PHOTOCATALYTIC DEGRADATION OF PARAQUAT BY USING TIO$_2$ AND PHOTO FENTON

A Dissertation

submitted in partial fulfillment of the requirement

for the award of degree of

Masters in Technology

in

ENVIRONMENTAL SCIENCE & TECHNOLOGY

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July 2016

CERTIFICATE

This is to certify that thesis entitled, **"Photo catalytic degradation of paraquat by using TiO_2 and Photo Fenton "** submitted by **Chirag** in partial fulfillment of the requirements for the award of degree of **Masters of Technology** in **Environmental science** at **Thapar University, Patiala** is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in this thesis has not been submitted in part or full to any other university institute for award of any Degree.

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DECLARATION

I hereby declare that the project work entitled **"Photocatalytic Degradation Of Paraquat By TiO_2 & Photo Fenton"** is an authentic record of my own work carried out at Thapar University campus as requirements of one year project internship for the award of degree of M.Tech. **"School Of Energy And Environment"**, Thapar University, Patiala, under the guidance of **Dr. Anita Rajor**, during June 15, 2015 to June 15, 2016.

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ABSTRACT

Pesticide paraquat dichloride is most widely used as herbicide in the world, it kills a wide range of annual grasses and broad leaved weeds and it is very fast reacting therefore it is mostly used in farming to protect plants and foods. But on the other hand it is a highly toxic substance. It causes contamination of air, water and soil. It enters the food chain and cause bioaccumulation and biomagnifications. Exposure can lead to diseases of eyes, skins, inhalation and ingestion. Therefore an alternate solution must be there so it can be used as an environmentally friendly product. One of the methods is by photo degradation.

Photo degradation was performed in a UV chamber. During experiment TiO_2 was used as photo catalyst degradation of paraquat dichloride as it is the best photo catalyst due to its chemical and biological inertness when compare to other photo catalyst. During experiment it was found that degradation of 20ppm paraquat with proper agitation and aeration for 420min. with pH 11 and TiO_2 content 0.4gm in 250ml solution showed maximum degradation of 98%. When same experiment was conduct in sunlight it show even higher degradation of 98% as compaired to UV light. This showed that optimum catalytic properties enable demonstrate TiO_2 has good behaviour to photocatalytically degrade paraquat dichloride to relatively safe and tolerable compunds in the enviornment.

To reduce the paraquat impact, more powerful treatment processes as compared to traditional treatment for its complete degradation in environmental water are needed. Photo Fenton is one of the clean technologies based on the generation of extremely reactive and non-selective hydroxyl radicals, with very high oxidative power. Due to their powerful capability to oxidize numerous organic compounds into CO_2 and H_2O. Fenton's reagent is a solution of hydrogen peroxide and ferrous ions. Experiment conducted with Photo Fenton showed higher degradation as compared to TiO_2. Result obtained by the degradation of paraquat when performed with optimum conditions by addition of 20ppm paraquat, pH 3, Fe^{2+} 5.5 and H_2O_2 0.1ml for 300 min. showed maximum degradation of 89% which is more than degradation done by TiO_2 which showed 77% degradation in 300min. This result showed that with Photo Fenton process even better and faster degradation can be obtained as compared to TiO_2. Even it is possible to achieve complete degradation of paraquat by Photo Fenton process by increasing reaction time.

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CHAPTER 1

INTRODUCTION

1.1 Environmental Pollution

It is defined as the addition of different harmful pollutants into the environment which make it unhealthy to live in. The most common types of pollutants are usually garbage, hazardous substances, and waste water. They bring undesirable change in the physical, chemical or biological characteristics of the environment. Environmental degradation is a worldwide problem, which happens mainly in the form of air and water pollution. These make the environment unhealthy for all the living beings including humans, plants, microorganisms, wildlife and livestock.

1.2 Water Pollution

Over 71% of our Earth's area is covered with water. But only 2.4% of it is available as fresh water out of which only ~1% is usable for direct human uses. This is the water found in lakes, rivers, reservoirs and underground sources like wells, springs etc. The main concern is water pollution due to its universal solvent property for which it can dissolve almost all the substances in it which makes it easily get polluted. The pollution can be caused by point sources and non point sources. Waste water from industries, domestic houses, agricultural fields etc. makes it polluted and affects the health humans and plants. The main water pollutants are heavy metals like cadmium, lead, mercury etc., inorganic substances such as sodium chloride, sodium carbonate etc and organic sources like pesticides paraquat, malathion, etc. These substances are harmful and cause bioaccumulation and biomagnifications in living organism. This waster pollution is increasing annually. A efficient treatment technology should be investigated which can make the polluted to degrade effectively and minimize its toxic component to lowest level so it can be made environmental friendly product. Even the technology used should be clean so that residue left and product obtained will not affect the environment example treatment of some of the pesticide using Advance oxidation process which is taken to be clean technology because by product are carbon dioxide and water. Further more research is needed in this field control water pollution. The water cycle and its pollution are shown in the figure below. Which show hydrology of water and pollution from different source.

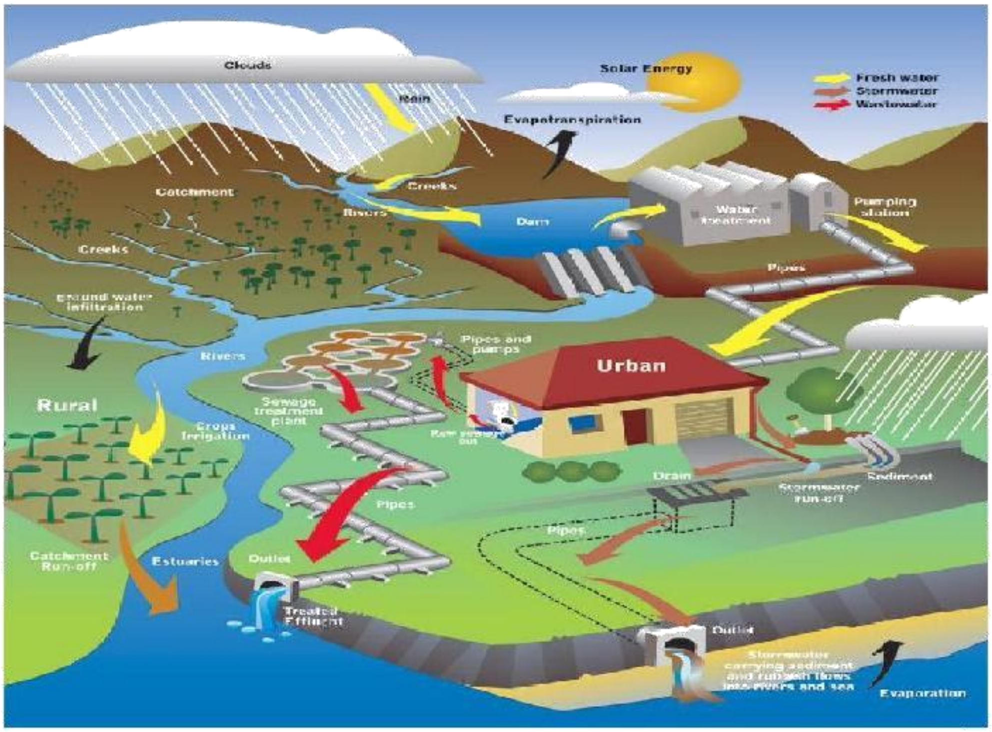

Fig: 1.1. Water cycle and its pollution

(Source:*web link http://thewatercycle7.weebly.com/)*

1.3 Pesticide

Pesticides are substances which are used for destroying any pest. It is mainly used for plant weeds, fungi and insects. It is also used for non-agricultural purposes. There are many form of pesticide which includes: herbicide, fungicide to control fungus, insecticide to control insect growth, nematicide etc. The problem of pesticide pollution is increasing drastically due to its vast usage in agricultural field in order to have maximum yield. Agricultural pesticides, has been categorized as a major environmental problem due to the toxic nature of these compounds. Because pesticides are generally persist for long time. Residues of pesticides may remain in treated products. Humans are exposed to pesticides found in soil, water, air and food by different routes of exposure such as inhalation, ingestion and dermal contact. Exposure to pesticides have various effects on health like irritation of eyes, cancer, vomiting, nausea, diarrhea and many other health related problems. These residues should not exceed a limit above which they may pose risks to human health. They are extremely mobile all over the environment and some of them present carcinogenic and mutagenic properties, there with drawl has become a field of growing interest (*Posecion et al., 2008*). The existence of these pesticides in water and food cause adverse affect on human health and for balance of ecosystems.

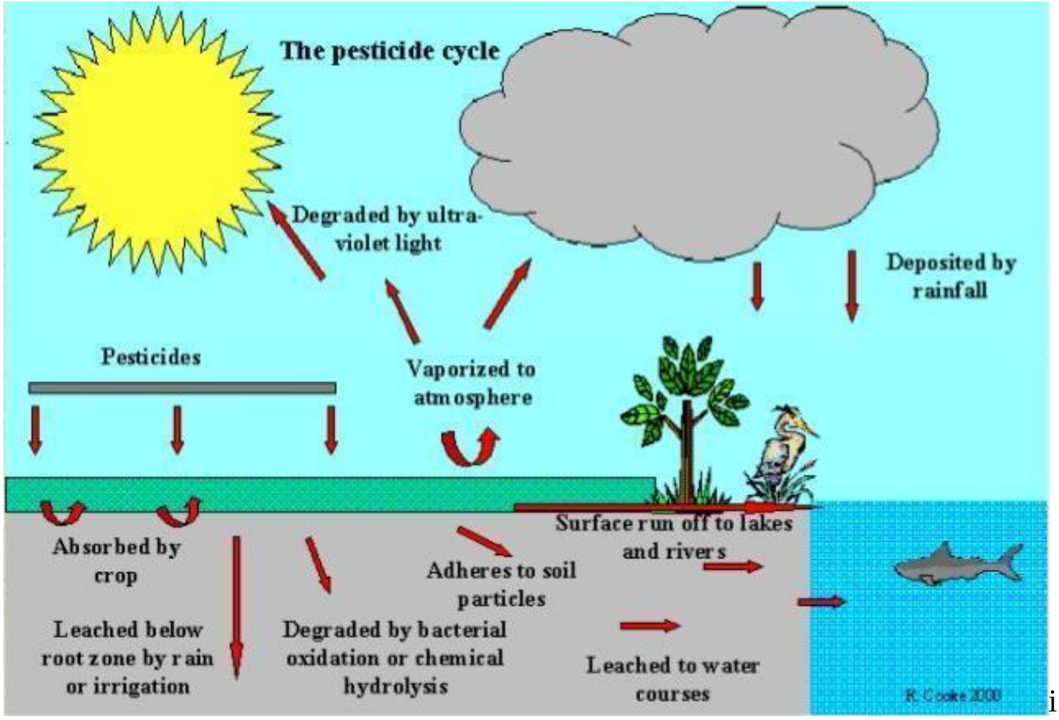

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Fig: 1.2. Pesticide cycle

(Source:*web link http://www.ecifm.rdg.ac.uk/pesticides.htm*)

Runoff of pollutant into a watercourse occurs when fertilizers and pesticides from a ground is carried into a river by surface run-off. Pesticides can enter water bodies even through leaching process. These two primary processes are related to the earth's hydrological cycle. With increase in global demand for food, the situation does not likely to improve. The critical nature of this environmental problem has imposes the development of faster and more accurate methods for characterization and quantification of pesticides dispersed in the environment (*Amondham et al., 2006*). When wastes generated from animals, fertilizers, insecticides, herbicides and fungicides are applied to cropland, some residues reside in the soil after plant uptake and may percolate into subsurface waters, or the residues may drift to surface water by dissolving in runoff or adsorbing to the sediments (*Hertzmann et al., 1990*). Spray drift during application may carry pesticides to surface waters too. Chemical or physical processes transform residues into products that may also contaminate water. A simple familiarized example is, nitrogen fertilizer or nitrogen from animal waste may be transformed first into ammonium and then into nitrates. Nitrates can turn into nitrites and both are detrimental to human health (*Alberdi et al., 1996*). Once a pesticide is introduced into the environment, either through an application, removal or a spill, it is influenced by processes, such as adsorption, transfer, breakdown and degradation. These natural processes determine their persistence, movement and its final fate in the environment. In recent years the growing awareness of the risk associated with intensive use of the pesticides has led to a more critical attitude towards the use of agrochemicals (*Kearney et al,. 1995*). Analyzing and monitoring exposure data are critical to accurately determine the negative effect of pesticides on human health and environmental degradation. Several methodical techniques that have been used broadly for the analysis of pesticides include fluorimetry, capillary electrophoresis, spectrophotometry, mass spectroscopy and mainly gas or liquid chromatography (Kambhampati *et al*., 1994). These techniques operate reasonably well with high sensitivity but they do present a certain form of disadvantages. Among the disadvantages of these techniques are, they are restricted to laboratories, requires specialized and sophisticated instrumentations, more time consuming, costly, and have to be performed by well trained technicians (Shivhare et al., 1991). Besides, the determination of pesticides and their residues in both water or soil solutions is a serious problem as each of these chemicals display specificity in terms of reactivity and numerous active ingredients of pesticides are often present in the same matrix. Therefore, the need to plan convenient tools for the study of pesticides in environment remains an unending and challenging question (*Du et al., 2007*).

1.3.1 Properties Of Pesticides

There are quantity of other properties of pesticides which verify their performance and fate. One is volatility of pesticide. The ones that are most volatile have the maximum potential to go into the atmosphere and, if persistent, to move long distances. Another main property is solubility in water; or how simply they dissolve in water. If a pesticide is very soluble in water, it is more easily drain off with rainfall, as runoff or through the soil has potential groundwater contaminant. In addition, the water-soluble pesticide is more likely to stay mixed in the surface water where it can have adverse effects on fish and other organisms.

If the pesticide is very insoluble in water, it regularly tends to stick to soil and also settle to the bottoms of bodies of surface water, making it less accessible to organisms.

1.4 Environmental Characteristics

It is feasible to predict in a general sense behavior of pesticide. Unfortunately, more precise prediction is not feasible due to complexity of environment. for example, there are vast numbers types of soil varying in the concentration of sand, organic matter, metal content, acidity, etc. All of these soil behaviors control the pesticide activities so that a pesticide which might be possible to contaminate groundwater in one soil may not do so in another. Similarly, surface waters have different properties, such as acidity, depth, temperature, clarity (suspended soil particles or biological organisms), flow rate, and general chemistry. These properties and others have influence pesticide movement and fate. With such great complexity, scientists unable to conclude exactly what will pesticide behaves once it has entered the environment. However, they can partition pesticides into general categories with regard to, for example, persistence and possible for groundwater contamination and they can also gives some idea as to where the pesticide released will most possible be found at its highest levels. Thus, it is possible to collect information which can help make informed decisions about what pesticides to use in which situations and what possible risks are being faced due to a particular use.(*weblinkhttp://extoxnet.orst.edu/tibs/movement.htm*)

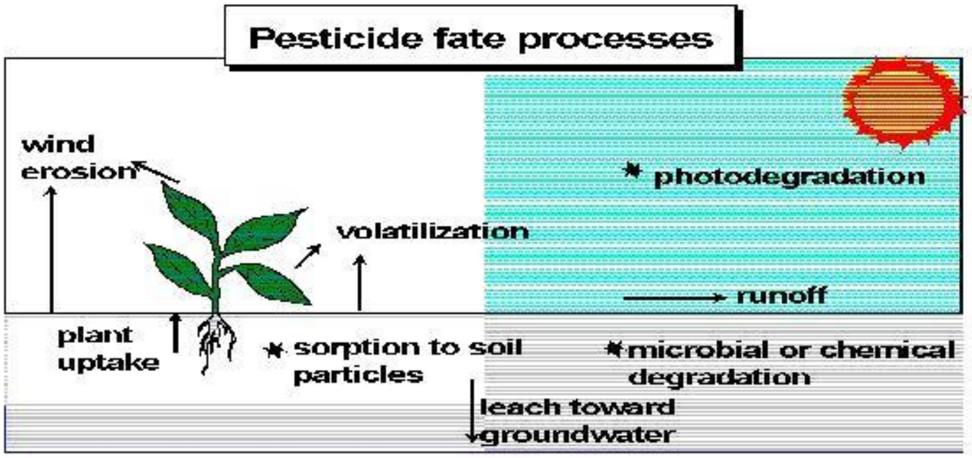


Fig: 1.3. Pesticide fate process

(Source:*we blink http://extoxnet.orst.edu/tibs/movement.htm*)

1.4.1 Impact on Air

Pesticides can cause air pollution. Pesticide flow occurs when pesticides suspended in the air as particle are carried by wind to other areas, potentially contaminate them. Pesticides that are sprayed to crops can volatilize and may be blown by effect of winds into close by areas, potentially posing a threat to wildlife. Weather conditions at the time of application as well as temperature and relative humidity change the spread of the pesticide in the air. As wind velocity increases so does the spray drift and also droplets of sprayed pesticides or particles from pesticides applied as dusts may travel on the wind to other areas, or pesticides may hold to particles that blow in the wind, such as dust particles. Farmers can take up a buffer zone about their crop, consisting of empty land or non-crop plants such as evergreen trees to serve as windbreaks and absorb the pesticides, preventing drift into other areas.

1.4.2 Impact on water

There are four key routes by which pesticides enter the water: It may flow outside of the proposed area when it is sprayed, it may infiltrate, or leach, through the soil, it may be carried to the water as runoff, or it may be spilled, for example by chance or through neglect. They may also be carried to water by eroding soil. Factors that affect a pesticides ability to contaminate water include its water solubility, the distance from an purpose site to a body of water, weather, soil type, presence of a growing crop, and the method used to apply the chemical.

1.4.3 Impact on soil

Many of the chemicals used in pesticides are persistent soil contaminants, whose impact may undergo for decades and negatively affect soil conservation. The utilize of pesticides decreases the common biodiversity in the soil. Not using the chemicals results in higher soil quality, with the additional effect that extra organic matter in the soil allows for high water retention. This helps raise yields for farms in famine years. Degradation and sorption's are both factors which influence the persistence of pesticides in soil. Depending on the chemical nature of the pesticide, such processes control directly the transportation from soil to water, and in turn to air and our food. Breaking down organic substances, degradation, involves exchanges among microorganisms in the soil. The table below lists some of the more normally used pesticides with an estimate of their persistence in soil. If a pesticide's half-life is 30 days, half will be left after 30 days, ¼ after 60 days, 1/8 after 90 days and so on. It might seem that a short half-life would mean a pesticide would not have a ability to move extreme in the environment. This is generally true; however, if it is also very soluble in water and the circumstances are right, it can move speedily through certain soils. As it moves away from the surface, it moves away from the agents. Which are degrading it such as sunlight and bacteria. As it gets deeper into the soil, it degrades more gradually and thus has a probability to get into groundwater.

The descending movement of non-persistent pesticides is not an unlikely scenario and several pesticides with short half-lives, such as aldicarb, have been broadly found in groundwater. In contrast, very persistent pesticides may have other properties which limit their potential for movement throughout the environment. Many of the chlorinated hydrocarbon pesticides are very persistent and slow to breakdown but also very water insoluble and lean not to move downward through the soil into groundwater. On the other hand, they become problems in other ways since they stay on the surface for a more time where they may be subject to runoff and likely to evaporate. Even if they are not very volatile, the immensely long time that they reside can lead, over time, to measurable concentrations moving through the atmosphere and accumulating in remote area So far, the discussion has focused on air, soil and water. However, living organisms may also play a important role in pesticide division. This is particularly important for pesticides which can build up in living creatures. An example of accumulation is the uptake of a very water-insoluble pesticide, such as chlordane, by a creature living in water. Since this pesticide is stored in the organism, the pesticide accumulates and levels rise over time. If this organism is eaten by a higher organism which also can store this pesticide, levels can reach higher values in the higher organism than is present in the water in which it lives. Levels in fish, for example, can be tens to hundreds of thousands of times better than ambient water levels of the same pesticide. This type of accumulation is called bioaccumulation. In this regard, it should be remembered that humans are at the top of the food chain and so may be exposed to these high levels when they eat food animals which have bioaccumulated pesticides and other organic chemicals. It is not only fish but also domestic farm animals which can be accumulators of pesticides and so care must be used in the use of pesticides in agricultural situations.

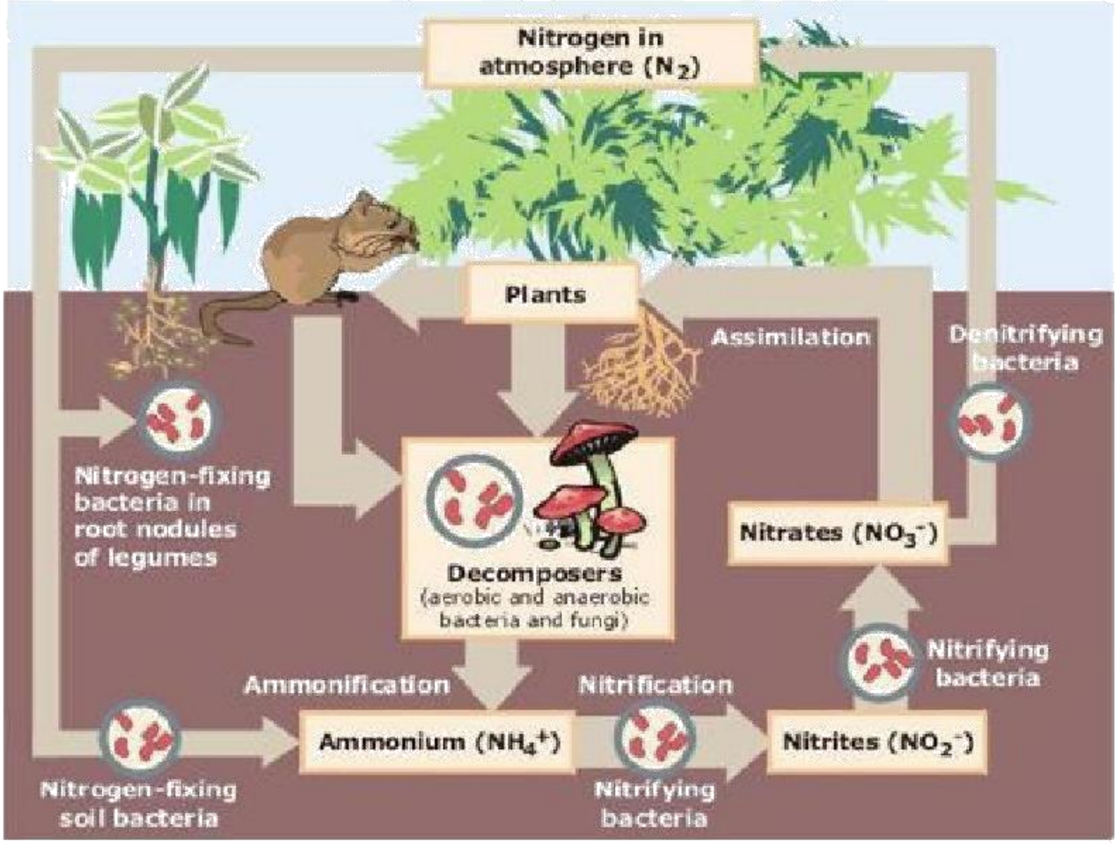


Fig: 1.4. Nitrogen Fixation

(Source:*Web link http://www.slideshare.net/kunaltribhuvan7/pesticides-14223207*)

1.4.4 Effect on plants

Nitrogen fixation, which is required for the enhance of higher plants, is caught up by pesticides in soil. The insecticides DDT, methyl parathion, and especially pentachlorophenol have been shown to obstruct with legume- rhizobium chemical signaling. Reduction of these symbiotic chemical signaling results in reduced nitrogen fixation and thus reduced crop yields. Root nodule creation in these plants saves the world economy $10 billion in synthetic nitrogen fertilizer every year. The fate of pesticide is shown in figure below how it reach and then contaminate the plant as well as soil and its surrounding.

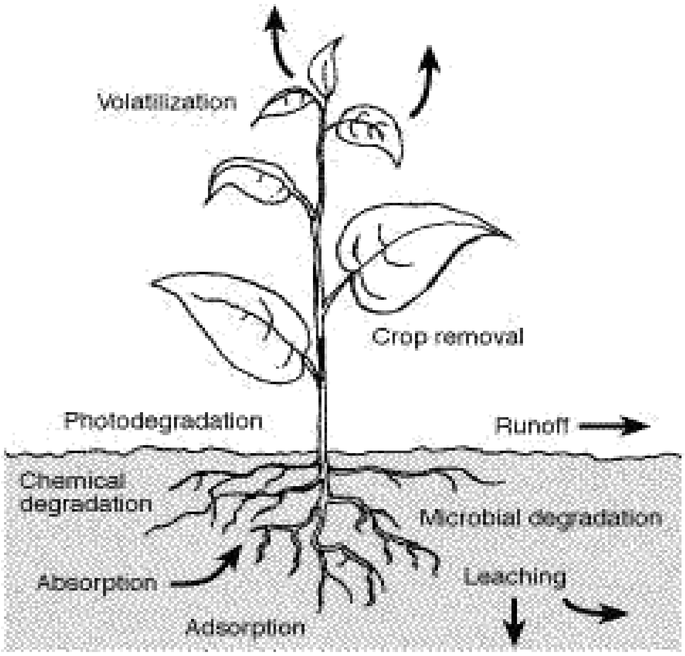


Fig: 1.5. Pesticide fate in plant

(source: *web link http://extension.missouri.edu/p/G7520*)

1.5 Paraquat Dichloride

Paraquat is a herbicide which is widely used in the world for agriculture practices for controlling broad weeds and grasses. Chemically, it belongs to the group of bipyridilium herbicides.

1.5.1 Crops in which paraquat is used

Paraquat is used includes cereals, pulses, oil seeds, vegetables and in horticulture. Farmers use paraquat for controlling weeds in 25 crops. As of now, there is no implement in India to monitor and make sure that paraquat is used only on crops for which it is legally permitted. There is also no system to prevent the illegal use of paraquat.

1.5.2 Application of paraquat in the field

Paraquat is sprayed in the field mostly during pre-planting, pre-sowing, seedling or vegetative stage as a pre-emergence measure as well as useful for post-emergent weed control. Pre-planting or pre-sowing application is reported by 71 % of the respondents. The pre-sowing or pre-planting application was observed for crops such as cereals, pulses and vegetables. Paraquat is applied in the field about 16 – 21 days before the planting date, followed by field training once the weeds are burnt and then the crop is sown or planted. Paraquat is applied for weed control in station crops as well. 56% percent of the respondents reported that they use paraquat for controlling weeds in spaces between the rows, ridges and furrows, as well as field bunds and boundaries of crops such as paddy, wheat and vegetables. Paraquat is applied in two ways, one is by spreading and the other is through spraying. The CIBRC data shows that paraquat is approved only for spraying. In addition, information obtained from the leaflet of Gramoxone, the manufacturer (Syngenta) only recommends use through spraying(*Dileep kumar*, *2015*).

1.5.3 Limitation-

1) Toxicity - Paraquat is acutely toxic and highly toxic by the inhalation route and has been put in Toxicity Category I (the highest levels) for acute inhalation effects. Paraquat is moderately toxic (Category II) by the oral route and slightly toxic (Category III) by the dermal route. Paraquat will cause moderate to severe eye irritation and minimal dermal irritation, and has been placed in Toxicity Categories II and IV for these effects. Paraquat is corrosive to the skin. The lethal doses of paraquat are relatively low. Examples of lethal dosages are ca. 33 and 36–54 mg/kg for human beings and cattle, respectively. *(United States Environmental Protection Agency August* 1997; *Kanchanatip et al.*, *2011*).

2) It is an ecological contamination both in soil and in surface waters that is dangerous to people and creatures. It appeared to be extremely fixed in soil. Paraquat does not hydrolyze, does not photo degrade in fluid arrangements, and is impervious to microbial debasement under vigorous and anaerobic conditions.
3) The farmers and laborers reported various problem due to paraquat, for example, aggravation, tingling, cerebral pain, spewing, copying sensation, breathing trouble, muscle torment, stomach distress, laziness, skin hypersensitivity and shading change, tiredness, queasiness, happiness, fever, eye smolder, discombobulating, loose bowels, throat drying, shuddering, sniffling and change in heart beat rate. Some animals also affected by it e.g. passing of a cow and a goat in the wake of eating paraquat splashed

fields causes obviousness, stomach extension, the runs and tiredness among them. In towns, retailers offer paraquat in plastic conveys packs and refill bottles which are against the Insecticides Act.

4) It has been utilized for suicides as a part of different parts of the nation and has a high death rate. There is no cure for paraquat. The death rate for paraquat suicide endeavors is relatively high, at 42 to 80 % (*Kumar, 2015*).
5) Due to its physical properties such as low vapour pressure and high solubility in water. It cause contamination of rivers, sea, and is able to change the activity of several enzymes of fish, affecting the cardiac contraction and ventilation, effects that can alter the initial development of these organisms (*kanchanti et al., 2010*).
6) It ties firmly to the dirt and gets to be dormant in the dirt, which cause barrenness of soil and over the long haul it cause debasement of soil (*Syngenta Australia Pty Ltd 2013*).
7) Among the natural impacts of these chemicals, it can bring various physiological changes. A few herbicides, when at low dosage, bring about various noticeable impacts in the life forms, in any case, in long run it can decrease the lifespan (*Morales et al., 2013*).

1.6 Objective

The main objectives of proposed study are:

- Removal of paraquat by using TiO_2 in aqueous suspension and by Photo Fenton
- process. Optimization different conditions for removal of paraquat by TiO_2 and Photo Fenton process.

1.7 Approach

- The selected paraquat would be treated with TiO_2 and Photo Fenton process.
- The Degradation condition would be optimized by varying catalyst concentration, pH, paraquat concentration, volume of solution and distance from UV rays.

CHAPTER 2

REVIEW OF LITERATURE

2.1 Pesticide Scenario

Paraquat is a kind of herbicide which is typically applied in horticulture field for manage of weeds. It react during the process of photosynthesis and expel the moisture content from the greener parts of the plant with which it comes into touch and adsorption from the surface of leaf, is increased due to excessive humidity and cause drying of the leaf. The paraquat reacts with electrons produced during the photo system and produces free radicals that destroy cellular membranes and then plant's tissues. It possess risky substance that is hazardous for each human and animals(*Haley et al., 1979*). Paraquat has been open to agriculturists over 53 years and it causes environment degradation both in water and in soil, due to its huge use. It is necessary to develop a crucial technique to minimize its effect (*Kunz et al., 2002*). It is continuously used to demolish weeds to make filed ready for farmers in so to have less work out in combine with no till farming practices which minimize ploughing. Paraquat is available as paraquat dichloride. It turned into enrolled in several countries as a non unique agrochemical herbicide item for the manipulate of weeds completely from the field of agrarian regions and further non-crop areas, as an instance, such as near open plane terminals, streets, electric powered transformer stations, railroad and commercial buildings(*Bromilow, 2004*). It is also used to kill oceanic weed. The presence of little amounts of paraquat herbicide inside the oceanic surroundings would possibly adversely affect the respiration problem in aquatic creatures,(*Cheah U et al., 1998*). Paraquat strongly adsorb via soil particles, and drain to aquatic environment during run-off from agriculture(*Hance R.J et al., 1980*). Also, herbicides in the soil stop the growth of mycorrhizal fungi, which grows with the root of many plants and aid in nutrient uptake, by decreasing the number of fungal spores produced (*Mackinnon et al., 1993*). The heavy use of pesticide in treatment of soil causes populations of beneficial soil micro-organisms to low level, causing degradation of soil. These pesticides are subsequently washed into the aquatic environment through run-offs and leaching and cause negative effect to the aquatic flora and fauna (*USEPA, 2007*). It is difficult to measure the level of toxicity of pesticides on organisms in the aquatic environment because of the complex nature of aquatic ecosystems (*Rand and Petrocelli, 1985*). Farmers and workers were conscious that it is acutely toxic, but because of labour issues they felt forced to apply these chemicals. Lack of professional laborers, non availability of labourers at some critical periods, increases labour cost were the important reason for them in using paraquat. similarly, farmers claimed that paraquat dichloride is available at reasonably priced and controlling of weed can be carried out with lesser effort. The farmers and workers reported numerous unfavorable fitness which causes infection, headache, vomiting, burning sensation, breathing problem, muscle pain, skin hypersensitive reaction, tiredness, nausea, fever, eye burn, diarrhea, throat drying, sneezing, respiratory issues including low beat of heart price etc. additionally the chemical enters the food that is harmful for individuals who eat it which cause biomagnifications and bioaccumulation(*Kumar, 2015*).Thus its necessary to have some measure to minimize toxicity from herbicide and makes it much closer to environment friendly product. There are some of advantage why it is popular among farmer.

1) It has physical properties such as high solubility in water and low vapour pressure (*kanchanti et al., 2010*).
2) Paraquat kill weeds efficiently within a small time period, therefore, cultivator feel that using paraquat is an simple method to control weeds.
3) It is less inexpensively compared to the cost incurred for manual weeding.
4) It is economical than other herbicides (*Kumar, 2015*).
5) It binds tightly to the soil and becomes inert in the soil, so does not leach into river or marine environments.
6) It can be used during wet climates also.
7) It is a contact herbicide and does not affect roots or bark of plant, so can be sprayed to control weeds much closer to, and under, vines and fruit trees, in comparison to other herbicides. (*Syngenta, 2013*).

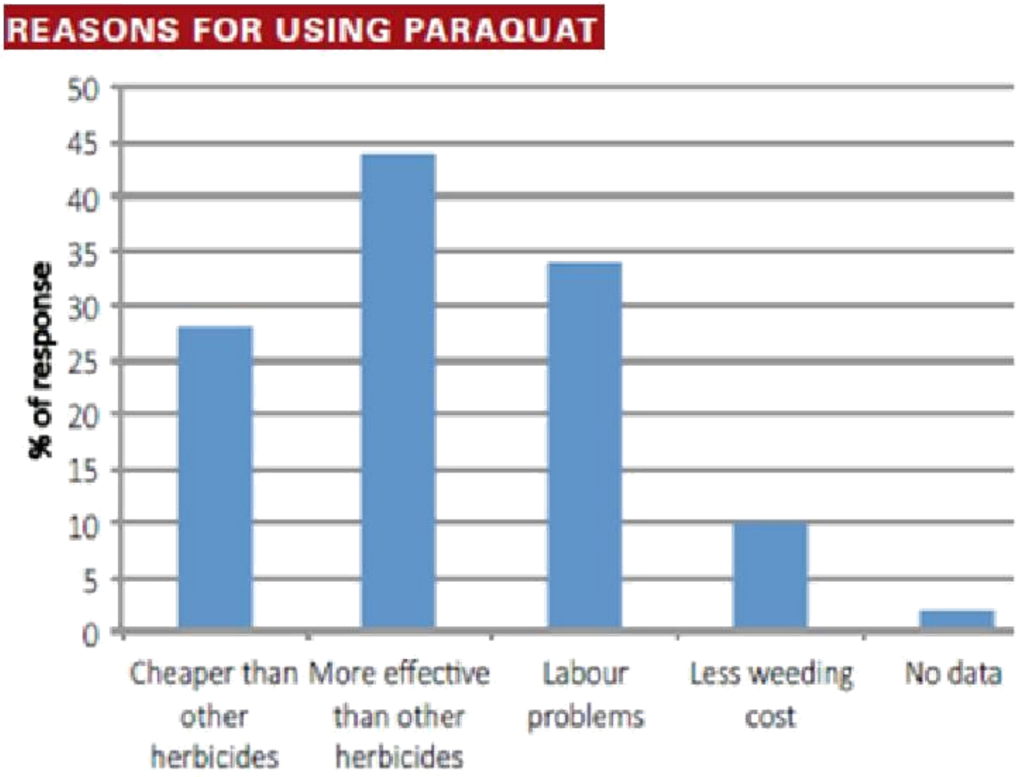


Fig: 2.1. Reason for using paraqaut

(source: *kumar, 2015*)

2.2 International Scenario

Paraquat is sold around 132 countries. But, paraquat is banned in 33 countries which includes countries of the European Union due to its adverse health consequences. In Switzerland, the home united states of Syngenta, the principle manufacturer of paraquat, it's far banned for the reason since 1989. It changed into first synthetic and bought via in early 1963, and today it is most usually used herbicides. It is the most deadly herbicide used in market for 70 years. Yet it is one of the most extensively used herbicides in the world, and in most countries where it is registered it can be used without any restriction. It is used on more than 80 crops in about 110 countries. Gramoxone, manufactured by Syngenta, is the most common trade name for paraquat, but the herbicide is also sold under many different names by many different manufacturers.

China is now the world's largest manufacturer of paraquat, producing more than 100,000 tonnes per year. As paraquat has been banned, or use prohibited, in 32 countries, mainly for health causes. But there has been tough industry resistance to including paraquat in the Rotterdam

Convention on Prior Informed Consent and it remains outside the PIC list. Syngenta, the world‘s largest agrichemical corporation, is the chief manufacturer (with plants in UK and China), selling the product under the trade name Gramoxone. It is formed in many other countries under different trade names. China is reported to be the world's major manufacturer of paraquat, and production is increasing. In 2005 China had 18 active ingredient producers and another 118 formulators – at that stage with a production capacity of 24,000 tonnes. By 2009 it was producing 108,000 tonnes/year and exporting 54,000 tonnes .Construction began on another plant in March 2010,which will increase China's paraquat capacity by another 21,000 tonnes/year. Paraquat was first synthesised in 1881. Its herbicidal properties were exposed in 1965 by ICI, and registered in England in 1961. However, it was introduced in Malaysian rubber plantations in 1962. It is now approved for use in about 110 countries, according to industry.

2.3 Regional and national bans

Paraquat is prohibited in 33 countries, including the 26 countries of the European Union. After a successful legal challenge launched by Sweden. The Court ruled that a 2002 Directive authorizing the use of paraquat within the European Union failed to assure the need of protection of human health, particularly involving topexposure. It also unsuccessful to assess

the risk of Parkinson's disease, and to properly assess risk to animals. Prior to this decision a number of EU countries had already banned in following countries for various reasons:

Country	Year	Reason for ban
Sweden	1982	Very acute toxicity, irreparable toxic effects and risk of accidents while handling and use.
Kuwait	1984	expelled for all uses, for health and environmental concern.
Finland	1985	highly toxic even in tiny doses, consequential lead to death.
Hungary	1990	Accidental poisoning; the mortality rate was inappropriately high.
Germany	1990	not a ban, but a severe constraint because of extreme persistence in soil (half-life of 16 years).
Austria	1992	Very acute toxicity, irretrievable effects (especially on lungs) and various fatal accidents.
Denmark	1994	Reside in soil; very toxic to non-target organisms and death had occurred in rabbits eating or walking on spraying grass.
Slovenia	1996	human and environmental toxicity; lethal toxic in small amounts with no antidote; worry about high rate of suicide in Slovenia.
Cambodia	2002	All uses banned from December 14, 2002; however there are reports of illegal use of paraquat smuggled in from Vietnam and Thailand.
Ivory Coast	2003	Prohibition of import, produce and use in agriculture.
Malaysia	2004	Acutely toxic with irreversible effects and no known antidote; high annual statistics of human poisoning. However in 2005 the ban was reversed, and restricted use permitted in oil palm plantations.

T: 2.1. Country & Reason for ban
(Source: *UNEP Data 1999*)

2.3.1 Restrictions

Paraquat is also severely restricted or restricted in at least 10 other countries.

Country	Year	Cause of restriction
Columbia	1988	expelled for aerial application.
Philippines	1988	Limited.
Indonesia	1989	Severely limited, use only for certain estate crops by professional applicators possessing special permit. May induce symptoms in affected humans too late to cure.
S Korea	1986	Severely limited because of high acute toxicity; must contain emetic, colourant and stenching agent.
USA	2000	Can only be sprayed under the administration of a certified applicator. Its use is banned in homes, schools, recreational parks, golf courses, and playgrounds. There is a necessity to wait 12 or 24 hours before re-entering any area where paraquat has been sprayed.
Belize	2002	Limited to ground application.
Chile	2002	Banned for aerial application.
Costa Rica	2004	limit on aerial application
Sri Lanka	2006	considering the extremely high rate of deaths due to paraquat poisoning

T: 2.2. Country and cause for restriction

(Source: *UNEP Data 1999*)

In 1990, paraquat was expelled in the Dominican Republic. However agrochemical companies effectively argued that the herbicide posed no serious health effects and was essential because of high labor costs. Its regulatory status was reduced to "restricted" and the herbicide is now broadly used all over the country *(Meriel Watts 2011).* In the US, they account for about 70% of all agricultural pesticide use. The global sales of Paraquat dichloride are expected to grow about 3.7 percent between 2015 and 2020 in North and South America, and Europe and Asia regions. The growths of Paraquat dichloride formulations are spurring the demand for Paraquat dichloride. Unite States, Japan, Germany and China supply more than 85 percent of Paraquat dichloride sold in the world. China has become the major manufacture base of chemical technical in the world in terms of ability and output and has been playing a more and more important role in the global chemistry industry. The reasons are strong demand within the country and cost advantages over Western industrial countries both in the manufacture of chemical products and for key customer industries building up manufacture capacities. Furthermore, construction costs are fairly low and licensin procedures are considerably shorter than in Europe. These favorable conditions are attracting more chemicals companies. So China Paraquat dichloride market has played an vital role in global Paraquat dichloride market. This research from ChemReport.Net provides a professional and in detail study on the current state of the China Paraquat dichloride industry, focusing on the capacity and production volumes, manufacturers, prices, import & export, marke forecast and consumers, including the historical data 2011 - 2013 and long-term forecasts through 2014 - 2019.*(Paraquat dichloride Global Market and Forecast Research 2015)*

2.4 National Scenario

Paraquat dichloride (24 % SL) is registered in India by the Central Insecticide Board and Registration Committee (CIBRC). This is the only formulation registered in India. CIBRC has categorized paraquat dichloride as extremely toxic. Although CIBRC has not provided any recommendations, it has accepted the use of this herbicide in 8 crops. Another formulation, paraquat dimethyl sulfate was banned in India in 1992 (CIBRC 2013). It is one amongst the 19 most commonly used and suggested pesticides in the country.

2.4.1 Consumption Of Paraquat Dichloride In India

The chart given below shows the consumption data of paraquat dichloride and total herbicide consumption in India for the period between 2007 – 08 and 2013 – 14 (as on December 17, 2014). The data reveals that the volume of paraquat consumed is much less when compared to the total herbicide consumption in the country. However, in spite of paraquat not being the herbicide used in the key quantities in contrast with other herbicides in India, its conditions of use are unsafe with many opportunities for severe exposure and risks to human health to farmers, agricultural workers, and others who handle paraquat, such as applicators and retailers.

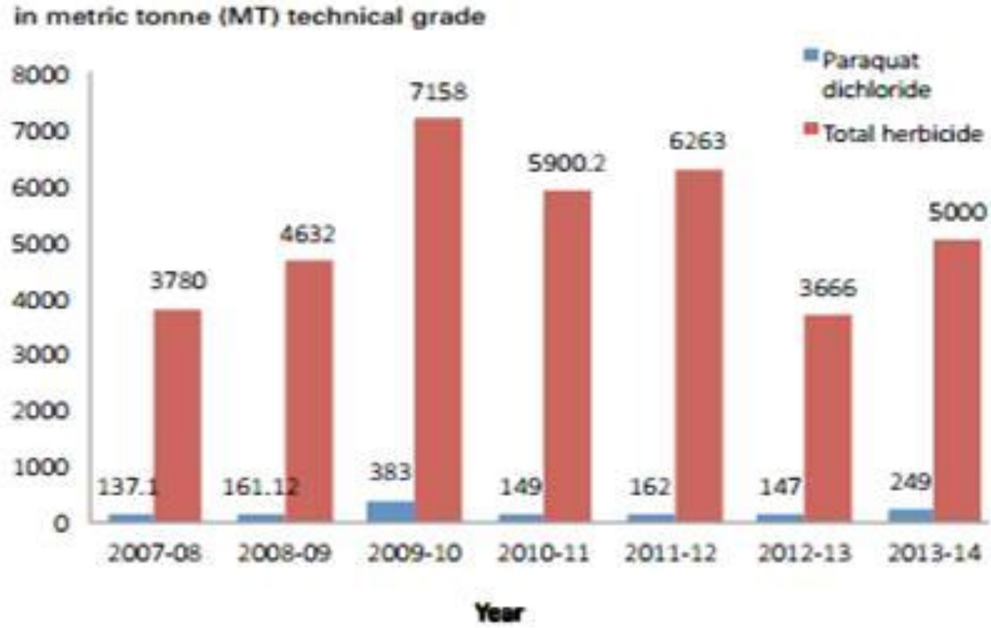
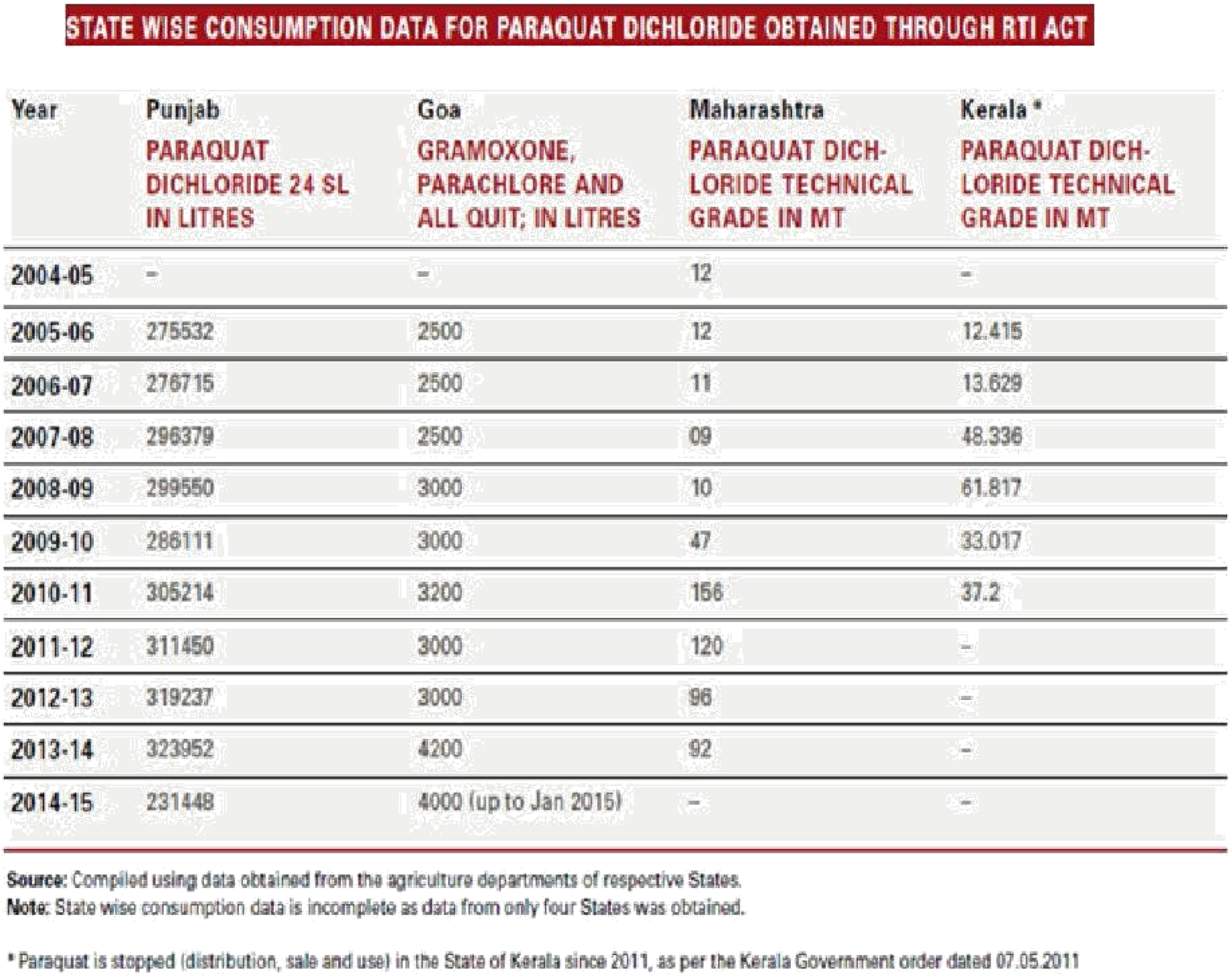


Fig: 2.2. Consumption of paraquat dichloride and total herbicide (source: *kumar, 2015*)

2.4.2 State Wise Consumption Of Paraquat Dichloride

The consumption data for paraquat dichloride was collected during the Right to Information (RTI) Act. Below are the responses acknowledged from 4 States. State wise consumption data of paraquat dichloride for the 4 States in India – Punjab, Goa, Maharashtra and Kerala – reveals that it continues to be used in fairly large volume in 3 of the States except Kerala, where paraquat was banned since 2011, mainly because of health reasons.



STATE WISE CONSUMPTION DATA FOR PARAQUAT DICHLORIDE OBTAINED THROUGH RTI ACT

Year	Punjab PARAQUAT DICHLORIDE 24 SL IN LITRES	Goa GRAMOXONE, PARACHLORE AND ALL QUIT; IN LITRES	Maharashtra PARAQUAT DICHLORIDE TECHNICAL GRADE IN MT	Kerala * PARAQUAT DICHLORIDE TECHNICAL GRADE IN MT
2004-05	–	–	12	–
2005-06	275532	2500	12	12.415
2006-07	276715	2500	11	13.629
2007-08	296379	2500	09	48.336
2008-09	299550	3000	10	61.817
2009-10	286111	3000	47	33.017
2010-11	305214	3200	156	37.2
2011-12	311450	3000	120	–
2012-13	319237	3000	96	–
2013-14	323952	4200	92	–
2014-15	231448	4000 (up to Jan 2015)	–	–

Source: Compiled using data obtained from the agriculture departments of respective States.
Note: State wise consumption data is incomplete as data from only four States was obtained.

* Paraquat is stopped (distribution, sale and use) in the State of Kerala since 2011, as per the Kerala Government order dated 07.05.2011

Fig: 2.3. State wise consumption in india

(Source: *kumar, 2015*)

2.5 Case Study In Punjab

Environmental changes: The advent of Green Revolution with its chief components of consolidation of land holdings, land reforms, high yielding seed varieties, irrigation, use of chemical fertilizers and pesticides, agricultural credit, rural electrification and farm mechanization heralded a new era in history of Indian agriculture(*Chopra, 1985*). Whereas the early raise in production was mostly due to raise in the area under cultivation but a spectacular rise of 17.36 million tons in food grain production from 1972 to 2006 could be largely credited to intensive use of inputs like fertilizers, pesticides, insecticides, herbicides, etc.(*Punjab State Council for Science and Technology, 2007*)The great scale use of pesticides to control pests resulted in the development of pesticides resistance in different pests and insects which in turn led to the resurgence of insect pests and turn down in population of the natural enemies of pests. In order to minimize the crop loss, farmers insistently adopted self-defeating practices such as growing either dosage or frequency of pesticides application, in spite of of its effects on environment, health and socioeconomic conditions of the community (*Shetty, 2004*).

However, the assumption of nature as a source of scarcity, and technology as a source of abundance lead to the creation of technologies which shaped new scarcities in nature through ecological destruction. The reduction in availability of fertile land and genetic diversity of crops as a result of the Green Revolution practices indicated that at the ecological level, the Green Revolution produced scarcity and not abundance (*Shiva, 1991*). Further, the damaged ecology of Punjab amplified the cost of agriculture by growing the expenditure on irrigation, fertilizers, land reclamation and pesticides. Apart from this, the depleting water table badly affected soil properties which further cause damage to Punjab’s ecology. There are studies which link environmental degradation with various diseases in Punjab. It is found the premature greying of hair in children as early as ten years old, ageing and predisposition to cancer in Jajjal village of Bathinda district of Punjab (*Thakur et al., 2008*) Study has found the prevalence of various pesticides above the permissible limits in tap water and vegetable samples in Talwandi Sabo area in Bathinda district of Punjab. The Age Adjusted Prevalence Rate of confirmed cancer cases was found to be 123 in the same region which is higher than the national average of 60(*Tirado, 2009*). It is found the nitrate levels as high as 611.6 mg/l in village Doda of district Muktsar as against the prescribed level of 51 mg/l for safe drinking by World Health Organization. The study linked the superior incidence of blue-baby syndrome and cancer to the upper levels of nitrate in the district(*Agnihotri, 2010*) linked the rising instances of abortion, early menarche, fetal abnormalities especially neural tube defects and early ageing to the higher pesticides levels in Punjab.(*Reetinder Kaur and A. K. Sinha, 2011*).

CHAPTER 3

DEGRADATION STUDY

3.1 Degradation of Pesticide

Degradation of pesticides means to break down the pesticides inside the environment. The degradation may occur during photo degradation, chemical degradation or biodegradation (*Topp E et al., 1997*). In some cases there is a complete mineralization of the pesticides whereas in other cases only a partial degradation takes place. This may potentially lead to an accumulation of metabolites, which sometimes are more toxic, i.e. more hazardous, than the mother-compound (*Giacomazzi S and Cochet N, 2004*). Sometimes the pesticides are not degraded even though they have proven to be biodegradable. This may, as mentioned above, be due to different environmental factors affecting the activity of the degrader organisms; essential nutrients may be missing, environmental conditions may be unsuitable, or the concentration of the pesticide may be too high or too low (*Jones WJ, and Ananyeva ND, 2001*). All chemicals are subject to photo degradation to some level. The degree of photo degradation will depend on the intensity of the sunlight and the exposure time. However numerous pesticides move quite rapidly into the soil and are thus no longer exposed to sunlight and therefore not susceptible to photo degradation (*Gavrilescu M, 2005*). Chemical degradation is due to reactions of the pollutant with e.g. oxygen, water or other chemicals. Biodegradation means the degradation of the pesticides by organisms; most often microorganisms similar to bacteria and fungi, but in some cases plants may be implicated in the degradation as well. The degradation rates are affected by soil properties, e.g. pH and temperature. Lower degradation rates have been observed with a pH above 6.5 and higher rates with pH below 5. However the effect of pH will depend on the compound being degraded and the organisms responsible for the degradation, and studies by Walker et al showed a more rapid degradation in soils with higher pH. The temperature of the soil also influences degradation rates; the rate of most reactions catalyzed by enzymes tends to double for every 10 ^{o}C increase in temperature [between 10 and 45 ^{o}C]. An increase in soil temperature will thus lead to an increase in degradation rate (*Walker et al., 2001*).

3.2 Suitability of AOPs as water treatment technology

In recent years, advanced oxidation processes (AOP's) have received increasing attention as they are successful in degradation of bio-resistant and toxic compounds without creating secondary pollution. These processes are based upon the production of OH* radicals, which are able to oxidize and mineralize almost every organic molecule, yielding CO_2 and inorganic ions. The hydroxyl radical is having an oxidation potential of 2.8 eV, the second strongest known oxidant after fluorine.

Defined by Glaze et al. (1987), AOP's are water treatment processes that work near ambient temperature and pressure; involve the generation of highly reactive radicals in sufficient quantity to effect oxidation/reduction of bio-recalcitrant compounds. For the degradation of non-biodegradable organic pollutants present in contaminated surface, ground, and wastewaters, these treatment processes are considered as very promising.

3.3 Photo degradation (by means of UV rays)

It means degradation of pesticide under UV rays with help of suitable catalyst. The mainly used catalyst is TiO_2 and is reported to be one amongst the top 20 inorganic chemicals of industrial Importance It is widely used as a pigment in paints, coatings, sunscreens, ointments, and toothpastes because of its brightness and a very high refractive index *(Jitlada chumee et al., 2010*). TiO_2 and may have capacity to decompose paraquat dichloride to several harmless compounds in the environment (*MOHD HASMIZAM RAZALI et al., 2013*). In the presence of UV light irradiation redox reactions and charges separation are promoted, leading to the formation of hydroxyl radicals (•OH) and superoxide ions ($\bullet O^{2-}$). These species are able to induce oxidation reactions promoting the degradation of organic compounds. The principle of heterogeneous photo catalysis is based on the activation of a semiconductor particulate material (CdS, TiO_2, ZnO, WO3 etc.) by the action of radiation with an suitable wavelength. With the absorption of photons by the semiconductor particle possessing enough energy to endorse the conduction of an electron (e−) from its valence band (VB) to the conduction band (CB) (a transition called band gap energy), activation is achieved and creating holes in the valence band (h+) that will act as oxidizing sites. The hydroxyl radical is used as a powerful oxidizing agent to convert organic pollutants into CO_2 and less toxic by-products(*Mota et al.*, *2008*).The best result obtained by using UV light over commercial TiO_2 to remove paraquat under operating conditions.(*Moctezuma et al. 1999; Florêncio et al. 2004*).

3.3.1 What is Photo catalyst?

Photo-Catalysis is known as "speeding up the presence of as catalyst". A catalyst does not modify in itself or being consumed in the chemical reaction. This definition includes photosensitization, a process by which a photochemical modification occurs in one molecular entity as a result of initial absorption of radiation by another molecular entity called the photosensitized. Chlorophyll of plants is a type of photo catalyst. Photo catalysis compared to photosynthesis, in which chlorophyll captures sunlight to turn water and CO_2 into oxygen and glucose, photo catalysis creates strong oxidation agent to breakdown any organic matter to CO_2 and H_2O in the presence of photo catalyst, light and water. Chlorophyll of plants is a type of photo catalyst. Photo catalysis compared to photosynthesis, in which chlorophyll captures sunlight to turn water and carbon dioxide into oxygen and glucose, photo catalysis creates strong oxidation agent to breakdown any organic matter to carbon dioxide and water in the presence of photo catalyst, light and water.

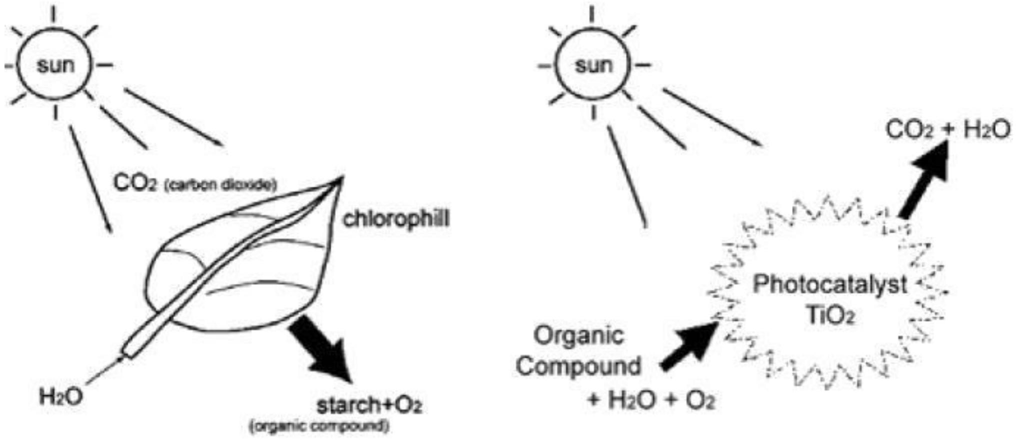


Fig: 3.1. Chlorophyll of plants

(Source: ***web link http://www.abolinco.com/downloads/downloads/What_is_Photocatalyst.pdf*****)**

3.3.2 Mechanism

When photo catalyst titanium dioxide (TiO_2) absorbs Ultraviolet (UV) radiation from sunlight or illuminated light source, it will create pairs of electrons and holes. The electron of the valence band of titanium dioxide becomes excited when illuminated by light. The excess energy of this excited electron promoted the electron to the conduction band of titanium dioxide therefore creating the negative-electron (e-) and positive-hole (h+) pair. This stage is referred as the semiconductor's ' **photo-excitation** ' state. The energy variation between the valence band and the conduction band is known as the ' **Band Gap** '. Wavelength of the light necessary for photo-excitation is: 1241 (Planck's constant, *h)* / 3.1 ev (band gap energy) = 389 nm

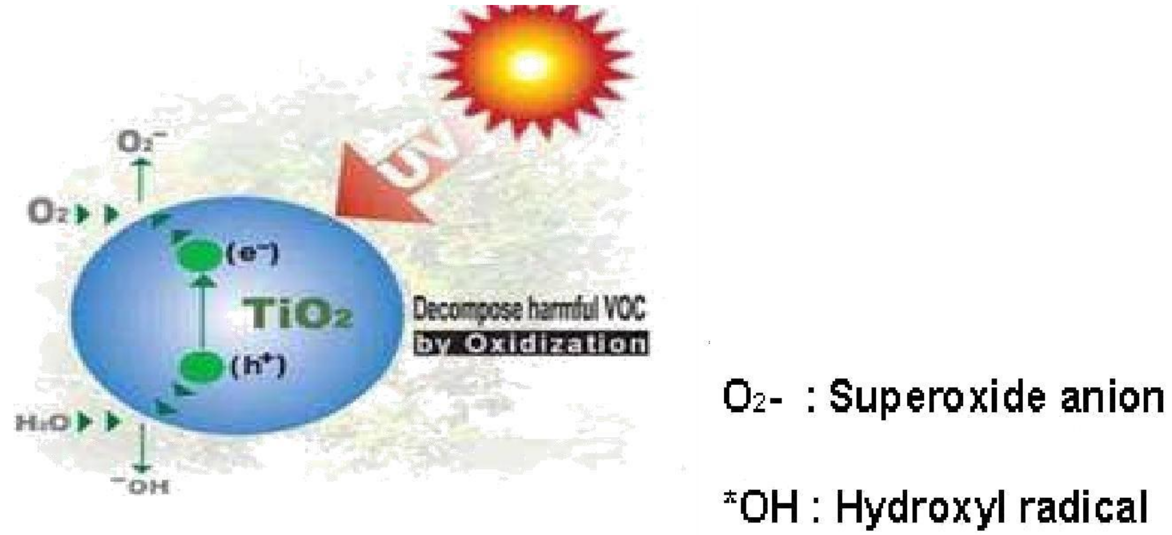


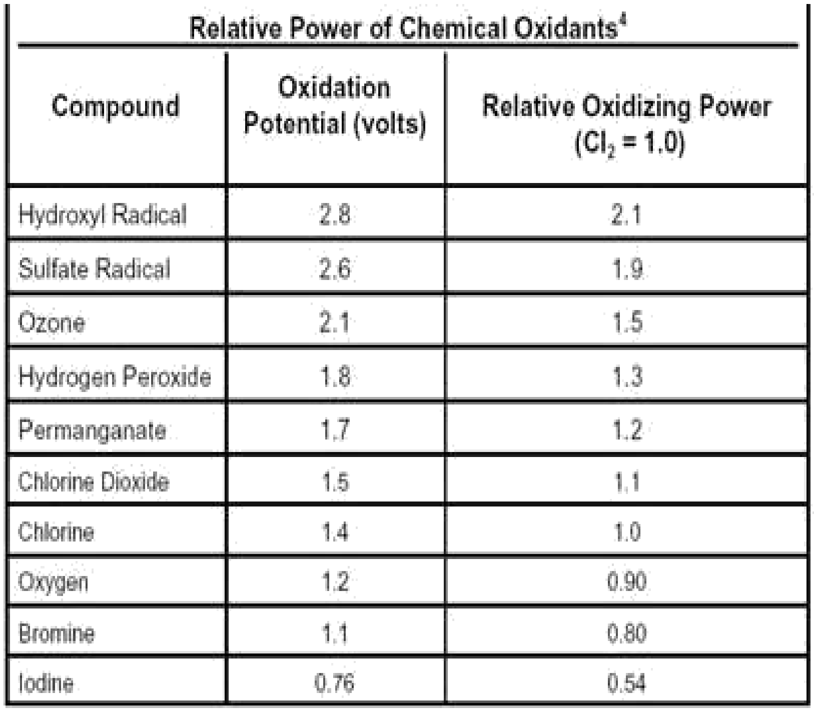
Fig: 3.2. Photo excitation State

(Source*: web link http://www.abolinco.com/downloads/downloads/What_is_Photocatalyst.pdf*)

The positive-hole of titanium dioxide breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available. The overall mechanism of Photocatalytic reaction of titanium dioxide.

3.3.3 Photocatalytic Oxidation

The most powerful advanced oxidation systems are based on the generation of hydroxyl radicals. The hydroxyl radical is an enormously powerful oxidation agent, second only to Fluorine in power (2.23 in Relative Oxidizing Power). Following is a listing of common chemical oxidants, placed in the order of their oxidizing strength:



Relative Power of Chemical Oxidants[4]

Compound	Oxidation Potential (volts)	Relative Oxidizing Power (Cl_2 = 1.0)
Hydroxyl Radical	2.8	2.1
Sulfate Radical	2.6	1.9
Ozone	2.1	1.5
Hydrogen Peroxide	1.8	1.3
Permanganate	1.7	1.2
Chlorine Dioxide	1.5	1.1
Chlorine	1.4	1.0
Oxygen	1.2	0.90
Bromine	1.1	0.80
Iodine	0.76	0.54

T: 3.1. Relative power of chemical oxidant

(Source: ***web link http://www.abolinco.com/downloads/downloads/What_is_Photocatalyst.pdf*****)**

Utilizing the strong oxidation strength of hydroxyl radical, Photocatalytic oxidation can Effectively disinfect, deodorize, and purify air, water, and different surface area.

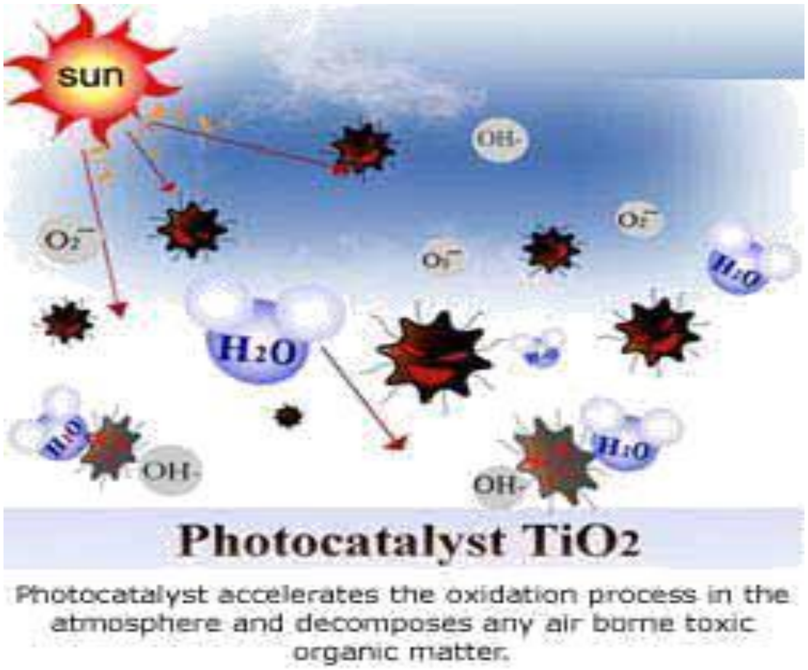


Fig: 3.3. Decomposition by TiO_2

(Source:***http://www.abolinco.com/downloads/downloads/What_is_Photocatalyst.pdf*****)**

3.3.4 Type of photo catalyst:-

3.3.5 Homogenous photo catalysis

In homogenous photo catalysis, the reaction takes place in similar or homogenous phases like liquid – liquid phases examples are dye with soluble metal catalyst. Discovered by H.J. Fenton in 1890’s (Fenton, 1894), it remains one of the most reliable AOP for its ability to degrade high loading of organic compounds. In homogenous photo catalysis, a powerful UV lamp is used to illuminate the contaminated water in the presence of Fe^{3+}, O3 or H_2O_2 which act as a catalyst and the reaction takes place in the bulk solution. The mechanism of the hydroxyl radical production by the ozone is as follows,

O3 + hν → O2 + O (1D) (2.2) O
(1D) + H2O → •OH + •OH (2.3)

O (1D) + H2O → H2O2 (2.4)
H2O2 + hν → •OH + •OH (2.5)

3.3.6 Heterogeneous photo catalysis

It can be defined as catalytic process during which one or more reaction steps occur by means of generation of electron-hole pair by suitable light on the surface of the solid semiconductor materials. Heterogeneous photo catalysis using semiconductor oxides are gaining more importance, has demonstrated to be very efficient to degrade pollutants either in gas or in liquid phase. Photocatalytic degradation of organic compounds is based on semiconductor photochemistry. The most effective and commonly photo catalyst for this purpose is titanium dioxide (TiO_2). TiO_2 is biologically and chemically inert material, commonly used as constituent of toothpastes, pharmaceuticals, and many cosmetics. Heterogeneous photo catalysis is a complex sequence of the reactions. Its mechanism composes of five steps , which are:

(i) Mass transfer of the organic contaminant in the liquid phase to the TiO_2 surface
(ii) Adsorption of the organic contaminant onto the photon activated TiO_2 surface
(iii) Photo catalysis reaction for the adsorbed phase on the TiO_2 surface
(iv) Desorption of the intermediate from the TiO_2 surface

(v) Mass transfer of the intermediate from the interface region to the bulk fluid. (Augugliaro et al., 2006).

3.3.7 Photocatalytic degradation pathways

It is well established that conduction band electrons (e−) and valence band holes (h+) are generated when aqueous TiO_2 suspension is irradiated with light energy greater than its band gap energy (e.g. 3.1 eV). The photo generated electrons could decrease the organic substrate or react with electron acceptors such as O_2 adsorbed on the Ti(III)-surface or dissolved in water, reducing it to superoxide radical anion O^{2-}. The photo generated holes can also oxidize either the organic molecule directly, or the OH^- ions and the H_2O molecules adsorbed at the TiO_2 surface, to OH• radicals. Together with other extremely oxidant species (peroxide radicals) they are reported to be responsible for the heterogeneous TiO_2 photodecomposition of organic substrates. According to this, the relevant reactions at the semiconductor surface causing the degradation of pesticides can be expressed as follow

$$TiO_2 + h\nu \rightarrow e^- + h^+ \tag{1}$$

$$(O_2)_{ads.} + e^- \rightarrow (O_2^{\bullet -})_{ads.} \tag{2}$$

$$Ti(IV) - OH + h^+ \rightarrow Ti(IV) - OH^\bullet \tag{3}$$

$$Ti(IV) - H_2O + h^+ \rightarrow Ti(IV) - OH^\bullet + H^+ \tag{4}$$

$$\text{compound} + h^+ \rightarrow \text{compound}_{\text{oxidized}} \tag{5}$$

(*Serpone et al., 1989; . Bahnemann et al., 1994*). The resulting OH• radical, being a extremely strong oxidizing agent (standard redox potential + 2.7V) can oxidize most of organic pesticides to the mineral end products. Substrates not reactive toward hydroxyl radicals are degraded employing TiO_2 photo catalysis with rates of decay highly subjective by the semiconductor valence band edge position(*Maurino et al., 1999*). This suggests that the exact mechanism is inclined by several factors and the organic substrates depending on their nature and on the experimental conditions can react throughout direct interaction with the carriers and/or with the trapped holes. Studies with pulse radiolysis experiments have examined the reaction of halo aromatics. The role of reductive pathways in heterogeneous photo catalysis has been envisage in the degradation of numerous compounds.(*Muneer and Bahnemann, 2002*).

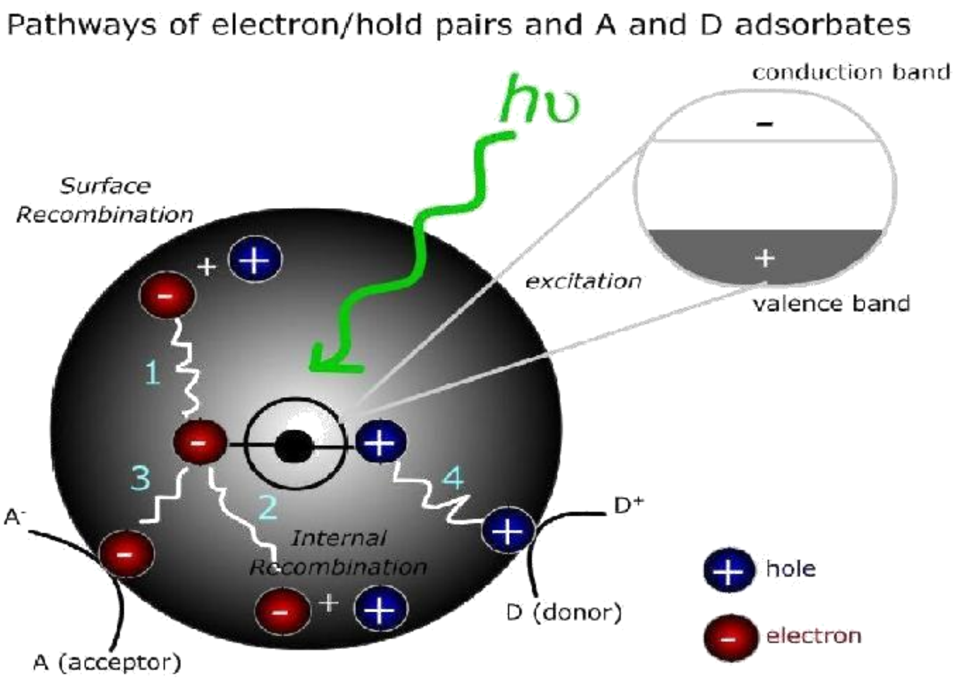


Fig: 3.4. Mechanism of Photocatalytic reaction in TiO_2

In particular, a great number of organic compounds dissolved or dispersed in water can be mineralized; the photo degradation is moderately high if large surface areas of the photo

catalyst are available; TiO_2 is economical and can be recycled on a technical scale; UV lamps emitting in the spectral region required to initiate the Photocatalytic oxidation are simply available in different sizes or shapes. Furthermore, surface modification of the photo catalyst to increase the UV light absorption efficiency as well as doping process of transition metal-ion to

Utilize the visible light like free sunlight instead of expensive UV light, have enhanced the commercial applications of photo catalyst to water purifications (*Legrini et al., 1993*). Although the efficiency of the photo-process due to a hole-electron recombination can slightly be reduced, the doping of TiO_2 with transition metal ions makes the amount of adsorbed visible light enhanced, and the doping effect of the metal ions increases with the low field of light intensity, the result of photo-oxidation parameters on the paraquat removal has been investigated in a photo reactor with suspended TiO_2 particles, where UV lamps were immersed at the regular spatial intervals to enhance the light availability and TiO_2 Particles were prepared by a hydrothermal method to enhance their photo activity (*Joon-Chul Lee et al., 2003*).

3.4 Degradation by Photo-Fenton process

Advanced oxidation processes (AOPs) due to their recognized efficiency in the treatment of recalcitrant organic matter, through the efficient generation of OH· radicals. From the variety of existing AOPs, particular attention has been given to photo-Fenton process and heterogeneous photo catalysis due to the possibility of use of solar radiation, reducing the energetic costs(*wang, 1994*). The photo-Fenton process has the advantage to be a homogeneous process, avoiding an additional step of removal of catalyst, usual when dealing with a heterogeneous process. Another advantage is the fact that homogeneous processes favor a greater contact between reagent species, with favorable implications for process performance (*Amiri, 1996*). the Photo-Fenton process can be applied as an alternative to the wastewater treatment containing this herbicide in large scale and using solar radiation, once that the toxicity decreased significantly with the paraquat concentration reduction and intermediates more oxidized were obtained. In addition, the use of solar radiation is completely advantageous, mainly in tropical countries (*Tomlim, 2000*).

Fenton’s reaction is a non-expensive and environmental friendly oxidation method, which appeared in 1894 when Fenton robustly improved tartaric acid oxidation by the use of ferrous ion and hydrogen peroxide. This process is widely used in wastewater treatment. Fenton’s reagent is a solution of hydrogen peroxide and ferrous ions and this process has a complex mechanism, which can even though be simplified by the following equations.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + HO^\bullet \qquad (2)$$

$$Organic\ matter + HO^\bullet \rightarrow Oxidation\ intermediates \qquad (3)$$

$$Oxidation\ intermediates + HO^\bullet \rightarrow CO_2 + H_2O \qquad (4)$$

$$H_2O_2 + HO^\bullet \rightarrow H_2O + HO_2^\bullet \qquad (5)$$

$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + HO^- \qquad (6)$$

$$HO^\bullet + HO^\bullet \rightarrow H_2O_2 \qquad (7)$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe^{III}(HO_2)^{2+} + H^+ \qquad (8)$$

$$Fe^{III}(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2^\bullet \qquad (9)$$

Briefly, the reaction between iron and hydrogen peroxide produces hydroxyl radicals with high oxidative power (Eq. (2), which attack the organic matter present in the water (Eq. (3)).

Unfortunately, some equivalent reactions occur (Eqs. (5)–(7)), and so the hydroxyl radicals are not only consumed to degrade the organic matter but also to produce other radicals, with less oxidative power, or other species (scavenging effect of HO•). Besides, this leads to the undesired consumption of hydrogen peroxide (Eq. (5)). On the other hand, Eqs. (8) and (9) indicate a generation of Fe^{2+} by the reaction between H_2O_2 and Fe^{3+} (Fenton-like process); this way ferrous ion is restored, acting as catalyst in the overall process (*Santos et al., 2011*).

3.5 Degradation by Electrochemical process.

In electrochemical processes, hydroxyl radicals can create by two means: anodic oxidation (AO) (direct form) and mediated electro oxidation (indirect form). In anodic oxidation, the hydroxyl radical is generate in the anode (Pt, PbO_2, doped with SnO_2 etc.) of an electrochemical cell from water oxidation (Eq. (10)). In mediated electro-oxidation, chemical species, such as H_2O_2, are continuously generate in the cathode by the reduction of two electrons of dissolved oxygen (Eq. (11)) (*Mota et al., 2008; Brillas et al., 2002*)

$$H_2O \rightarrow HO^{\bullet} + H^+ + e^- \qquad (10)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (11)$$

The generated H_2O_2 can act as a reagent for Fenton's system, with the adding of iron, leading to the arrangement of hydroxyl radicals (Eq. (2)) (electro-Fenton (EF) process). If the Fe^{3+} obtains with Fenton's reaction (Eq. (2)) or add to the solution, can be constantly reduce to Fe^{2+}, creating an electrochemical catalysis process (Eq. (12)) (*Mota et al., 2008; Oturan and Brillas, 2007*).

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (12)$$

With the opening of UV to help reduce Fe^{3+} to Fe^{2+}, the oxidation power of the system can also be increased (photoelectron-Fenton (PEF) process) (*Mota et al., 2008; Wang, 2008*). Fenton's electrochemical course can also be used by means of an electrochemical cell with Fe electrodes (cathode and anode), in which the anode has the function of transferring Fe to the solution and the cathode functions as an inert electrode for water decline, as shown in Eqs. 13-14. The Fe2+ transferred by the cathode acts in the Fenton's reaction (Eq. (2)), with the addition of hydrogen peroxide to the system (*Mota et al., 2008; Saltmiras and Lemley, 2002*).

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (13)$$

$$2H_2O + 2e^{-} \rightarrow H_2(g) + 2OH^{-} \qquad (14)$$

Degradation of paraquat by electrochemical methods have tested and compared 4 different advanced oxidation methods in the degradation of paraquat: anodic oxidation, electro-Fenton, photoelectro-Fenton and classic Fenton. The photoelectro-Fenton has been the most efficient treatment method (*Santos et al., 2011; Dhaouadi and Adhoum, 2009*).

3.6 Biodegradation of paraquat dichloride in soil by microorganism

Degradation of pesticides is the isolating of dangerous chemical compounds into dependable mixes and, from time to time, over into their unique components. The corruption or breakdown of pesticides can appear in flora, creatures, and in the dust and water; or it may arise upon presentation to extremely-violet radiation. There are some totally substance responses which occur in soil that manual in corruption, notwithstanding, the most extensively recognized type of debasement there occurs through the motion of microorganisms, particularly the parasites and bacteria(*Burns, 1970*). Paraquat is a divalent cation that is adsorbed emphatically to soil debris with terrible rate, especially to dust minerals (*Khan, 1973*). The adsorption of paraquat by earth colloids renders the herbicide occupied for microbial by-product attack. Paraquat likewise is through all bills stable to substance debasement in soil along these strains, it's been regarded as that paraquat remains unaltered in soil inconclusively (*Hance, 1980*). Its dwelling association time in soils can shift from 1 to 6 years depending upon the focal point, soil attributes, temperature and precipitation (*Cheah, 1998*). there may be nothing puzzling about microbial corruption of insecticides. Microorganisms basically supply a medium and a power hotspot for alternatively primary concoction responses to appear. They, therefore, get sustenance, crucial additives, or power to bear on their existence capacities. The dust fumigant, the herbicide dalapon, is illustrations of pesticides which might be debased by microorganisms. The corruption of CH is a simple technique consisting of the freedom of methane gasoline deserting the bromine to will undoubtedly soil particles or to turn out to be part of some new compound. A 2d instance, dalapon, is a more convoluted compound, but it's detoxification still consists of simple artificial responses. Dalapon can be detoxified via the evacuation of the chlorine atoms to leave pyruvate or pyruvic corrosive. Pyruvate may be aminated into amino corrosive, which thusly can be modified over into protein, it can be decarboxylated and be used inside the development of lipids. It could enter the Kreb Cycle and emerge as a piece of this energy growing cycle. Any other possibility is the completed debasement of dalapon into CO2 and CH4, gasses which show up usually in nature. The third response includes a fungicide chloroneb, that is less understood, but it's the main pesticide for which both debasement and resynthesis via microorganisms has been regarded. It ought to be introduced up that chloroneb is basically like greater widely recognized pesticides; the herbicide dicamba and the worm spray methoxychlor. Chloroneb is separated with the aid of microorganisms to two, five-dichloro-four-methoxyphenol . One-of-a-kind microorganisms, together with a number of the same ones accountable for degradation, are capable of resynthesize chloroneb by remethylating it. 20% of it is modified over again to chloroneb. It illustrates that corruption can be a straightforward artificial reaction and that the opposite procedure can likewise occur. insecticides which might be promptly depredated in nature are called non-persevering in correlation with the ones which aren't right away depredated, that are known as consistent. it's far those two popular classifications to which i might now want to coordinate my comments. the subsequent is a rundown of diligent and non-persist he factor of interest of determined insecticides is their lengthy haul adequacy in infection manipulate. it may be season-considering a long time in the past weed manipulate with simonize, weeks of disorder control with mercury fungicide, or seasons of creepy crawly manage with chlordane. however, the industrious insecticides have an plain downside; they taint nature for drawn out stretches of time. There are likewise specific drawbacks to steady pesticides. Imperviousness to persevering Trojan horse sprays has passed off significantly extra regularly than to no persistent Trojan horse sprays. The housefly's imperviousness to DDT and the Japanese creepy crawly grub's imperviousness to chlordane are cases. Tenacious herbicides have created troubles where overdoses had been connected seeing that quick prompt re foundation of appealing species is unrealistic; or wherein delicate non-bug species had been delivered into a range once handled with a constant herbicide. Where in non-consistent herbicides were utilized, replanting or edit revolution after an overdose is not a tough problem. Persevering fungicides appear to have the slightest authentic signs and symptoms, from a purposeful attitude, of any of the diligent pesticides(*Vargas, 2013*).

CHAPTER 4

METHODOLGY

4.1 Specification of chemicals

Paraquat Dichloride	42% technical grade
TiO_2	P25 Degussa
$FeSO_4$	Ferrous sulphate AR grade
H_2O_2	30% by weight/volume

4.2 Procedure

4.2.1 Preparation of stock Stock solution

From 42% technical grade (420000ppm) pesticide paraquat dichloride 500ppm is prepared by dissolving 0.595 liter of paraquat in 500ml distilled water.

4.2.2 Degradation study

Different concentration 10 15 20 30 40 and 50 was prepared including control of solution with 250ml distilled water is prepared with addition TiO_2 initial taken 0.2 gm for trial and was kept in UV chamber. Before experiment start UV tube was turned on and allowed to warm up for 2 min.

4.2.3 Photocatalytic degradation of paraquat dichloride by TiO_2

Photocatalytic degradation of Paraquat dichloride was carried in a Photo reactor chamber (136×40×73 cm^3). It has equipped with six UV light lamps with 20 watt intensity giving overall intensity in chamber as 28watt/m^2. The supported photo catalyst (TiO_2) was dipped into the paraquat solution in a bowl having diameter approx 17cm. The sample was kept at height of 30cm from UV tube on magnetic stirrer then illuminated for five hours and 5 mL of sample was taken out every hour. The collected sample was then sent to UV/ Vis to obtain the percentage of degradation by the declining of absorbance of paraquat peaks at 258 nm. Degradation rate is calculated by formula:

$$\text{Percent of Degradation} = \frac{(A_0 - A_t)}{A_t} \times 100$$

Where

A_0 = initial absorption

A_t = absorption at t minute.

4.2.4 Effect of pH on degradation

pH study was performed with 10ppm of paraquat by using pH 3, 4, 5, 7, 9 for 5 hr reaction time. 2nd set is performed with pH 7 for 420 min. reaction time at different concentration 10, 20, 30, 40ppm. After second the 3rd set run with 20ppm concentration by using pH 3, 5, 7, 9, 10, 11, for 420 min. reaction time.

4.2.5 Effect of different concentration of catalyst (TiO_2)

The concentration dose 0.2, 0.4 and 0.6 gm was utilized for degradation study in 250ml solution with 20ppm concentration and pH 11 from 420 min. reaction time.

4.2.6 Comparison of UV light and sunlight

The same reaction was done in UV light as well as sunlight for 420 min.

4.2.7 Effect of aeration

Further the reaction was kept in both sunlight and chamber with aeration and after 420 min. the degradation recorded. In all experiment aeration was provided.

4.2.8 Effect of volume

The effect was noticed with 50, 100, 150 and 250ml volume with 20ppm concentration and pH 11 for 420 min.

4.2.9 Effect of distance

For effect of distance reaction is kept with varying distance as 10cm, 20 cm and 30cm from UV tube to the base of bowl for 360 min.

4.3 Reaction by Photo Fenton

4.3.1 Degradation study

Different concentration 10, 15, 20, 30, 40 and 50 was prepared including control of solution with 500ml distilled water and addition of Fe^{2+} initial by 7.5mg and H_2O_2 as 0.1ml for trial and was kept in UV chamber. Before experiment start UV tube was turned on and allowed to warm up for 2-3 min.

4.3.2 Effect of pH on degradation

pH study was performed with 10ppm of paraquat by using pH 1, 2, 3, 4. The experiment was carried out with proper aeration and agitation, reaction kept for 300 min. Further the reaction was carried out with pH 3 by taking different concentration of pesticide as10, 20, 30, 40 and 50 ppm of pesticide for 300 min. reaction time.

4.3.3 Effect of variation of Fe^{2+} concentration

With 20ppm pesticide and pH 3 different concentration of Fe^{2+} (2, 3.75, 5.5, 7.5, and 10.5mg) was added in 500ml solution for 300 min. reaction time.

4.3.4 Effect of variation of H_2O_2 concentration

Concentration of H_2O_2 0.025, 0.05, 0.1, 0.2, 0.3, 0.4ml for 500ml solution was utilized for degradation study for 300 min. reaction time.

4.3.5 Comparison of UV light and sunlight

The same reaction was done in UV light as well as sunlight for 300 min. as with catalyst TiO_2.

4.3.6 Effect of different volume

The reaction carried at different volume of 300, 500, 700 ml with optimum value of concentration 20ppm, Fe^{2+} 5.5mg, H_2O_2 0.1ml and pH 3 for 300 min. reaction time.

4.3.7 Effect of distance

For effect of distance reaction is kept with varying distance as 10 cm, 20 cm and 30cm from UV tube to the base of bowl for 240 min. reaction time.

4.3.8 Degradation study of wastewater with TiO_2 and photo Fenton

The waste water collected from Thapar university treatment plant (inlet). Instead of distilled water and all the optimum condition were remain same as concentration 20ppm, pH 11, TiO_2 dosage 0.4gm and volume 250ml with proper agitation and aeration for 6 hr reaction time. The same experiment was carried out for 6 hr time with photo Fenton considering all optimum value as concentration 20ppm, Fe^{2+} 5.5mg, H_2O_2 0.1ml, volume 500ml and pH 3.

4.4 Equipment and Instrument used:

4.4.1) pH meter - The pH of the solution was adjusted with the help of 1N HCL and 1N NaOH.

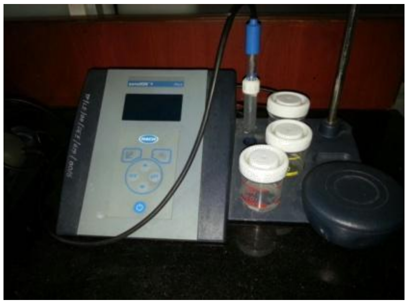


Fig: 4.1. pH meter

4.4.2) Filtration – Sample after Photocatalytic treatments were filtered through injection filters (pore size 0.22µm).

Fig: 4.2. Syringe filter

4.4.3) Reactors- The Photocatalytic chamber is rectangular in shape and made up of wooden material. It is equipped with UV lamps attached to the roof having wavelength of 365 nm fitted in parallel on the top of the chamber. Small holes are given on the side wall of the chamber to maintain a constant temperature and for proper circulation of air. The magnetic stirrer is placed on a lab jack so that required intensity could be attained by adjusting the distance from the UV tubes. The UV intensity in the reactor is corresponding to the average intensity of UV radiation in sunlight. Temperature inside the reactor is maintained by exhaust fan.

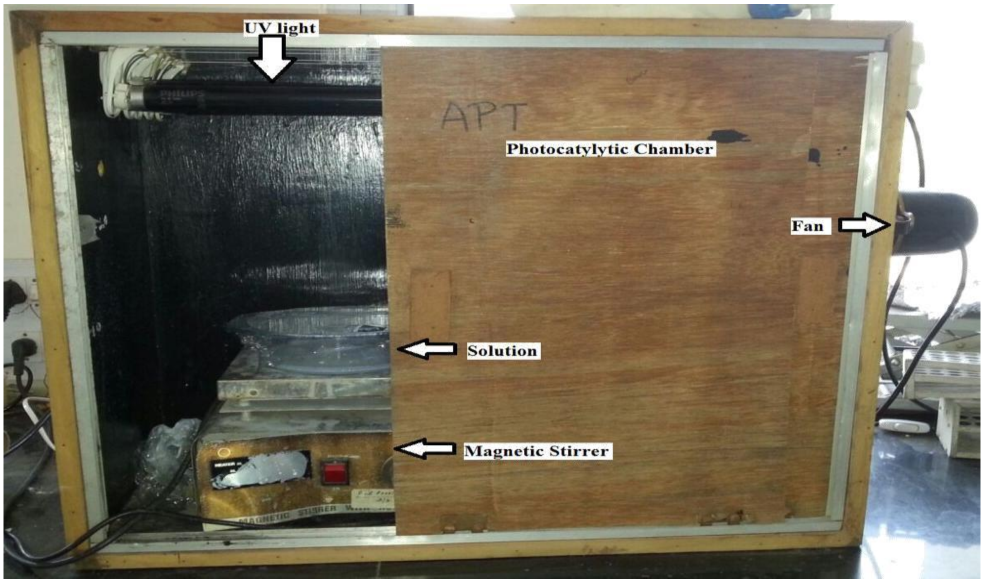


Fig: 4.3. UV Chamber

4.4.4) UV-Visible Spectrophotometer- The UV-Visible spectrophotometer was used for the wavelength scan of the pesticide sample and to measure the residual concentration of pesticide after degradation.

Fig: 4.4. Spectrophotometer

4.5 Standard calibration curve of paraquat dichloride

The absorbance of paraquat solution was studied between the wavelength of 200 to 800 nm and maximum absorbance (ƛmax) was obtained at 258 nm. Standard concentrations of paraquat were made from5 mgL-1 to 25 mgL-1 and their absorbance at 258 nm was measured. An absorbance was plotted against standard concentration of paraquat solution to get the calibration curve (figure 4.5). Regression coefficient was found to be 0.9992 and slope was 0.0374. From this calibration curve the unknown concentration of parqauat solution can be calculated.

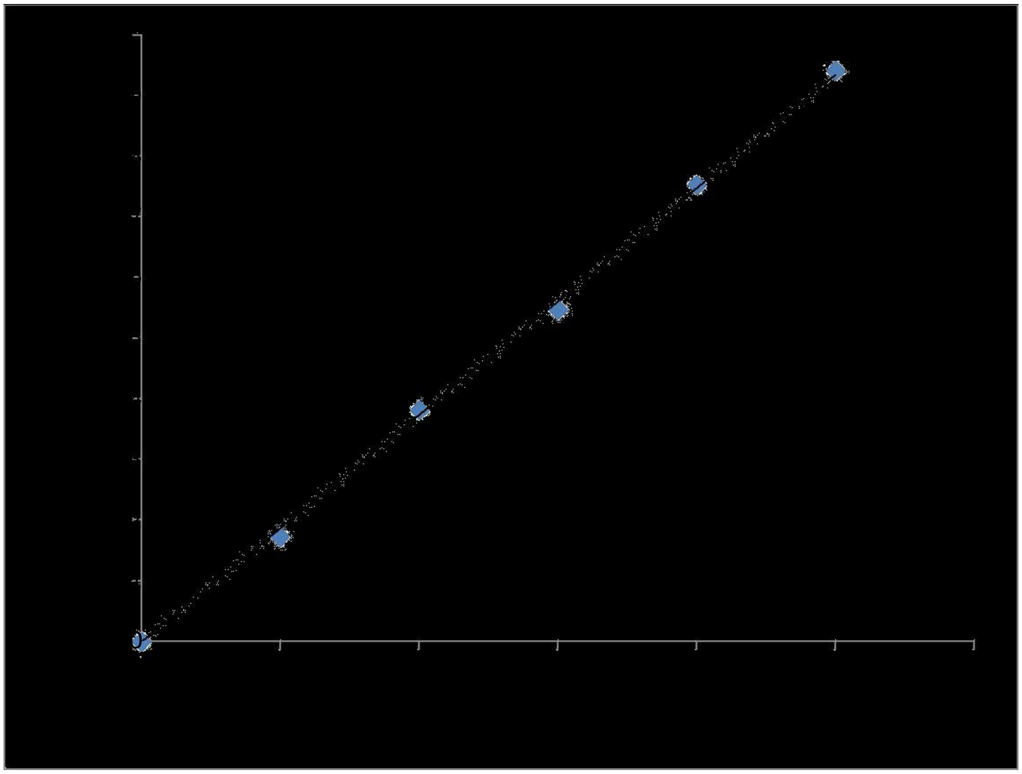


Fig: 4.5. **Calibration Curve of Paraquat In Water.**

4.6 Absorption spectra of raw pesticide sample

UV-visible spectra of 5 ppm solution technical grade paraquat dichloride pesticide showed sharp long peak at wavelength 258 nm. Which indicate that the pesticide is highly toxic and needs the effective degradation for the complete mineralization of the toxic compound to minimize the toxic effect.

4.7 TiO_2 Observation

Table: 4.1. Degradation of Paraquat at different concentration

	Absorbance			
Time(min.)	**10ppm**	**15ppm**	**20ppm**	**25ppm**
0	1.328 (0)*	1.577 (0)	1.929 (0)	2.235 (0)
60	0.963 (27)	1.228 (22)	1.558 (19)	1.927 (13)
120	0.719 (36)	1.081 (31)	1.375 (28)	1.874 (16)
180	0.622 (43)	0.962 (38)	1.309 (31)	1.756 (21)
240	0.551 (54)	0.779 (50)	1.016 (47)	1.421 (36)

(0)* represent percentage degradation of paraquat

(Degradation of Paraquat at different concentration with TiO_2 0.2gm in 250ml solution for 240 min. reaction)

Table: 4.2. Degradation of paraquat at concentration 10ppm

	Absorbance				
Time(min.)	**pH=3**	**pH=4**	**pH=5**	**pH=7**	**pH=9**
0	1.325 (0)	1.324 (0)	1.327 (0)	1.328 (0)	1.321 (0)
60	1.204 (9)	1.129 (14)	1.054 (20)	0.963 (27)	0.983 (25)
120	1.102(16)	1.004 (22)	0.939 (29)	0.849 (36)	0.905 (31)
180	0.971 (26)	0.921 (30)	0.832 (37)	0.752 (43)	0.798 (39)
240	0.892 (32)	0.805 (39)	0.747 (43)	0.581 (54)	0.695 (47)
300	0.834 (37)	0.752 (43)	0.587 (55)	0.524 (60)	0.563 (57)

(Degradation of paraquat 10ppm with different pH)

Table: 4.3. Degradation of Paraquat at different concentration with pH

	Absorbance			
Time(min.)	**10ppm**	**20ppm**	**30ppm**	**40ppm**
0	1.328 (0)	1.469 (0)	4.226 (0)	2.344 (0)
60	0.963 (27)	1.028 (30)	3.541 (16)	2.124 (9)
120	0.719 (36)	0.771 (47)	3.002 (29)	1.984 (15)
180	0.622 (43)	0.676 (54)	2.741 (35)	1.798 (23)
240	0.551 (54)	0.554 (60)	2.611 (38)	1.597 (31)
300	0.474 (60)	0.458 (65)	2.412 (43)	1.471 (37)
360	0.408 (64)	0.397 (72)	2.281 (46)	1.328 (43)
420	0.381 (68)	0.318 (78)	2.064 (51)	1.245 (47)

(Degradation of Paraquat at different concentration with pH 7, TiO_2 0.2gm for 420 min. reaction)

Table: 4.4. Degradation of paraquat at concentration 20ppm

	Absorbance					
Time(min.)	**pH=3**	**pH=5**	**pH=7**	**pH=9**	**pH=10**	**pH=11**
0	1.448 (0)	1.458 (0)	1.469 (0)	1.453 (0)	1.467 (0)	1.449 (0)
60	1.421 (1.7)	1.446 (5)	1.028 (30)	0.982 (32)	1.522 (35)	1.219 (12)
120	1.386 (4.0)	1.421 (8)	0.771 (47)	0.821 (47)	1.193 (49)	1.114 (23)
180	1.332 (8.0)	1.331 (14)	0.676 (54)	0.531 (59)	0.982 (63)	0.798 (45)
240	1.316 (9.0)	1.214 (22)	0.554 (60)	0.437 (65)	0.815 (69)	0.551 (62)
300	1.279 (11)	1.022 (34)	0.458 (65)	0.349 (71)	0.784 (74)	0.321 (77)
360	1.265 (12)	0.961 (38)	0.397 (72)	0.297 (75)	0.651 (78)	0.171 (88)
420	1.253 (13)	0.793 (49)	0.318 (78)	0.255 (81)	0.497 (84)	0.079 (94)

(Degradation of paraquat at concentration 20ppm with TiO_2 0.2gm at different pH for 420 min. reaction)

Table: 4.5. Degradation of pesticide with different TiO_2 dosage

	Absorbance		
Time(min.)	**0.2gm**	**0.4gm**	**0.6gm**
0	1.449 (0)	1.421 (0)	1.426 (0)
60	1.219 (12)	1.161 (18)	1.199 (15)
120	1.114 (23)	0.913 (35)	1.021 (28)
180	0.798 (45)	0.708(49)	0.579 (59)
240	0.551 (62)	0.348(75)	0.448 (68)
300	0.321 (77)	0.181(87)	0.241 (81)
360	0.171 (88)	0.074 (92)	0.104 (90)
420	0.079 (94)	0.026 (98)	0.045 (96)

(Degradation of paraquat at concentration 20ppm with different TiO_2 dosage at pH 11 for 420 min. reaction)

Table: 4.6. Degradation of paraquat in Sunlight & UV Chamber.

	Absorbance			
Time(min.)	**Sunlight**	**UV chamber**	**UV with aeration**	**Sunlight with aeration**
0	1.434 (0)	1.449 (0)	1.449 (0)	1.483 (0)
60	1.256 (12)	1.219 (15)	1.219 (15)	1.016 (31)
120	1.105 (23)	1.114 (23)	1.114 (23)	0.481 (67)
180	0.689 (51)	0.798 (46)	0.798 (45)	0.307 (79)
240	0.364 (74)	0.551 (61)	0.551 (62)	0.221 (85)
300	0.203 (85)	0.321 (77)	0.321 (77)	0.153 (89)
360	0.121 (91)	0.201 (86)	0.171 (88)	0.091 (93)
420	0.073 (95)	0.141 (90)	0.141 (95)	0.025 (98)

(Degradation of paraquat at concentration 20ppm with TiO_2 dosage 0.4gm at pH 11 for 420 min. reaction in Sunlight, UV Chamber and without aeration)

Table: 4.7. Degradation of paraquat with different area to volume ratio.

	Absorbance			
Time(min.)	**4.53***	**2.26**	**1.51**	**0.9**
0	1.434 (0)	1.445 (0)	1.424 (0)	1.449 (0)
60	0.834 (41)	1.077 (25)	1.081 (24)	1.219 (15)
120	0.324 (77)	0.631 (56)	0.732 (48)	1.114 (23)
180	0.091 (94)	0.202 (86)	0.534 (62)	0.798 (45)
240		0.108 (92)	0.355 (75)	0.551 (62)
300			0.324 (77)	0.321 (77)
360			0.309 (78)	0.171 (88)
420			0.278 (80)	0.141 (95)

*** Area to volume ratio (Dia. of bowl approx 17cm and volume varies as 50, 100, 150 & 250 ml. (Degradation of paraquat at concentration 20ppm, pH 11, TiO_2 dosage 0.4gm with different volume with aeration for 420 min. reaction time)**

Table: 4.8. Degradation of paraquat with different distance from UV tube

	Absorbance		
Time(min.)	**10cm**	**20cm**	**30cm**
0	1.445 (0)	1.451 (0)	1.449 (0)
60	1.112 (23)	1.218 (16)	1.219 (15)
120	0.437 (69)	0.708 (51)	1.114 (23)
180	0.164 (88)	0.287 (80)	0.798 (45)
240	0.073 (94)	0.199 (86)	0.551 (62)
360	0.034 (97)	0.141 (90)	0.181 (87)

(Degradation of paraquat 20ppm with TiO_2 0.4 gm at pH 11 with different distance from UV tube with aeration for 360 min. reaction)

4.8 Fenton Observation

Table: 4.9. Degradation of paraquat at concentration 10ppm

	Absorbance			
Time(min.)	**pH=1**	**pH=2**	**pH=3**	**pH=4**
0	1.226 (0)	1.224 (0)	1.226 (0)	1.227 (0)
60	1.131 (7)	1.003 (18)	0.645 (47)	1.117 (8)
120	1.108 (10)	0.836 (31)	0.439 (64)	1.073 (12)
180	0.957 (21)	0.717 (41)	0.274 (77)	0.976 (20)
240	0.817 (33)	0.608 (50)	0.241 (80)	0.834 (32)
360	0.729 (40)	0.518 (57)	0.188 (84)	0.798 (34)

(Degradation of paraquat at concentration 10ppm with different pH having H_2O_2 0.1ml, Fe^{2+} 7.5mg, volume 500ml for 360 min. reaction)

Table: 4.10. Degradation of paraqaut at different concentration with pH 3

	Absorbance				
Time (min.)	**10ppm**	**20ppm**	**30ppm**	**40ppm**	**50ppm**
0	1.226 (0)	2.223 (0)	2.846 (0)	3.096 (0)	3.334 (0)
60	0.645 (47)	1.048 (52)	1.985 (30)	2.299 (25)	3.055 (8)
120	0.489 (60)	0.739 (66)	1.469 (48)	1.651 (46)	2.265 (20)
180	0.364 (70)	0.476 (78)	1.231 (56)	1.541 (50)	2.205 (34)
240	0.251 (79)	0.356 (84)	0.981 (65)	1.404 (54)	2.003 (40)

(Degradation of pesticide at different concentration with pH 3 having H_2O_2 0.1ml, Fe^{2+} 7.5mg, volume 500ml for 300 min. reaction)

Table: 4.11. Degradation of paraquat at concentration 20ppm at pH 3

	Conentration (%)				
Time (min.)	**2mg**	**3.75mg**	**5.5mg**	**7.5mg**	**10.5mg**
0	2.387 (0)	2.389 (0)	2.215 (0)	2.223 (0)	2.243 (0)
60	1.819 (23)	1.321 (44)	1.102 (50)	1.148 (48)	1.371 (38)
120	1.664 (30)	1.226 (49)	0.932 (57)	1.029 (53)	1.164 (48)
180	1.391 (41)	0.987 (58)	0.681 (68)	0.876 (60)	0.998 (55)
240	1.092 (54)	0.841 (64)	0.476 (78)	0.596 (73)	0.754 (66)
300	0.946 (60)	0.701 (70)	0.234 (89)	0.331 (85)	0.538 (76)

(Degradation of paraquat at concentration 20ppm at pH 3 with different Fe^{2+} dosage having H_2O_2 0.1ml for 300 min. reaction)

Table: 4.12. Degradation of paraquat with different H_2O_2 concentration

Time(min.)	**0.025ml**	**0.05ml**	**0.1ml**	**0.3ml**	**0.4ml**
0	2.224 (0)	2.366 (0)	2.215 (0)	2.186 (0)	2.144 (0)
60	1.669 (24)	1.416 (40)	1.102 (50)	1.282 (41)	1.348 (37)
120	1.275 (42)	1.208 (48)	0.932 (57)	1.003 (54)	1.091 (49)
180	0.971 (56)	0.968 (59)	0.681 (68)	0.871 (60)	0.992 (53)
240	0.801(63)	0.728 (69)	0.543(75)	0.623 (71)	0.801 (62)
300	0.519 (76)	0.168 (84)	0.234 (89)	0.406 (81)	0.501 (76)

(Degradation of paraquat at concentration 20ppm with different H_2O_2 concentration having Fe^{2+} 5.5mg for 300 min. reaction)

Table: 4.13. Degradation of paraquat with at different area to volume ratio

	Absorbance		
Time(min.)	**0.75***	**0.45**	**0.32**
0	2.245 (0)	2.215 (0)	2.024 (0)
60	1.519 (32)	1.102 (50)	1.622 (19)
120	1.274 (43)	0.932 (57)	1.401 (30)
180	1.048 (53)	0.681 (68)	1.182 (41)
240	0.859 (61)	0.543(75)	0.881 (56)
300	0.473 (78)	0.234 (89)	0.508 (74)

*** Area to volume ratio (Dia. of bowl approx 17cm and volume varies as 300, 500 & 700 ml). (Degradation of paraquat at concentration at 20ppm with at different volume ratio at pH 3, Fe^{2+} dosage 5.5mg and H_2O_2 0.1ml for 300 min. reaction)**

Table: 4.14. Degradation of paraquat with different distance from UV tube

	Absorbance		
Time (min.)	**10cm**	**20cm**	**30cm**
0	2.217 (0)	2.213 (0)	2.215 (0)
60	1.261 (43)	1.316 (40)	1.102 (50)
120	1.012 (54)	1.073 (51)	0.932 (57)
180	0.831 (62)	0.941 (57)	0.681 (68)
240	0.308 (86)	0.393 (82)	0.476 (78)

(Degradation of paraquat 20ppm with H_2O_2 0.1ml, Fe^{2+} 5.5mg, at pH 3 with different distance from UV tube to base of bowl for 240 min. reaction)

Table: 4.15. Degradation of paraquat in sunlight.

Time (min.)	Concentration (%)
0	2.216 (0)
60	1.009 (54)
120	0.805(63)
180	0.608(72)
240	0.468(79)
300	0.394(82)

(Degradation of paraquat at concentration at 20ppm with 500 volume at pH 3, Fe^{2+} dosage 5.5mg and H_2O_2 0.1ml for 300 min. reaction in sunlight)

Table: 4.16. Degradation of paraquat in waste water with TiO_2 and Fenton

	Absorbance	
Time (min.)	TiO_2	Fenton
0	0.723 (0)	0.882 (0)
60	0.591 (18)	0.688 (22)
120	0.348 (52)	0.386 (56)
180	0.241 (66)	0.275 (68)
240	0.202 (72)	0.199 (77)
300	0.164 (75)	0.156 (82)
360	0.139 (80)	0.109 (87)

(Degradation of paraquat in waste water having 500ml volume with optimizes condition of TiO_2 and Fenton for 360 min. reaction in UV chamber)

CHAPTER 5

RESULT & DISCUSSION

5.1 Photocatalytic degradation of paraquat by TiO_2.

In the Photocatalytic oxidation process organic pollutants are destroyed in the presence of semiconductor photocatylysis(TiO_2, Fenton etc). The effective light source and an oxidizing agent such as oxygen air. This chapter presents the results of the Photocatalytic degradation of paraquat(pesticide).

The Photocatalytic process can efficiently degrade the pesticides using artificial UV light or sunlight radiation source. The molecular formula of paraquat is $C_{12}H_4Cl_12N_2$ and molecular mass is 257.16g/mol The IUPAC name is 1,1 dimethyl-4,4' bibyridinium dichloride 1, Its boiling point is 300^oC and melting point is 175^oC with 125 g/cm3 density.

Paraquat is a herbicide which is widely used in the world for agriculture practices for controlling broad weeds and grasses Experiment variables was developed in which effect of catalytic, effect of dose, pH, Volume, UV/Solar light, Volume of vessels etc discussed.

Paraquat is acutely toxic LD50 150 mg/kg and highly toxic by the inhalation route. As it discussed that it is a toxic chemical and dissolved in water, different concentration of pesticide was used for degradation study with catalyst. Photocatalytic process can efficiently degrade the pesticides using artificial UV-light or sunlight radiation sources. There is importance of choosing optimum degradation parameter to obtain high degradation rates which is most essential for any practical application of Photocatalytic oxidation process. The titanium dioxide (TiO_2) is used as catalyst for degradation of paraquat due to its high efficiency purification of hazardous compounds in polluted water and air. Thus TiO_2 have greater capacity to decompose paraquat dichloride to several harmless compounds in the environment. Thus making paraquat a environmental product, useful to farmer in increasing productivity in agriculture practices with safer side.

The study was carried out for 240 min. initially Table 4.1 & Fig. 5.1 showed 10, 15, 20 and 25 ppm of paraquat in 250ml liquid with 0.2 gm of TiO_2 in it. It was observed from the table that maximum

54% degradation was observed in 10ppm pesticides followed by 20, 15, 25 ppm which is 47%, 50% and 36% respectively.

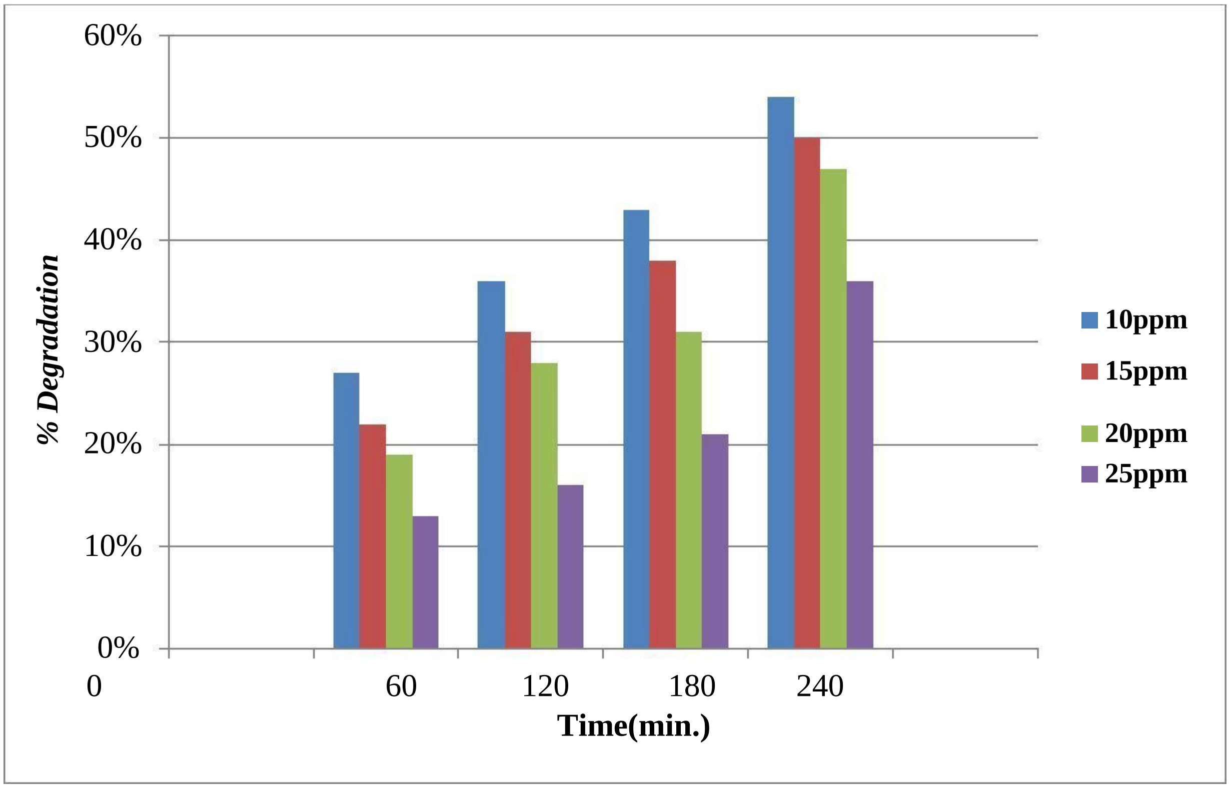


Fig: 5.1 Degradation of Paraquat at different concentration

After observing maximum degradation in 10ppm next experiment was planned with different pH keeping concentration of paraquat 10ppm and catalyst 0.2gm Table 4.2 & Fig. 5.2.

Effect of pH

These results showed the optimum pH at which maximum degradation is observed is pH 7. Here 60% degradation observed within 300 min. and 57% at pH 9.

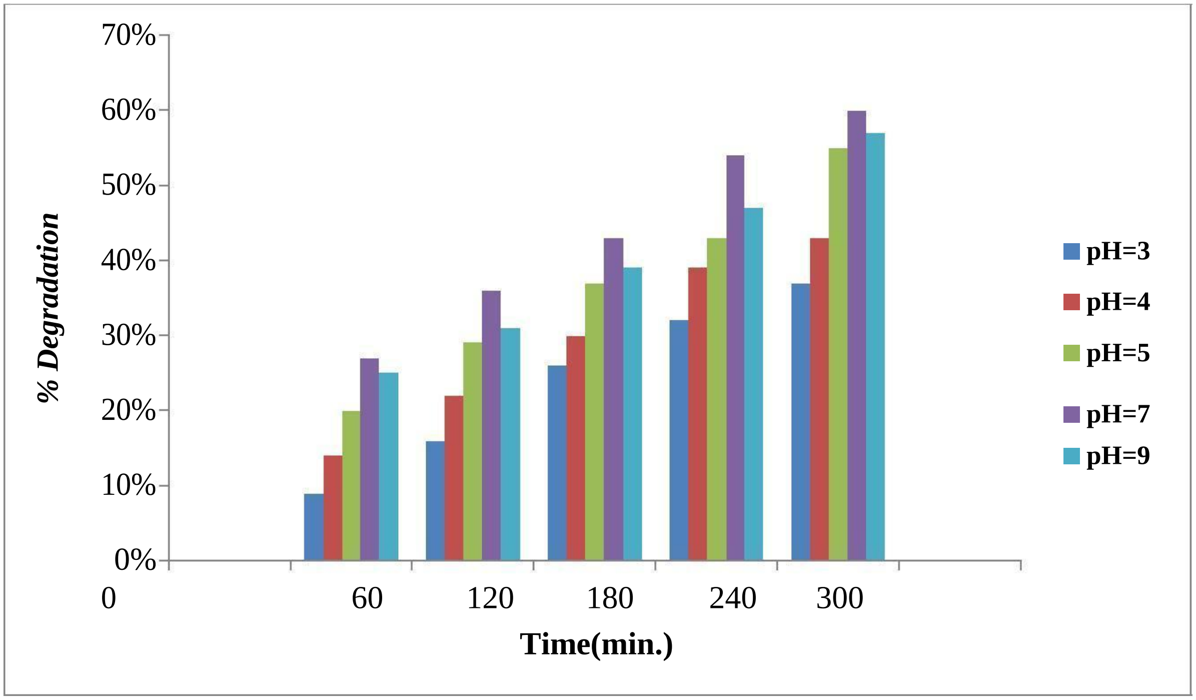


Fig: 5.2. Degradation of paraquat at concentration 10ppm

These results indicate that the photolysis reaction required higher pH which is above 5 or can say neutral condition. *Lock and winlks 2010* also observed that paraquat is photo chemically decomposed by ultraviolet radiation in aqueous solutions. It is more stable in neutral medium. It is highly soluble in water, 700g/l at 20^{o}C *Lock and Wilks 2010*, 625 g/l at 25^{o}C *Santos et al, 2011*, and 620 g/l *olivelra et al 2012* and practically insoluble in organic solvents with different concentration. Degradation of paraquat after selecting pH 7 another experiment was performed with different concentration of pesticides for 420 min. with 0.2 gm catalyst concentration Table 4.3 & Fig. 5.3. It was observed from the result that degradation rate of pesticide increases with 10ppm 68%, 20ppm 78% and afterwards it started decreasing.

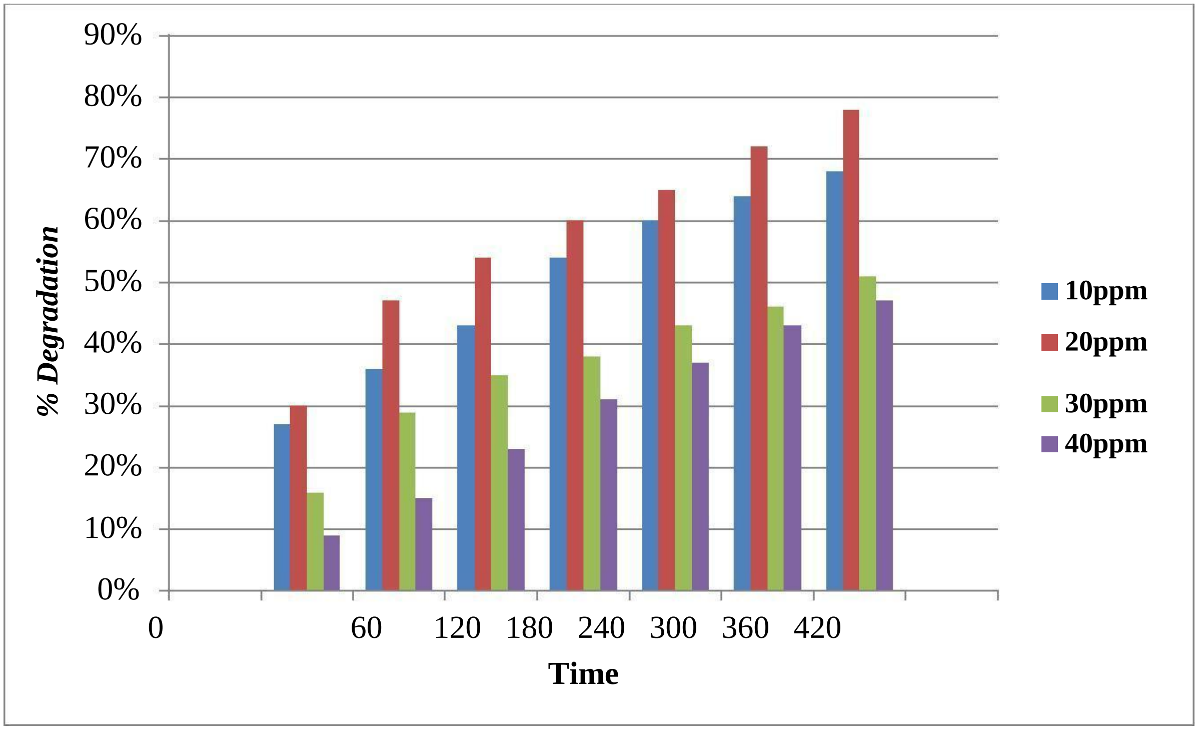


Fig: 5.3. Degradation of Paraquat at different concentration with pH

If we compared the results of all concentration, in 10ppm and 20ppm from the beginning degradation is high with both concentration compared to 30ppm 40ppm where they showed linear degradation figure 4.7 *Khatoon et al 2013* showed different analytical techniques for determination of paraquat in water especially spectro photo metrically. After getting maximum degradation with pH 7 with 20ppm paraquat some experiment planned with 20ppm of pesticide and varied pH from 3, 5, 7, 9, 10 and 11 for 360 min. Table 4.4 and Fig. 5.4 These values are average of three replicates and quite significant.

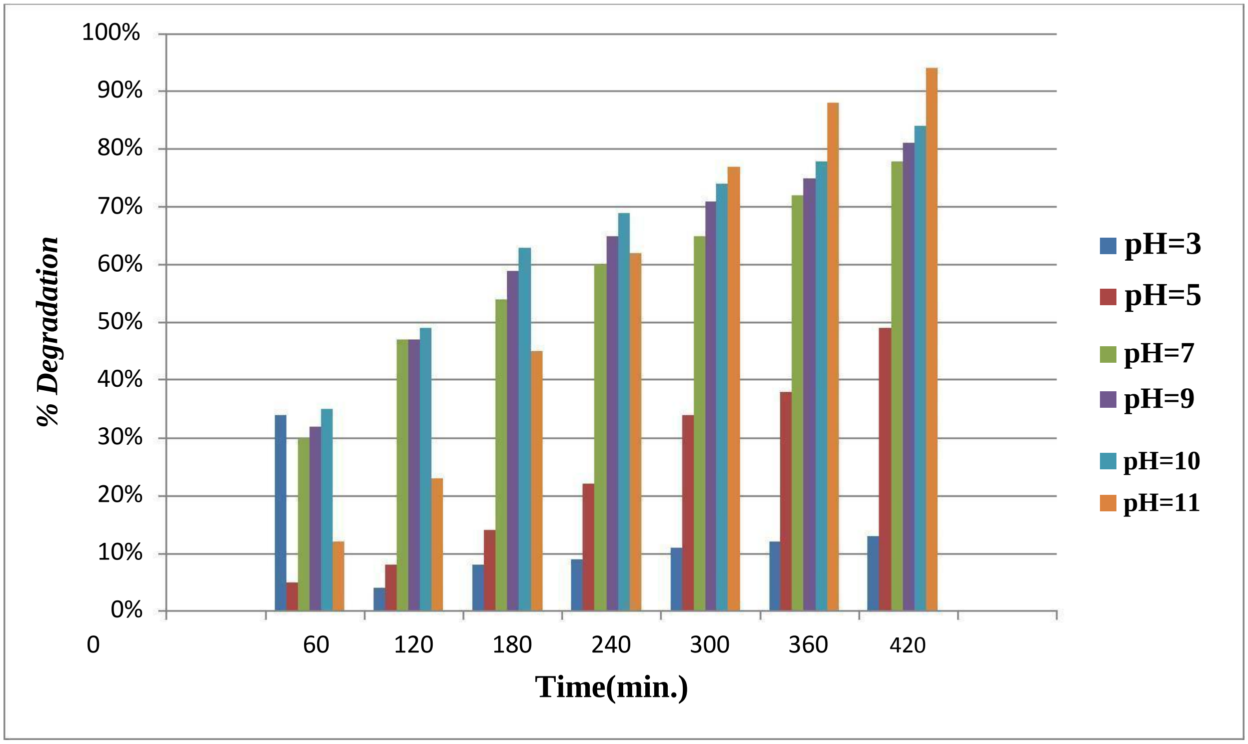


Fig: 5.4. Degradation of paraquat at concentration 20ppm

The pH plays an important role both in characteristics of pesticide and generation of hydroxyl radicals. With increase of pH the biodegradation also increases up to certain level and then it started decreasing. The pH of solution significantly affects TiO_2 activity including the charges on the particles, the size of the aggregate it forms, and the positions of the concentration and valence bonds. From the Table 4.2 it was observed that at pH 7 the maximum degradation 60% was observed compared to pH 3 and 5 which was 37% and 56% respectively in 300min.

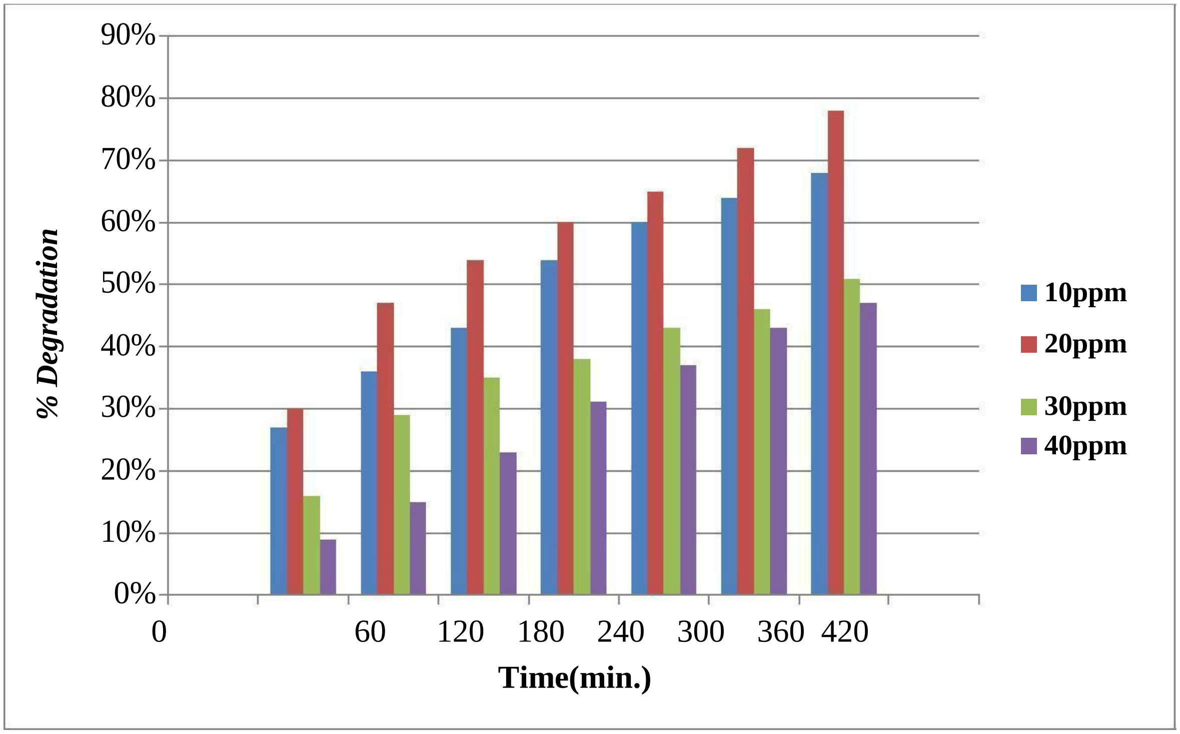


Fig: 5.5. Degradation of Paraquat at different concentration with pH

But when the pH increased to 9, 10, 11 94% degradation at pH 11 was observed followed by 84% and 81% respectively with pH 10 and 9 as indicated in Fig. 5.6.

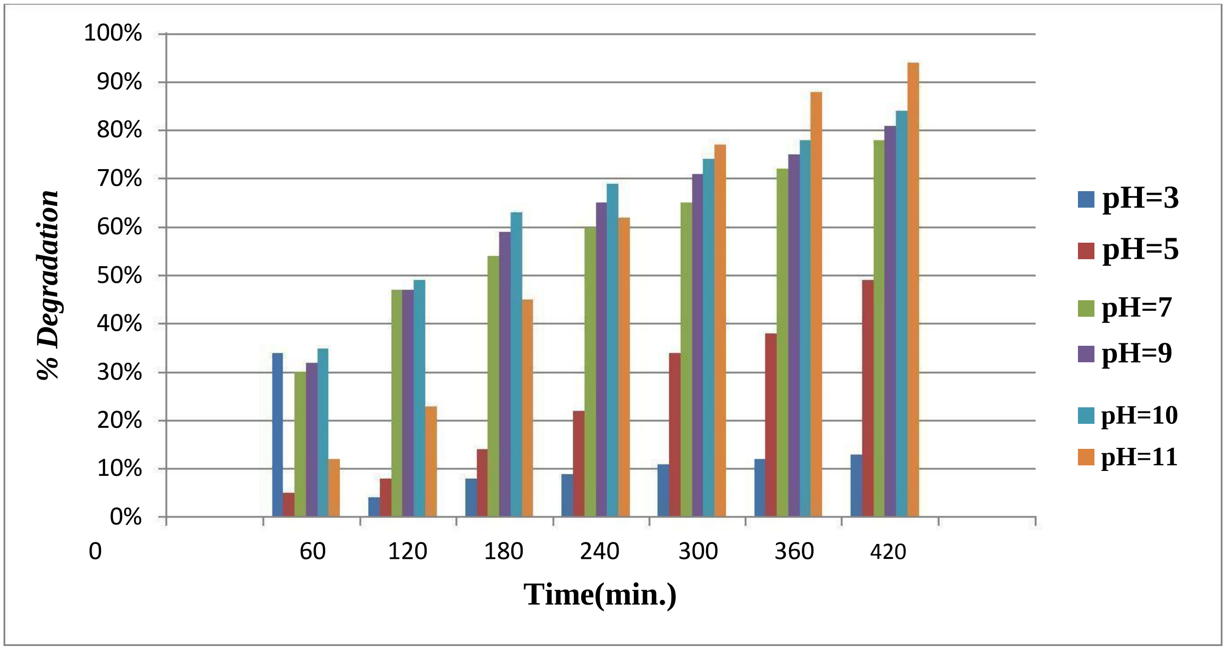


Fig: 5.6. Degradation of paraquat at concentration 20ppm

Chumee et al 2010 also studied degradation of pesticide beneath UV beams with the help of catalyst TiO_2 with optimum pH neutral.

Effect of different dosage of TiO_2 Table 4.5 & Fig. 5.7 showed the effect of different dosage of TiO_2 in degradation of 20ppm pesticides in 7 hrs with pH 11 maximum degradation of 98% pesticide was observed with 0.4gm/250ml of TiO_2 followed by 96% with 0.6gm of TiO_2.

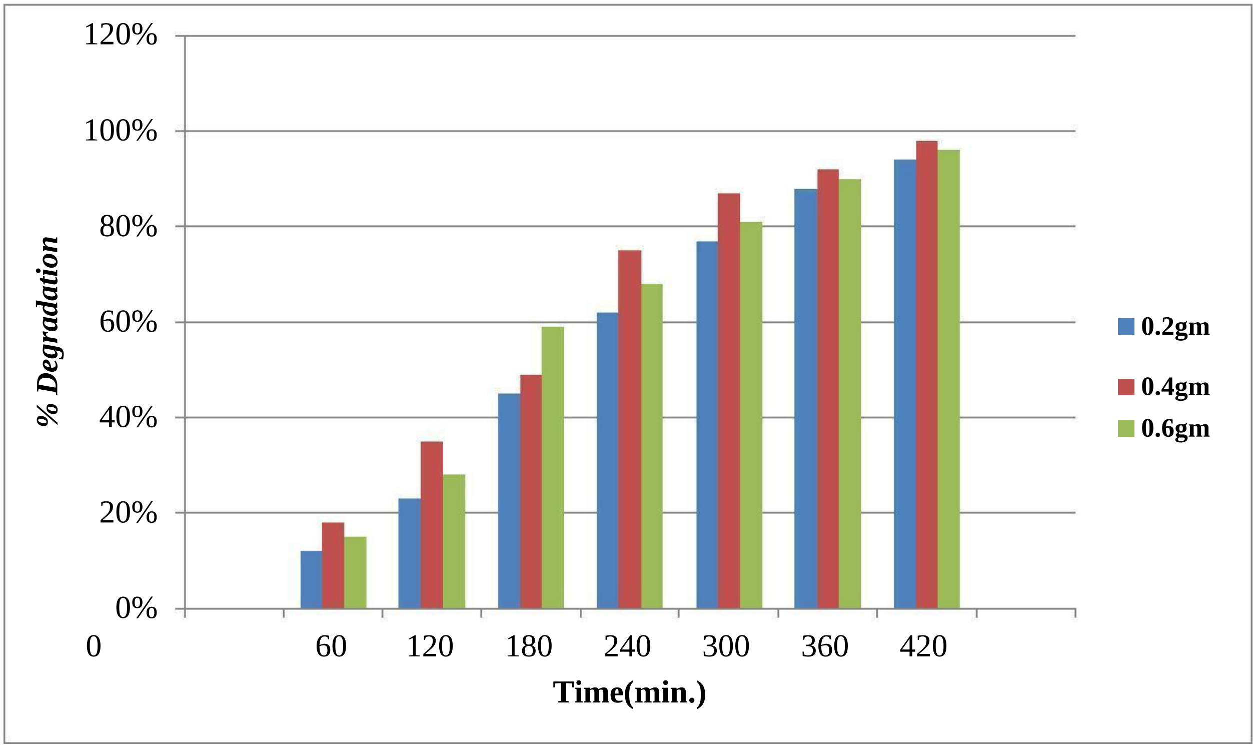


Fig: 5.7 Degradation of pesticide with different TiO_2 dosage

These results indicate that degradation rate of pesticide increases with increased catalyst concentration and become constant above certain levels Table at 0.6 gm TiO_2 there is marginal difference observed in percentage degradation after one hrs compare to 0.4 gm dosage this is may be due to aggregate of TiO_2 particles at higher concentration causes decrease in the number of surface active sites and decreased in opacity and light scattering of TiO_2 particles at higher concentration.

Moctezium et al 1999 have used commercial TiO_2 for removal of paraquat concentration 10, 20 and 40 mg/l. UV 365 nm and pH 4, 6.6, 7 and 9 in his result they showed 60% degradation in less than 3 hrs of reaction with 10mg/l at pH 6.6. *Santos et al 2011* also observed at high pH value in the presence of TiO_2 all species were consumed after three hrs of reaction.

Effect of aeration in sunlight and UV chamber- The experiment showed the results of UV light and sunlight .The 20ppm concentration of paraquat with 0.4gm/250ml of TiO_2 was used for experiment with pH 11.

Comparison UV light with sunlight- It was observed from table that sunlight gives better photocatylytic degradation 98% compared to UV light in aerated condition.

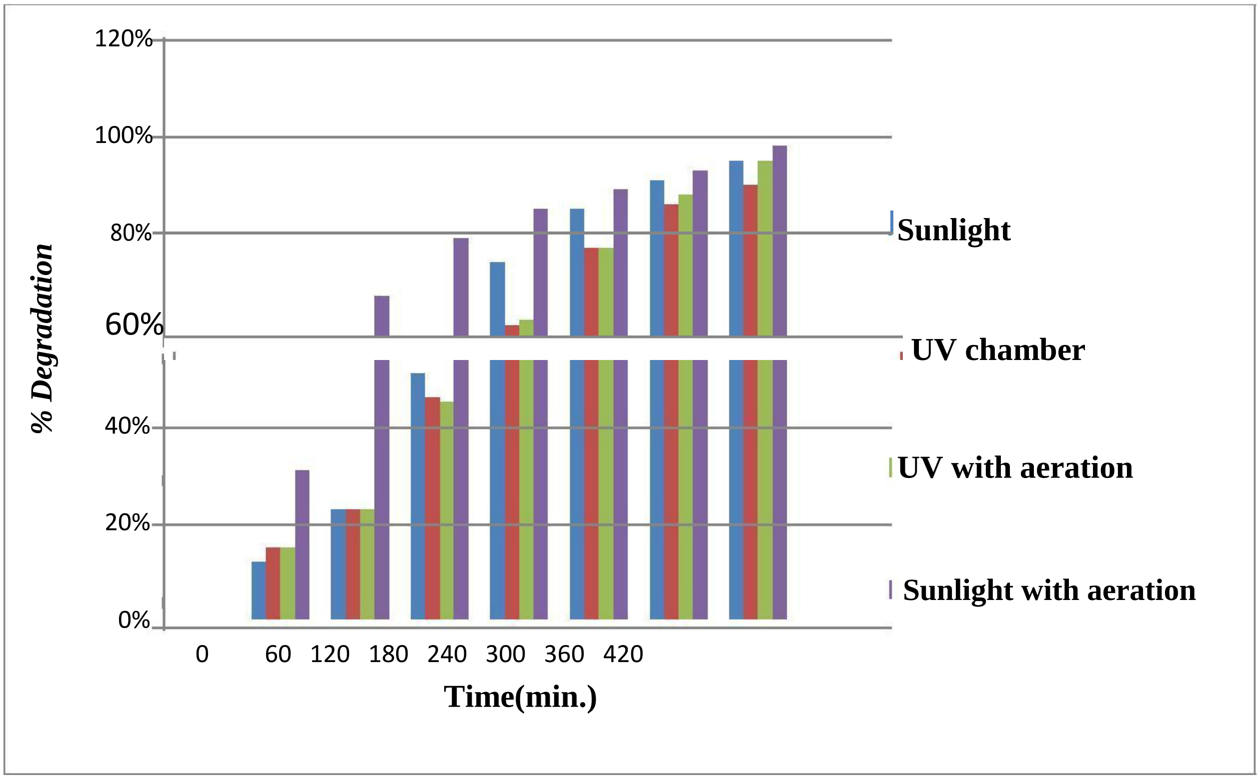


Fig 5.8. Degradation of paraquat in Sunlight & UV Chamber

As *Mota et al 2008* also mention that principle of photo catalysis is based on the activation of semi conductor materials such as TiO_2 , Zno etc by the action of radiation by different wavelength. These results also showed different radiation , whether it is agitated sample or without agitatation. Sunlight showed better results than UV lamp in the chamber. This is may be due to adiation which got from sunlight is higher than UV in the chamber. In the chamber UV having intensity 28W/m^2 which is may be lesser than sunlight which was present in that particular day. *Joon et al 2003* studied removal of paraqaut in aqueous suspension with and without air sparging. He found 50% higher degradation than that with only the UV lamp.

Degradation of paraquat with different doses of catalyst TiO_2 ; Experiment was performed with 20ppm of paraqaut at 11 pH by using different volume.

Effect of area to volume ratio----- The area and volume of the reaction vessel are the two different parameters which affect on the degradation of the pesticide used. If surface area is increased keeping the same volume the degradation will be more because of the surface area which is available for light to contact with the solution (TiO_2, pesticide, Fenton etc). In our case volume is variable but the surface area of the vessel is same.

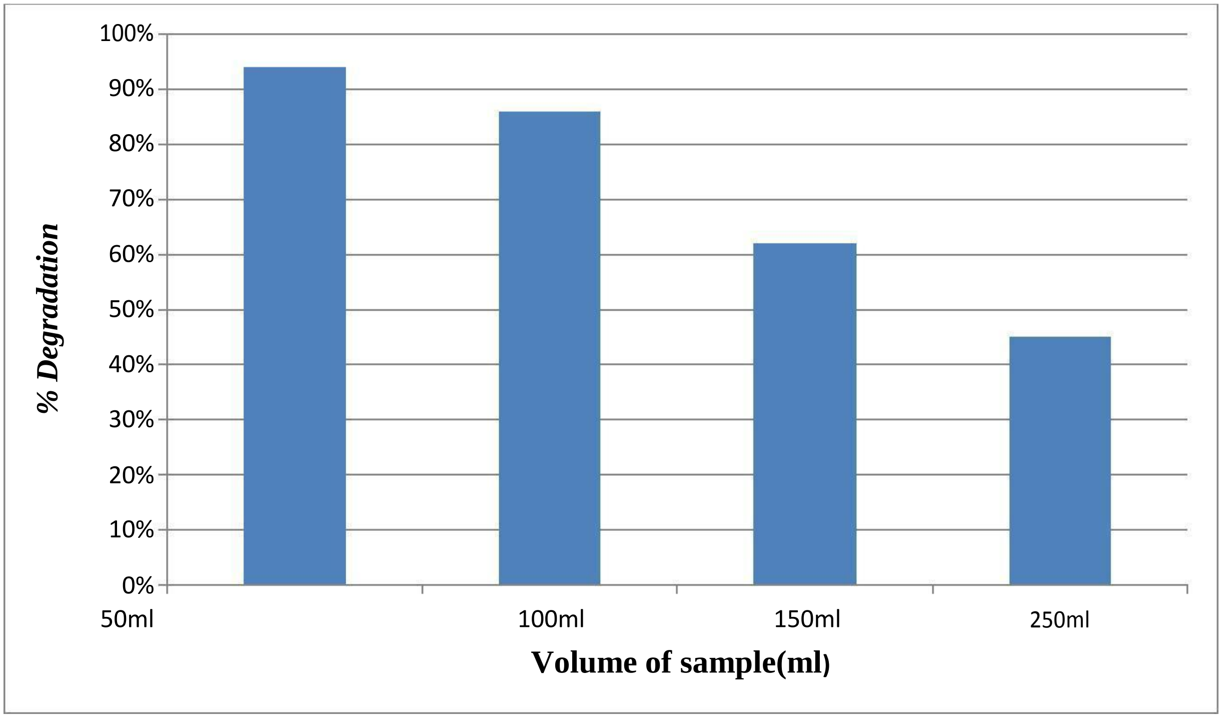


Fig: 5.9 Degradation of paraquat with different area to volume ratio for 180 min.

Volume of the sample is directly related to the light (radiation) which is passing through the solution. *Hoffmann et al 1999* mention in his paper that principle of photon oxidation is nothing but UV illumination onto a photocatylyst excites produce electron and hole pair with high energy state. This energy migrates to the particle surface and initiate a wide range of chemical redox relations. Results of table 4.7, Fig 5.9 and 5.10 also showed the same results when the volume is only 50ml than maximum degradation is 94% which works on the same principle mentioned above. Results showed as we increased the volume of water pesticide degraded was also increased but time taken is more with 150ppm 80% degradation was observed which further increased 95% with 250ml. After 7 hrs these results indicate that high energy state differ

according to the particle surface differ according to the chemical redox reaction. The TiO_2 in different volume reacts accordingly.

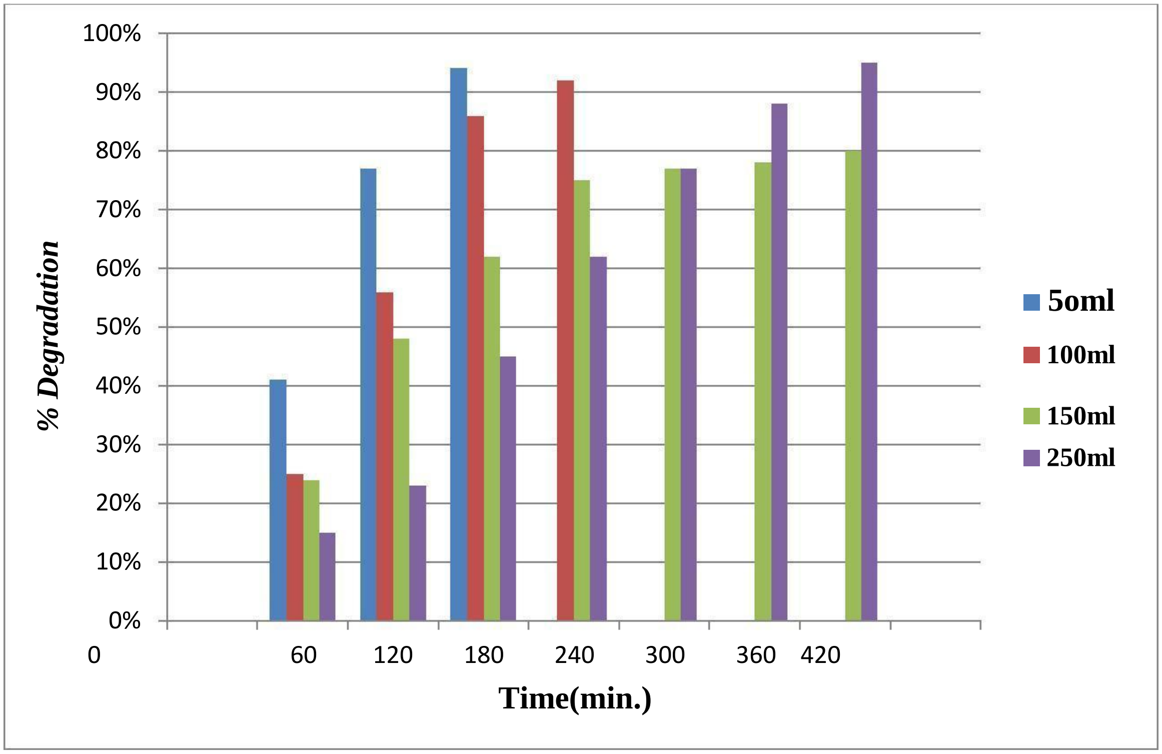


Fig: 5.10. Degradation of paraquat with different area to volume ratio.

Effect of UV intensity----Figure 5.11 show the effect of UV intensity on the degradation efficiency. It was observed from Table 4.8 that as the light intensity increase the photo degradation efficiency increases. This is due to the UV irradiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photo catalyst and the energy of a photon is related to its wavelength. The overall energy input in Photocatalytic process is dependent on light intensity. *Daneshvar et al 2004 and Kanstantinon of albaine 2004* stated that as more radiation fall on the catalyst surface, the ratio of degradation increases so producing more hydroxyl radicals.

Effect of UV light at different distance- The degradation of paraquat was studied with different length of the UV light lamp. The degradation was done with optimum dose 20ppm of pesticide with 0.4 gm of TiO_2 with pH 11 in 250ml solution. Results were shown in Table 4.8 & Fig. 5.11. It was observed from the table that as soon as we increased the UV light length from the base line, the photocatylytic degradation decreased. When the UV light was 10cm above from the base line degradation was 94 to 97% in 240 to 360min. where as it was keep on decreasing above the 20 cm 90% and 30 cm 87% .

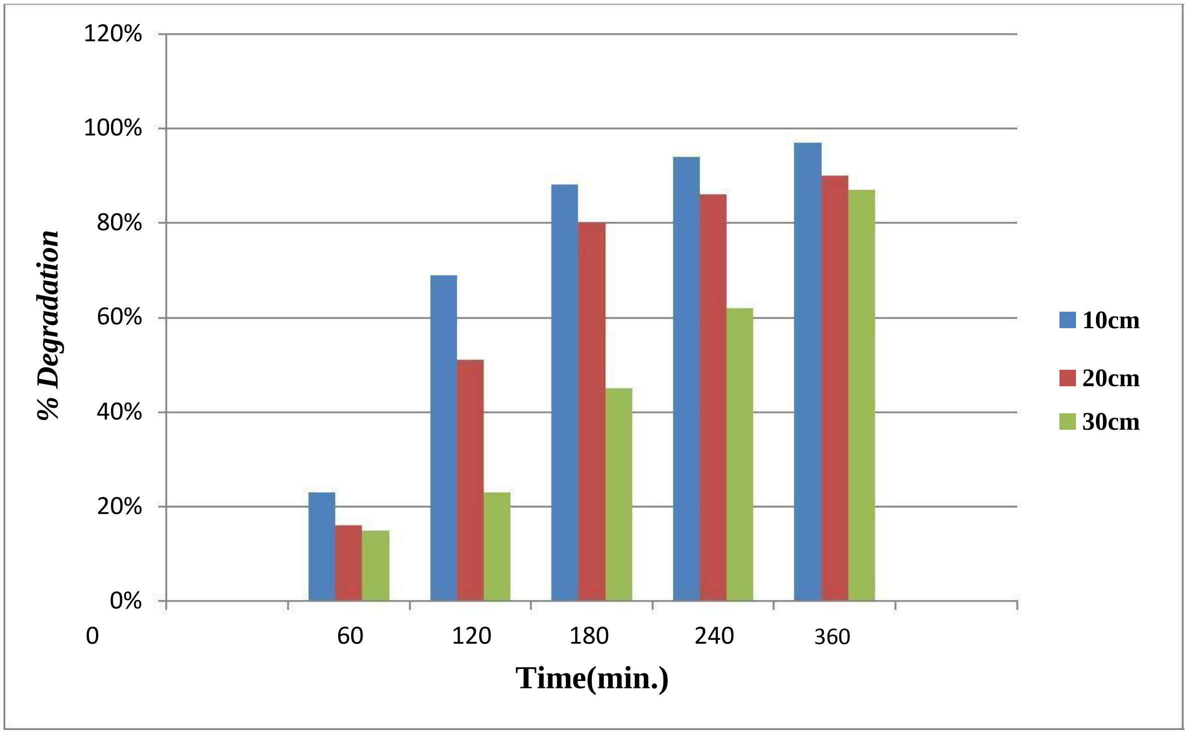


Fig: 5.11. **Degradation of paraquat with different distance from UV tube**

These results indicated that distance from base line should not be move than 10-20cm in artificial light. The intensity of UV lamp is 28 w/m2 if we varied the distance it will affect to the efficiency.

5.2 Photocatylytic Degradation Of Paraquat By Photo Fenton.

Here equipment used are same as photo catalysis experiments Fenton's reagent is a solution of hydrogen peroxide (30%) and ferrous ions as $FeSO_4$. Fe^{2+} in Fenton's reagent (Fe^{2+}/H_2O_2) is prepared by making a solution of Fe^{2+} salt and H_2O_2 obtained in liquid (30%). Fenton reaction is one type of advanced oxidation process which also generates hydroxyl radicals (OH) like TiO_2
But in this reaction H_2O_2 and ferrous ions (Fe^{2+}) generate hydroxyl ion (OH) according to this reaction

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + HO$$

Which was also observed by venny et al 2012 and *Ramirezetal 2007*.

Degradation of paraquat with H_2O_2 and Fe^{2+} with different pH

The degradation studies were carried out in glass bowl and exposed to UV light inside the chamber in the presence of 7.5 mg Fe^{2+} and 0.1ml H_2O_2 with 10ppm of paraquat table showed the results of experiment . It was showed by the experiment that pH 3 showed maximum reduction in absorbance which started with 1.226 at 0 hr and keep on decreasing up till 300 min (0.158) followed by pH 2. The decreased in absorbance is further decreases with pH 1.0 and after that pH 4. The percent degradation calculated maximum with pH 3 (87%) followed by pH 2 (57%), pH1 (40%) and pH 4 (34%).

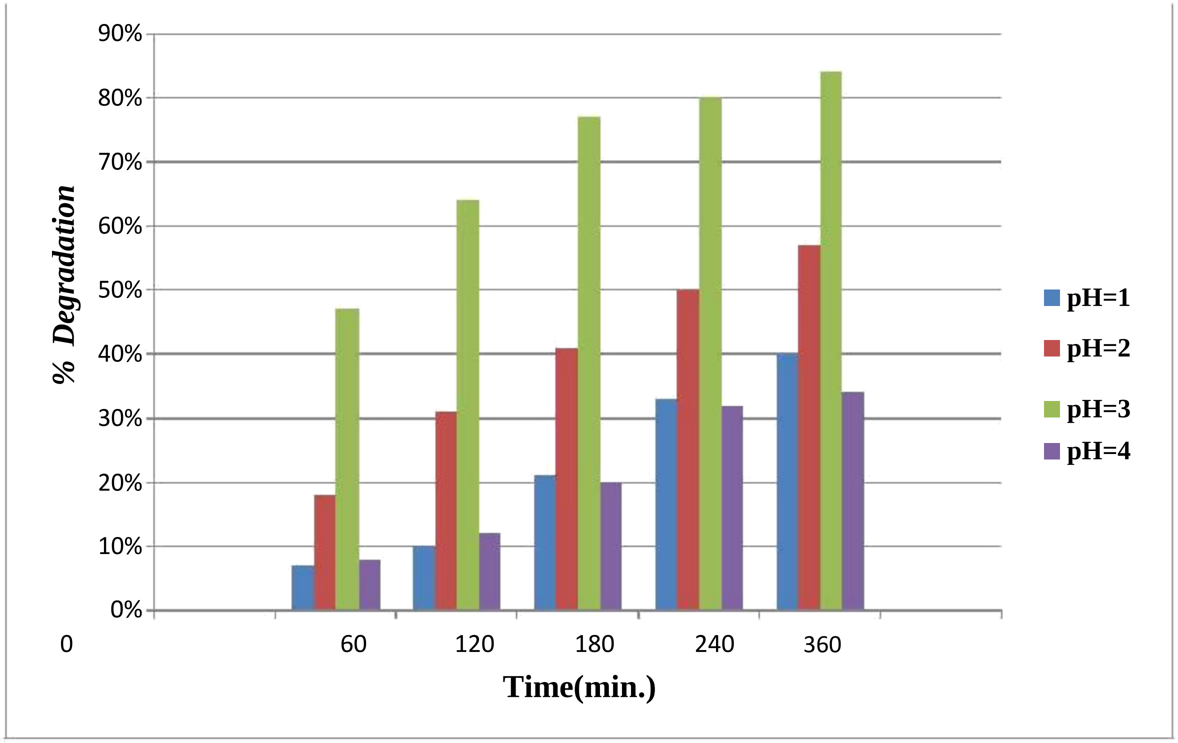


Fig: 5.12. Degradation of paraquat at concentration 10ppm

Oliveira et al 2014 also studied removal of pesticide with Fenton reaction. In his study he showed complete degradation of pesticide insitu water system their deposits and corroded pipes which acts as catalyst oxidation of pesticides because Fenton's process requires dissolved iron.

Oliveira et al 2012 also stated that pipe deposits can also act as a catalyst in AOP process.

Degradation of different concentration of paraquat.

A several authors were used Fe^{2+} 7.5 mg so this concentration was used with 10,20,30,40 and 50 ppm of paraquat with Fe^{2+} 7.5mg and H_2O_2 0.1ml and pH 3 in 500ml solution shown in Table 4.10 & Fig. 5.13. With this combination maximum degradation was observerved in 20ppm concentration(86%) followed by 10ppm (83%) , 30ppm 72% and then 40ppm and 50ppm.

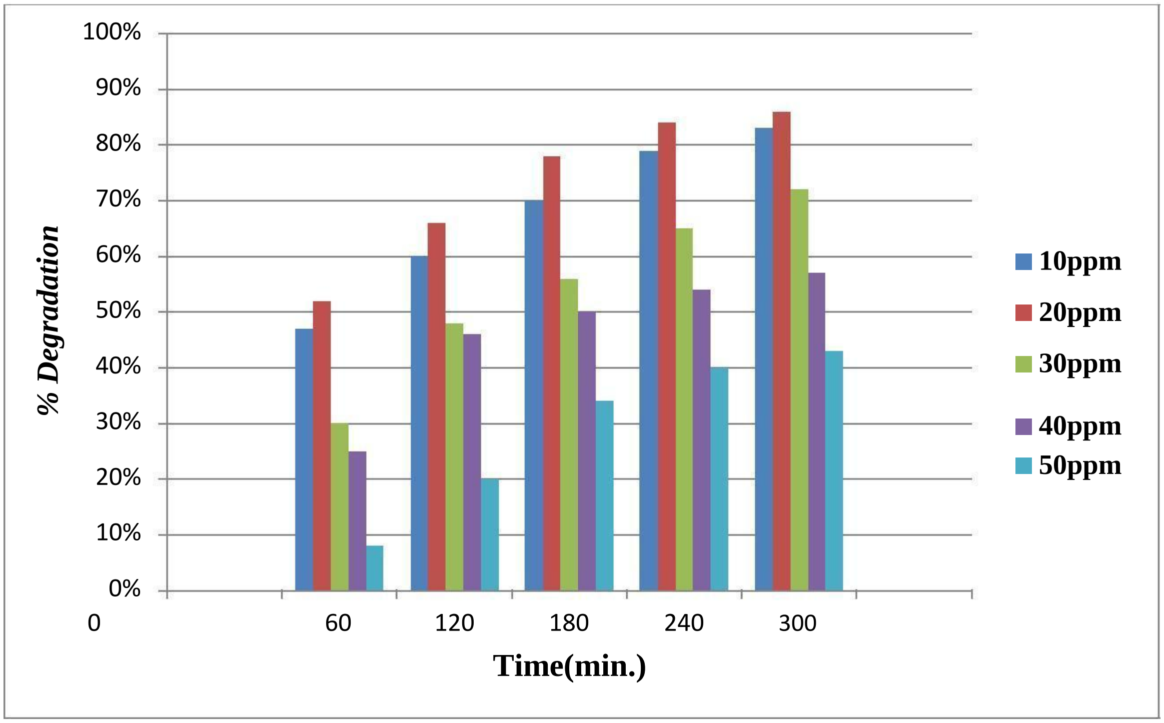


Fig: 5.13. Degradation of pesticide at different concentration with pH 3

Oliveira et al 2104 he also observed effect of pH on paraquat degradation. In his study he stated that initial pH has a significant impact in the catalytic process.

Degradation of paraquat with various Fe^{2+} concentrations

From the Table 4.10 & Fig. 5.13 it was observed that 20 ppm of pesticide had given maximum degradation so another experiment was planned with different concentration of Fe^{2+}. The Fe^{2+} concentration varied from 2, 3, 7.5, 5.5,and 10.5 mg with 20ppm paraquat 0.1ml H_2O and pH 3 in 500ml solution. Table 4.11 & Fig. 5.14 showed the results of different concentration of Fe2+. This experiment showed 5.5mg/500ml was found 2.215 which decreases to 0.234 which give 89% of degradation. The minimum degradation was found in 2mg Fe^{2+} which keep on increasing up till 5.5mg and after that it decreased gradually 85% (7.5mg) and 76% (10.5mg) respectively.

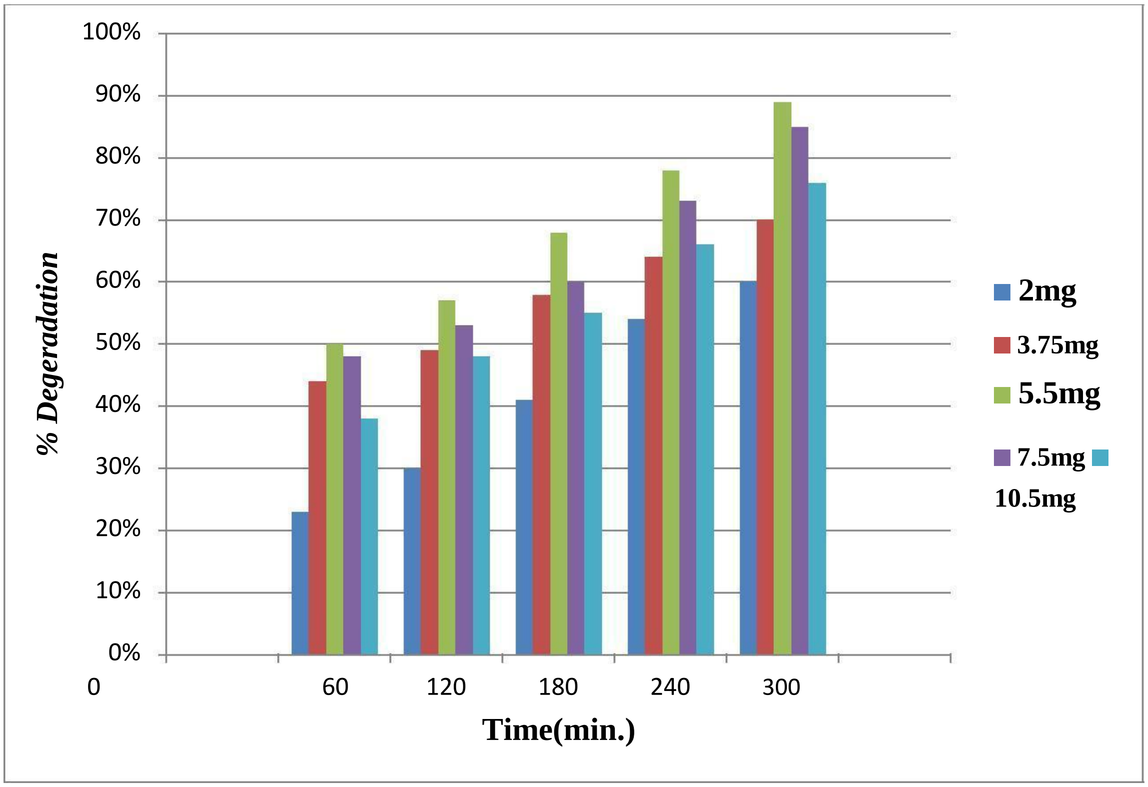


Fig: 5.14. Degradation of paraquat at concentration 20ppm at pH 3

Santos et al 2011 also studied paraqaut mineralization where he found best condition temp 30^{o}C, pH 3 H_2O_2 1.5×10^{-2} and Fe^{2+} 5×10^{-4}M.

Effect of different concentration of H_2O_2 on paraquat degradation

The results of different concentration of H_2O_2 showed in table 4.12 & Fig. 5.15 The experiment contian 20ppm paraquat 5.5mg Fe^{2+} with pH3 inhere the H_2O_2 concentration found maximum degradation with 0.1ml (89%) in 300min.

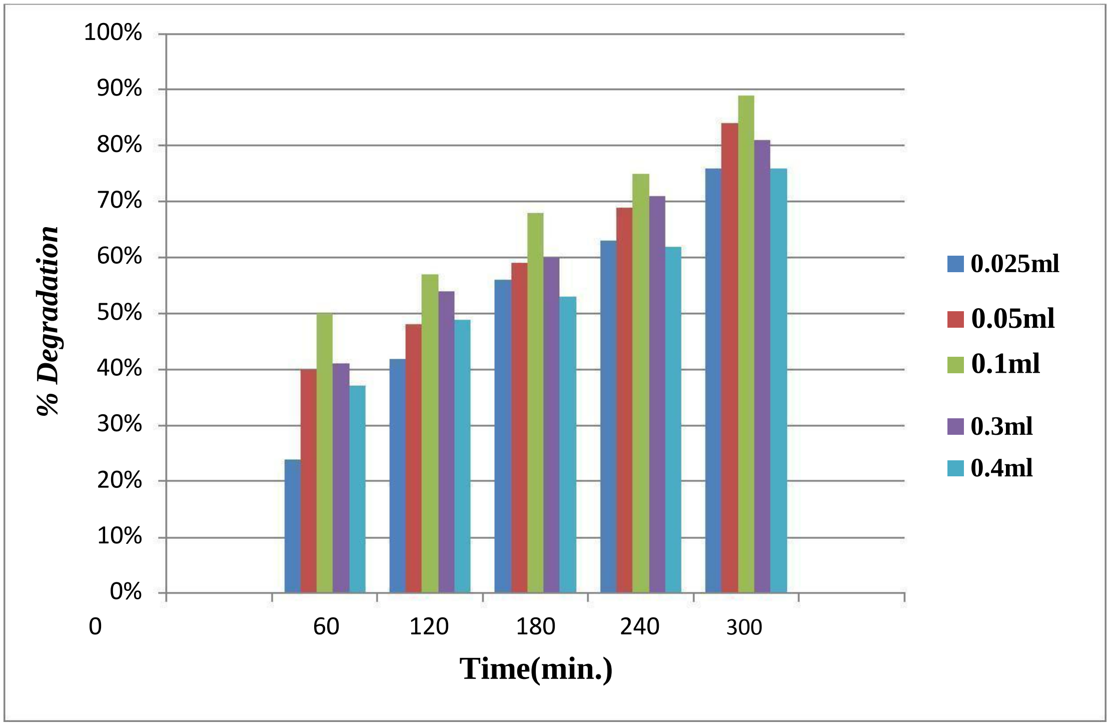


Fig: 5.15. Degradation of paraquat with different H_2O_2 concentration

These results indicates that if concnetration of H_2O_2 decreases below 0.05 degradation got decreased where as if concentration is more them also degradation get affected actually reaction between iron and H_2O_2 also produced hydroxyl radicals with high oxidation power which attack on pesticde present in water. The hydoxyl radicals are not only consumed to degrade the pesticide but also produce other radicals. *Oliveira et al 2014* have investigated degradation of pesticide in the pilot loop system achieving similar results as in a labscale reactor. Initial pH is also an important factor for fenton reaction. He also concluded that gradual addition of H_2O_2 showed the best option in the oxidation process for higher mineralization upto 60% within 24 hrs.

Effect of volume of degradation The degradation of paraquat was performed with optimum conditions by addition of 20ppm paraquat, pH3, Fe 5.5mg and H_2O_2 0.1ml in 500ml solution. The results showed in table Table 4.13 & Fig. 5.16. The maximum initial absorption 2.215 found in 0hr with 500ml volume which decreased to 0.234 in 300min from the results it showed that 500ml volume had maximum degradation 89% followed by 300ml (78%), 700ml(74%).

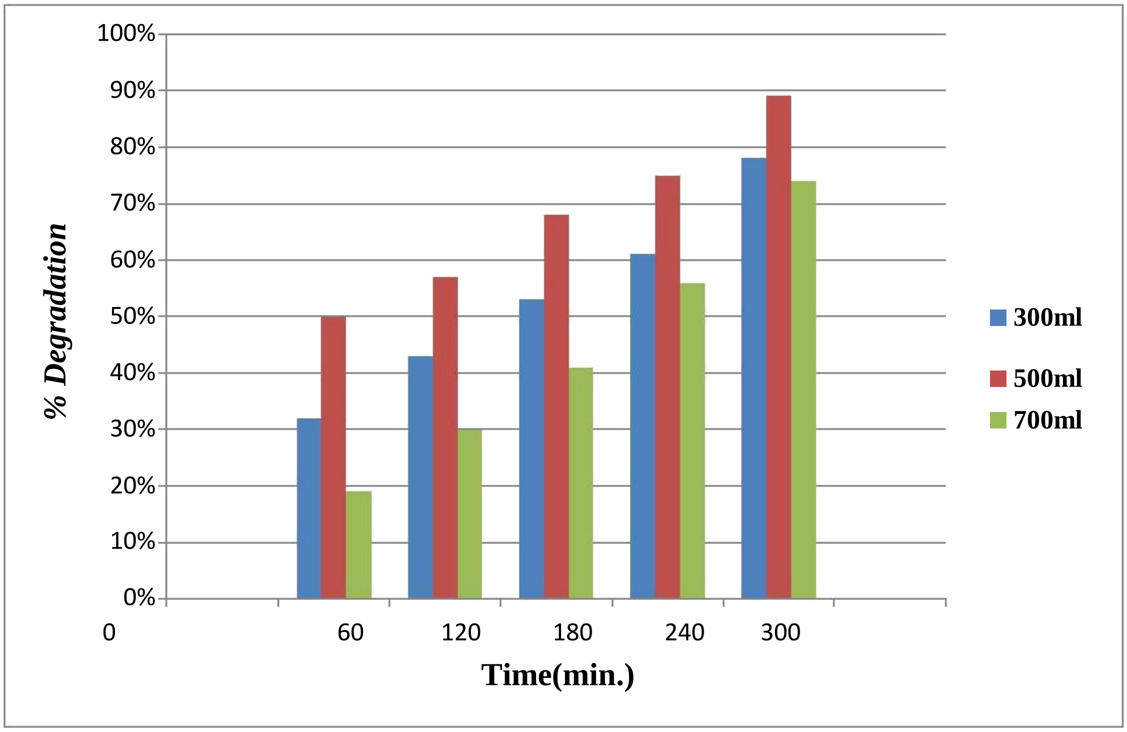


Fig: 5.16. Degradation of paraquat with at different volume.

Variation in volume but concentration of catalyst is same which cause decrease in degradation when volume increased due to low concentration of catalyst. The same results were obtained with TiO_2 where optimum volume found 250ml results directly related with the availability of catalyst present in the water and their irradiation with UV light.

Effect of degradation with distance from base line

This experiment was performed with optimum coniditon of Fe^{2+}, H_20_2, pH and dose of paraquat. Results showed in Table no 4.14 & Fig. 5.17 here the observation is same as with photocatalytic degradation with distance of 10cm maximum degradation was observed 86% followed by 20cm(82%) 30cm(78%).

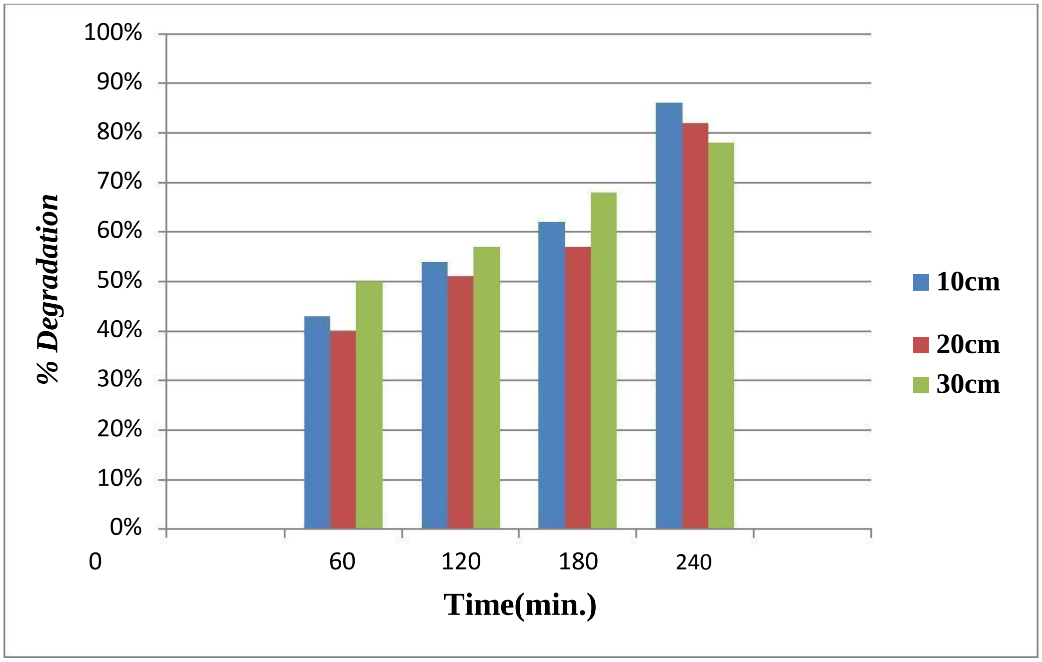


Fig: 5.17. Degradation of paraquat with different distance from UV tube

Percentage degradation showed that intensity of UV lamp having major impact on degradation with optimized condition. As soon as distance from base line increases the degradation decreases. Experiment run in sunlight also and found maximum degradation within 240min. which is totally depends upon the intensity of sunlight which is not known Table 4.15 & Fig. 5.18.

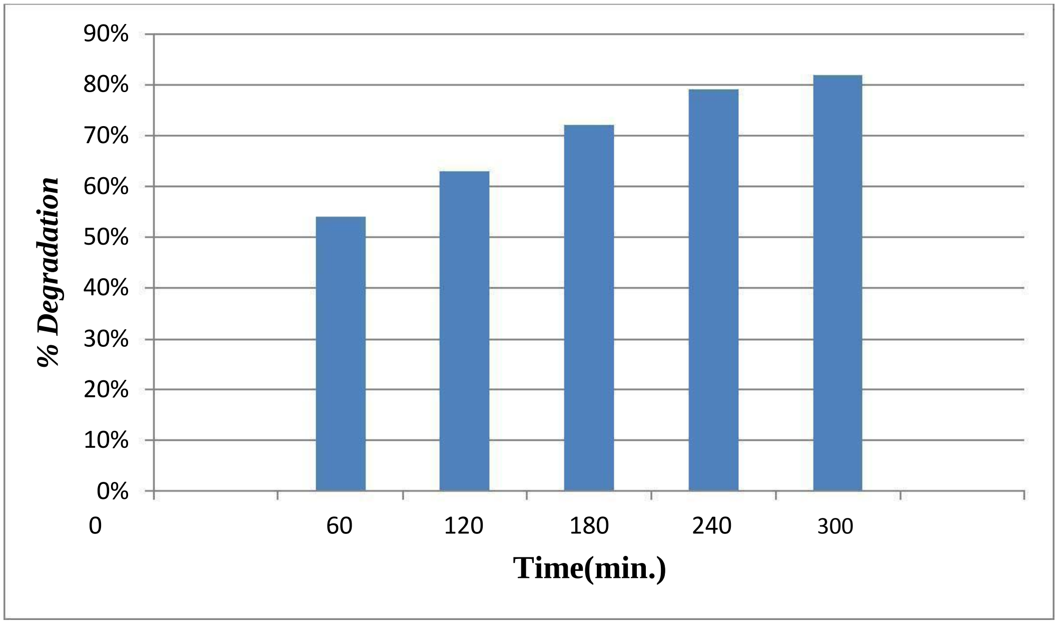


Fig: 5.18. Degradation of paraquat in sunlight.

kanchanatio et al 2011 invesitigate paraquat under visible light and observed 70% degradation. Which was also suppoted by *santos et al 2011*.

Degradation of wastewater

Paraqaut can be introduced in aquatic system especially in the river through runoff from agriculture application By application of pesticide for killing of weed etc. The advantages of using photodegradation and photofenton are, there are no sludge produced. Degradation of paraqaut in waste water was performed by addition of catalyst in waste water.500ml waste water collected from Thapar campus treatment plant was used for experimentation. The TiO_2 and Fenton reagent which got from optimized condition was added in waste water. The experiment performed in the same procedure as done previously for TiO_2 and Fenton reagent. Table 16 showed the result of waste water initially there is no pesticide present in waste water. The TiO_2/UV and Fenton/UV process have many advantages as number of organic and dissolved or dispensed matter can be mineralized by these process.

From the Fig. 5.18 it was observed that when waste water after addition of pesticide and TiO_2 was irradiated with UV light at pH 11 was showed 80% degradation as initially with waste water absorption spectra was 0.723 but after 360min. it absorption reduced to 0.139 which showed 80% degradation and with Fenton reaction it observed 87% degradation.

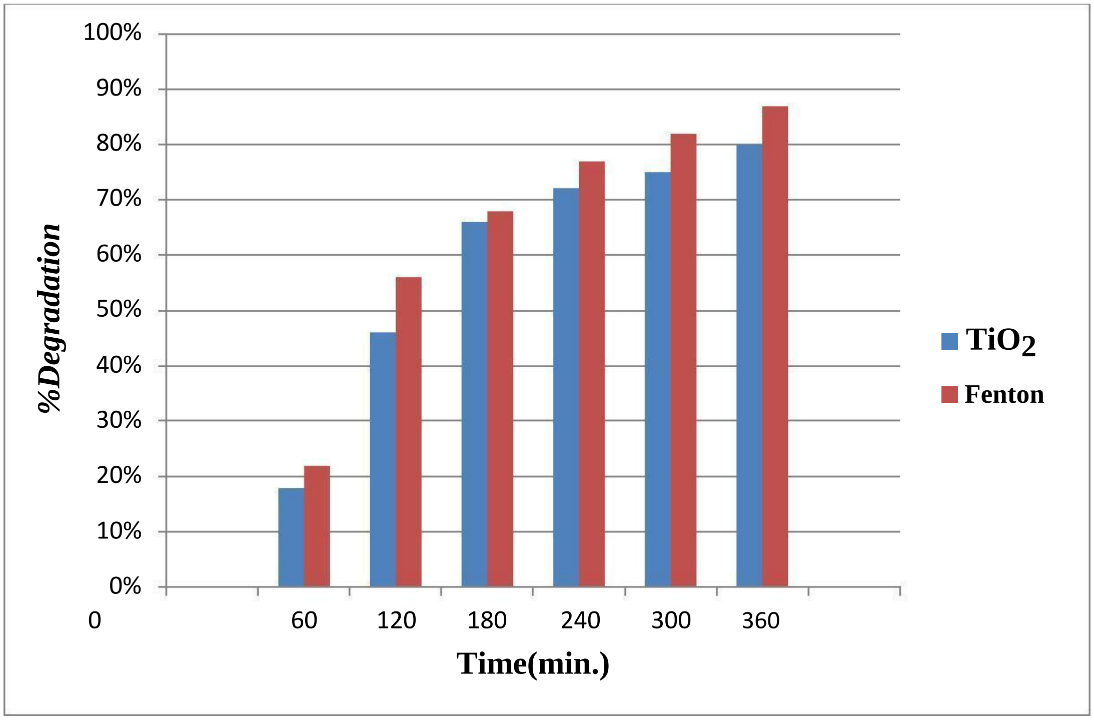


Fig: 5.18. Degradation of paraquat in waste water with TiO_2 and Fenton

It was investigated that reaction between iron H_2O_2 and TiO_2 produced hydroxyl ion, which attach on the organic matter. The hydroxyl radicals are not only consumed to degrade the organic matter but also produced other radicals with less oxidative power or produce other species also observed by Santos et al 2011.The production of again Fe^{2+} by the reaction between Fe^{2+} and H_2O_2 In this way ferrous ion is restored in the system acting as catalyst

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{III}(HO_2)^{2+} + H^{+}$$

$$Fe^{3+}(HO2)^{2+} \rightarrow Fe^{2+} + HO^{\cdot}_2$$

CHAPTER 6

CONCLUSIONS

6.1 Degradation By TiO_2

1) Photocatalytic process can efficiently degrade the pesticides using artificial UV- light or sunlight radiation sources. There is importance of choosing optimum degradation parameter to obtain high degradation rates which is most essential for any practical application of Photocatalytic oxidation processes.

2) The titanium dioxide (TiO_2) is used as catalyst for degradation of paraquat due to its high efficiency purification of hazardous compounds in polluted water and air and it is the best photo catalyst due to its chemical and biological inertness when compare to other photo catalyst. Thus Tio_2 have greater capacity to decompose paraquat dichloride to several harmless compounds in the environment. Thus making Paraquat a environmental product, useful to farmer in increasing productivity in agriculture practices with safer side.

3) Paraquat plays a very important role in agriculture. There is no other product more useful than paraquat, and for that reason, farmers want to use it. The farmers who use paraquat chemicals, some of which might be more hazardous and less environmentally benign and they might also employ women and children to weed by hand, with attendant injuries and costs that such work entails.

4) Photo degradation is excellent process as no sludge formation takes place.

5) The optimum dose of TiO_2 was found 0.4gm/250ml which give maximum degradation of paraquat.

6) The optimum catalytic properties enable demonstrate TiO_2 has good behavior to photo catalytically degrade paraquat dichloride to relatively safe and tolerable compounds in the environment.

7) For low concentration paraquat it has higher efficiency for degradation as low concentration paraquat solution are easily degraded and high concentration paraquat solution required longer times to degrade the original molecule.

8) From effect of area to volume it can be concluded there is variation in volume but concentration of catalyst is same which cause decrease in degradation when volume increased due to low concentration of catalyst.

6.2 Degradation By Photo Fenton

Results from the present study have demonstrated the effectiveness of the application of photo-Fenton reagent (Fe^{2+}/H_2O_2) in the treatment of paraquat. It is proven to be one of the clean technologies based on the generation of extremely reactive and non-selective hydroxyl radicals, with very high oxidative power. Advanced oxidation processes provide an efficient alternative for treating paraquat which is toxic compounds. With high oxidation power, the hydroxyl radicals are capable of totally or partially degrading practically all classes of organic compounds present in aqueous medium or in soils, resulting in the complete mineralization of these compounds or in their conversion to more biodegradable products. The response surface methodology for optimizing such process parameters was applied. This experimental design methodology was shown to be a valuable tool in optimizing the process, which could be satisfied with the minimum number of experiments. The three variables, Fe^{2+}, H_2O_2 concentrations, and pH, showed optimal values, giving maximum percentage degradation that reached 97%. This demonstrates the usefulness and effectiveness of the Fenton reagent as an advanced technique for the treatment process. In the present work, a detailed parametric study was performed to evaluate the effect of volume, H_2O_2 concentration, Fe^{2+} concentration, pH, iron source and paraquat concentration on the pesticide degradation by Fenton's reagent. Under selected conditions ($[Fe^{2+}]$ = 5.5mg/500ml, $[H_2O_2]$ = 0.1ml/500ml, and pH = 3.0 nearly all the initial paraquat dichloride present in the reactor was degraded after 300 min. Maximum degradation of 89% shown which is more than degradation done by TiO_2 which showed 77% degradation in 300min. The result show that Photo Fenton are powerful methods for degradation of paraquat and it is more efficient compared to degradation by catalyst TiO_2. Even it is possible to achieve complete degradation of paraquat by Photo Fenton process by increasing reaction time.

REFERENCES

[1] A. Kunz, P. Peralta-Zamora, N. Duran, "*Adv. Environ. Res*." Vol. 7, 2002, pp. 197–202.

[2] Agnihotri, A, Pesticide use takes toll on people's reproductive health, *The Asian Age* Available at http://navdeepasija.blogspot.com/2010/07/pesticide-use-takes-toll-on-peoples.html. 2010.

[3] Alam G. Trovó,*,a Oswaldo Gomes Junior,a Antonio E. H. Machado,a Waldomiro Borges Netoa and Jader O. Silvab, "Degradation of the Herbicide Paraquat by Photo-Fenton Process: Optimization by Experimental Design and Toxicity Assessment, *J. Braz. Chem. Soc.*, Vol. 24, No. 1, 2013, pp. 76-84.

[4] Alberdi, J.L., Saenz M.E., Di Marzio, W.D., and Tortorelli, M.C. (1996). Comparative acute toxicity of two herbicides, paraquat and glyphosate, to Daphnia magna and D. spinulata. *Bulletin of Environmental Contamination and Toxicology* 57, 229 -235.

[5] Amondham, W., Parkpian, P., Polprasert, C., Delaune, R.D., and Jugsujinda, A. (2006). Paraquat adsorption, degradation, and remobilization in tropical soils of Thailand. *J Environ Sci Health* B 41(5), pp. 485 - 507.

[6] Anoop Verma (2014) Degradation of Pesticides in Groundwater by Advanced Oxidation Processes(Master's thesis, Thapar University Punjab).

[7] Augugliaro V., Litter M., Palmisano L. and Soria J., The combination of heterogeneous photocatalysis with chemical and physical operations: A tool for improving the photoprocess performance, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 7 2006, pp. 127–144.

[8] Avimuktesh Bhardwaj and Savvy Soumya Misra "State of Pesticide Regulations in India," *Centre for Science and Environment*, New Delhi 2013.

[9] Berne Declaration. 2010a. Legal status of paraquat in different countries. Berne Declaration, Zurich. http://www.evb.ch/en/p5787.html.

[10] Brillas, E., Casado, J., 2002. Aniline degradation by Electro-Fenton and peroxicoagulation processes using a flow reactor for wastewater treatment, Chemosphere. 47, pp. 241–248.

[11] Bromilow R.H., Paraquat and sustainable agriculture, "*Pest Management Science*," vol. 60(4), 2004, pp. 340.

[12] Burns, R. G., and L. J. Audus. “Distribution and breakdown of paraquat in soil,” Weed Res. Vol. 10, 1970, pp. 49-58.

[13] Calderbank, A.,” The Bipyridylium Herbicides. Effects on Man”, *Advances in Pest Control Research. In: Metcalf, R.L. (Ed.), Interscience Publishers*, vol. 8, 1968, pp. 224.

[14] Cheah U., Kirkwood R.C. and Lum K., “Degradation of four commonly used pesticides in Malaysian agricultural soils,” *J. Agric. Food Chem*., vol. 46(3), 1998, pp. 1217.

[15] Cheah, U-B.; Kirkwood, R. C.; Lum, K.-Y.; *J. Agric. Food Chem.* Vol. *46*, 1998, pp. 1217.

[16[Chopra, RN, “*Green revolution in India,”* Intellectual Publishing House, New Delhi, 1985.

[17] Dr. Dharmendra Kumar “Use Of Photo-Fenton Reagent For The Degradation Of Thioglycolic Acid” *International Journal of Analytical, Pharmaceutical and Biomedical Sciences, Available online at www.ijapbs.com* Research article,Vol: 3: Issue-3: July-Sept-2014

[18] D.W. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat, N. Serpone, in: G.R. Heltz, R.G. Zepp, D.G. Crosby, (Eds.), Aquatic and Surface Photochemistry, Lewis Publishers, Boca Raton, FL, 1994, pp. 261.

[19] Dhaouadi, A., Adhoum, N., 2009. Degradation of Paraquat herbicide by electrochemical advanced oxidation methods, J. Electroanal. Chem., 637, pp. 33–42.

[20] Dileep Kumar A. D., “Conditions of paraquat use in india,” *Report*, April 2015.

[21] Du, D., Huang X., Cai, J. and Zhang, A. (2007). Amperometric detection of triazophos pesticide using acetylcholinesterase biosensor based on multiwall carbon nanotubechitosan matrix. Sensors and Actuators. B: *Chemical ,B* 127 (2),pp. 531- 535.

[22] Ekkachai kanchanti, ponghatwat khemtong, jitlada chumee, nurak grisdanurak, “Characterization of C_{60} modified V-Tio_2 Prepared by chelation method for degradation of paraquat,” *Asia pacific regional conference on particle environmental technologies*, March 2010.

[23] FAO of united nation, “specifications and evaluations for paraquat dichloride,” Available at http://www.fao.org/agriculture/crops/core-themes/theme/pests/jmps/en/.

[24] Farabi Barna, sh., 2011. Towars decomposition of phosphonates in water using catalytic membranes: paraquat on silica as a proxy, M.Sc. Thesis, University of Illinois at Urbana-Champaign.

[25] Florêncio, M.H., Pires, E., Castro, A.L., Nunes, M.R., Borges, C., Costa, F.M., 2004. Photodegradation of diquat and paraquat in aqueous solutions by titanium dioxide: evolution of degradation reactions and characterisation of intermediates, Chemosphere. 55: 345–355.

[26] Gavrilescu M, "Fate of Pesticides in the Environment and its Bioremediation*," Engineering in Life Sciences*, vol. 5, 2005, pp. 497-526.

[27] Giacomazzi S, and Cochet N, "Environmental Impact of Diuron Transformation: *a Review. Chemosphere*," vol. 56, 2004, pp. 1021-1032.

[28] Hance R.J., Byast T.H. and Smith P.D., Apparent decomposition of paraquat in soil, *Soil Biol. Biochem*., vol. 12, 1980, pp. 447.

[29] Hance, R. J.; Byast, T. H.; Smith, P. D. Apparent decomposition of paraquat in soil. Soil Boil. Biochem, vol. 12, 1980, pp. 447- 448.

[30] Hassan Shahgholi and Ahmad Gholamalizadeh Ahangar, "Factors controlling degradation of pesticides in the soil environment," Available at *www.tijournals.com,* Agric. *sci. dev*., Vol(3), No (8), August, 2014. pp. 273-278.

[31] Hertzmann, C., Wiens, M., Bowering, D., Snow, B. and Calne, D. Parkinson's disease: a case-control study of occupational and environmental risk factors, American *Journal of Industrial Medicine* 17(3), pp. 349 – 355.

[32] Hoffmann, H.R., Martin, S.T., Choi, W. and Bahnemann, D.W., "Environmental Applications of semiconductor Photocatalysis," Chem. Rev., 95,69 (1995).

[33] J.M.Vargas, jr. "PESTICIDE DEGRADATION," *Journal of Arboriculture* December 1975.

[34] Jones WJ, and Ananyeva ND, "Correlations between pesticide transformation rate and microbial respiration activity in soil of different ecosystems," BiolFertil Soils, vol. 33, 2001, pp. 477–483.

[35] Kambhampati, K.S., Roinestad, T.G., Hartman, J.D., Rosen, E.K., Fukuda, R.L. Lippincott, R.T. and Rosen. (1994). Determination of diquat and paraquat in water using high-performance liquid chromatography with confirmation by liquid chromatography-particle beam mass spectrometry, *J. Chromatogr. A* 688, pp.67 - 73.

[36] Kanchanatip, E., Grisdanurak, N., Thongruang, R., Neramittagapong, A., 2011. Degradation of paraquat under visible light over fullerence modified V-TiO_2, React. Kinet. Mech. Catal. 103, pp. 227-237.

[37] Kearney and D.D. Kaufmann. New York, N.Y.: Marcel Dekker, Inc. (Reprint; also in unpublished submission received Aug 22, 1977 under 239-1663; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:231430-D)

[38] Khan, *S.* U. Interaction of bipyridylium herbicides with organoclay complex. *J.* Soil Sci. vol. 24, 1973, pp. 244-248.

[39] Koivunen M.E., Gee S.J., Park E.K., Lee K., Schenker M.B., and Hammock B.D., "Application of an enzyme linked immunosorbent assay for the analysis of paraquat in human sample," *Arch. Environ. Contam.Toxicol.*, vol. 48, 2005, pp. 184.

[40] Kori-Siakpere, O., K. Adamu and J. Okenabirihie, "Sub-lethal effects of parequat on some plasma organic constituents (metabolic parameters) of African Catfish": *Clarias gariepinus.* Int. J. Zoo Res., vol. 3, 2007, pp. 213-217.

[41] Legrini, O., Oliveros, E. and Braun, A.M., "Photochemical Processes for Water Treatment," *Chem. Rev.*, vol. 93, 1993, pp. 671.

[42] Lock, E.A., Wilks, M.F., 2010. Chapter 83, "Paraquat, Hayes' Handbook of Pesticide Toxilogy", Elsevier Inc.

[43] M. Muneer, D. Bahnemann, Appl. Catal. B: Environ. 36 (2002) 95.

[44] Mackinnon, D.S. and B. Freedman, "Effects of silvicultural use of the herbcide glyphosphate on breeding and regenerating," *Can. J. Appl. Ecol.*, vol. 30, 1993, pp. 395-406.

[45] Maria Aparecida Marin-Morales, Bruna de Campos Ventura-Camargo and Márcia Miyuki Hoshina, "*Toxicity of Herbicides: Impact on Aquatic and Soil Biota and Human Health*," Available at http://dx.doi.org/10.5772/55851, 2013, pp. *978-953*.

[46] Mechanism of TiO_2 Available at:

http://www.abolinco.com/downloads/downloads/What_is_Photocatalyst.pdf

[47] Meriel Watts, "Paraquat," *link http:// www.stop-paraquat.net,* February 2011.

[48] Moctezuma, E., Leyva, E., Monreal, E., Villegas, N., Infante, D., 1999. Photocatalytic degradation of the herbicide “paraquat”, Chemosphere. 39: 511–517.

[49] Mota, A.L.N., Albuquerque, L.F., Beltrame, L.T.C., Chiavone-Filho, O., Machulek, J.A.,

[50] Nascimento, C.A.O., “Advanced oxidation processes and their application in the petroleum industry,” *A review, Braz. J. Petrol. Gas*, vol. 2, 2008, pp. 122-142.

[51] N. Serpone, E. Pelizzetti, Photocatalysis, Fundamentals and Applications, Wiley, New York, 1989.

[52] N.C. Posecion, E.M. Ostrea, D.M. Bielawski, J. Chromatogr. B862 (2008) 93–99.

[53] Oliveira, C., Santos, M.S.F., Maldonado-Hodar, F.J., Schaule, G., Alves, A., Madeira, L.M., 2012. Use of pipe deposits from water networks as novel catalyst in paraquat peroxidation, Chem. Eng. J. 210: 339-349.

[54] Oturan, M.A., Brillas, E., 2007. Electrochemical Advanced Oxidation Processes (EAOPs) for environmental applications, Portug. Electrochim. Acta. 25:1-18.

[55] Posecion N.C, Ostrea E.M, and Bielawski D.M., “Quantitative determination of Paraquat in Meconium by Sodium Borohydride- Nickel chloride chemical reduction and Gas chromatography/ Mass Spectrometry,” *J.Chromatogr.* vol. B862 (1-2), 2008, pp. 93.

[56] Punjab State Council for Science and Technology , “*State of Environment Punjab*,” Chandigarh: Punjab State Council for Science and Technology, 2007.

[57] Rand, G.M. and A.D. Petrocelli, “Fundamentals of Aquatic Toxicology,” *Hemisphere Publishing Corp., Washington, D.C.*, 1985, pp. 352-376.

[58] Reetinder Kaur and A. K. Sinha, “GLOBALIZATION AND HEALTH: A CASE STUDY OF PUNJAB**,”** *Journal of Studies and Research in Human Geography,* 2011, pp. 35-42.

[59] Safarzadeh-Amiri, A.; Bolton, J. R.; Carter, S. R.; *J. Adv. Oxid. Technol.* **1996**, *1*, 8.

[60] Saltmiras, D.A., Lemley, A.T., 2002. Atrazine degradation by anodic Fenton treatment, Water Res. 36: 5113–5119.

[61] Santos, M.S.F., Alves, A., Madeira, L.M., Paraquat removal from water by oxidation with Fenton’s reagent, Chem. Eng. J. vol. 175, 2011, pp. 279– 290.

Shetty, PK , 'Socio-ecological implications of pesticide use in India', *Economic and Political Weekly,* vol. 39 (49), 2004, pp. 5261-5267.

[62] Shiva, V, "*The Violence of the Green Revolution,"* Zed Books, New York, 1991.

[63] Shivhare, P. and Gupta, V.K. (1991). Spectrophotometric method for the determination of paraquat in water, grain and plant materials, *Analyst 116,* 391.

[64] Syngenta Australia Pty Ltd, "*The economic impact of Paraquat*," Available at www.deloitteaccesseconomics.com. August 2013.

[65] T.J. Haley, Clin. "Toxicol," Vol. 14 , 1979, pp. 1–46.

[66] Thakur, JS, Rao, BT, Rajwanshi, A, Parwana, HK, & Kumar, 'Epidemiological study of high cancer among rural agricultural community of Punjab in Northern India', *International Journal of Environmental Research and Public Health* vol. 5, 2008, pp. 399-407.

[67] Tirado, R, "*Chemical fertilisers in our water,"* Greenpeace Society, India, 2009.

[68] Tomlim, C. D. S.; *The Pesticide Manual*, 12th ed.; British Crop Protection Council: UK, 2000.

[69] Topp E, Vallayes T, and Soulas G, Pesticides: Microbial degradation and effects on microorganisms. In: Modern soil microbiology, 1997, pp. 547–575.

[70] UNEP. 1999. Interim Secretariat for the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade. United Nations Environment Programme. weblnk http://www.pic.int/en/Circular/CIRC10EN.pdf. PIC CIRCULAR X - December 1999.

[71] United States Environmental Protection Agency (USEPA), "Pesticides in the Environment. Office of water," *US, Environmental Protection Agency, Washington D.C.* 2007.

[72] United States Environmental Protection Agency archive document, "*R.E.D. FACTS Paraquat Dichloride*," August 1997.

[73] V. Augugliaro, L. Cavallero, G. Marc`ı, L. Palmisano, E. Pramauro, "*Stud. Surf. Sci. Catal."* Vol. 82, 1994, pp. 713–720.

[74] V. Maurino, C. Minero, E. Pelizzetti, M. Vincenti, Coll. Surf. A 151, 1999, pp.329.

[75] Walker A., Jurado- Exposito M, Bending GD, and Smith V J R,”Spatial variability in the degradation rate of isoproturon in soil,” *Environmental Pollution* vol. 111, 2001, pp. 407±415.

[76] Wang, S., 2008. A Comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater, Dyes and Pigm. 76(3): 714-720.

[77] Wang, Y.; Yen, J.; Hsien, Y.; Chen, Y.; *Water, Air, Soil Pollut.* Vol. *72*, 1994, pp. 1.

[78] Water Cycle Available at http://www.jointheevolution.ca/blog/2009/06/22/the-water-that-flows-part-1/

[79] WHO, Environmental Health Criteria 39: Paraquat and diquat. World Health Organization, Geneva, 1984.

[80] Wise guy report, “Paraquat dichloride Global Market and Forecast Research,” link www.wiseguyreports.com, June 2015.

[81] Woo kim, Joon-Chul Lee, Moon sun kim, Gui young han, Ki june yoon, “Removal of paraquat in aqueous suspension of TiO_2 in an immersed UV phoreactor”, *korean J. Chem. Eng.*, vol. 20(5), 2003, pp. 862-868.