

**USE OF COUPLED PHOTOCATALYSIS AND PHOTOFENTON  
PROCESSES FOR DEGRADATION OF CONTAMINATED SOIL**

**A PROJECT REPORT**

*Submitted in partial fulfilment of the requirements for the award of the  
degree*

*of*

**BACHELOR OF TECHNOLOGY**

**IN**

**CIVIL ENGINEERING**

*Under the supervision of*

**Dr. Saurabh Rawat**

**(Assistant Professor)**

*by*

**Shivam Nag [161666]**

**Siddharth Verma [161686]**

*to*



**JAYPEE UNIVERSITY OF INFORMATION TECHNOLOGY**

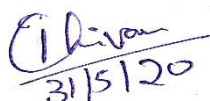
**WAKNAGHAT, SOLAN – 173234**

**HIMACHAL PRADESH, INDIA**

**MAY-2020**

## STUDENT'S DECLARATION


I hereby declare that the work presented in the Project report entitled  
**“USE OF PHOTO CATALYSIS AND PHOTO FENTON TO PURIFY SOIL”**  
submitted for partial fulfilment of the requirements for the degree of Bachelor of Technology in Civil Engineering at **JAYPEE UNIVERSITY OF INFORMATION TECHNOLOGY, WAKNAGHAT** is an authentic record of my work carried out under the supervision of **DR. SAURABH RAWAT**. This work has not been submitted elsewhere for the reward of any other degree/diploma. I am fully responsible for the contents of my project report.

  
31/5/20

**Shivam Nag**

**161666**

Department of Civil Engineering  
Jaypee University of Information  
Technology, Wagnaghat, India

  
31/5/20

**Siddharth Verma**

**161686**

Department of Civil Engineering  
Jaypee University of Information  
Technology, Wagnaghat, India

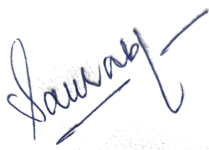
**Dated:** 30 May 2020

## CERTIFICATE

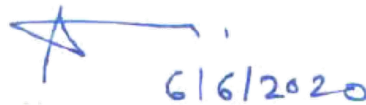
This is to certify that the work which is being presented in the project report titled “**USE OF PHOTO CATALYSIS AND PHOTO FENTON TO PURIFY SOIL**” in partial fulfilment of the requirements for the award of the degree of Bachelor of Technology in Civil Engineering submitted to the Department of Civil Engineering, **JAYPEE UNIVERSITY OF INFORMATION TECHNOLOGY, WAKNAGHAT** is an authentic record of work carried out by **SHIVAM NAG (161666) SIDDHARTH VERMA (161686)** during a period from August, 2019 to May, 2020 under the supervision of **DR. SAURABH RAWAT** Department of Civil Engineering, Jaypee University of Information Technology, Wagnaghat.

The above statement made is correct to the best of our knowledge.

**Date:** 30<sup>th</sup>.May. 2020



Signature of Supervisor  
Dr. Saurabh Rawat  
Assistant Professor  
Department of Civil Engineering  
JUIT, Wagnaghat



Signature of HOD  
Prof. Ashok Kumar Gupta  
Head of Department  
Department of Civil Engineering  
JUIT, Wagnaghat

External Examiner

## **ACKNOWLEDGEMENT**

It has been a wonderful and intellectually stimulating experience working on “**USE OF PHOTO CATALYSIS AND PHOTO FENTON TO PURIFY SOIL**” which gives us full knowledge and innovative ideas in this field.

We gratefully acknowledge the management and administration of **JAYPEE UNIVERSITY OF INFORMATION TECHNOLOGY** for providing us the opportunity and hence the environment to initiate and complete the project till now.

We would like to express our sincere gratitude to our project guide **DR. SAURABH RAWAT**, Assistant Professor, Department of Civil Engineering at Jaypee University of Information Technology for his guidance regarding this project.

Shivam Nag (161666)

Siddharth Verma (161686)

# **TABLE OF CONTENTS**

	Page No.
DECLARATION	i
SUPERVISOR'S CERTIFICATE	ii
ACKNOWLEDGEMENT	iii
ABSTRACT	vii
LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF ABBREVIATION	x
<b>CHAPTER</b>	<b>DESCRIPTION</b>
<b>1.</b>	<b>INTRODUCTION 1-7</b>
1.1	General 1
1.2	Process to purify contaminated soil 2
1.2.1	Bioremediation 2
1.2.2	Photocatalysis 4
1.2.3	Fenton-process 6
1.3	Organization of the report 7
<b>2.</b>	<b>LITERATURE REVIEW 8-18</b>
<b>3.</b>	<b>MATERIAL AND METHODOLOGY 19-37</b>
3.1	General 19
3.2	Pond Ash 19
3.3	Soil Sampling 20
3.4	Preparation of Soil Sample 22
3.5	Materials and Apparatus 24

3.5.1	Titanium dioxide	24
3.5.2	EDTA	24
3.5.3	Hydrogen peroxide	26
3.5.4	Ferrous Sulphate heptahydrate	26
3.5.5	Propanol	27
3.6	Apparatus	28
3.6.1	Degradation Chamber	28
3.6.2	UV-Lamp setup	29
3.7	Use of Hydrogen peroxide	31
3.8	Preparation of sample	32
3.8.1	Preparation of TiO <sub>2</sub> sample	32
3.8.2	Action of FeSO <sub>4</sub> .7H <sub>2</sub> O, EDTA and Propanol	33
3.8.3	Preparing setup for UV action	35
<b>4.</b>	<b>RESULTS &amp; DISCUSSION</b>	<b>38-41</b>
4.1	Pond ash samples degradation test results	38
4.2	Result of un-purified sample	40
4.3	Inference of test results	40
<b>5.</b>	<b>CONCLUSION</b>	<b>42-43</b>
5.1	General	42
5.2	Conclusion	42
5.3	Future scope	43
<b>6.</b>	<b>REFERENCES</b>	<b>48-52</b>

## ABSTRACT

Soil is the one of the most extensive part of civil engineering. Every structure from minor to a super structure is built over the soil, not even from the perspective of civil engineering soil is also necessary for the survival of all living beings on earth, for agricultural practices. So the quality and purity of the soil is an important parameter to be achieved from the perspective of agriculture practices as well as humans health. Soil provides shelter to various living beings and helps in maintaining the balance in ecosystem, so it is important to prevent soil from contamination and photo catalysis and photo Fenton are the two useful processes which helps in purification of soil containing heavy metals.

Heavy metals are toxic to soil, plants, aquatic life and human health if their concentration is high in the compost. Heavy metals exhibit toxic effects towards soil biota by affecting key microbial processes and decrease the number and activity of soil microorganisms. Advanced oxidation processes (AOPs), namely photo-Fenton, Fenton-like, Fenton and UV/H<sub>2</sub>O<sub>2</sub>, have been investigated in the removal of organic matter and colour from landfill leachates. The leachate was characterised by high COD, low biodegradability and intense dark colour. Evaluation of COD removal as a function of the operation variables (H<sub>2</sub>O<sub>2</sub>, Fe<sup>2+</sup>, Cu<sup>2+</sup>, UV) led to results that ranged between 28% and 75% and it was observed that the removal efficiencies decreased in the order: photo-Fenton > Fenton-like > Fenton > UV/H<sub>2</sub>O<sub>2</sub> > UV. Thus, a detailed experimental analysis was carried out to analyse the effect of the hydrogen peroxide and iron concentrations and the number of reagent additions in the photo-Fenton process, observing that: (i) the COD removal ranged from 46% to 77% depending on the H<sub>2</sub>O<sub>2</sub> dose, (ii) the total amount of organic matter removed was increased by adding the reagent in multiple steps (83%), (iii) iron concentration corresponding to a Fe<sup>2+</sup>/COD mass ratio = 0.33 was found to be the most favourable and, (iv) after a neutralization step, the colour and residual concentrations of iron and H<sub>2</sub>O<sub>2</sub> were practically negligible in the final leachate solution.

*Keywords:* Advanced oxidation processes; Purified soil; ecological cycle; photo catalysis; COD removal; Landfill leachate; Photo-Fenton process, heavy metals.

## LIST OF TABLES

<b>Table No.</b>	<b>Caption</b>	<b>Page No.</b>
3.1	Equipment used for soil sampling	22
3.2	Materials used for preparing initial sample	23
3.3	Chemicals used in the reactor chamber	28
3.4	Specifications of UV-tube	31
3.5	Soil samples and their description	37
4.1	Heavy metal test results for sample 1 purified	38
4.2	Heavy metal test results for sample 2 purified	39
4.3	Heavy metal test results for sample 3 purified	39
4.4	Heavy metal test result for un-purified sample.	40



## LIST OF FIGURES

<b>Fig. No.</b>	<b>Caption</b>	<b>Page No.</b>
1.1	Bioremediation process in contaminated soil	3
1.2	Decomposition of TiO <sub>2</sub> to form free radicals to perform photocatalysis	5
1.3	Catalytical decomposition of H <sub>2</sub> O <sub>2</sub> to form OH ion	7
3.1	NTPC Ropar Ash pond site	20
3.2	Sample collection in a tight bucket	21
3.3	Unit meter square area for sampling	21
3.4	Pond ash solution	23
3.5	Titanium dioxide (TiO <sub>2</sub> ) 99.0% AR	24
3.6	EDTA as a chelating reagent	25
3.7	Hydrogen peroxide	26
3.8	Degradation tube	29
3.9	Wooden frame setup to place degradation tube	29
3.10	UV-lamp rod	30
3.11	UV-lamp setup inside the reactor	31
3.12	Stirring of TiO <sub>2</sub> in water	32
3.13	Gradually mixing of TiO <sub>2</sub> to avoid formation of lumps	33
3.14	Addition of EDTA	33
3.15	Addition of FeSO <sub>4</sub> .7H <sub>2</sub> O	34
3.16	Pouring of solution into prepared soil sample	35
3.17	Installation of sample under UV-light setup	35
3.18	Extraction of water from the sample using pump	36
3.19	Oven dried sample	37
3.20	Packed sample	37

## LIST OF ABRIVATIONS

<b>Abbreviation</b>	<b>Full Form</b>
<i>EDDs</i>	Ethylenediamine-N, N'-disuccinic acid
<i>XRD</i>	X-Ray Diffraction
<i>TCFR</i>	Tourmaline chyrosporium
<i>PBDE3</i>	Polybrominated Diphenyl Ethers
<i>PCBs</i>	Polychlorinated biphenyls
<i>COD</i>	Chemical oxygen demand
<i>FA</i>	Fluorapatite
<i>AOPs</i>	Advance oxidation processes
<i>AR</i>	Analytical regency

# CHAPTER 1

## INTRODUCTION

---

### 1.1. GENERAL

Combustion of coals in thermal power plants is one of the major sources of environmental pollution due to generation of huge amounts of ashes, which are disposed of in large ponds in the vicinity of the thermal power plants. These problems are very significant in nations like India where almost total thermal installed capacity is about 223 GW out of which 85% of thermal power is obtained from coal which generates a huge amount of fly ash and pond ash which contains highly toxic elements such as Mo, As, Cr, Mn, Cu, Ni, Co, Pb, Be, V, Zn. Now these contaminants when dumped on ground or site they get mixed up with soil and due to rain and seepage action they end up mixing with ground water which further contaminates the surrounding areas soil. Since the most of the thermal power plants and pond ash dump areas are located in densely populated areas, there is a huge risk of contamination of soil and the ground water of the surrounding areas from the toxic elements in the ash. The global energy demand have been increased because of rapid stride of technology and to full fill this need massive energy generation system and power plants were required and mostly they run on coal, the coal is used as a fuel in these power plant and ash is the residue generates from it which leads to the contamination of surrounding grounds. This problem is particularly important for Indian power stations because most of the power stations use poor quality coal with 7–55% ash yielding about 100 million tons of ash per annum.

The solid wastes produced from the coal fired thermal power plant are of two types: fly ash and bottom ash. Bottom ash also known as pond ash is the coarse-grained fraction that is collected from the bottom of the boiler and fly ash consist of fine sized particles size from 0.5 to 200  $\mu\text{m}$ . Due to its relatively small size and, hence, large surface area, the ashes have a greater tendency to absorb trace elements that are transferred from coal to waste products during combustion. It migrates through pores along with trace particles and end up mixing with ground water which further contaminates crop and vegetation. The major contamination starts from the depth of 15cm from the surface layer.

Coal ash contains high concentration of trace elements like Pb, Cu, As etc which affect the soil properties and the vegetation over it. In eastern portion of India almost 80% of power plants run on coal which generates tones of fly ash and pond ash which further leads to the soil contamination. The main contamination is due to the increment of heavy metal in soil which disturbs the property of the soil as well as harmful for the vegetation present on the soil surface. The enrichment of individual elements in the top soil around the ash pond was estimated with respect to the crustal abundance and also with respect to the background to show the effect of ash deposition in soil. Now the major challenge arises is how to deal with this contaminations, various processes and conditions were taken under consideration to deal with it and the most commonly used is bioremediation. It's a well-known and most practised method to purify the soil but its very time consuming and efficiency is about 60-70%. But there are some other processes like photocatalysis and photo fenton which are very effective as compare to bioremediation with an efficiency of 85-90% or may be more if we combine them together and also very time efficient.

## **1.2 Processes to purify contaminated soil**

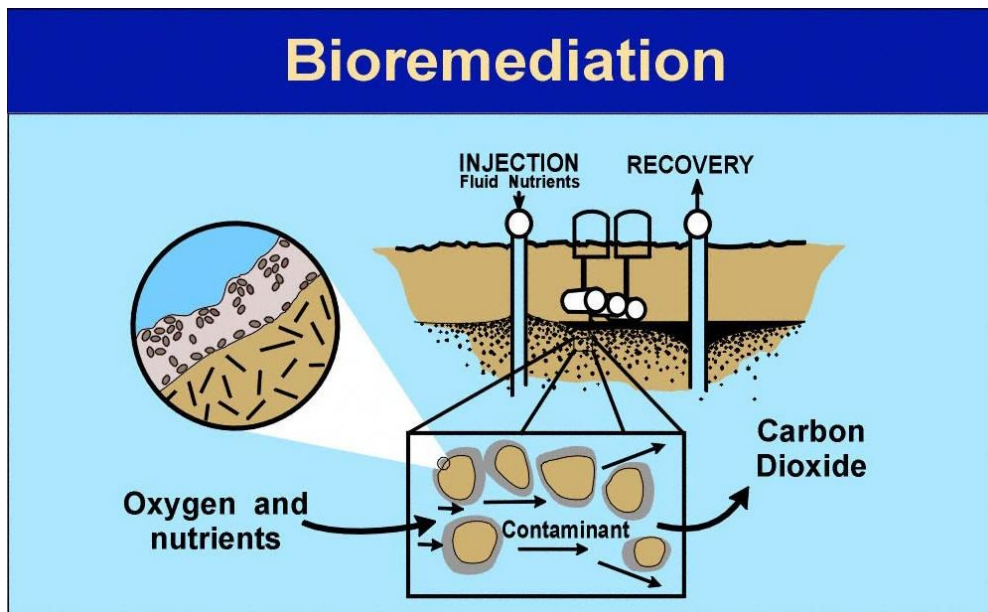
There are many processes to purify contaminated soil but, in this chapter, we mainly discussed about three methods.

### **1.2.1 Bioremediation**

It is the most commonly used process to purify soil, in this process pollutants or waste is treated with the help of microorganisms. What microbes do they break down the undesirable substances present in the soil. Its main principle is complete removal of organic toxic pollutants and convert it into harmless or naturally occurring compounds like carbon dioxide, inorganic compounds which are snug for human, animal and the vegetation around.

Bioremediation is taken out mainly in two ways i.e. **In-situ** and **Ex-situ**:

In-situ in which the process is carried out directly on the contamination site while on the other hand in ex-suit the sample is collected from the site and then taken to the desired location or laboratory to conduct the process.



**Figure 1.1 Bioremediation process in contaminated soil and oxidizing of harmful substance.**

In in-suit we have four different processes to purify the soil.

**a) Bioventing**

In bioventing to draw down the oxygen to the vadose zone of the soil to activate the microorganism present over there and thus they can decompose and breakdown the unwanted organic waste present in that portion of soil.

**b) Bio-spraying**

In bio-spraying we inject oxygen below the groundwater level to activate the microbes present in that portion of soil to breakdown the unwanted substances present in the soil.

**c) Bio stimulating**

In bio-stimulation we stimulate the microorganism in the soil by providing them nutrients so that they become active and decomposing organic waste.

**d) Bio-augmentation**

In bio-augmentation we provide the bacteria and microbes from the outside to the contaminated zone so that these microbes activate inside and start decomposing the waste and convert it into organic compound.

Similarly, in **ex-suit** there are four type of processes.

**a) Compositing**

In compositing we use non-hazardous organic amendments like manure, organic waste which helps in increasing the population of microorganism so that they perform their work of decomposing of organic waste.

**b) Land farming**

In land farming we mix the contaminated soil with the purified soil and done farming over it so that the demand of oxygen in contaminated soil can be fulfilled due to which the microbes present in it can perform their work easily and oxidized the organic waste present in it.

**c) Bio-piling**

In bio-piling we generate the enough amount of pressure by inserting pipe inside the soil that can trigger the action of microbes and thus they can decompose the hazardous waste.

**d) Bioreactor**

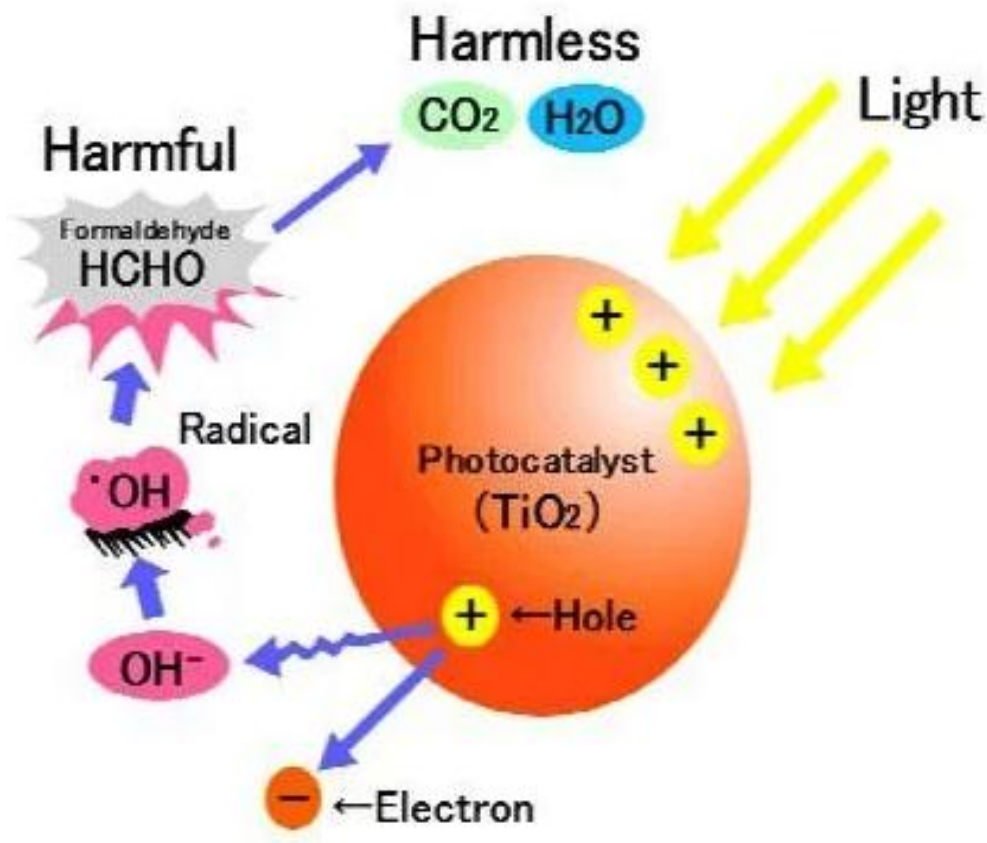
Bioreactor is an electronic device or a system of devices which support biological activities, it is also called fermenter in which we obtained a new product with the help of microorganisms. Its vessel in which chemical reaction takes place due to the action of microbes to generate new product. The proceeds in the various steps, first we provide nutria for the growth of microbes and to increase the growth of microbes we have to perform certain chemical reaction s which takes place inside the reactor and finally proceed with the increased population of microbes. Now these are the various ways to conduct bioremediation, but there are some flaws are also associated with it like it's a biological process therefore its very time consuming also it is not very effective in removal of heavy metal which is a very major disadvantage is associated with it, another this is it requires a lot of labour work.

### **1.2.2 Photocatalysis**

Photocatalysis was first discovered in Japan by professor Fujishima of university of Tokyo in 1976, when he accidentally discovered the splitting of water into hydrogen and oxygen when titanium dioxide powder is irradiated with light.

In photocatalysis when light radiation from sunlight or fluorescent light is irradiated on titanium dioxide a strong powerful decomposition is generated on the surface of titanium dioxide by its properties which decomposes hazardous waste on it until it becomes harmless. Photocatalysis effect is almost permeant effect.

When light energy is radiated over the surface of  $\text{TiO}_2$  electrons are released, the released electrons binds with the oxygen in the air to form superoxide anion and the surface of titanium oxide becomes positively charged and takes electrons from the moisture present in the air and the moisture that has loss electrons becomes hydroxyl radical than the superoxide anion and hydroxyl radical by their power of oxidation decompose organic compounds such as oil, unwanted bacteria, hazardous gases, fungus etc turn them into water or any other harmless substance.

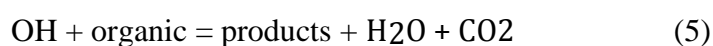
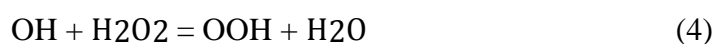
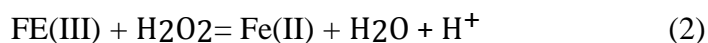
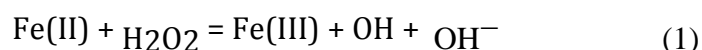


**Figure 1.2 Decomposition of  $\text{TiO}_2$  to form free radicals to perform photocatalysis**

TiO<sub>2</sub> photocatalysis is widely use in various fields but mainly use in sanitizing processes which includes cleaning, oxidizing, water purification system, soil purification. Photocatalysis is a surface phenomenon in which the main action takes place on the surface of the reagent. It is a very promising technology and has so many applications and helpful technique to efficiently removal of hazardous waste from our surrounding environment.

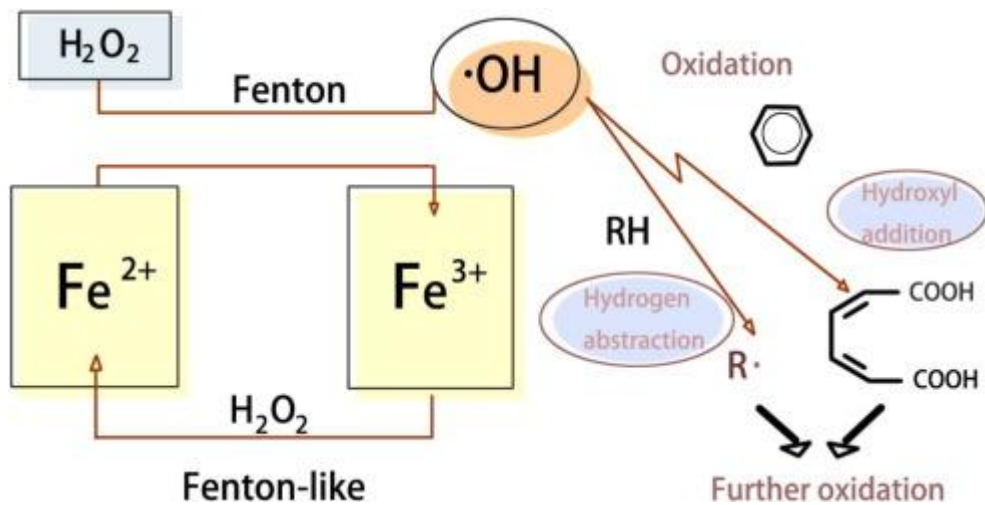
### 1.2.3 Fenton processes

Fenton Technology is a smart, efficient and time saving technology and hence a promising method for treatment processes. It basically uses Hydrogen peroxide as an oxidant, and Fe<sup>2+</sup> as a catalyst here, and when the reaction takes place, the H<sub>2</sub>O<sub>2</sub> undergoes more of a catalytic decomposition, in the presence of Fe<sup>2+</sup> and it makes more of a chain reaction here. The reactions are as follows-



In more simplified form the reaction starts like H<sub>2</sub>O<sub>2</sub> undergoes more of a catalytic decomposition in the presence of Fe<sup>2+</sup> and OH is generated. The optimum pH required or this reaction is 2.8-3.0, because at this pH, the Fe<sup>3+</sup>/Fe<sup>2+</sup> can undergo catalytic changes and change in pH could spoil that. The major point to notice here is that these reactions can be performed at room temperature and ordinary pressures, so no extra setup is required for the same. Hence, these factors enable it to be used in abundance for the treatment of variety like pesticide, pharmaceutical, laboratory and fermentation to name a few. Still it has some limitation like, high costs of reagents in the process, high volume of iron sludge required, that need to be sorted out to bring the best out of it.





**Figure 1.3 Catalytic decomposition of  $\text{H}_2\text{O}_2$  to form  $\text{OH}$  ion**

### 1.3 ORGANIZATION OF THE REPORT

- 1) Chapter 2 it's the review about the literatures, studies and researches that we have followed and studied during the course of this project.
- 2) Chapter 3 is about the methodology and the procedure that has been followed in the research.
- 3) In chapter 4 we discuss the results and outcomes of this research.
- 4) Chapter 5 is the conclusion of the respective results and the procedure has been followed to achieved these results.

## **CHAPTER 2**

### **LITERATURE REVIEW**

---

#### **2.1 GENERAL**

There are various studies, articles and news reports which shows that how our action disturbing the surrounding environment and soil contamination is one of the major issues arising today. Many studies have been done and various methods and processes have been developed to overcome this problem, no doubt these methods and processes are very effective in conquering these complications. The main objective of this literature review is to provide in-depth knowledge about mechanism and the procedures followed in resolving this problem. The following studies have been promoted the concept photocatalysis and Fenton process and their application in purification of contaminated soil.

#### **2.1 PREVIOUS STUDIES**

Neil and Nzegung (2004) studied the effective in-situ bioremediation and phytoremediation technique which was developed to remove perchlorates and chlorinated volatile organic compounds (CVOCs) e.g. trichloroethylene, methylene, 1,1-dichloroethane. A new surface technology has been developed known as “Surface application and mobilization of nutrients” (SAMNA). In this technique a suitable carbon source is provided to trigger the population of microbes which further decompose these volatile organic compounds. Organic manure like cow dung, horse manure, ethanol, methanol is also use for rapid action of microbes. More than 70% of hazardous substances has been removed within a few months. Some of the key points from their study are:

The study has been conducted in 6 different plots each of dimension 4.50 x 2.75m and the rate of degradation of perchlorate from the top layer of soil is approximately 7mg/kg soil/day.

#### **2.2 PREVIOUS STUDIES**

Liang and Liu (2010) examined the degradation of Formaldehyde (HCHO) with the help of UV-Fenton process. We briefly studied the fenton process and its application along with the UV light. The process become more significant with the use of hydrogen peroxide

(H<sub>2</sub>O<sub>2</sub>), in this reaction H<sub>2</sub>O<sub>2</sub> consumed exponentially which affect the decomposition rate of fenton action which is rapid than addition of 2Fe<sup>+</sup> and the UV light to the system.

**Key points: -**

The photo-fenton reaction activates the ferrous ion (Fe<sup>2+</sup>) to react with hydrogen peroxide under the presence of UV-light, which forms very strong oxidizing reagents known as hydroxy radicals (-OH) which helps in the degradation of hazardous particles.

### **2.3 PREVIOUS STUDIES**

Satyro & Marotta et al. (2016) studied about the properties of chelating agent, how they react with the metal ions to form water soluble complex. The technique of soil washing is a very effective method to deal with the heavy metals like Cu, Zn, Fe etc along with the photocatalysis in a combined form.

The photocatalysis is carried out by using UV-lights along with the titanium dioxide to oxidize the harmful heavy metals from the soil. The chelating agent most frequently use for soil washing is ethylenediaminedisuccinic also known as EDDS. The main aim of using UV-lamps is to improve the heavy metal removal efficiency from the soil.

**Key points: -**

The washing is carried out in ideal conditions like the pH should lies between 7-7.5 and the solution ratio (L/S) is 10:1, the sample is shaken in a mechanical shaker at 190 rpm for the proper mixing of the chemicals into the solution.

### **2.4 PREVIOUS STUDIES**

Matavos and Moussavi (2017) studied the advancements in the field of improving and treating of various environmental pollution sources like soil and various wastewater sources by using Fenton and Fenton-based systems as the solution for treating these pollution sources and how these oxidation process degrade the harmful pollutants so that they can be disposed of properly.

So, by undergoing the complex catalytic reactions of oxidation processes, activation of H<sub>2</sub>O<sub>2</sub> by Fe salts, in other words, called Fenton's reagent, which allowed the generation of OH radicals, which gave the breakthrough of elimination of these pollutants.

Key points: -

1. High efficiency of OH radicals that converted the pollutants into non-toxic CO<sub>2</sub>.
2. No complex conditions were required as these radicals were generated at normal conditions of temperature and pressures.
3. Fenton reaction involves rapid release of radicals owing to the short reaction time involved with the reaction, hence enabling it to become quite favourable for use.
4. Very cost effective, easy to use and continue with, and moderately reactive, which made it practical for use.

## **2.5 PREVIOUS STUDIES**

Li and Wang et al. (2016) studied the combined technology of Tourmaline Fenton like reaction (TCFR) alongwith the Phanerochaete Chyrosporium (TCFR+P) for the soil remediation process of soil containing contaminated Polybrominated Diphenyl Ethers (PBDEs). PBDEs are organobromide compounds commonly employed as flame retardants in variety of products in circuits, textiles etc. But they pose a great threat as they are quite dangerous and serious threat to life.

So, for this test on PBDEs, a remediation process was conducted in a period of 70 days, and the conclusion derived was that TCFR was instrumental in removing these compounds with low Br atoms concentration, while TCFR+P was good with high Br atoms concentration. Added to this, it was derived that both these methods were in-fact valuable as they improved the soil properties like SOM content, aromaticity, polarity index etc. which in turn paved a way for the removal of PDEs.

## **2.6 PREVIOUS STUDIES**

Zaho & Dong et al. (2016) the purification of PCBs contaminated soil which is mainly due to the capacitor oil. The removal of PCBs by normal water- based processes is quite difficult because of its non-aqueous nature, PCBs exist as a non-aqueous phase liquid due

to which they have low solubility and slow dispersion rate in aqueous medium and thus difficult to remove.

Fenton reaction is proceeds to oxidize PCB28 in soil wash along with the formation of Fe<sup>3+</sup> free radicals which plays the main role in detoxification of PCBs.

Key points: -

The chemical used in the process are Brij 58, Brij 30, Tween 80 and 2-hydroxypropyl- $\beta$ -cyclodextrin which enhance the solubility of 2,4,4'-trichlorodiphenyl.

The fenton process develops free radicals which plays a major role in the reaction and act as a catalyst.

## **2.7 PREVIOUS STUDIES**

Villa & Trovo et al. (2009) studies about the coupled action of soil washing and photo-Fenton in purification of soil contaminated with *p,p'*-DDT (DDT) and *p,p'*-DDE (DDE) and its significant success in removal of diesel waste from the soil.

The process is proceeded with three subsequent wash using TX-100 in aqueous solution at different concentration to obtain wastewater solution each having different concentration and this waste water is further treated with photo-Fenton process under the presence of solar light.

The results were very significant about 90% of efficiency has been achieved for DDT and DDB and almost 100% for diesel waste.

Key points: -

Along with diesel waste heavy metals like Pb, Cr, Ni, Cd were also removed and the dissolved organic carbon content is also decreased at a very significant rate almost about 90-95% of degradation is observed.

## **2.8 PREVIOUS STUDIES**

Zhang and Tong et al. (2010) studied the aspects of using the combination of soil washing treatment followed by some chemical stabilization that was achieved by using EDTA as a chelating agent. The main objective here, to investigate whether soils treated with EDTA washing, and chemical stabilization and to check the feasibility of this method.

The techniques available are mainly differentiated into two groups; namely separation i.e. soil washing, and immobilization such as chemical stabilization. The main purpose of this combined method was to use this method in a way that the contaminants could be separated from the bulk using soil washing techniques by dissolving them into a solution and then separating them from soil by concentrating them into a smaller volume. Then the work of EDTA comes up, or Ethylenediaminetetraacetic acid, comes up, as a washing agent that increases their dissolution and mobilizes but, still some portion is left in the residue part on the account of them being weakly absorbed, hence more easily leachable, whilst the use of chemical stabilizers comes up. These chemicals react with the metal fractions to immobilize them. But these are required in much larger quantities, which may not be good on costs. Hence, it is a plausible method, with soil washing eliminating them to be cornered, and eventually EDTA and chemicals discarding them off. But the problem of cost effectiveness is still a major problem here.

## **2.9 PREVIOUS STUDIES**

Sun and Wang et al. (2011) studied the toxification of soil due to the presence of heavy metals in the soil, preferably for this study sands and clays were taken. With the constant development and industrialization, human wastes continue to be invested directly and indirectly into soils, posing a difficult problem to everyone about their disposal and secondly, a threat to all with their toxicity problems. The points of significance here are-

1. Microbial activity of any kind cannot decompose heavy metals.
2. They could very easily seep into the soil and into the crops too.
3. Underground water pollution a big risk to all.

Hence, a major breakthrough had to be attained for the successful removal of these heavy metals from the soil, and just relying on methods of dilution and purification wasn't going to do any good. Hence, a need was there to take up more chemical methods of treatment to solve the big issue. As a result, chemical leaching techniques were taken into account as they enjoy having a good status in the heavy metal reduction techniques. In this, a variety of chelating agents, accompanied by an eluent, like an acid, accompanied by a reducing agent was taken up. In this, oxidation was taken into account, and an effort was made to remove them from surface using surfactants. In this process, a small amount of solvent significantly decreases the surface tension, eventually decreasing the hydrophilic and adsorption properties. As the metal atoms need to achieve a stable state, but solvent

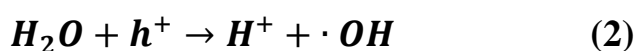
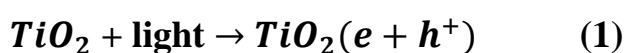
doesn't allow them to do this. The metal ions don't form lipophilic groups so that they may seep with the water groups. Hence, using this lucrative feature, surfactants can achieve the removal of heavy metals from sediments into the water phase, therefore enabling it for testing of this feature in soils too.

## 2.10 PREVIOUS STUDIES

Wahyuni and Siswanta et al. (2017) studied the removal of Heavy metals in wastewater through Photo-Fenton method. Metals like lead especially, are the main reasons for a majority of harmful effects in humans like organ and brain damages, mental retardation, a majority of them temporary which may even lead to death. So, there is a desperate need to get rid of these properly. These heavy metals were found frequently in wastewater of manufactures of paint, batteries and metal plating industry.

Through was desperate, so techniques were employed to get a breakthrough. To remove  $Pb^{2+}$  ions present in the wastewater, various techniques of adsorption and even bioremediation techniques were taken up. Through simple and effective they were, they weren't just good enough as they didn't fully remove the toxic traits that were there hence not fulfilling the need of the hour. Therefore, a combined technique of oxidation reaction called Photocatalytic Oxidation was taken up. Basically, UV light was exposed along with the  $TiO_2$  that generates the  $OH$  radical responsible for treating the  $Pb$  ions in water.

The reactions are as follows-



## 2.11 PREVIOUS STUDIES

Moghadam and Bagheri et al. (2017) studied the elimination cadmium from the water with the help of advance chemical oxidation processes like Fenton process. A standard approach has been followed to achieve the ideal results data analysis has been carried out by using SPSS. The data analysed in four steps of experiment and each step is based on optimum pH, contact time and removal rate.

The standard pH is maintained between 5-7 and the contact time lies between 15 to 20 minutes. Cadmium is very harmful for human beings, it effects the tissues and direct contact with skin can leads to skin cancer, so getting rid of it is very necessary.

Key points: -

For first stage pH observed 5 with the contact time observed to be 20 minutes. The ratio of  $H_2O_2/Fe^{+2}$  ions is about 1.7 and about 75 to 80% of efficiency have been achieved

## **2.12 PREVIOUS STUDIES**

Singh and Chaudhary et al. (2011) studied to understand the efficiency of photocatalysis in purification of air, water, soil and surrounding environment. The treatment technology includes AOPs and solar irradiation in a combined manner to achieve magnificent results that normal methods can-not achieved.

Advantages and disadvantages of these processes have been compared and two type of reactors have been used, non-concentration reactor and concentration reactor. The analysis is made on the principle and uses of both the reactor.

Key point: -

The main applications of this technology are removal of colour, reduction of COD, decomposition of hazardous substances, treatment of heavy metals. pH plays a significant role in the oxidation of substances the pH at which the surface of an oxide is uncharged is define as zero-point charge and the prescribed Ph for  $TiO_2$  is 7.

## **2.13 PREVIOUS STUDIES**

Saud and Pant et al. (2014) studied the advantage of the  $TiO_2$  in decomposition of hazardous compound. Titanium dioxide has a very good oxidizing property especially in presence of sunlight also known as photocatalysis process in which titanium dioxide in presence of sunlight losses an electron which combines which combines with the oxygen in the air to form an oxidizing compound.

Fly ash is a by-product of coal generated thermal power plant and is very toxic if not decomposed properly, the properties of fly ash is improved further by incorporating it metals, in such way we can make it use to proceed further in the process.



Key point: -

Electrospinning utilized with the concentration of FA/TiO<sub>2</sub> and their first composition is made by mixing 1g titanium tetraisopropoxide with 2 g of acetic acid and the time of contact is about 10 minutes, further the proceed at different concentration.

## **2.14 PREVIOUS STUDIES**

Dixit and Malaviya et al. (2015) focuses on the major threats heavy metals possess as contaminants, and by using different methods of treatment and remediation, which can be successfully employed for successful treatment and removal of these metals from their depositories. Heavy metals are something quite natural and also basic to the environment, but they also possess a huge risk to everyone due their altered used in various spheres, both on human, plants and aquatic lives, and posing a greater risk to life, even risking the future generations to come. Metals like arsenic, cadmium, mercury and lead, are some of the examples of these harbingers to problems like toxicity and soil leaching. These don't get broken down easily to non-toxic forms, and even at low concentrations, are carcinogenic and mutagenic in nature. Hence, a desperate need to come up with more effective solutions towards it.

The first steps needed to be taken are to get rid of the soils containing them, and several techniques are available like oxidation, reduction, chemical precipitation etc. But they aren't effective when these metals exist in very low concentrations below 100mg/L, in fact water soluble, so these methods wouldn't do any good. Added to this, costs are high and ineffective.

To break this problem down, emphasis was laid on the process of Bioremediation. The use of the power of microorganism's ability to break matter down was taken up as a possible solution to this. To counter the low concentration problem, ions were displaced to solve the issue. Since these microorganisms developed new strategies with time against pollutants, various methods like Biosorption, bioaccumulation etc. were employed as detoxifying techniques. Also among all the other techniques, Bioremediation proves to be most effective as it seems feasible on large scale with cost effectiveness and high efficiency rates. In view of this, more advancements are being done in the process of bioremediation to make it more cheaper and safer.

## **2.15 PREVIOUS STUDIES**

Kyriacou and Pilidis et al. (2004) studied the process of combined bioremediation and Advanced Oxidation Processes (AOPs) for the treatment of wastewater containing Olive oil. This Olive Oil was discharged by the manufacturing industries pertaining to various agro-industrial activities. This wastewater contained antimicrobial activities and phytotoxic properties which resists biological degradation. As a result, numerous attempts at its disposal failed drastically. Hence, processes of AOP and aerobic pre-treatment with various types of fungi for phenol removal was tested. Firstly, the table olive processing wastewater (TOPW) was studied to know about the history and nature of these pollutants and their constituents, like olive variety, maturity and treatment etc.

This wastewater is generally disposed into water bodies, or sometimes treated in evaporation ponds where its treated by anaerobic methods, but applicable to green olives that have the characteristics of alkaline pH and high phenol content.

So, a combined method of aerobic and anaerobic biological processes, with advanced oxidation processes as the phenolic compounds, which tend to have high toxic content, can be neutralized by biological treatment method with *Aspergillus* sp., that were able to degrade phenol and remove their colour efficiently. This was done on lab scale systems of high capacities, to demonstrate high scale efficiency.

## **2.16 PREVIOUS STUDIES**

Hamerski and Moravasaki et al. (2009) studied weather the method of photocatalysis could be employed for the purification of soils particularly contaminated with oils. It is a well- known fact nowadays that oil present in the environment, along with its derivatives is the harbinger for major ecological problems in our environment. Basically, oils are classified as one of the most harmful compounds in the environment today, both having consequences in plant and aquatic life. But it's harsh to see that it's not still considered a major problem till date. This is due to the fact that the existing methods we have, are just not efficient and effective, accompanied by not time efficient, high on costs and also risk of secondary pollution.

In recent years, many tests have been done with the application of photocatalysis and solar energy, in the view of using them as a catalyst and an activator, in the process of degradation of these organic pollutants. In this photocatalytic procedure, Titanium dioxide

is mainly used as its ion electron configuration, which aided to the decomposition of the pollutants, and could be used for the purification of oil and its derivatives using titanium dioxide, modified with barium, potassium, arsenic etc.

## **2.17 PREVIOUS STUDIES**

Malto and Hernando et al. (2001) studied the various factors associated with the Photo-Fenton method and Titanium oxide catalysis in the presence of artificial light, the factors majorly being feasibility, mechanisms and the level of performance for the degradation of the pollutants. In this, artificial light in the form of UV light was employed. This setup was employed for the tests of pesticides that have been in water all back to the decades of 1950s, with their use demand increasing in high numbers. The work focuses on the major sources of these, majorly agriculture in greenhouses. The sources of pollution were mainly from agricultural practices, spraying of crops, waste water from industry, and from plant residue containing contaminants. Hence, there was a desperate need for a low cost, efficient, and on-site treatment method for pesticide-contaminated wastewater.

Alternative air stripping with activated carbon was employed, but wasn't a long-term solution. Incineration was thought of, but owing to negative public perception this idea was dropped, accompanied by high costs and proper work facility. Direct photolysis wasn't competitive due to low efficiency. Hence, Advanced oxidation Process was selected who produced the OH radical as it was the most successful one. This system makes use of systems well defined with reliability of long-term solution. In this Photo-Fenton method along-with UV light was used, photocatalysis by Titanium dioxide was done. This process was employed to one of the major pollutants, Imidacloprid ( $C_9H_{10}ClN_5O_2$ ), one of the most used pesticides in the market, and the results showed comprehensive progress in the wastewater treatment program.

## **2.2 SUMMARY OF LITERATURE REVIEW**

In this review we studied about the various methodology and processes have been followed to purify contaminated soil, water and air. In case of soil contamination, we studied contamination through dyes, capacitor oil, industrial waste and chemicals and the process used in the purification. The main target is reduction of heavy metals like Pb, As, Hg, Cr etc because they are the main reason behind the contamination of the soil.

Processes like bioremediation, phytoremediation, photocatalysis and photo-fenton has been followed in most of the researches but also have certain limitations and flaws associated with them, in terms of efficiency photocatalysis and fenton processes are much effective than the bioremediation and these processes are significant in dealing with heavy metals. The efficient use of titanium dioxide in oxidation of dyes, chemicals and oil pollutants shows how vast is this technology have become and also the combine oxidation of photo-fenton with other remediation have been used widely, some studies shows that UV photocatalysis can also be used in combination with Fenton reaction to achieve more efficiency.

### **2.3 OBJECTIVES**

The main aim of the present work is the purification of contaminated soil. There are various methodology to purify the soil as we discussed above but in this chapter we mainly focused on two methods. These processes are **PHOTOCATALYSIS & PHOTO FENTON**. Both the methods are very useful for the purification of soil.

To achieve the most effective result we use them in a combined manner and to achieve this aim following objectives have been framed: -

- a) To check the efficiency of both the process, individually as well as a combined process.
- b) To check the advantages of this process over the other process applicable in same field.
- c) To reduce the percentage of heavy metal present in the soil to maintain and stabilize the properties of soil.
- d) To check whether the remaining residue can be used as a fertilizer.

# CHAPTER 3

## METHODOLOGY

---

### 3.1 GENERAL

This Chapter deliberates the material acquisition process, which are used in this study. Methodology followed in preparation of sample, collecting method, about the apparatus and the chemicals used in the purification of soil.

### 3.2 POND ASH

Pond ash also known as the coal ash basin is a structure or we can say is a site near a coal power station to dispose the combustion residue of coal. There are mainly two type of ash generates in coal combustion: bottom ash and fly ash. The site is used as a landfill or dumping yard for the ash residue to prevent its expose in the atmosphere which is more catastrophic. How-ever there are wet scrubbers are provided which reduces the risk of airborne pollutants but the structure leads to the severe health risks to the encompassing environment. Ash pond works on the principle of gravity to separates ash particle from the waste water from the power plant. Specific gravity lies between 2.23 to 2.28 and is determined on the basis of inflow and outflow of pond ash sample. The pond ash is generally obtained as a waste in the boiler where coal is burn to generate steam, which is normally done in coal generated power plants. As it contains highly track particles hence required a safe dispose. Pond ash is a mixture of both fly ash and bottom ash the only difference between pond ash and fly ash is in their particle size.

The pond ash sample is collected from NTPC Ropar power plant, Punjab. The sample is collected in a plastic bucket and sealed with plastic tape to prevent sun exposure, to preserve the properties of the ash and also to maintain the moisture content of the ash.



**Figure 3.1 NTPC Ropar ash pond site**

### **3.3 SOIL SAMPLING**

The soil is collected from the superficial layer of the soil about 20 cm below the top surface. We select an area of 1m square with the help of measuring tape and marked the area with cord and spikes so that area should be uniform after that we excavate the top soil up to 20 cm from the top and measure the depth with the help of measuring tape.

Then we collect the sample from the superficial layer into a air tight container and seal with a plastic sheet to keep the property of the soil stable. The main contamination zone lies between 15 to 20 cm below the top layer that's why its suggested to collect the superficial layer.



**Figure 3.2 Sample collection in an air tight bucket**



**Figure 3.3 Unit meter square area for sampling**

**Table 3.1 Equipment used for soil sampling**

<b>S. No.</b>	<b>Equipment</b>	<b>Purpose</b>
1	Rake	To excavate the top soil
2	Garden folk	For scooping
3	Measuring tape	To measure and select the area
4	Gloves	For safety purpose
5	Cord	To bind the area uniform
6	Spikes	To bind the cord

### **3.4 PREPARATION OF SOIL SAMPLE**

Preparing soil sample is the very first objective in the process of purification, about 730 grams of ash sieved through 2 mm sieve, used to prepare the first sample.

A solution having volume of 4000 ml in which 730 grams of ash by weight has been dissolved is prepared inside a cylindrical glass tube known as degradation tube. Then the next task is to check the pH of the solution, to check the pH we use digital pH meter and the ideal pH should lie between 2.5 to 3.5, to achieve this range of pH we use about 25 ml of concentrated H<sub>2</sub>SO<sub>4</sub> acid.



**Table 3.2 Materials used for preparing initial soil sample**

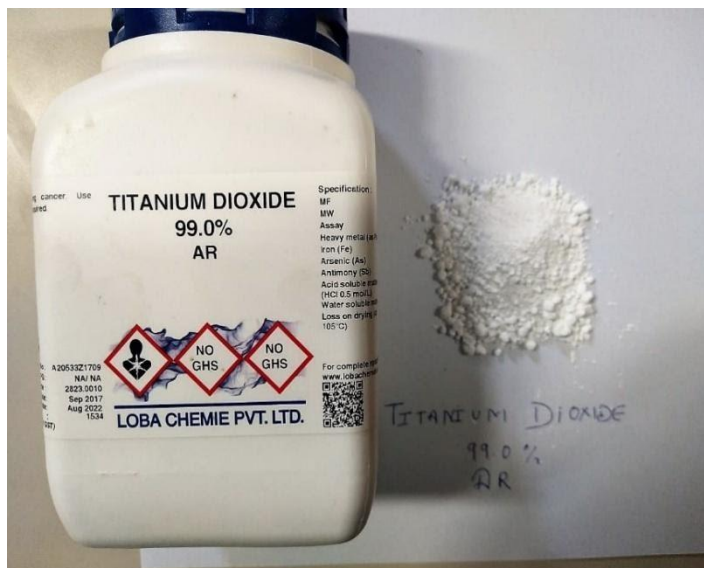
<b>S. No.</b>	<b>Material &amp; Chemicals</b>	<b>Quantity</b>
1	Pond ash	730 g
2	Water	4 L
3	H <sub>2</sub> SO <sub>4</sub> (concentrated)	25 ml



**Figure 3.4 Pond ash solution**

## 3.5 MATERIAL AND APPARATUS

### 3.5.1 Titanium dioxide (TiO<sub>2</sub>)



**Figure 3.5 Titanium dioxide (TiO<sub>2</sub>) 99.0% AR**

Titanium dioxide (TiO<sub>2</sub>) is used as a catalytical agent, it has specification attaining 99% analytical reagent (AR). The main property of titanium dioxide that it oxidizes in presence of sunlight or UV-light.

In presence of light titanium dioxide releases an electron which combines with the oxygen in the air to form a superoxide anion which is a very powerful oxidizing reagent and oxidize the hazardous substance present in the surrounding environment.

### 3.5.2 EDTA (Ethylenediaminetetraacetic acid)

Ethylenediaminetetraacetic acid (EDTA), also known by other names too, is a chemical used for both industrial and medical purposes. This happens to be colourless, water soluble and aminopolycarboxylic acid, with widespread used in the field to dissolve limescale. It finds its uses mostly as a chelating agent, and has its usefulness mostly because of its hexadentate structure. EDTA is produced in many forms of disodium EDTA, disodium EDTA, and tetra sodium EDTA.

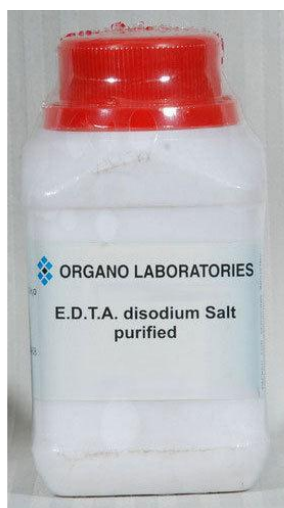
It finds its uses in the field of medicine, industries, laboratory applications, and cosmetics etc.

**INDUSTRY-** Mainly used to isolate metal ions in aqueous solution, hence prevents them from modifying the contents of products, notably colours of dyed products. Also used as a food preservative and added to foods because it prevents catalytic oxidation. Other uses include removing hardness of water in laundry and industrial boilers.

**MEDICINE-** Used for treating poisoning due to metals like lead and mercury. A form of EDTA, binds metal ions in the process, hence inhibits poisoning. Essential in dental procedures, as it removes the organic layer and lubricates root canals. Preservation of eyedrops, and acts as an anticoagulant too. Even used to trace back metal poisoning sources.

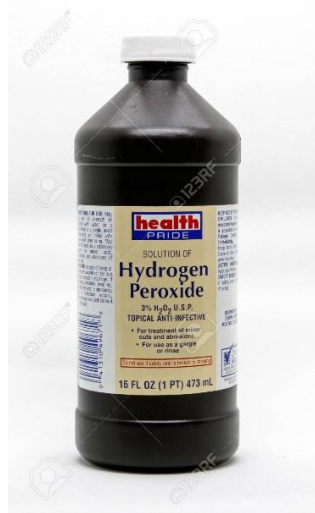
**LABORATORY APPLICATIONS-** Used for scavenging metal ions, to deactivate metal dependent enzymes, and to suppress DNA damage in biochemistry. Also used in biomedical labs, in veterinary procedures as an anticollagenase to prevent worsening of ulcers. Can be used as decalcifying agent to cut out minute sections in a tissue.

**COSMETICS-** Used in a variety of cosmetics like Shampoos, personal care products etc.



**Figure 3.6 E.D.T.A. as a chelating reagent**

### 3.5.3 Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)



**Figure 3.7 Hydrogen peroxide**

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is an important chemical used in pollution control treatment of domestic and industrial effluents. Hydrogen peroxide is an oxidizing agent use to remove contaminants from contaminated sites and ground water through a technology called in-situ chemical oxidation.

Physical properties: -

- a) H<sub>2</sub>O<sub>2</sub> is an almost colourless liquid in its pure state.
- b) It is miscible with water in all proportions and forms a hydrated H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O at a melting point of 221 K.
- c) The volume of 30% solution of hydrogen peroxide is marketed as 100 volume of hydrogen peroxide.

In acidic medium it acts as an oxidizing agent and form hydroxyl radical which reduces the quantity contamination.

### **3.5.4 Ferrous sulphate heptahydrate (FeSO<sub>4</sub>.7H<sub>2</sub>O)**

Ferrous sulphate heptahydrate also known as green vitriol, it's a blue green colour powder is mainly used to fulfil the iron deficiency. These compounds mainly exists in heptahydrate form in nature. We use this chemical to fulfil the need of Ferrous ion in oxidation process, in Fenton process these ions oxidized by hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and forming a hydroxyl free radical and a free ion of hydrogen.

Then these free radicals engage in the further steps and perform their action of oxidation to remove hazardous compounds in secondary stage.

Also, used to fortify foods and used as a synthetic agent in iron deficiency anaemia treatment, with its side effects being constipation. Used as artificial colour in canned olives. Promotes plant growth by lowering soil pH that are highly alkaline so that nutrients can be used easily. Can be mixed with compost for further uses.

In the middle ages, it was used even for the photo development in collodion processed images. It finds its uses in corrosion resistant protective coatings, and in gold refineries to separate metallic gold ions from solutions. Most importantly, a main reagent as a iron catalyst in Fenton process. For purification of water and to remove eutrophication in waterbodies, used in flocculation processes and for phosphate removal.

### **3.5.5 Propanol**

Propanol belonging to alcohol of primary type. It's a colourless liquid also known as propan-1-ol. The mainly use of propanol is as solvent or use to produce solvents, it acts as an intermediate. It's produced naturally during many fermentation processes, and employed as a solvent in pharmaceutical industry, and sometimes as a disinfectant, it has various medical purposes like it has been used in various medicines like in rubbing alcohol, used as an antiseptic and in hand sanitizers also.

**Table 3.3 Chemicals used in the reactor chamber**

<b>S. No.</b>	<b>Chemicals</b>	<b>Quantity</b>
1	EDTA	0.65 gm
2	Titanium dioxide (TiO <sub>2</sub> )	0.50 gm
3	FeSO <sub>4</sub> .7H <sub>2</sub> O	0.50 gm
4	Hydrogen peroxide	2.4 ml
5	Propanol	0.2 ml
6	NH buffer	0.4 ml

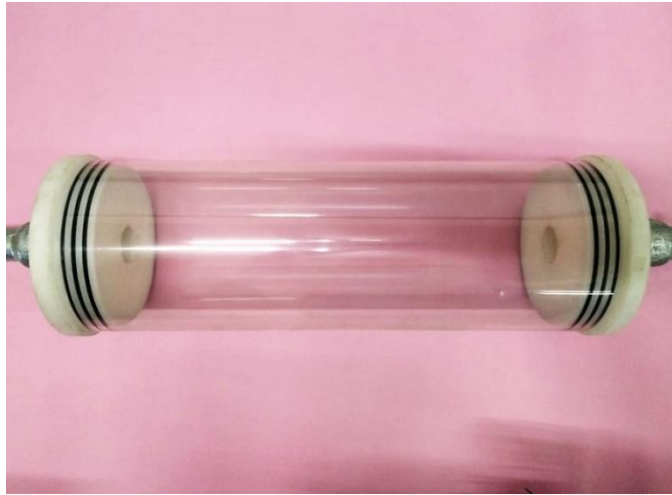
### **3.6 APPARATUS**

#### **3.6.1 Degradation chamber**

Degradation chamber is a transparent cylindrical glass tube used for the preparation of sample. Both the ends of the tube were covered with a plastic cap known as inlet cap and there is pipe connected to both the sections of the inlet cap.

Following are the specifications of the degradation chamber: -

- a) It's a transparent cylindrical tube having diameter 150 mm and length is 400 mm.
- b) The tube is made of a transparent acyclic material.
- c) The reactor is placed inside a wooden frame rectangular chamber consisting of UV-light.
- d) The reactor is placed inside the setup at a slant angle of 30 degrees.
- e) The UV-lamp is placed horizontally straight over the chamber for the direct fall impact on the solution.
- f) Proper electric setup also installed inside the wooden frame.



**Figure 3.8 Degradation tube**



**Figure 3.9 Wooden frame setup to place degradation tube**

### **3.6.2 UV Lamp and Setup**

Sunlight is very essential for the photocatalysis process without it, breakdown of titanium dioxide is not possible so it plays a vital role in this process. However the entire process takes place in-door that's why instead of sunlight we use UV-lamps which gives the same effect as sunlight.

UV-lamps of high intensity (240 to 270 nm) has been used to break down carbon based organic compounds in indoor conditions which is quite difficult with normal lamps having intensity between 100 to 160 nm.



**Figure 3.10 UV-lamp rod**



**Figure 3.11 UV-lamp setup inside reactor**



**Table 3.4 Specifications of UV-tube**

<b>S. No.</b>	<b>Specifications</b>	<b>Measurements</b>
1	Length of tube	11.9 inch
2	Diameter of rod	16 mm
3	Wattage	8 w
4	Intensity	270 nm

### **3.7 USE OF HYDROGEN PEROXIDE**

The main purpose of hydrogen peroxide is removal of organic impurities. It's mainly associated with the Fenton reaction as in advance oxidation processes Fenton reaction gives a free hydroxyl radical (. OH) which is highly reactive and degrades the organic compounds.

#### **Calculating the volume of H<sub>2</sub>O<sub>2</sub> use in process:**

H<sub>2</sub>O<sub>2</sub>> 30% w/v

30 gm in 100 ml

300 gm in 1000 ml

300000 ppm.

Addition of 0.2 ml of H<sub>2</sub>O<sub>2</sub> in pond ash sample.

$$300000 \times 0.2\text{ml} = X \times 250$$

$$X = 240 \text{ mg/l}$$

i.e. 2.4 ml

## 3.8 PREPARATION OF SAMPLE

### 3.8.1 Preparing TiO<sub>2</sub> sample.

Preparing titanium dioxide sample is a very important and crucial step and should be done carefully and properly.

We take about 25 ml of tap water in which we added 0.65 gm of titanium dioxide is added gradually and stir is continuously to avoid the formation of lumps. After complete addition of titanium dioxide, we put the mixture under Laboratory Stirrer at 90 rpm for proper mixing of titanium dioxide.



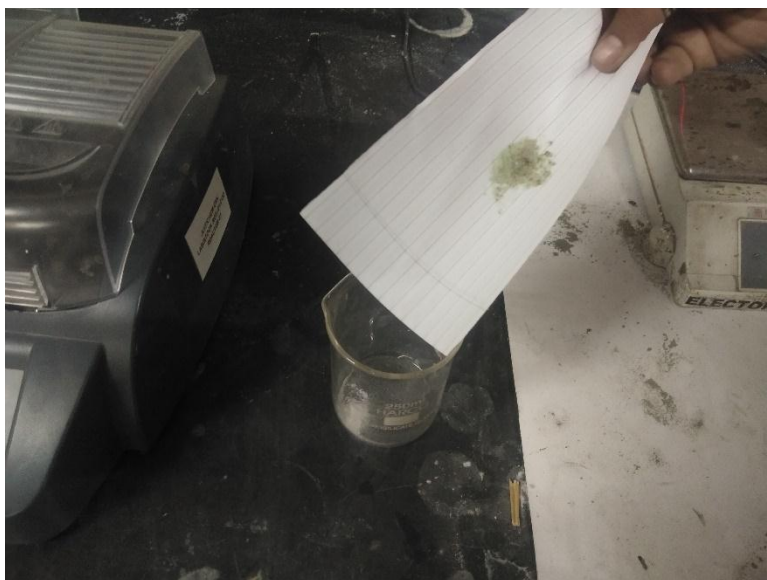
**Figure 3.12 Stirring of TiO<sub>2</sub> in water**



**Figure 3.13 Gradually mixing of TiO<sub>2</sub> to avoid formation of lump**

### 3.8.2 Action of ferrous sulphate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), EDTA & Propanol.

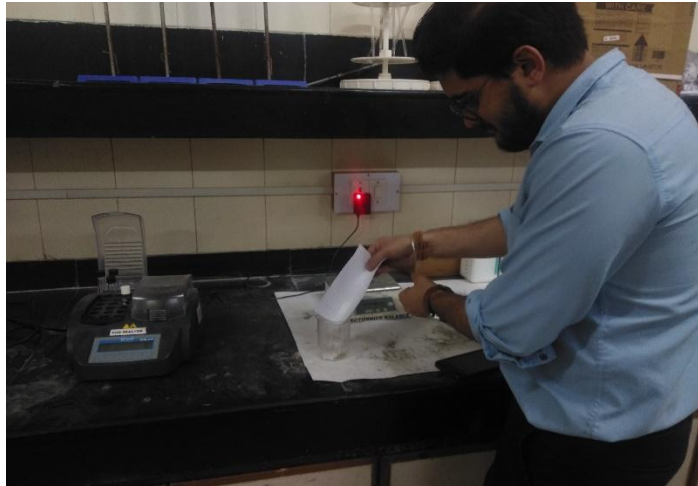
After preparing the titanium dioxide sample we add EDTA (Ethylenediaminetetraacetic acid) in the solution. As mention in **Table 3.3**, 0.65 grams of EDTA is added in the solution gradually and stir it side by side.



**Figure 3.14 Addition of EDTA**

EDTA is a chelating agent means act as a binder it binds the metal ions especially heavy metal ions in the reaction, it helps in controlling the bacterial growth and make solution more visible. Following EDTA we add our next chemical ferrous sulphate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) about 0.50 gram of ferrous sulphate is added in the solution, which is here to fullfil the demand of ferrous ion ( $\text{Fe}^{2+}$ ) used in fenton reaction to form free hydroxy radical when oxidized by hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).

After adding ferrous ions we proceede further by adding hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), it acts as an oxidizing agent in the peocess mainly purpose is to oxidize the ferrous ion present in ferrous sulphate heptahydrate and form and form very powerful free radicals.



**Figure 3.15 Addition of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$**

Following the procedure after adding ferrous sulphate we add 0.2 ml as mention before in **table 3.3**, propanol acts as a solvent in the reation.

Now after adding all these chemicals and make a solution out of it the next task arises is to maintain the pH of the solution the standardise pH lies in range of 2.5 to 3.5 so maintain which we have achieved already by using strong acid and to maintain this pH we add ammonium ( $\text{NH}_4^+$ ) buffer to the solution and stir it well, after preparing the solution we pouring it into the soil solution which we have already prepared in the in the degedration chamber tube and it well.



**Figure 3.16 Pouring of chemical solution into prepared soil sample**

### **3.8.3 Preparing the setup for UV action.**

After preparing the sample inside degradation tube we seal the chamber with inlet cap and shake the tube manually for couple of minutes and after that we put it inside the rectangular frame on a ramp which is installed at an angle of 30 degrees, so that proper penetration of UV-light will occur on the surface of the tube.



**Figure 3.17 Installation of sample under UV-light setup**

The chamber is equipped with UV-lamp setup with four tube-lights each of 8 watts and an operating switch is also provided outside the frame. After installing the sample, we seal the box with screws and wooden board and placed it in a dark corner to avoid any damage and switched on the UV-lamp.

The first sample is kept under UV-light for 26 hours, the second one for 34 hours and the third one for 42 hours. Now the next task is to extract out the water from the tube without disturbing the soil so we use a Tulu Pump of 1.5 HP. It's was very efficient and work smoothly without disturbing the soil takes out excessive amount of water.

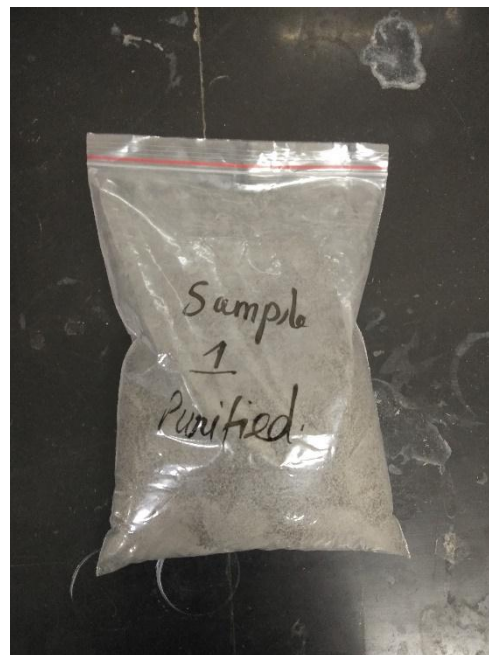


**Figure 3.18 Extraction of water from the sample using pump**

After extracting the water, the next task is to dry the soil sample, we take out the wet soil and weigh it than put it inside the oven at 105 degree Celsius for 16 hours for oven dry, the same procedure is followed for the next two samples, after oven drying it we pack the sample in vacuum bags and weight them.



**Figure 3.19 Oven dried sample**



**Figure 3.20 Packed sample**

**Table 3.5 Soil samples and their description**

<b>Soil sample</b>	<b>Time duration under UV (hrs)</b>	<b>Weight (grams)</b>
1	28	655 g
2	34	585 g
3	42	685 g

Most of the chemicals like Titanium dioxide, H<sub>2</sub>SO<sub>4</sub> are very dangerous for human beings so they should be handled properly with all the necessary precautions like wearing gloves and mask is mandatory while working with these chemicals to avoid any harm to yourself or your fellow project partner.

## CHAPTER 4

### RESULTS & DISCUSSIONS

---

#### 4.1 General

This chapter discusses the results obtained from the various experiments performed. Our main aim of this project is to reduce the heavy metal content from the contaminated soil sample and these are the following results we obtained:

#### 4.1 POND ASH SAMPLES DEGRADATION TEST RESULT

**Table 4.1 Degradation test results for sample 1 purified**

S. No.	Parameters	Units	Results
1.	Lead	mg/kg	BDL
2.	Arsenic	mg/kg	BDL
3.	Mercury	mg/kg	BDL
4.	Chromium	mg/kg	3.13
5.	Hexavalent Chromium (as Cr +6)	mg/kg	0.015

The above results are from a sample which is kept under the UV-light for 42 hours and as we can see there are some heavy metals like lead, arsenic and mercury that lies below detection level means no major percentage of these metals is founded in the sample, the metals like chromium and hexavalent chromium gets detected in the sample. Talking about the chromium especially Cr (+6) is one of the major cancer-causing heavy metal.



**Table 4.2 Degradation test results for sample 2 purified**

<b>S. No.</b>	<b>Parameters</b>	<b>Units</b>	<b>Results</b>
1.	Lead	mg/kg	BDL
2.	Arsenic	mg/kg	BDL
3.	Mercury	mg/kg	BDL
4.	Chromium	mg/kg	4.65
5.	Hexavalent Chromium (as Cr +6)	mg/kg	0.048

**Table 4.3 Degradation test results for sample 3 purified**

<b>S. No.</b>	<b>Parameters</b>	<b>Units</b>	<b>Results</b>
1.	Lead	mg/kg	2.30
2.	Arsenic	mg/kg	BDL
3.	Mercury	mg/kg	BDL
4.	Chromium	mg/kg	5.15
5.	Hexavalent Chromium (as Cr +6)	mg/kg	0.05

In the above two tables we the results of the soil kept under UV-lamp for 34 hours and 26 hours respectively. Let's talk about the table no. 4.2 its some-how seems similar to the results in table 4.1 as we can see majority of heavy metals like lead, arsenic lies below the detection level same as in the previous results and chromium is also get detected with less efficiency than the previous ones and same goes for the results in table 4.3 where more less efficiency has been achieved with the detection of lead.

## 4.2 Result of un-purified ash sample

**Table 4.4 Test results for un-purified sample**

<b>S. No.</b>	<b>Parameters</b>	<b>Units</b>	<b>Results</b>
1.	Lead	mg/kg	1.62
2.	Arsenic	mg/kg	BDL
3.	Mercury	mg/kg	BDL
4.	Chromium	mg/kg	13.14
5.	Hexavalent Chromium (as Cr +6)	mg/kg	0.075

In the above table we have the results of the contaminated soil sample as we can see the difference in the percentage of the heavy metals if compared with the results of the soil sample purified with TiO<sub>2</sub>.

## 4.3 Inference of the test result

We have prepared four samples of soil out of which three samples were purified by photocatalysis and photofenton process and one is totally raw un-purified sample, all the three samples were prepared by same procedure but the only difference is their time duration under UV-light contact, time interval difference between each sample is about 8 hours but that doesn't have any significant effect on the results.

Now let us discuss what we have achieved through our results by comparing the percentage of heavy metals of the purified sample with the un-purified sample. First of all let's talk about the lead as we can see in most of the purified samples it lies below the detection level while in raw sample it is detectable and amount is 1.62 mg/kg which shows we were able to reduce the quantity of lead below the contamination level. Next is arsenic and mercury and we can see both of them lie below detection level in all the three purified samples and in the un-purified sample. Now we come to the final two heavy metals i.e. chromium and hexavalent chromium on comparing the results of the chromium

content of both sets of samples of purified and un-purified we can see the difference in their percentage not just a slight difference but a noticeable difference.

First talk about the purified set in which we have three samples first one with contact time of 42 hours under UV-light the chromium content is 3.13 mg/Kg now comparing it with the other two we have second sample of contact time of 34 hours and chromium content is 4.65 mg/kg which is higher than the previous one and the last purified sample with the contact time of 26 hours and chromium content is 5.15 mg/kg as we can see there is a difference level of chromium in each sample what that concludes that this process is a time variant process as we go on increasing the UV contact time we will get more efficiency this can also be seen in chromium hexavalent as the contact time increases more efficiency will be achieved.

## CHAPTER 5

### CONCLUSIONS

---

#### 5.1 General

In this chapter we discuss the conclusion of our research and its result and talk about its practical applications on a large scale, how this technology performs on field level and also talks about its future scope.

#### 5.2 Conclusions

This study compares the application of Photocatalysis and Photo-Fenton and their use in a combined manner in reduction of heavy metal from the soil. Photocatalysis and Fenton processes were used widely to treat contaminated water and soil but separately, and no doubt the results were very good especially in case of reduction of heavy metals like Pb, As, Hg, Ni, Co, Cr etc which can not be achieved through normal reduction processes like Bioremediation. Conventional methods like bioremediation are useful in dealing with inorganic contaminants but have certain limitations like it can-not deal with the heavy metals, so in that case photocatalysis and Fenton processes comes in action as they are very useful in dealing with heavy metals and their combine application is more effective to degrade the heavy metals present in soil. We use pond ash for our project because it contains heavy metals like chromium which is the main reasons for groundwater contamination in areas surrounding NTPC Ropar, Punjab.

The coal fly ash sample from coal ash pond contains chromium have been collected to perform the experiment. The results show that the best for leaching of chromium at a significant rate with a contact time of 28 hours about 25% of results have been achieved. For next sample the contact time has been increased by 8 hours and similarly for the next sample, with increase time period more effective results have been achieved.

The sample prepared with titanium dioxide for photocatalysis process were studied by XRD technique, studies have been already done for the degradation of oil contaminants

present in soil by TiO<sub>2</sub> photocatalysis and very promising results have been achieved and the procedure is some-what similar with what we have followed in our study, heavy metals like chromium (+ 6) get oxidize by titanium dioxide in presence of UV-light.

Talking about contact time it lies between 24 to 48 hours or more and the results also varies with the time interval but not very significant, as we can see we have observed a very minor change in the reading with respect to time interval. In case of open field test under cloudy condition UV- radiation reaches the earth surface as diffused light in such cases the reaction rated were very slow and effectiveness is decreased by 40%. We perform the experiment in an indoor setup on a small scale but the results were promising, so in future these techniques will be very useful in water treatment and soil remediation with further more research and studies it can be implanted on huge scales with more advance setups and equipment's.

### **5.3 SCOPE FOR FUTURE STUDY**

This study is not new in the field of sciences and technology its was discovered back in 20<sup>th</sup> century but still there is so much yet to discover, its a vast ocean of knowledge and we have grasped only very few from it. In this project learn how to use photocatalysis and photofenton in a combine manner to get more prominent results that we can-not get by applying them separately and no doubt this works well but still there is lot to achieve. In countries like India where we still depend upon the processes like Bioremediation for soil purifications of soils but these processes still not very effective for heavy metals contamination, so we have to develop and learn about technologies like photocatalysis and photofenton and their applications so there is huge scope in this field in near future.

## REFERENCES

- [1] W. Zhang, Y. Yuan, L. Tong, L. Zhuang, H. Huang and Z. Liu, "Mobility of Metals Remaining in the Soils Treated by Edta Washing or/and Chemical Stabilization," *2010 4th International Conference on Bioinformatics and Biomedical Engineering*, Chengdu, 2010, pp. 1-4, doi: 10.1109/ICBBE.2010.5516713.
- [2] A. Barona, I. Aranguiz, and A. Elias, "Metal associations in soils before and after EDTA extractive decontamination: implications for the effectiveness of further clean-up procedures," *Environ. Pollu.*, Vol. 113, pp. 79-85, 2001.
- [3] Z. Wang, L. Huang, T. Tao, S. Fu, J. Zuo and B. Lv, "Treatment of Landfill Leachate by Combined Photooxidation and Biological Anaerobic-Aerobic Method," *2009 3rd International Conference on Bioinformatics and Biomedical Engineering*, Beijing, 2009, pp. 1-4, doi: 10.1109/ICBBE.2009.5163709.
- [4] C. Hofl, G. Sigl, O. Specht, I. urdack, D. Wabner, Oxidative degradation of AOX and COD by different advanced oxidation processes: A comparative study with two samples of a pharmaceutical wastewater, *Water Sci. Technol.* 35 (1997), pp. 257-264.
- [5] H. Zhou, D.W. Smith, *Advanced technologies in water and wastewater treatment*, J. *Environ. Eng. Sci.* 1 (2002), pp. 247-264.
- [6] D. Pangayao and S. Gallardo, "Leaching of chromium from coal ash using citric acid, oxalic acid and gluconic acid by batch leaching procedure," *2014 International Conference on Humanoid, Nanotechnology, Information Technology, Communication and Control, Environment and Management (HNICEM)*, Palawan, 2014, pp. 1-5, doi: 10.1109/HNICEM.2014.7016250.
- [7] M. Visa, C. Bogatu, A. Duta, "Simultaneous adsorption of dyes and heavy metals from multicomponent solution using fly ash", *Appl. Surf. Sci.* 256 (2010) 5486-5491.
- [8] Jiang yufeng, Zhan huiying, et al. Washing efficiency of heavy metals in soil with EDTA enhanced by surfactants[J]. *Journal of Agro-Environment Science*, 2006; 25(1): 119-123.
- [9] Jiantao Liang, Xiangxuan Liu and Yunchao Wang, "Notice of Retraction: Process mechanism of formaldehyde degradation in aqueous solution using the UV-Fenton method," *2010 The 2nd Conference on Environmental Science and Information Application Technology*, Wuhan, 2010, pp. 298-301, doi: 10.1109/ESIAT.2010.5568361.

- [10] Shyang-Chyuan Fang and Shang-Lien Lo, "Persulfate oxidation activated by peroxide with and without iron for remediation of soil contaminated by heavy fuel oil," *2011 Second International Conference on Mechanic Automation and Control Engineering*, Hohhot, 2011, pp. 2362-2366, doi: 10.1109/MACE.2011.5987455.
- [11] Xiaolian Hu and Xifeng Wang, "Photo-fenton treatment of dimethoate using TiO<sub>2</sub> film and UV radiation," *2010 2nd International Conference on Chemical, Biological and Environmental Engineering*, Cairo, 2010, pp. 110-113, doi: 10.1109/ICBEE.2010.5649070.
- [12] S. S. Hutagalung, I. Muchlis, P. Sebleku, M. F. Amri, H. Fakhurroja and A. Turnip, "Water purification technology based advanced oxidation processes emerging ozone," *2014 2nd International Conference on Technology, Informatics, Management, Engineering & Environment*, Bandung, 2014, pp. 292-295, doi: 10.1109/TIME-E.2014.7011634.
- [13] N. Wang, Z. Wu and G. Zhu, "Experimental Study of Nanometer TiO<sub>2</sub> Photocatalysis Material in Air Purification," *2009 International Conference on Energy and Environment Technology*, Guilin, Guangxi, 2009, pp. 56-59, doi: 10.1109/ICEET.2009.480.
- [14] Z. G. Ying, L. Lin, L. He and H. Yuanhao, "Microorganism-Plant Combined Bioremediation on Heavy Metal Contaminated Soil In the Industrial District," *2009 International Conference on Environmental Science and Information Application Technology*, Wuhan, 2009, pp. 273-276, doi: 10.1109/ESIAT.2009.462.
- [15] I. Arslan, I. A. Balcioglu, D.W. Bahnemann, Photochemical treatment of simulated dyehouse effluents by novel TiO<sub>2</sub> photocatalysts: Experience with the thin film fixed bed (TFFB) and double skin sheet (DSS) reactors, *Water Sci. Technol.* 44 (2001), pp. 171.
- [16] Y. Wang, Solar Photocatalytic Degradation of eight commercial dyes in TiO<sub>2</sub> suspension, *Water Res.* 34 (2000), pp. 990-994.
- [17] O.M. Alfano, D. Bahnenabb, A. E. Cassano, R. Dillert and R. Goslich, Photocatalysis in water environments using artificial and solar light, *Catal. Today.* 58 (2000) 199-230.
- [18] C.S. Turchi, J.F. Klausner and E. Marchand, Field test results for the solar photocatalysis detoxification of fuel-contaminated ground water, *Chemical Oxidation: technology for the Nineties*, 3rd International Symposium. (1993).

- [19] H. Fallmann, T. Krutzler, R. Bauer, S. Malato, and J. Blanco, Applicability of the Photo-Fenton Method for Treating Water Containing Pesticides, *Catal. Today*. 54 (1999), pp. 309-319.
- [20] A. Gonzalez-Martin, O. J. Murphy, and C. Salinas, Photocatalytic oxidation of organics using a porous titanium dioxide membrane and an efficient oxidant, *US patent*. 6 (2000), pp. 186.
- [21] A. Mills, J. Wang, The Kinetics of Semiconductor Photocatalysis: Light Intensity Effects, *Zeitschrift fur Physikalische Chemie*. 213 (1999), pp. 49-58.
- [22] E. Chamarro, A. Marco, S. Esplugas, Use of fenton reagent to improve organic chemical biodegradability, *Water Res.* 35 (2001), pp. 1047-1051.
- [23] S. Malato, J. Blanco, M. Maldonado, P. Ibanez, A. Campos, Optimising solar photocatalytic mineralisation of pesticides by adding inorganic oxidizing species; application to the recycling of pesticide containers, *Appl Catal B: Environ.* 28 (2000), pp. 163-174.
- [24] Z. Chen, J. Zhan and Z. Liu, "Pre-treatment of High-Strength Acid Dye Wastewater with Internal electrolysis-Fenton Process," *2012 Second International Conference on Intelligent System Design and Engineering Application*, Sanya, Hainan, 2012, pp. 472-476, doi: 10.1109/ISdea.2012.721.
- [25] "Bioremediation-cost-efficiency" <https://images.app.goo.gl/qWsu2286fyDvcMC86>
- [26] "Self cleaning & Air purification Nano Tio2 Photocatalyst Liquid Coating" <https://images.app.goo.gl/gvz9h9dyR5f9jFv9A>
- [27] Huang, D., Hu, C., Zeng, G., Cheng, M., Xu, P., Gong, X., ... Xue, W. (2017). <https://images.app.goo.gl/NGetNdqSRG3Q15nD8>
- [28] <https://www.google.com/imgres?imgurl=https://5.imimg.com/data5/CV/RA/MY-712037/edta-disodium-salt-purified-500x500.jpg&imgrefurl=https://www.indiamart.com/proddetail/edta-disodium-salt-purified-2061467730.html&tbnid=rLWkW3OApuzcgM&vet=1&docid=X3CIFUpZvswP8M&w=500&h=500&q=edta+bottle&source=sh/x/im>
- [29] [https://www.google.com/imgres?imgurl=https://previews.123rf.com/images/tiraspr/tiraspr1905/tiraspr190500078/133574742-bottle-of-hydrogen-peroxide-against-white-background-.jpg&imgrefurl=https://www.123rf.com/photo\\_133574742\\_bottle-of-hydrogen-peroxide-against-white-](https://www.google.com/imgres?imgurl=https://previews.123rf.com/images/tiraspr/tiraspr1905/tiraspr190500078/133574742-bottle-of-hydrogen-peroxide-against-white-background-.jpg&imgrefurl=https://www.123rf.com/photo_133574742_bottle-of-hydrogen-peroxide-against-white-)



background.html&tbid=T3aClBeToDN7QM&vet=1&docid=0N7ICEZJr7PdLM&w  
=791&h=1300&q=hydrogen+peroxide&source=sh/x/im

- [30] Villa, R. D., Trovó, A. G., & Nogueira, R. F. P. (2010). Soil remediation using a coupled process: soil washing with surfactant followed by photo-Fenton oxidation. *Journal of Hazardous Materials*, 174(1-3), 770–775.
- [31] Lin, S. H., & Chen, M. L. (1997). Purification of textile wastewater effluents by a combined Fenton process and ion exchange. *Desalination*, 109(2), 121–130..
- [32] Feng, F., Xu, Z., Li, X., You, W., & Zhen, Y. (2010). Advanced treatment of dyeing wastewater towards reuse by the combined Fenton oxidation and membrane bioreactor process. *Journal of Environmental Sciences*, 22(11), 1657–1665. doi:10.1016/s1001-0742(09)60303-x.
- [33] Dixit, R., Wasiullah, Malaviya, D., Pandiyan, K., Singh, U., Sahu, A., ... Paul, D. (2015). Bioremediation of Heavy Metals from Soil and Aquatic Environment: An Overview of Principles and Criteria of Fundamental Processes. *Sustainability*, 2015, 7, 2189-2212; doi:10.3390/su7022189.
- [34] Beltran FJ, Garcia-Araya JF, Frades J, Alvarez P, Gimeno O. Effects of single and combined ozonation with hydrogen peroxide or UV radiation on the chemical degradation and biodegradability of debittering table olive industrial wastewaters. *Water Res* 1999;33: 723–32.
- [35] M. Muneer, D. Bahnemann, Semiconductor-Mediated Photocatalysed Degradation of Two Selected Pesticide Derivatives, Terbacil and 2, 4, 5-Tribromoimidazole, in Aqueous Suspension, *Water Sci. Technol.* 44 (2001), pp. 331-338.
- [36] D.Y. Goswami, J.F. Klausner, G.D. Mathur, A. Martin, K. Schanze and P. Wyness, Solar Photocatalytic Treatment of Ground water at Tyndall AFB: Field Test Results, *Solar 93, Proceedings of the 1993 American Solar Energy Society Conference*, Washington, 1993 b, pp. 235-239.
- [37] D.Y. Goswami, A Review of Engineering Developments of Aqueous Phase Solar Photocatalytic Detoxification and Disinfection Processes, *J. Solar Energy Eng.* 119 (1997), pp. 101-107.
- [38] A. G. Rincón and C. Pulgarin, Photocatalytical inactivation of *E. coli*: effect of (continuous/intermittent) light intensity and of (suspended–fixed) TiO<sub>2</sub> concentration, *Applied Catalysis B: Environmental*. 44 (2003), pp. 263-284.
- [39] S.S. Block, V.P. Seng, D.W. Goswami, Chemically enhanced sunlight for killing bacteria, *J. Solar Energy Eng.* 119 (1997), pp. 85-91.

[40] R.P.S. Suri, J. Liu, D.W. Hand, J.C. Crittenden, D.L. Perram, M.E. Mullins,  
Heterogeneous photocatalytic oxidation of hazardous organic

**JAYPEE UNIVERSITY OF INFORMATION TECHNOLOGY, WAKNAGHAT**  
**PLAGIARISM VERIFICATION REPORT**

Date: 30-May-2020  
 Type of Document (Tick):  PhD Thesis  M.Tech Dissertation/ Report  B.Tech Project Report  Paper  
 Name: Shivam Nag; Siddharth Verma Department: Civil Enrolment No. 161686  
 Contact No. 854478643 E-mail. shivamnag123456789@gmail.co  
 Name of the Supervisor: Dr. Saurabh Rawat  
 Title of the Thesis/Dissertation/Project Report/Paper (In Capital letters): \_\_\_\_\_  
Use of coupled photocatalysis and photofenton processes for degradation of contaminated soil

**UNDERTAKING**

I undertake that I am aware of the plagiarism related norms/ regulations, if I found guilty of any plagiarism and copyright violations in the above thesis/report even after award of degree, the University reserves the rights to withdraw/ revoke my degree/report. Kindly allow me to avail Plagiarism verification report for the document mentioned above.

**Complete Thesis/Report Pages Detail:**

- Total No. of Pages = 57
- Total No. of Preliminary pages = 4
- Total No. of pages accommodate bibliography/references = 5

*Rawat*  
 31/5/20  
*Shivam*  
 31/5/20  
 (Signature of Student)

**FOR DEPARTMENT USE**

We have checked the thesis/report as per norms and found **Similarity Index** at 14 (%). Therefore, we are forwarding the complete thesis/report for final plagiarism check. The plagiarism verification report may be handed over to the candidate.

(Signature of Guide/Supervisor)

*★*  
 6/6/2020  
 Signature of HOD

**FOR LRC USE**

The above document was scanned for plagiarism check. The outcome of the same is reported below:

Copy Received on	Excluded	Similarity Index (%)	Generated Plagiarism Report Details (Title, Abstract & Chapters)	
Report Generated on	<ul style="list-style-type: none"> <li>• All Preliminary Pages</li> <li>• Bibliography/Images/Quotes</li> <li>• 14 Words String</li> </ul>		Word Counts	
			Character Counts	
		Submission ID	Total Pages Scanned	
			File Size	

Checked by  
 Name & Signature

Librarian

Please send your complete thesis/report in (PDF) with Title Page, Abstract and Chapters in (Word File) through the supervisor at [plagcheck.juit@gmail.com](mailto:plagcheck.juit@gmail.com)