Chapter-I

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1.1. INTRODUCTION

Survival through the ages has engaged man in a continuous struggle with his physical and biological environment. From being at the mercy of the nature he has reached a stage where he can control the environment and shape his own destiny. With the advancement of science and technology he has modified the natural environment into an artificial and highly productive system to get more energy and more nutrient resources and is able to control the natural calamities and conquer disease and pestilence. This has resulted in improvement of the quality of life and its expectancy. However, with the over increasing trend in the world population problems of food, health and hygiene are widening day by day [1], thus, putting pressure on man to increase agricultural production. The rapidly growing human population has jeopardized the environment and natural resources, which are already under great stress.

According to the latest UN projections [2], world population will rise from 6.8 billion today to 9.1 billion in 2050. To feed 9.1 billion humans as predicted by demographers for the year 2050, significant increase in food production will be required. At present India’s population is 1.198 billion and it is expected to reach 1.59 billion by 2050. Increase in population leads to decrease in farm size on one hand and reduction in per capita arable land area on the other. The per capita land area (ha) of India is expected to decrease from 0.136 in 2010 to 0.100 by 2050 [3]. The food grain production of India is static at an average of about 210 million tons since last ten years. To feed 1.59 billion people, as predicted, the 300 – 350 m tons of food grain production is required [4, 5]. The Food and Agricultural Organization (FAO) and United Nations foresee that by 2050 there will be scarcity of food. This challenge on the food front has to be met within the limited land resources.

The productivity of crops grown for human consumption is at risk due to the incidence of diseases and pests. The damage caused by various insects and diseases,
varies from crop to crop in different parts of the world. It has been reported that about
80,000 plant diseases, 30,000 species of weeds, 1000 species of nematodes and more
than 10,000 species of insects damages one third of the crops annually [6]. On an
average, farmers of the world lose between 40 to 50% of their crops before harvest.
As per the response to the starred question no.62 in Rajya Sabha on 2nd March 2007,
by the Union Minister of Agriculture, Government of India, the crop losses due to
pests, weeds and diseases were approximately assessed to be ranging from 10 to 30%.
In economic terms, at present prices, food grains worth Rs. 2.5 Lac Crores are lost
year after year [6].

So to achieve the above goal the role of pesticides cannot be ignored. It's wide
spread use had played an important role in the success of Green Revolution and in
solving the problem of adequate grain production in our country. Without pesticides
the benefits of all other costly inputs goes to waste. They have enhanced the
production of food, fodder and fibre not only in great quantity but better quality as
well. In addition to their contribution to a substantial growth of food, pesticides have
freed human beings from contagious diseases to a degree impossible to imagine in the
past. If we want to sustain or increase the current level of food production, further use
of pesticides is must.

India is the second largest manufacturer of pesticides in Asia (behind China)
and rank twelfth globally. At present only 231 pesticides are registered for use in
India [7] in comparison of 755 in USA, 600 in Europe, 495 in Pakistan, and 422 in
Vietnam. In spite of the fact that judicious use of pesticides can provide economic
benefits to the farmers, the pesticide consumption in India is limited to about 25% of
the arable land. Per hectare average use of pesticides in India is low at a minimum of
0.33 kg ha\(^{-1}\) in comparison to 1.6 Kg ha\(^{-1}\) in USA, 2 Kg ha\(^{-1}\) in U.K., 3 Kg ha\(^{-1}\) in
Germany, 3.07 kg ha\(^{-1}\) in France, 4.17 kg ha\(^{-1}\) in Italy, 6.6 Kg ha\(^{-1}\) in Korea, 10.5 Kg
ha\(^{-1}\) in Holland, 13.14 kg ha\(^{-1}\) in Japan and 17.0 kg ha\(^{-1}\) in Taiwan [8].

Despite of the fact that consumption of pesticides is low in India in
comparison of other countries, residues of chlorinated persistent pesticides have been
identified in various components of the environment in India [9]. India is one of only
two countries worldwide (along with United States) to have applied more than
100,000 tons of dichlorodiphenyl trichlorethane (DDT) since its initial formulation. Because of the excessive and indiscriminate use of pesticides in India, the total intake of organochemicals per person is highest in the world [9].

The chemical crop protection is indeed a profit induced poisoning of the environment. Only when viewed from a narrow and distorted economic perspective does the application of chemical pesticides seems beneficial. If the credits of pesticides include enhanced economic potential in terms of increased production of food and fibre, and amelioration of vector-borne diseases, then their debits have resulted in serious health implications to man and his environment. It has been estimated that less than 0.1% of pesticides applied to crops reach their target pests; however, most of the pesticides enter to the environment, and contaminate soils, water and air, which eventually affects non-target organisms [10]. The accumulation of pesticides in food and drinking water has generally been recognized as dangerous, and the long-term persistence and toxicity of pesticides in groundwater is potentially responsible for causing various kinds of human illnesses [11, 12]. Throughout the Developing World, it is estimated that close to a million people are annually poisoned by pesticides, of which 40,000 die. It is also well worth noting in comparison with the Developed World, "the incidence of pesticide poisoning is 13 times higher in the Third World." [13]. The World Health Organization estimated in 1992 that 3 million pesticide poisonings occur annually, causing 220,000 deaths [14, 15]. In India, the first report on poisoning due to pesticides was from Kerala in 1958, where over 100 people died after consuming wheat flour contaminated with parathion [16]. This was followed by the tragedy at Bhopal (M.P., India), where about 2,500 people have been reported to have died due to the leakage of methyl isocyanide (MIC) gas, an intermediate product used in the manufacturing of Sevin, from the Union Carbide Plant and several thousands have been seriously affected.

In order to provide awareness about the hazards of the pesticides, many books [17-25] and reviews [26-33] have been published and symposia [34-36] have been organized on the subject as a warning of the potential hazards. The first book written on this subject was "Silent Spring" by Rachel Carson, an American Journalist. She warned in her book that organo-chlorine compounds could pollute the tissues of virtually every life form on earth, the air, the lakes and the oceans, the fishes that live
in them and the birds that feed on the fishes [37]. This publication was followed by many books on the pesticides giving practical information on the assessment of the pesticide hazards. Two of these are “Hazards Assessment of Chemical” by Saxena and Fisher [24] and “A Growing Problem - The Pesticide and Third World Poor” by David Bull [25]. Recently, the US National Academy of Sciences stated that the DDT metabolite, DDE causes eggshell thinning and that the bald eagle population in the United States declined primarily because of exposure to DDT and its metabolites [38]. Certain environmental chemicals including pesticides termed as endocrine disrupters are known to elicit their adverse effects by mimicking or antagonizing natural hormones in the body and it has been postulated that their long-term, low dose exposure are increasingly linked to human health effects such as immune-suppression, hormone disruption, diminished intelligence, reproductive abnormalities and cancer [39-41].

Although several alternative methods to control pest and diseases have been suggested but where pest population reaches to a very high dimensions, pesticides have to be used. This is a dilemma with regard to the use of pesticides. But it is true that we need to use more pesticides to grow more food in the coming years and at the same time we must be careful about the impact of pesticides on human beings, animals and the environment. So there is a need of proper planning for the use of pesticides. Suspicion about chemicals in food is fuelling sales of organic crops [42] but it is by no means certain whether organic production could sustain the world’s growing population [43]. Moreover, the need for more food for an ever growing population and our dependence on these agricultural chemicals seem inevitable.

1.2. PESTICIDES

The term “pesticide” is used to denote the wide range of synthetically prepared organic compounds. The root word is Latin word ‘cide’ that means to kill. Environmental Protection Agency (EPA) defines a pesticide as a substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pests or intended for use as a plant growth regulator, defoliant or desiccants.

The use of pesticides is not new. As long as 79 A.D., Pliny recommended arsenic as an insecticide. The use of pesticides was practiced by ancient men also, e.g.
ancient Romans used “Tar” as a pesticide. About two and a half centuries back i.e. in the year 1763, nicotine (from the extract of tobacco leaves) was used for the first time as an insecticide for control of aphids. In 1818 A.D., Pyrethrum (extract from the flower heads of a species of Crysanthemum) was introduced. In 1865 A.D., Paris green was developed for the control of Colorado potato beetles. In 1886 A.D., arsenic containing pesticides were discovered. It was at the end of nineteenth century that the “first generation pesticides” such as lead arsenate, selenium compounds and several thiocyanates, came into existence. The Second World War brought about the emergence of what came to be known as “second generation pesticides”. It was around 1940 that two important groups of synthetic pesticides emerged. These were the organochlorine and organophosphorus compounds.

The pesticides are classified on the basis of target group of organisms such algaecides, avicides, bactericides, fungicides, herbicides, insecticides, miticides, molluscicides, nematicides, rodenticides, and virucides for the control of algae, birds, bacteria, fungi, weeds, insects, mites, slugs and snails, nematodes, rodents and viruses respectively.

1.3. FATE OF PESTICIDES

When pesticides are applied to soils or comes in its contact, whether by application by spraying, broadcasting granular formulation or fumigation, disposal or a spill, brings about the changes in the physico-chemical and biological properties of the soils which can influence many processes. These processes determine the ultimate fate of the pesticides in soils. It may be taken up by plants and/or ingested by animals, insects, worms, or microorganisms in soil; it may be adsorbed on soil particles and move downward in soil; it may dissolve; it may volatilize; it may be broken down into less toxic compounds; it may leach or moved out of the plant root zone by rain or irrigation; or it may be carried away by runoff water and erosion. Sannino et al. [44] and Cramer et al. [45] provided useful informations for predicting the behaviour of pesticides when entered into the soil. These processes determine the ultimate fate of pesticides by affecting its persistence and movement in the environment.
The fate processes can have both positive and negative influences on the pesticide's effectiveness or its impact on the environment. On the positive side, they can bring a pesticide into contact with target pest for effective control, or they can reduce biologically significant concentrations of the active ingredient to relatively harmless; and on the negative side they are phyto-toxic and destroy useful plants. They enter into the food chain causing toxicity to humans, animals and other creatures. Its loss from the area of application and contamination of non-target sites such as surface and groundwater represents a monetary loss to the farmers as well as a threat to the environment. Quite a large amount of pesticides reaches the water resources causing toxicity to flora and fauna.

The fate of pesticides in the environment is governed by the retention (adsorption, desorption, absorption, partitioning, ion-exchange), transformation (degradation), transport (volatilization, leaching, overland flow) processes and the interaction of these processes. Site characteristics, environmental conditions, crop management systems and chemical handling practices can all affect each process.

1.4. REVIEW OF LITERATURE
1.4.1. Adsorption of Pesticides on Soils

Adsorption is the attraction and repulsion phenomenon at the soil surface and exerts the most pronounced influence amongst the several processes operating to determine the fate and behaviour of pesticides in soil environment. It is influenced by several factors such as atomic and molecular structure of the pesticides, its solubility and concentration of the solvent and solvent itself, the lattice configuration of the adsorbent, the exchangeable cations and their hydration, the heat treatment of the surface, orientation of the molecules and the environmental conditions.

Adsorption processes play a vital role in determining the environmental fate of pesticides and in determining their efficacy for crop protection. United States Environmental Protection Agency (USEPA) has proposed guidelines for registration of pesticides requiring adsorption and movement studies in soils because adsorption
controls the quantity of a pesticide in soil solution which impacts almost all the
specific fate processes, including volatilization [46,47], bioavailability [48]
biodegradability [49-51], photolysis [52,53], hydrolysis [54,55], its persistence,
mobility, leachability and translocation [56].

Several researchers [57-105] have reported that the extent of adsorption of the
pesticides on soils depends upon the soil properties (organic matter quantity and type,
clay mineral content and type, CEC, pH, moisture, exchangeable cations); on the
physical and chemical parameters of the pesticides (such as particle size, shape,
configuration, molecular structure, chemical functions, water solubility, polarity,
polarizability, charge distribution and acid and base nature of the pesticide molecule);
and on temperature and other environment conditions. Literature on this aspect has
been reviewed by Cheng [58]; Bailey and White [67]; Hayes [106]; Wolcott [107];
Adams [108]; Khan [109]; Stevenson [110]; Weed and Weber [111]; Gevao et al.
[112]; Wauchope et al. [113]; Doucette [114]; Kah and Brown [115].

Organic matter may exert the most profound influence of the several processes
operating to determine the fate of pesticides in soils. Soil organic matter includes
plant and animal residues at various stages of decomposition, cells and tissue of soil
organisms, and substances synthesized by the soil population. Soil organic matter
contains proteins and lignin-like compounds as the major molecular groups, along
with small quantities of hemi-cellulose, cellulose, and ether and alcohol soluble
compounds. Non-humic substances in soil organic matter include carbohydrates,
proteins, peptides, amino acids, fats, waxes and low molecular weight acids.
Stevenson [116] pointed out that information on the nature of organic matter-
pesticide interaction may provide a more rational basis of effective use, thereby
reducing undesirable side effects due to carry over and contamination of environment.
However, a proper understanding of the exact nature of these interactions is hindered
due to complexities of organic matter and the numerous other interactions in soil
environment, all operating simultaneously. In recent years careful studies with
simplified systems involving well defined organic matter component such as humic
acid and fulvic acid have led us to understand that: (i) they can be readily extracted
from soil organic matter in relatively pure forms (ii) they can be thoroughly
characterized by various techniques, and (iii) they are major and common constituents
of organic matter.
Clay minerals also constitute the most important reactive surface of the soils and play a very important role in pesticide adsorption. Literature on this aspect has been reviewed by Rich and Thomas [117], Mortland [118] and Green [119]. Several researchers [120, 121] have reported that clay adsorbs strongly the organic cations and probably does not adsorb anions by anion exchange; the layer of OHn group of kaolinite is not exchangeable and the number of edge OH-groups in kaolinite and montmorillonite is small. Hydrated Fe and Al-oxide associated with clay are probably responsible for adsorption of anions by anion exchange. They have been reported to provide heterogeneous chemical spots in the form of adsorbed water around cations, hydroxyl at the edges, lattice surface oxygen’s and electrical double layer of changing polarity at the edges. They possess electron accepting sites in the form of exposed aluminum and transition metals in higher valance state at the edges. The location and distribution of exchanges sites on clays is an important factor in the nature and extent of adsorption.

A limitation that needs to be considered in organic matter pesticide interactions 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 identity and its relative contribution in pesticide adsorption will depends upon the extent to which the clay is coated with organic matter [116]. However, it should be realized that the association of organic matter with clay still provides an organic surface for adsorption [116].

The adsorption of pesticides that are neutral and hydrophobic is highly correlated with the organic matter content of the soils [122-124]. Walker and Crawford [125] suggested that for soils having organic matter content greater than 6%, adsorption occurs entirely on organic surfaces; whereas, for soils containing organic matter less than 6 %, both mineral and organic surfaces are involved in adsorption. Wahid and Sethunathan [126] demonstrated in their studies that beyond the level of 2% organic carbon content in soils the adsorption of pesticides takes place almost entirely on organic surfaces but at organic carbon level below 2% the adsorption was significant on clay surfaces or inorganic surfaces. The extent to which clay minerals contribute to adsorption depends on both the ratio of clay mineral (CM) to organic carbon (OC) fractions of the soil or sediment and on the nature of pesticide.
Means et al. [127] suggested that for CM/OC < 30, mineral contributions are masked, regardless of the mineral content. Green and Karickhoff [128] suggested a ratio of 40 as the cutoff of organic carbon-dominated adsorption and Liu et al. [129] suggested that for CM/OC ratio less than 60, adsorption occurs mainly on organic matter.

1.4.2. Effect of Surfactants on Adsorption of Pesticides on Soils

The word ‘surfactant’ is a contraction of the descriptive phrase “surface active agents”. A surfactant molecule is amphiphilic, having two distinct structural moieties, one polar and other non-polar. The polar moiety of the molecule has an affinity for water and other polar substances, while the non-polar moiety is hydrophobic. The polar and non-polar moieties of a surfactant molecule are referred as head and tail group, respectively. Surfactants are classified according to the nature of the hydrophilic portion of the molecule. The head group may carry a negative charge (anionic), a positive charge (cationic), both positive and negative charge (zwitterionic) or no charge (non-ionic). The differences in the chemistry of surfactants due to the nature of hydrophobic tails (degree of branching, carbon number and aromaticity) are usually less pronounced than those due to hydrophilic head.

A unique phenomenon of surfactants is the self assembly of molecules in to dynamic clusters called ‘micelles’. The surfactant concentration at which monomers began to assemble in to ordered, colloidal aggregates is termed as ‘critical micelle concentration’ (CMC). The CMC represents a narrow concentration range over which the partial derivatives, with respect to surfactant concentration, of many solution properties, e.g., surface tension, display abrupt changes in value [130]. In micelle forming solutions, the CMC approximates monomeric solubility. At surfactant concentrations greater than the CMC, the additional surfactant is incorporated in to the bulk solution through micelle formation [131]. The average number of surfactant molecules in a micelle is called aggregation number.

Surfactants are widely used in household cleaning detergents, personal care products, textiles, paints, polymers, pharmaceuticals, mining, oil recovery, pulp and paper industries and pesticide formulations. They play a very significant role for environmental interest because after use, a major portion is discharged into waste waters which eventually reach the natural waters.
When soil is exposed to a considerable quantity of surfactants, and even at low concentrations seems to alter soil physics, soil chemistry and soil biology with adsorption process playing a dominant role. Research in this direction has two fold purposes namely: (a) to determine how the adsorption and movement of hydrophobic organic compounds (HOCs)/pesticides is altered by the presence of surfactants when both coexist in soil as a result of human activity and, (b) to investigate the potential use of surfactants for solving soil pollution problems posed by HOCs/pesticides.

Anionic and non-ionic surfactants generally are found to enhance the apparent solubility of HOCs/pesticides and decreases their adsorption on soils [132-148]. This increase in apparent solubility may represent an important tool for chemical and biological remediation of contaminated soils and sediments [149-153].

Some researchers [143, 147, 148, 150, 154-161] have reported variations in anionic and non-ionic surfactant behaviour as a function of CMC. They reported that at below and at CMC level adsorption of pesticides increases; whereas at above CMC level adsorption decreases. The increase in adsorption at lower concentrations (below and at CMC level) was due the dispersion of soil particles or due to the adsorption of pesticides by the soil adsorbed surfactant or due to soil adsorption and co-precipitation of surfactant (especially anionic) with the divalent cations, followed by partitioning of pesticide into the adsorbed and precipitated surfactant. While the decrease in adsorption at above CMC level is attributed to competitive adsorption between surfactant and pesticide molecules on soil surfaces.

The variation in anionic and non-ionic surfactant behaviour as a function of soil organic matter (OM) and clay content has also been reported. Sanchez-Camazano *et al.* [162] and Sanchez-Martin *et al.* [163] reported that, at below CMC level, SDS only increases desorption of atrazine and linuron in the soil with the highest OM content. However, at above CMC level, the desorption of atrazine and linuron increases in all the soils, efficiency of desorption increasing with the OM content of the soils. Werkheiser and Anderson [164] showed that in presence of Triton X-77 adsorption of herbicide primisulfuron increased on low organic carbon soils whereas in high organic carbon containing soils its adsorption decreased. Rodriguez-Cruz *et al.* [165] showed that the addition of Triton X-100 decreases desorption of atrazine.
and linuron in soils containing low organic matter, whereas in soils containing high
organic matter desorption was not favourable. Brickell and Keinath [166] and Abu-
Zreig et al. [167] have reported variations in surfactant effect due to soil clay
mineralogy or soil textural characteristics. These variations in non-ionic and anionic
surfactant effect on adsorption and movement of carbaryl have recently been reported
by Singh et al. [154]. The physico-chemical properties of pesticide are also important
for surfactant effects on its adsorption, which was confirmed by the leaching behavior
of four herbicides in the presence of Tween 80 [168].

Other type of surfactants such as cationic ones may be retained by soil colloids
and enhances the adsorption of pesticides with a potential increase in the formation of
bound residues [148, 154, 159, 169-175]. This increase in adsorption is attributed to
the fact that cationic surfactants are positively charged and they are adsorbed on the
negatively charged soil surfaces through electrostatic interaction [176-183]. This
increases the hydrophobicity of soil surfaces and thus increases the adsorption of
pesticides. This concludes that the contamination by pesticides which are present in
soil due to their direct input/spills or illegal tipping may be hindered from migration
to groundwater by application of a cationic surfactant. Conversely, few authors [146,
184] have also reported a decrease in adsorption and thereby increase in movement of
pesticide in presence of cationic surfactant. This decrease in adsorption is due to the
competition between cationic surfactant and pesticide molecules for adsorption on soil
surfaces. The variation in cationic surfactant effect on the adsorption and movement
of pesticides has been observed by Sanchez-Camazano et al. [159] and Iglesias-
Jimenez et al. [147]. They found that for sparingly water soluble pesticides such as
diazinon and atrazine increase in adsorption is much less pronounced as compared to
the adsorption of moderately water soluble pesticide ethofumesate. Whereas for
acephate, a water soluble pesticide, no change in adsorption occurs. Similar results
were reported by Singh and Rajkumar [157].

Literature on this aspect has been reviewed by Haigh [185], Katagi [186] and
Laha et al. [187].
1.4.3. Effect of Co-solvents on the Adsorption of Pesticides on soils

Most of the data on pesticide adsorption on soils deal with aqueous solutions [75, 86, 188-206]. However, under waste disposal and land treatment sites it is likely that the soil solution will consist of a mixture of water and various miscible solvents (co-solvents). Due to this reason, in natural environment pesticide adsorption could occur in a mixture of water and various miscible organic solvents. The presence of these organic co-solvents may increase or decrease the adsorption of pesticides in soils. The extent of these effects depends on the specific interactions between soil, pesticide and liquid phases. Thus it is necessary to characterize pesticide adsorption by soils not only from aqueous solutions but also from aqueous-organic mixed solvents. Several researchers [207-214] have studied the adsorption of pesticides in soils from organic solvents and solvent-water mixtures. These water miscible co-solvents (eg. alcohols and ketones) have also been used as a means for enhancing the removal of organic substances adsorbed by the soils [215-222]. Rao et al. [223] has presented a theoretical approach for describing the effects of these co-solvents on HOCs adsorption on soils. According to this theory, HOC sorption from aqueous-organic binary solvent mixtures decreases exponentially as the fraction of organic co-solvent increases. This theory predicts a log-linear relationship between the mole-based partition coefficient \(K^m\) and volume fraction of co-solvents \(f_s\). This theory is particularly important because it enables accurate predictions of adsorption of HOCs from a specified mixture of water and miscible organic solvents because it is very difficult to determine their adsorption partition coefficient in pure water. This has implications in understanding the fate and transport of organic contaminants in real world, e.g. complex waste streams such as industrial wastes and landfill leachates. Nkedi-Kizza et al. [224] for the first time have successfully applied this theory for the sorption of two herbicides diuron and atrazine. Since then, this theory has been applied to the adsorption of several pesticides and other organic compounds having moderate and intermediate hydrophobicity [225-240] using methanol and acetone as co-solvents.

1.4.4. Mechanisms of Adsorption

Several mechanisms have been proposed for adsorption of pesticides on soils. These involve Vander Waals forces, hydrogen bonding, ligand exchange, ionic bonding, charge-transfer or electron donor acceptor mechanisms, hydrophobic
bonding or partitioning and covalent bonding. There are two types of adsorption: (a) Physical adsorption, which is called Vander Waal's adsorption and; (b) Chemisorption, which is the formation of a factual bond, usually covalent between the molecule and the soil surface molecules. The physical adsorption is due to the orientation of dipole-dipole or ion-dipole interactions in addition to bond repulsion. Chemisorption is due to the columbic forces and results from bond formation between the adsorbent and the adsorbate. Physical adsorption occurs with non-ionic pesticides, while chemisorption with cationic and anionic pesticides. Hydrogen bonding is intermediate between physical and chemical adsorption. Physical adsorption is generally reversible and involves several layers and low binding strength. Two or more mechanisms may occur simultaneously depending upon the nature of the functional group present on pesticide and soil surfaces and acidity of the system. The mechanisms involved in the adsorption of pesticides on soil surfaces are outlined below.

1.4.4.1. Vander Waals Forces

Vander Waals forces consists of weak short range dipolar or induced dipolar attractions that exist, in addition to stronger binding forces, in all adsorbent-adsorbate interactions particularly between non-ionic and non-polar pesticides on suitable humic acid molecules. These forces are additive [241] and increases with the size of the interacting molecule and decay rapidly with distance. Although there is paucity of experimental evidence, the involvement of these binding forces has been observed for a large number of compounds, including bipyridilium cations [242], carbaryl and parathion [243], benzonitrile and DDT [244] and has been shown to be the major adsorption mechanism for picloram and 2,4-D [245, 246]. Barriuso et al. [247] suggested that atrazine is primarily retained on surfaces of smectites with low surface charge density through relatively weak vander Waals forces. This mechanism was also proposed as contributing to sorption of imazethapyr [248] and fluridone [249].

1.4.4.2. Hydrogen Bonding (H-bonding)

H-bonding is an intra- or intermolecular dipole-dipole interaction that is stronger than vander Waals bonds. It is caused by the electron-withdrawing properties of an electronegative atom (F, O, N) on the electropositive hydrogen nucleus of
functional groups such as -OH and -NH. Humic substances with numerous oxygen- and hydroxyl-containing functional groups form H-bonds with complimentary groups on pesticide molecules. Pesticide molecules compete with water for these binding sites. H-bonding is suggested to play a vital role in the adsorption of several non-ionic polar pesticides, including substituted ureas and phenylcarbamates [250, 251]. Acidic and anionic pesticides, such as phenoxyacetic acids (2,4-D and 2,4,5-T) and esters, asulam and dicamba, can interact with soil organic matter by H-bonding at pH values below their pKa in non-ionised forms through their –COOH, –COOR and identical groups [252-254].

IR, differential thermal analysis (DTA) and 1H-NMR studies on interactions between atrazine and other s-triazine herbicides with humic substances suggest the occurrence of one or more H-bonds, possibly involving carbonyl groups of humic acids and secondary amine groups of the s-triazine. Nearpass [255] found that the adsorption capacity for the s-triazines depends on the proportion of humic substances and titrable acidity. It was inferred as a result that adsorption occurred by H-bonding between the amino protons of the triazine ring and humic acids. Martin-Neto et al. [256] found evidence for weak H-bonding between atrazine and humic substances using UV-visible, FT-IR and ESR spectroscopy. Piccolo and Celano [257] demonstrated the usefulness of IR in the study of H-bonding using complexes of glyphosate [N-(phosphonomethyl) glycine] with water-soluble humic acid. The hydrogen bonds were formed between the phosphono group of the glyphosate and the oxygen groups of the humic acids. Hydrogen bonding has also been proposed as a binding mechanism for primisulfuron [258], metribuzin [259], and 2, 4-D and triclopyr [260] on soils. It has been implicated in the adsorption of fluazifop-butyl on homoionic clays [261], atrazine on smectite [247], and atrazine [262, 263], imazethapyr [248], ethamethasulfuron-methyl [264], and imazaquin [265] on soil organic matter.

1.4.4.3. Ligand Exchange

Adsorption by ligand exchange involves the replacement of relatively weak ligands, e.g. H2O partially holding polyvalent cations associated with soil organic matter by suitable adsorbent molecules such as s-triazines and anionic pesticides [266,
The substitution may be facilitated by an entropy change, if a xenobiotic molecule succeeds in replacing several H₂O molecules associated with one or several complexed metal ions.

1.4.4.4. Ionic Binding

Pesticides and their metabolites adsorbed by ionic bonding, or cation exchange, exist either in the cationic form in solution or can be protonated and become cationic. Ionic bonding involves ionised, or easily ionisable, carboxylic and phenolic hydroxyl groups of soil humic substances. Bipyridilium pesticides (e.g. diquat and paraquat) bind to soil humic substances by ion exchange via their cationic group. They form highly stable and unreactive bonds with the carboxyl groups of the humic substances. However, possible binding sites on the humic complexes are not utilized due to steric hindrance effects [267]. The effect of pH on binding has been reported for less basic pesticides such as the triazine herbicides [268-270], amitrole [271], dimefox [272], propiconazole [273] and carbendazim [274], which become cationic depending on their basicity and the pH of the system, and also governs the degree of ionization of acidic groups of the humic substances. Infrared spectroscopic studies (IR) of s-triazine-humic acid systems have shown that ionic bonding can occur between a protonated secondary amino-group of s-triazine and a carboxylate anion and possibly, a phenolate group of the s-triazine [275, 276, 250]. In the late 1960s, Weber and colleagues [277, 278] working with the s-triazine herbicides provided compelling evidence to show that maximum adsorption of basic compounds occurs at pH values close to their pKa values.

1.4.4.5. Charge Transfer Complexes

Humic substances contain within their structure both electron-deficient moieties, such as quinines, and electron-rich centres, such as diphenols. Charge transfer complexes are formed via electron donor-acceptor mechanisms, with pesticides possessing, alternatively, electron donor or electron acceptor properties. IR spectroscopy revealed that the bipyridilium pesticides, paraquat and diquat, have been reported to form a charge-transfer complex with soil humic acids. Similarly, charge-transfer complexes have also been observed between methoxytriazines, substituted ureas and amitrole, and soil organic matter. Electron spin resonance spectroscopy
(ESR) has been employed to confirm the presence of these electron donor-acceptor mechanisms between pesticides and humic substances [250, 279]. The charge transfer interaction between humics and the pesticides can result in an increase in the free radical concentration relative to the unreacted humic acid, due to single-electron donor-acceptor mechanisms [279].

1.4.4.6. Hydrophobic Partitioning

Hydrophobic adsorption is proposed as the main mechanism for the retention of non-polar pesticides by hydrophobic active sites of humic substances or clay. Hydrophobic retention need not to be an active adsorption mechanism, but can also be regarded as a partitioning between a solvent and a non-specific surface. The partitioning theory, which treats soil organic matter as a water-immiscible liquid phase, has been found to explain the hydrophobic interaction between pesticides and soils [280]. This means that humic substances both in the solid- and dissolved-phase are treated as a non-aqueous solvent into which the organic pesticide can partition from water [281]. However, soil organic matter is a solid phase with pH-dependent functional groups and a matrix of internal and external hydrophobic surfaces.

Hydrophobic adsorption by soil organic matter and humic substances is suggested as an important mechanism for DDT and other organochlorine insecticides [243], oxidaizinon, butralin, methazole [253], metolachlor [246], picloram and dicamba [252]; 2,4-D [245] and it is considered a possible interaction mechanism for the s-triazine herbicides and polyureas [282, 283].

1.4.4.7. Covalent Bonding

The formation of covalent bonds between xenobiotic chemicals and/or their metabolites and soil humic substances, are often mediated by chemical, photochemical or enzymatic catalysts leading to stable, mostly irreversible incorporation into the soil. The pesticides which are most likely to bind covalently to humic matter have functionalities similar to the components of humus [284-285, 241]. Thus, pesticides that structurally resemble phenolic compounds can covalently bind to humus. This results in the formation of C – C and C – O bonds between phenolic
species and C-N and N-N between aromatic amines [286]. Compound classes that can bind covalently to soil humic material include acylanilides, phenylcarbamates, phenylureas, dinitroaniline herbicides, nitroaniline fungicides and organophosphate insecticides, such as parathion and methylparathion. They bind by two possible mechanisms involving carbonyl, quinine and carboxyl groups of humic substances leading to hydrolysable and non-hydrolysable bound forms [287, 288].

The complex and heterogeneous nature of environmental solids such as soil makes it difficult, if not impossible, to identify specific adsorption mechanisms for most soil-pesticide combinations [289] and in most situations, several mechanisms operate simultaneously. In most soils and under most conditions, pesticides are adsorbed on both organic matter and inorganic clay surfaces. The relative importance of organic versus inorganic constituents depends on the amount, distribution, and properties of those constituents and the properties of the pesticides. As the polarity, number of functional groups, and the ionic nature of the pesticide increase so too does the number of potential adsorption mechanisms [290]. Fortunately for many pesticide–soil interactions, the adsorption process is dominated by one or two mechanisms and generalizations regarding adsorption behaviour can be made.

1.4.5. Adsorption Isotherms

The relation between the amount of pesticide adsorbed per unit weight of the adsorbent and the pesticide concentration in the solution at equilibrium is called an adsorption isotherm. Adsorption of pesticides on soils was evaluated by adsorption isotherms which represents the relation between the amount of pesticide adsorbed per unit weight of the soil and pesticide concentration in the solution at equilibrium. According to the nature of the slope of the initial portions of the curves, Giles et al. [291] reported the relation between solute adsorption mechanisms on solid surfaces and the types of adsorption isotherms. They developed four main classes of adsorption isotherm i.e. S-type curves, C-type curves, L-type curves and H-type curves.
1.4.5.1. **S-type Curves**

S-type isotherm generally occurs when the solid has a high affinity for the solvent. The initial direction of the curvature shows that adsorption becomes easier as concentration increases. This type of isotherm usually appears when the solute molecule is monofunctional; has moderate intermolecular attraction, and meets strong competition for substrate sites from molecules of the solvent or other adsorbed species.

1.4.5.2. **L-type Curves**

The L-type curve, the normal or "Langmuir" isotherms, are best known and represent a relatively high affinity between the solid and solute in the initial stage of the isotherm. As more sites in the substrates are filled, it becomes increasingly difficult for solute molecules to find a vacant site available.

1.4.5.3. **C-type Curves**

C-type curve are given by solutes which penetrate into the solid more readily than does the solvent. These curves are characterized by the constant partition of solute between the solution and substrate, right upto the maximum possible adsorption, where an abrupt change to horizontal plateau occurs.

1.4.5.4. **H-type Curves**

H-type curves are quite uncommon and occur only when there is very high affinity between solute and solid. This is a special case of L-type curve, in which the solute has such a high affinity that in dilute solution it is completely adsorbed, or at least there is no measurable amount remaining in solution. The initial part of the isotherm is therefore vertical.

1.4.6. **Adsorption Models**

Generally two mathematical equations such as Freundlich and Langmuir equations have been used for quantitative description of pesticide adsorption on soils [292-294].
1.4.6.1. Freundlich Adsorption Equation

The Freundlich adsorption equation can be expressed as:

\[ \frac{x}{m} = K_F C_e^{1/n} \]  \hspace{1cm} (1.1)

where \( K_F \) and \( 1/n \) are empirical adsorption constants and \( x/m \) and \( C_e \) are the adsorbed (\( \mu g \) pesticide \( g^{-1} \) soil) and solution phase (\( \mu g \) pesticide \( mL^{-1} \) solution) concentrations, respectively. The adsorption coefficient \( K_F \), has unit of \( g^{1-n} \) \( mL^n \) g\(^{-1} \), while \( 1/n \) is dimensionless. Values of adsorption constants \( K_F \) and \( 1/n \) are estimated by linear regression of log-transformed data. The equation (1.1) is expressed in logarithmic form and a linear relationship is obtained:

\[ \log \frac{x}{m} = \log K_F + \frac{1}{n} \log C_e \]  \hspace{1cm} (1.2)

Generally, in the reasonable pesticide concentration range, the relationship between \( \log x/m \) and \( \log C_e \) is linear with \( 1/n \) being constant. In comparing adsorptive capacity of various pesticides by soils, the \( K_F \) value may be considered to be useful index for classifying the degree of adsorption because the use of \( K_F \) values has considerably increased as a result of the requirement by regulatory agencies for quantification of relative pesticide adsorption in soil water system (EPA, 1978). For soil–pesticide interaction, soil organic matter based or soil organic carbon based adsorption constant \( K_{OM} \) or \( K_{OC} \), respectively, was calculated by dividing the \( K_F \) value by organic matter or organic carbon content present in the soil \([295, 296]\). \( K_{OM} \) or \( K_{OC} \) are used to characterize the mechanism of adsorption of pesticide to organic components of the soil. The lower \( K_{OM} \) or \( K_{OC} \) values show that the chemical will be less adsorbed by the soil particles.

In general, the values of \( K_F \) for the adsorption on soils decreases with increase in the temperature and increase in value to \( 1/n \) takes place at higher temperature \([65, 193, 297]\).

1.4.6.2. Langmuir Adsorption Equation

Langmuir Adsorption Equation was initially derived from the adsorption of gases by solid using the following assumptions:

(i) The energy of adsorption is constant and independent of surface charge.
(ii) Adsorption is on localized sites and there is no interaction between adsorbate molecules, and
(iii) The maximum adsorption possible is that of a complete monolayer.

The Langmuir adsorption equation may be expressed in terms of concentration in the following form:

$$\frac{x}{m} = \frac{K_1 K_2 C_e}{1 + K_1 C_e}$$  \hspace{1cm} (1.3)

Where $K_1$ is a constant for the system dependent to temperature and $K_2$ is the monolayer capacity. The term $x/m$ and $C_e$ have been defined in the Freundlich equation. The reciprocal of equation:

$$\frac{1}{x/m} = \frac{1}{K_2} + \frac{1}{K_1 K_2 C_e}$$  \hspace{1cm} (1.4)

A plot of $1/(x/m)$ vs. $1/C_e$ should give a straight line with an intercept $1/K_2$ and a slope of $1/(K_1 K_2)$ when the Langmuir equation holds. The adsorption of pesticides on soils and clays was found to conform to an isotherm type which was similar to Langmuir model for adsorption [298, 299].

Under certain conditions both the Freundlich and Langmuir equations may reduce to linear relationship. In the case of Freundlich equation, if the exponent $1/n$ is 1, adsorption will be linearly proportional to the solution concentration. In practice, it has been found that adsorption of the pesticides on soils do fit the Freundlich equation with an exponent close to unity. In the Langmuir equation the denominator, $1 + K_1 C_e$, becomes indistinguishable from 1 at low concentrations. In this situation, the amount adsorbed becomes directly proportional to the concentration in the solution.

**1.4.7. Movement of Pesticides in Soils**

The movement of pesticides in soil affected their ability to effectively control the targeted pests and determine whether or not these chemicals may lead to an environmental impact. Due to this reason Soil Scientists and Environmental Scientists
both have equal interest in characterizing the fate and movement of pesticides in soils.
Over the last several years, the interest in this kind of research has been focused on
groundwater contamination due to the use of pesticides in crop protection.

Prior to 1979, groundwater contamination from field applied pesticides was
virtually unexpected. It was assumed that pesticide in the natural environment would
either breakdown, or that the soil, sand, gravel and rock formations would be adequate
to cleanse the water of its contaminants before it reached groundwater. Now it is clear
that human activities can lead to contamination of groundwater. Pesticides, especially
nematicides such as DBCP and EDB have been detected in groundwaters in several
regions of USA [300, 301]. A 1990 study by the USEPA highlighted the presence of
74 pesticides in the groundwater of 38 states of USA. Due to this reason, fumigants
such as DBCP and EDB have been banned by EPA and the use of non-fumigant
pesticides such as aldicarb, oxamyl, carbofuran and fenamiphos etc has increased.
However, another monitoring study has reported that aldicarb, oxamyl and carbofuran
were also found in groundwater samples [302-304]. So, to reduce the risk of
groundwater contamination, it is essential to understand the behaviour of pesticides in
natural environment.

Several workers [64, 67, 75, 305-320] have studied the movement of
organohalogenated, organophosphorous and carbamate group containing pesticides in
soils. The role of organophosphorous and carbamate group containing pesticides,
being more soluble in water than organohalogenated pesticides, in polluting soil
environment cannot be underestimated. Kaneko et al. [321] and Kaufmann et al.
[322] have also studied the movement of permethrin, cypermethrin and decamethrin
in soils.

The extent of movement of pesticides in soil depends upon the soil properties
such as texture, structure, porosity, organic matter content, clay content, moisture
content, pH and CEC [323-327] and on the nature and properties of pesticides itself
i.e. solubility of pesticides in water, formulation, rate of pesticide application or
degradation.

Soil texture and structure affects the movement of pesticides because fine
textured soil contains higher amount of moisture rendering a faster dilution of
toxicants. The movement of pesticide was less in fine textured soil than coarse
textured soil because equilibrium of pesticide between water and the interior soil
aggregates becomes slower with increasing aggregate size and relatively small zone
of pest control. It was also observed that an inverse relationship exists between clay
content and movement of pesticides. The sand particles being more permeable than
clay particles, allow an easy and deeper movement. Porosity is the function of the
pore size distribution determined by soil texture, structure and particle shape.
Pesticides are transported to a greater degree through more porous soil when other
things are equal.

Soil organic matter is another primary parameter that affects the movement of
pesticides in soils. The depth of penetration of pesticides has been found to be
inversely proportional to the organic matter content; higher organic matter content
greatly increases the retention of pesticides and therefore inhibits their movement into
groundwater.

Water flux affects the movement of pesticide in soil because it is the amount of
water that flows through the soil. In practice this is often less than the rainfall because
evaporation from the soil surface and uptake by the crop diminish downward
movement as a consequence chemical can move both downwards and upwards in
soils in response to water movement in wetting and drying cycles. However, in
laboratory condition water flux through the soil column can be accurately controlled.
Leaching of pesticides due to addition of water has been extensively studied by Davis
et al. [328], Friesen [329] and Bayer [330]. Some of pesticides are more mobile at
higher rates of percolation [331].

Water solubility of pesticides is an important property which affects their
movement in soil. Increased solubility of pesticides has decreased adsorption [332,
333] and therefore, increased the mobility. An inverse relationship has also been
observed between solubility and adsorption [334-336]. Organophosphorous and
carbamate pesticides are more soluble in water than chlorinated hydrocarbon
compounds. Reynolds and Metcalf [337], while studying the movement of several
phosphorous and carbamate group containing pesticides found that it was related to
their water solubility. This would indicate that they are much more susceptible to
leaching than the chlorinated compounds. Weber [338] reported that the amount of acidic herbicides adsorbed on soil was inversely related to the water solubility of the chemical. On the other hand, Hance [339] and Weber [340] observed no relationship between solubility and adsorption of certain pesticides.

The formulation in which a pesticide is applied influences the mobility. An increase in mobility of simazine has been observed by adding ammonium sulphate [341] and that of diuron by adding surfactants [342]. Solution formulations of some non-volatile fungicides were more mobile than suspension [343].

The rate at which the pesticides are to be applied may affect the movement of pesticides. Several workers [344-347] have studied the effect of rate of application on mobility of certain triazine herbicides and they have reported that higher application rates of herbicides increased their mobility.

Generally, the movement of pesticides has been estimated using soil column [78, 84, 348-353] and soil thin layer chromatographic (Soil TLC) techniques [305-377, 312-313, 354-358]. Data pertaining to soil column and field leaching studies were used to evaluate the simple piston displacement model [359]. The model accurately predicted the position of the wetting fronts, but under predicted pesticide leaching. Singh et al. [353], Kumari et al. [78, 84], and Bilkart and Rao [359] have studied the movement of certain pesticides in soil columns and estimated the distribution coefficients K_D values as described by Ketelle and Boyd [360] and used by Swoboda and Thomas [361]. The K_D values obtained from soil column studies were correlated with the K_D values obtained from batch equilibrium techniques. They demonstrated that higher movement of pesticides was observed in coarse textured soils than fine textured soils. The amount of rainfall required to leach pesticide up to a depth of '60 inches' was estimated by using the relation as described by Swoboda and Thomas [361] and later used by Singh et al. [353] and Kumari et al. [78, 84]. Recently, Fenoll et al. [362] have evaluated the movement and leaching potential of several insecticides and fungicides through disturbed clay-loam soil columns. Xu et al. [363-367] have studied the effect of methanol as an eluent in soil columns and developed a method to measure the capacity factors (k') and soil organic partition coefficient (K_OC) of pesticides by developing a relation between K_OC and k' and
evaluated the influence of different volume fractions of methanol on these parameters. Recently, Hua et al. [368] have studied the effect of surfactants on the leaching behavior of bentazone.

Before 1968, pesticide mobility in soils can be studied indirectly from their soil adsorption coefficient and directly using column leaching experiments. Helling and Turner [305] introduced the soil TLC technique as an alternative procedure for rapid, reproducible and inexpensive assessment of pesticide movement in soils with the use of soil instead of silica gel, oxides and other adsorbents as an stationary phase and they found it analogous to conventional TLC technique. They found that the Rf value determined by the soil TLC for the mobility of several pesticides were consistent to the field data and with the results of the laboratory studies using soil columns. Using Rf values as indices of mobility of a series of pesticides with different structures, they proposed a five level classification scale for pesticide mobility in soils. Helling [306-308] used the soil TLC technique to study the effect of different parameters such as soil particle size, run distance, plate thickness, sample size of pesticides etc. on the movement of pesticides in soils. Helling (1971 abc) [306-308] used three methods for detecting the movement of labeled pesticides on soil chromatoplates such as (i) analysis of the successive zones of the soil layers (ii) autoradiography and (iii) scanning radio chromatograms. All these methods yielded similar results, although at that time Helling considered autoradiography to be the best one. Helling et al. [310, 369] have also reported a bioassay technique for the detection of pesticide mobility in soil. Singh et al. [312-313, 352-353, 370] and Sharma et al. [356-358] however, used this technique for determining the movement of certain pesticides, amino acids and phenols in soils by detecting the movement with simple chemical detectors and the movement was expressed in terms of Rf values.

Recently, Singh and Singh [239], Singh et al. [154, 240], Sanchez-Camazano et al. [371], Ravanel et al. [372], Queiroz and Lancas [373], Singh and Rajkumar [157, 160, 174], Horvat et al. [374] and Crovotto et al. [375] have studied the movement of pesticides on soil and examined effect of organic matter, cosolvents, surfactants, fertilizers and mineral composition on pesticide mobility using soil TLC technique.
1.5. OBJECTIVES

The work on the aspects covering the effect of surfactants and co-solvents on the adsorption and movement of pesticides in soils currently used for agricultural purposes is still meagre. More studies are required to get the complete picture of this phenomenon on different types of soils. Keeping this in view, the present work was planned to study the effect of surfactants (cationic, non-ionic and anionic) and water miscible organic solvents (acetone and methanol) on the adsorption and movement of carbofuran, carbaryl and endosulfan in divergent textured Indian soils. These studies will help in providing the information with regard to the judicious and efficacious use of carbofuran, carbaryl, and endosulfan in soils and also for assessing near source of these pesticides’s movement/transport in soils in the event of spill or discharge of organic waste containing surfactants and water miscible solvents (co-solvents). The study conducted is interesting in that it covers three pesticides with different water solubility and hydrophobicity. The scheme of the chapters is as follows:

- Adsorption and Movement of Carbofuran in Non-Ionic and Anionic surfactant Amended Soils of Divergent Texture.
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