

**EVALUATION OF FENTON'S OXIDATION FOR
TREATMENT OF SELECTED PAINT EMULSIONS AND
ITS RESIDUAL TOXICITY IN WATER**

Thesis

Submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

SURYA NAIR K



Department of Civil Engineering

**NATIONAL INSTITUTE OF TECHNOLOGY KARNATAKA,
SURATHKAL, MANGALORE – 575025**

March 2024

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Register No: 187CV012

Under the Guidance of

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**NATIONAL INSTITUTE OF TECHNOLOGY KARNATAKA,
SURATHKAL, MANGALORE – 575025**

March 2024

DEDICATED

TO

MY PARENTS, IN-LAWS, HUSBAND,

DAUGHTER, FAMILY MEMBERS,

TEACHERS, FRIENDS

AND

MOTHER NATURE

DECLARATION
by the Ph.D Research Scholar

I hereby declare that the Research Thesis entitled "**EVALUATION OF FENTON'S OXIDATION FOR TREATMENT OF SELECTED PAINT EMULSIONS AND ITS RESIDUAL TOXICITY IN WATER**" which is being submitted to the **National Institute of Technology Karnataka, Surathkal** in partial fulfillment of the requirements for the award of the Degree of **Doctor of Philosophy in Civil Engineering** is a *bonafide report of the research work carried out by me*. The material contained in this Research Thesis has not been submitted to any University or Institution for the award of any degree.

Place: NITK, SURATHKAL

Date: 27th March, 2024.



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CERTIFICATE

This is to certify that the Research Thesis entitled “**EVALUATION OF FENTON’S OXIDATION FOR TREATMENT OF SELECTED PAINT EMULSIONS AND ITS RESIDUAL TOXICITY IN WATER**” submitted by **SURYA NAIR K (187009CV012)** as the record of research work carried out by her, *is accepted as Research Thesis submission* in partial fulfilment of the requirements for the award of degree of **Doctor of Philosophy**.



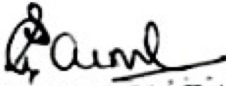
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ACKNOWLEDGEMENT

I am grateful to have Dr. Basavaraju Manu as my research supervisor, for his immense support throughout my research work. I thank him for all his patience and love so that I could carry out this research without much stress and could balance the family life along with it. His knowledge and expertise in the area of this research topic helped in the achievement of the best results. It has been a great experience to work with him.

I am indebted to my Co-Guide Dr. Adani Azhoni for his wonderful effort in guiding me throughout the research by giving proper directions to think and to arrange the thesis in the best way. He has really supported in improving the writing skills and suggested all the corrections in writings at the earliest possible. His interest in guiding students, punctuality, and friendly approach is truly appreciable.

I acknowledge my sincere thanks to Prof. S. Shrihari, Dept. of Civil Engineering and Dr. Hemantha Kumar, Dept. of Mechanical Engineering, the members of my Research Progress Assessment Committee, for their valuable suggestions and the encouragement provided at various stages of this work. Prof. S. Shrihari has always been a mentor and a well-wisher throughout my NITK life.

I wish to thank Dr. Subhash C. Yaragal, the Head of Civil Engineering Department, Dr. A.U. Ravishankar, Dr. K.S. Babu Narayan, Dr. Katta Venkataramana, Dr. B.R. Jayalekshmi, Dr. K. Swaminathan, Dr. M.C. Narasimhan, Dr. B M Sunil, Dr. Arun Kumar Talla, Dr. C. P. Devatha, Dr. Anupama Surejan, Dr. Palanisamy, and Dr. Mithun Mohan, secretary DRPC and all other faculty staff and supporting staffs of Civil Engineering Department for all their support and encouragement throughout my stay at the NITK campus.

I would like to thank Mr. Manohar Shanbhogue for all of the intellectual guidance, encouragement, and support he has provided me throughout, as well as Mr. Dheeraj for his unwavering assistance with lab work. I also like to extend my gratitude to Mr. Subhash, Computer lab staff for his helping mentality and kindness towards the scholars.

I appreciate the co-operation and help extended to me by all the members of the technical staff at the laboratories of the Civil Engineering Department. My special thanks to Mr. Akash, and other staffs of Central research facility for their kind help in completing my experimental work. I extend my sincere thanks to the members of the office staff, Mrs. Prabhavathi, Mrs. Anwitha, Mrs.Thara, and Mr. Monaappa for their kind support at various stages of this work. I also thank the cleaning staffs and security

staffs of NITK for providing me a clean and safe working atmosphere. I am greatly thankful to the staffs in Resident Engineers Office for their helping hands for the safe stay in NITK quarters.

I am thankful to BASF India limited, Mangalore and Central Plantation Crops Research Institute (**CPCRI**), Kasaragod for providing me the samples and materials required for the experimental studies.

I owe a debt of gratitude to all of my friends and fellow research scholars at this institute for their unceasing support and advice as I worked on my project. My friends' unofficial encouragement and support have been crucial. I thank my junior research scholars, M.Tech and B.Tech students, Interns who were working in the environmental laboratory for their co-operation.

I want to express my gratitude to my loving parents Sri. Sukumaran K. and Smt. Rema, husband Mr. Rajeesh, daughter Ardra Pournami, Sister Aishwarya, Father-in-law Mr. Radhakrishnan, Mother-in-law Mrs. Chandramathi, Sister-in-law Rajila, Brother in laws Vivek and Vyshakh, Aunt Susheela and other family members who have provided me the best available education and support and have encouraged in all my endeavors. They have always been a source of motivation for me.

Finally, I am grateful to the almighty and mother nature whose power has brought all of my people with their helping hands to support me in the achievement of the goals of my life.

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Date: 27-03-2024

ABSTRACT

Due to increasing water scarcity, recycle and reuse of wastewater is increasingly pertinent. Paint manufacturing industries emit enormous quantity of wastewater. This wastewater contains high Chemical Oxygen Demand (COD) and turbidity. Advanced oxidation process is increasingly recognized as an appropriate method among the chemical methods to reduce the toxicity of paint wastewater. In this study, the degradation of mixture of three different emulsion samples in water is investigated using laterite soil heated to 800°C as heterogeneous catalyst by Fenton-like oxidation process. Optimisation of different factors such as pH, H₂O₂ and catalyst concentration is done with the Design Expert 11 software using Central Composite Design (CCD), to evaluate their effects on COD removal efficiencies of the synthetically prepared paint wastewater. A remarkable result found was that the treatment efficiency of 98% was achieved for the mixture of emulsions with and without the addition of H₂O₂. The laterite calcined at 800°C could produce in-situ •OH radicals in the acidic pH which initiated the Fenton's reaction due to the bimetallic action of Fe³⁺ and Al³⁺ in the solution. Thereby, this experimental analysis provides an important breakthrough for treatment of paint industry wastewater, where it can overcome the disadvantages of using H₂O₂ and conventional Fenton process. The laterite calcined at 800°C is found to be remarkably stable and reusable and also it produced very less amount of sludge compared to conventional process. The remarkable property of the green synthesized heterogeneous catalyst particles (LSFeNP(TC)) using laterite extract and Terminalia catappa leaf extract made the catalyst wonderfully working in reducing the COD of paint wastewater upto 85% efficiency without an external oxidizing agent such as H₂O₂, and acid, thus reducing the cost of process and increasing the environmental sustainability. Although the reduction in chemical oxidation generally reduces toxicity, high efficiency of organic component breakdown does not always result in a drop in toxicity to a tolerable level. Hence, toxicity reduction studies for industrial effluent are required. Therefore, proxy tests, such as the use of indicator bacteria, have the potential to provide insights for toxicological studies of (treated) wastewater. Having reviewed various methods and indicators adopted for toxicity analysis of AOP treated wastewater, the toxicity of treated paint wastewater was studied by bacterial growth inhibition test using *Bacillus subtilis* and seed germination test using mung bean (*Vigna radiata*) and Bengal gram (*Cicer arietinum*). The results showed that the wastewater is completely toxic free

for the growth of indicator bacteria treated with LS 800 catalyst but it shows 38% inhibition for LSFeNP(TC) due to the presence of FeOCl. This indicates that the heterogeneous Fenton's oxidation using laterite as catalyst is an effective AOP in reducing the toxicity of paint wastewater. The finding reported in this research is significant because it proves laterite soil, which is abundantly available in tropical regions, to be an efficient catalyst for Fenton's Oxidation treatment of paint wastewater by considerable reduction in the sludge, which opens up further scope for treatment of other similar industrial effluents in tropical regions.

Keywords: Emulsions, Advanced oxidation, Fenton's catalysts, Laterite, Green synthesized nanoparticles, Ecotoxicity.

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NOMENCLATURE

Name	Full Form
AOP	Advanced Oxidation Process
BET	Brunauer–Emmett–Teller
COD	Chemical Oxygen Demand
CCD	Central Composite Design
DO	Dissolved Oxygen
DOE	Design Of Experiments
R²	Coefficient of Determination
RSM	Response Surface Methodology
SEM	Scanning Electron Microscope
UN SDGs	United Nations Sustainable Development goals
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Paint manufacturing industries are one of the major sources of wastewater containing high chemical oxygen demand and turbidity, besides biodegradable and non-degradable organic matter, suspended solids and heavy metals that cause enormous environmental damages. Safely treating this wastewater before being disposed of to the natural water sources is essential for attaining the UN SDGs, particularly Goal 14: Life under water. Besides being efficient, wastewater treatment techniques must be sustainable – environmentally, economically and ethically. The current treatment methods used for treating paint industry wastewater includes the physicochemical, biological and chemical treatment techniques. The physicochemical treatment techniques produce large amount of sludge making it difficult for disposal while biological treatment techniques are difficult to maintain because of the uncertainties in the chemical compositions of the paint wastewater. Advanced oxidation processes are emerging as preferred methods among the chemical methods for reducing the toxicity of the various components of the paint wastewater with a reduced sludge quantity.

1.2 EMULSIONS

To make the world more vibrant, colorful, and attractive, colors are conferred to buildings, vehicles, cloths, furniture and almost every human-made appliance, through equipment-maintenance, graphic arts, and coatings. These coatings are mostly used in the form of paints. The practicality and availability of various attractive colors and their ease of application increases the usage of paint coatings ubiquitous (Nascimento, Ribeiro, Minamidani, & Duarte, 2013). Most of the paints that are widely used are made of similar components containing pigments (a suspension of finely ground solids) in a liquid medium, called as vehicle, consisting of a binder (polymeric or resinous material), a volatile solvent and appropriate additives (Aniyikaiye, Oluseyi, Odiyo, & Edokpayi, 2019; El-Shazly, Hasanin, & Kamel, 2010; Kakoi, Kaluli, Ndiba, & Thiong'o, 2017; Körbahti, Aktaş, & Tanyolaç, 2007). Paints are often categorized by their function or application purpose as architectural coatings, industrial coatings, special purpose coatings, varnishes, lacquers, etc.

1.3 PAINT WASTEWATER

It is important to develop a wastewater treatment technique which is environmentally, economically and ethically sustainable along with the efficiency (Nair K, Manu, & Azhoni, 2021). Paint industry wastewater has been shown to be loaded with manufacturing wastes and causes major complications in treatment due to the indefinite chemical structure of the mixtures of compounds they are made of. In accordance with that, a suitable treatment methodology is to be adopted so as to reduce the impact of emulsions in water in terms of COD removal efficiency. The application of advanced oxidation processes (AOPs) in the mineralization and degradation of toxic and recalcitrant organic pollutants have been proven to be excellent from the past decades (Benatti, Tavares, & Guedes, 2006; Ganiyu, de Araújo Costa, Martínez-Huitle, & dos Santos, 2020; Garrido-Ramírez, Theng, & Mora, 2010; Nidheesh, 2015; Sangami & Manu, 2017a; Tarkwa et al., 2019).

1.4 HETEROGENEOUS FENTON'S OXIDATION

Among different AOPs, the classic Fenton and Fenton-like reagents remain attractive alternative for the removal of non-biodegradable contaminants.

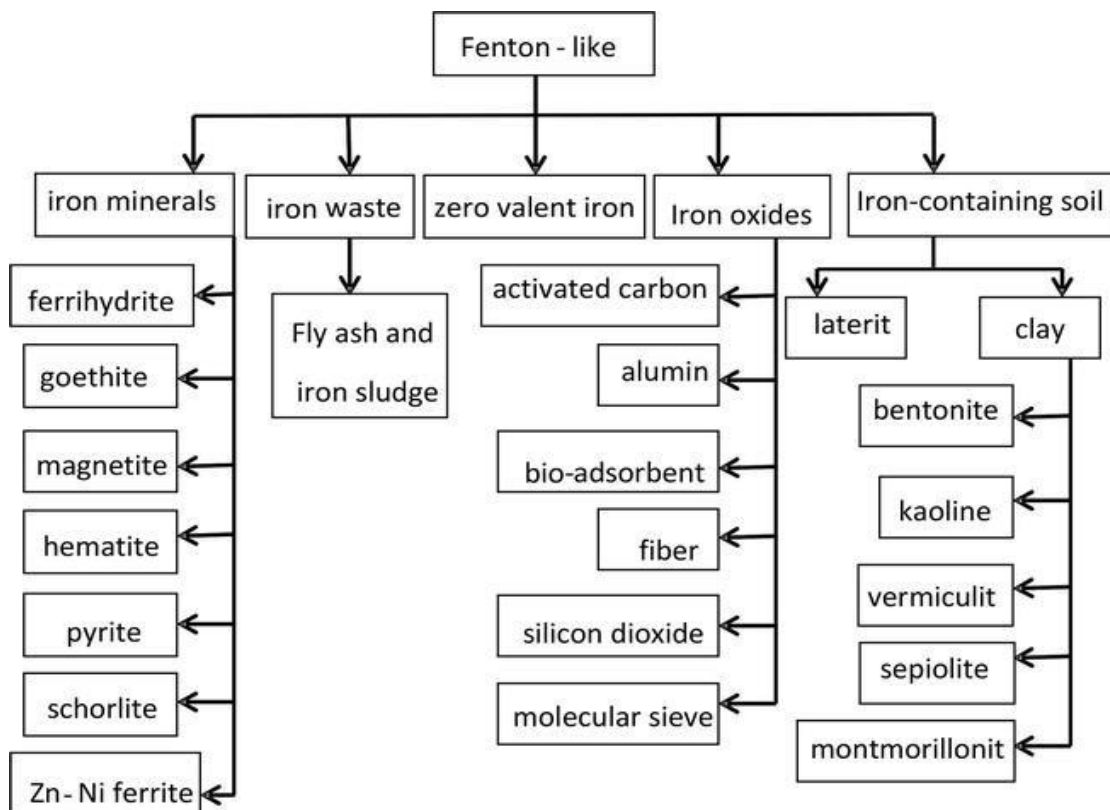


Figure 1.1 Various types of Fenton-like catalyst (Min Xu, 2015)

However these systems are seriously affected by the typical problems of homogenous catalysis (separation, regeneration) and also by ineffective consumption of H_2O_2 and acid range pH adjustment requirements. Thus, different Fenton like heterogeneous catalyst have been developed by immobilizing transition cations on adequate supports such as zeolites, pillared clays, silica, activated carbon, etc.

1.5 LATERITE SOIL

Laterite is a soil type rich in Iron, Aluminium, and Silica formed in hot and wet tropical areas. It is formed by intensive and long-lasting weathering of the underlying parent rock. Mineralogical and chemical compositions of laterite are dependent on their parent rocks. Laterisation, also known as tropical weathering, is a protracted chemical and mechanical weathering process that produces a wide range of soils in terms of their chemistry, grade, thickness, and ore mineralogy. India's flat uplands are often covered in laterite soil, which is also dispersed along the western coast and receives exceptionally strong rainfall. Additionally, there are minor areas of Karnataka, Tamil Nadu, Orissa, the Chota Nagpur Plateau in the north, and Meghalaya that are bordered by lateritic soil along the eastern edge of the plateau. Compared to other methods, using iron and aluminium from laterite soil is more affordable and environmentally friendly.

Various heterogeneous catalysts and the advances of their uses in efficient treatment of different wastewaters in recent years have been reviewed in Nidheesh (2015). Among the recently considered heterogeneous catalysts, laterite is one of the important and novel catalysts (A. R. Khataee & Pakdehi, 2014) which is known for its richness in iron oxides (Ganiyu et al., 2020; A. Khataee, Salahpour, Fathinia, Seyyedi, & Vahid, 2015; Gloria Murielle Rostandi Kpinsoton et al., 2018; R. Nagarajan, 2015) such as Fe_2O_3 (hematite) and Fe_3O_4 (magnetite) (Changduang, Limpiyakorn, Punyapalakul, & Thayanukul, 2021; Koottatep et al., 2017; Sen, Takahashi, Fortin, Spottiswood, & Yasar, 1987) that can be utilized as a catalyst in both homogeneous Fenton process (Karale, Manu, & Shrihari, 2014; Sangami & Manu, 2017b) as well as heterogeneous Fenton-like oxidation (Kamagate et al., 2018; A. Khataee et al., 2015; Koottatep et al., 2017). In addition, laterite has a natural mesoporous structure (A. Khataee et al., 2015; Koottatep et al., 2017) with spherical particles and large specific surface area (Sen et al., 1987). This can be a boon for its use as heterogeneous Fenton's catalyst. Moreover, laterite is found in abundance in the tropical and subtropical areas (R. Nagarajan, 2015), considerably

cheaper and is suitably unaffected by thermal and chemical processes (Ganiyu et al., 2020; Han et al., 2020; Nidheesh, 2015)

Earlier studies have identified the potential to improve the catalytic properties of laterite with heat treatment or calcination at different temperatures (Ganiyu et al., 2020; A. Khataee et al., 2015; Gloria Murielle Rostandi Kpinsoton et al., 2018). Laterite soil calcined at 350°C for 3hrs was used for the treatment of an azo dye C.I. Acid Red 17 with heterogeneous photo Fenton-like process. The decolorization efficiency was increased beyond 95% compared with around 35% using uncalcined laterite. This showed that the calcination of laterite soil improved the treatment efficiency (A. Khataee et al., 2015). Effect of different calcination temperatures 400°C, 600°C and 800°C on efficiency of laterite soil as heterogeneous Fenton's catalyst for removal of Methylene Blue was investigated by Gloria M.R. Kpinsoton et al. (2018). The laterite calcined at 600°C was found to be most effective in the degradation of methylene blue with 99% degradation after 100 minutes of treatment at room temperature.

1.6 GREEN SYNTHESIS OF FENTON'S CATALYSTS

Numerous chemical and physical processes, such as chemical reduction, pyrolysis, electrochemical, template-assisted synthesis method, hydrothermal synthesis, vapor-solid growth techniques, sol-gel process, etc. are used to produce nanoparticles. Iron nanoparticles (FeNPs) have shown to be extremely effective for the removal or remediation of a wide range of pollutants, including azo dye, antibiotic, insecticide, nitrate, alkaline-earth metals. Among these methods, the chemical reduction method is most often used for its simple operation and equipment. In this method, using a reducing agent, the metal salt in aqueous solution is reduced to metal nanoparticles, and the particles are prevented from aggregation by a stabilizing agent.

The removal or remediation of a variety of pollutants, including azo dyes (Jadidi Kouhbanani et al., 2018; Lazaar et al., 2022; Z. Wang, Fang, & Megharaj, 2014), antibiotics, insecticides, herbicides (Sangami & Manu, 2017d), brominated and chlorinated organic compounds (Kuang, Wang, Chen, Megharaj, & Naidu, 2013; Smuleac, Varma, Sikdar, & Bhattacharyya, 2011), etc., has shown iron nanoparticles (FeNPs) to be incredibly successful. In general, a variety of chemical and physical processes, such as chemical reduction, pyrolysis, electrochemical, template-assisted

synthesis, hydrothermal synthesis, vapor-solid growth techniques, sol-gel process, and chemical co-precipitation, are employed to make nanoparticles. The chemical reduction process is one of these that is most frequently employed due to its easy operation and equipment. These techniques have a lot of drawbacks even if they can create nanoparticles with appropriate sizes and shapes. These procedures employ chemicals like organic solvents, reducing agents, and stabilisers that are not biodegradable, pose environmental risks, and may be hazardous to people and other living things (Jadidi Kouhbanani et al., 2018). The metal salt in aqueous solution is reduced to metal nanoparticles using a reducing agent in this process, and a stabilising agent prevents the particles from aggregating. Chelating agents and several dispersants/surfactants are utilised in the chemical production of nanomaterials to prevent agglomeration. However, a lot of organic chelating and dispersing chemicals are found to be toxic enough to contaminate the environment when used in the mass manufacture of nanomaterials (Mohan Kumar, Mandal, Siva Kumar, Sreedhara Reddy, & Sreedhar, 2013).

1.7 THE INDIAN ALMOND (*Terminalia catappa*)

The huge tree species known as Indian almond (*Terminalia catappa*) is primarily found in the tropics and is a member of the Bàng (Combretaceae) family (Hung et al., 2022). The natural range of the tree is unknown because people have widely dispersed it. It has long since been a part of nature throughout a vast region that stretches from Africa to northern Australia, New Guinea, and the Indian subcontinent through Southeast Asia and Micronesia. Parts of the Americas have recently received the plant's introduction (Fan et al., 2004). The abundant presence of phenolic compounds or polyphenolic acids is a characteristic particular of the leaves of this plant, such as the acid Gallic (Tanaka et al., 1986). The leaves also include phytosterols, saponines, various tannins, including punicalin, punicalagin, and tercatin, as well as a number of flavonoids, including kaempferol and quercetin (Gutiérrez-Pineda & Herrera, 2022). The leaves (and the bark) are utilised in many herbal remedies for a variety of purposes as a result of their chemical richness. Although they have no proven anticarcinogenic qualities, the leaves may include antioxidants, anticlastogenic capabilities, and compounds for cancer prevention (Hung et al., 2022). It is well-known to reduce pH and heavy metal content of the water in the aquariums, and fish breeders have been using it in this way for many years. Additionally, it is thought to aid in preventing the growth of fungus on fish eggshells (Malawa et al.,

2022). The aqueous leaf extract of *T. catappa* was used in the creation of silver nanoparticles, which involved polyphenols as the predominant component (Muthulakshmi et al., 2022). Plant-based metal nanoparticle synthesis is shown to be nontoxic and environmentally safe (Naseem & Farrukh, 2015).

1.8 TOXICITY EVALUATION

Due to the harmful effects of various compounds to the living things at concentrations below chemical detection limits, toxicity tests have become more important (Barbusiński, 2005). Recycling of the treated industrial wastewater by using it for gardening and agricultural activities has been followed in recent decades. Thus, it is necessary to do the toxicity analysis for the plants and the soil bacteria before the application of treated wastewaters.

From the above brief introduction, it can be concluded that Fenton's oxidation process can be an economical technique for the treatment of paint industry wastewater. However, the treatment of paint wastewater using laterite soil as sorbent/catalyst is rarely investigated to the best of my knowledge. At present, the industries are following the conventional physical chemical treatment where the chemicals are not degraded but instead form large amounts of sludge. So, in order to degrade the toxicity of the emulsions in water and reduce the sludge, Fenton's process is adopted.

1.9 RESEARCH OBJECTIVES

The purpose of this research is to reduce the toxicity of emulsions in water. The objectives of the present study are as follows:

1. To evaluate the Fenton's oxidation process for the treatment of three different emulsions in water.
 - (a) By optimizing the pH, hydrogen peroxide dosage and iron concentration (iron extracted from laterite soil and nano catalyst synthesized using iron from laterite soil and a suitable plant leaf extract)
2. To investigate the toxicity of the raw wastewater and treated water using lab scale model.

1.10 ORGANIZATION OF THESIS

Chapter 1 This chapter provides the introduction to Paint industry wastewater, their effects on the environment, a brief idea on advanced oxidation process, Fenton process, laterite soil, green synthesized catalysts, toxicity evaluation of treated water, need, significance, and objective of the research.

Chapter 2 It deals with the review on conventional treatment techniques for paint wastewater used, its advantages and disadvantages, and identifies the need for a sustainable treatment technique. Also, the relevance of Heterogeneous Fenton's oxidation, the knowledge gap in the area is discussed. A brief review on the green synthesized heterogeneous Fenton's catalyst, the need to improve the catalyst efficiency is described. It also gives the importance of toxicity analysis of treated wastewater using advanced oxidation process.

Chapter 3 It provides a brief idea on the details about the sampling, materials, experimental methodology with a novel catalyst, analytical techniques, and the tools used for the optimization of process.

Chapter 4 The results and discussion on the synthesis of heterogeneous catalyst and FeNPs from laterite using sustainable plant extracts and its application as a Fenton like catalyst to treat paint wastewater is explained in detail in this chapter. Also, the results of the toxicity analysis done for the treated wastewater are discussed in the chapter.

Chapter 5 It gives the information about the conclusions drawn, based on the experimental results along with the recommendations and scope for the future work.

CHAPTER 2

LITERATURE REVIEW

2.1 OVERVIEW OF PAINT INDUSTRY: PRODUCTION, USE AND DISPOSAL OF PAINTS

Paint manufacturing industries uses large quantities of water and chemicals, and hence, produces large volume of wastewater. According to one estimate (Nicholas, 2018), paint manufacturing industries, worldwide, use about 75 to 85 million gallons per day out of which only about 4% of it is recycled. Nearly 70% of this wastewater is discharged untreated in the natural water bodies while about 25% gets evaporated (Nicholas, 2018). Depending on the manufacturing processes of individual industrial units, the composition of paint industry wastewater varies widely (Dovletoglou, Philippopoulos, & Grigoropoulou, 2002). Usually, they consist of the cleansing water from polymerization and mixing tanks (Dovletoglou et al., 2002; Güven, Hanhan, Aksoy, Insel, & Çokgör, 2017; Zagklis, Koutsoukos, & Paraskeva, 2012). Therefore, the discharge of the effluents from these industries straight to the water bodies causes severe ecological instability, including direct poisoning of the animal biota and inhibition of photosynthesis of aquatic plants (since the presence of color impedes sunlight penetration) (Aboulhassan, Souabi, Yaacoubi, & Baudu, 2014a; da Silva, Barbosa, de Paula, Romualdo, & Andrade, 2016). Such impacts on the quality of the receiving streams lead to the exhaustion of Dissolved Oxygen (DO).

Some of the hazardous chemical elements also infiltrate and leach into the subsurface environment and gradually settle in the soil and sediment of water bodies (Aniyikaiye et al., 2019). Moreover, even the meager presence of toxic elements in water bodies has the potential to create adverse effects on living beings including affecting the food chain of organisms and to aquatic life (Aboulhassan et al., 2014a; Aniyikaiye et al., 2019; da Silva et al., 2016; Menkiti, Okoani, & Ejimofor, 2018). Therefore, reducing their concentrations to tolerable limits prior to disposing into the environment (Aniyikaiye et al., 2019; Menkiti et al., 2018) is essential. The discharge effluent standards of industrial wastewater as per Bureau of Indian Standards and the characteristics of a paint industry wastewater (Aboulhassan et al., 2014a) is tabulated below in **Table 2.1** for comparison.

Table 2.1 Characteristic of a paint industry wastewater and limits as per Indian Standards

Parameters	Characteristic of a paint industry wastewater (Aboulhassan et al., 2014a)	Discharge standards			
		Into inland Surface Waters (IS2490-Pt-1:1981)	Into Public Sewers (IS3306:1974)	On Land for Irrigation (IS3307:1977)	Marine Coastal (IS7968:1976)
pH	6.7 – 7.8	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0
BOD (5 days at 20 ⁰ C), max	960-968	30	350	100	100
COD mg/l, Max	4438-25100	250	-	-	250
Temperature (°C)	30 – 45	Shall not exceed 40	45, at the		45 at the point of discharge
Suspended Solids, mg/l, max	220-1200	100	600	200	For process wastewaters - 1000
Dissolved Solids(inorganic) mg/l, Max		2100	2100	2100	-
Oil and grease mg/l, max	22-138	10	20	10	20

2.2 EFFECTS OF PAINTS ONTO ENVIRONMENT AND THE NEED FOR TREATMENT OF PAINT INDUSTRY WASTEWATER

Wastewater from paint industries contain significant organic content and thus environmentally toxic for direct disposal (Zagklis et al., 2012). Various organic substances such as acids, alkalis, solvents, surfactants found in the paint wastewater constitute toxic pollutants (Kakoi et al., 2017). These toxic effluents containing obstinate compounds (like phenols) in the wastewater (de Oliveira et al., 2007) cause particular

threats to the aquatic life. The characterizations of wastewater from the paint industry (Güven et al., 2017) show their non-biodegradability with high chemical oxygen demand (COD) and suspended solids, heavy metals (such as Zn, Ni, Pb, Cu, Cr and Cd), toxic compounds, and color, (Aboulhassan et al. 2014; Aniyikaiye et al. 2019; Balik and Aydin 2016a; Barbosa et al. 2018; Güven et al. 2017; Krithika and Philip 2016; Menkiti, Okoani, and Ejimofor 2018), besides odor, and large amounts of organic and toxic chemical compounds such as surfactants, organic micro pollutants (like monocyclic and polycyclic aromatic hydrocarbons) (Güven et al., 2017), bactericides, oils, solvents, and preservative agents (da Silva et al. 2016). Paint wastewater has been thus shown to be severely loaded with manufacturing wastes and causes major complications in treatment due to the indefinite chemical structure of the mixtures of compounds they are made of (Dovletoglou et al., 2002).

The sludge from the paint wastewater treatment is a substantial waste byproduct which poses a serious challenge for disposal and hence requires careful control (Güven et al., 2017). The sludge can be solvent-based or water-based, according to the paint type. By the distillation process, the solvent constituent of the solvent-based paint sludge can be recovered. But there is no common or efficient and sustainable methodology to recycle or reuse the water-based paint sludge produced (Salihoglu, Ucaroglu, & Salihoglu, 2018). Hence, a combination of various methods to effectively treat such wastewater, so as to safely discard or reuse it in its production processes, (Barbosa et al., 2018) is essential. A few recent reviews on treatment of paint industry related wastewater treatment methods are summarized in Table 2.2. Among them, a one (Putatunda, Bhattacharya, Sen, & Bhattacharjee, 2019) reviewed recently proposed methodologies of treating emulsified oily wastewater from various industrial effluents including from paint industries, petrochemicals, food processing and automobile.

Sustainability is often understood exclusively as environmental sustainability or economic and resources sustainability such that the need for enabling those very processes that makes the environment or the resources sustainable, for example the sustainability of waste treatment processes itself, is overlooked. From resources point of view, sustainability is often understood as the level of consumption that satisfies the demand of the present without compromising the need for the future (Kaminsky & Javernick-Will, 2015).

Table 2.2 Recent reviews on treatment methods related to wastewater from paint industries.

Author and year	Source	Summary
(Vinay Kumar & Dwivedi, 2021)	Journal of Cleaner Production	Removal Nickel and Chromium from various industries including paint
(D. Sharma, Chaudhari, Dubey, & Prajapati, 2020)	Journal of Environmental Engineering	Electrochemical methods of effluent treatment including paint
(G. Sharma & Kandasubramanian, 2020)	Journal of Chemical and Engineering Data	Applications of various Molecular-imprinted polymers in the elimination of heavy metal ions and some common toxic dyes
(Jha & Kumar, 2019)	Bioprocesses and Biosystems Engineering	Different extraction techniques of biopolymers from waste and paints
(Putatunda et al., 2019)	International Journal of Environmental Science and Technology	Different treatment processes for emulsified oily wastewater from petrochemical, heavy metal, food processing, paint, automobile industries
(Popli & Patel, 2015)	International Journal of Environmental Science and Technology	Application of biological processes for azo dyes removal from industrial effluents.

In the context of the United Nations Sustainable Development Goals, sustainability is understood in a much broader sense to include socio-economic and ethical aspects of sustainability. Goal No. 14 of the UN SDG, life below water, is particularly pertinent in the light of wastewaters often being discharged directly into the water sources (Riveros,

2018) which ultimately finds its way into the sea and thereby affecting the attainment of the Sustainable Development Goals. Developing sustainable methods of treating wastewaters from industries in general will go a long way in attaining the United Nations Sustainable Goals sooner than later.

The aim of this review is thus, to evaluate the state-of-the-art of the current practices and advances in treating wastewater effluents with a particular focus on treatment of wastewater from paint industries and thereby identify sustainable and efficient techniques.

2.3 AVAILABLE TREATMENT TECHNIQUES FOR PAINT WASTEWATER

The commonly used treatment technologies implemented by paint industries include physicochemical treatments (Aniyikaiye et al., 2019; Huang & Ghadirian, 1974) like coagulation, flocculation and sedimentation (Balik and Aydin 2016; Dovletoglou, Philippopoulos, and Grigoropoulou 2002; Eremektar et al. 2006; Kakoi et al. 2017; Mamadiev and Yilmaz 2011; Menkiti, Okoani, and Ejimofor 2018; Riveros 2018), electrocoagulation (Barbosa et al., 2018; da Silva et al., 2016; Körbahti et al., 2007; Körbahti & Tanyolaç, 2009), microfiltration, dissolved air flotation (El-Shazly et al., 2010), electroflotation (Mohtashami & Shang, 2019), membrane filtration process (Mamadiev & Yilmaz, 2011; Vishali, Roshini, Samyuktha, & Ashish anand, 2018; Zagklis et al., 2012), adsorption (Malakootian, Almasi, & Hossaini, 2008; Malakootian, Nouri, & Hossaini, 2009) and ionizing radiation (Nascimento et al., 2013). Multilevel Contact Oxidation (Zhu, Zhu, Fienko, Yuanhua, & Kuo, 2017) and advanced oxidation processes like Fenton's oxidation (de Oliveira et al., 2007; Kurt, Avsar, & Talha Gonullu, 2006; Mamadiev & Yilmaz, 2011) have been adopted by various studies. On the other hand, the combined effectiveness of chemical and biological processes (Aboulhassan et al., 2014a), thermo-chemical combined processes (Sahu, 2016), radiation combined with coagulation and adsorption (Sawy, Sokker, Hassan, & Anadouli, 2012) have also been studied. Among the biological methods, activated sludge process (Satyanarayan & Kaul, 2001), submerged attached growth reactor (Krithika & Philip, 2016), sequencing batch reactor (SBR) (Güven et al., 2017), bioremediation (Nharingo & Moyo, 2016), and bio-composting (Salihoglu et al., 2018) have been reported in literature. Paint wastewater is thus well-thought-out as a severely loaded manufacturing waste and causes major complications in treatment due to the indefinite chemical structure of the mixtures of

compounds made of toxic effluents that contain obstinate compounds (like phenols) are present. Moreover, depending on the definite production procedures of individual industrial units, the composition of paint industry wastewater varies (Dovletoglou et al., 2002). Usually, they consist of the cleansing water from polymerization and mixing tanks, comprising ultimate compounds diluted in order to obtain the specific product (Zagklis et al., 2012).



Figure 2.1 Various treatment techniques adopted for PIWW (Nair K et al., 2021)

2.3.1 Physicochemical treatment

Physicochemical treatment of wastewater mainly involves processes such as sedimentation, coagulation, flocculation and filtration. These processes primarily focus on separating the colloidal and suspended particles. Coagulation and flocculation is achieved through the addition of chemicals called coagulants and flocculants that enables the

particles to form flocs and settle down under gravity during sedimentation after which the solids can be separated by filtration depending upon their particle size.

Physical-chemical treatability and the effect of pH and polymer addition is an important characteristic of latex paint wastewater (Huang & Ghadirian, 1974). Studies (Huang & Ghadirian, 1974) have shown that wastewater remains stable at neutral pH, and very little effect on treatability such as, sedimentation rate and removal efficiency of Chemical Oxygen Demand (COD), Total Solid (TS), Volatile Solids (VS), and alkyl benzene sulfonate (ABS), is observed in the presence of polymer unless a critical polymer concentration is reached. A low pH of 3.5 is observed as a critical pH for effective treating (90% solids removal) while less removal efficiency is observed for pH more than 10. With the amount of polymer added, the removal of solids, ABS, and COD is increased.

In order to ensure that the treated wastewater meets the safe disposal limits, physicochemical parameters of raw and treated wastewater, the effectiveness and the agreement level of different paint industries wastewater treatment plants were studied by Aniyikaiye et al., 2019. Studies on five wastewater treatment plants in Lagos, Nigeria (Aniyikaiye et al., 2019), conducted with some regulatory standards in South Africa, revealed that the plants of the companies considered for the study were ineffectual in decreasing the TS, Total Suspended Solids (TSS), Biochemical Oxygen Demand (BOD), COD and oil & grease to standard values. The experimental data reported high level of pollution released into the environment by paint industries. Similarly, another study (Riveros, 2018) investigating wastewater from latex paint industries in Peru showed large concentration of suspended solids (SS) (>5,000 ppm), COD > 1,000 ppm and bacterial content (>100,000 CFU/mL) even after treatment using physico-chemical treatment. It was reported that many paint industries do not treat their effluent before discharging, while the WWTP (wastewater treatment plant) of the few is inefficient to bring the quality of the effluents to environmentally acceptable safe limits. A summary of the various physicochemical treatment methods surveyed is provided in Table 2.3. Each of these treatment methodologies are elaborated in the following subsections.

Table 2.3 Summary of surveyed literatures on physicochemical treatment technologies

References	Treatment method	Results and conclusion	Remarks
(Balik & Aydin, 2016b)	Coagulation with alum, FeSO ₄ , and PACl.	COD removal- 88% SS removal- 100% Color removal- 46-72%	FeSO ₄ is most economic.
(Eremektar et al., 2006)	Coagulation-flocculation with sodium bentonite, alum, FeCl ₃ and FeSO ₄	50 mg/l of FeCl ₃ at pH 5.9 COD removal 40%.	Efficiency is very low.
(Zagklis et al., 2012)	Coagulation-flocculation with poly electrolytes, further ultrafiltration and reverse osmosis.	93% efficiency	The problem of fouling of membrane and also costlier.
(Riveros, 2018)	Coagulation with PAC and Flocculation with PAM. Also, disinfection with sodium hypochlorite	56% of raw wastewater obtained for recycling.	Sludge management not considered
(El-Shazly et al., 2010)	Coagulation/flocculation and filtration using palm hemp	Removal of COD, TSS and BOD ₅ - 85%, 91% and 90%, respectively	The use of hemp as makes the system difficult to maintain and operate well.
(Kakoi et al., 2017)	Coagulation and flocculation using bio-coagulant Maerua Decumbent	turbidity, COD, lead, and chromium removals of 99.2, 78.6, 100, and 99.97%, respectively	treatment will depend on the availability of bio-coagulant.
(Nharingo & Moyo, 2016)	Coagulation and flocculation by Opuntia ficus-indica	removal efficiency of 50-98.7%, 11-93.62% and 17-100% for turbidity, chemical oxygen demand and	treatment will depend on the availability of bio-coagulant

		heavy metals respectively.	
(Vishali et al., 2018)	Coagulation using <i>Moringa oleifera</i> , flocculation sedimentation, sand filtration, and membrane filtration	90% and 88% for color and turbidity removal, respectively	filtration techniques will require O & M cost and also treatment will depend on the availability of <i>M. oleifera</i>
(da Silva et al., 2016)	coagulation (aluminum sulfate) coupled to electrochemical methods (BDD electrode).	Optimum values: 12 mL/L of $Al_2(SO_4)_3$ dosage $i = 10 \text{ mA/cm}^2$ and $t = 90 \text{ min}$	Sludge management not considered
(Körbahti et al., 2007)	Electrochemical oxidation	Removal of COD- 65.68%, color- 98.74% and turbidity-96.56%	less economic and requires skilled supervision
(Barbosa et al., 2018)	Natural coagulation using <i>Moringa oleifera</i> aqueous extract and electrolytic flow process	85% organic load removal.	treatment will depend on the availability of bio-coagulant
(Menkiti et al., 2018)	Adsorptive component of coagulation– flocculation using <i>Brachystegia eurycoma</i> (seed)	Process efficiency 96.50% at coagulant dosage of 5 g/L, pH 8 and coagulation temperature of 35 °C	treatment will depend on the availability of bio-coagulant
(Nascimento et al., 2013)	Ionizing radiation	COD removal 30%	little-known technology, more expensive, less efficiency

(Mohtashami & Shang, 2019)	continuous-flow electro flotation reactor and stainless-steel electrodes	TSS removal rate 95±7% under initial total solids 500 mg/L, current density 100 A/m ² , retention time 8 min	little-known technology, more expensive
(Malakootian et al., 2008)	Adsorption using wood ash.	The maximum Pb removal efficiency- 96.1% maximum Co removal efficiency- 99 %.	adsorption rate increased as the amount of wood ash increased
(Malakootian et al., 2009)	Adsorption with light expanded clay aggregate (leca)	The maximum removal efficiency for Pb- 93.75 % while for cadmium, it was nearly 89.7 % at the same condition.	Leca suggested as a cheap and easily obtainable adsorbent

2.3.1.1 Coagulation

Coagulation and flocculation are well-known techniques used in treatment of wastewater containing colloids or suspended particles and metal ions. The effect of dosage of coagulant and effective pH on the quality of wastewater treated is an important factor in coagulation process. Various studies have investigated the coagulation of paint industry wastewater using different coagulants such sulfates of iron and aluminum (Dovletoglou et al., 2002) and polyaluminum chloride (PACl) (Balik & Aydin, 2016b). On the other hand, the COD removal efficiencies and operating costs using coagulants such as sodium bentonite, alum, FeCl₃, and FeSO₄ have been assessed (Eremektar et al., 2006). The key findings of these papers are highlighted below.

Findings from Dovletoglou, Philippopoulos, and Grigoropoulou (2002) concludes that the most favorable pH for FeSO₄ was around 9.7, with an average efficiency of the process ranging from 30 to 80% for COD and 70 to 99% for turbidity, at a coagulant dose of about 2 g/L, for a varied range of batch of wastewater. The need of pH adjustment was not there in case of aluminum sulfate while the effective dose of coagulant was 25g/l and efficiency of process ranged from 70 to 95% for COD and 90 to 99% for turbidity

(Dovletoglou et al., 2002). In addition, the raising of pH of the alum-sludge supernatant to 10 showed improved process efficiency. With PACl as the coagulant, an efficiency of 98% removal of both COD and turbidity was found at an optimum pH near 7 and an effective dose of 4g/L. The excessive application of coagulants was found to have negative effect on the treatment processes of paint industry wastewater as is evident from measuring the organic load in the form of COD, particle size distribution, pH, and ζ potential of suspended solids (Zagklis et al., 2012).

Besides the removal of COD and other organic loads, minimizing the sludge produced from the coagulation process is also essential since sludge disposal is an additional task. Studies (Balik & Aydin, 2016b) conducted with varying concentrations of coagulants to evaluate the amount of sludge shows that with lower concentrations, COD removal efficiency was reduced by 10%, whereas color and SS removal improved. Initial tests with higher concentrations of alum, PACl, and FeCl_3 were found to be 86-88%, 100% and 46-72% efficient for COD, suspended solids, and color respectively. The most favorable removal efficiency was attained by 250mg/l alum and FeCl_3 dosage, and 4mg/l of optimum anionic polyelectrolyte dose (Balik & Aydin, 2016b). When coagulants were dosed in equal quantities, the sludge amounts were found to be $\text{FeCl}_3 > \text{PACl} > \text{FeSO}_4 \geq$ alum. Thus, it was concluded that process efficiency was not increasing with increased quantity ($> 2,000$ mg/l) of coagulants, but rather it produced more sludge.

The efficiency of the coagulation process varies with the dosage and experimental conditions. High removal efficiencies ($>95\%$) were attained by introducing lesser doses of coagulants (<500 mg/l) under suitable experimental conditions. FeCl_3 and alum showed the highest treatment efficiencies, whereas FeSO_4 gave economic treatment (Balik & Aydin, 2016b). Compared to 63% of method efficiency for the anionic flocculants that act as primary coagulants, cationic polyelectrolytes are found to have a higher potential than them, with process efficiency in the range of 85–90%. High efficiency (in the range of 80–90%) is achieved with a blend of aluminum sulfate and PACl with polyelectrolytes (Dovletoglou et al., 2002). A study (Zagklis et al., 2012) conducted on different polyelectrolytes for optimizing the prevailing processes by using new chemical reagents showed a percentage removal of about 93%. It was observed that high percentage removal was attained for the lesser concentration of polyelectrolytes (400 mg/L instead of 1000 mg/L), in comparison with that utilized by the industry.

2.3.1.2 Coagulation with flocculation and filtration

Coagulation is a process of applying coagulants to destabilize the suspended particles and flocculation is done to agglomerate them so as to form flocs and promote settling. Paint industry effluent treatment using aluminum polychloride (PAC) as a coagulant and anionic polyacrylamide (PAM) as flocculant (Riveros, 2018) showed that it was possible to produce three varieties of acrylic latex paintings with treated water which met the quality standards such as pH, viscosity, and density. Recycling of about 56% of the raw wastewater produced was reported (Riveros, 2018). However, the suspended particles after coagulation have to be removed through the process of filtration in which the suspended solid matters are separated from the liquid by passing the mixture through a membrane or filter. Filtering the flocs after coagulation and flocculation is usually done using different filtration techniques, such as ultrafiltration, microfiltration, and bio-filtration (Smidova et al. 2005, El-Shazly, Hasanin, and Kamel 2010; Zagklis, Koutsoukos, and Paraskeva 2012). In order to remove the residual organic matter after the coagulation/flocculation, (Zagklis et al., 2012) a combination of ultrafiltration and reverse osmosis which removes nearly all organic load is often applied. Ultrafiltration does not change the waste considerably but is successful in removing all the larger suspended solids, making it capable for reverse osmosis process. The organic content of the wastewater decreased to 30 mg/L with the use of reverse osmosis membrane, and the ultimate discharge was fit to use for recycle, irrigation, or disposal to water sources (Zagklis et al., 2012). Other studies (Šmídová, Mikulášek, & Skoupil, 2005) used microfiltration as separation process for removal of solid particles in wastewater from a water-based paint industry. For this, (Šmídová et al., 2005) conducted experiments on tubular ceramic membranes made from α -Al₂O₃ with the mean size of pores reaching 0.1 μ m which conclusively demonstrates that cross-flow microfiltration is an appropriate process for the treatment paint industry wastewater.

A treatment technique was proposed by El-Shazly, Hasanin, and Kamel (2010) in which physicochemical treatment is tailed by filtration method using palm hemp as filtration media with aeration for 1 hour and Dissolved Air Flootation (DAF) unit when needed. The chemicals used were NaOH, Alum, FeSal. and polymer. The removal efficiencies in average for COD, BOD₅, and TSS after the application of proposed treatment technique

were 85%, 91%, and 90%, respectively. But, the use of hemp as filtration media makes the system difficult to maintain and operate well.

Processes involving a treatment series comprising of coagulation, flocculation, sedimentation, sand filtration, and membrane filtration is also reported in literature. The use of the coagulation unit, with sand filtration and membrane filtration unit, helped in achieving total color removal of effluent and 99% turbidity removal.

2.3.1.3 Coagulation/Flocculation using Bio-coagulants.

Coagulation process can be enhanced using natural coagulants in the form of seeds, mucilage, leaves, grains, fruits, gum and foliage of plants. Biocoagulation process mainly works by the mechanism of adsorption, polymer bridging and charge neutralization. In all these processes biocoagulant makes the smaller suspended particles collectable and make them settle (Saleem & Bachmann, 2019). The bio-coagulants are said to have many advantages including cost effectiveness (Maduabuchi MN, 2018), biodegradability, ability to maintain the pH, producing toxin-free treated water and low sludge volume (Vishali et al., 2018). One of such study (Kakoi et al., 2017) was carried out by applying response surface methodology (RSM) to optimize the coagulation and flocculation of the wastewater using the bio-coagulant *Maerua decumbent*. Optimum settings for *Maerua* in turbidity removal was dosage :1 kg m⁻³, pH- 5.56 and settling time- 52.31 min; COD: dosage-0.8 kg m⁻³, pH-5.11, and settling time-53.53 min; Lead: dosage-1.165 kg.m⁻³, and pH-6.81; and Chromium: dosage-1.03 kg.m⁻³ and pH-5.78. At these conditions, *Maerua* attained turbidity, COD, Pb, and Cr removals of 99.2, 78.6, 100, and 99.97%, respectively, which was comparatively favorable than 98.6, 66.2, 96.16, and 94.38% removals for alum. In the similar manner, another study (Ezemagu, Ejimofor, & Menkiti, 2020) was done with *Mucuna seed*, which showed that the use of this bio-coagulant gave 89.54% particle load removal efficiency. Optimization of the parameters dosage, time and temperature was done by RSM by Central composite design (CCD) and the coagulation-flocculation process was found to follow Langmuir isotherm.

Moringa oleifera is used as a bio-coagulant in treating a refabricated water-based paint wastewater (Vishali et al., 2018). The study confirms that *M. oleifera* has a positive coagulation property so that it can be utilized as a good substitute for chemical coagulant. The results proposed that to treat one liter of effluent, 80mL *M. oleifera-eluate* was made

using 3g *M. oleifera* and 1N NaCl at actual pH of effluent which gave the most efficient removal for color and turbidity from the actual paint effluent of 90% and 88%, respectively. In another study (Barbosa et al., 2018) the treatment of paint (water-based) wastewater was done with bio-coagulant *Moringa oleifera* aqueous extract (MOAE), fortified with Ca^{2+} (from nitrate and chloride salts). The optimum coagulation-flocculation was achieved at pH 6.5 by using 80 mL of MOAE (50 g/L of MO and 0.125 mol/L of Ca^{2+}) per liter of wastewater. The reuse of extract is only likely if it is linked with Ca^{2+} ions from a nitrate salt.

The most appropriate coagulation methodology was reported to be adsorption-charge neutralization and adsorption-bridging which was due to the anionic and macromolecular nature of the deprotonated polygalacturonic acid in OFI materials that has been ascertained to have substantial coagulation capacity (Nharingo & Moyo, 2016). Also, the adsorption capacity of *Brachystegia eurycoma* (seed) as coagulant in coagulation/flocculation of paint wastewater is reported (Menkiti et al., 2018) to have achieved a treatment efficiency of 96.5% at coagulant dose of 5g/L, pH 8 and temperature of 35°C.

2.3.1.4 Coagulation and electrochemical process

Electrochemical processes are accompanied by the passage of electric current and helps in coagulating the particles by transfer of electrons. The oxidation of paint wastewater (water-based) electrochemically by batch-study using NaCl electrolyte with carbon electrodes show that the electrochemical technique can be used as a good substitute for traditional physico-chemical processes in treating water-based paint wastewater (Körbahti et al., 2007). By minimizing the potential difference, reaction temperature, and electrolyte concentration and maximizing the percentage removal of COD, color and turbidity at 100% pollution load, optimized electrochemical treatment conditions using response surface methodology gave maximum removal efficiencies for COD, color and turbidity as 65.68%, 98.74%, and 96.56%, respectively.

The practicality of reutilizing the water-based acrylic textured paint wastewater that is treated by the process of coagulation using aluminum sulfate and electrochemical method (BDD electrode), individually and combined together and the likelihood of discharging it to the water sources was examined (da Silva et al., 2016). Toxicity, color, turbidity, organic load, dissolved Al, alkalinity, odor, and hardness, were assessed. Under

optimized conditions, using only the chemical coagulation (12 mL/L of $\text{Al}_2(\text{SO}_4)_3$) method the viability of wastewater reuse was ascertained (da Silva et al., 2016). Whereas by using the electrochemical method ($i = 10 \text{ mA/cm}^2$ and $t = 90 \text{ min}$) the treated wastewater becomes appropriate for disposal into water sources, the problems accompanying the sludge generated in the chemical coagulation process are not taken into account and focus is more on water management.

An electrolytic flow process consisting of a filter-press reactor having a boron-doped diamond (BDD) electrode accompanied the treatment unit of paint (water-based) wastewater to develop the quality of the treated wastewater and make it apt for discharging (Barbosa et al., 2018). 35 mA/cm^2 of limiting current density and 90 minutes of electrolysis time were utilized in the electrochemical treatment. Besides eliminating the odor and organic load (85%), there was huge reduction in the number of mesophiles and the thermo-tolerant coliform growth. The method is said to meet the proposals for disposal, and for the reuse of treated wastewater.

In an experimental study (Mohtashami & Shang, 2019), a continuous-flow electroflotation apparatus having an effective volume of 38.4L and stainless-steel electrodes were designed and applied for the treatment of auto paint wastewater, with respect to the key process variables such as initial solids concentration, retention time and applied current density. The system efficiency in the removal of total suspended solids increases by increasing the applied current and retention time, while it has an inverse relationship with initial solids concentration. The highest percentage removal of the system was $95 \pm 7\%$ under initial total solids concentration of 500 mg/L, current density of 100 A/m^2 , retention time of 8 min, respectively.

2.3.1.5 Adsorption

Adsorption is a surface phenomenon in which an atom, ion or molecule of gas, liquid or soluble solid adheres to a surface. Various chemical and natural adsorbents (Malakootian et al., 2008, 2009; Menkiti et al., 2018; Nharingo & Moyo, 2016) are used to remove the heavy metals from the paint wastewater. A study (Malakootian et al., 2008) shows that wood ash, an easily obtainable as well as cheap adsorbent, can be used for removing heavy metals from the paint industry and similar wastewater. Batch experimental study was conducted in the heavy metal removal (Lead and Cobalt) from Binalood paint

industry (Kerman, Iran) effluent. In a similar way, the capability of light expanded clay aggregate (leca) in removing Pb and Cd from paint industry wastewater at various levels of adsorbent, contact time and pH was studied (Malakootian et al., 2009).

The influence of pH and the adsorbent quantity was found to be an important parameter in the treatment efficiency. The adsorption rate increased as the amount of wood ash increased. At pH 2, a contact time of 3h and wood ash 100g/L the removal efficiency was maximum for lead (96.1%) and cobalt (99%). Co had a greater affinity for wood ash than Pb at constant and varying pH (Malakootian et al., 2008). At an exposure of 10g/L of leca and pH 7, the removal efficiency for Pb was maximum (93.75%), while at the same condition it was about 89.7% for Cd.

Adsorption isotherms help in finding the pattern of adsorbance. The adsorption process was fitted with the Langmuir isotherm (Malakootian et al., 2008) and also Freundlich adsorption isotherm (R^2 Pb = 0.97 and R^2 Cd = 0.98) and the adequate contact time was estimated as 1-2 h for Pb and Cd (Malakootian et al., 2009). From the study, Leca is suggested as a cheap and easily obtainable adsorbent in removing Pb and Cd from the paint industry wastewater.

2.3.1.6 Radiation methods

Radiation methods are used in the treatment of wastewater that uses the short lived reactive species formed during the radiolysis of water for the efficient decomposition of pollutants. A decrease in organic compounds and suspended solids during the initial phase of degradation of the contaminants in wastewater from the polymeric coatings for the automotive and repainting process using the ionizing radiation was observed (Nascimento et al., 2013). But the efficiency of COD removal is only about 30%. Further research is to be conducted to enhance the methods of oxidation and degradation of complex molecules.

2.3.2 Advanced Oxidation Process

In recent years, advanced oxidation processes (AOPs) have been identified as an attractive option for wastewater purification, particularly in cases where the contaminant species are difficult to remove using biological or physicochemical processes. Advanced oxidation processes (AOP) are chemical treatment methods to remove organic materials from wastewater. It is usually achieved through various oxidation processes, such as

ozonation, photocatalytic degradation, Fenton's reagent, photo-Fenton, wet air oxidation (Abid, Alwan, & Abdul-Ridha, 2016), supercritical wet air oxidation and supercritical wateroxidation (Mishra et al., 2017). A great number of methods have been classified under the broad definition of AOPs (Figure 2.2). AOPs are those processes which rely on the generation of very reactive oxidising agents, i.e. free radicals such as the hydroxyl radical can initiate oxidative degradation reactions of refractory, synthetic and natural organic compounds and is capable of mineralising them ultimately to carbon dioxide and water owing to their high oxidation potential in aqueous solution.

Most of them use a combination of strong oxidising agents (e.g. Hydrogen peroxide and/or ozone) with catalyst (e.g. transition metal ions like ferrous salts) and irradiation (e.g. ultraviolet). Fenton like reactions ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$) generates hydroxyl radicals (OH^\bullet) by means of the reaction of H_2O_2 with ferrous ion, which is efficient and low-cost method, taking place at room temperature and at atmospheric pressure compared to all other advanced oxidation processes (Poyatos et al., 2010).

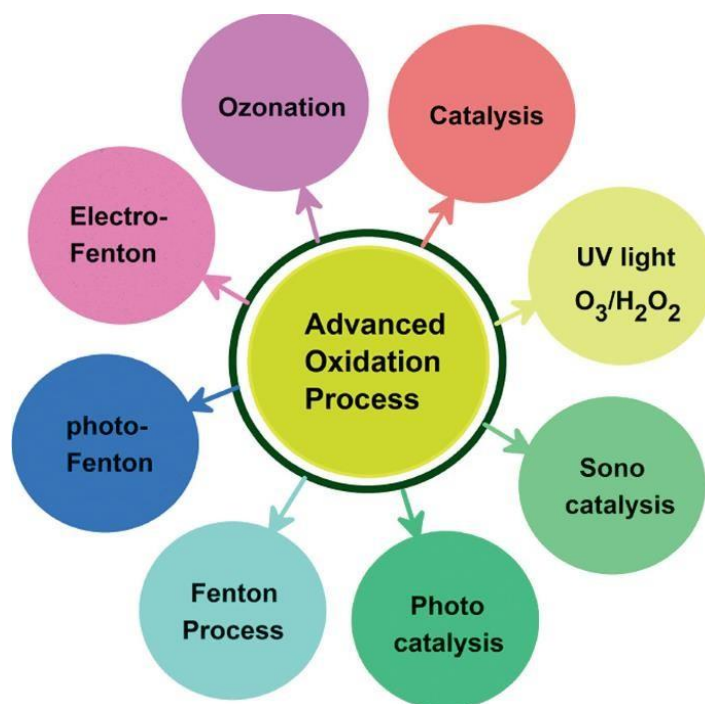


Figure 2.2 Types of AOPs (Poyatos et al., 2010)

They have been reported to be very effective for toxic and refractory organics in wastewater in dye-containing effluents (Marco A, Erick R., and Carlos A. 2011.). Of the many AOPs developed, the Fenton's oxidation process (FOP) is studied in paint

wastewater treatment. A summary of some of the Advanced Oxidation Process surveyed in paint industry wastewater is provided in Table 2.4 and are elaborated in the following subsections.

Table 2.4. Paint industry wastewater treatment with Advanced Oxidation Process

References	Treatment method	Results and conclusion	Remarks
(Kurt et al., 2006)	Fenton oxidation process using rust particles	COD removal 80%	rust materials practically not an efficient source of Fe ions.
(de Oliveira et al., 2007)	Fenton and photo-Fenton processes.	With photo-Fenton process assisted with solar radiation, reductions of 99.5 and 99.1% of COD and TOC levels	photo-Fenton's is very efficient in treating alkyd resin using solar light than artificial source.
(Mamadiev & Yilmaz, 2011)	Fenton oxidation process	81% of COD removal	sludge generated in the Fenton's process was not as much as in coagulation, hazardous chemical sludge clearance necessary

2.3.2.1 Fenton's oxidation process

Fenton's process is used to oxidize contaminants in wastewater with a solution of hydrogen peroxide and ferrous ion. This process is influenced by the pH, dosage of H₂O₂, and the concentration of the catalyst. Treatment of paint (water-based) wastewater using Fenton's oxidation process (Mamadiev & Yilmaz, 2011) was experimented using different Fenton's catalysts (Kurt et al., 2006) and photo-Fenton's (de Oliveira et al., 2007). In order to evaluate the effects of column dimension, size of packing material, the dosage of reactive, pH and reaction time, based on packed columns and mixed reactors, (Kurt et al., 2006) conducted experiments to improve the COD removal efficiency. The

experiments were done with rust particles as oxidized iron from the discard in the metal rolling process, as the catalyst for Fenton's process. By adjusting the pH, the COD removal was about 20%. But, by the influence of Fenton's method, in column and mixed-reactor studies, the removal efficiency was enhanced to around 80%. But, the use of rust materials as a catalyst is not a practically efficient source of Fe ions because the dissolved metal ions could be generated in significantly low pH (1.5) values and are comparatively trivial in size while the small particles of Fe may affect the rate of filtration undesirably.

2.3.2.2 Photo-Fenton's oxidation

The effectiveness of the Fenton's and photo-Fenton's oxidation, in presence of sunlight or artificial radiation, for the removal of COD, TOC and phenolic compounds from wastewater produced during alkydic resin production was correlated in a study (de Oliveira et al., 2007). The optimum conditions for treatment were: pH 3.0, 15.15×10^{-3} mol/L FeSO₄ and 0.30 mol/L H₂O₂ for 6 hours reaction. The finest outcomes were attained with photo-Fenton's process aided with solar radiation, with removal efficiencies of 99.5 and 99.1% of COD and TOC, respectively, whereas presented a lesser but a noteworthy removal of 60-80% for both COD and TOC, with artificial irradiation. Whereas, an exceptional removal (95%) of total phenols was attained using photo-Fenton's process aided with artificial irradiation. It is suggested that the process of photo-Fenton's in treating alkyd resin wastewater is very efficient using solar light.

The treating and reusing possibilities of extremely contaminated paint (water-based) wastewater from the electronics industry were studied (Mamadiev & Yilmaz, 2011) by coagulation/flocculation, Fenton's oxidation and membrane processes. The wastewater utilized in this work was characterized by high concentrations of COD (55,000–144,000 mg/l) and SS (9,500–32,000 mg/l), alkaline nature and black color. Coagulation/flocculation was done with alum and FeSO₄. The COD removal efficiency of 67% was attained at alum dosage of 1000mg/l but only 45% removal at 750mg/l dosage with FeSO₄. 81% of COD removal was reached using Fenton's oxidation process at a molar ratio of $[H_2O_2]/[Fe^{+2}] = 10:1$. The sludge generated in the Fenton's process was not as much as in coagulation, however hazardous chemical sludge clearance was necessary. By using the membrane filtration, there was no sludge discarding problem because the filtrate was reused or reprocessed. Analyzing the cost involving investment, operation,

and maintenance, and waste sludge disposal must be done to resolve the feasibility of treatment and/or recycling technique.

AOPs are found (Mishra et al., 2017) to be effective in the degradation of toxic organic and inorganic pollutants, emerging pollutants like endocrine disrupting chemicals, persistent organic pollutants, dyes and heavy metals (Putatunda et al., 2019). Since paint industry wastewater would contain similar pollutants, AOPs can be effective in improving the discharge effluent quality. Hence more studies have to be carried out for different AOPs in the paint wastewater management.

2.3.3 Biological Methods

In biological methods of wastewater treatment, the biological factors/organisms are utilized to treat or engineer the wastewater.

Table 2.5. Biological methods of paint industry wastewater

References	Treatment method	Results and Conclusion	Remarks
(Salihoglu et al., 2018)	Composting of paint sludge	85% bio-dried using corncob as bulking Agent	corncob can be used as a good bulking agent
(Krithika & Philip, 2016)	Submerged attached bioreactor	organic loading rate of 0.89 kg COD/m ³ /d, the maximum removal efficiency of 97% was achieved.	feasible and efficient for degradation of toxic organic solvents
(Satyanarayan & Kaul, 2001)	Activated sludge system	87.8-93.6% COD, and 97.7-99.2% of BOD Removal	efficient in treating mixture of sewage and paint wastewater
(Güven et al., 2017)	Sequencing Batch Reactor (SBR)	Carbon and nitrogen removal performance of the SBR feeding with MSW alone were obtained as 89% and 58%, respectively.	treatment is challenging due to presence of potential toxic organic and inorganic micropollutants and high Chemical Oxygen Demand (COD) content

Different biological methods experimented for treatment of paint wastewater are composting (Salihoglu et al., 2018), attached growth system (Krithika & Philip, 2016),

activated sludge process (Satyanarayan & Kaul, 2001), and sequencing batch reactor (Güven et al., 2017) (Table 2.5).

2.3.3.1 Composting

The ability of water-based paint sludge to compost, which originated in the automotive industry by operating 6 reactors was investigated (Salihoglu et al., 2018). Wastewater treatment sludge was taken as the extra substrate from the industry, and corncob as a bulking agent. All the reactors gained a temperature rise to the thermophilic stage (> 40 °C) for at least five days, and organic matter and C/N losses were checked. Since Ni and Sn concentrations of the ultimate product surpassed the standard composts limit values, the method can be developed as bio-drying phase prior to incinerating in the cement kilns. About 85% of paint waste sludge could be bio dried with corncob as a bulking agent and could achieve higher calorific values.

2.3.3.2 Attached Growth System

A study (Krithika & Philip, 2016) on the individual and simultaneous degradation of toxic organic solvents such as ethylene glycol, propylene glycol and isobutanol from paint (water-based) industry in batch and continuous mode was conducted. The submerged attached bioreactor performance on the percentage removals and efficiency at different airflow and organic loading rates showed that at an organic loading rate of 0.89 kg COD/m³/d, the highest percentage removal of 97% was attained. The results showed that the organic loading rate and nature of pollutant influenced the removal efficiency significantly. From the study (Krithika & Philip, 2016), it was concluded that the submerged attached growth reactor is feasible and efficient for the treatment of wastewater from water-based paint industries. Out of the three pollutants considered in the study, propylene glycol required longer duration for degradation. Thorough treatment was attained at an organic loading rate of 1.4 kg COD m⁻³d⁻¹. Out of the bio kinematic models like Monod, Monod inhibition and Haldane, the best fitting model describing the bio degradation of primary substrate was found to be Haldane model.

2.3.3.3 Activated Sludge Process

Pure oxygen-based activated sludge system was used for treating a mixture of sewage and paint wastewater (Satyanarayan & Kaul, 2001). From the results, it was observed that removal efficiencies of 87.8-93.6% and 97.7-99.2% were achieved for COD and BOD,

respectively, resulting in effluent quality conforming to the recommended pollution standards. DO content in the system ranged between 3.26 and 3.9mg/l throughout the tank, showing good aeration in the system. The sludge produced in the ASP (3.0 kg/d) was found to have good manure value with N, P, K of 112, 68 and 32mg/L, respectively. The dissolved air flotation system (clarifier) set up also showed capable performance.

2.3.3.4 Sequencing Batch Reactor

A Sequencing Batch Reactor (SBR) at lab-scale was designed to observe the treatment of paint wastewater biologically and its kinetic characteristics, along with mainstream wastewater of a bus production factory (Güven et al., 2017). With only mainstream wastewater (MSW), the removal efficiency of carbon and nitrogen by the SBR were attained as 89% and 58%, respectively. With the introduction of paint wastewater to MSW, both carbon and nitrogen removal was worsened. The additions of paint wastewater lead to inhibition in growth kinetics to 21% and hydrolysis kinetics to 33%. It was concluded that the biodegradability and suppressing characteristics of paint wastewater has to be taken into account while introducing it into the prevailing biological wastewater treatment system. Thus, concentrated paint shop wastewater should not be discharged to the full-scale treatment system.

2.3.4 Combination methods

The applicability of treatment of emulsions in water using different combinations of physicochemical and biological process experimented (Aboulhassan et al., 2014a; Eremektar et al., 2006; Sawy et al., 2012; Zhu et al., 2017) are briefly summarized below (Table 2.6). A complete analysis of optimum coagulant applicable to water-based paint and ink industry effluents from a prevailing wastewater treatment plant (with a coagulation-flocculation unit followed by an activated sludge process) was conducted ((Eremektar et al., 2006). The COD removal efficiencies and operating costs of coagulants like sodium bentonite, alum, FeCl_3 , and FeSO_4 have been assessed. The coagulant yielding the optimal output has been addressed by evaluating the refractory COD content of the consequent activated sludge system outlet. The results show that among all the coagulants applied, the dosage of 50 mg/l of FeCl_3 at the real pH (5.9) of the wastewater produces the most appropriate solution.

Table 2.6. Combined methods of paint industry wastewater treatment.

References	Treatment technology	Results and conclusion	Remarks
(Sawy et al., 2012)	Radiation combined with coagulation (aluminium sulphate) and adsorption (Granular activated carbon)	reduction in sulphate concentration 50%, COD 92% and BOD 98.5%.	Improved the quality of the treated paint effluent
(Zhu et al., 2017)	multilevel contact oxidation system	removal rate of COD and suspended solid (SS) were 84% and 82.5% respectively with the Hydraulic Retention Time (HRT) of 8 hours	
(Aboulhassan, Souabi, Yaacoubi, & Baudu, 2014b)	combination of a chemical coagulation/flocculation step with an aerobic biological process	96% of COD, 97% of colour and 92.5% of BOD removals	

The effectiveness of radiation in combination with coagulation using $Al_2(SO_4)_3$ and adsorption with granular activated carbon (GAC) of paint wastewater treatment and reusing the treated effluent for various purposes was examined (Sawy et al., 2012). Complete process (with GAC dose of 2 g/100 ml supernatant) presented a decrease in sulfate concentration of 50%, COD of 92% and BOD of 98.5%. Radiation process alone did not meet the effluent discharge standards. Hence, coagulation with $Al_2(SO_4)_3$ was done to improve the quality of the treated paint effluent, and the sulfate concentration in the supernatant was reduced by adsorption with activated carbon.

A contact oxidation system with multilevel was designed (Zhu et al., 2017) with a pilot-scale experimental setup for treating the actual wastewater from the automobile painting process. The wastewater was poorly biodegradable with a high concentration of COD and was initially treated by the physicochemical method. The results revealed that the system could effectively decrease the COD of the paint wastewater, by growing activated sludge and monitoring method conditions. Under steady process conditions, the final rate of removal of COD and SS were 84% and 82.5% respectively with a retention time of 8hrs. The COD value of treated wastewater effluent was less than 500mg/l, meeting the industry discharge levels for paint factories. In addition, the process was successful in decreasing the excess sludge generation significantly, that would make the treatment process more economical. Also, the reactor has a simple structure, small cover space, easy operation, and stable running condition. It can also degrade the obstinate organic matters in paint wastewater.

The combined effect of chemical coagulation/flocculation method and anaerobic biological process, with feed-batch setup, for treating actual paint producing wastewater was investigated (Aboulhassan et al., 2014a). The observations showed that the combined coagulation/flocculation and biological process could be an effective method for treating the paint manufacturing wastewater. Initial COD (18590 mg/L), BOD (1492 mg/L) and color (0.9 absorbency) is removed to efficiencies of 92%, 44.5%, and 97%, respectively by the coagulation-flocculation with iron chloride and chimec5161. This mixture of chemical and biological processes produces a clean effluent with COD and BOD removal efficiencies of 96 and 92.5%, respectively.

2.4 GREEN SYNTHESIS OF NANOPARTICLES

Because of this, naturally occurring laterite was taken into consideration as an iron source, and Terminalia catappa extract was used in the nanoscale manufacture of the heterogeneous catalyst. Because of its numerous benefits, including its availability everywhere, nontoxicity, affordability, and temperature susceptibility, laterite has already gained popularity as a method of removing many harmful substances. Additionally, it is claimed that iron taken from laterite degrades less than iron from other sources, and that this can be remedied by synthesizing nanoparticles from laterite (Sangami & Manu, 2017c).

Due to their unique features that make them relevant in numerous fields of science and technology, metallic nanoparticles made by green synthesis have attracted enormous interest over the past ten years. With this process, hazardous chemicals, high temperatures, and energy requirements are not necessary. Better influence, control over crystal development, and durability are achieved by green synthesis. Nanoparticles produced by green synthesis are affordable, practical, and have a wide range of uses (Naseem & Farrukh, 2015). In terms of both kinetics and % removal, GT-Fe nanoparticles outperformed iron nanoparticles made using borohydride reduction as a Fenton-like catalyst. The steric stabilisation of iron nanoparticles against aggregation and the problems associated with employing sodium borohydride as a reducing agent in ordinary synthesis are being addressed through the development of green synthesis of iron nanoparticles. This chemical is noted for its corrosiveness and flammability (Shahwan et al., 2011).

These production techniques, however, are generally costly, labor-intensive, and possibly harmful to the environment and living things (Naseem & Farrukh, 2015). Although green synthesis of nanoscale metals has a lot of potential, it is hindered by material choice, synthesis circumstances, product quality control, and product application. The adoption of industrial manufacturing and widespread use of green-synthesised nanoscale metals is hampered by these factors. Studies on diverse plant materials indicate the possibility of environmentally friendly nanoscale metal production. Numerous studies on the green production of nanoscale metal have been published recently. However, green synthesis faces multiple challenges and drawbacks, including low yield, irregular particle sizes, difficult extraction processes, seasonal and regional raw material availability, and other issues that must be resolved for the practical production and use of green synthesised nanomaterials (Ying et al., 2022).

The future of research must therefore focus on increasing the production of nanoscale metal particles, using inexpensive raw materials, and implementing straightforward energy-saving technology. Use of the reducing agent sodium borohydride, NaBH₄, and hydrazine hydrate makes it simple to create iron nanoparticles. But these procedures are expensive, and they also produce by-products that could be harmful to the environment (Sastry et al., 2003)

Numerous species serve as safe, environmentally acceptable, and long-lasting precursors to create stable, well-functionalized nanoparticles. Bacteria, actinomycetes, fungi, yeast, viruses, etc. may be among them with environmentally friendly production methods based on nanotechnology function without the use of hazardous chemicals (Saif et al., 2016).

Materials that act as both a reducing agent and a capping/stabilizing agent are therefore of great interest and show great promise in the biosynthesis (Mohan Kumar et al., 2013). As a result, attempts are being made to create alternative synthesis techniques that follow the ideals of green chemistry: they should be inexpensive, employ environmentally "friendly" reagents (such as solvents and reducing agents), prevent the production of waste, and be energy-efficient. The phrase "green synthesis" is frequently used in this context to describe processes that use water as a solvent and microorganisms or plant extracts as reducing agents of Fe in solution, resulting in the creation of nZVI. The life cycle inventory assessment methodology (LCIA), used to conduct an environmental analysis of the most widely employed nZVI production processes on a laboratory and industrial scale, revealed that green synthesis is currently one of the best options (Puiatti et al., 2022).

2.5 TOXICITY EVALUATION OF TREATED WATER

Microorganisms, plants and algae, invertebrates, and fishes can all be used in toxicity bioassays as test organisms (Idel-aouad et al., 2015). The selection of the organisms for toxicity studies mostly depends on the type of pollutant in the wastewater (Dias & Kapanen, 2006; Fanny et al., 2019; Pérez-Moya, Kaisto, Navarro, & del Valle, 2017). For example, Pérez-Moya et al (2017) found the infeasibility of tracking the toxicity of bisphenol A (BPA, 0.5 L, 30 mg L⁻¹) and by-products using *E. coli* and *S. epidermidis* bacteria in the degradation study by photo-Fenton treatment due to higher LD50 (4 × 10⁴ mg L⁻¹) of BPA for these organisms. However, the cytotoxic effect of in vitro cultured mammalian cells, such as VERO cell line was found to be efficient in determining the presence of BPA and its by-products. From the comparative study (Dias & Kapanen, 2006) of different bacterium *Vibrio fischeri*, microalga, *Selenastrum capricornutum* and ciliate *Tetrahymena pyriformis* in the toxicity study of various dyes (azo dyes (Reactive Orange 16 (RO16); Congo Red (CR)) and anthraquinone dyes (Remazol Brilliant Blue R (RBBR); Disperse Blue 3 (DB3))), it was found that the algal test was the most appropriate.

The importance of study of interaction between toxicity and biodegradability, where AOPs are employed as a pretreatment step to enhance industrial wastewater biodegradability is discussed by Rizzo (2011). Bioassays are useful tools for establishing the right experimental conditions so as to eliminate the possible toxicity in the process of advanced oxidation of various complex organic pollutants that generally involves the generation of intermediary products that are more harmful than the original chemicals (Rizzo, 2011). Also, it can be useful in selecting the most appropriate AOP among different AOPs for specific wastewater treatment after comparative investigation of final toxicity. Evaluating the toxicity of the water at various steps of AOP treatment using toxicity bioassays can also help to reduce AOP operating costs (Hernando, Aguera, & Caceres, 2002). This can also predict the bio-degradability in a better reproducible way because toxicity assays are standardised and reliable compared to normal biodegradability tests, which depends on the selected biomass by the researchers.

Due to the fact that many compounds are harmful to living things even at concentrations below chemical detection limits, toxicity tests are becoming increasingly relevant (Idel-aouad et al., 2015). Various studies reviewed the generation of intermediate products of oxidation and toxicity effects of insecticides (Hossaini, Moussavi, & Farrokhi, 2017), pharmaceuticals (Fent, Weston, & Caminada, 2006), endocrine disrupting chemicals (EDCs) and personal care products (Esplugas, Bila, Krause, & Dezotti, 2007), phenols (Zazo, Casas, Molina, Quintanilla, & Rodriguez, 2007), coke wastewater (Kwarciak-Kozłowska & Krzywicka, 2016), textile industries (Na, Yoo, Nam, & Jung, 2017) and dyes (de Luna, da Silva, Nogueira, Kummrow, & Umbuzeiro, 2014; Idel-aouad et al., 2015) over AOPs treatment. Table 2.7 describes a few relevant studies on toxicity analysis of treated wastewater using advanced oxidation processes.

Table 2.7 Various toxicity analysis of treated wastewater using advanced oxidation processes

Sl No.	Type of wastewater	Toxicity test organisms	Treatment process	Reference
1	Textile Industry	<i>Daphnia magna</i>	Fenton process	(Na et al., 2017)
2	Insecticide,	<i>Vibrio fischeri</i>	Photocatalytic	(Hossaini et

	diazinon		oxidation	al., 2017)
3	Dye wastewater	Seed germination	Heterogeneous Fenton process	(Vijyendra Kumar et al., 2019)
4	Raw surface water and distilled water	<i>V. fischeri</i> and <i>P. subcapitata</i>	Fenton-like process	(Dogan, Ozturk, Olmez-Hanci, & Arslan-Alaton, 2016)
5	Dyes	<i>Daphnia similis</i> , <i>Ceriodaphnia dubia</i> and <i>Pseudokirchneriella Subcapitata</i>	Photo-Fenton process	(de Luna et al., 2014)
6	Textile industry	<i>Daphnia magna</i>	Fenton's oxidation (FO) process and ozone (O ₃) oxidation	(Meriç, Selçuk, & Belgiorno, 2005)
7	Coke wastewater	Algae growth inhibition and <i>Lepidium sativum</i> germination test	Fenton process	(Kwarciak-Kozłowska & Krzywicka, 2016)
8	Bisphenol A	In vitro assay of VERO Cells	Photo-Fenton process	(Pérez-Moya et al., 2017)
9	Hazardous industrial wastewater	<i>Vibrio fischeri</i>	Fenton process	(Barbusiński, 2005)
10	Phenols	<i>Vibrio fischeri</i>	Fenton process	(Zazo et al., 2007)

Since the water bodies are the major receiver of all the waste streams from past years, ecotoxicology studies are largely focused on aquatic systems particularly freshwater organisms. Also, estimating the amount of bioaccumulation of a chemical within the food

web and its persistence in the ecosystem help in evaluating the amount and duration of the environmental exposure. Fish and marine animals, which are at the top of the food chain, are the organisms most impacted. They consume other fish that are contaminated or are exposed to high amounts of toxins in the water directly (Tiwari, Bulai, Misra, & Venturino, 2017). *Daphnia magna* is considered as one of the most efficient organisms to test aquatic toxicity due to various industrial effluents (Meriç et al., 2005). Flathead grey mullet (*Mugil cephalus*) is found to be effective as a bio indicator for bio monitoring polluted coasts (Ouali, Belabed, & Chenchouni, 2018). To characterise the spatiotemporal variation of trace metals (TM) such zinc, copper, lead, cadmium, and mercury and their contamination and consequences on the growth of the *Mugil cephalus*, five different locations scattered around the Gulf were considered for sampling (Ouali et al., 2018). The rainbow trout (*Oncorhynchus mykiss*), and bluegill sunfish (*Lepomis macrochirus*), are also recommended to study the acute toxicity in the aquatic environment due to its good sensitivity and availability of data base on the response to various contaminants (Rizzo, 2011). Nonetheless, it is crucial to take into account in vitro assays or other processes to reduce the frequency of acute fish testing for evaluating the ecotoxicity of chemicals, both for reasons of animal welfare and economic implications (Fent et al., 2006).

For determining the ecotoxicity of different compounds degraded by the fentons process, bioassays are conducted with different organisms. The photobacterium *Vibrio fischeri* (*V.fischeri*) and the freshwater microalga *Pseudokirchneriella subcapitata* (*P. subcapitata*) are the commonly used test organisms (Arslan-Alaton, Olmez-Hanci, Dogan, & Ozturk, 2017; Barbusiński, 2005; Dogan et al., 2016; Hossaini et al., 2017; Idel-aouad et al., 2015; Lee, Choi, & Gu, 2003; Yangin-Gomec, Olmez-Hanci, Arslan-Alaton, Khoei, & Fakhri, 2018). *Vibrio fischeri* (*Photobacterium phosphoreum*) is found to be highly sensitive to a wide range of toxicants and is a bioluminescent organism producing light as a by-product of its normal metabolism which is used as indication of level of toxicity (de Schepper, Dries, Geuens, & Blust, 2012; Hossaini et al., 2017; Idel-aouad et al., 2015; Jennings, Rayner-Brandes, & Bird, 2001; Rizzo, 2011; Wei, Song, Meng, & Pic, 2015; Xu et al., 2018). The bioluminescence of *Vibrio fischeri* and its extinction was helpful in conducting toxicity bioassay evaluation of intermediates from the degradation of an insecticide, diazinon (Hossaini et al., 2017). The short time required for the analysis and easy operation, makes it more advantageous among other toxicity

tests (Rizzo, 2011). The toxicity towards the photobacterium *V. fischeri* and the acute toxicity to freshwater microalgae *P. subcapitata* were determined to evaluate the efficiency of advanced oxidation (using zero-valent aluminum activated persulfate) of some target micropollutants in raw surface water and distilled water which showed acute toxicity in terms of relative luminescence inhibition percent with respect to a control (Dogan et al., 2016).

Any chemical agent, such as high concentrations of fertilisers, herbicides, heavy metals, or nanoparticles, can have negative effects on a plant's development, physiology, or metabolism, which is termed as phytotoxicity (Hasanuzzaman et al., 2020). Common phytotoxic consequences include plant death, decreased metabolism, or growth suppression (Tripathi et al., 2017). Disrupted physiological processes, such as those that prevent photosynthesis, water and nutrient intake, cell division, or seed germination, affect a plant's metabolism and growth (Hasanuzzaman et al., 2020). Seed germination test has been found to an easy and effective test to understand the toxicity levels of raw and treated industrial wastewater. Mung bean (*Vigna radiata*) and *Lepidium sativum* seed were used to analyse the phytotoxicity of treated mixed dye wastewater (Vijyendra Kumar et al., 2019) and coke wastewater (Kwarciak-Kozłowska & Krzywicka, 2016), respectively using advanced oxidation by Fenton process; which could give a reliable data regarding the toxicity removal efficiency of the treatment process.

Recycling of the treated industrial wastewater by using it for gardening and agricultural activities has been followed in recent decades. Thus it is necessary to do the toxicity analysis for the plants and the soil bacteria before the application of treated wastewaters. *Bacillus subtilis* is a commonly found rod-shaped bacterium. *B. subtilis* is simple to culture and safe to work with in a laboratory. *B. subtilis* is a naturally occurring organism that lives in soil, plant roots, and aquatic settings, and is considered as non-pathogenic bacteria (Martinez, 2013).

2.6 OUTCOME OF THE LITERATURE REVIEW

Paint industry wastewater is found to be a highly polluted wastewater which needs an immediate attention for its treatment methodology before its disposal. Different treatment techniques have been experimented for emulsions in water such as physicochemical processes, biological processes and combined chemical and biological processes. The

physicochemical processes mainly used are coagulation, flocculation, sedimentation, filtration, electrocoagulation, radiation, and adsorption.

Even though coagulation and flocculation processes are found to be easier compared to other techniques, the effect of dosage of coagulant and effective pH on the quality of wastewater treated is an important factor (Dovletoglou et al., 2002) to be considered. Different coagulants both chemical and bio-coagulants has been used to treat paint industry wastewater. It is observed from various results that using cladodes, fruit pulp and peels mucilage and electrolytes on varieties of polluted water, the capability of pollutant sorption and removal efficiencies is high (Nharingo & Moyo, 2016). Because of the low/no toxicity presented by the use MOAE, from the environmental point of view, particularly in areas where the plant is easily grown, it is found to be a potential alternative for chemical coagulants (Barbosa et al., 2018). But, the use of bio-coagulant depends on its availability and proper maintenance and skill is required for its practical use. The further disposal of adsorbed chemicals has to be considered with precaution which is a major disadvantage of coagulation technique.

The filtration process helps in removing the larger settled particles and the advanced treatment of filtrate but it has the disadvantages such as fouling and sludge removal. Hence, further experiments must be conducted to determine the conditions which can reduce similar issues. In addition, the process is less economical (Vishali et al., 2018). These treatment techniques are capable of removing the color and the solids to a large extent but the chemicals are precipitated in its toxic form and thus produce large sludge.

Electrochemical oxidation of the paint wastewater is found to be effective and a viable treatment technique when compared to the current chemical treatment methods, but the method is less economic and requires skilled supervision (Körbahti & Tanyolaç, 2009). The complex chemical structure of the polymers used in emulsions makes the biological treatment techniques less efficient. Therefore, treating the paint wastewater biologically is complicated because of the potential toxic organic and inorganic micro pollutants present in it and its high COD content. Advanced oxidation techniques can be comparatively efficient since it can oxidize the toxic form of the chemicals and reduce the amount of sludge compared to physicochemical process. Among the most investigated AOPs, the Fenton's process is one of the most effective process for the degradation of recalcitrant

water pollutants (Pliego et al., 2015) in which the high reactive potential of the hydroxyl radicals (generated from the dissociation of hydrogen peroxide through the catalytic reaction of $\text{Fe}^{2+}/\text{Fe}^{3+}$) is utilized for the oxidation of compounds (Garrido-Ramírez et al., 2010; Kamagate et al., 2018; Nidheesh, 2015; N. Wang, Zheng, Zhang, & Wang, 2016; Q. Wang, Tian, & Ning, 2014). However, homogeneous Fenton's oxidation has certain limitations. This includes the narrow working range of pH (2 to 4) (Garrido-Ramírez et al., 2010), the non-reusability of the catalyst since their separation is difficult (Hartmann, Kullmann, & Keller, 2010), and production of huge amount of iron sludge (H. L. Lien, Yu, Kamali, & Sahu, 2019). Application of heterogeneous Fenton-like oxidation in treatment of various types of waste water and the selection of the best heterogeneous catalyst for a particular type of pollutant and the optimization of different variables such as pH, H_2O_2 dosage, catalyst dosage and the reaction time in the Fenton-like oxidation processes is critical to develop an efficient and sustainable treatment methodology.

But in order to have a proper control of the sludge management, it is important to study the degradation process of the chemicals. Also more studies on application of different AOPs for paint industry wastewater have to be carried out. Further, identifying the best combination methods can also help in improving the efficiency of treatment of the industrial effluents. The selection of the best heterogeneous catalyst for a particular type of pollutant and the optimization of different variables such as pH, H_2O_2 dosage, catalyst dosage and the reaction time in the Fenton-like oxidation processes is critical to develop an efficient and sustainable treatment methodology. Various heterogeneous catalysts and the advances of their uses in efficient treatment of different wastewaters in recent years have been reviewed in Nidheesh (2015). The properties, stability, and efficiency of different catalysts such as iron minerals, zero-valent iron, waste materials, iron- and iron oxide-loaded materials, and clay, are critical in the selection of heterogeneous catalysts (Nidheesh, 2015) for wastewater treatment with economic feasibility, stability, and sustainability.

Laterite has been proven to be efficient in the degradation of pharmaceutical compounds and antibiotics like paracetamol (Manu, 2011), 3-aminopyridine (Karale et al., 2014), acetaminophen (Kootatep et al., 2017), flumequine (Kamagate et al., 2018), penicillin, tetracycline, and pleuromutilin (Changduang et al., 2021) in water, dyes such as Orange G (Tarkwa et al., 2019), Methylene Blue (Gloria M. R. Kpinsoton, Karoui, Richardson,

& Yacouba, 2018), C.I. Acid Red 17 (A. Khataee et al., 2015), food colorant Bordeaux Red (Ganiyu et al., 2020). Laterite soil has also been studied as an adsorbant for removal of various contaminants such as phosphorus (L. Zhang, Hong, He, Gan, & Ho, 2011), arsenate ions (Maiti, DasGupta, Basu, & De, 2008), fluoride (Sarkar, Banerjee, Pramanick, & Sarkar, 2006) and was found to very effective in removing these pollutants from water. Thus, it can act as a sorbent apart from iron rich catalyst which would be an added benefit in the removal of contaminants. Thus, calcined laterites provide a potential sustainable and eco-friendly wastewater treatment catalyst particularly in the tropical and sub-tropical region where it is found in abundance.

Utilizing biological entities such as bacteria, plant extract, or plant biomass for the environmentally friendly synthesis of nanoparticles is an alternative to traditional processes (Sastry, Ahmad, Islam Khan, & Kumar, 2003). Numerous studies have used the FeSO_4 and FeCl_3 iron sources to create iron nanoparticles from various plant extracts (Puiatti, de Carvalho, de Matos, & Lopes, 2022). Plant-based metal nanoparticle synthesis is shown to be nontoxic and environmentally safe (Naseem & Farrukh, 2015). The potential of *Terminalia catappa* has not been explored for synthesis of iron nanoparticles (Sadhasivam, Vinayagam, & Balasubramanian, 2020). The huge tree species known as Indian almond (*Terminalia catappa*) is primarily found in the tropics and is a member of the Bàng (Combretaceae) family (Hung et al., 2022). The abundant presence of phenolic compounds or polyphenolic acids is a characteristic particular of the leaves of this plant, such as the acid Gallic (Tanaka et al., 1986). It is well-known to reduce pH and heavy metal content of the water in the aquariums, and fish breeders have been using it in this way for many years (Malawa, Nuntapong, Suanyuk, & Thongprajukaew, 2022).

Due to the harmful effects of various compounds to the living things at concentrations below chemical detection limits, toxicity tests have become more important. Toxicology tests should be included in the evaluation of wastewaters in addition to the chemical characterization (Barbusiński, 2005). The final application of the treated water should be taken into consideration when choosing the organisms to be tested for bioassays. Studies on chronic effects should be further developed as some acute toxicity tests may not be appropriate to assess toxicity in the presence of low/realistic concentrations of target contaminants (Rizzo, 2011).

CHAPTER 3

MATERIALS AND METHODOLOGY

Paint industry wastewater is one among the most contaminated industrial wastewater. This chapter deals with the materials used and with the various experimental procedures adopted to conduct the different laboratory investigations towards the treatment of emulsions in water. The preliminary tests conducted include extraction and characterization of laterite soil, COD tests. The iron nanoparticles using laterite soil and *Terminalia catappa* leaf extract is synthesized and characterized for using as catalyst in Fenton-like oxidation of the emulsion in water. Finally the treatment of the emulsion samples in water is carried out using calcined laterite (LS 800) and iron nanoparticles (LSFeNP(TC)) and the COD removal efficiencies are measured. In the subsequent sections the methods adopted for various tests are briefly discussed.

3.1 MATERIALS

3.1.1 Procurement of Paint Industry Samples

Three different emulsions namely **ACRONAL IA 734 AP**, **ACRONAL 295 D AP**, and **ACRONAL IN 296 D AP** are collected from BASF India limited, an emulsion manufacturing industry in Mangalore (Figure 3.1 (a)). The chemical properties of the samples are studied. The laterite soil used for treatment is collected from a quarry near Kasaragod, Kerala. The reagent hydrogen peroxide (H_2O_2 , 30% w/w) was purchased from Medilise chemicals, Azhikode; hydrochloric acid (HCl , 35%) and sulfuric acid (H_2SO_4 , 98%) are purchased from Isochem Laboratories, Kochi. The other chemicals for reagent preparation of various experiments are procured from Merck India.



Figure 3.1 a) Collected emulsion samples from BASF India Ltd., Mangalore. **b)** Synthetically prepared wastewater samples.

3.1.2 Collection of plant leaves

The laterite soil used for treatment is collected from a quarry near Kasaragod, Kerala. The other chemicals for reagent preparation of various experiments are procured from Merck India and Sigma Aldrich. Terminalia catappa (TC) leaves (littered) were collected from the premises of NITK. The other chemicals for reagent preparation of various experiments are procured from Merck India and Sigma Aldrich.

3.1.3 Materials used for measuring toxicity

The toxicity analysis of treated samples is done by bacterial growth inhibition test using *Bacillus subtilis* and seed germination test using mung bean (*Vigna radiata*) and Bengal gram (*Cicer arietinum*). *Bacillus Subtilis* (BS) and Tryptone Soya Broth (TSB) obtained from the Central Plantation Crops Research Institute (CPCRI), Kasaragod, is used in this study.

3.2 EXPERIMENTAL METHODOLOGY

3.2.1 Preparation and characterization of synthetic wastewater

Synthetic samples are prepared from the emulsions by dilutions using deionized water (Figure 3.1 (b)). Various parameters such as pH, COD, and BOD are determined in the laboratory following the standard procedures outlined in Standard Methods for the examination of water and wastewater (APHA,1998). The initial characterization of the emulsions to identify the presence of organic compounds is done using FT-IR (PerkinElmer Spectrum IR Version 10.6.2) and Smart UV-VIS double beam Spectrophotometer, (Systronics).

3.2.2 Preparation and characterization of heterogeneous Fenton's catalyst

The natural laterite was prepared for use as a heterogeneous catalyst in the Fenton-like oxidation of two different emulsions in water. The natural laterite samples collected were powdered and sieved through 150-micron sieve and heated under normal air supply in the muffle furnace at different temperatures viz 105°C, 300°C, 600°C and 800°C. Based on their heating temperatures, samples were named as LS105, LS300, LS600 and LS800 respectively. The tests were conducted for varying pH in the range of 2 to 8 and H₂O₂/COD in the range of 1 to 4 with fixed amount (10g/L) of laterite soil heated at different temperatures for a mixing time of 120 min at 210rpm at room temperature. The characterization of the laterite sample was done using XRD, BET, and HR-FESEM to

study the changes in the physical and elemental properties of the catalyst due to heating. In order to determine the crystal structure of the laterite, XRD diffractogram were recorded on a Empyrean 3rd Gen, Malvern PANalytical, Netherlands, using Cu Ka radiation ($k = 1.54 \text{ \AA}$) and equipped with a PIXcel 3D Detector. The X-ray generator was set to 40 kV and 40 mA, the recorded angular range was 20–80 with a step size of 0.02. The quantitative analyses were performed using the Rietveld method with the PANalytical X'Pert HighScore Plus software and Matched with ICDD 2020 database. HR-FESEM [GEMINI 300, Carl Zeiss, Germany], with Schottky type field emitter and resolution: 0.7 nm @15 kV, 1.2 nm @1 kV is used to get the microphotographs and particle size distribution of the catalysts. The determination of isotherm type and the pore structure was studied by the nitrogen adsorption–desorption isotherm using BET Surface Area Analyzer [*Autosorb IQ-XR-XR, Anton Paar, Austria*].

The laterite sample that exhibited the highest performance in the degradation of the two emulsions in water at varying pH and H₂O₂ was found from the experimental results and was fixed as the heterogeneous catalyst for Fenton-like degradation of paint wastewater for further treatment process.

3.2.3 Design of Experiments

The design of experiments (DOEs) for determining the optimum values of different parameters affecting the treatment efficiency is done using Response Surface Methodology (Myers & Montgomery 2016) with the help of Design Expert 11 software. DOEs is the process of choosing a suitable group of points within a particular space for conducting experiments. Factorial, RSM (response surface methodology), mixed, and Taguchi design are the four varieties of DOE. The goal of the RSM, a statistical tool for the design of experiments, is to maximise the response or to improve the models by modelling and analysing problems where the response of interest is influenced by multiple factors. The RSM is of two categories: 1) Central Composite Design (CCD), and 2) Box-Behnken design (BBD) (Sahoo & Barman, 2012). Central Composite Design (CCD) was adopted with three variable factors and one response. pH, H₂O₂/COD and catalyst concentration are the factors considered and their effects in maximizing the response (% removal of COD) is studied by analyzing the results with ANOVA.

3.2.4 Heterogeneous Fenton's oxidation

Initially, preliminary experiments were performed to determine the range of values for all

independent variables; pH, H₂O₂/COD, catalyst concentration and reaction time. From the preliminary experiments suitable range for different parameters were fixed as shown in Table 3.1 and mixing time of 120 minutes was fixed. Total 20 experiments were performed for each sample in a 250 ml Erlenmeyer flask with sample size of 50 ml according to the CCD (Central composite design) matrix at room temperature (29-31⁰C). The heterogeneous iron catalyst was added and the pH of the solution was adjusted using 6N NaOH and 0.2 N HCl. This was followed by addition of H₂O₂. The mixing was done in a rotary shaker with shaking speed of 210 rpm for 2 hours and the samples were kept for 24 hours so that hydrogen peroxide decomposes completely (zero residual hydrogen peroxide). The experiments were conducted in duplicate sets at different pH with different dosages of hydrogen peroxide and catalyst as per design. After the reaction time (24hrs), the supernatant solution was taken and COD removal efficiency determined. It is calculated by using the following equation.

$$\% \text{ COD removal efficiency} = ((\text{COD}_i - \text{COD}_f) / \text{COD}_i) \times 100 \quad (3.1)$$

Where, COD_i is the initial COD (mg/L) and COD_f is the final COD (mg/L) after the reaction time. Without adding oxidant and catalyst, the experiment was conducted (24 hrs) and no reduction in COD was observed.

Table 3.1 Range of values for different parameters in treatment process

Factor	Name	Minimum	Maximum
A	pH	3	7
B	H ₂ O ₂ /COD	1	4
C	Catalyst dosage(g/L)	5	15

3.2.5 Preparation and characterization of iron nanoparticles (LSFeNP(TC))

The iron nano particles were synthesized using laterite (sampled from Surathkal, Karnataka, India). The laterite was crushed to a finer material and removed the lighter particles with water. The remaining particles were dried, sieved (105 micron) (PLPs-powdered laterite particles) and preserved in dark bottles for further use. Typically, 3 g of sieved soil was mixed with 15 ml concentrated HCl (35%) and the total mixture was heated till all acid was fully evaporated. Further, once again 15 ml of acid was added and heated till dryness. Then, 20 ml of hot distilled water was transferred to a reaction mixture and vacuum filtered (Whatman 42). The filter paper containing mixture was

ignited in a muffle furnace (650⁰C) and final residue was considered as silicon dioxide. The filtrate is the mixture of aluminium and iron oxides and other traces of elements. The reaction mixture is diluted to 250 ml and 50% of the liquid was used for the extraction of iron (IS-2720 (Part- XXV)-1982).

Around 100 g of *Terminalia catappa* (TC) leaves were collected from NITK campus, washed with water, and dried at room temperature. 60g of dried TG Leaves were dissolved in 1 liter of boiling water (Temp 80 ⁰C, 1h) and the whole solution was filtered and stored in grey bottles (Sangami & Manu, 2017d). Nanoparticles were synthesized by mixing 2.6 g/L of extracted iron with plant extract in different volume proportions (1:1, 1:2, 1:3 and 1:4) at room temperature in magnetic stirrer, for 60 min. The formation of black color liquid confirms the production of nanoparticles (LFeNPs-laterite based iron nanoparticles) and liquid was dried at 100 ⁰C and preserved in grey bottles.

The potential of these leaves in the green synthesis of iron nanoparticles from laterite extract as precursor is studied. The morphology and elemental composition of laterite based iron nano particles (LFeNPs) was obtained using XRD, BET, and HR-FESEM to study the changes in the physical and elemental properties of the catalyst due to heating. In order to determine the crystal structure of the laterite, XRD diffractogram were recorded on a Empyrean 3rd Gen, Malvern PANalytical, Netherlands, using Cu Ka radiation ($k = 1.54 \text{ \AA}$) and equipped with a PIXcel 3D Detector. The X-ray generator was set to 40 kV and 40 mA, the recorded angular range was 20–80 with a step size of 0.02. The quantitative analyses were performed using the Rietveld method with the PANalytical X'Pert HighScore Plus software and Matched with ICDD 2020 database. HR-FESEM [GEMINI 300, Carl Zeiss, Germany], with schottky type field emitter and resolution: 0.7 nm @15 kV, 1.2 nm @1 kV is used to get the microphotographs and particle size distribution of the catalysts. The determination of isotherm type and the pore structure was studied by the nitrogen adsorption–desorption isotherm using BET Surface Area Analyzer [Autosorb IQ-XR-XR, Anton Paar, Austria]. The FT-IR spectra were recorded using a PerkinElmer Spectrum IR Version 10.6.2 and samples were measured in the region 4000 – 450 cm^{-1} .

3.2.6 Fenton-like oxidation of emulsion samples using LFeNP(TC)

Initially preliminary experiments were performed to know the range of values for all independent variables (pH, catalyst concentration and reaction time). From the

preliminary experiments suitable range for mixing time was fixed as 120minutes. The experiments were performed in a 250 ml Erlenmeyer flask with sample size of 50 ml according to the design at room temperature (29-31 °C). The mixing was done in a rotary shaker with shaking speed of 210 rpm for 2 hours. The experiments were conducted in duplicate sets at different pH with different dosages of catalyst. After the reaction time, the supernatant solution was taken and COD test of the treated sample was done to determine the COD removal efficiency, which is calculated using Eq. 3.1.

3.2.7 Toxicity Evaluation

a) **Bacterial inhibition growth test.** The stock culture of bacteria was prepared with 100 mL Tryptone Soya Broth (TSB) prepared by dissolving 3g in 100ml of distilled water. The TSB was incubated for 24 h at 37 °C in a shaker at 120 rpm, resulting in tremendous growth in BS cells (Amjad, Arsalan Khushnood, & Ali Memon, 2023). Thereafter, at a specific contact period, 0.1mL of each bacterial stock was introduced to the test tube containing 1mL of the Fenton-treated sample and 9mL of fresh TSB broth. The tubes were shaken at 150 rpm for 16 hours, incubated at 37 °C (Y. Zhang, Xiao, Zhong, & Lim, 2019). The absorbance at 600 nm was used to measure bacterial growth in triplicate, using Smart UV-VIS double beam Spectrophotometer, Systronics. Growth control was carried out without the addition of treated samples. The difference in turbidity between the treated samples and the growth control was used to calculate the percent growth inhibition (Strotmann, Eglsäer, & Pagga, 1994).

The extent of inhibition is obtained by

$$I = [(OD600 \text{ control} - OD600 \text{ test}) * 100] / [OD600 \text{ control}] \quad (3.2)$$

b) **Seed germination test.** The phytotoxic effect was determined by the seed germination test using mung bean (*Vigna radiata*) and Bengal gram (*Cicer arietinum*). Seeds of each species used in the germination test were each put in a petri dish lined with two tissue papers. These tissue papers were then irrigated with 5 ml of the untreated and treated wastewater sample, and distilled water for control each day (Ramana, Biswas, Kundu, Saha, & Yadava, 2002). The growth in the length of the root of the seed after 5 days was measured to determine toxicity (Vijyendra Kumar et al., 2019).

For the treatment of paint wastewater, optimised conditions (pH of 3 and catalyst dosage of 5g/L, initial COD of 1500 mg/L pollutant concentration) were used. The treated wastewater had a pH of 4.5, COD of 32mg/L and also sample of treated water with pH 7 was also tested for the growth inhibition check.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter deals with the treatment of mixture of emulsion samples (**ACRONAL IA 734 AP, ACRONAL 295 D AP, and ACRONAL IN 296 D AP**) in water by Fenton-like oxidation. The response surface methodology is used for the design of experiments (DOEs). The laterite is used as the source of iron as a catalyst in the process. The set of experiments as per the design are conducted and the results are interpreted with ANOVA (analysis of variance), coefficient of determination (R^2), Fisher's test (F-test) along with the 2nd order polynomial equation. Optimum values for various parameters like pH, H_2O_2/COD and catalyst concentration for maximum removal efficiencies are obtained and the effects of respective parameters on the treatment process are studied. The laterite calcined at $800^\circ C$ and the green synthesized nanoparticles with laterite and *Terminalia catappa* extracts is used as the source of iron as a catalyst in the process. The treatment of the emulsion samples in water is carried out using LS 800 and LSFeNP(TC) as catalyst and the COD removal efficiencies are measured. The set of experiments are conducted to find the optimum amount of catalyst.

4.1 PHYSICAL AND CHEMICAL PROPERTIES OF THE EMULSIONS

The initial characteristics of the synthetic paint wastewater prepared by emulsion samples **ACRONAL IA 734 AP, ACRONAL 295 D AP, ACRONAL IN 296 D AP and the mixture of three emulsions** are shown in Table 4.1.

Table 4.1 Characteristics of the emulsions in water (concentration 1040mg/L)

Properties	ACRONAL IA 734 AP	ACRONAL 295 D AP	ACRONAL IN 296 D AP	Mixture of three emulsions
Colour & appearance	White viscous liquid	White viscous liquid	White viscous liquid	White viscous liquid
pH	8.03	7.48	7.36	8.03
COD (mg/L)	1056	1504	1376	1312
BOD (mg/L)	21.266	22.716	21.266	21.75
Density (g/cc)	1.04	1.04	1.04	1.04

Application	For premium exterior applications. The cross-linking gives best of mechanical properties without compromising on dirt pick up resistance.	Applicable in general purpose exterior/interior or paints, premium exterior / interior paints, texture paints, flexible coatings, primers	Used in the production of adhesives, coatings, textured finishes, surface binders for nonwoven and textile coatings and as an additive for hydraulic binders.
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The initial absorbance of the synthetic wastewaters prepared by the three emulsions and the mixture of emulsions was recorded using UV/VIS spectrophotometer at a wavelength range of 190 to 900nm.

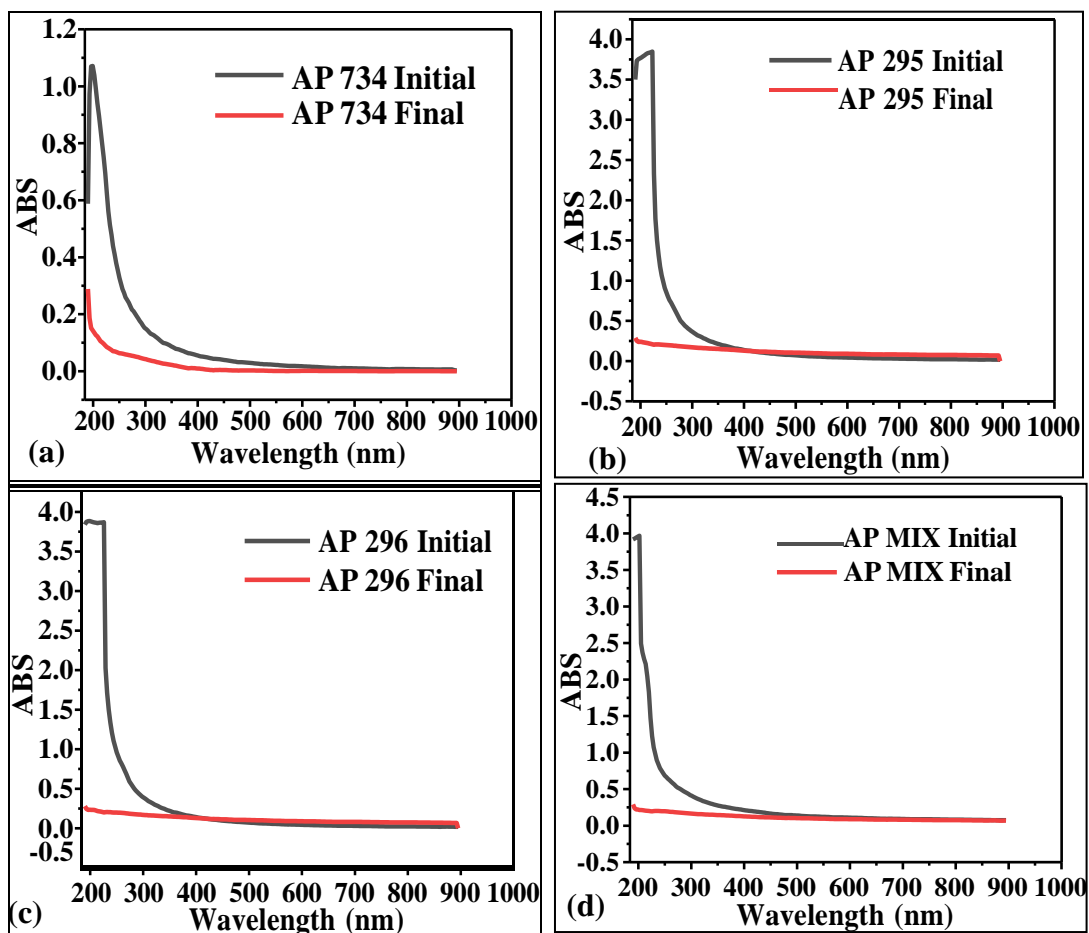


Figure. 4.1 UV/VIS spectrum before and after treatment (a) ACRONAL IA 734 AP; (b) ACRONAL 295 D AP; (c) ACRONAL IN 296 D AP; and (d) Mixture of emulsions

A peak was observed in all the samples in the range of 190 to 350nm, which signifies the presence of poly-unsaturated and aromatic compounds (von Elbe & Schwartz, 2018). The final treated samples were also analysed. The spectrums (Figure 4.1 (a-d)) show that there is a considerable removal of the suspected compound and there is no production of other peaks in the entire wavelength range, which suggests that there is no formation of any other intermediate compound after the treatment process.

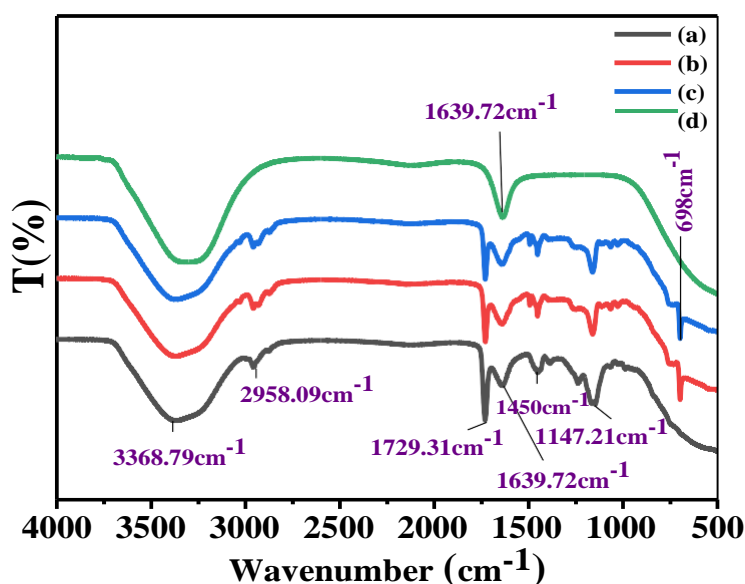


Figure. 4.2 Fourier-transform infrared (FTIR) spectra of the following samples: (a) ACRONAL IA 734 AP; (b) ACRONAL 295 D AP; (c) ACRONAL IN 296 D AP; and (d) PWW treated with LS800

In the FTIR spectra of the three emulsions (Figure 4.2), the following bands (common to all three materials) stand out at: $\approx 3369 \text{ cm}^{-1}$, associated with the O-H stretching vibration (Wang et al., 2014a); $\approx 2959 \text{ cm}^{-1}$, associated with the aromatic C-H stretching vibration (Junfei, Yimin, & Qiang, 2016); $\approx 1730 \text{ cm}^{-1}$, associated with strong C=O stretching α,β unsaturated ester or formates; $\approx 1640 \text{ cm}^{-1}$, associated with strong C=C stretching monosubstituted alkene; $\approx 1450 \text{ cm}^{-1}$, associated with medium C-H bending alkane (methyl group) and due to aromatic C=C stretching vibration absorption. These absorption peaks indicate the existence of benzene rings (Junfei et al., 2016); $\approx 1148 \text{ cm}^{-1}$, associated with the strong C-O stretching vibration (aliphatic ether) (Puiatti et al., 2022); and $\approx 698 \text{ cm}^{-1}$ associated with the strong C-halogen stretching of halo compound. Therefore, the results of the FTIR analysis indicate the presence of poly-unsaturated, aromatic and halo compounds in the emulsion samples. The FTIR

spectra of the treated paint wastewater using calcined laterite suggest the removal of all the unsaturated compounds.

4.2 CHARACTERIZATION OF HETEROGENEOUS CATALYST

The laterite samples heated at 105°C and at 800°C were characterized and analyzed using XRD, BET, and FESEM to study changes in the physical and elemental properties of the catalyst due to temperature treatment. Fig. 4.3 shows the XRD pattern of laterite samples LS105 and LS800. From the analysis it was found that the main phases in the LS105 are Fe₂O₃ (Hematite), Fe₃O₄ (Magnetite), SiO₂ (Quartz), Al₂(SiO₄)O (Sillimanite) and TiO₂ (Titanium oxide). Further, in LS 800, the main phases are Fe₂O₃ (Hematite) and SiO₂ (Quartz) with traces of Al₂(SiO₄)O (Sillimanite) and TiO₂ (Titanium oxide). The diffraction peaks at 2θ values of 24.25°, 33.31°, 35.77°, 41.04°, 49.68°, 54.32°, 57.88°, 62.72° and 64.28° are characteristics of (012), (104), (110), (113), (024), (116), (018), (214) and (300) plane of hematite crystal structure, respectively in the diffractogram of both LS105 and LS800 (JCPDS 01-085-9166). In the spectrum of LS105, the peaks at 2θ values of 34.75°, 43.87°, 44.99° and 48.25° can be assigned respectively to (230), (301), (311) and (321) space plane of magnetite (JCPDS 01-074-4121). These peaks disappear upon heating as seen in the pattern (Fig. 4.3), at 800°C since the magnetite is completely oxidized into hematite (Monazam, Breault, & Siriwardane, 2014). The intensity of the peaks corresponding to hematite for LS800 increased and stabilized which confirms the oxidation of Fe₃O₄ to Fe₂O₃, thus increases the fraction of active sites for the heterogeneous Fenton-like oxidation process. The diffraction peaks at 2θ value of 20.86° and 26.42° corresponds to (100) and (011) plane of SiO₂ crystal structure, respectively in the diffractogram of both LS105 and LS800 (JCPDS 01-087-2096). Furthermore, the characteristic peaks of Al₂(SiO₄)O at 2θ values of 26.65°, 35.47°, 41.17°, 50.44°, 54.89°, and 59.61° which can be assigned, respectively, to the spacing planes (210), (112), (122), (410), (420) and (142) (JCPDS 01-075-1576) disappear at 800°C, except (210) and (122). This can be due to the dissociation of unstable Al₂(SiO₄)O into SiO₂ upon the heating of the catalyst in the presence of air, which can be attributed to the increased peaks of SiO₂ (Induja & Sebastian, 2018; Lima, Silva, Menezes, Santana, & Lira, 2022).

The diffraction peaks at 2θ value of 24.95° corresponds to the (101) plane of TiO₂ crystal structure in both LS105 and LS800 diffractogram (JCPDS 01-076-8999). The presence of element Titanium in the laterites has been reported in different studies (Ganiyu et al.,

2020; A. Khataee et al., 2015; Tarkwa et al., 2019). Also, all these elements are detected in the EDS analysis of the laterite sample (Figure 4.5 (c)).

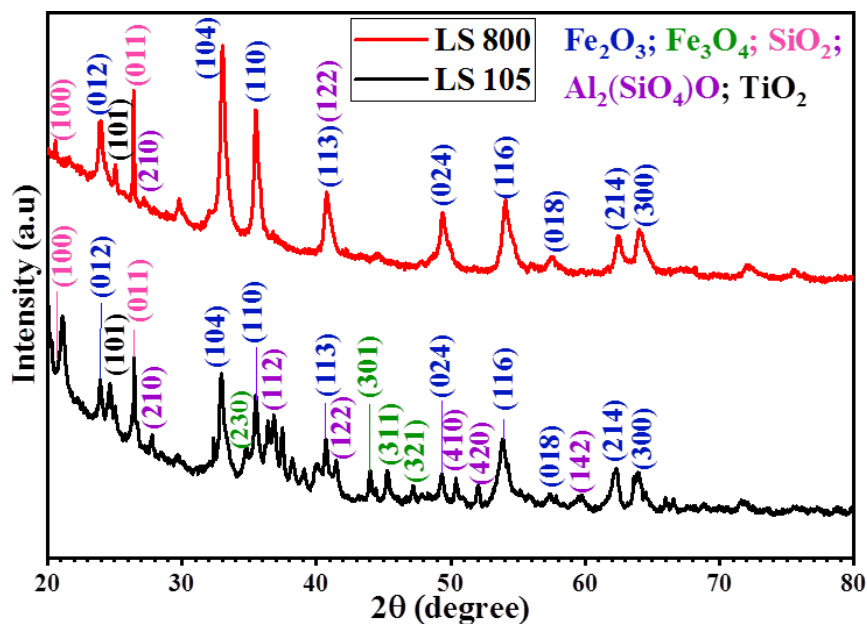


Figure. 4.3 XRD pattern of laterite samples LS105 and LS800

Thus, the transformation of magnetite to hematite during heating can be attributed to the higher efficiency of LS800 as heterogeneous catalyst for Fenton-like oxidation of organic pollutants.

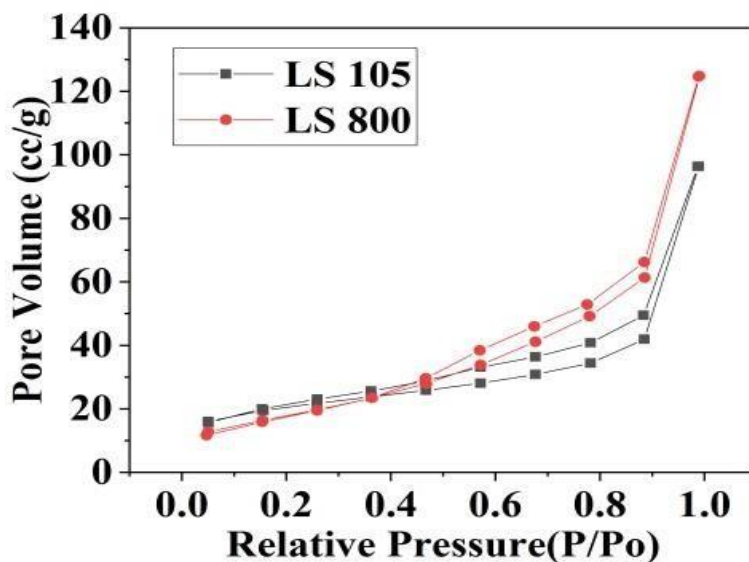


Figure 4.4 N₂ adsorption–desorption isotherm of the catalyst samples

The determination of isotherm type and the pore structure was studied by the nitrogen adsorption–desorption isotherm using BET Surface Area Analyzer. Fig. 4.4 indicates N₂ adsorption–desorption isotherm of the catalyst samples that is measured at 77.350K.

Table 4.2 Textural properties of LS105 and LS800 samples

Samples	LS105	LS800
Surface area (m ² /g)	66.614	66.530
Total pore volume (cc/g)	0.15	0.20
Average pore size (nm)	4.47	5.80

Based on the isotherms, the surface adsorption properties were calculated and listed in Table 4.2.

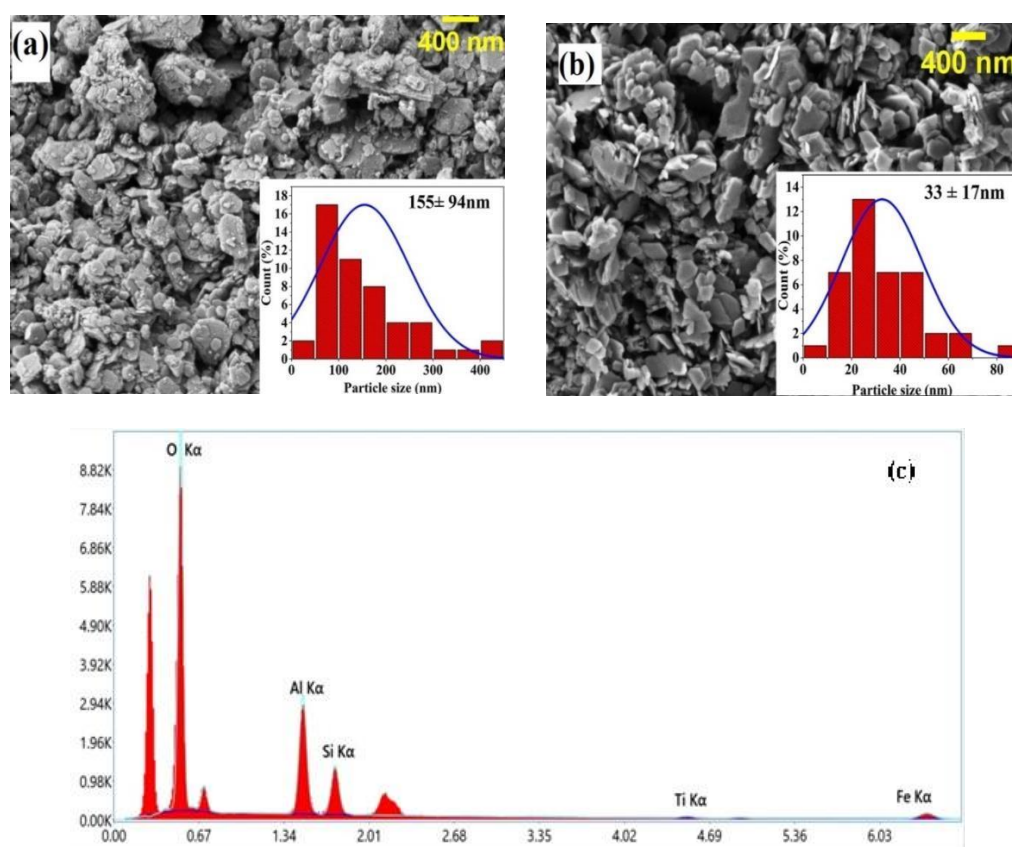


Figure. 4.5 SEM micrographs with particle size distribution curve for laterite samples (a) LS105 and (b) LS800 (c) EDS of laterite sample

The laterite exhibited a slight reduction in the surface area together with an increase in pore radius. The surface area was reduced from 66.614 to 66.530 m²/g after heating to 800°C, and the pore radius increased from 4.47 to 5.80 nm. These diameter ranges in between 2 to 50nm which corresponds to the mesoporous structure and it is also visible from the adsorption-desorption isotherm that both the catalysts represent the Type IV

isotherm, according to the IUPAC classification and the hysteresis loop of H3 (Changduang et al., 2021; Thommes et al., 2015). The H3 signifies that it is non-rigid aggregates of plate-like particles with slit-shaped pores. Fig. 4.5 (a, b) gives the SEM micrographs and particle size distributions of samples. It can be seen from the images that the samples have plate-like particles. The average size of particles of LS800 was 33 ± 17 nm and lesser compared to LS105 (155 ± 94 nm) that could be probably due to the recrystallization of the mineral oxides in the laterite during heating.

4.3 TREATMENT OF EMULSIONS IN WATER BY FENTON-LIKE OXIDATION

Response surface methodology was applied to study the effect of variables (pH (A), H₂O₂/COD (B) and catalyst concentration (C)) on responses (%COD removal). The effect of various parameters on the treatment efficiency is analysed and discussed in the following sections for each type of emulsions.

Table 4.3 The levels of parameters studied in the CCD for the emulsions.

Fac Tor	Name	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	pH	1.64	8.36	-1 ↔ 3.00	+1 ↔ 7.00	5.00	1.70
B	H ₂ O ₂ /COD	-0.0227	5.02	-1 ↔ 1.00	+1 ↔ 4.00	2.50	1.27
C	Catalyst dosage(mg/L)	1.59	18.41	-1 ↔ 5.00	+1 ↔ 15.00	10.00	4.24

Table 4.4 CCD design matrix with responses for all the three emulsions.

Run	Factor1	Factor 2	Factor 3	Response		
				ACRONAL IA 734 AP	ACRONAL 295 D AP	ACRONAL IN 296 D AP
	A:pH	B: H ₂ O ₂ /COD	C:Catalyst dosage g/L	COD removal %	COD removal %	COD removal %
1	7	4	5	15.91	3.72	9.88
2	5	2.5	10	22.73	20.21	14.54
3	1.64	2.5	10	87.12	98.94	98.26
4	5	2.5	10	18.94	15.42	10.46

5	3	4	15	31.82	96.28	91.86
6	5	2.5	10	22.73	24.47	9.30
7	5	2.5	10	20.45	26.60	9.88
8	8.36	2.5	10	24.24	19.15	9.88
9	5	2.5	10	9.85	23.40	8.72
10	5	2.5	1.6	10.61	25.53	16.28
11	3	1	15	21.97	80.32	91.28
12	5	5.02	10	27.27	22.34	17.44
13	3	4	5	78.79	91.46	91.28
14	7	1	15	3.79	27.66	17.44
15	5	2.5	18.41	0.76	52.13	20.93
16	5	-0.02	10	25.76	25	21.51
17	7	1	5	1.515	22.87	16.28
18	3	1	5	97.73	82.93	93.02
19	5	2.5	10	18.94	20.74	14.54
20	7	4	15	21.97	18.09	18.60

4.3.1 Fenton-like oxidation of emulsion sample ACRONAL IA 734 AP

All the three independent variables with their levels are listed in Table 4.3 and design matrix is shown in Table 4.4 and the response data is shown in table 4.5. The response functions along with interaction coefficients of independent variables are presented in Eq. 4.1. The equation involves one constant term, three linear terms (A, B, C), three quadratic terms (A*A, B*B, C*C) and two interaction terms (A*B, A*C).

$$\text{Sqrt(COD removal)} = +4.31 - 1.81 A + 0.4167 B - 0.8079 C + 0.6943 A * B + 1.23 A * C + 1.06 A * A + 0.3595 B * B - 0.7313 C * C \quad (4.1)$$

The response ranges from 0.76 to 97.73. Hence the ratio of maximum to minimum is 129 which is greater than 10. It is recommended to apply power transformation and thus square root transform is applied to fit the model. In the coded equation (4.1) for the model, the intercept value is +4.31 which shows a positive effect. So as to improve the model, model reduction was done by eliminating terms with p-values greater than 0.10.

Table 4.5 Response data from the design for ACRONAL IA 734 AP

Response	Name	Minimum	Maximum	Mean	Std. Dev.	Ratio	Transform	Model
R1	COD removal (%)	0.76	97.73	28.14	27.27	129.00	Square Root	Reduced Quadratic

To find out the relation between the mean square (MS) and the residual error of the model, the F test (Fisher's test) analysis was performed. The Model F-value of 19.87 implies the model is significant. The Lack of Fit F-value is 2.29, which is not significant (Table 4.6). The Predicted R^2 of 0.7086 is in reasonable agreement with the Adjusted R^2 of 0.8882; i.e. the difference is less than 0.2. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Here, the ratio of 17.802 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.6 ANOVA results of the quadratic models for COD removal percent for ACRONAL IA 734 AP

Source	Sum of squares	Degrees of freedom	Mean square	F-Value	Prob > F
Model	99.73	8	12.47	19.87	< 0.0001
Residual	6.90	11	0.6275		
Lack of Fit	5.06	6	0.8438	2.29	0.1902
Pure error	1.84	5	0.3680		

$R^2=0.9353$, R^2 adj = 0.8882, Predicted $R^2 = 0.7086$; Adequate precision = 17.8019

4.3.2 Fenton-like oxidation of emulsion sample ACRONAL 295 D AP

All the three independent variables with their levels are listed in Table 4.3, design matrix is shown in Table 4.4 and the response data is shown in Table 4.7. The response functions along with interaction coefficients of independent variables are presented in Eq. 4.2. The equation involves one constant term, three linear terms (A, B, C), two quadratic terms (A*A, C*C) and one interaction term (A*B).

$$\begin{aligned} \text{Sqrt(COD removal)} = & +4.79 - 2.24 A - 0.2206 B + 0.4795 C - 0.6458 A * B \\ & + 0.9877 A*A + 0.6253 C*C \end{aligned} \quad (4.2)$$

Table 4.7 Response data from design for ACRONAL 295 D AP

Response	Name	Minimum	Maximum	Mean	Std. Dev.	Ratio	Transfo Rm	Model
R1	COD removal (%)	3.72	98.94	39.86	31.11	26.57	Square Root	Reduced Quadratic

The response ranges from 3.72 to 98.94. Hence the ratio of maximum to minimum is 26.57 which is greater than 10. It is recommended to apply power transformation and thus square root transform is applied to fit the model. In the coded equation (4.2) for the model, the intercept value is +4.79 which shows a positive effect. So as to improve the model, model reduction was done by eliminating terms with p-values greater than 0.10.

To find out the relation between the mean square (MS) and the residual error of the model, the F test (Fisher's test) analysis was performed. The Model F-value of 25.30 implies the model is significant. The Lack of Fit F-value is 4.71, which is not significant (Table 4.8). The Predicted R² of 0.7082 is in reasonable agreement with the Adjusted R² of 0.8847; i.e. the difference is less than 0.2. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Here, the ratio of 18.3230 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.8 ANOVA results of the quadratic models for %COD removal for ACRONAL 295 D AP

Source	Sum of squares	Degrees of freedom	Mean square	F-Value	Prob > F
Model	94.07	6	15.68	25.30	< 0.0001
Residual	8.06	13	0.6197		
Lack of fit	7.12	8	0.8901	4.76	0.0512
Pure error	0.9351	5	0.1870		

R²=0.9211, R² adj = 0.8847, Predicted R² = 0.7082; Adequate precision = 18.3230

4.3.3 Fenton-like oxidation of emulsion sample ACRONAL IN 296 D AP

All the three independent variables with their levels are listed in Table 4.3, design matrix is shown in Table 4.4, and the response data is shown in Table 4.9. The response functions along with interaction coefficients of independent variables are presented in Eq. 4.3. The equation involves one constant term, three linear terms (A, B, C), and three quadratic terms (A*A, B*B, C*C).

$$\begin{aligned} \text{Log}_{10}(\text{COD removal}) = & +1.01 - 0.3339 A - 0.0254 B + 0.0353 C + 0.2332 A*A \\ & + 0.1338 B*B + 0.1264 C*C \end{aligned} \quad (4.3)$$

Table 4.9 Response data from design for ACRONAL IN 296 D AP

Response	Name	Minimum	Maximum	Mean	Std. Dev.	Ratio	Transform	Model
R1	COD removal (%)	8.72	98.26	34.04	35.24	11.27	Base 10 Log	Reduced Quadratic

The response ranges from 8.72 to 98.26. Hence the ratio of maximum to minimum is 11.27 which is greater than 10. It is recommended to apply power transformation and thus Base 10 Log transform is applied to fit the model. In the coded equation (4.3) for the model, the intercept value is +1.01 which shows a positive effect. So as to improve the model, model reduction was done by eliminating terms with p-values greater than 0.10.

To find out the relation between the mean square (MS) and the residual error of the model, the F test (Fisher's test) analysis was performed. The Model F-value of 25.44 implies the model is significant. The Lack of Fit F-value is 4.02, which is not significant (Table 4.10). The Predicted R² of 0.6969 is in reasonable agreement with the Adjusted R² of 0.8853; i.e. the difference is less than 0.2. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Here, the ratio of 15.703 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.10 ANOVA results of the quadratic models for %COD removal for ACRONAL IN 296 D AP

Source	Sum of squares	Degrees of freedom	Mean square	F-Value	Prob > F
Model	2.64	6	0.4397	25.44	< 0.0001
Residual	0.2247	13	0.0173		
Lack of fit	0.1944	8	0.0243	4.02	0.0711
Pure error	0.0302	5	0.0060		

$R^2=0.9215$, R^2 adj = 0.8853, Predicted $R^2 = 0.6969$; Adequate precision = 15.703

4.3.4 Fenton's oxidation of mixture of emulsion samples in water

A mixture of emulsion sample was prepared by mixing the synthetic samples of three different emulsions in equal proportions. The experiment was conducted in the similar conditions and same reaction time as that for individual emulsion samples. From the results of COD removal efficiencies of each sample and also considering the cost effectiveness of the process experiments were conducted at optimum and minimum catalyst and H₂O₂ quantities without compromising much with the efficiency of treatment. Thus, a pH of 3, H₂O₂/COD ratio of 1 and catalyst dosage of 5g/L was considered as optimum for treating the mixture of emulsions. A COD removal efficiency of 95% was achieved at this treatment condition. The treatment of water-based paint wastewater using conventional Fenton oxidation process using FeSO₄·7H₂O as an iron source showed a COD removal efficiency of 80% at pH-3. But the H₂O₂/COD ratio was 2 and the Fe concentration more than 15 mg/l (Kurt et al., 2006).

4.3.5 Effect of independent variables on the response

The effect of various factors such as pH, H₂O₂/COD, catalyst dosage, and calcination temperature which contribute to the overall efficiency of the treatment process is discussed in the following sections.

4.3.5.1 Effect of pH

Due to the high sensitivity of pH in conventional Fenton's process in the treatment of wastewater containing organic pollutants, (Nidheesh, 2015; M. hui Zhang, Dong, Zhao, Wang, & Meng, 2019), heterogeneous Fenton's process was adopted to find out the efficient pH range for paint industry wastewater using laterite as catalyst. Even though the

heterogeneous Fenton-like oxidation is found to work in wide range of pH (2 to 5) (Vijyendra Kumar, Pandey, Dharmadhikari, & Ghosh, 2019) and in alkaline pH (Boczka & Fernandes, 2017), it depends on the type of wastewater and the catalyst used (A. Khataee et al., 2015). In this study, a pH value of 3 was found to be the most efficient which is similar to the conventional Fenton's oxidation. The oxidation potential of hydroxyl radicals is lower in basic solutions compared to the acidic ones (A. Khataee et al., 2015). The variation in pH during the reaction time is shown in Fig.4.6. It is found that the final pH of the treated water comes to the range of 4-5, which makes the treated water less acidic than the initial pH.

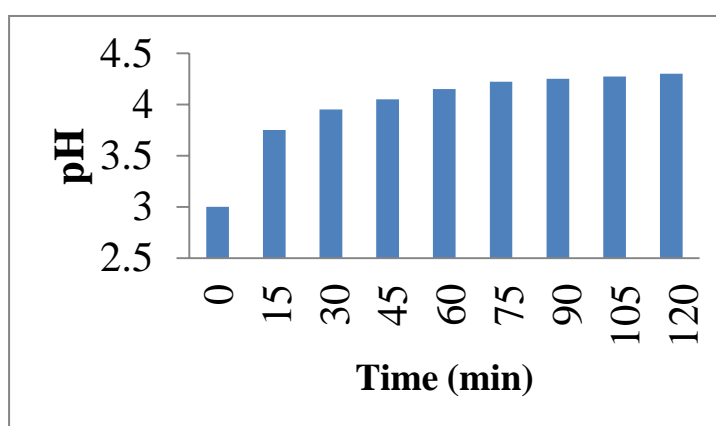


Figure 4.6 Variation of pH during treatment

The effect of pH on the %removal of COD of the emulsion **ACRONAL IA 734 AP** in water is shown in Fig 4.7 (a). It can be observed that the decrease of pH from 7 to 3 led to the increase of COD removal to 97.72%, with 120 min of treatment at room temperature. This result shows that the acidic pH is more favorable for Fenton-like degradation of the selected emulsion. With 5 g/L of heated lateritic soil and H₂O₂/COD ratio 1, the above efficiency was achieved. With increase in these two parameters at pH 3, it was found that the efficiency is decreasing.

The effect of pH on the %removal of COD of the emulsion **ACRONAL 295 D AP** in water is shown in Fig 4.7 (b). It can be observed that the decrease of pH from 7 to 3 led to the increase of COD removal to 96.27%, with 120 min of treatment at room temperature. This result shows that the acidic pH is more favorable for Fenton-like degradation of the selected emulsion. With 15 g/L of heated lateritic soil and H₂O₂/COD ratio 4, the above efficiency was achieved. With decrease in these two parameters at pH 3, it was found that

the efficiency is decreasing. But almost similar efficiency of 91.46% was attained at lesser catalyst dosage of 5g/L and same H₂O₂/COD ratio.

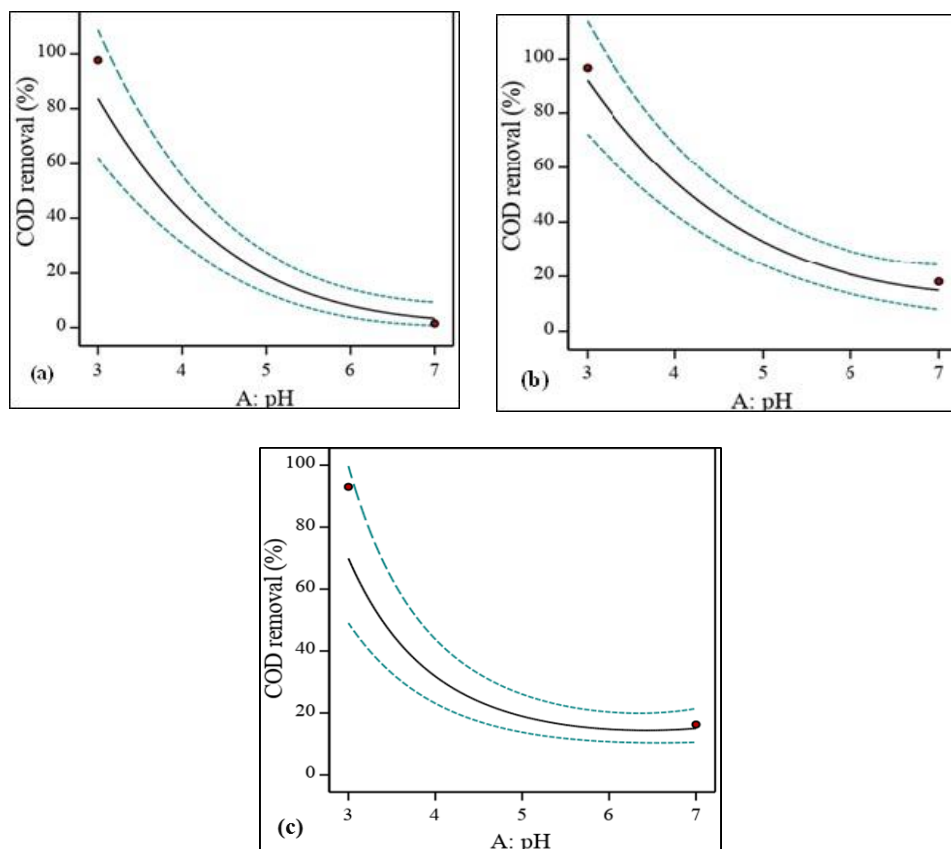


Figure 4.7. Effect of pH on % COD removal of (a) ACRONAL IA 734 AP (At H₂O₂/COD-1 and catalyst dosage 5g/L, room temperature); (b) ACRONAL 295 D AP (At H₂O₂/COD-4 and catalyst dosage 15g/L, room temperature); (c) ACRONAL IN 296 D AP (At H₂O₂/COD-1 and catalyst dosage 5g/L, room temperature)

The effect of pH on the %removal of COD of the emulsion **ACRONAL IN 296 D AP** in water is shown in Figure 4.7 (c). It can be observed that the decrease of pH from 7 to 3 led to the increase of COD removal to 93%, with 120 min of treatment at room temperature. This result shows that the acidic pH is more favorable for Fenton-like degradation of the selected emulsion. With 5 g/L of heated lateritic soil and H₂O₂/COD ratio 4, the above efficiency was achieved.

4.3.5.2 Effect of H₂O₂

The effect of H₂O₂ dosage on the %removal of COD of the emulsion **ACRONAL IA 734 AP** in water is studied by varying the parameter H₂O₂/COD ratio from 1 to 4 (Fig 4.8 (a)). The figure depicts that with the increase in hydrogen peroxide, the COD removal was not

increasing, because even though more hydroxyl radicals were formed, it was not useful. Maximum degradation was achieved as 97.72% at H_2O_2/COD of 1 that is 3.17 (mL/L) at pH 3 and catalyst dosage 5g/L. Excess hydrogen peroxide led to scavenging effects or produced less powerful oxidizing agent like per hydroxyl radical (A. R. Khataee & Pakdehi, 2014). Therefore, when increased amount of H_2O_2 was employed, degradation was lowered.

The effect of H_2O_2 dosage on the %removal of COD of the emulsion **ACRONAL 295 D AP** in water is studied by varying the parameter H_2O_2/COD ratio from 1 to 4 (Fig 4.8 (b)). It depicts that with the increase in hydrogen peroxide, the COD removal was increasing, which explains that this emulsion has more complex organic substance compared to **ACRONAL IA 734 AP** which requires higher amount of hydroxyl radical. Maximum degradation was achieved as 96.27% at H_2O_2/COD of 4 that is 18.07 (mL/L) at pH 3 and catalyst dosage 15g/L. Decreasing the volume of H_2O_2 to the minimum of H_2O_2/COD ratio of 1 gave efficiency of 83%, which was also appreciable.

The effect of H_2O_2 dosage on the %removal of COD of the emulsion **ACRONAL IN 296 D AP** in water is studied by varying the parameter H_2O_2/COD ratio from 1 to 4 (Fig 4.8 (c)). It depicts that, the COD removal was almost similar at H_2O_2/COD ratio 1 and 4, which explains that the organic substances present in the emulsion are degradable even at lower H_2O_2/COD ratio. Maximum degradation was achieved as 93.02% at H_2O_2/COD of 1 that is 4.13 (mL/L) at pH 3 and catalyst dosage 5g/L. Increasing the volume of H_2O_2 to the minimum of H_2O_2/COD ratio of 4 gave efficiency of 91.28% at 5g/L of catalyst dosage which was also appreciable. At this H_2O_2/COD ratio, increasing the catalyst dosage to 15g/L gave higher efficiency of 91.86%. And, at lower H_2O_2 and higher catalyst dosage the efficiency was almost similar i.e., 91.28%. Thus an optimum value of H_2O_2 has to be decided considering the cost effectiveness. These results explains that the effect of H_2O_2 concentration in the treatment process, depends on the characteristics of wastewater (N. Wang et al., 2016) as much as it depends on the type of advanced oxidation process (M. hui Zhang et al., 2019).

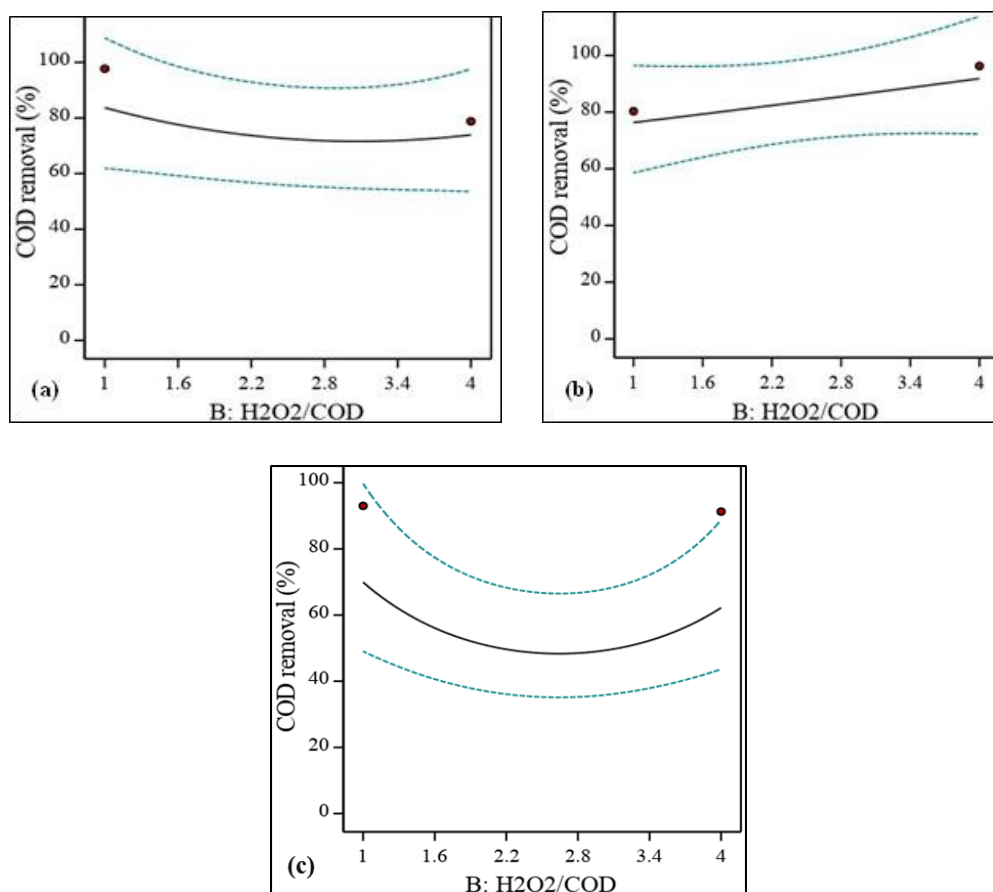


Figure. 4.8 Effect of H_2O_2/COD on % COD removal of (a) ACRONAL IA 734 AP (At pH-3 and catalyst dosage 5g/L, room temperature); (b) ACRONAL 295 D AP (At pH-3 and catalyst dosage 15g/L, room temperature); (c) ACRONAL IN 296 D AP (At pH-3 and catalyst dosage 5g/L, room temperature)

The treatment of organic waste depends on H_2O_2 , which is the primary source of HO during catalysis in Fenton-like actions. To determine the optimal H_2O_2 dose, experimental research is needed. Inadequate H_2O_2 dosage will lessen the efficiency of treating organic wastewater due to a lack of HO generated by H_2O_2 decomposition under catalysis. On the contrary, utilising H_2O_2 excessively is also not advised. Firstly, when Fenton-like processes are used to pre-treat high concentration organic WW in order to improve the ratio of BOD to COD (BOD/COD or B/C), an enormous quantity of H_2O_2 could have a detrimental effect on the reactivity of the microorganisms that are used to treat the pretreated organic wastewater in the subsequent bio-treatment process. Second, an excessive H_2O_2 dosage would significantly increase the cost of treatment when the amount of organic wastewater is quite high. Thirdly, utilising too much H_2O_2 may cause the COD of the effluent to increase. Although this sort of COD cannot harm the

environment, it may hinder the treated wastewater quality from fulfilling the discharge criteria because of the innocuous COD. The last and most crucial element is that HO will be more strongly scavenged by an excessive H₂O₂ dosage (N. Wang et al., 2016). In addition, any leftover H₂O₂ will make the effluent more hazardous and indicate inefficient oxidant consumption, which adds to the overall expense of this treatment. The expense of H₂O₂ and the volume of sludge (Fe(OH)₃) created during the neutralisation step of the treated solution before disposal are the main drawbacks for using the Fenton procedure. It is difficult to come up with methods to enhance the Fenton technology given these limitations and the increasingly strict water regulations (Pliego et al., 2015).

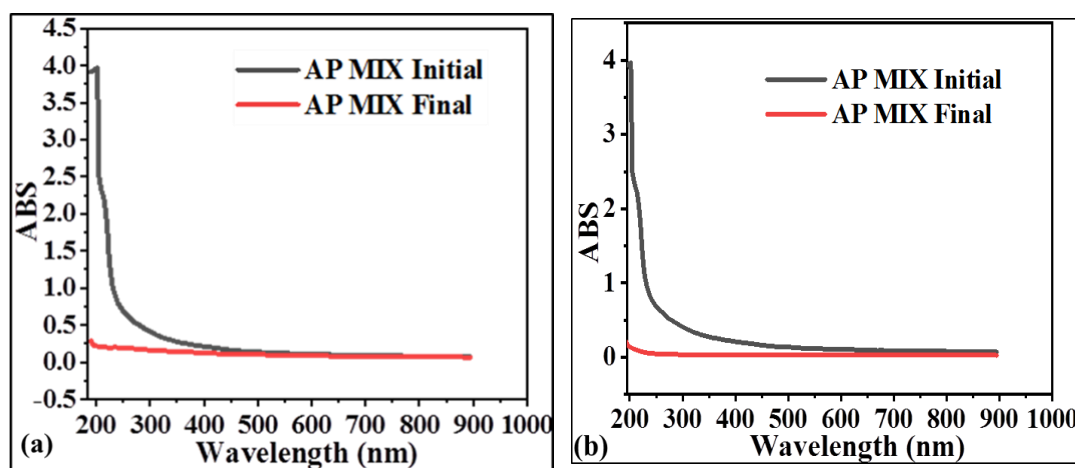


Figure 4.9 UV/VIS spectrum before and after treatment for Mixture of emulsion (a) with H₂O₂; (b) Without H₂O₂

The use of laterite calcined at 800°C in treating paint wastewater could overcome these drawbacks and is found to be an excellent catalyst which does not require external addition of H₂O₂. A COD removal efficiency of 98% is achieved using the catalyst at acidic pH of 3. The initial absorbance of the synthetic wastewaters prepared by the three emulsions and the mixture of emulsions was recorded using UV/VIS spectrophotometer at a wavelength range of 190 to 900nm. A peak was observed in all the samples in the range of 190 to 350nm, which signifies the presence of poly-unsaturated and aromatic compounds (von Elbe & Schwartz, 2018). The final treated samples were also analysed. The spectrums (Fig. 4.9 (a-b)) show that there is a considerable removal of the suspected compound and there is no production of other peaks in the entire wavelength range even without the addition of H₂O₂, which suggests that there is no formation of any other intermediate compound after the treatment process and the treatment can occur without H₂O₂.

4.3.5.3 Effect of catalyst dosage

The effect of heterogeneous catalyst LS800 on the %removal of COD of the emulsion **ACRONAL IA 734 AP** in water is shown in Fig 4.10 (a). In this case, optimization of catalyst dosage was done by varying it from 5 to 15g/L. for this emulsion sample in water, it is observed that at pH-3 and H₂O₂/COD-1, maximum COD removal efficiency of 97.72% is obtained at 5 g/L and there is a decrease in the efficiency with increase in the catalyst. Even though increasing the catalyst would give more iron active sites for degradation, this trend can be due to excess iron.

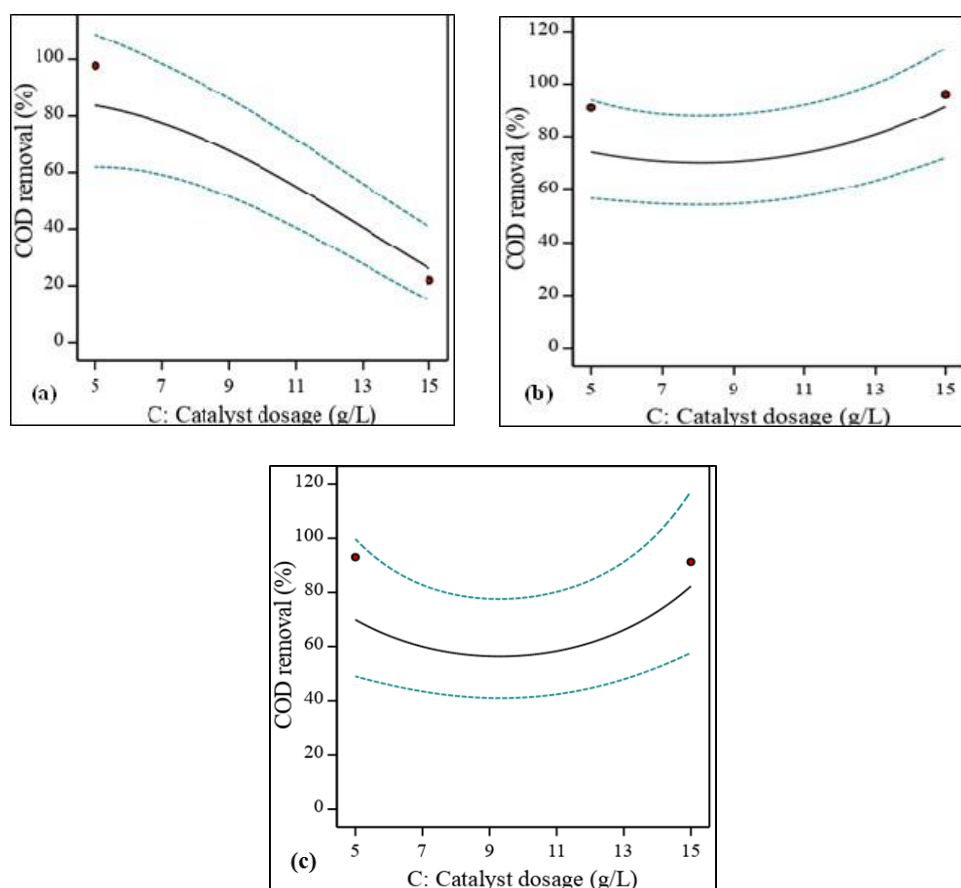


Figure. 4.10 Effect of catalyst dosage on % COD removal of (a) ACRONAL IA 734 AP (At pH-3 and H₂O₂/COD-1, room temperature); (b) ACRONAL 295 D AP (At pH-3 and H₂O₂/COD-4, room temperature); (c) ACRONAL IN 296 D AP (At pH-3 and H₂O₂/COD-1, room temperature)

The effect of heterogeneous catalyst LS800 on the %removal of COD of the emulsion **ACRONAL 295 D AP** in water is shown in Fig 4.10 (b). In this case, optimization of catalyst dosage was done by varying it from 5 to 15g/L. For this emulsion sample in

water, it is observed that at pH-3 and H₂O₂/COD-4, maximum COD removal efficiency of 96.27% is obtained at 15 g/L. But, almost similar efficiency of 91.46% was attained at lesser catalyst dosage of 5g/L and same H₂O₂/COD ratio of 4. This may signify that 5g/L of the heterogeneous catalyst was sufficient so as to activate the increased amount of H₂O₂ which was required to degrade the organic compound in the emulsion.

The effect of heterogeneous catalyst LS800 on the %removal of COD of the emulsion **ACRONAL IN 296 D AP** in water is shown in Fig 4.10 (c). In this case, optimization of catalyst dosage was done by varying it from 5 to 15g/L. For this emulsion sample in water, it is observed that at pH-3 and H₂O₂/COD-1, maximum Cod removal efficiency of 93.02% is obtained at 5 g/L. It was observed that with lower H₂O₂/COD, increasing the catalyst dosage also gave similar COD removal. This may signify that 5g/L of the heterogeneous catalyst was sufficient so as to activate the amount of H₂O₂ which was required to degrade the organic compound in the emulsion.

4.3.5.4 Effect of calcination temperature on treatment efficiency

The natural laterite was prepared to be used as a heterogeneous catalyst in the Fenton-like oxidation of mixture of three different emulsions in water. The natural laterite samples collected were powdered and sieved through 150 micron sieve and heated under normal air supply in the muffle furnace at different temperatures viz 105°C, 300°C, 450°C, 600°C and 800°C.

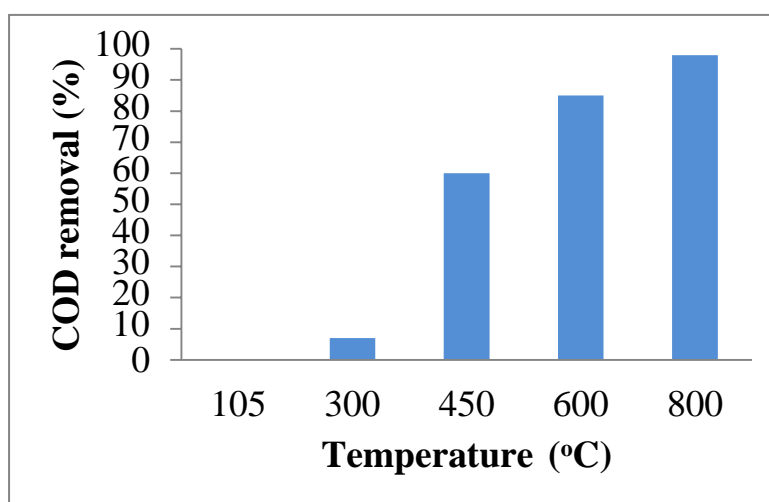


Figure 4.11. Effect of calcination temperature on treatment efficiency

Based on their heating temperatures, samples were named as LS105, LS300, LS450, LS600 and LS800 respectively. From the experimental results, laterite soil sample heated

at 800°C was found to be the most effective in reducing the COD of the three emulsions in water (Fig. 4.11). Further raising the calcination temperature to 1000°C caused the disappearing of Fe₂O₃ peaks which will destroy the efficiency of catalyst for Fenton-like reaction (Han et al., 2020).

The comparison of XRD pattern of laterite samples calcined at different temperatures viz. 105,300,450,600 and 800°C are shown in Fig. 4.12.

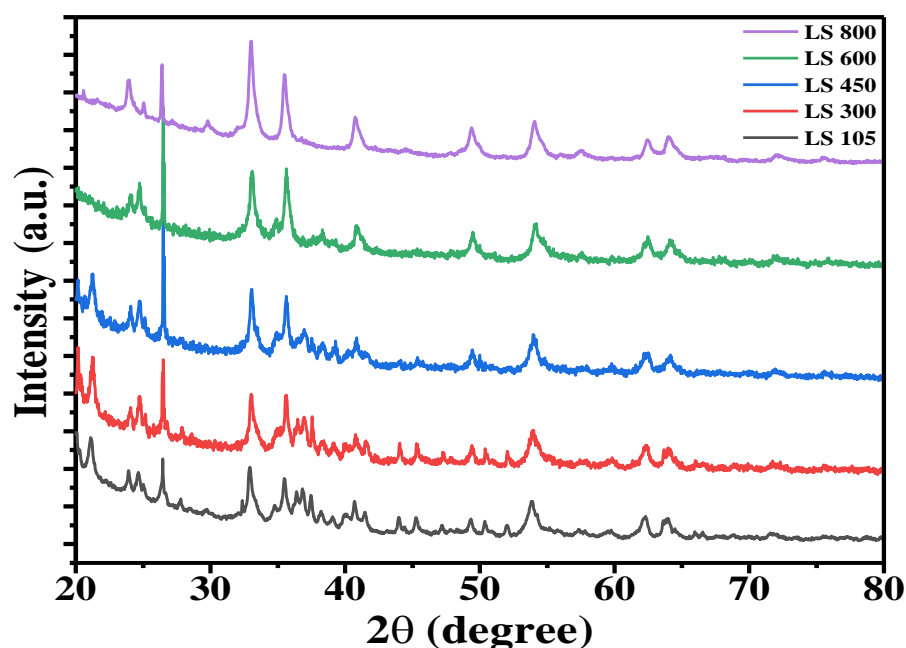


Figure 4.12 Comparison of XRD pattern of laterite samples calcined at different temperatures viz. 105,300,450,600 and 800°C

4.3.6 Catalyst stability and reusability

One of the important factors to be considered in improving a heterogeneous Fenton-like process is the stability of the catalyst (Ganiyu et al., 2020). As we aim to make the process economical and eco-friendly, the recovery and reusability capacity of the catalyst should also be studied (Tarkwa et al., 2019). Also, the leaching of metal ion (iron) from the heterogeneous catalyst into the treated water affects the recycling or reuse efficiency (Ganiyu et al., 2020; Nidheesh, 2015). With this purpose, experiments were conducted for three cycles for the above mentioned optimum experimental conditions with the mixture of emulsions. The catalyst was washed with deionised water and reused for the next cycle. The COD removal efficiency was found to be 95%, 73%, and 60%. Catalyst is found to be 30% less efficient after three cycles which could be possibly due to the deactivation of catalyst (Tarkwa et al., 2019) and also due to the loss of catalyst particles

during washing (Ganiyu et al., 2020) or due to the leaching phenomenon of iron from the heterogeneous catalyst into the solution (Changduang et al., 2021; Han et al., 2020). The dissolved iron concentration in the treated water after the first cycle was 0.26mg/L, which shows the remarkable stability of laterite catalyst in the treatment process.

It is found that the laterite soil heated to 800°C is highly stable and remarkably reusable. The peaks of Fe₂O₃ from the XRD results (Fig.4.13), is found to remain exactly the same before and after use for treatment except a very small reduction in the peak owing to the reaction of iron as catalyst or leaching into the sample for the degradation reaction.

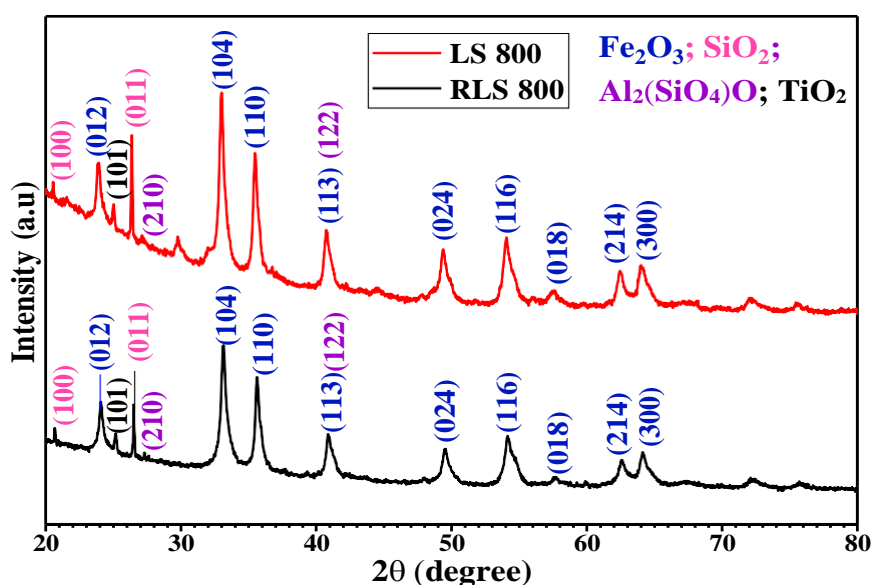


Figure 4.13 XRD pattern of laterite sample LS800 and reused laterite RLS800

4.4 CHARACTERIZATION OF GREEN SYNTHESISED HETEROGENEOUS CATALYST- LSFENP(TC)

Fig. 4.14 shows the XRD pattern of LSFENP(TC). From the analysis it was found that the main phases in the catalyst are Fe₃O₄ (Magnetite), FeOCl (Iron oxide chloride), Ca(Fe₂O₄) (Calcium Iron Oxide), and KFeO₂ (Potassium Iron Oxide). The diffraction peaks at 2θ values of 34.54°, 36.51°, 38.61°, 46.02°, and 49.17° are characteristics of (023), (111), (040), (131), and (132) plane of magnetite crystal structure (JCPDS 01-082-3508). The peaks at 2θ values of 26.45°, 29.45°, 38.15°, 43.48°, 44.88° and 55.66° can be assigned respectively to (110), (011), (111), (121), (031) and (002) space plane of FeOCl (JCPDS 01-076-2300). The diffraction peaks at 2θ value of 26.04°, 27.32°, 34.36°, 36.24°, 41.18°, 50.69°, and 56.37° corresponds to (220), (310), (230), (021), (311), (421),

and (620) plane of $\text{Ca}(\text{Fe}_2\text{O}_4)$ crystal structure in the diffractogram (JCPDS 01-078-4318). Furthermore, the characteristic peaks of KFeO_2 at 2θ values of 20.91° , 22.99° , 24.38° , and 31.78° which can be assigned, respectively, to the spacing planes (112), (121), (113), and (124) (JCPDS 01-084-9871).

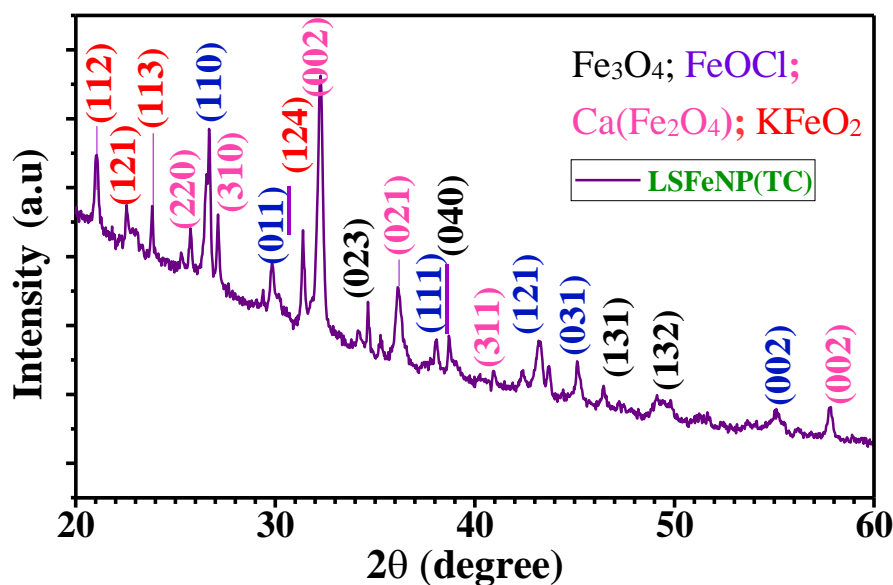


Figure 4.14 XRD pattern of LSFenP(TC)

In comparison to other Fe-based catalysts, iron oxychloride (FeOCl) has recently been shown to be a highly efficient and pH-insensitive Fenton catalyst. Self-stacked iron layers connected by van der Waals interactions make up the distinctive structure of FeOCl , which has a favourable catalytic performance. Through electron transfer between FeOCl and intercalated materials (such as polyaniline and Na) (the presence of Na was discovered in the EDS analysis as stated in Table 4.11), Fe^{3+} in FeOCl is easily reduced to Fe^{2+} (Chen, Miller, Collins, & Waite, 2021). In iron-based oxidation systems, structural management of the active centres is crucial in regulating the catalytic activities. Using an oxidative coupling or polymerization, the K- FeOCl catalyst may effectively remove a variety of organic contaminants with nearly 2 orders of magnitude faster reaction kinetics than other Fe-based materials.

A reaction-filtration coupled process based on K- FeOCl showed tremendous promise for sustainable pollution removal technologies, with the potential to reduce energy usage by over 50% (Jinling Wang et al., 2022). A potential substance for heterogeneous catalysis, orthorhombic KFeO_2 has a special structure that allows K^+ cations to move inside the Fe-O skeleton (S. Zhang et al., 2022). Divalent cobalt ion (Co^{2+}) has also received a lot of

attention as a Fenton-like catalyst for the oxidation of organic contaminants (Bokare & Choi, 2014). The presence of Co was discovered in the EDS analysis, as indicated in Table 4.11.

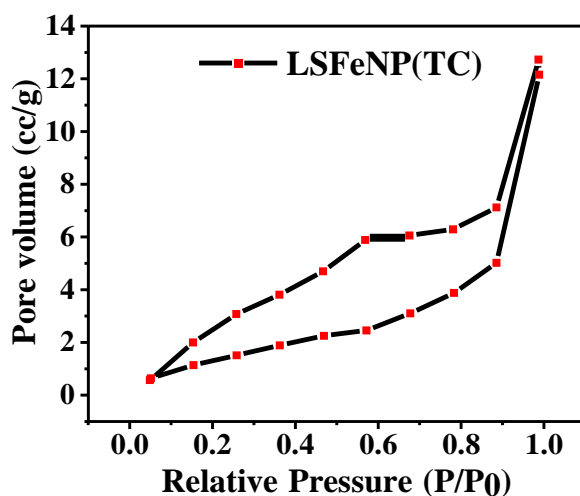


Figure 4.15 N₂ adsorption–desorption isotherm of the LSFenP(TC)

These diameter corresponds to the macroporous structure and it is also visible from the adsorption-desorption isotherm that the catalyst represent the Type IV isotherm, according to the IUPAC classification and the hysteresis loop of H3 (Changduang et al., 2021; Thommes et al., 2015). The H3 signifies that it is non-rigid aggregates of plate-like particles with slit-shaped pores. The SEM micrograph of the catalyst is shown in Fig. 4.16.

Table 4.11 Chemical components of LSFenP(TC) from EDS analysis

Component	O	Cl	Fe	K	Ca	Al	Co	Na	Mg	Si
Weight (%)	45.1	28.3	11.2	4.4	1.6	3.6	1.9	1.6	1.2	1.2

The determination of isotherm type and the pore structure was studied by the nitrogen adsorption–desorption isotherm using BET Surface Area Analyzer. Fig. 4.15 indicates N₂ adsorption–desorption isotherm of the catalyst sample that is measured at 77.350K. Based on the isotherms, the surface adsorption properties were calculated. The surface area was found to be 5.87m²/g, and the average pore radius is 64.42nm.

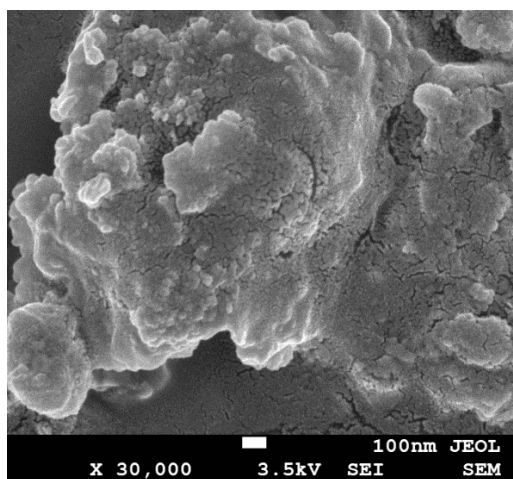


Figure 4.16 SEM micrograph of LSFenP(TC)

4.5. TREATMENT OF EMULSIONS IN WATER BY FENTON-LIKE OXIDATION USING LSFENP(TC) AS CATALYST

A mixture of emulsion sample was treated using the synthesized nanoparticles LSFenP(TC). The catalyst particles could be obtained from 1:3 ratio of precursor to leaf extract and also till 1:10 ratio. It was observed that just addition of this catalyst could reduce the pH of the wastewater from basic to acidic (upto 1), values depending on the amount added. This remarkable property of the catalyst could be due to the presence of FeOCl which has the capability to reduce the pH of the solution (Jie Wang, Li, Jiang, & Tong, 2023). The ability of Terminalia catappa leaves in reducing the pH of water is also well established (Malawa et al., 2022) . Hence, this catalyst could give 85% efficiency in removing COD from the prepared paint wastewater (initial COD 1500g/l, pH-8) at 3g/l dosage (which made the pH to 3) for a mixing period of 120minutes at 210rpm at room temperature without addition of external H₂O₂ and acid for regulating pH in the heterogeneous Fenton-like process.

4.6 TOXICITY EVALUATION OF TREATED WATER

The toxicity analysis of treated samples done by bacterial growth inhibition test using *Bacillus subtilis* and seed germination test using mung bean (*Vigna radiata*) and Bengal gram (*Cicer arietinum*) was analysed as below.

4.6.1 Bacterial growth inhibition test

The growth inhibition of *Bacillus subtilis* in the Fenton-treated solution was used to evaluate the toxicity of the Fenton oxidation products. The bacterial growth inhibition due

to the degradation products was measured as per equation (3.2). The treated wastewater (pH= 4.75) showed 0.23% growth inhibition. This shows that even slight inhibition in the growth of the *Bacillus subtilis* in the actual treated water is not found. The bacterial species could also grow in the moderately acidic pH.

4.6.2 Seed germination test

The seed germination of Bengal gram and Mung bean seed is depicted in Fig. 4.17(a-d) for untreated and treated wastewater using laterite soil as a catalyst in heterogeneous Fenton process. The germination of seed was prevented in the raw wastewater mostly due to the presence of soluble and harmful chemicals, which can make it difficult for seeds to germinate (Kwarciak-Kozłowska & Krzywicka, 2016). The root length was measured to be at an average 3mm for Mung bean and 6mm for Bengal gram, whereas a higher root growth of 22mm and 32mm, respectively was observed for treated water which is almost similar to that of control. For control sample seed root was grown till 22.5 mm and 33mm respectively after 5 days.



Figure 4.17 5 day germination of seeds (a-b) Bengal gram irrigated with treated and untreated water, (c-d) Mung bean irrigated with treated and untreated water.

The results from both the bacterial inhibition test and seed germination test (Table 4.12) suggests that Fenton-like oxidation (with OH• radicals) of paint wastewater using calcined laterite (800°C) as catalyst remarkably degraded the toxic organic compounds in it, with no toxicity towards the selected indicator species, making it an eco-friendly treatment technique.

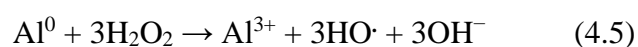
Table 4.12 Bacterial growth inhibition test

Sample	pH	OD 600 control	OD 600 test	% growth Inhibition
LS 800 treated	4.5	0.6740	0.6725	0.23

LS 800 treated (diluted)	6.85	0.6740	0.6732	0.12
LSFeNP(TC) treated	3.2	0.6740	0.4175	38
LSFeNP(TC) treated (diluted)	6	0.6740	0.5675	15

4.7 DISCUSSION

A mixture of emulsion sample was prepared by mixing the synthetic samples of three different emulsions in equal proportions. From the experimental results, laterite soil sample heated at 800°C was found to be the most effective in reducing the COD of the three emulsions in water. A COD removal efficiency of 98% was achieved at a pH of 3 and catalyst dosage of 5g/L (for an initial COD of 1500mg/l) without the addition of H₂O₂. The mechanism behind this reaction is understood by carrying out experiments with synthetic form of Fe³⁺ and Al³⁺ separately as well as combined. It is observed that similar reaction as that of the solution with LS800 as catalyst is observed due to bimetallic Fe/Al. To develop the novel bimetallic Fe/Al for the treatment of persistent pollutants in water and wastewater through the enhanced and rapid OH[•] generation (H. L. Lien et al., 2019). Aluminum serves as a reductant to create favorable reducing conditions (H.-L. Lien & Zhang, 2002). The excellent oxidative powder of ZVAl/H+/air system is mainly due to the formation of hydroxyl radical (Bokare & Choi, 2009; H. Zhang, Cao, Liu, Lin, & Feng, 2012), which is explained by the following equations



The stable iron in LS800 accelerated the removal mainly through its transformation to Fe²⁺ in the acidic solution, which subsequently triggered Fenton reaction (H. Zhang et al., 2012) and degraded the emulsions in water with very less amount of sludge compared to conventional paint wastewater treatment processes such as coagulation-flocculation (Balik & Aydin, 2016b).

CHAPTER 5

CONCLUSIONS

5.1 GENERAL CONCLUSION

In the light of large volumes of wastewater being generated various methods including physic-chemical and biological methods have been developed over the past decades. However, these processes are inadequate in effectively treating the wastewater from paint industries due to its various disadvantages discussed earlier. The survey of the state-of-the-art literature shows that advanced oxidation processes are increasingly being recognized as a potential effective method to address the challenges of large wastewater often being disposed directly to the surface water source or the challenge of managing the large volume of sludge being generated. However, it is not clearly understood as to how these processes can be made more efficient, sustainable and economically viable. In order to address these challenges, further research investigations should focus on making it more feasible and eco-friendlier. Also identifying the best methodology for characterizing the chemical compounds and degraded products and conducting ecotoxicity studies is necessary in order to achieve better efficiency. This will go a long way in addressing the global challenges. According to Goal No. 14 of the UN SDG, as much as 40 percent of the ocean is heavily affected by pollution, depleted fisheries, loss of coastal habitats and other human activities. Thus, treating these industrial wastewaters which are being disposed of to the large water bodies, up to the desired disposal quality is essential to save the environment. The conclusions of this research are summarized below-

- In this study, the degradation of mixture of three different emulsion samples in water is investigated by Fenton-like oxidation process using laterite soil as heterogeneous catalyst prepared by heating soil (sieved through 150-micron sieve) under normal air supply in the muffle furnace to a temperature of 800°C.
- A remarkable result found was that COD removal efficiency of 98% was achieved for the mixture of emulsions without the addition of H₂O₂. The catalyst is found to be stable and reusable. Also, the remarkable property of the green synthesized heterogeneous catalyst particles using laterite extract and *Terminalia catappa* leaf extract is that, they can reduce the pH of the wastewater to very highly acidic pH even if added in very less concentration and thus reducing the COD of paint wastewater upto 85% efficiency without an external oxidizing agent such as H₂O₂.

- The review on various methods and indicators adopted for toxicity analysis suggests the high significance for conducting ecotoxicity studies for the AOP treated wastewater, to make the process more efficient and sustainable.
- The survey of the state-of-the-art literature shows that various organisms can be used for studying the toxicity and their selection depends on the intended use of the treated water.
- In vitro assays, tests on indicator microbes and phytotoxicity tests can be more practicable considering the animal welfare, economic, relative speed and simplicity of the toxicity analysis process.
- Focusing on the recycling of the treated industrial wastewater for gardening and agricultural activities, the toxicity of treated paint wastewater was studied by bacterial growth inhibition test using *Bacillus subtilis*, which is a common soil bacteria and seed germination test using Mung bean (*Vigna radiata*) and Bengal gram (*Cicer arietinum*), widely grown crops in the South Asia.
- The results showed that the treated wastewater is completely toxic free for the growth of selected indicator bacteria and the seeds. This indicates that the heterogeneous Fenton's oxidation using laterite as catalyst is an effective AOP in reducing the toxicity of paint wastewater, and thus making it possible for the reuse of treated water.

Hence it will be of significant interest to both academic researchers and practitioners as these results brings up an economic, ecofriendly and efficient treatment technology for sustainable treatment of industrial wastewater.

5.2 SUPPORTING EXPERIMENTS FOR CONCLUSION

The novelty of the research lies in the catalytic oxidation of the organic compounds there by giving 98% COD removal efficiency without the addition of external oxidizing agents such as hydrogen peroxide etc. Apart from reducing the cost of process it also helps in reducing the sludge compared to conventional paint wastewater treatment techniques as discussed earlier. The novelty of the experimental process and the results was validated by conducting set of experiments. The expected mechanism discussed in section 4.6 is understood by trying to replicate the actual process using synthetic form of the compounds in the natural catalyst prepared. Initially the reaction was carried out using Fe_2O_3 at pH-3 without H_2O_2 to check if the efficiency is due to Fe^{3+} alone. It was

observed that there was no reaction Fig. 5.1 (a). This proves that Fe_2O_3 alone does not have the ability to produce oxidizing radicals to cause degradation of the compounds. It requires addition of H_2O_2 which is the conventional Fenton's process. Secondly, the experiment was conducted using only Aluminum salt at pH-3 without H_2O_2 . It was observed that Aluminum salt was acting as a coagulant alone and all the paint particles settled at the bottom of the flask producing the sludge Fig. 5.1 (b). Finally, the experiment was conducted using both Fe^{3+} and Al^{3+} salts at pH-3 without H_2O_2 and observed that the sludge produced was very minimal Fig. 5.1 (c). Only the Fe_2O_3 was remaining at the bottom of flask and COD removal efficiency of 98.5% was obtained. Thus, the bimetallic mechanism of the Fe/Al for the treatment of persistent pollutants in water and wastewater through the enhanced and rapid OH^\bullet generation is validated.

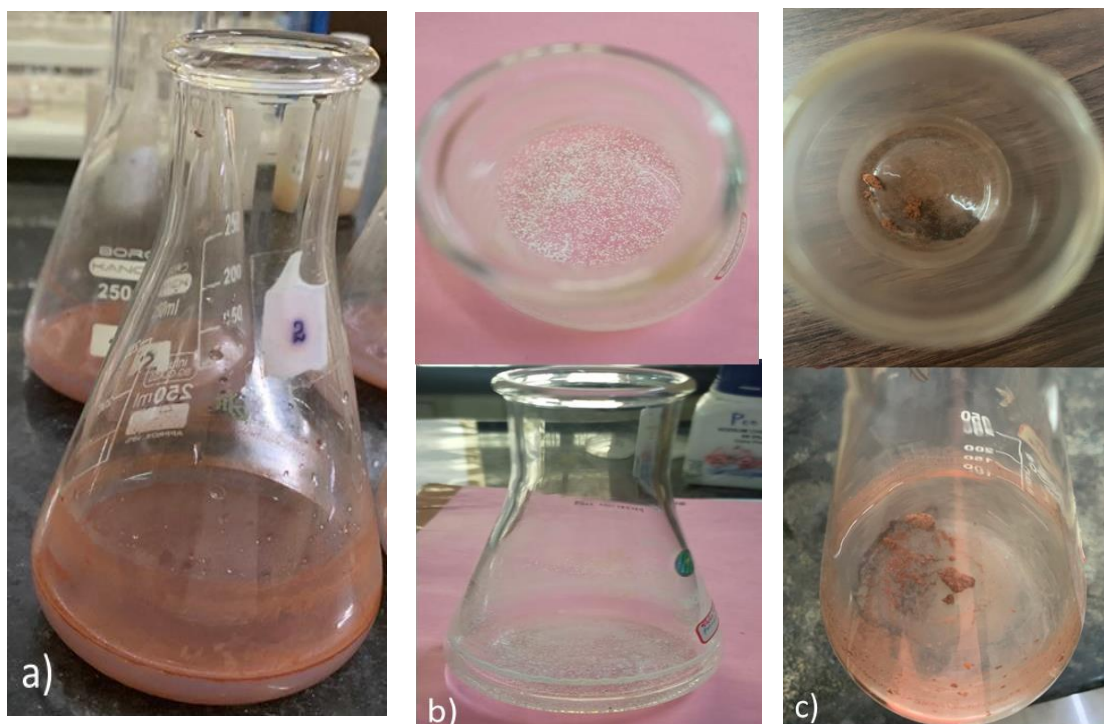


Figure 5.1 PWW treated using a) Fe^{3+} b) Al^{3+} and c) both Fe^{3+} and Al^{3+}

5.3 LIMITATIONS OF FIELD APPLICABILITY

In order to make the technique in this research into a technology it is important to understand the limitations and scope of the findings. This can be better understood by preparing a lab-scale model and running the process which can give an idea on scaling up of the project in treating the paint industry waste water and similar waste water more efficiently. To understand the economical benefit, a cost analysis of the process and comparison with

current treatment techniques can be carried out using the model.

The availability and utilization of the natural catalyst without affecting the environmental stability would be a challenge. But considering the reusability and efficiency of the treatment and comparing the environmental impacts of various techniques, an optimized model can be designed.

5.4 SCOPE FOR THE FUTURE WORK

The present research work can be extended:

- To understand the field applicability by using model treatment system and optimizing various parameters.
- To study the usability of the novel catalyst from laterite for degradation of various other toxic organic compounds in water.
- To explore the potential of FeNPs from Terminalia catappa leaves in disinfection capacity and degradation of more compounds.

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1. Nair K. Surya, Basavaraju Manu, and Adani Azhoni. (2021). “Sustainable Treatment of Paint Industry Wastewater: Current Techniques and Challenges.” *Journal of Environmental Management* 296(May): 113105. <https://doi.org/10.1016/j.jenvman.2021.113105>.

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PATENT (UNDER REVIEW)

1. Nair K. Surya, Basavaraju Manu, and Adani Azhoni (2023). Calcined Laterite Soil as a Novel Catalyst for Hydrogen Peroxide Free Heterogeneous Fenton-Like Oxidation of Paint Emulsions in Water.
2. Nair K. Surya, Basavaraju Manu, and Adani Azhoni (2023). Green Nanocatalyst as Hydrogen-Peroxide Free and pH-Insensitive Heterogeneous Catalyst for Fenton-Like Oxidation of Paint Emulsions in Water.

RESUME

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B Tech	Civil Engineering	CUSAT	2010-2014	78.5%