ADSORPTION OF SOME ORGANIC MOLECULES ON CLAYS AND SOILS

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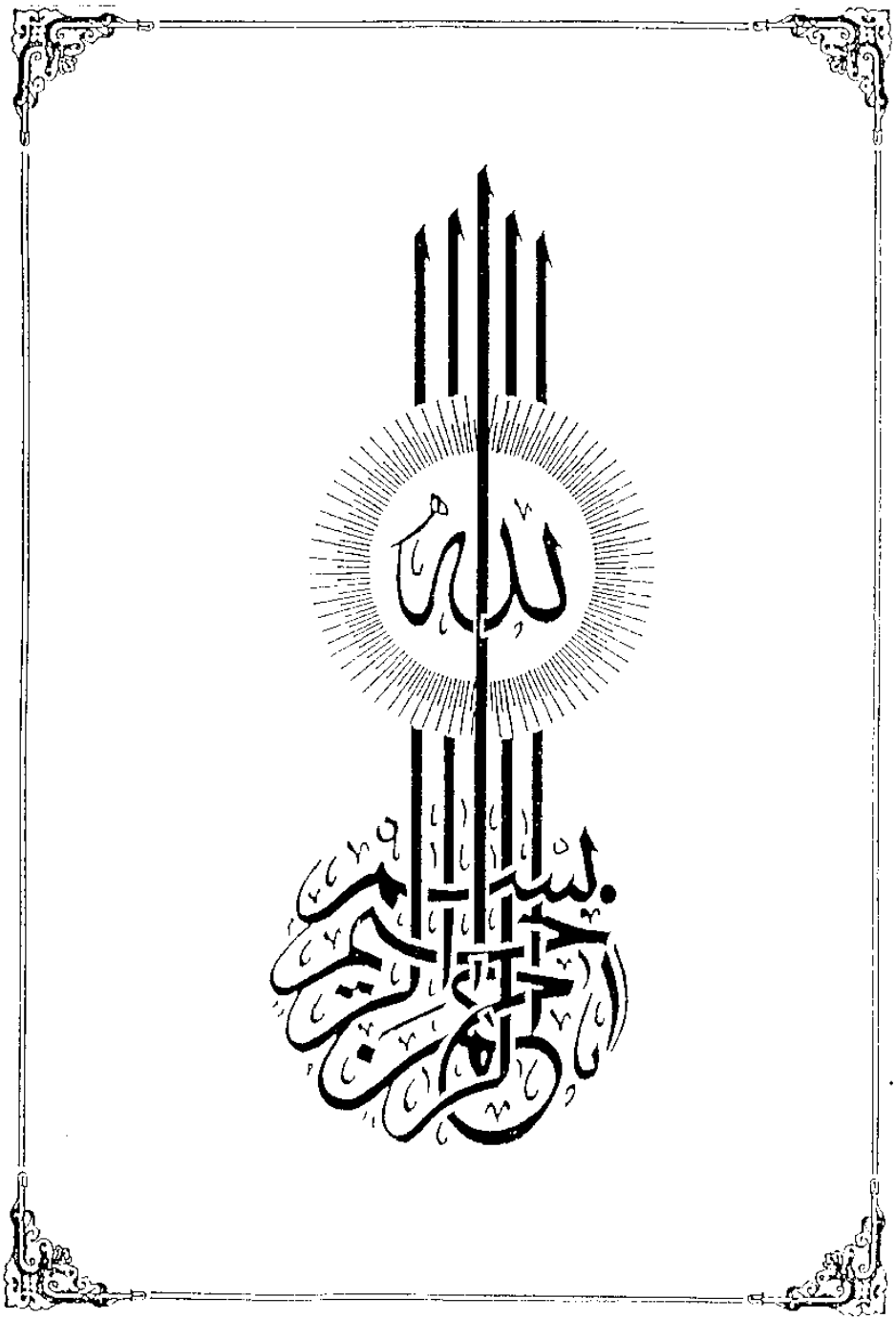

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INTRODUCTION

Adsorption is the phenomenon of binding molecules or ions on the surface of solids. Such phenomenon may cause deviations of the properties of both adsorbate and adsorbent. Studying the adsorption of organic molecules has drawn the attention of many investigators because of the widely usage of organic compounds in our practical life. Organic herbicides give an evident example for such argument; they represent one of the broad categories of pesticides used for weed control.

Applied soil herbicides are known to be absorbed by plant roots as solutes with soil water. Soil constituents modify the degree of adsorption and hence they govern the availability and/or activity of herbicides to plant.

As the application of herbicides is becoming increasingly practised in agriculture, it seems a fruitful choice to study the adsorption of some organic herbicides by clays and soils. Such study may shed light on the behaviour of some of commonly used herbicides in the soils of Egypt, namely paraquat and atrazine. Paraquat is non selective herbicide, it is used as herbicide for non crop usage, mainly for orchard weed control, as a pre-emergence herbicide and as a direct post emergence herbicide. While atrazine is a widely used selective herbicide for control of weeds grown in corn, sorghum, sugar cane and in certain orchards.

It has been believed that soils receiving heavy application of pesticides show some changes in their physical and chemical characteristics. One thought that such changes are due to herbicides application, therefore the aim of this investigation is to study such phenomina. For achieving this, adsorption and desorption of either paraquat or atrazine by soils and clays were studied. Different alluvial and calcareous soils as well as clay minerals known to be predominant in such soils were used as adsorbents. Changes in some chemical, physical and mineralogical properties of such soils and clay minerals were also investigated. X-ray diffraction and infrared spectroscopic techniques were implicated to elucidate adsorption phenomina and to follow the changes in some properties of utilized adsorbents as well.

2. REVIEW OF LITERATURE

2.1. Adsorption of herbicides on soils and clays:

It is a common notation to call synthetically prepared organic compounds used in control and/or eradication of unwanted organisms as pesticides. Herbicides are broad categories of pesticides; they are used for weed control.

The fate and behaviour of pesticides in soil systems are dependent on many factors; chemical decomposition, volatilization, movement, plant uptake and adsorption. The phenomenon of adsorption-desorption seems to influence, directly or indirectly, the magnitude of the effect of the other factors. Adsorption, therefore, appears to be one of the major factors affecting pesticide-soil colloid interactions, Bailey et al. (1968). The factors affecting the adsorption and desorption of organic pesticides are reviewed by Bailey and White (1964). Such factors are soil or colloid type, physico-chemical nature of the saturating cation on the colloid exchange site, soil moisture content, nature of formulation and temperature all directly influence the adsorption of pesticides by soil systems, whereas the physical properties of soils as a substrate as well as climate exert more indirect influence. Greenland (1965) referred two factors of importance in the adsorption of organic ions; the large number of possible points of contact between ion and adsorbent, which leads to large change

in the entropy of the system and the occurrence of specific adsorption sites which depend on the particular molecular characteristics of the cation and substrate.

Pesticides may be classified into three classes depending on their predominant charge characteristics; cationic pesticides, anionic pesticides and non-ionic or polar pesticides. Pesticides of the first group are completely ionized, adsorbed by soils and clays through ion exchange processes and also replace the inorganic cations initially present at exchange surfaces, Khan (1978).

The forces involved in the adsorption and desorption of some herbicides were studied by McCall et al. (1972) using ionic and nonionic exchange resins. They found that Picloram was adsorbed mainly in the anionic form by Coulombic forces and, to a lesser degree, by weak physical bonds at sites on the resins where there were no Coulombic forces.

Soil properties that may contribute to the adsorption of herbicides have been studied by many investigators. Harris and Warren (1964) stated that adsorption of herbicides by organic matter in soil tended to be less reversible and might actually increase with an increase in temperature. Hance (1965) concluded that organic matter content was the only soil property that could be correlated with adsorption of Diuron. Similar statement was introduced by Liu and Cibes-Viade(1973)

in their study on Fluometuron adsorption. They stated that the nature of clay minerals did not influence the amount of Aldrin adsorbed. This amount was found to be dependent on mechanical composition and organic matter content. Savage and Wauchope (1974) examined the adsorption-desorption equilibria of Fluometuron. Successive equilibrations resulted in a shift in the equilibria towards the adsorbed state, most likely due to a physical change in the adsorption capacity of the soil with repeated agitation. Desorption studies with different soils proved the importance of soil organic matter content on adsorption-desorption equilibria. Clay content of these soils was not significantly correlated with Fluometuron equilibrium constants. Day et al. (1968) found a negligible correlation between the amount of simazine causing 50% reduction in growth (GR_{50}) and pH and clay content. They added that there was a marked interrelationship between organic matter, cation exchange capacity, equilibrium concentration of simazine in the soil solution, and GR_{50} which was more closely correlated with organic matter percent than with any other factor. Swanson et al. (1954) found that the retention of Lindane was related to soil porosity which could explain why fine textured soil requires heavier application of BHC for effective results in comparison with coarse textured soils. Similar results were obtained by Kishk et al. (1979) in their

study on the adsorption of Parathion by sandy soils of El-Tahrir and the alluvial soil of El-Nahda. They concluded that clay content is an important factor in the adsorption of Parathion.

The adsorption of many pesticides, however, depends on pH. Frissel (1961) found that the adsorption of herbicides having widely different molecular structures increased as the pH decreased. There exists a negative relationship between pH and maximum adsorption. He observed a negative adsorption of certain acids as 2.4 D and 2,4,5-T on both montmorillonite and illite over certain pH ranges. The pH value at which negative adsorption ceased and positive adsorption commenced was found to be a function of both adsorbent and the adsorbate. Baily and White (1964) summarized the role of pH in the adsorption of pesticides and referred to the effect of pH on the degrees of dissociation or association of the compound, total charge on the inorganic soil colloids and solubilities of certain elements in soils that may form stable complexes with pesticides.

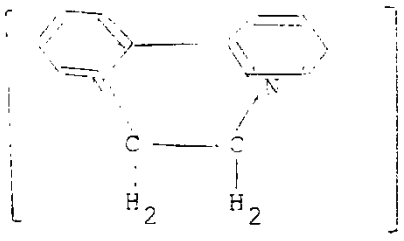
Clay minerals and amorphous materials in a soil greatly affect the adsorption process of pesticides. Jurinak (1957) indicated that the adsorption of EDB (ethylene dibromide) by natural soils is a function of the predominant clay minerals present in soil. Kaolinite and illite had higher adsorption per unit surface than montmorillonite. Frissel (1961)

reported that montmorillonite adsorbed considerably more of various herbicides, of widely different chemical character, than did illite or kaolinite as the magnitude of the exchange capacity of these minerals are in this order, thereby the suggested mechanism of adsorption is dependent on the number of exchange sites. Harris and Warren (1964) observed that adsorption of herbicides was readily occurred on bentonite than on organic matter. Dickens and Hiltbold (1967) found that the adsorption of methane arsenate by kaolinite and vermiculite increased with increasing concentration of DSMA in the equilibrium solution. Kaolinite and limonite adsorbed much more methane arsenate than vermiculite. Baily and White (1964) reviewed that clay minerals of a high cation exchange capacity such as montmorillonite and vermiculite have a great capacity for adsorption of pesticides due to the Coulombic and Van der Waals' forces, while clay minerals of low cation exchange capacity e.g. illite, Kaolinite and chlorite would not have as large an adsorption capacity as montmorillonite and vermiculite. They also mentioned that the surface area of crystalline and amorphous oxides and hydroxide of silica, iron, and aluminium appears to be similar in magnitude of that of montmorillonite and vermiculite.

2.2. Adsorption of paraquat and diquat on soils and clays:

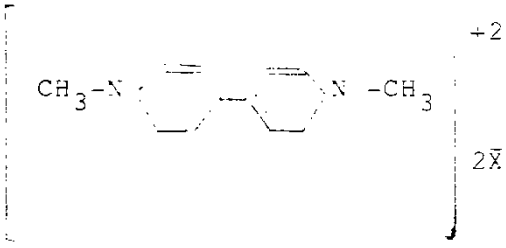
Paraquat and diquat are contact organocation herbicides usually supplied as chloride or bromide salts. Their chemical

structure are given below :



Diquat

1,1 ethylene-2,2 bipyridinium
where x: bromide



Paraquat

1,1 dimethyl-4,4 bipyridinium
where x: chloride

They are usually nominated as bipyridiniums. The common trade name of paraquat is Gramoxone, whereas for diquat is Reglone, Church (1968). Both compounds are soluble in water and dissociate to give divalent organic cations similar in compositions but differ only in the location of nitrogen atoms and, in turn, in the charges of the pyridine rings, Philen et al. (1971).

According to Knight and Tomlinson (1967) the adsorption of paraquat in mineral soils is characterized by three factors: (1) Up to a limiting value defined as the strong adsorption capacity (SAC), the solution concentration of paraquat is reduced below the level of chemical detection by suspended soil (2) Removal of soil organic matter does not greatly change SAC. Strong adsorption of paraquat is primarily a property of clay minerals and the presence of expanding lattice minerals is of particular importance (3) The adsorption of paraquat is strongly influenced by factors other than simple

electrostatic interaction. Weber et al. (1965) found that diquat and paraquat were completely adsorbed by montmorillonite and Kaolinite clays to the CEC. Adsorption on montmorillonite appeared to be primarily by the Coulombic forces of ion exchange supplemented by Van der Waals' forces. The cations were held in the clay lattice with the plane of the ring parallel to the silicate sheets. Adsorption of the cations by Kaolinite was on the edges or faces of the clay particles and the bonding was not as strong as that of the montmorillonite system. Haqua et al. (1970) in their study on the adsorption of paraquat on montmorillonite using infrared and ultraviolet spectroscopy, found that diquat and paraquat form associated complexes on montmorillonite surface. They concluded that the charge transfer mechanism between the organic cation and the anionic silicate framework may also be involved. Philen et al. (1971) postulated that the relative preference for diquat demonstrates two linear relationships, one for internal adsorption and the other for external adsorption. Internal adsorption is characterized by a strong preference for paraquat on low charged smectites; a relative decreasing preference for paraquat with higher charged smectites, and a strong preference for diquat on highly charged expanded vermiculite. They also showed that preferential adsorption for paraquat by Kaolinite is quite similar to its adsorption on the external sites of vermiculites. Weber and Weed (1974)