Chapter – I

INTRODUCTION

1.1 General

Water is a source of life and energy. Groundwater is one of the major sources of drinking water. Many organic pollutants in ground and surface water are proven to be toxic and harmful even when present at very low concentrations. For this reason, their removal from the contaminated water is of high priority (Babuponnusami and Muthukumar, 2014). Wastewater is categorized and defined according to its origin. Agro-industrial wastewater has considerable impact on the environment in terms of pollutant strength. Agriculture is the backbone of India's economic development, utilizes large quantities of pesticides and other chemicals that penetrate plants besides killing pests and reach human body leading to various health problems (Bhatnagar and Sillanpaa, 2010).

1.2 Historical Background of Pesticides

Pests are affecting every aspect of human life, right from the food we eat, to the clothes we wear. The crop losses in the country due to various pests range from 10-30% of total production per year depending on the severity of pest attack. To meet the increasing demand of food, control of these pests is essential (Dhaliwal and Arora, 1996). With the innovation in research, synthetic pesticides also called chemical pesticides were developed, which were highly effective against pest. The era of chemical pesticides for pest control began around the World War II (Shawaqfeh, 2010). The insecticidal potential of dichloro-diphenyl-trichloroethane (DDT) was discovered in 1939 by Paul Muller in Switzerland and the development of organophosphorus insecticides in 1945 in Germany (Casida, 2009). The first soil-acting carbamate herbicides brought to light in the United Kingdom in 1970 and simultaneously the organochlorine insecticide chlordane was introduced in Germany and the United States (WHO, 2009). Towards the end of 1960s, the importance of the pesticides was well recognized for the pest control and pyrethroids were introduced in 1980 (Bosch and Stern, 1962). A pesticide consists of an active ingredient coupled with inert ingredients. Raw materials used in the production of pesticides might include a large number of organic and/or inorganic compounds.

1.3 Classification of Pesticides

Pesticides can be classified in three most popular ways which are based on the mode of action, the targeted pest species and the chemical composition of the pesticide. In India, there are seven ways to classify pesticides based on the chemical nature, as shown in Figure 1.1. (Aktar et al., 2009; www.fehd.gov.hk).

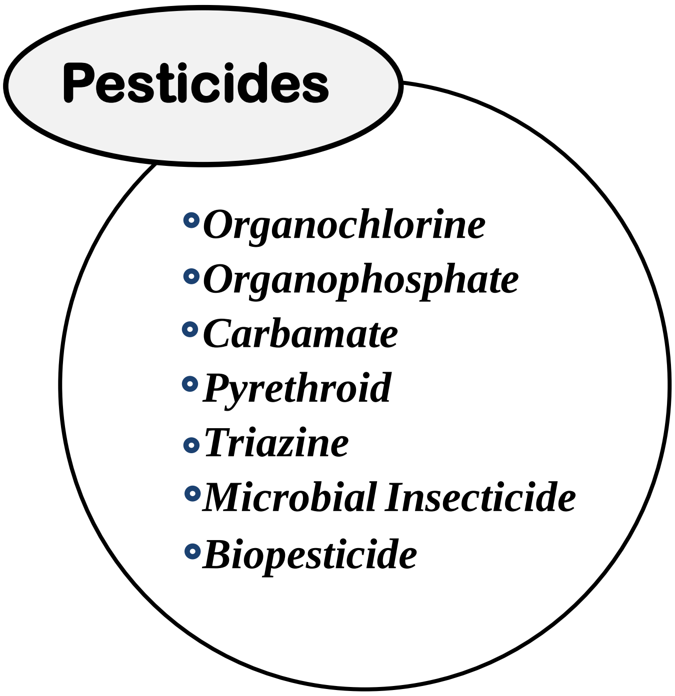

Figure 1.1: Classification of pesticides based on the chemical nature.

1. Organochlorines**:** These organic compounds have several atoms of chlorine per molecule and have broad-spectrum characteristics. Dichloro-diphenyl-trichloroethane (DDT), lindane, endosulfan, endrin, aldrin, dieldrin, chlordane and Benzene hexachloride (BHC) are organochlorine pesticides (Aktar et al., 2009). Prolonged use of these compounds in large quantities will easily contribute to environmental pollution, resulting in accumulative poison or damage to the environment. These compounds have a stable chemical nature; and are hard to break down in the natural environment. Organochlorine pesticides are highly toxic in nature and the rate of degradation of these compounds is slow, therefore is banned for general use and is gradually replaced by other pesticides.

2. Organophosphates**:** Organophosphorus compounds are the most commonly used pesticides in the western countries which are toxic in nature and enter into the body through contact with skin, ingestion, and inhalation. These pesticides are characterized by their multiple modes of action and the capacity to control a broad spectrum of pests. They are highly effective on the nervous system (nerve poisons). After sometimes these pesticides are biodegraded in the environment, cause slow pest resistance and minimum environmental pollution. Temephos, parathion and fenitrothion are typical examples of these pesticides.

3. Carbamates**:** The working principle of these pesticides is the same as organophosphate pesticides, affecting the nervous system and resulting in the death of the pests. These pesticides are stomach poisons, contact poisons as well as fumigants. They can be easily degraded in the environment with minimum environmental pollution. Carbofuran (furadon) and propoxur (baygon) are examples of carbamate pesticides.

***4. Pyrethroids*:** These are synthetic products synthesized by imitating the structure of natural pyrethrins, a plant chemical extracted from chrysanthemum cinerarifolium. Synthetic-pyrethroid pesticides are comparatively more stable than natural pyrethrins. These are highly toxic to insects but only slightly toxic to mammals. Permethrin and allethrin are examples of pyrethroid pesticides.

***5. Triazines*:** These compounds are like atrazine and simazine derived from urea. These compounds are effective herbicides and used to control weeds of tea, cotton, and tobacco.

***6. Microbial Insecticides*:** These insecticides are used to control pests by means of pathogenic micro-organisms including fungus, viruses, and bacteria. Bacillus thuringiensis israelensis (B.t.i.) is an example of microbial insecticides.

7. *Biopesticides*: Biopesticides are the pesticides derived from animals, plants and certain minerals canola oil. Baking soda also considered as biopesticides and has several pesticidal applications.

Pesticides can also be classified on the basis of their hazardous nature (LD_{50} value) as shown in Table 1.1 and sub classification of pesticides based on their targeted organism/pest is given in Table 1.2.

Table 1.1: Classification of pesticides on the basis of hazardous nature (LD_{50} value) (WHO, 2009).

Classification of pesticide	Lethal dose (oral route) (LD_{50}) mg/kg*	Lethal dose (dermal route) (LD_{50}) mg/kg*	Examples
Extremely toxic	1-50	1-200	Phorate, Parathion
Highly toxic	51-500	201-2000	Carbofuran, Endrin
Moderately toxic	501-5000	2001-20000	DDT, Lindane
Slightly toxic	5000	20000	Malathion
Unlikely to toxic	More than 5000	More than 20000	Atrazine

* Body weight of test animals

Table 1.2: Sub classification of pesticides based on the targeted organism/pest.

S. No.	Type of pesticides	Target organism/pest
1.	Algicides or Algaecides	Algae
2.	Avicides	Birds
3.	Bactericides	Bacteria
4.	Fungicides	Fungi and Omycetes
5.	Insecticides	Insects
6.	Miticides or Acaricides	Mites
7.	Nematicides	Nematodes
8.	Molluscicides	Snails
9.	Rodenticides	Rodents
10.	Virucides	Viruses

1.4 Usage of Pesticides

Pesticides are known as agrochemicals, mainly used for crop protection and public health. Application of chemical pesticides is the quickest method as compared to natural pesticides to control weeds, insect, fungi, rodent, bacteria by attacking on nervous system, affecting photosynthesis, smothering, dehydration, inhabitation of blood clotting, widely used to enhance the agriculture production e.g. Green revolution in countries like India and Mexico (Pinto et al., 2010).

As 30% of the crops are lost due to different pests, insects, mites etc., so the use of pesticides has become unavoidable. The use of pesticides in agriculture, forest, garden, park and in non-agricultural sectors such as wood preservation, disinfection or household use is increasing day by day, thus polluting water resources (Gupta et al., 2006; Pinto et al., 2010; Reis et al., 2014). Some of carbamates are used as pesticides and some of them (e.g. physostigmine, pyridostigmine) are registered as human drugs (Jokanovic, 2009). Carbamate also reversibly inhibits the enzyme activity. Table 1.3 shows the applications of pesticides on crop protection and Figure 1.2 shows the consumption of pesticide on crops according to classification.

Table 1.3: Major application area of pesticides (TATA, 2015).

Segment	Major applications area
Insecticides	Cotton, Rice
Fungicides	Fruits, Vegetables, Rice
Herbicides	Rice, Wheat
Bio-pesticides	Rice, Maize, Tabacco
Others	Stored produce

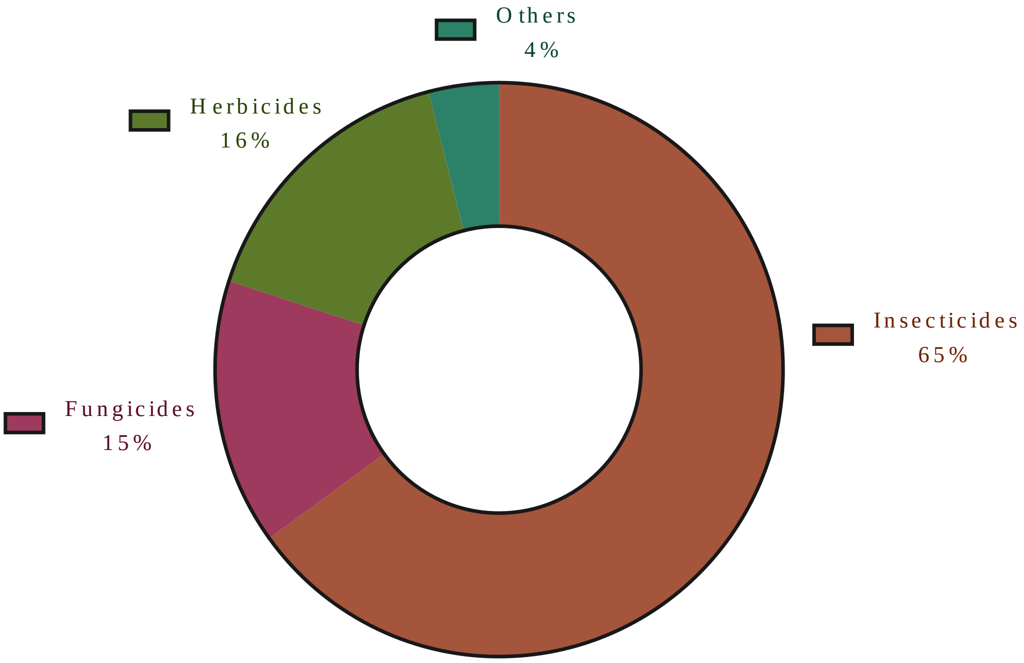

Figure 1.2: Consumption of pesticides by crop protection (www.krishijagran.com, 2015).

1.4.1 World scenario of pesticides

Around two million tons pesticides per year are consumed worldwide. In 2015 USA consumed 24%, Europe 45% and the rest of the world 25%. India used only 0.6 kg/ha pesticides (Table 1.4), which is lowest in the world.

Table 1.4: Worldwide pesticide consumption (kg/ha) **(**TATA, 2015).

S. No.	Country	Pesticide consumption (kg/ha)
1.	Taiwan	17
2.	China	13
3.	Japan	12
4.	USA	7
5.	Korea	7
6.	France	5
7.	UK	5
8.	India	0.6

1.4.2 Indian scenario of pesticides

Pesticides that have been used in India are regulated by the Central Insecticides Board and Registration Committee (CIBRC) and the Food Safety and Standards Authority of India (FSSAI). The CIBRC registers pesticides for crops while the FSSAI sets the maximum residue limits (MRLs) of pesticides, which have been registered for the crops (Bhushan et al., 2013). The total number of pesticides registered in 2013 by CIBRC including endosulfan is 234 (www.cseindia.org). The use of endosulfan was banned in May 2011 in India. Most of the pesticides have either been banned or restricted by some countries, but in India these are allowed to be used on the crops.

In India, pesticide industry started in 1952 for the production of BHC at Rishra near Kolkata (Abhilash and Singh, 2009; Kavitha and Sureshkumar, 2016). Soon, Hindustan Insecticides Ltd. followed suite and set up two units for DDT manufacture. In 1969, Union Carbide installed a small plant (Union Carbide India Ltd. (UCIL)) at Bhopal, to formulate pesticides. According Green Peace Report, India is producing 90,000 metric tons (MT) of pesticides per year which is the second largest producer of pesticides in Asia after China and has twelfth rank globally in the world (Amalraj and Pius, 2015; www.greenpeaceindia.org).

The major category of insecticides, which are available and continuously being used in India include 2,4–dichlorophenoxyacetic acid, acephate, phorate, captan, monocrotophos, cypermethrin, paraquat, carbofuran, carbendazim, dimethoate, dichloride, methyl parathion, phosalone mancozeb, malathion, paraquate quinalphos, chlorpyrifos, fenvalerate, dichlorvos, triazophos, and zineb (IPCS, 2008; Abhilash and Singh, 2009; Bhushan et al., 2013; Amalraj and Pius, 2015).

The usage of pesticides is high in some parts of the country such as Maharashtra, Karnataka, Gujarat, Andhra Pradesh and Punjab. In which, Andhra Pradesh

(Seemandhra and Telangana) and Punjab consume the largest amount of pesticides. Yearwise consumption of pesticide is presented in Figure 1.3. Pesticides commonly used in India are described in Table 1.5. State and cropwise consumption of pesticides in India are presented in Figures 1.4 and 1.5, respectively.

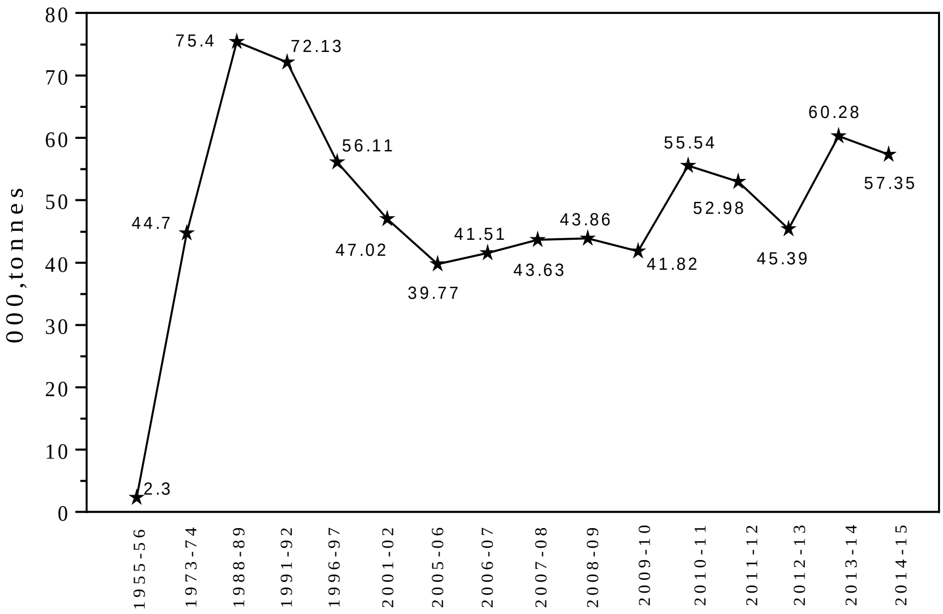

Figure 1.3: Yearwise consumption of pesticides in India (www.pib.nic.in, www.krishijagran.com).

Table 1.5: Commonly used and recommended pesticides in India (US EPA, 2007; Bhushan et al., 2013).

Name of Pesticide	Consumption (MT, 2009-10)	Crops Registered	R_fD (mg/kg BW/day)	TMDI (adult) (mg/day)	Category
Phorate	3284	23	0.0005	0.0564	-
Mancozeb	3118	23	0.05	0.565	-
Methyl Parathion	2739.32	7	0.00025	0.52	I
Cypermethrin	2473	8	0.01	0.0885	II
Carbendazim	1992	18	0.025	0.71	-
Monocrotophos	1815	14	-	0.17	I
Malathion	1739.39	16	0.02	3.756	-
Quinalphos	1595	32	0.0005	0.00176	II
Acephate	1513	3	0.003	0..025	III
Triazophos	1164.48	4	-	0.0096	-
Dichlorvos	960	10	0.0005	0.535	-
Fenvalerate	776	4	0.025	0.15	II
2,4 – D	662	8	0.01	0.243	-
Dimethoate	636	24	0.0002	1.2	-
Captan	471	14	0.13	9	-
Zineb	462	18	0.05	0.565	-
Paraquat dichloride	NA	10	0.0045	0.0924	-
Chlorpyrifos	NA	13	-	0.13	I
Phosalone	NA	1	-	0.864	-
Carbofuran	NA	27	0.005	0.122	I

** Reference Doses (R_fD), Theoretical Maximum Daily Intake (TMDI).

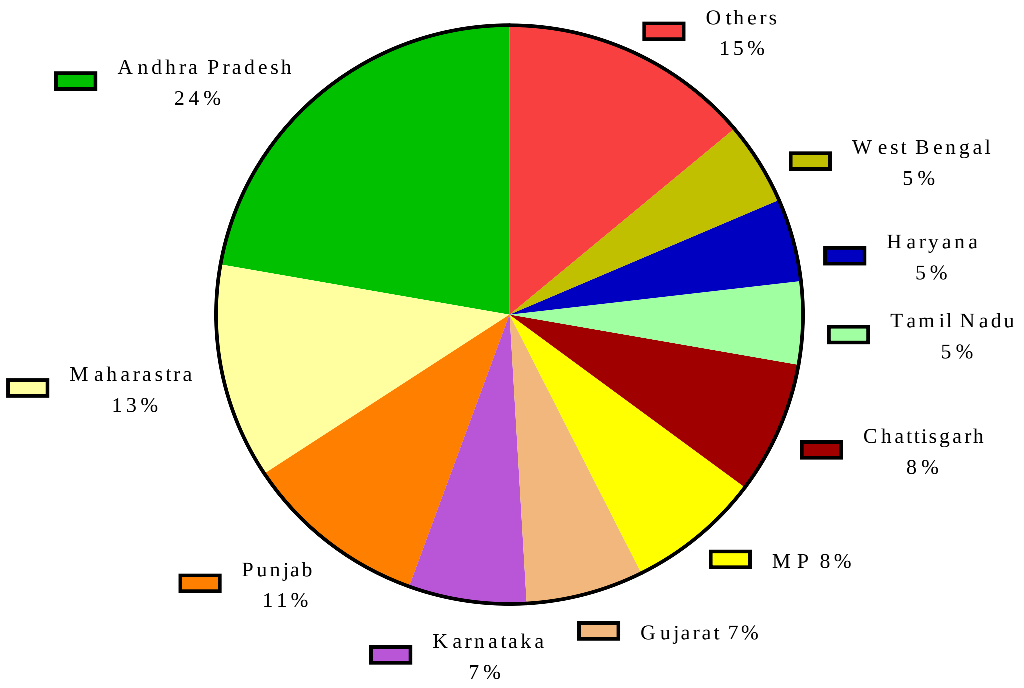

Figure 1.4: State wise consumption of pesticides in India (Kavitha and Sureshkumar, 2016).

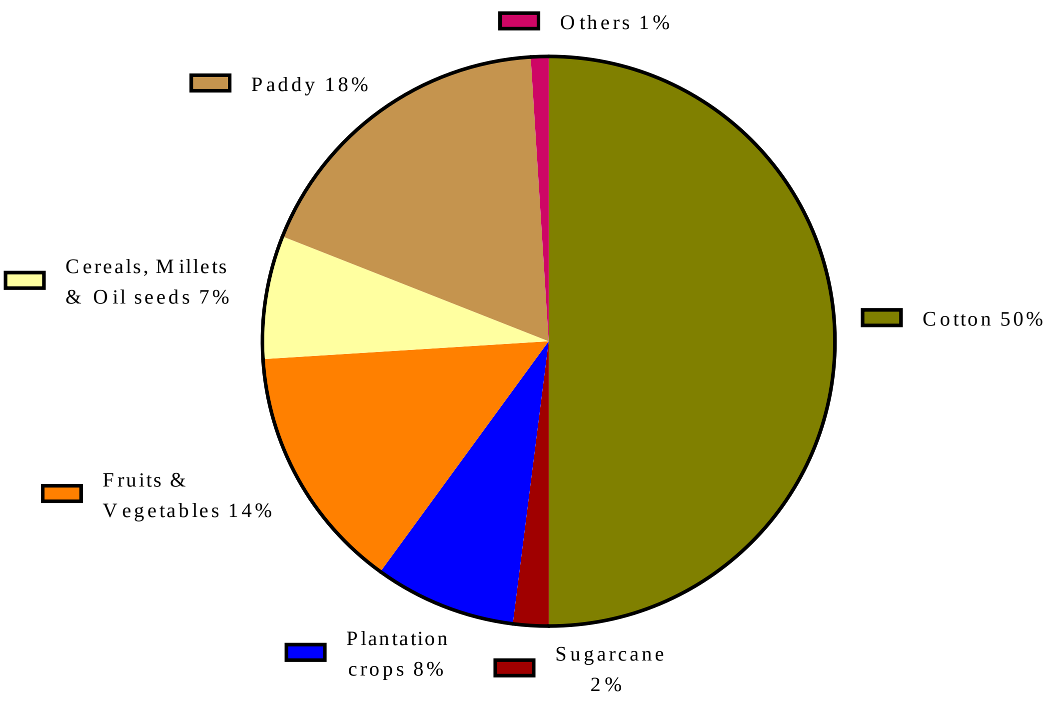

Figure 1.5: Crop wise consumption of pesticides in India (Kavitha and Sureshkumar, 2016).

1.5 Sources of Pesticides in Environment

Due to the rapid growth in industrialization, the discharge of chemicals through the use of fertilizers, pesticides, herbicides, heavy metals, and other hazardous chemicals, including organic matter and microorganisms have contributed substantially to the environmental pollution (Ova and Ovez, 2013). Pesticides are generally used to increase production and quality of crops. Extreme usage of pesticides increases the pesticide level in drinking water and eventually causing syndrome to human beings (Ng and Zhang, 2011). Globally 4.6 million tons of pesticides are annually sprayed into the environment, out of which 98% reach into non-targeted species like air, water bodies and soil (Jeyanthi and Kombairaju, 2005). Dispersion of pesticide in the environment is shown in Figure 1.6.

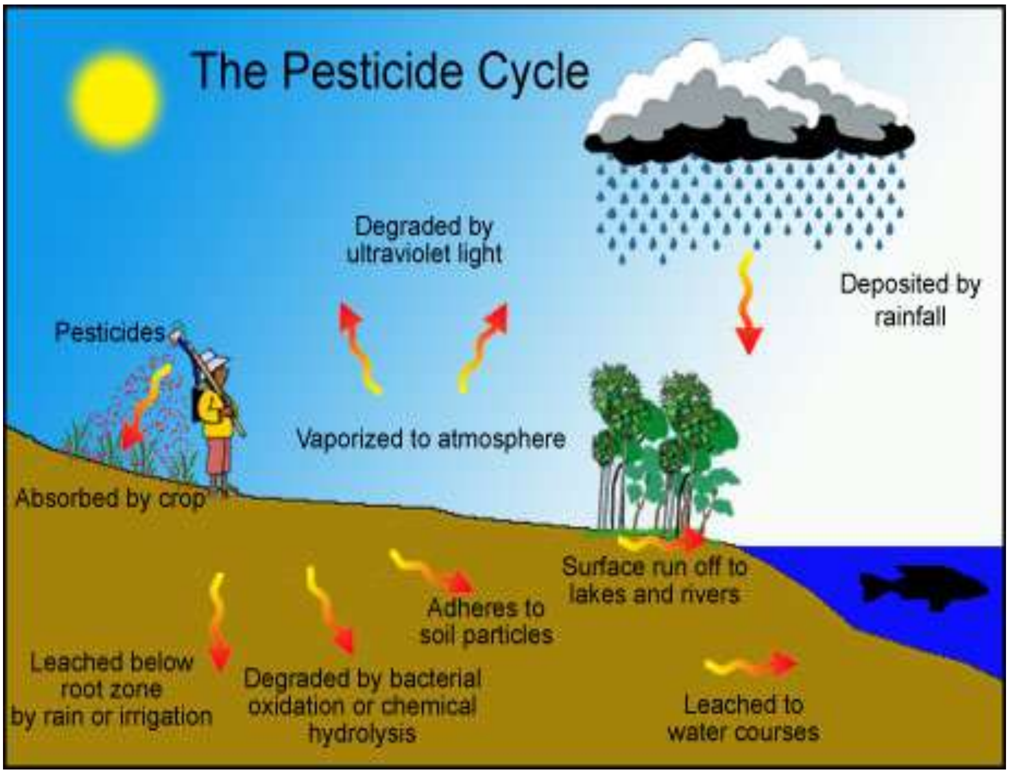

Figure 1.6: Pathways of pesticides spread in the environment.

The transmission of pesticides in soil and in other environmental compartments depends on a change of physical, chemical and biological processes, including adsorption–desorption, uptake by plants, volatilization, chemical/biological degradation, runoff and leaching. However, adsorption plays a crucial role in the persistence, bioaccumulation and transformation of pesticides in environments (Jonge et al., 1996; Vryzas et al., 2007; Arias-Estevez et al., 2008; Geronimo et al., 2014).

Emissions of pesticides are generally subdivided into diffuse and point sources. The pesticide effluents into the water resources and aquifer systems, by the spray drift, soil leaching, tile drainage outflow, base-flow seepage, surface run-off, volatilization (diffuse-source inputs), sewer overflows, improper handling of tank mix left overs, leaking of faulty equipment, incorrect storage of canisters, dripping from agricultural practices, accidental spillage, farm yard runoff, improper disposal of pesticides and direct entry into surface water (point-source inputs) (Reichenberger et al., 2007). Agro-industrial sites are the largest easily identifiable point sources of pollutant.

1.6 Adverse Effects of Pesticides

The Food and Agriculture Organization (FAO, 2001) reported more than 500,000 tons of unused and out-of-date pesticides, that are threatening the public health and environment in many countries.

1.6.1 Health effects

According to World Health Organization (WHO) every year there are 3 million pesticide poisoning cases, most of which were due to organophosphate i.e. methyl parathion and chlorpyrifos, and 200,000 deaths worldwide due to either occupational exposure or self-poisoning (Alavanja and Bonner, 2012). Pesticides have toxic effects such as reproductive, teratogenic, mutagenic and carcinogenic on humans. There are many sources of exposure to pesticides. Pesticides enter in human body through different routes of exposure such as inhalation, ingestion, and dermal contact as shown in Figure 1.7 (WHO, 2008). Carbofuran is very toxic to aquatic life with long lasting effects and fatal if swallowed or inhaled. At extremely low doses, carbofuran can cause transient alterations in the concentration of many hormones in humans and animals.

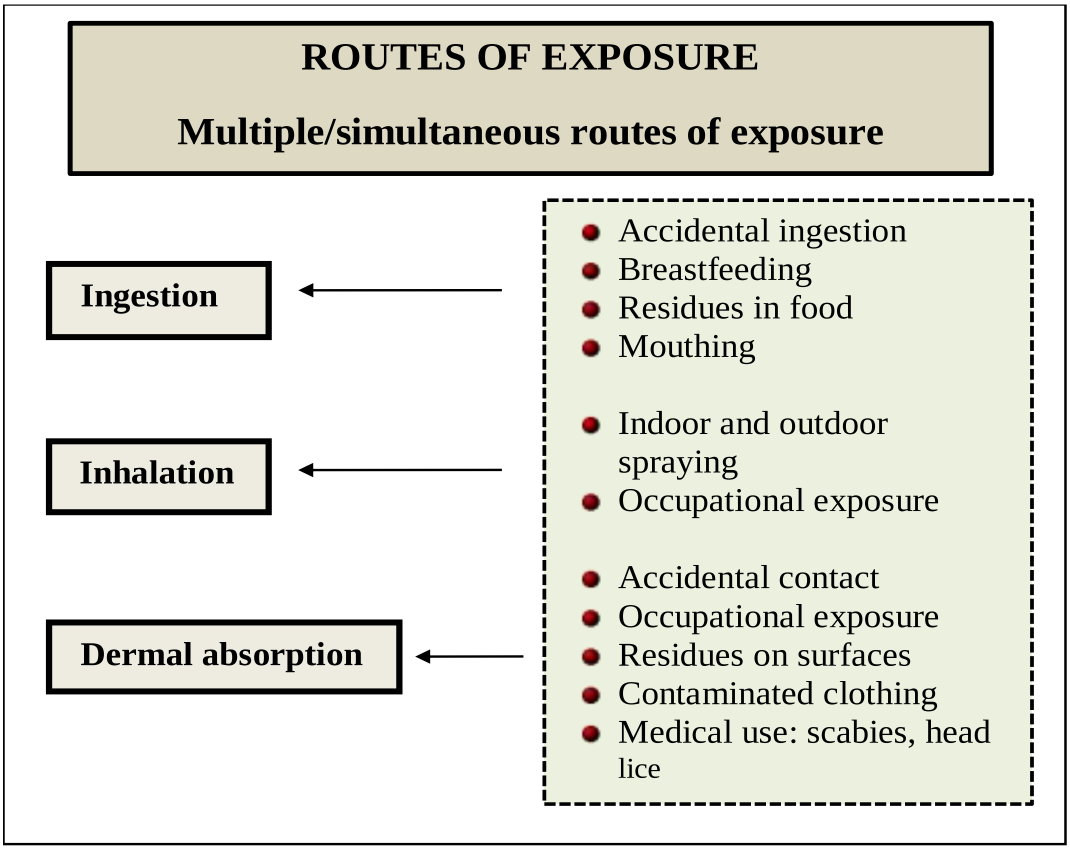

Figure 1.7: Routes of exposure of pesticides on human body.

1.6.2 Environmental effects

Pesticides also affect the lives of domestic animals, birds, fish, wildlife and livestock. Application of pesticides in inappropriate doses is only destroying the healthy pool of bio-control agents that normally co-exist with the vegetation but also disturbing the soil circumstances (California EPA 1999; EPA, 2000; Brkic et al., 2008; Casida, 2009).

1.7 Pesticides Regulations

Pesticides manufacture, storage and transport are governed in India under the following Acts/Rules:

1. Hazardous Waste (Management & Handling) Rules, 1989
2. The Environment (Protection) Act, 1986
3. Air (Prevention & Control of Pollution) Act, 1981
4. Water (Prevention & Control of Pollution) Act, 1974
5. The Insecticides Act, 1968 and Rules, 1971
6. Prevention of Food Adulteration Act, 1954
7. The Factories Act, 1948
8. Bureau of Indian Standards Act

There are total 234 pesticides registered in India under Section 9(3) of the Insecticides Act, 1968. Out of these, 4 are WHO Class Ia pesticides, 15 are WHO Class Ib pesticides and 76 are WHO Class II pesticides, together constituting 40% of the registered pesticides in India (Cohen et al., 1984; IPCS, 1993; US EPA, 2007).

1.8 Pesticides Control Technologies

Pesticides present in industrial wastewaters can be decomposed by various treatment technologies, such as physical treatments (Gupta et al., 2006; Memon et al., 2008; Hussain et al., 2013; Henych et al., 2016), chemical treatments (Affam et al., 2014; Chang et al., 2014; Amor et al., 2015; Cui et al., 2015;) and biological treatment (Shawaqfeh 2010; Chen et al, 2012; El-Helow et al., 2013; Pailan et al., 2016) as shown in Figure 1.8. The physical treatment processes are not efficient enough because they do not degrade pollutants, but simply transfer them from one phase to another (e.g. liquid–liquid extraction, adsorption or ion exchange). The biological treatment occurs at low rates and does not biodegrade many of the compounds present in the effluent.

To overcome these limitations chemical treatment has been proposed (Duarte et al., 2009). In this section, basics of various techniques such as adsorption, photodegradation, coagulation-flocculation, Fenton oxidation, etc. for the removal of pesticides from water and wastewater are described.

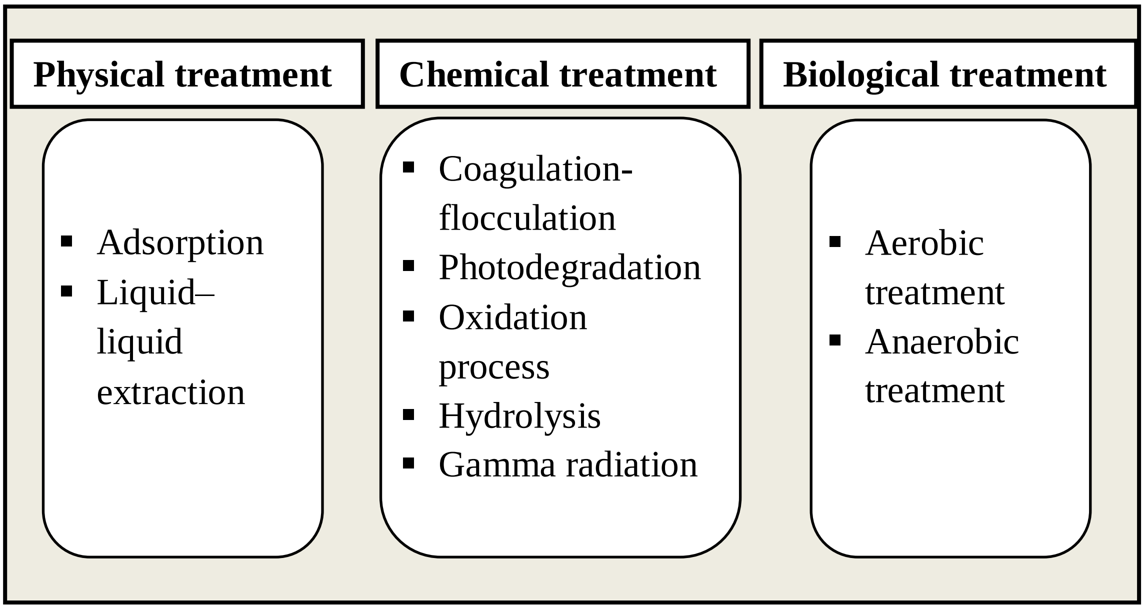

Figure 1.8: Technologies have been used for the treatment of pesticides.

1.8.1 Adsorption

Adsorption is advantageous in comparison to other removal methods because of being simple in operation, ease of design, and low investment in terms of initial cost and land required. Adsorption is a process of deposition of a substance at the interface between two phases such as solid and liquid or solid and gas, that depends on various properties of solids such as the number of available sites, porosity, size, shape, specific surface area, and molecular structure and also on solubility, polarity, polarizability and charge distribution of interacting species, and the acid-base nature of the pesticide molecule (Gevao et al., 2000). Unbalanced forces of attraction at the surface of the solids are responsible for adsorption (Bhatnagar and Sillanpaa, 2010). Pesticides which are insoluble in water (e.g. DDT), or which are easily decomposed can be effectively removed by the conventional adsorbents.

Activated carbon has good efficiency for the removal of pesticides from water and wastewater, but because of its high cost the researchers had attempted to use low-cost adsorbents. A variety of adsorbents have been used for the removal of insecticide, such as, granular activated carbon filtersorb 300 (GAC F300) (Salman et al., 2010a), powdered activated carbon (PAC) (Fernndez-Prez et al., 2005), banana stalks (Salman et al., 2010b), date seed activated carbon (Salman et al., 2011), standard activated charcoal (Gupta et al., 2006), chestnut shells (Memon et al., 2007), rice straw activated carbon (Chang et al., 2014), soil (Bermudez-Couso et al., 2012), and other low cost materials.

1.8.2 Coagulation − flocculation

Coagulation - flocculation is a physico-chemical process and is widely used as both pre and post treatment steps in wastewater treatment. Coagulation-flocculation has appeared as an efficient method in many applications including treatment of industrial wastewater containing alkaline cleaning solution (Memon et al., 2008), drinking water (Trinh and Kang, 2011; Theodoro et al., 2013; Hussain et al., 2014; Hu et al., 2015), humic substances (Koparal et al., 2008; Kourdali et al., 2014), heavy metals, phenols, cyanides (Wang et al., 2014; Golbaz et al., 2014; Cui et al., 2015) and landfill leachate (Moradi et al., 2014; Oloibiri et al., 2015; Amor et al., 2015), etc. Simultaneous removal of toxic aqueous solutions has attracted the attention of engineers throughout the world. Being simple and cost-effective, chemical coagulation and precipitation have traditionally been used in water treatment to decrease turbidity and colour and attracted global attention for simultaneous removal of toxic inorganic and organic contaminants from wastewater (Golbaz et al., 2014).

Electro-coagulation methods seem to be effective for the treatment of different effluents, i.e. pesticide wastewater, textile wastewater, laundry wastewater, food industry wastewater (Gatsios et al., 2015), pistachio processing industry (Bayar et al., 2014) and olive mill wastewater (Inan et al., 2004) etc., which involve in the application of electric current across metal electrodes (Gatsios et al., 2015).

1.8.3 Photo-degradation

Toxic organic compounds may be difficult to totally eliminate from water and wastewater by conventional methods, such as adsorption on low cost and activated carbon. Alternative treatment methods, such as advanced oxidation processes (AOPs), have been explored for the treatment of ground, surface and wastewaters having organic compounds (Oliveros et al., 1997). These processes can be divided in to three sections: (1) photochemical processes, (2) ozonation, and (3) technologies based on generation of free hydroxyl radicals. Photochemical treatments are light induced reactions, generally oxidation that depend on the formation of hydroxyl radicals by the combination with added oxidants or semiconductors (Benitez et al., 2002; Mahalakshmi et al., 2007). Photo-degradation process is simple in handling, economical and gives rapid degradation.

1.8.4 Oxidation process

Fenton reaction was efficiently employed in wastewater treatment process for the removal of many toxic organics from wastewater (Bautista et al., 2008). Among the advanced oxidation processes, Fenton reaction had wide attention in the treatment of wastewater because of the reactions have strong oxidative capacity for the degradation of organic contaminants (Perez et al., 2002). Fenton reactions incorporate the reactions of peroxides (usually hydrogen peroxide (H_2O_2)) with iron ions to form active oxygen species that oxidize organic or inorganic compounds at acidic pH. Fenton process is one of the most effective AOPs for industrial wastewater treatment in terms of cost (Sanchis et al., 2014). Fenton process is strongly dependent on the solution pH mainly due to iron and hydrogen peroxide factors (Babuponnusami and Muthukumar, 2011). Usharani et al. (2012) used ozone as an oxidant in the ozonation process for degradation of pesticides.

1.8.5 Gamma radiation

Radiation process is one of the most powerful treatment technologies in wastewater treatment, where irradiation with gamma rays or a beam of accelerated electrons is employed for the decomposition of various organic contaminants. Gamma radiation process has been successfully applied for the degradation of pesticides (Ismail et al., 2013; Hossain et al., 2013).

1.8.6 Biodegradation

Biodegradation is the process of breaking down of the organic materials by bacteria, fungi, or other biological means. Biodegradation has received increasing attention in wastewater treatment as a reliable, eco-friendly and cost-effective approach. Degradation of pesticides by several bacterial strains had also been testified by several workers (Farhan et al., 2012; El-Helow et al., 2013; Tiwari and Guha, 2014; Pailan et al., 2016).

1.9 Problem Identification

The presence of pesticides in drinking water has become significantly high and is a big environmental concern. Pesticide bearing wastewater has high chemical oxygen demand (COD), high biological oxygen demand (BOD), high total dissolved solids and high alkaline pH (Senn et al., 2014). The wastewater consisting of methyl parathion, chlorpyrifos, carbofuran etc. must be treated as a hazardous waste because it comes in the category of highly hazardous substances (Kavitha and Sureshkumar, 2016).

All these are commonly used pesticides for both indoor and outdoor (agricultural field, plantation etc.), pest control, hence their residual amount is also large. Thus these have been selected as target pollutants for this study. Methyl parathion, chlorpyrifos and carbofuran are significant pollutants because of their extensive use, persistence in the environment and wide distribution (Salman et al., 2010a). Carbofuran is highly toxic (LD_{50} 11 mg/kg in mice) and widely used on agricultural crops as an insecticide (Lopez-Alvarez et al., 2011). Contamination of methyl parathion, chlorpyrifos and carbofuran found in various water bodies are polluting the water resources. So, it is important to study the removal and degradation methods for such pesticides. Various methods that have been used for removal of pesticides from wastewater have been critically reviewed in Literature Review (Chapter II). Based on this reviewed as well simplicity and efficacy of the treatment process were used as the basis for selecting coagulation/flocculation, Fenton oxidation, and their combination. In view of the above, a detailed, objective has been framed.

1.10 Objective of the Present Study

In the present work, an attempt has been made to investigate degradation of three pesticides methyl parathion, chlorpyrifos and carbofuran from simulated wastewater using cost effective materials as well as treatment methods.

The objectives fixed for the present work are following:

- ✓ To optimize the coagulation and Fenton process using response surface methodology (RSM) and support the results obtained, statistically using adaptive neuro fuzzy inference system (ANFIS).
- ✓ To evaluate the removal efficiency of pesticides methyl parathion, chlorpyrifos and carbofuran in terms of its COD and absolute concentration.

- ✓ To evaluate the efficiency of coagulation using jar-test experiments and alum [$Al_2(SO_4)_3.18H_2O$] and ferric chloride ($FeCl_3$) as coagulants and investigate the effects of various operational parameters.
- ✓ To explore the capability of Fenton process using Fe^{2+} as a catalyst and investigate the effects of various operating parameters.
- ✓ To evaluate the degradation kinetics of methyl parathion, chlorpyrifos and carbofuran by Fenton oxidation and examine the effects of various influencing parameters.
- ✓ To explore the possibility of coupled Fenton and coagulation process as a viable treatment method.
- ✓ To evaluate the toxic effects of pesticides on human cells.