chlorophenol by ADL (alumina-

delaminated Laponite) indicated that equilibrium was achieved within 10 hr at pH 7.4 with using of batch-equilibrium technique. The pH decreased, adsorption increased in a more or less linear fashion. At a pH equal to or lower than the PKa of PCP (~ 4.7), adsorption was constant. At pH 7.4, the phenol exists almost exclusively in the anionic form. To investigate the possibility of coulombic interactions being involved in the binding of PCP, the pH dependency of adsorption by ADL was investigated. PCP binding to ADL at pH 4.7 was also about 13 times as greater as the amount bound at pH 7.4, at the same equilibrium concentration.

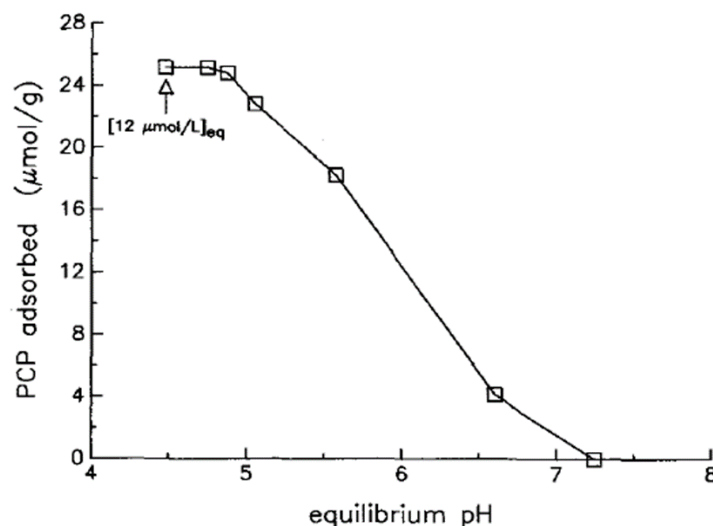


Fig.14. Effect of pH on pentachlorophenol (PCP) uptake by alumina-delaminated Laponite (ADL).

Equilibration time were 24 hr, initial PCP concentration were 38 /mole L⁻¹, solid/solution ratio = 100 mg 100 ml⁻¹.

Thus, the adsorption capacity was greater for the neutral phenol than for the phenolate form. The adsorbents used in the present investigation had pore volumes capable of accommodating between 200 and 900 μmole perfluro-tributyl-amine/g clay by vapor-phase adsorption. In contrast, the maximum amount of PCP adsorption observed in the discribed work was only 28 μmole/g for ADL (alumina-delaminated-Laponite).

Effect of time on herbicide adsorption-

Zielke and Pinnavaia¹²¹, studied that the affinities of 3,5-DCP and 3,4,5-TCP for ADL were somewhat greater, but not nearly as high

as for PCP at pH 4.7. First, the initial uptake was rapid, with more than 70% of the equilibrium loading being achieved in less than 2 hours reaction time. Second, the equilibrium loading increased as the extent of chlorination increased in the order 3-CP < 3,5-DCP < 3,4,5-TCP *i.e.*, the binding capacity was not limited by the size of the adsorbate molecule. PCP (pentachlorophenol) is a slightly different type of adsorbate than the partially chlorinated phenols. It is very sparingly soluble in water, and, consequently, the range of concentration available for investigation is more limited.

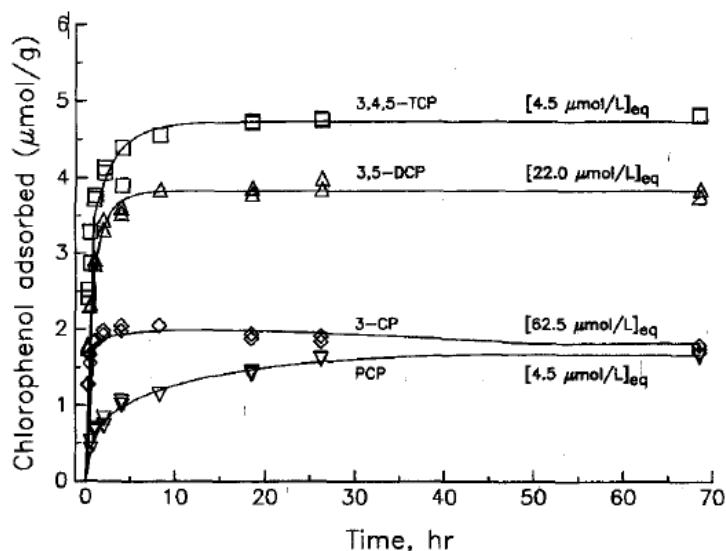


Fig. 15. Chlorophenol uptake by alumina-delaminated Laponite (ADL), Initial chlorophenol concentrations: 3-chlorophenol (3-CP), 3,5-dichlorophenol (3,5-DCP), 3,4,5-trichlorophenol (3,4,5-TCP) = 100 µmole/liter; pentachlorophenol (PCP) = 38 µmole/liter. Solid/solution ratio = 1.0 g/50 ml, equilibrium pH = 7.4.

Significantly, the amount of time required to achieve equilibrium was much longer for PCP than for the partially chlorinated phenols. Carrizosa *et al.*¹⁰, studied that the amount of non-mobile or sorbed Bentazone was greater in OCI-treated soil than un-treated soil in a given period. The amount of methanolic extractable bentazone (Fig.16) decreased as

the sorption capacity of the OCIs increased AHDT2 and with the amount of OCI added to the soil. The difference in methanol extractable bentazone between untreated and OCI-treated soil corresponds to that strongly sorbed or bound to organoclays added to the soil. 10% AHDT2 added to soil appears to be a potential tool to facilitate bioremediation.

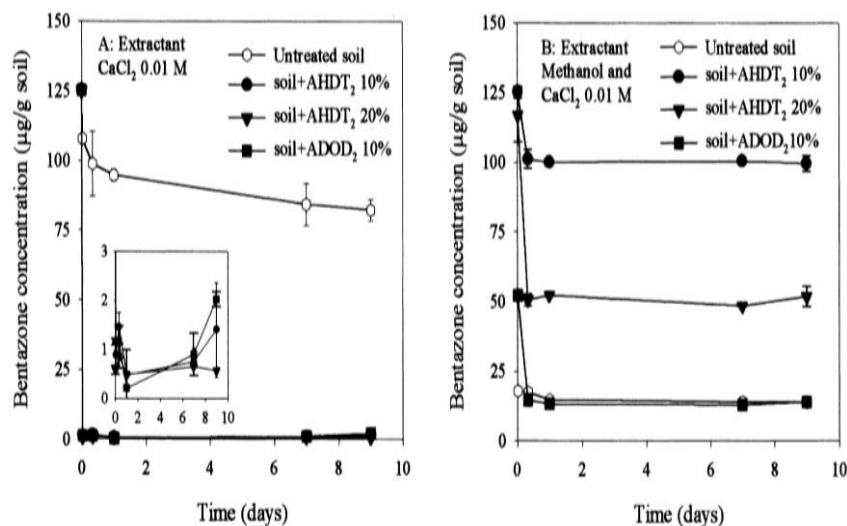


Fig. 16. Mobile (CaCl₂ 0.01 M extracted) and residual (methanol:CaCl₂ 0.01 M 80:20 extracted) Bentazone in untreated and OCI-treated soil. Initial amount of Bentazone in soil: 125 µg/g.

The total bentazone extracted from the untreated and OCI-treated soils. The total bentazone extracted with 0.01 M CaCl₂ and methanol 0.01 M CaCl₂ from the untreated and OCI-treated soils. There was a great decrease

in the availability of soil applied bentazone in the presence of the OCIs, particularly ADOD2. Despite the same sorption capacity as indicated by the isotherms for AHDT2 and ADOD2, ADOD2 showed the greatest efficacy

in arresting bentazone in soil. ADOD2 had a lower CaCl_2 : methanol extractable amount of bentazone as compared to AHDT2 and hence most of the immobilized herbicide would not be available for bioremediation. The total extractable bentazone slightly decreased in

untreated soil from 1 to 9 days, whereas it remained constant in OCl-treated soils. Pignatello and Xing⁶⁹, advised that OCl is blocking the late disappearance of bentazone in soil, which could be related to slow irreversible sorption or biodegradation.

Table 5 Total bentazone (% applied) extracted (CaCl_2 0.01 followed by methanol: CaCl_2 0.01) from untreated soil and soil-OCl mixture.

Time (days)	Untreated soil	Soil AHDT ₂ 10%	Soil AHDT ₂ 20%	Soil ADOD ₂ 10%
0.01	100 1	99 1	94 1	42 2
0.3	93 1	92 1	41 2	12 1
1	88 2	80 1	42 1	11 1
7	78 2	81 1	39 2	11 1
9	73 2	81 1	42 1	12 1

The results of bentazone desorption kinetics (Fig.17) in water, at the first sampling time, 10 min, the herbicide concentration in solution was 80% and 60% for WC-AC181-bentazone and SC-AC181-bentazone, respectively, but only 30% and 20% for WC-ADOD2-bentazone and SC-ADOD2-bentazone complexes, respectively. In all cases, the bentazone released from complexes reached the maximum concentration rapidly after 8 to

10 h. and then remained constant throughout the experiment. Less bentazone was released from ADOD2 complexes than from AC181 complexes, mainly due to the low sorptive capacity of the AC181 as compared to ADOD2. These results suggest that a part of the bentazone associated with the organic clay may be unavailable to be effective, particularly in the case of ADOD2 complexes.

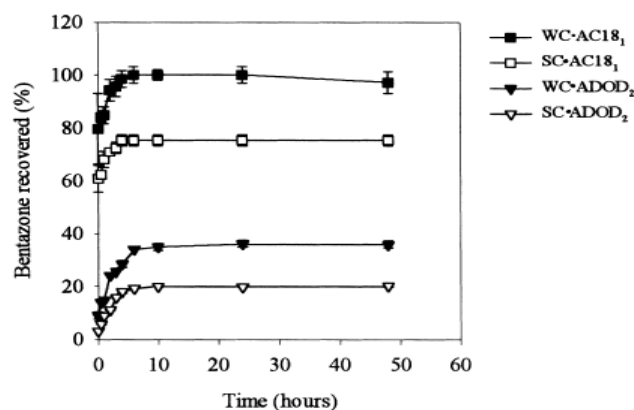


Fig. 17. Bentazone release in water from the Bentazone OCl (Organoclay) WC and WS complexes with 4% Bentazone content 10 mg complexes in 300 ml water.

The WCAC181-bentazone released (Fig.17) upto 100% of the associated herbicide suggesting this OCl was not appropriate for slow release formulations. In contrast SC-AC181-bentazone would have potential to be a controlled release formulation because 60 to 80% of bentazone would be available in water from 1 to 10 hours after that.

The maximum bentazone concentration (Fig.18) was reached after 8 h, and the concentrations decreased in the order WC-AC181>SCAC181>WC-ADOD2>SC-ADOD2. After 8 hours, a small decrease of the bentazone concentration in both technical compound and bentazoneAC181complexes WC and SC was investigated.

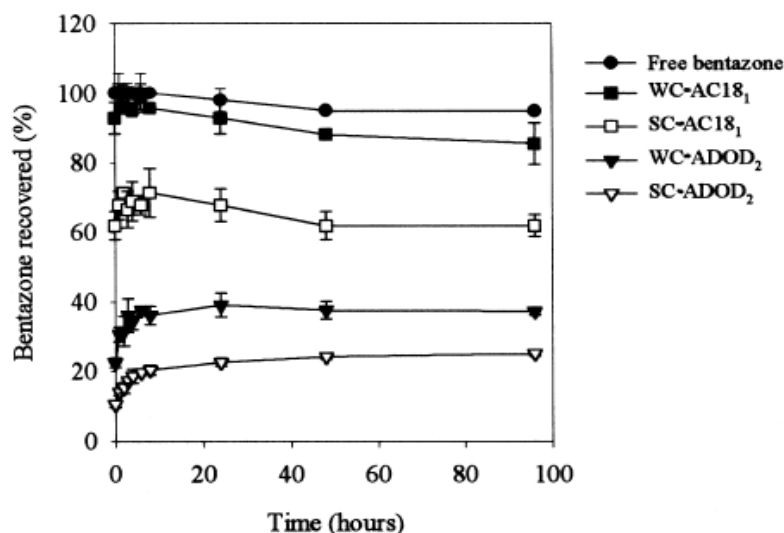


Fig.18. Bentazone release in soil/water suspension 50 g/250ml. from WC and SC bentazone OCI complexes 10 mg. with 4% bentazone complex. Free bentazone refers to the technical compound 0.4 mg. added to the soil.

The bentazone release (Fig.18) side view from soil/water suspensions for OCI-Bentazone-complexes and technically free bentazone applied to soil. The decreases in herbicide concentration could be due to slow sorption on the OCIs or degradation in soil, enhanced by the higher amount of herbicide available from low sorptive capacity of complexes SAC181 and free bentazone.

Effect of Specific Surface Area-

Carrizosa *et al.*¹⁰, also studied that the behavior of the surface-active species of the clay had an uniform more striking effect than texture on the power to bind PCP from aqueous solution. The parent clays Na-Laponite and Na-montmorillonite adsorbed no detectable amounts of PCP from aqueous solution at pH 4.7. The absence of PCP binding cannot be attributed to the lack of sufficient surface area. Na-Laponite and Na-montmorillonite have surface areas in the dry state of 269 and 75 m²/g, respectively. If these materials are dispersed in solution, the specific surface should be even larger because of swelling and layer delamination. The replacement of Na⁺ on the surface of Laponite with Keggin-like hydroxy-Al cations dramatically enhanced PCP binding. In fact, as much as 8 μmole/g was adsorbed quantitatively on HAL: The conversion of HAL to ADL on calcinations at 350~

increased the ability of the clay to adsorb PCP at higher concentration. For example, the binding capacities at an equilibrium concentration of 10 μmole/liter for ADL and HAL were 28 and 20 μmole/g, respectively.

Effect of texture –

Zielke and Pinnavaia¹²¹, investigated that the order of size difference in pore filling is compatible with the interaction of Pentachlorophenol with the dispersed surface-oxide aggregates and not with the layer silicate basal planes or edge surfaces. The greater adsorption capacity observed for aluminium-delaminated-laponite (ADL) relative to APM may have arisen because of greater dispersion and availability of the oxide aggregates in the clay having the delaminated texture.

CONCLUSIONS

Herbicide is necessary evil for whole world including India, Modified clay can decline in herbicide losses through various processes such as leaching, volatilization, runoff and Physical drift (Movement due to wind action Wind speed, drop sizes) because of high adsorbability, the herbicide retain in soil for long duration and release as required to crop plant protection. This review suggest for recommendation of modified clay with herbicide for enhance the availability of herbicides.

Researchable issues

Keeping in view the manufacturing cost of modified clay, commercial production at economic scale helps the farmers to future cultivation as a decline in the chemical cost (input).

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