# EVALUATION OF THE WATER TREATMENT TECHNOLOGY FOR THE REMOVAL OF MALATHION (ENDOCRINE DISRUPTOR CHEMICAL)

## A Thesis

**Submitted in partial fulfillment of the requirement for the award of the degree of**

**MASTER OF SCIENCE**
**IN**
**BIOTECHNOLOGY**

| | |
|---|---|
| **Under the guidance of:** | **Submitted By:** |
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# CANDIDATE'S DECLARATION

I, hereby declare that the work presented in this thesis entitled "**Evaluation of the water treatment technology for the removal of Malathion ( Endocrine Disruptor chemical)**" in partial fulfilment of the requirement for the award of the degree of Masters of science in Biotechnology, Department of Biotechnology and Environmental Sciences (DBTES), Thapar university, Patiala, is an authentic record of my work during the period of six months from January, 2011 to June 2011, under the guidance of Dr. Moushumi Ghosh, Assistant Professor, Thapar University, Patiala. I have not submitted the matter embodied in this thesis for the award of any other degree or diploma.

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# CERTIFICATE

This is to certify that the thesis entitled **"Evaluation of the water treatment technology for the removal of malathion (Endocrine disruptor chemical)"** submitted by Pansy Sethi in partial fulfilment of the requirement for the award of Degree of Masters of Science in Biotechnology to Thapar University, Patiala, is a record of student's own work carried out by her. The report has not been submitted for the award of any other degree or certificate in this or any other University or Institute.

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# ABSTRACT

Endocrine disruptor chemicals have become major concern to the public, as they impair hormonal functioning and leads to innumerable adverse effects on humans and wildlife. Endocrine distruptor chemicals include plasticizers, metals, food antioxidants and pesticides. Malathion is one of the most potent pesticide which is known to produce adverse effects on human health. Although, malathion has amazing benefits on crops but its regular usage is leading to problems including surface water pollution. Thus, the removal of such EDCs from water has become a necessity. The conventional water treatment processes may be inadequate for reducing certain EDCs as they present great diversity of structural and chemical properties. In the present study, coagulation and flocculation process has been evaluated for the removal of malathion from water. Conventional jar test was employed, by taking different malathion concentration (0 ppm-10 ppm), varying turbidity groups (10-300 NTU), different coagulant dose (25 mg//L-200 mg/L) and flocculant dose (10-30mg/ml) at different contact times of 30 min, 60 min and 90 min. Although, significant reduction of malathion (78%) was observed at 100mg/L of coagulant dose at low turbidity levels at 90 min.  But it was found that higher concentrations of malathion could not be removed below the permissible limit at any of the coagulant and flocculant dose. In the case of flocculants 30 mg/ml was the appropriate dose found for the malathion removal. Overall the result of the current study suggests that conventional coagulation/flocculation processes need further improvement and optimisation to remove malathion from water.

.**Keywords:** Endocrine disruptor chemicals, malathion, coagulation, flocculation, Jar test.

# List of Abbreviations

| | |
|---|---|
| Alum | Aluminium sulphate |
| BHA | Butylated hydroxyl anisole |
| BPA | Bisphenol A |
| Da | Dalton |
| DES | Diethylstilbesterol |
| DDT | Dichlorodiphenyltrichloroethane |
| EDC | Endocrine disruptor chemical |
| EPA | Environmental protection agency |
| GAC | Granular activated carbon |
| HAA | Haloacetic acid |
| NBS | N-bromosuccinamide |
| NTU | Nephlerometeric turbity unit |
| OWC | Organic waste contaminants |
| PCB | Polychlorinated biphenyl |
| PPCP | Personal care products |
| PAC | Powdered activated charcoal |
| THM | Trihalomethane |

# List of Symbols

| | |
|---|---|
| G | Gram |
| Ml | Millilitre |
| mg/ml | Milligram per milliliter |
| mg/L | Milligram per litre |
| µg | Microgram |
| µl | Microlitre |
| Min | Minute |
| N | Normality |
| Ppm | Parts per million |
| % | Percentage |
| Rpm | Revolutions per minute |
| Sec | Second |
| w/v | Weight by volume |

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# CHAPTER 1
# INTRODUCTION

# 1. INTRODUCTION

In recent years, rapid industrialisation, extensive use of agricultural land, generation of chemically transformed product has led to the introduction of enormous quantities of pollutants in the water. Among these pollutants endocrine disruptor chemicals (EDC's) are one of the most potent pollutants causing great threat to human population. Endocrine disruptor chemicals are described as chemicals interfering at multiple levels of the endocrine pathways; these compounds disrupt the physiological processes including development, reproduction, general metabolism and behaviour. They are present in every product used for human betterment like food, cosmetics, pharmaceuticals and pesticides. For the high yield of crops, the use of pesticide has become indispensable. Besides the amazing benefits of pesticides in increasing the productivity, some pesticide (Malathion as EDC) has generated many problems including surface water pollution. In addition, it affects human health by causing lung cancer, prostate cancer, adverse effects on fertility, disruption of hormonal functioning etc. Thus, the removal of EDC from the water bodies has become a necessity.

The water treatment technology which is globally accepted is approximately five decades old now, when such types of EDCs were not even known. Therefore, the conventional water treatment processes may be inadequate for reducing certain EDCs as they represent a great diversity of structural and chemical properties which makes their removal from water quite difficult. The vast progress has been made worldwide in water treatment technology to deliver potable water, but no significant research has been carried for EDC removal from water. So, the conventional practice of water –

treatment process needs immediate attention on the fact that whether they are able to remove EDCs or not.

EDCs are among the emerging contaminants and they include plasticizers, metals, food antioxidants and pesticides. Amongst the pesticides, malathion is one of the potent EDCs and is known to produce adverse developmental, reproductive, neurological and immunological effects in humans. Malathion is a general purpose organophosphorus insecticide. It is of low toxicity however, absorption or ingestion into the human body readily results in its metabolism to malaoxon, which is substantially more toxic than malathion. According to EPA the permissible limits of malathion in water is 0.1 milligrams of malathion per litre of drinking water (0.1 mg/L). But, the magnitude of usage of malathion is quite high as it is registered for use on more than 100 agricultural crops and on an average, approximately 3.1 million acres of agricultural crops are treated per year with malathion. So, malathion enters the environment primarily through spraying on farm crops. Drift, evaporation, wind erosion can carry these residues to atmosphere from where they can fall as rain or snow to contaminate the surface water. Once malathion has reached surface water, it causes many problem to humans, that’s why removal of the malathion from water is necessary.

Conventional water treatment processes such as coagulation/flocculation involves the addition of chemicals like iron salts, aluminium salts, that coagulate and destabilize particles suspended in the water. The suspended particles are ultimately removed via clarification and/or filtration. These conventional processes may be inadequate for substantially removing malathion from water as it is being reported that malathion has been found to be present above its permissible limit in surface water. Therefore, a systematic study focusing on the evaluation of present water treatment technology for the removal of EDCs from potable water would be crucial to adopt these treatment processes.

# CHAPTER 2

# REVIEW OF LITERATURE

The water harbour many pollutants coming into it from different sources like food, cosmetics, electrical products, pharmaceutical products, which have become major concern currently. These pollutants have the potential to disrupt endocrine development in humans, animals and even in wildlife. They are known as endocrine disruptor chemicals (EDC's). Large numbers of endocrine disruptor chemicals is being introduced into water every year, from most of the products used by human. They are posing significant challenge to water utilities through their presence in drinking water, as many water treatment plants do not have facilities to treat these chemicals. In case, removal is possible, the treatment is incidental and does not have the ability to remove a large enough percentage of the chemicals from the water stream, because of the concentration at which they occur is, quite low. EDC's have diverse structural and chemical properties due to which their removal during water treatment process becomes challenging.

## 2.1 Endocrine Disruptor Chemicals (EDC's)

The discovery that certain compounds can mimic the natural hormones of animals was reported as early as the 1930s. These hormonally active chemicals, collectively called as endocrine disrupting chemicals (EDCs), are known to mimic or block natural hormones in animals. EDCs acts as xenobiotic (agents foreign to an organism) that interfere with the "synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behaviour (Juvancza *et al.*, 2008).

They are grouped under emerging contaminants because of real threat caused by

EDC's to human health. The different classes of emerging contaminants include pharmaceuticals and Personal care products (PPCPs), Organic wastewater contaminants (OWCs), Endocrine disrupting chemicals (EDCs). There is growing interest in the possible health threat posed by endocrine- disrupting chemicals (EDCs), which are substances in our environment, food, and consumer products, that includes Pesticides (chlordane DDT, endosulfan, heptachlor, methoxychlor, toxaphene, zineb, ziram and malathion), Food antioxidants such as Butylated hydroxyl anisole (BHA), detergents, flame retardants, toys, cosmetics, pharmaceuticals (dioxin and dioxin-like compounds), Plasticizers (Bisphenol A and Bisphenol F), Metals (arsenic, cadmium, lead and mercury).These chemicals have also been referred to as endocrine modulators, environmental hormones, and endocrine active compounds.

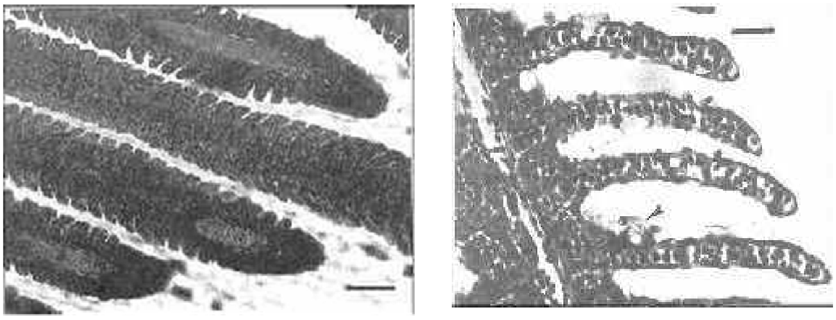
## 2.2 Potential health effects

People may be exposed to endocrine disruptors through the food and beverages they consume, medicine they take, pesticides they apply and cosmetics they use. Industrial activities such as pulp and paper production can also release large quantities of phytoestrogens that may have adverse impact on reproductive system function of aquatic animals. The degradation of vegetable matter and paper products in wastewater treatment plants also may contribute to releases of phytoestrogens into the aquatic ecosystem. So, exposure may be through the diet, air, skin, and water.

Although EDC's have been reported to be present in minute quantities in the environment but, the impact of these trace concentrations lead to concerns about their potential effects on humans and wildlife.

The best-documented example of endocrine disruption in humans involved is exposure to the synthetic estrogen diethylstilbestrol (DES), a pharmaceutical administered to pregnant women to prevent miscarriage (Colborn *et al.*, 1993). Its use resulted in adverse reproductive impacts in human offspring. Decreases in human sperm quality and quantity, increase in some cancers abnormalities in male reproductive organs, female reproductive health issues, including fertility problems, early puberty and early reproductive senescence, increase in mammary, ovarian, and prostate cancers, increase in immune and autoimmune diseases, and some neurodegenerative diseases (Schworer., 2010) are among the potent effects of EDC on humans.

Exposure to endocrine-disrupting chemical in the environment has been associated with irregularities in animals and birds also, that includes abnormal thyroid function in birds and fish, decreased fertility in birds, fish, shellfish, decreased hatching succession fish, birds (Colborn *et al.*, 1993), turtles, demasculinization and feminization of male fish, birds, mammals and gastropods, alteration of immune function in birds. Gills damage has also been reported in fishes (Fig 2.2).



Normal fish gills Malathion exposed gills

Fig 2.2 Difference between gills of normal fish and gills affected by EDC (Malathion) (Journal Bulletin of Environmental Contamination Toxicology)

Disruption of the hormonal functions have also been linked to reproductive failures in animals such as, sheep that graze on certain strains of clover as that contains high levels of phytoestrogens. These deleterious health effects have been observed in many areas where the presence of multiple man-made chemicals, such as by-products of industrial chemical synthesis (chemical waste) and pesticides has been established. The effects were not reported before the 1950s and are currently observed in many areas such as the Great Lakes in North America (Colborn *et al.*, 1993). Other health effects are difficulty in breathing, headaches, neurological or psychological effects, irritation of skin and mucous membranes, skin disorders, spontaneous abortions, premature birth, low birth weight, developmental abnormalities and ovarian disorders.

## 2.3 Types and Effects of some EDCs

All people are exposed to chemicals with estrogenic effects in their everyday life, because endocrine disrupting chemicals are found in low doses in literally thousands of products. The most commonly detected chemicals in environment include Bisphenol A (BPA), Polychlorinated biphenyls (PCB's), Malathion. In this section, brief descriptions of potential EDCs, its major uses, health effects, chemical structure and human exposure are discussed.

### 2.3.1 Bisphenol A (BPA)

Bisphenol A, commonly abbreviated as **BPA**, is an organic compound with two phenol functional groups. It is used to make polycarbonate plastic and epoxy resins, along with other applications such as water bottles, sports equipment, medical and dental devices, baby bottles dental fillings (Ubelacker., 2008), sealants, eyeglass lenses, CDs/DVDs, and household electronics.

It is known to be estrogenic since the mid-1930s and a known endocrine disruptor, which can mimic the body's own hormones (Okada *et al.*, 2008) and may lead to negative health effects such as diabetes, mammary and prostate cancers, decreased sperm count, reproductive problems, early puberty, obesity and neurological problems (Connor *et al.*, 2003).

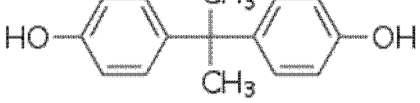


Fig 2.3 Structure of Bisphenol A

Exposure to Bisphenol A occurs mainly through leaching from the plastic lining of canned foods especially those which are cleaned with harsh detergents or those which contain acidic or high-temperature liquids. It is an ingredient in the internal coating of metal food and beverage cans used to protect the food from direct contact with the can. A recent finding suggests that the majority of canned soft drinks tested had low, but measurable levels of Bisphenol A (Walsh., 2010). Mostly human exposure is through diet, exposure can also occur through air and through skin absorption.

### 2.3.2 Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) are a class of chlorinated compounds used as industrial coolants and lubricants, dielectric fluids in transformers and capacitors.

PCBs are created by heating benzene, a by-product of gasoline refining, with chlorine. They were first manufactured commercially in 1927. The health effects of PCB includes severe acne-like condition called chloracne (Tang *et al*., 2008), skin cancer, liver cancer (Brown *et al*., 1987), and brain cancer (Loomis *et al*., 1997), children exposed prenatally have the risk of developing diabetes (Uemura *et al.,* 2008).

Other symptoms included dermal and ocular lesions, irregular menstrual cycles and lowered immune responses, fatigue, headaches, coughs, and unusual skin sores.

It is shown to have toxic and mutagenic effects by interfering with hormones. Imitation of the estrogen compound can leads to breast cancer cells and possibly cause other cancers, such as uterine or cervical. Inhibition of estradiol can lead to serious developmental problems for both males and females, including sexual, skeletal and mental development issues.

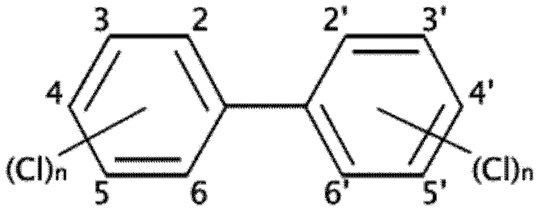


Fig 2.4 Structure of Polychlorinated biphenyls

Individuals can be exposed to PCBs through breathing in contaminated air, consuming contaminated food and by skin contact with old electrical equipment that contain PCBs. Once exposed, some PCBs may change to other chemicals inside the body. PCBs may also collect in milk fat and be transmitted to infants through breast-feeding**.**

Another very important EDC is malathion, a class of pesticide sprayed on crops and leads to disruption of hormones in humans and even in animals.

## 2.4 Malathion

Malathion is an organophosphate parasympathomimetic insecticide of relatively low human toxicity, however, absorption or ingestion into the human body readily results in its metabolism to malaoxon (Neal *et al*., 1993) which is 61 times more toxic than malathion (Edwards., 2006).

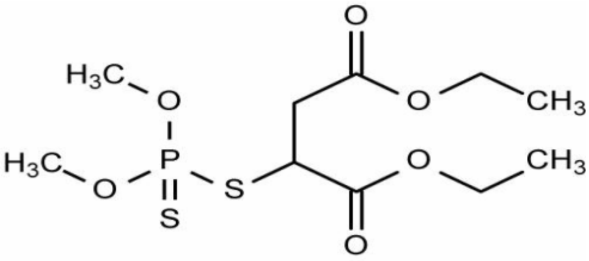


Fig 2.5 Structure of Malathion

Malaoxon is an oxygen analogue of malathion. It is widely used in agriculture, residential landscaping, public recreation areas and in public health pest control programs such as mosquito eradication. Over 100 food crops can be treated with malathion and about half of total applications are on alfalfa, cotton, rice, sorghum, and wheat. Annual use of malathion is over 1.5 million lbs active ingredient (ai) per year (Edwards., 2006). Besides the wonderful benefits of malathion, in increasing productivity, it has also generated many problems that includes surface pollution and adverse effects on human health.

### 2.4.1 Exposure routes of Malathion

The general population is not likely to be exposed to large amounts of malathion. Populations living within or very near areas of heavy malathion use are, at an increased risk of exposure to malathion. The persons utilizing malathion for extensive home and garden use, particularly if they consume contaminated, unwashed backyard produce are at increased risk of getting ill due to effect of malathion. The highest levels of exposure occurs to the individual who are involved in the production, formulation, handling and application of malathion as well as farm workers who enter treated fields.

Exposure through dermal contact occurs with contaminated plants and is the major route of exposure. While inhalation of the mist formed from the applied insecticide or by ingestion of water or food-borne residues may also be an important route of exposure.

Chronic exposure to low levels of malathion have been hypothesized to impair memory. Acute exposure to extremely high levels of malathion will cause skin and eye irritation, cramps, nausea, diarrhoea, excessive sweating, seizures and even death. Most symptoms tend to resolve within several weeks. However recent studies have shown that children with higher levels of malathion in their urine seem to be at an increased risk of attention deficit hyperactivity disorder (Maugh *et al.*, 2010). Malathion present in untreated water is converted to malaoxon during the chlorination phase of water treatment, so malathion should not be present in water that may be used as a source for drinking water or any upstream waters.

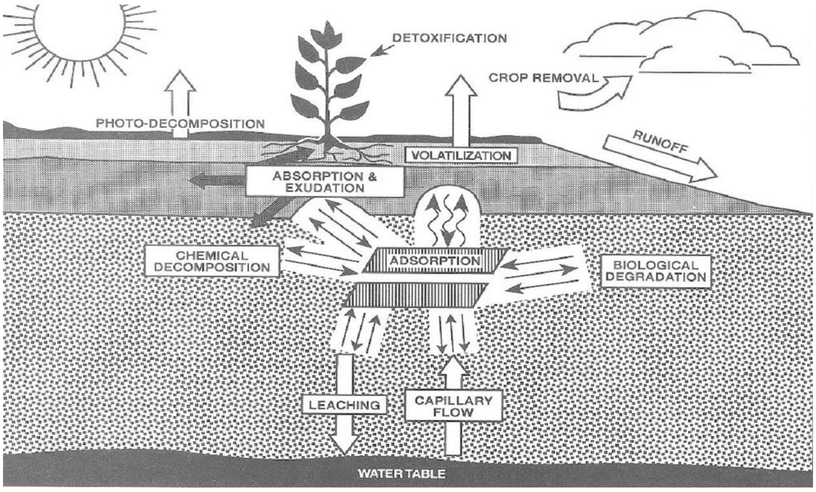


Fig 2.6 Environmental fate of Malathion

## 2.4.2 Fate of malathion

When malathion is released to the atmosphere it may be subject to direct photolysis (Newhart., 2006). It enters to air, malathion is degraded in the atmosphere by reaction with photochemically produced hydroxyl radicals; the half-life for this reaction in air is estimated to be approximately 5 h.

If malathion is released to water it may moderately adsorb to sediment but will not be expected to bioconcentrate in aquatic organisms. Biodegradation may be an important process, especially in waters < pH 7.0 where the rate of hydrolysis may be slow relative to the rate of biodegradation. The half-life of a pesticide of 10 days in the laboratory increases to one year if the pH of the water is 6 and the temperature 5°C (Valaragnarsdottir., 2000)**.** The water solubility of malathion is relatively high from an environmental fate perspective at 145 mg/L leading to a high potential for its transport in surface water and ground water. Their presence is in trace concentrations, which makes the removal difficult from surface water.

## 2.4.3Health Effects

Malathion is sprayed on almost all crops and is reported to be a potent EDC, affecting health of large population in India. A study of 7,500 workers in 1976 in Pakistan who sprayed various malathion formulations reported that five workers died, probably as a result of exposure to it. (Baker *et al.*,1978). Poor work practices (e.g., wearing clothing soaked with pesticide for several days without washing, mixing chemicals with bare hands) resulted in excessive skin contact and absorption of the pesticide through the skin.

It was estimated that the daily dermal exposure for the spraymen was 330 mg of malathion. Ramu *et al* in 1973 reported that dyspnea and excessive secretions in the respiratory tract occurs in children by dermal application to the hair when solution contains 50% malathion in xylene. Many *in vivo* and *in vitro* studies in humans and animals have investigated the genotoxic effects of malathion. Evidences suggested that technical-grade malathion to be a genotoxic agent.

Most studies (many with positive results) have used technical or commercial grades of malathion rather than the purified form. The result of these studies suggests the possibility that impurities in commercial formulations might be the active genotoxicity agents (Flessel *et al.*1993). There is another evidence that suggests malathion is a weak DNA alkylating agent *in vitro.* Male mice dermally exposed to single or multiple treatments (5 days/2 weeks) showed that the ability of Malathion to induce chromosome aberrations in somatic (bone marrow) and germ cells (primary spermatocytes). Statistically significant increase of chromosome aberrations in bone marrow cells occurred after single treatment (500 and 2000 mg/kg body wt) when chromatid gaps were included and after multiple treatment (250 and 500 mg/kg) when they were excluded. In germ cells, malathion induced a significant increase of univalent in both types of treatment but structural chromosome aberrations were induced only by multiple treatment (Salvadori *et al.*, 1986).

## Other Effects

Hyperglycemia and glucosuria were found in four children with severe malathion intoxication following application to the hair of a solution containing 50% malathion in xylene (Ramu *et al.*,1973). Since the hyperglycemia was accompanied with hyperinsulinemia.

Because of these many potential health effects of malathion on humans, it has become necessity for the removal of malathion from water. Extensive research on removal of EDCs is being carried out from last few years.

## 2.5 Water Treatment Technology

An estimated 32 percent of the population in developing countries do not have an adequate water supply. At present, there are some five million known substances registered, of which approximately 70,000 are widely used worldwide and it is estimated that 1000 new chemical substances are added to the list each year. One of the concerns is towards removing harmful contaminants like EDC. There are many problems in creating potable water such as difficulty in identifying of EDC and determining their sources. The goal of all water treatment processes to remove existing contaminants in the water (EDC’s) or to reduce the concentration of such contaminants so the water becomes fit for its use.

Water purification describes all those processes that make water more acceptable for a desired end-use. The treatment processes may include processes such as coagulation/ flocculation (Lofrano *et al.*, 2006), sedimentation and filtration to remove colloidal and suspended solids; ion exchange, carbon adsorption and membrane processes to remove dissolved solids and a disinfection step often achieved by chlorination (Mosoarca *et al.*, 2008) ozonation, and ultraviolet radiation (UV).

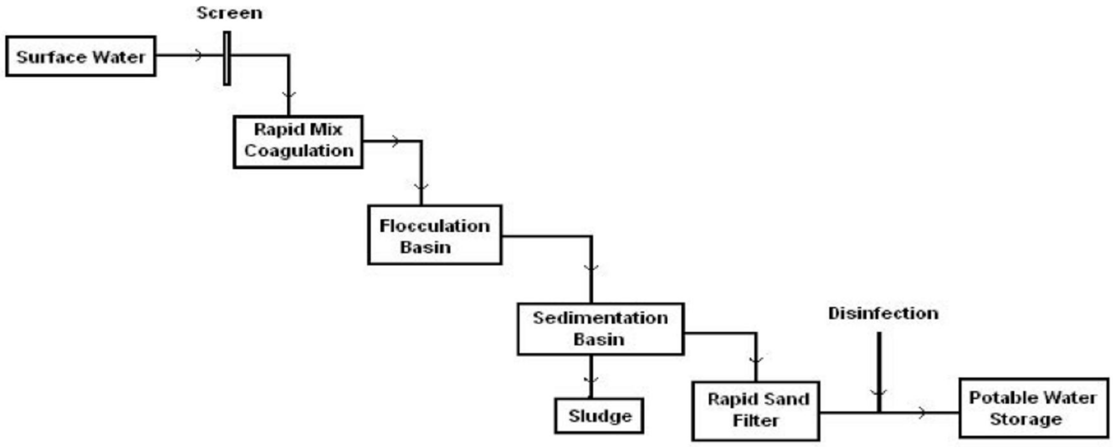


Fig 2.7 Flow diagram of a conventional potable water treatment plant

The conventional practises to treat polluted water are as follows:

Raw water is fed to grit chamber from where course particles are removed, followed by aeration then coagulation/flocculation is done to remove colloidal particles, which get collaese on addition of coagulant/flocculants, sedimentation allows them to settle at the bottom and filtration helps in the removal of these particles. At the end chlorination is done to remove any pathogenic micro-organisms.

### 2.5.1 Treatment technologies for the removal of water pollutants

The existing water treatment technologies for the removal of water pollutants are coagulation/flocculation, ozonation, chlorination and powdered/Granular activated charcoal (PAC/GAC).

#### 2.5.1.1 Coagulation/Flocculation

All water, especially surface water, contain both dissolved and suspended particles. Coagulation and flocculation processes are used to separate the suspended solids portion from the water. Coagulation is the process by which colloidal particles and very fine solid suspensions initially present in a wastewater are combined into larger agglomerates that can be separated via sedimentation, flocculation, filtration, centrifugation or other separation methods. Coagulation is commonly achieved by adding different types of chemicals (coagulants) to the wastewater to promote destabilization of the colloid dispersion and agglomeration of the resulting individual colloidal particles (Lofrano *et al.*, 2006).

Coagulation and flocculation occur in successive steps intended to overcome the forces stabilizing the suspended particles. The first step destabilizes the particle's charges. Coagulants with charges opposite those of the suspended solids are added to the water to neutralize the negative charges on dispersed non-settable solids such as clay and colour- producing organic substances. Following the first step of coagulation, a second process called flocculation occurs. Flocculation, a gentle mixing stage, increases the particle size from sub microscopic microflocs to visible suspended particles.

### 2.5.1.1.1Coagulants and Flocculants

Particles finer than 0.1 µm ($10^{-7}$m) in water remain continuously in motion due to electrostatic charge (often negative) which causes them to repel each other. Once their electrostatic charge is neutralized by the use of coagulant chemical, the finer particles start to collide and agglomerate (combine together) under the influence of Van der Waal forces. These larger and heavier particles are called flocs. Flocculants or flocculating agents (also known as flocking agents) are chemicals that promote flocculation by causing colloids and other suspended particles in liquids to aggregate, forming a floc**.**

The commonly used metal coagulants fall into two general categories: those based on aluminium and those based on iron. Long-chain polymer flocculants, such as modified polyacrylamides can also be used in treatment processes. Alum is the name used for aluminium sulphate. It is also known as soda alum, filter alum, concentrated alum, pearl alum, pickle alum, cake alum, papermaker's alum and patent alum. In water treatment, it is used primarily for the removal of colloidal particles present in the raw water (Guida *et al.*, 2006) which are too small to settle by itself and the negative charge on the colloidal particles does not allow them to adhere and they tends to repel each other. For the proper functioning of alum the pH of the water needs to be near 7. Both low and high pH, makes it worthless. The alum works by neutralizing the charge, in which net charge on the colloidal particles (negatively charged) will be cancelled by adsorption of an equal number of opposite (positively) charges (of aluminium sulphate). Polyacrylamides are the organic compounds made up of long chain of smaller particles acting as flocculants that facilitate flocculation or floccing up of suspended solids in liquid, resulting in the formation of floc or wooly mass (Bae *et al.*, 2007).This process applies to wastewater treatment and processes like paper making. The mechanism involved in polymer addition is the “bridging type” in which large polymeric molecules attach to the colloidal dispersion forming bridges. Due to the length of the polymeric chain the motion of the colloid-polymer particle is hindered.

The polymer chains protruding from colloid-polymer particles can interact with similar particles and finally becomes heavy and settles at the bottom as floc.

### 2.5.1.2 Ozonation

Ozone is made by passing oxygen through ultraviolet light or a "cold" electrical discharge. Some of the advantages of ozone include the production of fewer dangerous by-products (in comparison to chlorination) and the lack of taste and odour produced by ozonation. It is an oxidant gaining popularity in water treatment applications since 1906, because it is powerful disinfectant and effective in removing organic compound. Oxidation of EDC by ozonation depends on the chemical structure of compounds and ozone dose (Snyder *et al*). The oxidation efficiency was lower at low initial EDC concentrations than at high concentrations (Choi *et al*., 2006). It has been observed from studies that ozone could remove the ketone steroids (testosterone, progesterone and androstenedione), which were not appreciably removed using free chlorine. It also appears that aliphatic compounds can be challenging for ozone removal (e.g. TCE & meprobamate). Overall, removal of target compounds increased by 10-20% using ozone/peroxide over ozone alone (Snyder *et al.*, 2005).

### 2.5.1.3 Activated carbon (granular and powdered)

PAC is powdered activated charcoal and is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve or sieve is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions.

Granular activated carbon has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface. EDC investigated so far, expected to show satisfactory removal by GAC/PAC but due to presence of number Optimization studies for maximum removal of malathion of factors that affects removal efficiency of EDC i.e. they have been related to water-octanol partition coefficient. From studies it has been observed that GAC/PAC had relatively low removal efficiencies (25-40%). So, it may not be an acceptable alternative for removing EDCs (Choi *et al.*, 2006).

### 2.5.1.4 Chlorination

Chlorination is the process of adding the element chlorine to water as a method of water purification to make it fit for human consumption as drinking water. Disinfection by chlorine can be problematic, in some circumstances. Chlorine can react with naturally occurring organic compounds found in the water supply to produce dangerous compounds, known as disinfection byproducts (DBP’s). The most common DBP’s are trihalomethanes (THMs) and haloacetic acid (HAAs).

A finding says about the efficient removal of phenolic steroids (i.e., estradiol, ethynylestradiol, and estrone) by chlorination, while steroids lacking the phenolic moiety were not (i.e., androstenedione and testosterone) (Snyder *et al*).

Although significant progress has been made across the globe for water treatment technology to deliver potable water, but no significant research has been carried for EDC removal from water.

So, the present work is an attempt towards filling the knowledge gap as no studies were carried out so far for the removal of particular compound (malathion) from water through coagulation and flocculation and to know whether the existing technology is capable of removing EDC present in water or not.

## OBJECTIVES

1. Simulated study for evaluating the removal of malathion from water by coagulation/flocculation.

2. Optimisation studies for maximum removal of Malathion

# CHAPTER 3

# MATERIALS AND METHODS

The parameters which affect the coagulation-flocculation process are initial turbidity, dosage of coagulant, physical and chemical characteristics of coagulant, mixing time, settling time, jar configuration/container geometry. Amongst listed variables the study was limited to the optimization of coagulant dosage and time of treatment.

## Optimisation studies for maximum removal of Malathion

### 3.1 Test of coagulation flocculation (Jar test)

The simulation of coagulation flocculation process was carried out through a Jar test apparatus having six paddle stirrers, with six 2-L jars. As soon as coagulant solution was added, the suspended solution was strongly mixed at 100 rpm for one minute and this step was followed by a slow mixing (20 rpm) for 15 minutes. Thereafter, the solution was allowed to get settled for 30 minutes to 90 minutes. Finally, to assess analytically the effectiveness of the coagulation flocculation treatment, the supernatant was removed from the top of the suspension by siphoning for measurement of the turbidity, pH and conductance, using turbidimeter (Trademark Spectra labs), pH meter and conductivity meter respectively. Experiments were done in triplicates and mean was taken.

### 3.1.2 Optimisation of coagulant dose

In order to study the effect of coagulant doses, experiments were run using turbid water having low, medium and high turbidity and was spiked with malathion in concentration range of 0 ppm-10 ppm. Three types of turbid water solutions low, medium and high turbidity within the range of 10-30 NTU, 50-150 NTU and 200-300 NTU respectively.

***Preparation of coagulant solution*:** It was prepared by dissolving 300 mg Alum ($Al_2(SO4)_3.18\ H_2O$) in distilled water and the solution volume was increased to 1 L thus, stock solution was 300mg/L. Dilutions were made to achieve the concentrations of 25 mg/L, 50mg/L, 100mg/L, 150 mg/L and 200mg/L.

***Preparation of Turbid solution***: 5 gm. of Kaolin (Himedia) was added to 1 L of distilled water and the suspension was stirred slowly for uniform dispersion of kaolin particles. This suspension was used as the stock solution for the preparation of turbid water samples of varying turbidity for the coagulation tests. Jar test apparatus was used for the whole procedure. Malathion with range of concentration 0 ppm-10 ppm was spiked into turbid water. Coagulant doses (25mg/L -200mg/L) were added to the samples at a flash mixing speed of 100 rpm. After one minute, the stirring speed was lowered to 20 rpm for 15 min. At the end, the beakers were left undisturbed and flocs were allowed to settle down for 30 to 90 minutes. The samples were withdrawn from top of the suspension, at the interval of 30 min, 60 min and 90 min.

In order to analyse the coagulation efficiency of coagulant doses (25mg/L - 200mg/L), it was necessary to measure the pH, before starting the experiment and to determine the effect of coagulant dose on conductance. The pH not only affects the surface charge of coagulants, but also affects the stabilization of the suspension. Aluminium sulphate (Alum) was used as coagulant and it works best at pH 7.0-7.2. pH was adjusted with 0.1N NaOH and 0.1N HCl. If the operating pH was near 8.0, the floc remained unstable and begins to come apart and if the pH was below 6.5, the coagulant was dissolved in the water making it worthless. Observations were made as discussed in results and discussion.

Turbidity was measured in triplicates and average was taken.

### 3.1.3 Optimisation of time of coagulation process

For the study of effect of time on coagulation process three different contact times were chosen viz 30 minutes, 60 minutes and 90 minutes where 0 ppm-10 ppm was the concentration of malathion that was spiked into turbid water. Different coagulant doses (25mg/L - 200mg/L) were used. Jar test apparatus was employed for the whole procedure. Experiment was run at a flash mixing speed of 100 rpm. After one min. the stirring speed was then lowered to 20 rpm for 15 min after one minute, at the end, the beakers were left undisturbed and flocs were allowed to settle for 30 to 90 minutes. The turbidity, pH and conductance of samples were measured at 30 minutes, 60 minutes and 90 minutes.

## **3.2 Malathion Estimation** (Mathew *et al.,* 2006)

Malathion concentrations in water samples were measured before and after the treatment with coagulant. Malathion was procured from AccuStandards. Stock solution of 10 mg/ml of malathion was prepared by dissolving 1000 mg in a minimum amount of glacial acetic acid (Merck) and then diluting it to 100 ml with distilled water. An aqueous solution of 0.01% (w/v) N-bromosuccinimide (NBS) (Loba Chemie) was freshly prepared. A solution of 4.0 M HCl which was purchased from Loba chemie was prepared and standardized prior to use. The 0.02% (w/v) aqueous solution of RhodamineB (Loba chemicals) was prepared by dissolving an accurate weight of dye in the least amount of water and completed to the mark in a 100 ml calibrated flask.

A sample solution containing malathion were transferred into the 25 ml calibrated flasks to which 1.5 ml of NBS, 1 ml of glacial acetic acid and 0.5 ml of hydrochloric acid were added. The solution was kept for with occasional shaking for about 10 min at ~30°C and then 0.7 ml of rhodamine B solution was added and mixed thoroughly. The absorbance was measured at 550 nm against a reagent blank. A blank without pesticide (dye and NBS) and dye (devoid of pesticide and NBS) were prepared in the same way and its absorbance was measured against distilled water. The decrease in absorbance corresponding to consumed oxidant, which reflects the pesticide concentration was obtained by subtracting the decrease in absorbance of the test solution (dye minus test) from that of the blank solution (dye minus blank). Calibration graph was prepared by plotting the decrease in absorbance of dye against amount of the malathion.

### 3.3 Determination of the Flocculating activity

Flocculating activity of the polyacrylamide was measured using kaolin clay suspension and malathion as test material. 4.8 ml of kaolin and sample were added to test tube followed by 100µl of $CaCl_2$ and 100µl of different polyacrylamide concentration. The mixture was stirred at 60 rpm for 30sec. with a vortex mixer and then kept still for 5 min. The absorbance of the supernatant and the blank as control without flocculant was measured at 550 nm with a spectrophotometer.

The flocculating rate was defined and calculated as $\mathbf{[(B-A)/B]\times 100\%}$, in which $A$ and $B$ were the absorbance at 550 nm for sample and blank, respectively.

### 3.3.1 Optimisation of Flocculant efficiency for maximum removal of Malathion

Polyacrylamide ($5\times10^6$ Da) was purchased from Himedia, used as a flocculant and its flocculating activity was checked by flocculation of kaolin suspension and mixture of kaolin with known concentrations of malathion. A stock solution of flocculant was prepared (100mg/ml). The flocculant dose optimization and treatment time optimization studies were carried out. Flocculation studies were carried out at pH 7-8. Kaolin suspension was prepared by dissolving 5 g in 100 ml of water and turbidity was set as low, medium and high for different concentrations of kaolin clay. This suspension was used as the stock solution for the preparation of turbid water samples ,of varying turbidity's for the flocculating activity tests. The experiment was run using turbid water having low, medium and high turbidities, with malathion concentration in range of 0 ppm-10 ppm. Three groups of turbidities were considered: low (10-30 NTU), medium turbidity (50-150 NTU) and high turbidity (200-300 NTU). The flocculation activity was determined as above. Experiments were done in triplicates and mean was taken.

# CHAPTER 4
# RESULTS AND DISCUSSION

# 4. RESULTS AND DISCUSSIONS

## 4.1 Effect of coagulant dose on removal of Malathion (EDC)

Malathion was spiked in turbid water at the concentration of range 0-10 ppm and coagulant dose of 25 to 200 mg/L was added to evaluate the removal efficiency of malathion by coagulation. The turbid solution using kaolin suspension clay was prepared and the turbidity range for initial experiments was kept as 10-30 NTU. It was found that the very low concentration of malathion (below 0.2 ppm) could not be detected in control sample but the removal of low concentration (0.2-2 ppm) of malathion could be achieved with higher coagulant dose. The maximum reduction (65%) was achieved after 30 minutes at the initial concentration of malathion of 4 ppm than that usually practised (~30 ppm) at all the coagulant doses (Table 4.1). No significant reduction was observed in malathion when malathion concentration in range of 4-10 ppm was considered. The results were consistent in all turbid solutions (10-30 NTU). Hence, in the further studies on optimization of coagulant dose and treatment time, 4 ppm was used as the initial malathion concentration.

Table 4.1 Percentage reduction of malathion at different coagulant doses

| **Malathion conc.(ppm)** | **Reduction in malathion (%)** | | | | |
|---|---|---|---|---|---|
| | Coagulant Dose (mg/L) | | | | |
| | **25** | **50** | **100** | **150** | **200** |
| **2** | 28.9±0.3 | 44.5±0.5 | 48±0.2 | 48.8±0.4 | 47.5±0.1 |
| **4** | 30.5±0.2 | 65±0.8 | 65.2±0.4 | 64.5±0.7 | 64.3±0.1 |
| **6** | 31.6±0.1 | 65.5±0.1 | 66±0.1 | 65.8±0.8 | 65.5±0.4 |
| **8** | 32±0.1 | 66±0.3 | 66.8±0.7 | 65.9±0.5 | 65.6±0.6 |
| **10** | 32.2±0.1 | 66.9±0.6 | 67.5±0.9 | 66.7±0.3 | 66.5±0.1 |

Values are mean ± standard deviation

The coagulant dose is one of the most important parameter in determining the optimum condition for the performance of coagulation, one of the coagulant selected for the study was aluminium sulphate (alum). Basically insufficient dose or overdosing might result in the poor performance (Hassan *et al.*, 2009). Also, it is crucial to determine the optimum dosage to minimize the dosing cost. The series of experiments were run using turbid water with three levels of turbidity: low (10-30 NTU), medium turbidity (50-150 NTU) and high turbidity (200-300) in the presence of malathion concentration (4 ppm). The study was carried out at pH 7.0-7.2, 100 rpm of mixing rate for one minute and 20 rpm of mixing rate for 15 minutes and settling time for different concentration of alum (25mg/L, 50mg/L, 100mg/L, 150mg/L and 200mg/L) were 30 min, 60 min and 90 min.

Table 4.2: Percent reduction of malathion at different turbidity and coagulant doses

| | | **Reduction in malathion (%)** | | | | |
|---|---|---|---|---|---|---|
| **Turbidity (NTU)** | Time (min.) | Dose (mg/L) | | | | |
| | | **25** | **50** | **100** | **150** | **200** |
| **Low (10-30)** | 30 | 30.5±0.2 | 65±0.8 | 65.2±0.4 | 64.5±0.7 | 64.3±0.1 |
| | 60 | 38.2±0.3 | 69±0.1 | 70±0.2 | 70.2±0.2 | 69.5±0.1 |
| | 90 | 46.3±0.1 | 78±0.2 | 78±0.3 | 78.5±0.1 | 78.2±0.1 |
| **Medium (50-150)** | 30 | 28±0.3 | 57.8±0.1 | 60.1±0.1 | 60.8±0.2 | 59±0.1 |
| | 60 | 34.2±0.2 | 63.5±0.2 | 65.3±0.2 | 65.5±0.3 | 64±0.1 |
| | 90 | 43±0.1 | 72.5±0.3 | 74±0.3 | 72.6±0.1 | 72±0.2 |
| **High (200-300)** | 30 | 24±0.1 | 50±0.2 | 53.3±0.1 | 56±0.4 | 55.4±0.1 |
| | 60 | 31±0.1 | 56±0.2 | 60.4±0.2 | 60.8±0.7 | 60.5±0.8 |
| | 90 | 39±0.1 | 60.5±0.1 | 65.7±0.1 | 65.9±0.5 | 65.6±0.3 |

Values are mean ± standard deviation

The maximum reduction (78%) was observed when coagulant dose of 50 mg/L was used in low turbidity level (10-30 NTU). The reduction in turbidity was found to be increasing with increase in coagulant dose. When the medium turbidity level was considered, it was found that coagulant dose of 100 mg/l resulted in maximum reduction (74 %) of malathion (Table 4.2). The reduction in malathion concentration was found to be consistent at higher turbidity level even after using higher coagulant doses, as no significant reduction was observed. The table 4.1 clearly depicted that reduction in malathion concentration increased with increase in time of treatment. The treatment time of 90 minutes resulted in maximum reduction at all the coagulant doses.

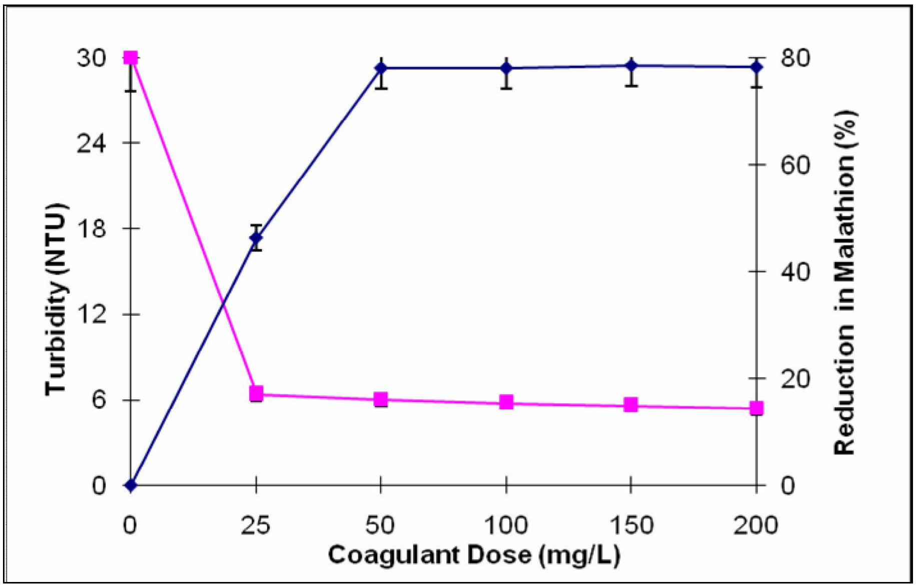


Figure 4.1 (a) Effect of coagulant dose on malathion concentration and turbidity (10-30 NTU). --◊---, Reduction in malathion (%)., --□--, Turbidity (NTU)

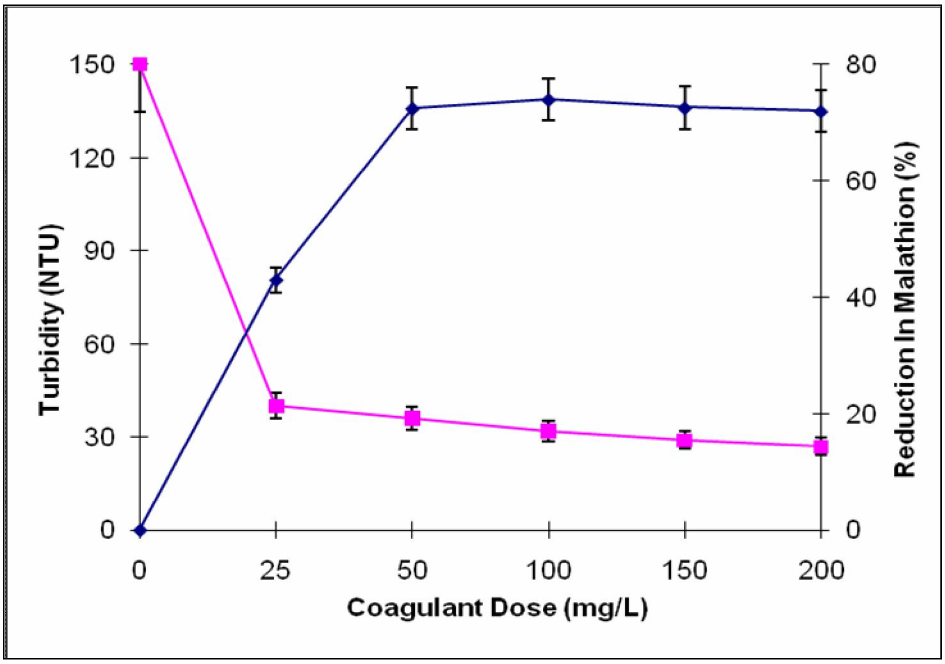


Figure 4.1(b) Effect of coagulant dose on malathion concentration and turbidity (50-150 NTU). --◊---, Reduction in malathion (%)., --□--, Turbidity (NTU)

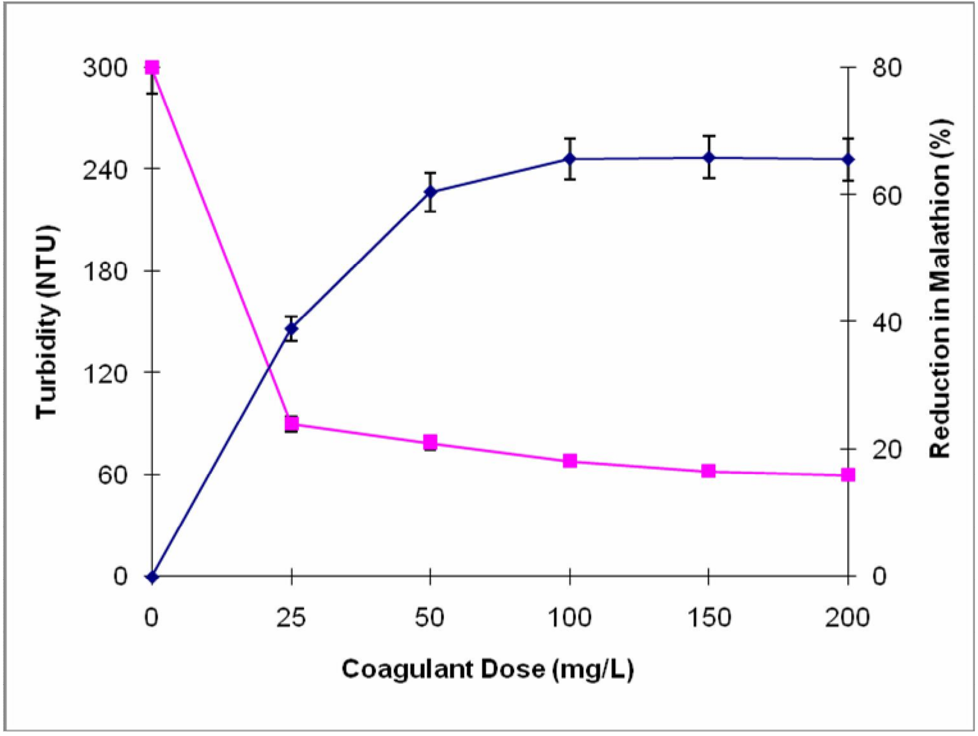


Figure 4.1 (c) Effect of coagulant dose on malathion concentration and turbidity (200-300 NTU). --◊---, Reduction in malathion (%)., --□--, Turbidity (NTU).

The results revealed that the higher coagulant doses (>100mg/L) did not produce much reduction in malathion at any of the turbidity level (Fig. 4.1(a-c)). The significant reduction of 78% in malathion concentration was observed at low turbidity when the coagulant dose of 50 mg/L was used. At the medium turbidity and high turbidity levels, the coagulant dose of 100 mg/L and 150 mg/L led to 74 % and 72.6 % reduction in malathion concentration respectively. The reduction in turbidity was recorded at different coagulant doses and maximum reduction of 82%, 81% and 80% was observed at low, medium and high turbidity levels respectively. For the optimum coagulant dose of 100 mg/l, coagulant recorded the highest reduction in malathion concentration as well as in turbidity at all the turbidity levels. Therefore, the optimum coagulant dose used in the further study was 100 mg/l.

## 4.2 EFFECT OF CONTACT TIME ON THE REMOVAL OF MALATHION

Besides the effect of coagulant dose and turbidity, the contact time also play a crucial role in the treatment of malathion with coagulation/ flocculation process. The effect of treatment time was analysed at optimum coagulant dose of 100mg/L. As the contact time was increased, the removal rate of turbidity and reduction in malathion concentration increased gradually. When the contact time was 30 min, reduction in malathion concentration was observed as 65.2%, 60.1% and 53.3% at low medium and high turbidity levels respectively. This might be due to time required for coagulation was insufficient. The results obtained for contact time of 60 minutes and 90 minutes were satisfactory. Measurements beyond 90 minutes revealed that the reduction in malathion concentration was consistent which might be due to long treatment time, the additional flocs so formed might have broken down and the coagulation effect becomes constant ( Hassan *et al*., 2009).As the maximum reduction in malathion concentration and turbidity was observed at 90 min of treatment, it was selected as optimum contact time for our experimental studies.

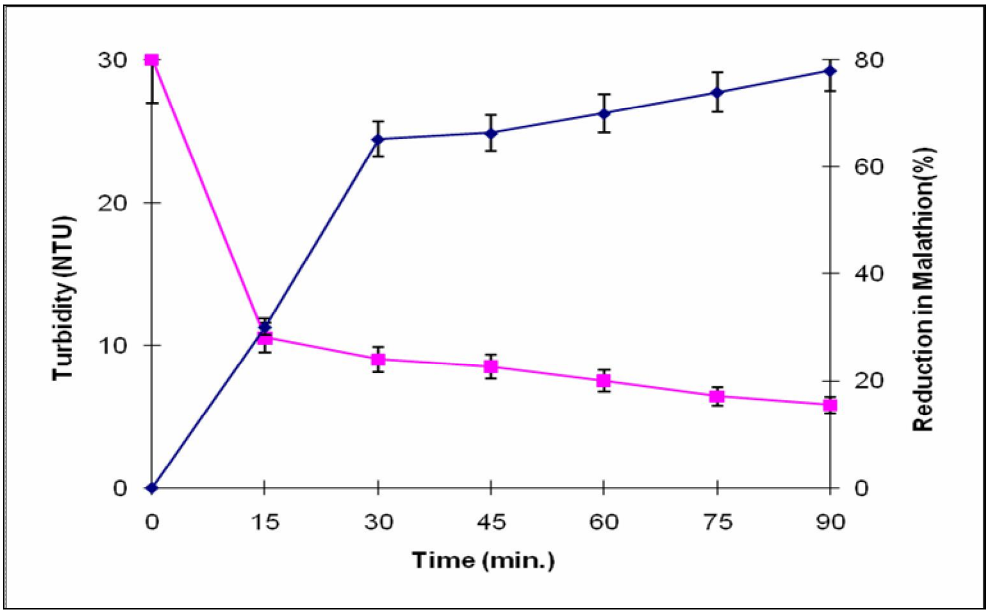


Figure 4.2 (a) Effect of treatment time on malathion and turbidity (10-30 NTU). --◊---, Reduction in malathion (%)., --□--, Turbidity (NTU)

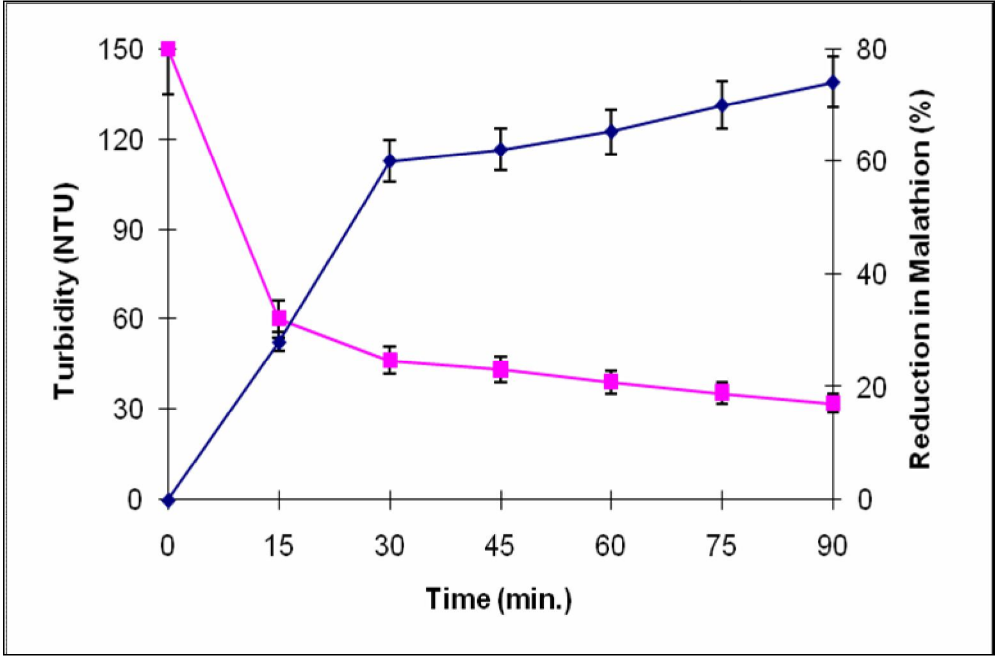


Figure 4.2 (b) Effect of time of treatment on malathion and turbidity (50-150 NTU) --◊---, Reduction in malathion (%)., --□--, Turbidity (NTU)

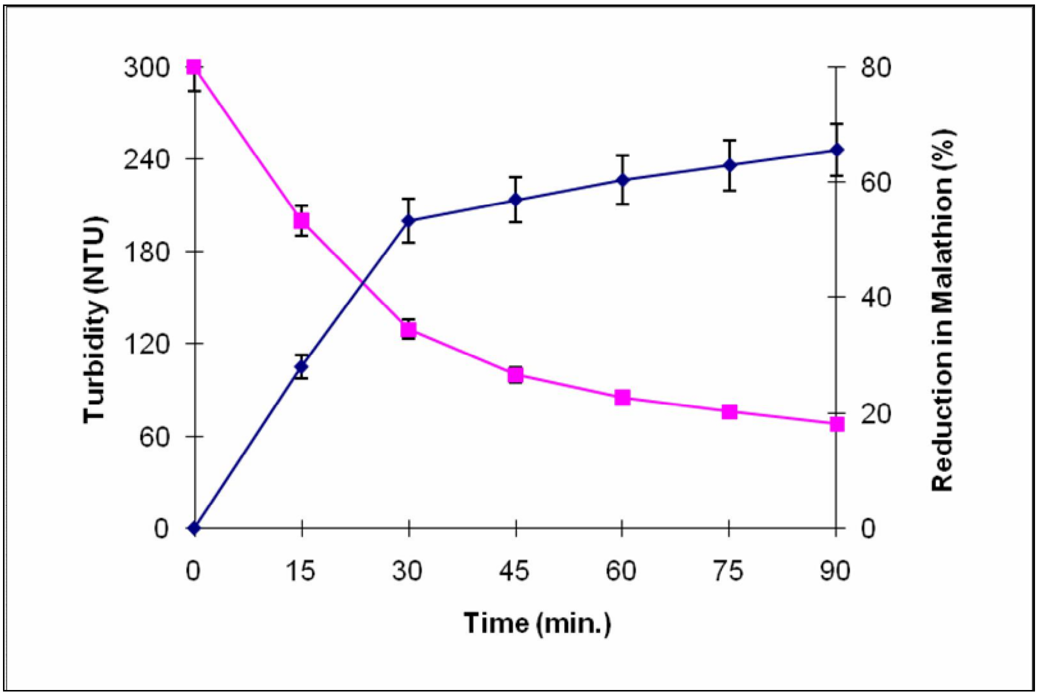


Figure 4.2 (c) Effect of time of treatment on malathion and turbidity (200-300 NTU)

--◊---, Reduction in malathion (%)., --□--, Turbidity (NTU)

From Figure 4.2 {a-c}), it was depicted that the significant reduction in malathion concentration was observed at 90 minutes when optimized coagulant dose of 100 mg/L was used. The removal of turbidity of 82%, 81% and 80% was achieved at low, medium and high turbidity levels respectively. The maximum reduction in malathion concentration was found as 78%, 74% at low and medium turbidity levels respectively as higher percentage of reduction in malathion (78%) required longer mixing time (i.e. 90 minutes).

The results were found in agreement with the earlier findings of Preston *et al.*, 2010, where it was found that with continued increase in coagulant dose, the repulsion between colloidal particles increases and the flocs formed were dispersed to stable colloidal particles again.

### 4.3 Effect of Turbidity on the removal of Malathion

Kaolin was used to make the water samples turbid. The mixture of kaolin particles in distilled water induces detachment of them due to their strong hydration. The dispersion of kaolin releases very fine colloidal particles. They remain in the state of suspension and could not be removed from the dispersion by sedimentation and ultracentrifugation. The two mechanisms (strong hydration and dispersion) play an important role in the stabilization of the colloidal system (Hassan *et al.*, 2009).The concentration of colloidal particles in water was very important, because they serve as the core to the coagulation. If the concentration of colloids was too low, there are too few particles to ensure good flocculation.

Table 4.3 Reduction in Malathion (%) at different Turbidity levels

| | **Reduction in Malathion (%)** | | | | |
|---|---|---|---|---|---|
| **Turbidity (NTU)** | Malathion concentration (ppm) | | | | |
| | **2** | **4** | **6** | **8** | **10** |
| **Low<br>(10-30)** | 56±0.1 | 78±0.1 | 79±0.8 | 79.6±0.4 | 79.9±0.4 |
| **Medium<br>(50 -150)** | 46±0.7 | 74±0.2 | 75.4±0.6 | 75.9±0.2 | 76±0.6 |
| **High<br>(200-300)** | 38±0.3 | 65.7±0.6 | 67.2±0.1 | 67.9±0.1 | 68±0.1 |

Values are mean ± standard deviation

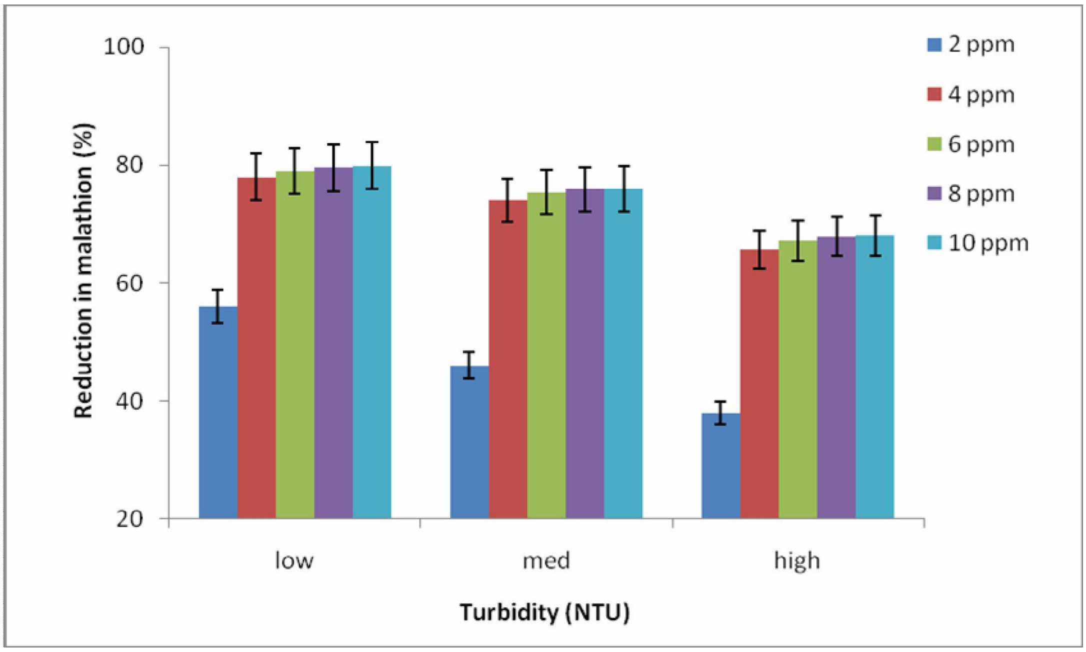


Figure 4.3 Effect of turbidity (low, medium and high) on reduction on malathion concentration.

Table 4.3 and Figure 4.3 presents the effectiveness of coagulant dose 100mg/L in removing different concentrations of malathion from water of different turbidity range. Significant reduction was observed in malalthion at low turbidity levels whereas at high turbidity level, the reduction in range of 38 to 68% was observed for all coagulant doses (0-10 ppm). The reduction of malathion was found to be more in solution of low turbidity levels. It was observed that it was difficult to achieve higher reduction in malathion concntration in solutions having high turbidity.

### 4.4 Malathion reduction by flocculation

Polyacrylamide ($5\times10^6$ Da) was used as flocculant in this study. The flocculating activity of the flocculant against turbid solutions containing kaolin and different concentration of malathion was measured. In order to determine optimum dose of flocculant for maximum removal of malathion, experiments were conducted by varying the dose of flocculant between 10 to 30 mg/ml on turbid water having turbidity ranging from low turbidity (10-30) NTU, medium turbidity (50-150 NTU) and high (200 -300 NTU).

Table 4.4(a) Flocculating activity of flocculant against various malathion concentration at low turbidity 10-30 NTU).

| Concentration of Malathion (ppm) | Turbidity (NTU) | Flocculation activity (%) |
|---|---|---|
| **2** | 25±0.3 | 9±0.8 |
| **4** | 14±0.5 | 20±0.4 |
| **6** | 12±0.2 | 22±0.4 |
| **8** | 10±0.4 | 23±0.8 |
| **10** | 8±0.1 | 25±0.3 |

Values are mean ± standard deviation

The data shown in Table 4.4 (a) , clearly depicted that the flocculating activity (%) was found to be maximum for higher concentration of malathion with 30 mg/ml of flocculant dose.

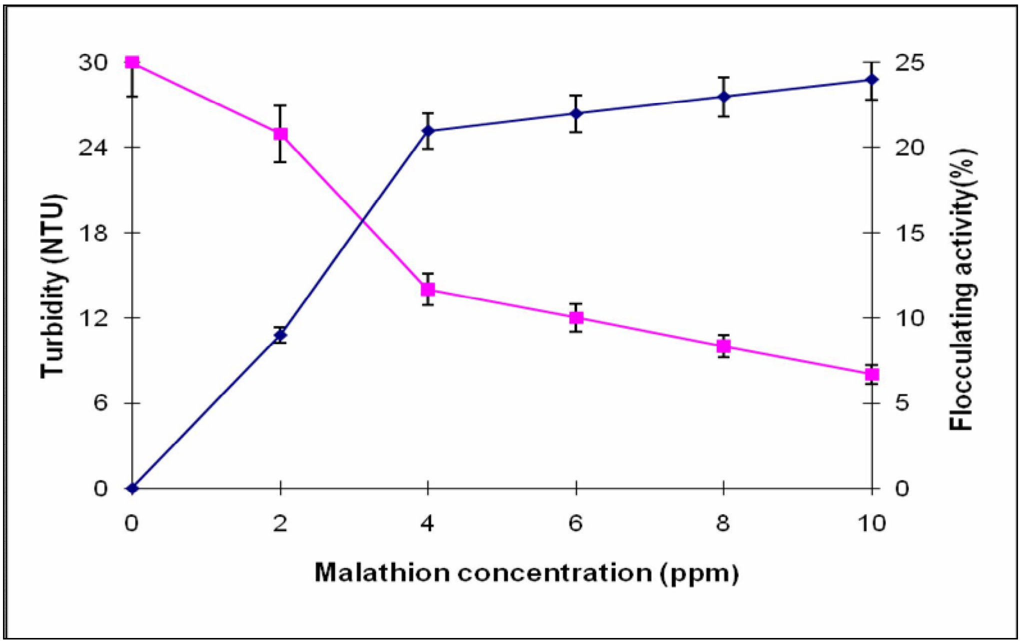


Figure 4.4 (a) Effect of flocculant (as flocculating activity) on malathion concentration and Turbidity (10-30 NTU) ). --◊---, Flocculating activity (%). --□--, Turbidity (NTU)

The maximum flocculating activity has been observed against the higher concentrations (> 4ppm). The flocculant dose of 30 mg/ml was found effective against all the malathion concentrations. The maximum reduction (73.3%) in turbidity was observed, when the initial concentration of malathion was 10 ppm.

Table 4.4(b) Flocculating activity of flocculant against various malathion concentration at medium turbidity (100 -150 NTU)

| Concentration of malathion (ppm) | Turbidity (NTU) | Flocculation activity (%) |
|---|---|---|
| **2** | 130±0.5 | 8±0.4 |
| **4** | 75±0.2 | 19±0.3 |
| **6** | 65±0.2 | 21±0.3 |
| **8** | 54 ±0.2 | 22±0.3 |
| **10** | 42±0.2 | 23±0.1 |

Values are mean ± standard deviation

In the case of low and medium turbidity levels, maximum reduction in turbidity and high flocculating activity was found at low concentrations of malathion.

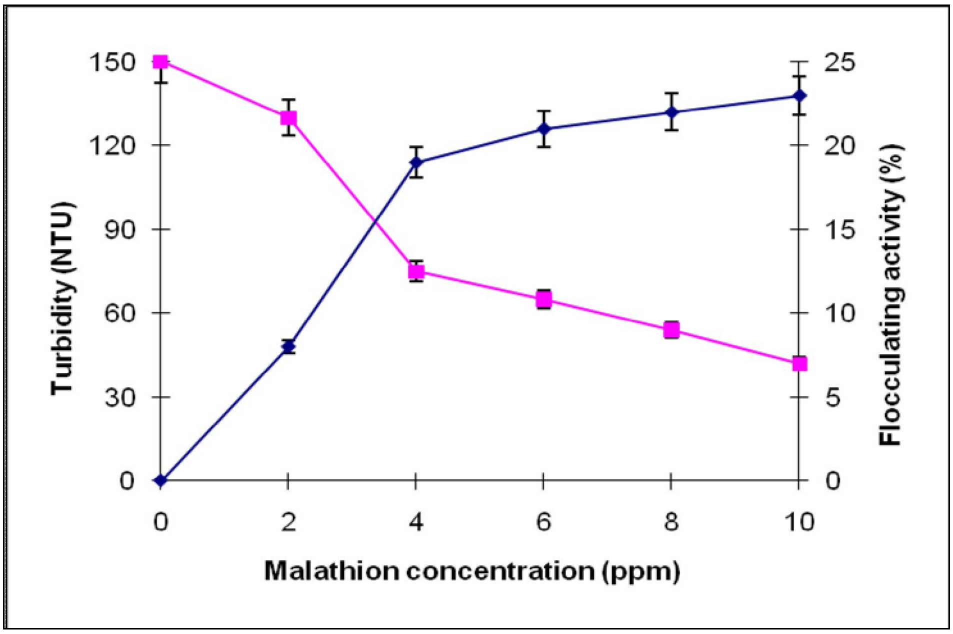


Figure 4.4 (b) Effect of flocculant (as flocculating activity) on malathion concentration and Turbidity (50-150 NTU). --◊---, Flocculating activity (%). --□--, Turbidity (NTU).

Table 4.4 (c) Flocculating activity of flocculant against various malathion concentration at high turbidity (200 -300 NTU)

| **Concentration of malathion (ppm)** | **Turbidity (NTU)** | **Flocculating activity (%)** |
|---|---|---|
| **2** | 270±0.3 | 8±0.3 |
| **4** | 160±0.5 | 19±0.1 |
| **6** | 145±0.5 | 20±0.1 |
| **8** | 125±0.3 | 21±0.8 |
| **10** | 100±0.3 | 22±0.2 |

Values are mean ± standard deviation

At high turbidity levels (200 -300 NTU) , optimum flocculant dose of 30 mg/ml was found to be effective in achieving satisfactory flocculating activity (%). The reduction in turbidity increased with increase in flocculant dose at all the turbidity levels.

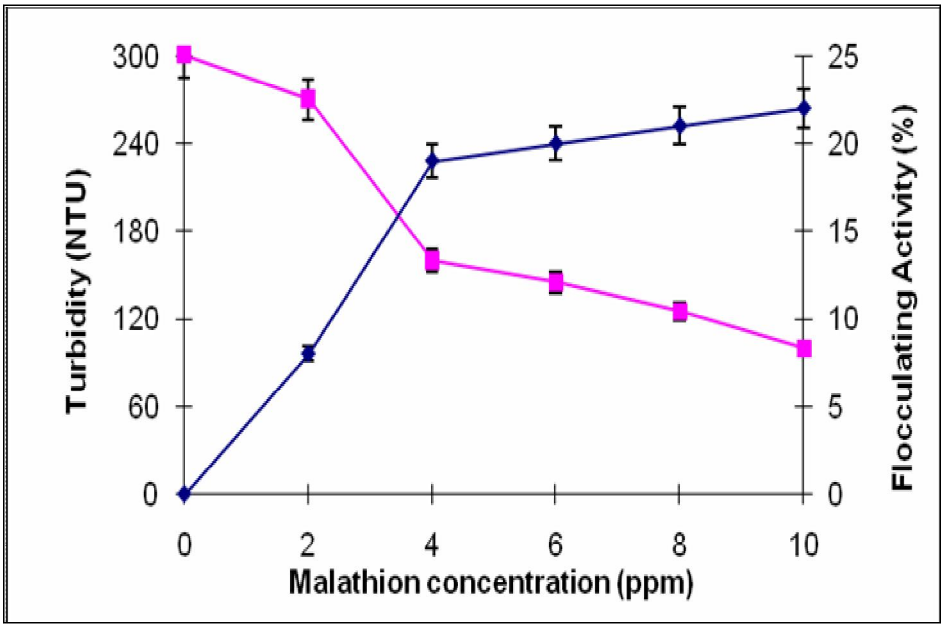


Figure 4.4 (c) Effect of flocculant (as flocculating activity (%)) on Malathion concentration at turbidity (200-300 NTU). --◊---, Flocculating activity (%). --□--, Turbidity (NTU)

The optimum flocculant dose of 30 mg/ml was found to show maximum reduction in turbidity and malathion concentration. This behaviour could be explained by the fact that the microflocs were generated by attraction and charge neutralization and this optimal dose of flocculant in suspension caused the larger amount of solids to aggregate and settle.

# *CONCLUSION*

# CONCLUSION

This study aimed to optimize coagulant/flocculant dose, time of treatment and level of turbidity for the maximum removal of malathion from water.

Significant reduction of malathion (78%) was observed at 100mg/L of coagulant dose at low turbidity levels at 90 min. In the case of flocculants, 30 mg/mL was the appropriate dose found for the malathion removal. The study evidenced that coagulation/flocculation process can assure the limits of malathion for water treatment providing high efficiency using relatively low levels of coagulants if the process is well optimized before operation.

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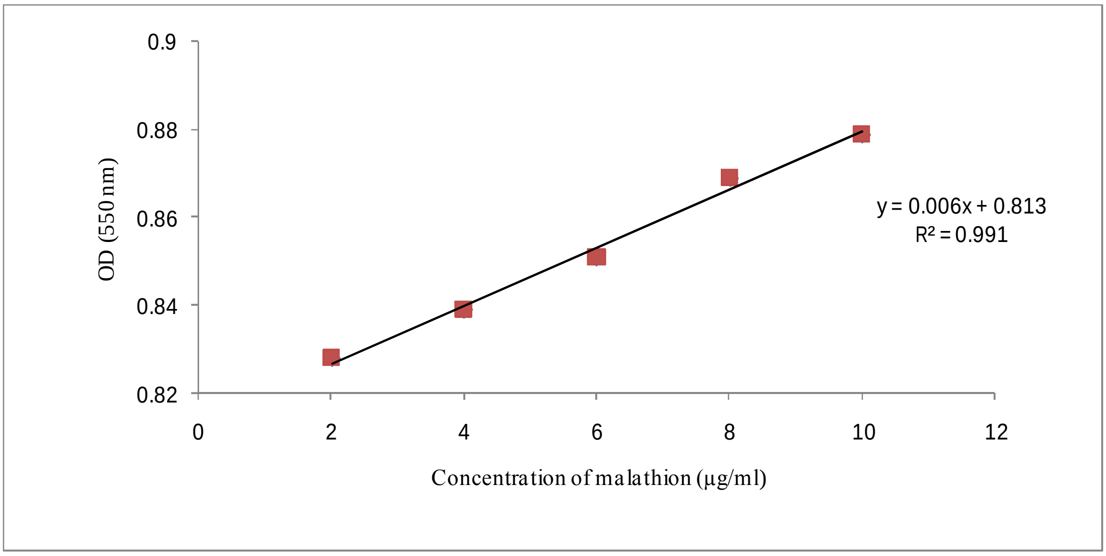
# ANNEXURE

## REQUIREMENTS FOR STANDARD CURVE (Malathion)

| **S.No.** | **Chemicals** | **ml** |
|---|---|---|
| 1. | NBS | 1.5 |
| 2. | Glacial acetic acid | 1 |
| 3. | HCl | 0.5 |
| 4. | Rhodamine B | 0.7 |

## Standard curve of Malathion

| Conc. (µg/ml) | OD (550 nm) |
|---|---|
| 2 | 0.828 |
| 4 | 0.839 |
| 6 | 0.851 |
| 8 | 0.869 |
| 10 | 0.879 |


0.9
0.88
0.86
0.84
0.82
OD (550 nm)
0
2
4
6
8
10
12
Concentration of malathion (µg/ml)
y = 0.006x + 0.813
R² = 0.991

b