CHAPTER I

INTRODUCTION
Ion exchange is one of the most versatile techniques of separation science. It is at present a standard analytical tool and is widely used in inorganic, organic and biochemical separations. In laboratories ion exchangers are being used as an important tool to solve new problems. Rapid and accurate determination of the constituents of a sample or contaminants of alloys, biological substances and fission products of radioactive elements has become possible by the use of ion exchangers. The use of ion exchangers on large scale may provide mankind with pure water and may be useful for the concentration and extraction of important metals and raw materials which are becoming more and more difficult to produce. Ion exchange has also been established as one of the most powerful techniques in the field of soil analysis thus proving its worth in soil pollution control.

Ion exchange was first reported by the name of base exchange nearly 150 years ago when an English land owner H.S. Thompson became interested in studying the loss of ammonia from manure heaps. He engaged a York Scientist named Spence to investigate this loss. Spence discovered this loss as an exchange
process between calcium (from soil) and ammonia (from manure).

\[ \text{Ca (soil)} + (\text{NH}_4)_2\text{SO}_4 \rightarrow \text{NH}_4 \text{(soil)} + \text{CaSO}_4 \quad \text{(1)} \]

Spence reported his discoveries to the Royal Agricultural Society [1]. These were further confirmed by another agricultural chemist G.T. Way [2] who described this exchange by the name of base exchange. This phenomenon could not be elaborated further as much was not known about the ionic nature of solutions and the crystal structure and composition of the clay minerals present in the soil. Many hypotheses were given to explain this exchange in soils [3] but ultimately it was traced mainly due to the presence of aluminosilicates [4]. The two principal causes responsible for ion exchange property of soils are organic matter and clay minerals [5,6]. The soils rich in organic matter contain humins and humic acid which on decomposition produce a wide variety of organic species, possessing -OH or -COOH groups. These groups are responsible for the ion exchange property in such soils. The soils which do not contain much organic matter also possess a considerable ion exchange property due to
the presence of crystallographic surfaces (clay minerals) with exchangeable sites.

Ion Exchange in soils is a reversible process. Of the two phenomena, cation and anion exchange, the first is generally considered to be more important since the anion and molecular retention capacity of most agricultural soils is much smaller than the cation retention capacity. This property of cation exchange is one of the major distinguishing features between soils and other plant rooting media. Because cations are positively charged, they are attracted to surfaces that are negatively charged. In the organic fraction these arise from the dissociation of $H^+$ from certain functional groups particularly from carboxylic ($-\text{COOH}$) and phenolic ($-\text{C}_6\text{H}_4\text{OH}$) groups.

$$-\text{COOH} \rightleftharpoons \text{COO}^- + H^+ \quad ....(2)$$

$$-\text{C}_6\text{H}_4\text{OH} \rightleftharpoons -\text{C}_6\text{H}_4\text{O}^- + H^+ \quad ....(3)$$

The carboxylic and the phenolic groups dissociate leaving a negative charge at the site of the functional groups (equations 2 and 3). It is estimated that 85 to 90% of the negative charge of
humus is due to these two functional groups. Two other groups enol (\(-\text{COH} = \text{CH}\)) and imide (\(=\text{NH}\)) also contribute to the negative charge of the organic matter. Negative charges in the clay fraction generally arise from two sources. The first is isomorphous substitution in layer silicate minerals and the second is caused by the deprotonation of both (i) hydroxyl groups (\(-\text{OH}\)) attached to the silicon atoms at the broken edges of the tetrahedral planes and (ii) exposed \(\text{AlOH}\) groups in layer silicates. The charge resulting from isomorphous substitution arises from the replacement of a silicon or aluminium atom by an atom of similar geometry but of lower charge (e.g. \(\text{Mg}^{2+}\) for \(\text{Al}^{3+}\) or \(\text{Al}^{3+}\) for \(\text{Si}^{4+}\)). This produces a net negative charge which is fairly uniformly distributed over the plate shaped clay particles. Negative charges also form at the edges of clay plates by reactions such as

\[
-\text{SiOH} + \text{OH}^- \rightleftharpoons \text{SiO}^- + \text{H}_2\text{O} \quad \ldots(4)
\]
\[
-\text{AlOH} + \text{OH}^- \rightleftharpoons \text{AlO}^- + \text{H}_2\text{O} \quad \ldots(5)
\]

The negative charge that develops on organic and mineral colloids is neutralized by cations attracted to the surfaces of these colloids. The quantity of cations expressed in milliequivalents is termed the
cation exchange capacity of the soil. It is one of the important chemical properties of soils and is usually closely related to soil fertility. Carboxyl and phenolic hydroxyl functional groups contribute most to the cation exchange capacity. This can be predicted from the analysis of titration data [7,8], from functional group analysis, infrared spectroscopy (in the case of carboxyls) and from the identification of products released from the degradation of the polymer [9]. Base saturation is another important property of a soil and generally reflects the extent of leaching and weathering of the soil. It is defined as the percentage of the total cation exchange capacity occupied by such basic cations as calcium, magnesium, sodium and potassium. Cation exchange capacity of a soil is not a fixed quantity but is dependent on the soil pH. Numerous studies have shown that the cation exchange capacity of soils is a continuous function of pH, with this value being lowest in the acid range, pH 3 to 4 and increasing continuously as the pH increases up to the alkaline range, pH 8 to 9. This increase in cation exchange capacity with increasing pH is caused by the ionization of the OH groups at the edges of the clay
lattice and on the hydrous Al or Fe oxides and from the carboxyl and phenolic groups present in soil organic matter. Contrary to cation exchange, the capacity for retaining anions increases with a decrease in soil pH. Further anion exchange is much greater in soils high in clays and those containing hydrous oxides of iron and aluminium. Anions may be retained by soil particles through a number of reactions, some of which are simply electrostatic [10] and are described as non specific. The positive charge sites responsible for electrostatic adsorption and exchange of anions originate in the broken bonds primarily in the alumina octahedral sheet, exposing OH groups on the edges of clay minerals.

A spectacular revolution began in 1935 with the discovery by two English Chemists, Adams and Holmes, that crushed phonograph records exhibit ion exchange properties. This led them to the synthesis of organic ion exchange resins [11], which consist of three dimensional networks of polymeric chains cross linked with short chains containing ionizable functional groups. Various improvements were made in the resins. A typical resin is prepared by polymerization of styrene and divinyl-benzene. The number of
cross-linkage is governed by divinylbenzene to styrene ratio. Organic ion exchange resins are stable towards acids. Their structure can be varied as desired. An increase in cross linkage increases rigidity, reduces swelling and the solubility of polymeric structure. Organic resins have been used in laboratories and industries for separations, recoveries of metals, purification of water, concentration of electrolytes and elucidation of the mechanism of many reactions. Several commercial resins, both cation (strong and weak acid) and anion (strong and weak base) exchangers are available for this purpose.

Cation exchange in soils is of great importance as it can alter the availability of several micronutrients [12]. In soils a number of cations may be present in trace quantities such as cobalt, copper etc., which are very beneficial to plants. A study of cation exchange in soils gives an idea about the capability of the soils to store [13] and supply [14] the nutrient elements to plants.

Adsorption at soil surface exerts the most profound influence of the several processes operating to determine the fate and behaviour of pesticides in
soil. It governs the relative availability of a pesticide, its volatilisation, physical distribution, breakdown, biological activity and even its susceptibility to microbial metabolism. It depends upon the nature and properties of the pesticide such as acidity, basicity, solubility, shape and configuration, charge distribution, polarity of molecule, molecular size and polarizability and its concentration in the solvent. The literature on this aspect has been reviewed by Bailey and White [15].

Several workers [16-33] have reported that the extent of pesticides on soils depends upon the clay content, organic matter content, cation exchange capacity, pH, moisture, exchangeable cations, temperature and other environmental conditions.

Organic matter is the most important of factors operating which determine the adsorption and fate of pesticide in soil. Stevenson [34] pointed out that information on the nature of organic matter-pesticide interactions may provide a more rational basis for their effective use, thereby reducing undesirable side effects due to carry-over and contamination of the environment. However, a proper
explanation of the precise nature of these interactions is hindered due to the complexity of organic matter and the numerous other interactions in the soil environment all operating simultaneously. In recent years careful studies with simplified systems involving well-defined organic matter components have resulted in the elucidation of some of the mechanisms of interactions. The merits of using organic matter components, such as humic acid and fulvic acid are:

1. They can be readily extracted from soil organic matter in relatively pure form
2. They have been thoroughly characterized by various techniques and
3. They are the major and common constituents of soil organic matter.

A limitation that needs to be considered in adsorption of pests on soil surface is that in most mineral soils, organic matter and clay minerals are intimately associated in the form of clay-organic matter complexes. Thus, organic matter may not function as a separate entity and its relative contribution in pesticide adsorption will depend upon the extent to which the clay is coated with organic matter [34]. However, it should be realized that the
association of organic matter with clay still provides an organic surface for adsorption [34].

The texture and structure of soil also play a very important role in adsorption process. The soils having two layer clay mineral i.e. kaolinite, three layer clay minerals, montmorillonite, illite or hydrated aluminium and iron oxide surfaces of oxygen atoms or OH-groups are available for adsorption including hydrogen bonding. The clay are generally negatively charged and have exchangeable cations such as $\text{H}^+$, $\text{Na}^+$ and $\text{Ca}^{2+}$ on their exterior surfaces (two layer minerals) or on their both exterior and interior surfaces (three layer minerals). Montmorillonite clays have higher surface area and cation exchange capacities followed by illite and kaolinite. All these clays strongly adsorb organic cations [35-37]. Clay minerals probably do not adsorb anions by anion-exchange, the layers of OH-groups of kaolinite are not exchangeable and number of edge OH-groups for kaolinite and montmorillonite is small. Hydrated Al and Fe-oxide associated with clay are probably responsible for adsorption of anions by anion-exchange.
Adsorption is of two types physical and chemical called as "physisorption" and "chemisorption" respectively. In the former the molecules are adsorbed to a solid surface by essentially the physical forces. In chemisorption, however, the molecule forms the chemical bonds with the solid surface. In case of physical adsorption there are vander waal's interactions (for instance dispersion or polar interaction) between the surface and the adsorbed molecule. These are weak types of interactions and the amount of energy released when a molecule is physisorbed is of the order of 25 kJ mol\(^{-1}\) i.e. the enthalpy of condensation. This energy can be adsorbed by the vibration of the lattice and is dissipated as heat. A molecule bouncing across the surface will loose its kinetic energy and stick to the surface resulting in the rise in temperature of the system, i.e. heat is evolved. In chemisorption which is shortening of chemical adsorption the molecules stick to the surface as a result of the formation of chemical bonds, usually covalent bonds and tend to find the sites that increase their coordination number.
with the temperature. Thus the energy of attachment is greater than in that of physical sorption and is in the range of 40 KJ mol\(^{-1}\) to 200 KJ mol\(^{-1}\). Sorption equilibria of Pb and Cu\(^{2+}\) has been discussed in our earlier studies \[38,39\]. For a spontaneous process chemisorption must be exothermic (barring the exceptional case). This can be explained as follows:

For a spontaneous process \(\Delta G\) should be negative. As the species is adsorbed there is a reduction in its translational freedom so \(\Delta S\) is also negative. Hence \(\Delta H\) must be negative if \(\Delta G=\Delta H+T\Delta S\) is to be negative and a negative \(\Delta H\) value corresponds to the exothermic process. But sometimes the adsorbate dissociates at high temperature leading to breaking of bonds and thus has high translational mobility on the surface as in case of the adsorption of hydrogen on the glass surface, enthalpy is small and positive.

A formal distinction between the chemisorption and physiosorption was formerly the magnitude of the enthalpy of adsorbed ion. \(\Delta H\) for physiosorption is rarely more negative than about -25 KJ mol\(^{-1}\) while that for chemisorption it is usually more negative and sometimes much more negative than -40 KJ mol\(^{-1}\).
Plotting of adsorption isotherms is the most convenient way of studying and understanding the nature of adsorption taking place in a particular system. The isotherms are obtained by plotting the amount adsorbed against the equilibrium concentration at any instant at a particular temperature. Thus different types of curves with different slopes and initial portion of the curve are obtained. Based on these factors adsorption isotherms can be divided into four main classes and thereafter into subgroups. The main classes are as follows:

(a) Langmuir isotherm or L curves
(b) S. type of isotherms
(c) High affinity isotherm or H curves
(d) Constant partition or C curves.

Langmuir isotherms indicate that molecules are adsorbed flat on the surface or sometimes vertically oriented with strong intermolecular attraction. This is the best known isotherm. These curves occur in majority of cases of adsorption from dilute solution and for cases of the other types appear to have been previously recorded. The initial slope depends on the rate of change of site availa-
bility with increase in solute adsorbed. As more solute is taken up, there is usually progressively less chance that a bombarding solute molecule will find a suitable site on which it can be adsorbed. The initial curvature shows that as more sites in the substrate are filled it becomes increasingly difficult for a bombarding solute molecule to find out a vacant site available. This implies that either the adsorbed solute molecule is not vertically oriented or there is no strong competition from the solvent. The types of systems which give this curve have one of the following characteristics.

(i) The adsorbed molecules are most likely to be adsorbed flat eg. resorcinol on alumina (ii) if adsorbed end on they encounter little solvent competition eg. high polar solute on substrate or systems with monofunctional ionic substances with strong intermolecular attraction.

S type curves indicate the vertical orientation of the adsorbed molecule at that surface. The initial part of the S curve shows that more solute is already adsorbed and it is easier for the additional amount to become fixed.
High affinity curves are given by solutes adsorbed as ionic micelles and by high affinity ions exchanging with low affinity ions. This is a special case of L curve in which the solute has such high affinity that in dilute solution it is completely adsorbed or at least there is measurable amount remaining in the solution. Thus the initial part is vertical. The adsorbed species are often large units i.e. ionic micelles or polymeric molecules, but sometimes they are apparently single ions which exchange with other ions of much lower affinity for the surface eg. sulfonated dye ions exchange with Cl⁻ alumina, cyanide dye on silver halide. In the most extreme cases the curve is a horizontal line running into the vertical axis.

And lastly the constant partition curves or the linear curves are obtained when the solute penetrates into the solid more readily than does the solvent. There is a constant distribution of solute between solution and substrate up to the maximum possible adsorption where an abrupt change to a horizontal plateau occurs. Such type of curves are obtained for the partition of a solute between two immiscible solvents. Favourable conditions for "C"
curve to appear are: (a) A porous substrate with flexible molecule and regions of differing degree of crystallinity and a solute with (b) higher affinity for the substrate than the solvent has and with (c) better penetrating power by virtue of conditions (d) and of molecular geometry, into the crystalline regions of the substrate.

The subgroups of these classes are arranged according to the shape of the parts of the curves farther from the origin, and the significance of plateau and changes of slope are described. Fundamentally, the linearity shows that the number of sites for adsorption remain constant i.e. as more solute is adsorbed more sites must be created. Such a situation arises when the solute has a higher attraction for the adsorbent than the solvent itself has. Thus the solute can break the inter substrate bond more readily than the solvent could, and if its molecular dimensions were suitable, it could penetrate to the structure of the substrate in regions not already penetrated by the solvent. This action has been compared to the opening of a zip fastener, the fastening represents the intermolecular bonds of the substrate, and the slider represents the first molecule or group of molecule of solute to penetrate.
This opens up the structure and allows more solute molecule to enter. This action stops abruptly when more highly crystalline regions of the substrate are reached. In fact the isotherms usually do suddenly change direction to give the horizontal plateau. Thus a linear isotherm indicates that the solute is penetrating the regions inaccessible to the solvent.

Nearly all sufficiently complete curves have either a plateau or an inflection (knee). Those that do not have plateau or knee are clearly incomplete i.e. surface saturation is not reached probably because of experimental difficulties. The plateau or the beginning of the linear portion above the "knee" must represent the "first degree saturation" of the surface i.e. the condition in which all possible sites in the original surface are filled and further the adsorption can take place only in new surface. For convenience this degree of coverage may be called the formation of a complete monolayer but this does not necessarily imply that it is a close packed layer of single molecule or ions, as in a compressed monolayer on water. It may be so in some cases and when it is specific surface area determination can readily be made. Generally however the layer may (a)
contain solvent as well as solute molecule or (b) consist only of isolated cluster of solute molecule adsorbed on the most active sites or (c) consists of ionic micelle either packed closely or well separated.

The significance of a long plateau must be that a high energy has to be overcome before additional adsorption can occur on new sites, after the surface has been saturated to the first degree. The solute has high affinity for the solvent but low affinity for the layer of solute molecule already adsorbed. Adsorption of ionic micelles give curves with long plateau. In this case the solid surface when covered will tend to repel other micelles holding the same charge. A short plateau means that the adsorbed solute molecule expose a surface which has nearly the same affinity for more solute as the original surface had.

Second rise or plateau are attributed to the development of a fresh surface on which adsorption can occur. The second plateau represents the complete saturation of the new surface.
The different models for adsorption applicable to both gases and liquids, are available in literature. They are however being discussed in brief as follows.

(1) Langmuir Model

Langmuir proposed

$$\frac{C_e}{A_m} = \frac{1}{K} x \frac{1}{b} + \left(\frac{1}{b}\right) C_e$$       \hspace{1cm} ....(6)

Where $C_e$ is the equilibrium concentration and $A_m$ is the amount adsorbed per specified amount of adsorbent. $K$ is the equilibrium constant and $b$ is the amount of adsorbate required to form a monolayer. Hence a plot of $C_e/A_m$ Vs $C_e$ should be a straight line, with a slope equal to $1/b$ and $\frac{1}{K} \cdot \frac{1}{b}$ as intercept.

(II) Freundlich Model

According to this model

$$A_m = K \ C_e^{1/n}$$       \hspace{1cm} ....(7)

$$\ln A_m = \ln K + \frac{1}{n} \ln C_e$$       \hspace{1cm} ....(8)

Where all the terms have the usual significance and $n$ is an empirical constant, thus a plot of $\ln A_m$ Vs $\ln C_e$ should give a straight line with a slope equal to
$1/n$ and intercept gives the value of $\ln K$.

This model deals with the multilayer adsorption of the substance on the adsorbent.

Pollution is an undesirable change in the physical, chemical and biological characteristics of our air, water and soil that may or will harmfully affect human life, industrial progress, living conditions and cultural assets. Pollution is a man-made problem. Man-made pollutants not only damage environment, health, vegetation and materials, but also interfere with climate. Pollution involves an unhealthy mixture of foreign matter or energy into air, water and soil which makes it harmful to life activities. Air is easily polluted by gases, smoke, dust, etc., which are lighter objects and get mixed up in the atmosphere. Effluent from industry and human settlements have turned many great rivers and lakes murky. Dumping of industrial wastes containing poisonous chemicals has caused serious damage to agricultural lands and destruction of scenery. Effect of polluted irrigation water on crop plants show deleterious effects and decreases productivity. The grain quality is affected by heavy metals i.e. lead,
zinc etc. and pesticides which get accumulated in these. Soil provides us a place to live and is a reservoir of minerals but with accelerating growth of the world's population and rapid urbanisation tremendous pressure has been created on it.

Insecticides, Herbicides and other pesticides aiding agricultural development and health protection are very potent pollutants having long range effects and their indiscriminate use poses a serious danger to the structure and function of the ecosystems. To contain the menace of pollution it is necessary to educate people at all levels to conserve the environmental resources, and to find ways and means to effectively reduce the pollution hazards which are already existing. Man pollutes the environment by using it too much and then throwing off too much of the unused matter this brings an imbalance in the ecosystem.

With the emerging new Science and technology there has been improvement in the quality of life and its expectancy. With the ever increasing trend in the world population, problems of food, health and hygiene are widening day by day [40] and putting
pressure on man to increase agricultural production which has led to greater exploitation of land, frequent use of pesticides and other agrochemicals. When soils come in contact with pesticides their physico-chemical and biotic properties are affected. The indiscriminate use of pesticides can pose a serious danger both to the human health and the environment [41]. Pesticides while eliminating the beneficial insects may cause ecological imbalance. At the same time they are phytotoxic and destroy useful plants. They enter the food chain causing toxicity to human beings, animals and other creatures. Quite a large amount of pesticides reaches the water resources causing toxicity to flora and fauna. By and large, pesticides are toxic chemical substances which are used to kill pests of widely different taxonomic categories. The pesticides are commonly characterized on the basis of target group of organisms such as fungicides against fungus, insecticides against insects, herbicides against herbs, nematicides against nematodes etc. Roughly one third of the crops are lost due to insects, pests, weeds and other diseases. On an average, farmers lose between 40 to 50 percent of their crops before harvest. Although, the turn of the present century
would see an enormous increase in food production, particularly in the developing countries, still the Food and Agricultural Organisation of United Nations foresee that by the year 2000 A.D. there will be scarcity of food especially in Africa, Latin America and parts of Asia. This brings into sharp focus the dire need for plant protection. The use of pesticides is expected to increase immensely as the crops would need an effective plant protection umbrella in the time to come.

This chemical crop protection is nothing but a profit induced poisoning of the environment. Many books [42-47] and reviews [48-50] have been published and symposia organised on the subject as a warning of the potential hazards. According to the World Health Organisation report every minute someone is poisoned by pesticides in the developing countries. A pesticide caused death occurs every one hour and 45 minutes in the third world countries. Consequently there is a growing concern about the use of pesticides throughout the world. A matter of serious thought is the fact that about half of the pesticide poisoning cases leading to death are from the third
world countries although these account for only 15 percent of the total consumption of pesticides. This is a pointer towards indiscriminate use and lack of awareness about the hazardous side effects of pesticides.

Generally pesticides are classified into two broad categories namely -

(i) Inorganic Pesticides
(ii) Organic Pesticides

**Inorganic Pesticides** : Several, inorganic compounds containing arsenic, lead, copper, antimony, boron, and zinc are known as inorganic pesticides. Some of the examples of well known inorganic pesticides are

(I) arsenic compounds such as paris green\(\{(CH_3COO)_2Cu_2 \cdot 3Cu(AsO_2)\_2\}\), basic copper arsenate \(\text{Cu (CuO \cdot HAsO}_4\) \)

(ii) fluorine compounds such as calcium fluosilicate \((\text{CaSiF}_6 \cdot 2\text{H}_2\text{O})\)

(iii) Mercury compounds such as mercuric chloride \((\text{HgCl}_2)\)

(iv) boron compounds such as borax \((\text{Na}_2\text{B}_4\text{O}_7)\).

The use of inorganic pesticides [44] to kill pests is not a new concept. These inorganic pesticides are known to cause several harmful effects. Arsenical
poisons and boron causes mutations in the reproductive parts of the plants causing semi-permanent sterility while copper ions react with enzymes having reactive sulphydryl groups, which explains their toxicity to all forms of plant life. Many enzymes containing iron, calcium, magnesium are inhibited by fluoride ions. Accumulation of lead in the body causes coagulation of body protein disrupting seriously the metabolic activities, it is also mutagenic when accumulated in the body tissues, mercury causes blurred vision, severe illnesses, headache and abnormalities not only in the person exposed but also in the next generation to come. Zinc accumulation results in the disintegration of liver, kidneys and heart.

Organic Pesticides : The era of organic pesticides began in 1939 [51] when the first wonder pesticide Dichlorodiphenyl trichloroethane (DDT) was discovered, although it was synthesised in 1874 by Zeidler. Its insecticidal properties were discovered by Muellarr in 1939 for which he was awarded the Nobel Prize. This was soon followed by Benzenehexachloride (BHC). Since then thousands of compounds have been synthesized and
tested for their pesticidal properties. More than 1200 pesticides were registered by the United States Environmental Protection Agency (USEPA) [52]. Of these, 275 were herbicides, 400 were insecticides, 200 were fungicides and nematicides, 100 were rodenticides and 275 were disinfectants, all being sold in the form of 30,000 or so products or formulations.

Organic Pesticides have been classified as:

(a) Organohalogenated Pesticides.
(b) Organophosphorus & Sulphur containing pesticides.
(c) Organocarbamate pesticides.
(d) Pyrethroids.
(e) Miscellaneous Pesticides.

**Organohalogenated Pesticides**: Several organohalogenated pesticides such as Aldrin, DDT, BHC, Endosulphan etc. are used for crop protection. These pesticides belong to the following sub-groups (I) Diphenyl aliphatics having an aliphatic or straight carbon chain with two diphenyl rings attached e.g. DDT, DDD chlorobenzilate, dicofol, perthane. (II)
Chlorinated benzene ring structure e.g. BHC and lindane (III) Cyclodienes having three dimensional structure with active stereoisomers e.g. aldrin, dieldrin, endosulphan and heptachlor(IV) Polychloroterpenes e.g. strobane and toxaphene.

These pesticides are toxic to insects and other arthropods at very low dose. The cost is low because of their high persistency. Few annual treatments are necessary to maintain pest at low levels. These compounds tend to accumulate in food chains. These compounds are well soluble in organic solvents including fat but are poorly soluble in water.

Organophosphorus and Sulphur containing pesticides:

These pesticides have a wide range of toxicity. They are known to inhibit the activity of the enzyme, acetylcholinesterase. During the course of their action they result in excessive sweating, headache, giddiness, blurred vision and muscular weakness. They also bring about destruction of myelin sheaths of sciatic and spinal nerves. High dosage leads to rapid paralysis and possible death.
Organocarbamate Pesticides: Carbamate belong to a new and comparatively small group of pesticides of growing utility. They bridge the gap between the persistent organochlorine and the short lived but excessively toxic organophosphorus pesticides. This group includes highly effective systemic pesticides such as aldicarb, baygon, carbaryl, carbofuran, lannate and oxamyl. The mode of action of carbamate is similar to that of organophosphorus pesticides.

Pyrethroids: The first synthetic pyrethroid was described in 1973 and many new photostable pyrethroids were synthesized between 1973-1977. These compounds exhibit high activity against insects, low mammalian toxicity, greatly increased stability effectiveness at very low dosages, rapid action and degradation to innocuous residues. These compounds are more effective as contact pesticides and a lesser extent as stomach poisons. The following compounds are registered to be marketed in India - Permethrin, Cypermethrin, Decamethrin and Fenvalerate.

Miscellaneous Pesticides: Since search and synthesis of new pesticides has always been in consideration
and with time more and more pesticides are being listed which do not fall in any of the above categories. To cite a few are formamidines, amitraz and chlorodimeform, thiocyanates, lethane 384 and thanite dinitrophenol dinocap, organotins, pyrethrins, rotenones and triazines. These compounds also have slow deleterious effect on the health of the crops, soil organisms and human beings. When these compounds are applied to soil or to standing crops, they are adsorbed and move to a certain depth in soil depending upon various soil properties and may pollute the sub-soil water.

Pesticides are introduced into the soil for destroying soil-dwelling pests, nematodes and the pathogens of bacterial and fungal diseases. Pesticides also get into the soil after treatment of the green organs of plants: they are washed off by atmospheric precipitation and carried off by the wind. The property of pesticides to withstand the decomposing action of physical, chemical and biological (biochemical and microbiological) processes characterize their persistence. Depending on the conditions, poisonous chemicals may remain in the soil unchanged and retain their toxicity for a
more or less prolonged period. The persistence of various compounds when studied in the same conditions (or of the same compound but in different soils) is characterized by the parameter $t_\frac{1}{2}$ (the half life) which denotes the time during which the content of the relevant pesticide in the soil is halved in comparison with the original amount.

The persistence of pesticides in the soil depends on their chemical and physical properties, the dose, formulation (powder, liquid etc.) the type of soil, its moisture content, temperature and physical properties, the composition of the soil microflora, the specific composition of the growing plants and the features of soil tilling. Pesticides incorporated into the soil in the form of granules persist in it for a longer time than powders or liquid substances. Pesticides as a rule are more persistent in soils with a high content of organic matter and a silt fraction. Pesticides and their metabolites are found in the soil in a labile state with all three of its phases and can therefore migrate along the soil profile in a horizontal and vertical directions. Poisonous chemicals move in the soils owing to molecular diffusion with the capillary
moisture, the descending flow of gravitational water, the root system of plants and as a result of displacement when the soil is being tilled. Pesticides travel over large distances with the stream of water appearing after rainfall or irrigation. The rate and depth of vertical movement depend on the solubility and dose of the pesticide, the features of its adsorption and desorption, its volatility (vapour pressure), and also on the intensity of evaporation of the soil moisture.

Pesticides become modified or completely decomposed in the soil as a result of physicochemical processes, microbiological decomposition and the sorption by higher plants and the soil fauna. Many pesticides become detoxicated owing to their adsorption by humus and other colloids or to the formation of stable complexes in the soil. Poisonous chemicals are removed from the soil as a result of volatilization, evaporation with water vapour, migration beyond the root habitat layer, washing out by rain water, melted snow, irrigation, ground and soil water.

Pesticides incorporated into the soil lose a part of their activity because of their being
adsorbed by the soil colloids. The degree of adsorption of most pesticides largely depends on the humus content in the soil. In the adsorption of pesticides, the adsorption surface of the soil and the degree of its affinity to a given pesticide (the magnitude of the surface energy) are of major importance. Adsorption of some pesticides may also depend on the pH, pK, and hydrolytic acidity of the soil. The degree of adsorption of pesticides depends not so much on the content of the clay and silt particles in the soil as on the nature and origin of the clay minerals that are distinguished by the magnitude of the surface of the particles and the structure of their crystal lattice. Consequently, the nature of adsorption of a pesticide will vary depending on whether an anion or a cation is the active part of a pesticide molecule or whether its molecule is ampholytic or electrically neutral and does not dissociates. The degree of adsorption of pesticides by the soil depends greatly on its moisture content. The larger the amount of water sorbed by the colloids, smaller is the free space remaining for the adsorption of pesticides. The nature of adsorption also depends on the chemical structure of the pesticide, its basicity and on the properties of its functional groups to form hydrogen
and dipole bonds. The adsorption of pesticides in the soil also depends on its temperature. This is of practical significance because triazine incorporated into the soil in cold and damp weather are adsorbed in the top layer of the soil, which prevents their being washed out or decomposed. Becoming desorbed when the weather gets warmer, they again exhibit their activity. Precipitation and elevation of temperature facilitates the desorption of pesticides sorbed by the soil. Evaporation with water vapour is one of the factors leading to the loss of toxicity in the soil of insecticides such as heptachlor. Pesticides may also decompose in the soil under the influence of elevated temperatures. The hydrolytic and oxidation transformations of many pesticides in the soil appreciably lowers their toxic action.

An important role is also played by the chemical structure of the pesticide and its properties. The kind and number of halogen atoms and their arrangement in a molecule affects the rate of decomposition of halogenated pesticides and their derivatives. The length of the hydrocarbon chain in aliphatic acids also affects the persistence of such
pesticides. The decomposition of most pesticides in the soil is associated with microbiological activity through reactions such as dehalogenation, dealkylation, amide or ether hydrolysis, oxidation, reduction breaking of an ether bond, hydroxylation of an aromatic ring and breaking thereof. The nature of decomposition also depends on the features of the enzyme produced by the microorganisms. Several enzymes produced by various microorganisms are responsible for decomposition at definite stages. As a rule aromatic substances with a cyclic structure decompose considerably with more difficulty than compounds of the fatty series. Dehalogenation consists in the detachment of halogen atom from a pesticide molecule. Of major significance for the dehalogenation of pesticides is the number, position and kind of halogen atoms in the compound. An increase in the number of halogen atoms in a pesticide molecule and also an increase in the distance from the functional group lowers the rate of decomposition reaction. This is why a compound in para-position is decomposed more readily than when it is in meta-position. Dealkylation of pesticides in the soil may take place with breaking of the bond C-R, N-R or O-R. Oxidation of pesticides in the soil by microorganisms proceeds
differently, relatively stable organochlorine compounds having a double bond may be oxidized to epoxides. Organochlorine insecticides as a rule are the most resistant to microbiological decomposition in comparison with other derivatives but microorganism oxidise heptachlor to neptachlor epoxide. The accumulation of persistent pesticides in the soil in a number of cases leads to their translocation into the stems, leaves and root vegetables. The level of the content of a pesticide in a plant is determined by sorption, the supply and decomposition of the toxicant in the plant and the soil. As a whole the intensity of migration of a pesticide from the soil into a plant and its accumulation in the productive organs depend on its content in the soil, although there is not always a direct relation between these parameters.

Pesticides incorporated into the soil may change the composition of the soil microflora. Organochlorine insecticides in the doses recommended for controlling soil-inhabiting pests do not have a negative influence on the number of soil microorganisms. Rapidly decomposing organophosphorus insecticide in the recommended doses stimulate the development of separate groups of microorganisms and
in increased doses first cause suppression and then stimulation of the soil microflora. Soil fungicides and fumigants as a rule, have a negative effect on the soil microflora. The biological activity of the soil or the intensity of soil respiration (the absorption of $O_2$ and the evolution of $CO_2$) may be used as a general parameter showing how pesticides act on the soil microflora. The change in the activity of the soil enzymes in definite conditions characterises the effect of pesticides on the microbiological activity in the soil. The effect of pesticides on biological processes in the soil comes to light the most clearly only upon a repeated or multifold application of the toxicants. The nature and degree of action of pesticides on soil fauna are due to the properties of the substances, their content in the soil the composition of the fauna and to the soil and climatic conditions. In some cases, pesticides stimulate the reproduction of the soil fauna, in others they cause its suppression and extermination. Unstable rapidly decomposing pesticides are less dangerous to the soil fauna. Persistent compounds upon their surplus accumulation are a great danger. Organochlorine insecticides such
as heptachlor and toxaphene in their usually recommended doses act weakly on or are completely harmless to earthworms and nematodes but are toxic to soil arthropods.

Several mechanisms have been reported for adsorption of pesticides on soil such as Vander Waal's attractions, Hydrogen bonding, Hydrophobic bonding, charge transfer, ion exchange and ligand exchange.

**Vander Waal's Attraction:**

Vander Waal's forces are involved in the adsorption of nonionic, nonpolar molecules or portions of molecules. Vander Waal's forces result from short range dipole-dipole interactions of several kinds. The additive nature of Vander Waal's forces between the adsorbate and adsorbent may result in considerable attraction for large molecules. The adsorption of carbaryl and parathion on soil organic matter in aqueous system is considered to be physiosorption involving Vander Waal's bonds between the hydrophobic portions of the adsorbate molecules and the adsorbent surface. Nearpass [53] suggested that the principal adsorption mechanism for
picloram by humic materials was molecular adsorption due to Vander Waal's forces. Singh et al. [54] found that adsorption of dimethoate decreased with the rise of temperature indicating the involvement of Vander Waal's forces during adsorption process.

**Hydrogen Bonding** : This is a special kind of dipole-dipole interaction in which the hydrogen atoms serve as a bridge between two electronegative atoms, one being held by covalent bond and the other by electrostatic forces. There is a difference between hydrogen bonding and protonation [55]. Protonation may be considered as a full charge transfer from the base to the acid while hydrogen bonding interaction is a partial charge transfer interaction [56]. Erik et al. [16] suggested that H-bonding was considered the most feasible adsorption mechanism of lindane. Hayes [57] stressed the participation of a hydrogen bonding mechanism in S-triazines and organic matter interactions. Borggard and Streibig [58] have suggested hydrogen bonding as an adsorption mechanism in atrazine adsorption by soils.

**Hydrophobic Bonding** : Nonpolar pesticides are likely to adsorb onto the hydrophobic regions of the soil.
Water molecules present in the system will not compete with nonpolar molecules for adsorption on hydrophobic surfaces. This type of bonding may be largely responsible for the strong adsorption by soil organic matter of organochlorine pesticides. Lipids are also associated with soil humus [59].

Thus association of nonpolar (chlorinated hydrocarbons) pesticides with the lipid fraction of soil organic matter and humus might be described by hydrophobic bonding [60]. This also explains the relative independence of pesticide adsorption on moisture in soils with high organic content [60]. The adsorption of pesticides involving this mechanism would be independent of pH [61]. Methylation of organic matter or humic substances to block hydrophilic OH groups would increase the adsorption by this mechanism. Kozak et al. [62] also suggested hydrophobic bonding as a possible explanation in prometryn and metolachlor adsorption.

**Charge Transfer**: Charge transfer interaction will take place only within short distances of separation between the interacting species. In the formation of charge transfer complexes, electrostatic attraction
takes place when electrons are transferred from an electron rich donor to an electron deficient acceptor. Burns et al. [63] postulated the involvement of charge transfer mechanisms in paraquat adsorption by humic acid.

**Ion Exchange**: Ion exchange adsorption takes place for those pesticides which either exist as cations or which become positively charged through protonation. Adsorption of pesticides, such as paraquat and diquat, via cation exchange functions through -COOH and phenolic-OH groups associated with the soil organic matter [64]. Bansal [22] also suggested this type of mechanism in the adsorption of oxamyl and dimecron by some soils. The cationic adsorption mechanism is also responsible for the adsorption on organic matter of less basic pesticides, such as S-triazines [65].

**Ligand Exchange**: Adsorption by this mechanism involves replacement of one or more ligands by the adsorbent molecule [66, 67]. The necessary condition is that the adsorbent molecule be a stronger chelating agent than the replaced ligands [68].
This type of mechanism may be involved for the binding of S-triazines on the residual transition metals of humic acid [69].

In ligand exchange partially chelated transition metals may serve as possible sites for adsorption [57]. Coordination through an attached metal ion, ligand exchange was considered to be the main process in the adsorption of linuron by peat samples saturated with different cations [70].

The chemical and physical properties of soils are influenced strongly by soil constituents which have high surface area and surface density of charge. The colloidal fraction of the soil, is thus the dominant factor in influencing interactions between pesticide molecules and the soil. The colloidal components of soil may be divided into the mineral fraction and organic fraction.

**Factors influencing the adsorption of pesticides by Soil Colloids**

(1) **Physico-chemical character of the adsorbent:** The properties of the adsorbent which influence its behaviour in interactions with the adsorbate are
primarily related to the area and configuration of the surface and to the magnitude distribution and intensity of the electrical field at the surface. The manner in which the surface charge density can be of importance in understanding the adsorption of pesticides has been illustrated in a very elegant manner by Weed and Weber [71]. The compounds used in this study were diquat and paraquat. Paraquat charges are about 7Å apart whereas the diquat charge centres are 3.5Å apart. It was observed that at low surface charge densities paraquat was preferentially adsorbed over diquat. With increase in surface charge density the adsorption sites are more closely spaced and diquat was preferentially adsorbed due to the shorter separation of its charge centres (3.5Å).

The adsorbent may influence adsorption through its effect on the orientation of the adsorbate. Information in this aspect has been primarily derived from x-ray diffraction studies. Green-Kelley [72] found that saturated and unsaturated ring compounds formed two main types of complexes, depending upon whether the rings lie parallel to $d_{001}$ of montmorillonite or perpendicular to $d_{001}$. 
(2) **Physico-chemical character of the adsorbate:**

Examination of a pesticide's structure and physico-chemical properties often permits estimation of its adsorption behaviour. These include (a) overall chemical character, shape and configuration (b) acidity or basicity (c) solubility (d) electronic effects (charge distribution, polarity and polarizability) and (e) molecular size [73]. These factors are of help in isolating the important pesticide characteristics affecting adsorption. The chemical character is largely determined by the number, nature and relative position of functional groups. Adsorption is characteristically increased with functional groups such as $R_3N^+$, $CONH_3$, $-OH$, $-NHCOR$, $-NH_2$ and $NHR$. Several workers have attempted to correlate molecular structure and adsorption to soil. In a study [73] on the effect of functional group, nature and position of ring substitution on the magnitude of adsorption of a wide variety of compounds, concluded that the chemical character of the molecule affects retention by colloidal systems in three different ways: (1) determines if the molecule is fundamentally acidic or basic in nature and the relative acidic or basic strength (2) affects the
water solubility of the molecule and (3) determines the relative importance to (1) and (2) of Vander Waal's type forces. A fundamental relationship [73] between adsorption by soils and chemical structure of certain classes of chemicals has been mathematically derived. This relationship is based on extra-thermodynamic linear free energy approximations.

(3) **Soil Reaction**: The importance of soil pH as a factor affecting pesticide adsorption depends largely on the pesticide itself. pH is manifested in determining the degree of dissociation or association of the compound, that is whether the compound is still a molecule or has dissociated into either a cation or anion. This in turn may affect the amount that is adsorbed and the strength with which it is held, since the energy of adsorption may be vastly different between the dissociated and associated form. Adsorption of herbicides with different molecular structures generally increases as pH decreases. The pH where maximum adsorption occurs is a function of the particular compound and the adsorbent. Herbicides are adsorbed in highest amounts at pH levels in the vicinity of their respective pK values. For instance, maximum adsorption of promethone...
(pKa 4.28) occurs in the range of pH 4.2 to 5.2. Addition of HCl or NaOH to lower or raise the pH results in decreased adsorption.

(4) **Effect of temperature**: Increased temperature, in general, leads to decreased adsorption as physical adsorption is characteristically an exothermic process. This corresponds to a weakening of attractive forces between the solute and the solid surface with increasing temperature and corresponding increase in solubility of the solute in the solvent. In a study of the adsorption of chloropicrin by soil, it was found that lowering of temperature resulted in increased adsorption but this increase was completely recovered by bringing the samples back to the original temperature. Since desorption is interrelated with bioactivity, the bioactivity of pesticide might be expected to be different at various temperatures.

(5) **Effect of salts**: Soils generally contain inorganic salts such as sodium chloride or magnesium sulphate which may influence the adsorption equilibrium. It appears that at normal pH's dilute
salts slightly increase adsorption while concentrated solutions sharply increase adsorption. Work on the effect of salts on anionic materials has not been reported.

The cosolvent theory was proposed to describe sorption of hydrophobic organic compounds to soils from water/miscible solvent mixtures [74]. It has been applied to the sorption of several organic compounds of moderate and intermediate hydrophobicity. [75, 76]. The theory predicts a log-linear relationship between the mole-based equilibrium sorption partition coefficient (Km) and volume fraction solvent (fs). In its simplest form, the theory can be expressed as

\[ \log \left( \frac{K_{mi}}{K_{mw}} \right) = -\alpha \sigma_s \text{fs} \quad \text{....(9)} \]

where \( K_{mi} \) and \( K_{mw} \) are mole-based partition coefficients (mol/g) for water/solvent mixture \( i \) and solvent free water, respectively. The term \( \sigma_s \) in equation 9 reflects solute-liquid interactions in that it is the slope of the log-linear relationship between mole fraction solubility and fs [77].

The term \( \alpha \) in equation 9 is related to solute-soil and solvent-soil interactions via liquid and organic carbon phase activity coefficients [74, 76].
The cosolvent theory is important for two reasons. First, the theory enables prediction of sorption of an organic solute from a specified mixture of water and miscible organic solvent. This has implications on understanding fate and transport of organic contaminants in real-world, complex waste streams such as industrial wastes and landfill leachates. Second, the theory can be utilized to estimate $K_D$ (Partition coefficient) for sorption from aqueous solution by log-linear extrapolation of $K_{Di}$ data generated at higher $fs$, where $K_{Di}$ is the volume-based sorption partition coefficient (mL/g) corresponding to liquid phase $i$, and is related to $K_{mi}$ by the expression

$$K_{mi} = K_{Di} / V$$

where $V$ is the molar volume of the liquid phase (mL/mol). This is particularly significant for highly hydrophobic compounds because direct experimental determinations of sorption from water are extremely difficult to make.

Helling and Turner [78 - 80] introduced Soil Thin layer chromatography technique as an
alternative procedure for rapid reproducible and simple assessment of pesticide movement in soil. Some progress has been made in this technique in detail by autoradiography. Singh et al.[81-83], Sharma et al. [84 - 87] have studied the movement of certain pesticides on soil TLC plates and the movement was expressed in terms of $R_f$ values which is measured using the following relation.

$$R_f = \frac{R_L + R_T}{2} \quad \ldots(11)$$

Where $R_L$ and $R_T$ denotes the $R_f$ of the leading and trailing regions respectively.

Thermodynamics is an appropriate means of describing the theoretical behaviour of sorption/ion exchange equilibria. Equilibria can be described in general by means of rigorous thermodynamics. This requires no model and no assumptions about the mechanism of sorption/ion exchange phenomena. However, rigorous thermodynamic treatment gives a minimum of information about the physical causes of the phenomena; therefore its practical utility is restricted. An interpretation in terms of the underlying physical forces requires a model. The
Properties of any particular model are reflected in form of the equations obtained and usually also in the physical interpretation to which these equations lead. This suggests that there are a number of different theoretical approaches. Two most appropriate theoretical approaches are usually applied for this purpose.

In the first approach more and more elaborate models are designed for deriving equations which reflect the action of various physical forces. These models have particular properties resembling those of ion exchangers. This approach gives a semiquantitative picture to understand the physical causes of the phenomena.

In the second approach various attempts have been made to correlate the activities, with some measurable quantities; the thermodynamic equations. The earliest approaches were based on semiempirical or empirical equations to fit the experimental results. Probably the first quantitative formulation of sorption/ion exchange equilibria was made by Gans [88]. For this purpose he used the law of mass action in its simplest form, without involving the
concept of activity coefficient. This concept was accounted for by Kielland [90]. Gaines and Thomas [89] gave a general treatment using an expression for the calculation of thermodynamic equilibrium constant which is a suitable choice for this purpose.

The thermodynamic equilibrium constant \( K_o \) for sorption on soils can be calculated by Biggar and Cheung method [19] where

\[
K_o = \frac{C_s}{C_e} \frac{\nu_s}{\nu_e} \quad \cdots (12)
\]

where \( C_s \) is the amount of solute per gram of the solvent in contact with the soil or exchanger phase, \( C_e \) the concentration of the solute in solution phase, \( \nu_s \) the activity coefficient of solute in soil and \( \nu_e \) the activity coefficient of solute in solution phase. From the value of thermodynamic equilibrium constant, free energy changes \( (\Delta G^o) \) during the sorption/ion exchange phenomena can be calculated from the relationship

\[
\Delta G^o = -RT\ln K_o \quad \cdots (13)
\]
where $R$ is universal gas constant and $T$ the absolute temperature.

The enthalpy change of the system can be calculated by using the integrated form of the Van't Hoff equation

$$\ln \left( \frac{K_{T_2}}{K_{T_1}} \right) = -\frac{\Delta H^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad \ldots (14)$$

The change in enthalpy predicts whether the reaction is endothermic or exothermic. Enthalpy change of the system is directly related to changes in the number and strength of the bonds in the ion exchange process. The randomness of the ion exchange process may be predicted from the values of the free energy and enthalpy changes. The entropy changes can be calculated from $\Delta H^o$ and $\Delta G^o$ values using the equation

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \quad \ldots (15)$$

at a given temperature, the overall entropy of the system reflects the extent of order produced during the ion exchange process.
In the present work sorption equilibria of cobalt(II) was studied on Indian soils - the natural ion exchangers with the purpose of understanding the basic chemistry of cobalt(II) in soils and to evaluate thermodynamic parameters for its interaction with the soils.

Sorption equilibria of pesticide, endosulphan was studied on Indian soils - the natural ion exchangers under the influence of organic solvents methanol and acetone by creating an adsorption system consisting of a liquid phase water with an organic solvent, soil and the pesticide. The applicability of the co-solvent theory was also evaluated. The effect of different factors such as exchangeable cations (H\(^+\) and Na\(^+\)) organic matter, surfactants (non-ionic and anionic) and temperature on the sorption equilibria of pesticide, endosulphan; on soils was also studied. Thermodynamic parameters were evaluated for the interaction of endosulphan with soils. These studies will be helpful towards assessing endosulphan movement in soil and controlling soil pollution.
Movement of different pesticides in soil has been studied using thin layer chromatographic technique. The data obtained will be helpful in examining the probability of pollution of groundwater by the pesticides.
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