ADDIS ABABA UNIVERSITY

INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

TUNGSTEN-BASED ACTIVATED CARBON MATRIX FOR THE CATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS (VOCS) IN LEATHER INDUSTRIES

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“I hereby declare that this research paper entitled “tungsten-based activated carbon matrix for the catalytic oxidation of volatile organic compounds (VOCs) in leather industries” is my own and to the best of my knowledge and belief, it contains no material previously published or written by another person, nor material which to a substantial extent that has been submitted for the award of any other degree or diploma of a university or other institution of higher learning.”

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Abbreviations and Acronyms

ACM	Activated carbon matrix
CLRI	Central leather research institute
COD	Chemical oxygen demand
DSC	Differential scanning calorimetry
ECW	Ethyl benzene contaminated water
EDAX	Energy dispersive X-ray analysis
FTIR	Fourier Transform Intra-Red
GWP	Global Warming Potential
HPLC	High Performance liquid chromatography
LVOC	Leather Volatile Organic Compounds
LW	Leather Waste
MTBE	Methyl Tert Butyl Ether
ORP	Oxidation Reduction Potential
PAH	Polycyclic Aromatic Hydrocarbons
PCMs	Polychloromethanes
PBCR	Packed bed catalytic reactor
PID	Photo ionization detector
RH	Rice husk
SEM	Scanning electrone microscopy
TCW	Tolune contaminated water

TDS	Total dissolved solid
TGA	Thermo gravimetry analysis
TSS	Total suspended solid
VOC	Volatile organic compounds
WACM	Tungsten based activated carbon matrix
XRD	X-ray Diffraction

Abstract

The term "leather waste water" refers to the liquid waste that tanneries produce as a consequence of tanning leather. Among the numerous components that made up effluents from tanneries, VOCs make the largest portion of it. VOCs are compounds that volatilize readily when exposed to air. Due to their volatility, these substances cause air pollution, water and soil contamination by the portion that rains and snowmelt can carry deep in to the soil.

Because of this VOCs pose a threat to people, animal and plants. Thus it is important to identify the sources of VOCs, to characterize and treat them before releasing to the environment. In this VOCs treatment process catalytic oxidation is one of the effective procedure that may be used to remove VOCs. Generally the objective of this study was to investigate the catalytic degradation of VOCs from leather waste water using tungsten based activated carbon matrix.

Tungsten based activated carbon matrix was prepared from rice husk. A Tiger SXT gas detector was used to investigate the VOCs found in leather effluent. Physico chemical characterization was performed using parameters like COD, TDS, TSS, density, ash content, PH, ORP and TOC. Instrumental characterization of tungsten impregnated catalyst was conducting using FTIR, XRD, EPR, TGA, DSC and SEM. The COD of the aerated sample was 35000 mg/L during the physical-chemical characterisation of leather waste (tannery waste), and it was reduced to 180 mg/L following tungsten treatment. In addition, the TOC in the aerated sample was reduced to 160 mg/L following treatment from 6460 mg/L. TDS concentration was 260 mg/L following treatment, whereas the parameter was 17000 mg/L in aerated water. This outcome was obtained with an optimal WACM of 3%. Following treatment, the lowering of the indicated parameters denotes a decrease in VOCs. In this investigation, water polluted with toluene, ethyl benzene, chlorobenzene, and LVOCS was produced in an optimal environment for catalytic oxidation. Regarding TOC, the relative VOC removal efficiencies were 80.5%, 85.5%, 80.9%, and 85.4% for toluene, ethylbenzene, chlorobenzene, and LVOCs.

Keywords: Activated carbon matrix, Volatile organic compounds, tungsten, catalytic oxidation.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Leather waste water made up of both organic and inorganic chemical substances and contributes to the effluent from tanneries. Among the numerous components that make up this mixture are tannins (from sources like chromium or vegetable extracts), dyes, acids, bases, and oils. It is further distinguished by a high concentration of suspended organic materials made from a range of animal hides and skins. The organic components found in leather waste water include volatile organic compounds (VOCs).

VOCs are the compounds that volatilize easily when exposed to air. Thus, these substances cause air pollution through their vapour, and water and soil contamination by the portion that rains and snowmelt can carry deep into the soil (Rusu & Dumitriu, 2003).

VOCs pose a threat to people, animals, and plants alike. First off, it has been demonstrated that these substances can have a wide range of harmful impacts on health, including allergic skin reactions, headaches, dizziness, coughing, respiratory tract and eye irritation, memory loss, disorientation, anemia, and exhaustion. Long-term exposure can harm the kidneys, liver, brain, heart, and reproductive systems in addition to the neurological, reproductive, and immune systems. Moreover, VOCs are "endocrine impostors." Certain ones are also suspected or confirmed to cause cancer. Certain volatile organic chemicals can also disrupt or kill the natural processes of plants. These substances are changed in the atmosphere into other substances that are considerably more harmful to people, animals, and plants. (Aguero *et al.*, 2013). An important component of urban smog, ground level or "bad" ozone is produced chemically when sunlight interacts with nitrogen oxides (NOx) and volatile organic chemicals. (Rusu & Dumitriu, 2003).

Numerous health issues may arise from prolonged exposure to ozone smog pollution. Tree growth and agricultural productivity are also slowed down by ozone. Acid rain, the greenhouse effect, and stratospheric or "good" ozone depletion are all major environmental issues that are

exacerbated by VOCs (Stutte et al., 2005). Consequently, VOCs are a great group of air pollutants. Thus, it is important to identify the sources of VOCs and to characterize them first.

For the treatment of VOCs, two main approaches are utilized: destructive techniques (such as incineration, thermal, catalytic, and photocatalytic oxidation) and non-destructive techniques (such as adsorption, absorption, condensation, etc.) (Song et al., 2021). Catalytic oxidation is one of the effective procedures that may be used to remove VOCs. (Kamal et al., 2016).

Despite its great efficiency, the gas-phase oxidation of VOCs has a number of drawbacks, including a large energy input, handling challenges, and the need for complex equipment for monitoring and operation. Gas-phase oxidation techniques can produce significant amounts of secondary organic aerosols, which are also responsible for air pollution, even in agricultural settings (Zhao et al., 2022). In addition to being expensive and requiring specialized equipment, the photocatalytic oxidation approach loses photon efficiency and is not practical on an industrial scale. This study suggests utilizing an effective catalyst to oxidize VOCs in the liquid phase in order to address this issue. Compared to gas phase oxidation, liquid phase oxidation requires an effective catalyst but is simpler to manage, less expensive, more effective at removal, and requires less monitoring (Song et al., 2021). The low working temperature of tungsten metal oxide for several gaseous species makes it useful for gas sensors.

VOCs are eventually released into the atmosphere by the traditional aerobic treatment methods; this should be avoided by treating the materials prior to their atmospheric entry. Therefore, the goal of this work is to use metal-impregnated carbon catalysts to successfully treat (VOCs without releasing them into the environment. Toluene, ethylbenzene, and chlorobenzene are the main constituents of leather wastewater; hence, these were chosen as the Model VOCs (MVOCs) and individually processed prior to being applied to actual wastewater. This work focused on the catalytic oxidation of the LVOCs using a Tungsten-impregnated Activated Carbon Matrix (WACM). The proposed method can proceed under relatively ambient conditions to implement at the industrial level. This study can be used to solve the industries' current environmental problem of wastewater pollution and sustainability issues.

1.2 Statement of the Problem

Nowadays, air purification is a major issue that the general population is concerned about. Many studies are being conducted to treat or limit these emissions of pollutants in order to treat atmospheric pollution. VOCs are a prominent category of air pollutants that possess the unique properties of being primary pollutants, precursors of secondary pollutants, and secondary pollutants in its own right (Rochard et al., 2021). Several things can release VOCs, including indoor and outdoor sources such as furniture, building materials, automobiles, energy-related processes, and home goods. (Doggali et al., 2012). The leather industry contributes more than other industries to various major sources of VOC emissions. Therefore, there are various effects of VOc emissions on people, the environment, and the economy at various scales. Many destructive (incineration, thermal, catalytic, and photocatalytic oxidation, etc.) and non-destructive (adsorption, absorption, condensation, etc.) techniques have been used to reduce the amount of VOCs released into the environment. Every technique has its own drawbacks, such as high energy requirements, handling challenges, and the need for complex equipment for monitoring and operation. This work focused on the catalytic oxidation of the LVOCs using a Tungsten-impregnated Activated Carbon Matrix (WACM) and physico-chemical characterization of activated carbon and tungsten based activated carbon matrix.

1.3 Objective of the Study

1.3.1 General Objective

To Investigate tungsten-based activated carbon matrix for the catalytic oxidation of volatile organic compounds (VOCs) in leather industries.

1.3.2 Specific Objectives

- To determine physico chemical characteristics of activated carbon and tungsten based activated carbon matrix.
- To determine physico chemical characteristics of leather waste weter
- To produce toluene, ethyl benzene, and chloro benzene-contaminated water under ideal conditions for catalytic oxidation

- To investigate the efficiency of tungsten based activated carbon matrix in VOCs treatment.

1.4 Significance of the Study

This study can assist the company that is being considered, Leather Industries, in thoroughly examining the treatment of volatile organic compounds from the waste water of the industry. Furthermore, it offered more catalyst for the catalytic oxidation of volatile organic molecules. Another important aspect of the study is that it can serve as a reference for other researchers studying the treatment of volatile organic compounds. It can assist them in understanding the main theoretical concepts surrounding the catalytic oxidation of volatile organic compounds using tungsten as a catalyst.

1.5 Scope of the Study

Geographically the scope of this study was limited to leather industry in Indian central leather research institute (CLRI). The operational scope of the study has covered activated carbon matrix characterization, determination of physico chemical characteristics of tungsten based activated carbon matrix and evaluation of the degree of treatment of volatile organic compounds in waste water by tungsten based activated carbon matrix.

1.6 Frame Work of the Study

The study is organized in to four sections. First Activated carbon matrix and tungsten based activated carbon matrix was prepared. Then physico chemical and instrumental characterization of tungsten based activated carbon matrix was done using FTIR, XRD, SEM, EPR, TGA and DSC. In third section Catalytic destruction of toluene, ethyl benzene and chloro benzene contaminated water was performed with optimization studies. Catalytic oxidation of leather VOCs was conducted in the fourth section of the study.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction to Leather Waste Water

The term "leather wastewater" refers to the liquid waste that tanneries produce as a consequence of tanning leather. Leather processing requires the use of a number of chemicals and compounds, all of which add to the distinctive qualities of the effluent produced throughout the process. These features distinguish this type of wastewater from others.

2.1.1 Characteristics of Leather Waste water

The effluent from tanneries is enriched with both organic and inorganic chemical compounds found in leather waste water. Tannins (from sources such as vegetable extracts or chromium), dyes, acids, bases, and oils are just a few of the several elements that go into this mixture. Furthermore, it can occasionally be identified by a high level of suspended particles and organic materials made from a range of animal hides and skins. The tannery effluent's characteristic dark brown or black hue is caused by pigments and tannins, which are part of the tanning process.
The pH readings of leather wastewater frequently indicate a noticeably greater alkalinity. The tanning process's use of lime and other alkaline chemicals is mostly to blame for these phenomena. High pH levels have the potential to have negative effects on aquatic ecosystems if appropriate management methods are not implemented. Because chromium is required for the chrome tanning process, there are higher concentrations of heavy metals, like chromium, in the wastewater released by leather processing factories. One element that is well known for its intrinsic dangers is chromium. These attributes have the potential to seriously jeopardize human health as well as the health of the environment if they are not adequately controlled and maintained.

There is a significant organic load in the wastewater, which is indicated by the presence of organic materials such proteins, carbohydrates, and fats. When organic debris accumulates in water bodies, it may lower the oxygen content of the surrounding water, which could have detrimental effects on the ecology and the creatures living there.

2.1.2 Significance of Leather Wastewater Treatment

For a variety of reasons related to environmental protection, public health, and the advancement of sustainable industrial processes, leather wastewater treatment is important (Louis & Kumar, 2024). Businesses in the leather processing industry work to turn animal hides and skins into leather products. The above indicated process generates large amounts of wastewater, which may be highly polluted and harmful if improperly managed. The need of treating wastewater originating from leather is highlighted by several noteworthy factors (Louis & Kumar, 2024).

For the sake of both environmental preservation and public health, the treatment of wastewater produced by the leather industry is crucial. The leather industry generates large amounts of effluent that contain heavy metals, organic pollutants, and a variety of dangerous compounds. When this effluent is left untreated, it poses a serious risk to the general public's health as well as the ecosystems it contaminates (Egrx & Dzdg, 2016).

When tannery effluent is not treated, it can contaminate nearby water sources and put nearby communities at risk of drinking tainted water. This can have negative health effects. This phenomena has the potential to cause serious health problems, including respiratory conditions, chronic health diseases, and dermatological irritations. It has been discovered that certain substances, such chromium, are carcinogenic when present in tannery effluent. When people are exposed to them, it can cause serious health problems. Furthermore, untreated tannery effluent discharge into rivers and streams can have detrimental effects on the local environment and aquatic ecosystem. Fish populations and other aquatic life are negatively impacted by the phenomenon's destruction of habitats and contamination of water sources (Goswami & Mazumder, 2015). Tannery effluent contains dangerous materials that could linger in the environment for a long time and have long-term negative consequences.

Using effective leather wastewater treatment techniques is not just required by law; it is also morally and environmentally imperative. Waste water can be made suitable for release into the environment or reuse by employing a variety of treatment techniques, such as chemical and biological processes, which can successfully remove or significantly reduce harmful contaminants. In addition to protecting human health, this practice helps to preserve important ecosystems, which goes a long way toward creating a cleaner and better planet for coming generations. It is commonly known that tannery effluent contains a variety of trace organic pollutants, and that improper handling and control of these contaminants can have detrimental

effects on both the environment and human health. These pollutants are often released as a result of the leather production process, which involves the application of various chemicals to animal hides and skins (Haydar et al., 2014).

The following are the most often found trace organic pollutants found in wastewater derived from leather:

Heavy Metals

Metals that have a density more than 4 g/cm3 are typically classified as heavy metals. The mining, mining, fertilizer, paper, and electroplating industries are the main sources of heavy metal release. In the lower regions, notable heavy metals with high toxicity levels encompass arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), mercury (Hg), and zinc (Zn). According to Saravanan et al. (2020a), Because heavy metals cling to surfaces and accumulate throughout the food chain, they have negative effects on terrestrial and aquatic ecosystems. Water sources eventually become contaminated with heavy metals due to their frequent introduction into the environment through man-made or natural channels. Heavy metals are drawn to humus, an organic substance present in soil, and as contaminated water passes through the soil, the metals leach out of it. (Iyare et al., 2020). Chromium, particularly in the form of hexavalent chromium (Cr (VI)), is a prominent contaminant found in tannery effluent.

Because of its toxic nature, chromium is used in the tanning process to stabilize the structure of leather, but its use poses serious risks to human health and the environment. When plant roots absorb water, heavy metals are transferred to animals that eat the plants. This process is known as heavy metal absorption. Sediments accumulate as a result of absorbed heavy metal particles sinking to the bottom of the sea. This buildup makes the risks to one's health from drinking such water worse. When it comes to human physiology, ingesting heavy metal ions can cause oxidative stress, which can then affect cellular organelles and constituents. The possible contribution of arsenic ingestion to aberrant gene expression and hypomethylation of DNA serves as one possible example. Wilson's disease may develop more as a result of copper exposure. On the other hand, it has been discovered that in human cells, chromium increases oxidative stress and DNA damage.

Organic Solvents

The tanning business is significantly impacted by organic solvents because they are commonly used in various processes to dissolve and alter the properties of leather (Khalid et al., n.d.). However, because these compounds have the potential to be poisonous and have negative impacts on aquatic ecosystems, their presence in the wastewater generated by tanneries has raised concerns about environmental impact. The frequency, properties, and mitigation techniques of organic solvents found in tannery wastewater have been the subject of numerous studies. Among the several organic solvents that are frequently found in tannery effluents are volatile organic compounds, or VOCs. Operations related to degreasing, dyeing, and finishing may release VOCs into water systems, such as toluene, xylene, and acetone (Wang et al., n.d.). The presence of these solvents poses risks to the environment and human health as well because of the possibility of respiratory and neurological issues from exposure to these compounds.

Phenolic Compounds

result of their poisonous and enduring characteristics (Haydar et al., 2014). Tanneries play a crucial role in facilitating the operations of the leather industry; nevertheless, they also produce significant volumes of wastewater that include phenolic compounds as a byproduct of the tanning process. Compounds such as phenol, cresols, and other polyphenols have a high degree of solubility in water, hence posing a risk of contaminating adjacent water bodies if appropriate management measures are not implemented.The presence of phenolic chemicals in tannery water presents notable environmental issues as a

The harmful effects of phenolic compounds on aquatic ecosystems are widely acknowledged. These compounds can upset the balance of aquatic life, harm fish and other organisms, and even make water supplies unfit for human consumption. For this reason, it is essential to employ effective methods of treatment and disposal in order to reduce the environmental effects of phenolic compounds found in leather wastewater.

Sulfides

Because of the tanning process, sulphides that are commonly found in leather waste water are a significant environmental concern. Tanneries employ many chemical agents and processes to transform raw animal skins into usable leather. Among these processes is the common application of sulfur-based chemicals, such as sodium sulfide. These chemicals aid in the extraction of hair and other unwanted materials from animal hides, but they also cause sulphides

to leak into wastewater. Sulfurides in tannery water have the potential to negatively affect the local ecology. They may contribute to water pollution and negatively affect aquatic organism biodiversity when introduced into rivers or other aqueous settings. Sulfides are harmful to a variety of aquatic organisms, which means they could upset the natural balance of ecosystems. Moreover, sulphides and other chemical substances found in water can react to generate hydrogen sulphide gas, which has a disagreeable odor and may be harmful to both human and animal health. Sulfur in tannery water can have a negative impact on health, thus efforts to reduce this impact include using wastewater treatment systems that can remove or neutralize these substances before they are released. Laws that limit the amount of sulfurides in industrial effluent have been put into place in a number of areas, encouraging tanneries to switch to greener and more sustainable tanning methods. An environmentally responsible and more conscious leather production sector can be fostered by acknowledging the presence of sulphides in tannery wastewater (Uddin et al., 2020).

Ammonia

This particular chemical compound is often found in leather waste water, where it plays an important role in the tanning process as well as the subsequent wastewater treatment process. In order to control the pH levels of water in tanneries—a crucial step in the production of leather—ammonia is commonly used. Hair and other unwanted materials removed from animal hides are made more suitable for tanning by means of this procedure. However, there is a creation of wastewater with high ammonia levels following the tanning process, which causes serious environmental problems (Uddin et al., 2020). It is concerning that ammonia in tannery effluent may have an adverse effect on the environment. Ammonia is hazardous to aquatic life, thus if it is introduced into bodies of water without being properly treated, it can contaminate the water and disrupt ecosystems. Because of this, tanneries need to treat their wastewater effectively in order to remove ammonia and other impurities before releasing the treated wastewater into the environment.

Ammonia in tannery water is managed using a variety of techniques, such as ion exchange, chemical precipitation, and biological treatment. By enabling the lowering of ammonia levels to acceptable thresholds, these methods ensure that tannery effluent complies with environmental regulations and reduces its ecological effects in the surrounding areas. In conclusion, in order to

properly handle any potential environmental effects of ammonia, it is essential that tannery operations treat and handle ammonia properly (Rahman et al., 2022).

Volatile Organic Compounds (VOCs)

Organic substances belonging to the class named as "volatile organic compounds" (VOCs) are also found in leather wastewater. The majority of VOCs are produced throughout the many different chemical processes involved in the creation of leather. The creation of VOCs, can be harmful to ecosystems and people alike. It's possible that the emissions will harm both parties. Due to the employment of chemicals, dyes, and solvents during the manufacturing and finishing phases of leather skin treatment, VOCs may be released into the environment. The human body may be harmed by these substances. The quality of the air could get worse if this keeps up. VOCs found in tannery effluent have the potential to harm adjacent water and air sources, which is cause for grave worry. In the case that these compounds are released into the atmosphere, there is a chance that they will react with other air pollutants, increasing the production of smog and ground-level ozone. These events might contribute to a rise in ground-level ozone and smog, both of which can be detrimental to the environment and people's respiratory systems. Tannery wastewater is known to contain VOCs, which, if improperly managed, can lead to the contamination of surface and groundwater, jeopardizing aquatic ecosystems and perhaps having an impact on human areas further downstream (Rahman et al., 2022).

Since tanning processes frequently use water containing VOCs, tanneries need to set up efficient wastewater treatment procedures. Utilizing state-of-the-art treatment techniques, like activated carbon adsorption or biological treatment, is the only way to ensure that water is free of VOCs before it is discharged into the environment. To limit the amount of VOCs in industrial wastewater, severe regulations and environmental standards have been put in place. These steps are intended to lessen the negative effects of tanneries on the quality of the air and water while encouraging ethical activities inside of them (Mahlaule-glory, 2022). In conclusion, for the leather industry to attain sustainable operations and reduce its environmental impact, the efficient management and mitigation of VOCs present in tannery water are essential.

Paints and Colors

One type of water pollution known to be hazardous to the environment and capable of changing the color of the water is paints. An estimated 10,000 paints have been used in industrial settings, and 0.7 million tons are synthesized annually worldwide. The release of a considerable amount

of paints into wastewater from industries like printing, paper, tanning, and textiles has been recognized as a major environmental risk (Mahlaule-glory, 2022).

Dyes have the ability to block or reduce the amount of sunlight that reaches the water, which lowers photosynthetic activity and affects aquatic life. Human usage of dyes has been linked to mutagenesis and carcinogenic consequences, as well as abnormalities and dysfunction in the liver, kidney, brain, and cerebrospinal nervous system. Leather coloring residue from the dyes and pigments used during the process may find its way into the wastewater produced by tanneries. These elements may contain substances that are hazardous to the environment and human health, and they may cause water to turn discolored (Bilal et al., 2022).

Herbicides and Pesticides

Although pesticides and herbicides are not intrinsically connected to the leather-making process, they can occasionally find their way into tannery water as contaminants resulting from nearby farming activities or agricultural runoff. There is a good deal of concern when these chemicals are found in tannery wastewater. Pesticides are designed to control or eliminate unwanted pests, and herbicides are used to control unwanted plants. When these chemicals are added to tannery water, it can have negative effects on human health and the environment (Louis & Kumar, 2024). Runoff from agricultural regions may contain pesticides and herbicides that find their way into water sources and end up being used as the water supply for tanneries. The surrounding area may become more polluted as a result of this procedure. Aquatic ecosystems and the animals that depend on them may be at peril due to the persistent and accumulating toxins and herbicides found in tannery wastewater. Additionally, these chemicals may interfere with the proper operation of wastewater treatment facilities, making it more difficult to remove them effectively before releasing them into the surrounding environment (Saleh et al., 2020).

It is essential for tanneries to continuously check and regulate the quality of their water sources in their operating operations since the water used in the tanning process may include pesticides and herbicides. Modern methods such as activated carbon filtration and complex oxidation processes can be used to treat wastewater efficiently and lower the levels of these contaminants. Establishing collaborative efforts between tanneries and agricultural stakeholders could expedite the decrease of pesticide and herbicide pollution in tannery water by reducing the use of these chemicals in adjacent areas. Cutting back on the use of pesticides and herbicides in nearby farms is one of the greatest ways to avoid tannery water contamination. The tanning industry may

contribute to environmental protection and improve the quality of its leather goods if it recognizes this issue and takes proactive measures to address it. (Louis & Kumar, 2024).

2.2 Overview of Volatile Organic Compounds

A broad category of organic chemical molecules that are present in many products and that, under typical circumstances, evaporate quickly and reach the environment is known as volatile organic compounds, or VOCs. As per the definition provided by the Environmental Protection Agency, VOC is any carbon-based compound that contributes to atmospheric photochemical processes, except for carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate. Once released into the environment, VOCs can travel great distances due to their high volatility, mobility, and robust resistance to degradation (Pandey & Yadav, 2018). The most frequently found VOCs are the aromatic hydrocarbons (benzene, toluene, ethyl benzene and xylene) and halogenated hydrocarbon like chloro ethylene and trichloroethylene (Azalim *et al.*, 2011).

2.2.1 Sources of VOCs

VOCs can have natural or man-made sources. Natural sources of VOCs include vegetation and tree emissions, naturally occurring forest fires, and anaerobic marshy bog processes. Hydrocarbon fuel evaporation, printing, building materials, pharmaceutical, septic system, chlorination, fumigation, textile cleaning, food extraction, pesticide and fertilizer application, landfill, hydrocarbon fuel storage, petroleum distribution and storage, and traffic are among the anthropogenic activities that produce VOCs. Due to their agricultural origins, which include burning agricultural waste, using fuels in agricultural machinery, and using VOCs as inert ingredients in pesticide formulation, VOCs are widely dispersed throughout the environment (Pandey & Yadav, 2018). VOCs were identified as indoor air contaminants, and a methodology for determining the sources of their indoor emissions was provided. These include carpets, paints, kerosene heaters, adhesives, insulating foam, perfumes, tobacco smoke, chlorinated water, paint removers, and new clothes. One of the main sources of VOCs released during the process's early stages and produced throughout the aerobic phase is composting (Ferrandon *et al.*, 2001). Major VOCs and their sources have been discussed as follows.

Halogenated VOCs

These are hazardous compounds due to their strong bioaccumulation potential, acute toxicity, and resistance to degradation ((ALONSO et al., 2002). Polychloromethanes (PCMs) are the most extensively employed halogenated VOC in a variety of applications. The waste products from evaporation and water purification systems are the primary sources of PCMs (Huang et al., 2014). The commonly came across PCMs are trichloromethane, carbon tetrachloride , dichloromethane and chloroform.

Furthermore halogenated VOCs consist of tetrachloroethylene, chlorobenzene, dichloroethane, trichloroethane, trichloroethylene, and tetrachloroethane (Giraudon et al., 2008). These substances are typically employed in the synthesis of polymers, the production of pharmaceuticals, paints, adhesives, chemical extractants, solvents in chemical processes, and cleaning agents. These substances frequently have lengthy atmospheric lives and are quite volatile. Halogenated VOCs can enter the human body through drinking water, inhalation, and adsorption when swimming (Huang et al., 2014). As a source of radicals in the atmosphere and a major contributor to the depletion of the ozone layer, halogenated VOCs have an impact on greenhouse gas effects. Halogenated VOCs have a global warming potential (GWP) of 10 to 1800, which is significantly greater than that of CO2, which has a GWP of only one (Abedi et al., 2015).

Aldehydes

The majority of reactive VOCs in the environment are made up of aldehydes. Of all the aldehyde VOCs, formaldehyde and acetaldehyde are the most often found.These are members of a group that contributes to the generation of new radicals that regulate the ozone layer. The breakdown of VOCs, which includes alcohol and other hydrocarbons, occurs in several stages and is the primary source of formaldehyde (Ivanova et al., 2013).

Aldehydes are among the main indoor pollutants that are contained in airtight buildings and released from ornamental materials. A wide range of industrial items, including treated wood resins, cosmetics, plastic adhesives, building supplies, cleaning chemicals, disinfectants, particle board, plywood, medium-density fiber board, carpeting, cigarette smoke, and fabrics, also release them (Li et al., 2014b). Another way that aldehydes might arise is when alkoxy radicals break their C-C bond. Seawater, burning biomass, decomposing biowaste, and living and dying plants are all potential sources of biogenic aldehyde. Low-exposure to aldehyde might result in

tightness in the chest, eye irritation, throat irritation, and shortness of breath (Zhu and Wu et al., 2015). Chronic toxicity may result from long-term exposure to aldehyde, which can have detrimental consequences on human health. Acute poisoning is more common when exposed to large concentrations of the chemical. Chronic exposure may also result in nasal tumors, respiratory tract irritation, rashes on the skin, and irritation of the eye mucous membranes (Collins, 2001; Yu and Crump, 1998). Aldehydes derived from biofuels have been present in the atmosphere at notably higher levels in recent years due to the growing usage of ethanol-based biofuels in transportation vehicles. These factors make the atmospheric reduction of aldehyde—especially through low-temperature processes—extremely interesting.

Aromatic compounds

Natural aromatic chemicals found in petroleum products, such as gasoline and other fuels made from crude oil, include benzene, toluene, and ethyl benzene. As a result, large volumes of aromatic chemicals are released into the atmosphere when liquid fuels in cars are not completely burned. Additionally, these substances are utilized in a wide range of formulations and goods, including detergents, paint, petrochemicals, and medications. Aromatic chemicals are not only harmful and carcinogenic, but they also seriously destroy the ozone layer, create photochemical smog, and have the potential to trigger mutations. Priority pollutants are the aromatic solvents that are frequently found in paints, thinners, gums, adhesives, lacquers, and printing inks (Shahna et al., 2010). Low exposure levels to aromatic VOCs might result in fatigue, loss of appetite and memory, nausea, weakness, dizziness, and blindness. Exposure to elevated levels of aromatic chemicals in the air might result in unconsciousness, vertigo, and fatality (Suib, 2013). For drinking water, the maximum permissible limit for aromatic compounds is 1 mg/L, and for air, it is 200 ppm.

Polycyclic aromatic hydrocarbons

Combustion operations are the primary source of polycyclic aromatic hydrocarbons (PAH), a class of VOCs. These substances' structures include several benzene rings. Three rings of phenanthrene, four rings of pyrene, and two rings of naphthalene are common instances of PAH. Power plants that use coal, asphalt processing facilities, and incomplete fuel combustion are the primary sources of PAHs. It is crucial to minimize the emission of PAHs since they have been found to be harmful (Kim et al., 2007b).

Ketones and Alcohols

Common cosmetics and personal care items that contain alcohols and ketones include rubbing alcohol, hair spray, colognes, perfumes, nail polish removers, and nail polish polish. Adhesives, paint thinners, varnishes, aerosols, and window cleaners all contain ketones. Acetone, methacrylates (methyl or ethyl), ethyl acetate, and methyl ethyl ketone are examples of ketone-based VOCs, whereas common alcohol-based VOCs are ethyl alcohol, isopropyl alcohol, and benzyl alcohol. Chest tightness, eye irritation, throat discomfort, and shortness of breath are caused by the secondary reactions that alcohols (mostly ethanol) produce to promote the synthesis of aldehydes (Zhu and Wu, 2015).

Extended exposure to short-chain alcohols such as n-butanol, isopropanol, and ethanol can result in depression of the central nervous system. Ketones in high quantities can irritate the throat, nose, and eyes. Acute inhalation exposure in humans has also been linked to headache, nausea, and depression of the central nervous system. Studies have shown that exposure to ketones might cause harm to nerves.

Miscellaneous VOCs

A number of alkenes fall under the VOC classification as well. Since it has a high photochemical ozone creativity potential (POCP), propylene is regarded as being particularly polluting. Due to its employment as a raw ingredient in numerous petrochemical syntheses, ethylene has significant importance (Patdhanagul et al., 2012). Fruits and vegetables can undergo chemical and physical alterations as a result of ethylene produced during agricultural product storage. Due to its low toxicity, strong solubility, and good volatility, ethylene is widely employed as a solvent in the manufacturing of varnishes, synthetic resins, adhesives, printing ink, and organic pharmaceutical intermediates. It is also utilized in the synthesis of perfumes. Methyl tertbutyl ether (MTBE) is a fuel enhancer that raises the fuel's octane rating and oxidation capacity. It is classified as a semi-volatile VOC (Kujawa et al., 2015). In the USA and Europe, the presence of MTBE in sources of drinking water has grown to be a serious problem. Air deposition, watercraft exhausts, and leaks from subterranean storage tanks are the main sources of MTBE. In addition to having a negative taste and odor, MTBE may be carcinogenic. It is critical to eliminate VOCs from the phases of generation since some, like formaldehyde and toluene, are mutagenic, carcinogenic, and teratogenic. These effects not only endanger human health but also contribute to the creation of photochemical smog (Pandey & Yadav, 2018).

2.3 Volatile Organic Compounds Treatment

Many methods have been developed and used for the removal of VOCs) for many years, including thermal incineration, membrane separation, condensation, adsorption, absorption, and photocatalysis (Bernal & Giraldo, 2018). Their extensive applications are limited, though, by the high cost of membrane separation and incineration, the difficult handling of spent coolants and condensation solvents, the choice of solvents for selective adsorption of different VOCs, and the production of secondary toxic substances that resemble formaldehyde when wall paints are photocatalyzed. When compared to conventional techniques, catalytic oxidation is a more environmentally and financially viable method of removing VOCs. At relatively low temperatures (<500 °C), it is capable of entirely converting organic contaminants into innocuous chemicals like water (H2O) and carbon dioxide (CO2). The main concern for the catalytic oxidation of VOCs is how to rationally design catalysts that have high activity and stability at cheap cost and environmental friendliness (Pandey & Yadav, 2018).

2.3.1 VOCs Catalytic Oxidation

In most cases, adsorption is preferred as the technique for reducing VOCs in the air. While certain molecules can be recovered using this method; the procedure is highly costly when dealing with low VOC concentrations (Dégé *et al.*, 2001). The process of thermal combustion has been used to remove VOCs, but it needs temperatures above 800 ^{o}C and can produce compounds that are even more hazardous than the ones that need to be removed. Because catalytic combustion may save a significant amount of energy when compared to thermal combustion, it seems to be a very attractive alternative for the removal of VOCs (Palacio *et al*., 2008).

A large body of research on the behavior of catalysts based on noble and transition metals has been identified in the literature about the catalytic combustion of VOCs. Activated carbon, alumina, and silica are typically used as supports for Pt, Pd, and Rh. Catalysts of this class exhibit good selectivity and activity at temperatures below 200 °C, but they are exceedingly costly and unstable when exposed to chloride compounds. Because of their stability and low cost in comparison to noble metals, transition metal oxides have also been extensively researched and employed successfully in the catalytic combustion of hydrocarbons. They are often employed as bulk catalysts without support or supported over porous oxides. Numerous findings using various transition metals (Fe, Co, Ni, Cu, Zn, Mn, Ag, V, Cr, W, etc.) have been documented; the

copper-based studies showed the lowest combustion temperatures. Perovskites based on La, Sr, and Mn also exhibit highly intriguing catalytic behavior; for instance, complete conversion can be reached at 235 8C in the case of toluene combustion. In an effort to investigate novel substances that might have catalytic qualities, Hoyos created a number of vanadates that are members of the so-called Fz family (Rusu & Dumitriu, 2003). The presence of Brucite-type layers (having scattered vacancies) joined by pyrovanadate groups is what distinguishes this structure. Water molecules and compensatory actions are present between the layers of these lamellar materials (Palacio *et al.,* 2008).

2.4 Activated Carbons

Activated carbon (AC), which is typically obtained from charcoal, is a type of carbon that has been processed to have tiny, low volume pores that enhance the surface area. The history of activated carbon (AC) dates back to 1500 BC, when the Egyptians used it for medical and water purification due to its adsorption properties (Commission & Ahsan, 2016). In the early 1900s, Germany's first AC production plant was put into service specifically for the sugar refining business. Certain facilities have recently surfaced to generate AC for use in wastewater treatment procedures. These days, air conditioners are widely used to remove pollutants from the atmosphere, clean the color of exhaust from cars and industries, deodorize refrigerators with food and pharmaceuticals, and even power complexes like nuclear power plants. With regard to both gaseous and aqueous phase applications, AC unquestionably gained enormous pace and appeal in the industrial sectors in the late 1930s. In actuality, a number of novel methods for producing carbon were created in order to satisfy the steadily rising demands of industry. A significant breakthrough occurred between 1939 and 1945 when various chemically saturated carbon were created for the purpose of capturing nerve gasses during combat (Commission & Ahsan, 2016).

AC is a black carbonaceous, tasteless, anamorphic, nonhazardous, very porous substance with a complicated structure composed of carbon atoms and an interior surface area that ranges from 300 to 3500 m2/gm (Bari *et al.,* 2022). This surface area is explained by the internal atomic structure of activated carbon, which is made up of hierarchical pores with diameters of less than two nm, two to fifty nm, and more than fifty nm, respectively. The surface area, high micro-porosity, and adsorption capacity of AC make them ideal as an adsorbent in the water treatment

process, as well as for the removal of both organic and inorganic contaminants. The use of ACs is highly recommended because of their highly developed interior surface area, porosity, and enormous adsorption capacity, as well as how easy they are to operate and construct (Bari et al., 2022).

There are three primary kinds of activated carbon that are available: powder, granular, and pellet. Nevertheless, granular and powdered AC are the most commonly utilized. Additionally, there exist alternative kinds of AC that remarkably capture the interest of academics. Among them are felts, clothing, and fiber, which are mostly derived from petroleum pitch and isotropic coal.

Figure2. 1: Activated Carbon (Granular)

The growing awareness of environmental conservation is driving up demand for air conditioners. But even with pricey natural predecessors like coal and wood, the cost of producing commercial air conditioners remains high due to the machinery and maintenance involved. As a result, extensive study has led to the discovery of more affordable production prices and environmentally benign substitute materials that can be used to create inexpensive air conditioning. Previous studies have shown that agricultural wastes, such as animal bones, leftover bamboo shoots, mangosteen peel, sludge, used tires, durian shells, coconut shells, and rice husks, can be useful sources of raw materials for the synthesis of activated carbon. Several elements, including price, accessibility, simplicity of activation, renewable nature, inorganic content, and carbon yield, impact the selection of raw materials for the manufacturing of AC.

Instead of being recycled, rice husk (RH), an agricultural waste with little commercial value, is typically burned or thrown in the open. It is a significant by-product of the rice milling industry

in Bangladesh. Furthermore, around 20% of the weight of paddy is composed of RH, with about 120 million metric tons produced worldwide. The process of making activated carbon from rice husk can raise the value of this agricultural waste and lower the cost of disposal, making it a less expensive option than the activated carbon that is now sold commercially (Bari et al., 2022).

2.4.1 Activated Carbon Production

Numerous scholars have reported on the production of AC, which can be divided into four primary stages. These include the processes of pyrolysis, carbonization, steam/thermal activation, and physical and chemical activation. Steam and carbon dioxide (CO2) are the most widely utilized reagents in the physical activation process, which involves carbonization and activation stage and greatly affects the porosity of the AC. Chemical activation produces AC in a single step utilizing readily available chemical reagents such as zinc chloride, phosphoric acid, and potassium hydroxide that can be utilized at room temperature. However, impurities like zinc (Zn) and phosphorus (P) might be detected in AC products depending on the chemical reagents employed. This can result in increased operating costs because more chemicals will need to be utilized (Bae et al., 2014).

Pyrolysis process

Pyrolysis is the process of converting organic material thermochemically, without the presence of halogen (mostly oxygen), into gaseous or liquid fuels at very high temperatures. Pyrolysis is an irreversible simultaneous process that modifies the physical phase and chemical makeup of materials.

Materials that are exposed to greater temperatures are more frequently detected during the pyrolysis process. Some pyrolysis parameters, such temperature, have the biggest effects. These are followed by nitrogen flow rate, retention period, and heating rate. Raising the pyrolysis temperature often results in a decline in solid yield and an increase in the yield of both gases and liquid percentages. Often, raising the reaction temperature also causes a reduction in the generation of char and AC. However, when volatile matter decreases, increased temperatures result in higher ash and AC percentages. Consequently, higher temperatures provide AC that is of higher quality. Moreover, a temperature increase that ultimately results in a decrease in char yield may also be caused by the primary breakdown of biomass at high temperatures or by the secondary breakdown of char leftovers. Higher temperatures for secondary decomposition may

also result in some non-condensable gaseous products, which would ultimately increase the gas output (Ioannidou and Zabaniotou, 2007).

Physical activation process

There are two steps involved in physical activation. Carbonization of carbonaceous materials occurs initially, followed by high-temperature activation of the resulting char in the presence of air, steam, carbon dioxide, or three combinations acting as oxidizing gases. The CO2 is typically employed as an activation gas because it is clean, easy to handle, and has a slow reaction rate at a temperature of about 800°C, all of which help to manage the activation process. It was discovered that the carbonization temperature ranged from 400°C to 850°C, with occasional highs of 1000°C, and the activation temperature ranged from 600°C to 900°C. It is not appropriate to use the AC created by the physical activation approach as filters or adsorbents because it lacks certain necessary properties. It is important to note that different agricultural biomass residues, including mango pits, rice husk, rice hull, sawdust, sunflower shells, corncobs, olive pits, pine cones, wood waste, corn hulls, cotton residues, oak, tobacco stems, corn stover, coconut coir pith, almond shells, and peanut hulls, can be used for physical activation (Ioannidou and Zabaniotou, 2007).

Chemical activation process

In the two phases of the chemical activation process, which happen simultaneously, the precursor and the chemical activating agents mix as oxidants and dehydrates. Even though the use of chemical activation agents may be restricted due to concerns about environmental protection, superior porosity structures of AC are produced when activation and carbonization are carried out concurrently during the chemical activation process at lower temperatures. Furthermore, trihydroxidooxido phosphorus (H3PO4), potassium hydroxide (KOH), zinc chloride (ZnCl2), phosphoric acid (H3PO4), and potassium carbonate (K2CO3) are a few substances that are frequently utilized as activation agents. Agricultural wastes that are being decreased by the chemicals stated earlier include rice husks, rice straw, cassava peel, olive seed, apricot stones, macadamia, pecan shells, peanut hulls, nut shells, almond shells, corn cob, and hazelnut shells (Ioannidou and Zabaniotou, 2007).

Steam pyrolysis

The initial step in the steam pyrolysis process involves heating the raw agricultural waste materials to either 500–700°C or 700–800°C while pure steam is flowing through them.

Agricultural waste biomass, including rice husk, jujube seed, sawdust, tropical wood waste, palm shells, durian peel, maize cobs, coconut shells, tobacco stems, hazelnut shells, banana peels, mangosteen shells, etc., have all been extensively researched and effectively processed using steam pyrolysis. With the exception of those made from cherry, apricot, and almond shells, steam pyrolysis-produced AC was, nevertheless, widely acknowledged to be less effective (Behnamfard and Salarirad, 2013).

CHAPTER THREE

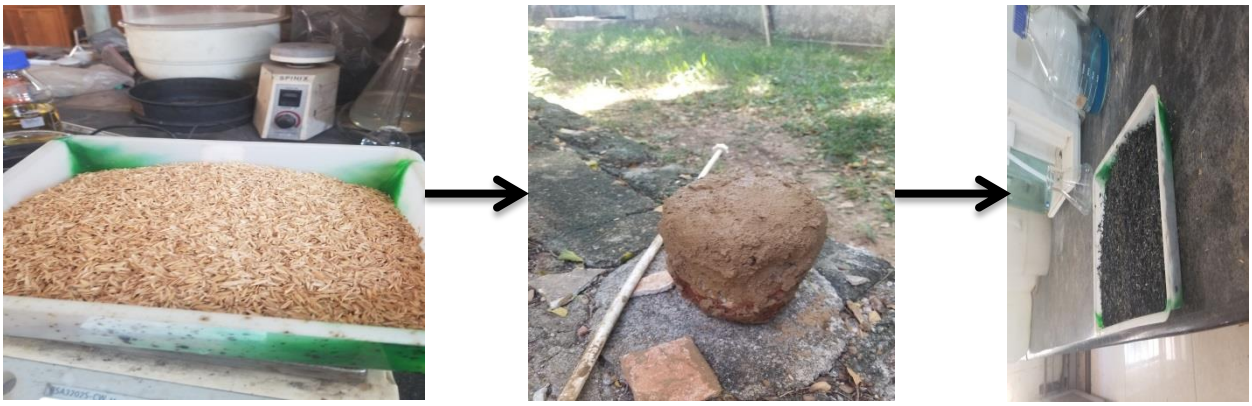
METHODOLOGY

3.1 Material and Equipment's

pH meter, ORP(Oxidation-reduction potential), analytical weighing balance, jar, oven, furnace, COD analyzer, aeration tank, pressure gauge, UV-spectroscopy, TOC analyzer, SEM, XRD, FTIR,EPR,TGA, DSC, PID ,sampling equipment, vacuum pump and safety equipment's, orbital shaker , separating funnel, were used to conduct this study.

3.2 Preparation of Activated Carbon

Rice husk (RH), which is readily available locally, was gathered from rice farms in Chennai. The study's RH had 62–65% volatility over the course of the investigation. To remove dirt and other materials from RH, raw rice husk was repeatedly washed with distilled water. After that, it was baked at 110°C for ten to twelve hours, or until the rice husk was totally dry. Rice husk carbon was made from this cleaned and oven-dried rice husk. The dehydrated husk was first pre-carbonized for four hours at a rate of five degrees Celsius per minute at 400 ^{O}C, and then it was activated with phosphoric acid at 700 ^{O}C. The carbon made from rice husk was retrieved when the electric furnace cooled. Ultimately, it served as a point of comparison for tungsten based activated carbon.



Raw Rice Husk Mud masked Rice Husk Activated Carbon

Figure3. 1: Activated carbon preparation

3.3 Tungsten Based Activated carbon Matrix Preparation

Rice Husk (RH), which is readily available locally, was chosen as the raw material for carbon catalyst synthesis. The tungsten (VI) chloride (WCl6) solution with known metal content of 1 to 5% was prepared accordingly (after taking into consideration RH volatility) and mixed well with RH in w/w separately. RH, which was utilized in the study, has volatility of 62-65% during the entire process. 3.775 g of WCl6 were dissolved in 250 ml of water to create 5%WACM, which was then thoroughly combined with 100 g of RH followed by a 12-hour capillary action soak to allow for absorption, and a 10- to 12-hour hot air oven drying period at 1100^{O}C. After being soaked in dry metal, the husk was pre-carbonized for four hours at a rate of five degrees Celsius per minute at 400 ^{O}C. Phosphoric acid was then used to activate it at 700 ^{O}C. The pre-carbonization and activation procedures were carried out in graphite crucibles. After being repeatedly cleaned with distilled water, the activated carbon was dried and given the designation 1-5%WACM. Metal-impregnated catalyst is expected to appear with the following formula.

RH + WCl6 $\longrightarrow$ [RH]-WCl6 (i)

[RH]-WCl6 $\longrightarrow$ [PRH-W] + H2O↑ + CO2↑ + Cl2 (g)↑ (ii)

2[PRH-W] + 2H3PO4 $\longrightarrow$ 2WACM + 1/2 P2O5↑ + 3H2O↑ (iii)

Tungsten chloride (WCl6) is absorbed by capillary action in rice husk (RH) according to Eq. (i). After being pre-carbonized at 400 ^{O}C, the metal-absorbed rice husk ([RH]-WCl6) formed PRH-W Eq. (ii) with the loss of simple gaseous molecules. Phosphoric acid was then used to chemically activate the PRH-W for one hour and thirty minutes at a temperature of 700 ^{O}C. The formation of P_2O_5 (liquid) in chemical activation was achieved through the desorption of water from H_3PO_4, which was then followed by evaporation within the temperature range of 580-585^{O}C Eq (iii). Additionally, the lightweight gasses were eliminated, leaving the catalysts' surface with active pores.

Figure 3. 2: Tungsten based activated carbon matrix preparation

3.4 Treatment of Volatile Organic Compounds

Using a 4mm acrylic sheet, the W-PBCR and A-PBCR were constructed independently. Its measurements are 50cm in height and 4.5cm in diameter. Its total capacity is 800ml, of which 500ml is its working volume. First, 5 cm of 5 mm quartz aggregate were packed into the reactor bottom. Next, 3 cm of aggregate and 2 mm of fine aggregate were packed into the reactor bottom to a height of 5 cm each. To obtain W-PBCR and A-PBCR, the catalysts of WACM and ACM were packed in separate columns, each with a height of 35 cm above the aggregate. Hydraulic Retention Time (HRT), pH, and hydrogen peroxide dose were optimized and applied to the reactor's top to treat the waters contaminated by volatile organic compounds (VOCs). To facilitate additional examination, the cleaned water was gathered from the reactor's bottom.

Every time it went through the metal catalysts column, it was examined for tungsten leaching and was determined to be below the detectable limit.

Figure 3. 3: Treatment Schemes of VOCs

3.4.1 Conceivable mechanism of VOCs degradation

The organic molecule on the matrix surface is adsorbed by the WACM, and the hydroxyl radical that is produced thereafter breaks down the VOCs. The tungsten oxides in the WACM are WO3 (W6+) and WO2 (W4+). The oxidation of VOCs and the production of hydroxyl radicals are anticipated to occur as follows.

$W^{4+} + H_2O_2 \rightarrow W^{5+} + OH^- + HO\bullet$ …….…….. (a)

$H_2O_2 + HO\bullet \rightarrow H_2O + HO_2\bullet$ …… (b)

$W^{6+} + HO_2\bullet \rightarrow W^{5+} + H^+ + O_2$….....(c)

$W^{5+} + HO_2\bullet \rightarrow W^{4+} + H^+ + O_2$ …….. (d)

$2HO_2\bullet \rightarrow O_2 + 2OH\bullet$…….. (e)

$2OH\bullet + VOCs \rightarrow CO_2 + H_2O$……..…… (f)

In addition to generating hydroxyl radicals, the W ion can oxidize pollutants through redox reactions. WO2, for example, reacts with hydrogen peroxide to produce hydroxyl radical and W5+ ion (Eq. a); it then reacts with hydrogen peroxide again to form hydroperoxyl radicals (Eq.

b). WO3, having a 6+ oxidation state of W, reacts with superoxide radicals to produce W5+ (Eq. c). The W5+ then reacts with hydroperoxyl radical to produce W4+ again, meaning that the hydroxyl radical generation continues (Eq. d). The hydroxyl radicals then react with volatile organic compounds to produce CO2 and H2O (Eq. f).

W4+ + R→ R● + W5+ ……(g)

R● + O2 → CO2 + H2O…… (h)

Following their adsorption on tungsten oxides (W4+), VOCs (R) cleave to generate VOC radical species (R•). This species then uses the dissolved oxygen to undertake additional cleavage and oxidation reactions (Eq. g & h). Hydroxyl radicals catalytically oxidized toluene to produce compounds like benzyl alcohol. After that, it underwent oxidation to produce benzoate, which underwent a ring cleavage event to produce maleic anhydride. At last, the maleic anhydride was oxidized to produce CO_2 and H_2O.

In order to prepare the fluids polluted with Toluene, Ethyl benzene, and Leather VOCs at the ideal timing, pH, and flow rate, the strip and dissolve method was employed. The reactor, designated R1, holds 100 milliliters of wastewater containing toluene, ethyl benzene, or leather. The wastewater is stripped using ambient air and a flow controller. After passing through B1 (for moisture condensation) and impinger B2, which contained 500 milliliters of distilled water to dissolve, the removed toluene or ethyl benzene gas, or LVOCs, were removed. It was therefore decided to create and employ Toluene Contaminated Water (TCW), Ethyl benzene Contaminated Water (ECW), and LVOCs Contaminated Water (LCW) for additional treatment tests.

To manufacture Chloro benzene Contaminated Water (CCW), the orbital shaking method was employed. A conical flask was filled with 100 ml of distilled water and 1 ml of chloro benzene. The flask was then carefully sealed. The chloro benzene was then allowed to dissolve at room temperature in an orbital shaker. A separating funnel was used to separate the un dissolved chloro benzene following shaking. It was put to use for more research on treatments.

Using the ACM-Packed Bed Catalytic Reactor (A-PBCR) and WACM-Packed Bed Catalytic Reactor (W-PBCR), the VOC-contaminated waters of TCW, ECW, CCW, and LCW were treated individually.

3.5 VOCs from Leather Waste Characterization

A Tiger SXT gas detector (ION Science, UK) was used to investigate the VOCs found in the leather effluent. An extensive spectrum of VOCs can be detected with the portable photo ionization detector (PID) Tiger SXT, which has an ultraviolet lamp with a 10.6eV output. VOC analysis was conducted on collected samples of untreated leather wastewater. Using known-concentration isobutylene calibration gas, the Tiger SXT was calibrated in accordance with the manufacturer's instructions. Less than 1 part per million (ppm) is the instrument's detection limit for the majority of VOCs. The effluent was moved into 500 ml glass bottles, sealed, and safely placed inside the closed flask for sample analysis. Next, the air pressure was varied to initiate a stripping procedure, with ambient air in our case being the passing air at a rate of 1 l/min. Inserting the Tiger SXT probe into the headspace above the glass bottle, it was equipped with a 0.2µm PTFE (polytetrafluoroethylene) filter. After giving each sample enough time to acclimate, triplicate measurements of the VOC concentrations were made, with the average results being used for quantification. To subtract background values, concurrent measurements of blank deionized water were also taken. This facilitated the selection of suitable treatment techniques by enabling quick field screening of leather effluent to identify main volatile organic compounds (VOCs) present above detection limits.

Figure 3. 4: Detection of VOC using Photo Ionization Detector

Physiochemical characterizations

S.No	*Parameter*	*Method*
1	Chemical Oxygen Demand (COD)	(APHA 5220 D)
2	Total Dissolved Solid (TDS)	APHA 2540 C
3	Total Suspended Solid (TSS)	APHA 2540 D
4	Density	APHA 2520 B
5	Ash content	APHA 2540 G
6	pH	APHA 4500-H+ B
7	Oxidation-Redaction Potential (ORP)	APHA 2580 B
8	Total Organic Carbon (TOC)	USEPA 9060A

Table 3. 1: Physico Chemical Characterization methods

Chemical Oxygen Demand (COD): COD quantifies the amount of oxygen needed to oxidize organic molecules present in the samples. It is a vital indicator of the load of organic pollutants and the effectiveness of the VOC reduction strategy.

$$\text{COD (mg/L)} = \frac{(A - B) * 1000 * N * 8 * D.F}{\text{Sample volume (ml)}}$$

Where

A= blank Titrant value

B= titrate value

N= normality of FAS

D.F= dilution factor (if any)

Total Dissolved Solids (TDS): The amount of organic and inorganic materials dissolved in the samples is measured by TDS. The overall quality of the water is evaluated, and the efficiency of VOC reduction measures in lowering the total pollutant load is assessed.

Total Dissolved Solids (mg/l) = $\frac{\text{(Final weight−initial weight)} \times 1000 \times 1000}{\text{Volume of sample (ml)}}$

Total Suspended Solids (TSS): The term TSS describes the amount of both organic and inorganic solid particles present in the samples. Assessing TSS levels helps to comprehend the existence of particulate matter and how it affects the environment.

Total Suspended Solids (mg/l) = $\frac{\text{(Final weight−initial weight)} \times 1000 \times 1000}{\text{Volume of sample (ml)}}$

Density: Density is a physical parameter that measures the mass per unit volume of the samples. It provides insights into the compactness.

$\rho = m / v$ whereas:

ρ = Density

m= mass

v= volume

Ash Content: The inorganic residue that remains after the samples have burned completely is represented by the term "ash content." Ash content analysis helps assess the purity of the sample and its possible influence on VOC reduction operations by providing information about the existence of inorganic contaminants.

% Ash = [(Weight of crucible + ash) – (Weight of empty crucible) x 100] /

(Weight of crucible + dry sample) – (Weight of empty crucible)* Moisture content

PH: pH measurement helps to identify the acidity or alkalinity of the samples.

Oxidation-reduction potential (ORP):- One way to quantify a solution's propensity for oxidation or reduction reactions is by its ORP value. The redox potential of a solution is measured by this method. The pH and temperature were measured using a Hanna Instruments HI2211 microprocessor-based bench top meter.

Total organic carbon (TOC):- TOC is a measure of the total amount of organic carbon in water. It is a measure of the total organic content of wastewater.

3.6 Instrumental analysis of carbon catalysts

X-ray Diffraction (XRD)

The carbon catalysts were characterised using powder X-ray Diffraction (XRD) of the Rich Siefert 3000 diffractometer model at a 4 deg min-1 scanning rate. It was done in the range of 5-80deg with step sampling of 0.005deg.

Fourier Transform Infra-Red spectroscopy (FTIR)

The functional group analysis was conducted using Perkin Elmer's Fourier Transform Infra-Red spectroscopy (FTIR). The samples were pelletized using the hydraulic pelletizer's piston at 15 kPa cm-2 pressure and 1 mm thickness and 13 mm diameter using the Merck spectroscopic grade KBr. The FTIR spectrum was obtained by scanning the materials between 4000 and 400 cm-1.

Thermogravimetry Analysis (TGA)

With a nitrogen atmosphere, the Q50 (V20.6 Build 31) instrument was used to obtain thermogravimetric analysis (TGA) by scanning from ambient temperature to 800 ^{o}C at a heating rate of 10^{o}C min-1.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) analysis was obtained using Q200 (V23.10 Build 79) from 300OC to 3000 OC.

Scanning Electron Microscopy (SEM)

Energy Dispersive X-Ray Analysis (EDAX) and Scanning Electron Microscopy (SEM) analyses were conducted using a Thermo Fisher Scientific Quanta200 (model).

Ultraviolet-Visible (UV/Vis) Spectrophotometer

Utilizing a nitrogen environment, thermogravimetric analysis (TGA) was obtained using the Q50 (V20.6 Build 31) equipment by heating the sample from room temperature to 800oC at a rate of 10oC per minute.

CHAPTER FOUR

RESULT AND DISCUSSIONS

4.1 Leather Effluent Physico Chemical Characterization

Parameters	***Aerated***	***Dissolved***	***Dissolved Effluent Treated with WACM***
pH	7.3	10.8	10.5
ORP	-160	-105	158.5
COD(mg/L)	35000	7500	180
TSS(mg/L)	2200	50	Not detected(ND)
TDS(mg/L)	17000	600	260
TOC(mg/L	6460	3230	160
Ammonia	26	17	Not detected(ND)

Table4. 1: Physico chemical characterization of leather effluent

The aforementioned findings show how well tungsten-impregnated activated carbon treats hazardous leather industry wastewaters in compliance with discharge regulations. The table displays the extremely high levels of total organic carbon (TOC) and chemical oxygen demand (COD) in the condensation and stripping tanks, which were 35,000 mg/L and 6460 mg/L, respectively. These levels far exceeded the general discharge limits for the leather industry, which are set at 100 mg/L for TOC and 250 mg/L for COD by the Central Pollution Control Board and Environmental Protection Agency, respectively. The ideal pH values of 7.3 in strippers and 10.5 in condensation tanks correspond with the extraction kinetics reported in the literature since COD and TOC were decreased by tungsten treatment at pH values of 9–11, 120 minutes, and 20 ml/min HRT rate.

4.2 Tungsten-loaded Catalyst Phisco-Chemical Characterization

WACM						***ACM***
	1%	***2%***	***3%***	***4%***	***5%***	
W metal content mg/g	7.1	15.2	24	31.1	35.4	--
W ion impregnated %	71	76	80	77.75	70.8	--
Density g/cm^3	0.3654	0.3932	0.4124	0.4952	0.5416	0.305
Moisture content %	3.5	3.4	3.3	3.2	3	3.4
Ash content %	83.14	80.52	78.35	75.64	74.87	85.39

Table4. 2: Physico Chemical Characterization of tungsten based catalyst

Catalysts with different metal (Tungsten) percentage loadings, including 1%, 2%, 3%, 4%, and 5% WACM, were made. While the ash content reduced, the catalyst density grew as the W % increased. Due to the extra metal ions, the W impregnation percentage decreased after increasing to 3%. As a result, when compared to the other percentage, the 3%WACM carbon matrix displayed the highest percentage of W impregnation. Thus, it was set to be optimal.

4.3 Tungsten-impregnated catalyst: instrumental characterizations

FTIR analysis

FTIR analysis was performed on the carbon catalysts of WACM and ACM (Fig 4.1 a). O-H stretching vibration of Si-O-H is responsible for the ACM peak at 3434 cm-1; this peak is moved to 3428 cm-1 by the production of Si-O-W. It is brought on by the W reaction with oxygen, which is created when W d-orbitals are donated. Because of the stretching vibration of C=O and Si-O-Si, the ACM peaks at 1621 cm-1 and 1097 cm-1. The metal influence caused the WACM to shift to 1634 cm-1 and 1096 cm-1. The shifting of these peaks validates W's interactions with the carbon matrix's functional groups. The W-O-W or O-W-O stretching vibrations are the cause of the steep peak in WACM at 804 cm-1. Within WACM, the W-O stretching vibration is responsible for the creation of another strong peak at 614cm-1. It verifies that W, as WO3 or WO2, is present on the carbon matrix's surface.

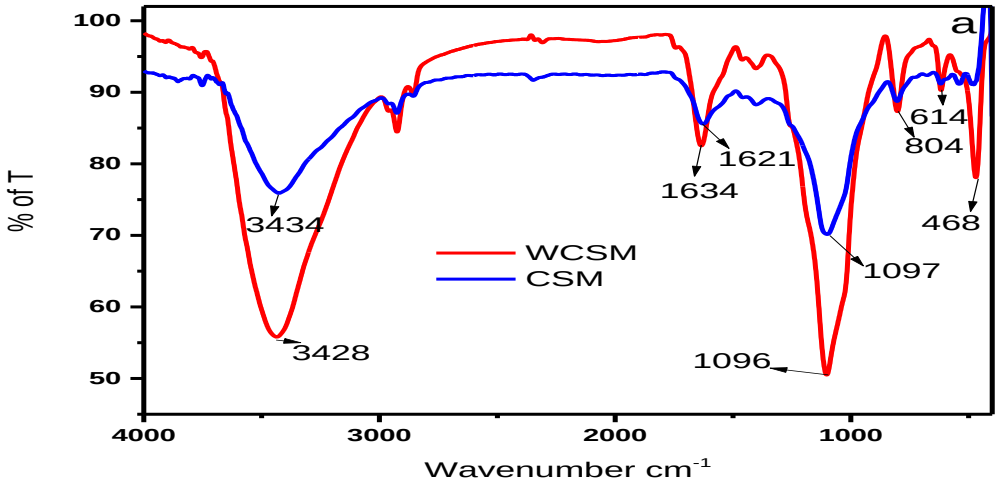


Figure 4.1 a: FTIR Analysis

XRD analysis

The amorphous form of the catalyst resulted in a large peak between 2θ 20 to 30, centered at 22.5 ^{O}, as seen in the XRD graph (Fig.4.1 b) of ACM. It has the potential to combine with the crystalline phases of tridymite and silica cristobalite at 21.9 and 24 degrees, respectively. The monoclinic form of the WO3 is shown by the peaks of WACM at 30^{O}, 35 ^{O}, 56 ^{O}, and 61.8 ^{O}. The (212), (202), (300), (310) peaks of WO3 are caused by the diffraction planes at these angles: 42.7^{O}, 52.9^{O}, 61.8 ^{O}, 35 ^{O} and 40 ^{O}. The WO2 planes (002) and (220) are responsible for the peaks located at 36.8 ^{O} and 52.9 ^{O}. WO3/WO2 was verified to be present on the carbon matrix by the XRD spectra.

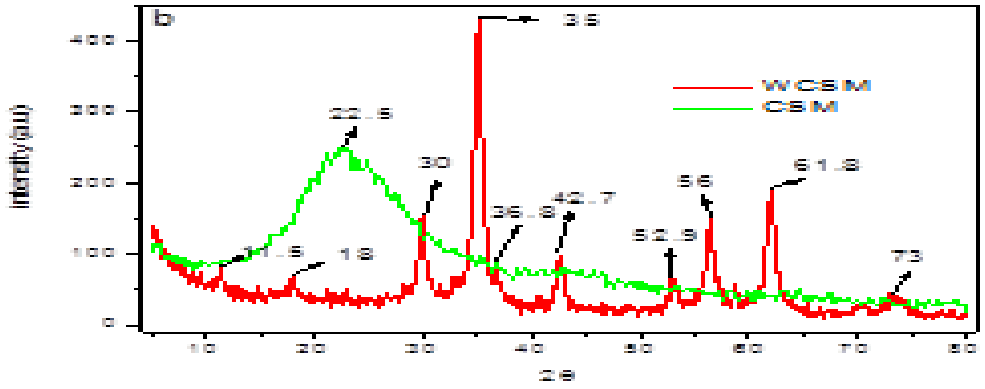


Figure 4.1 b: XRD Analysis

EPR Analysis

ACM and WACM EPR analyses were examined, and the g factor vs intensity plot was created. The EPR signals of ACM and WACM were discovered to include free unpaired electrons. There are two forms of tungsten oxides: dioxides and trioxides. Of these, WO3 has EPR active while WO2 does not. The increase in population and relaxation time of the free electrons in the carbon matrix clustered with WO3 could be the cause of the broadening of g-factors.

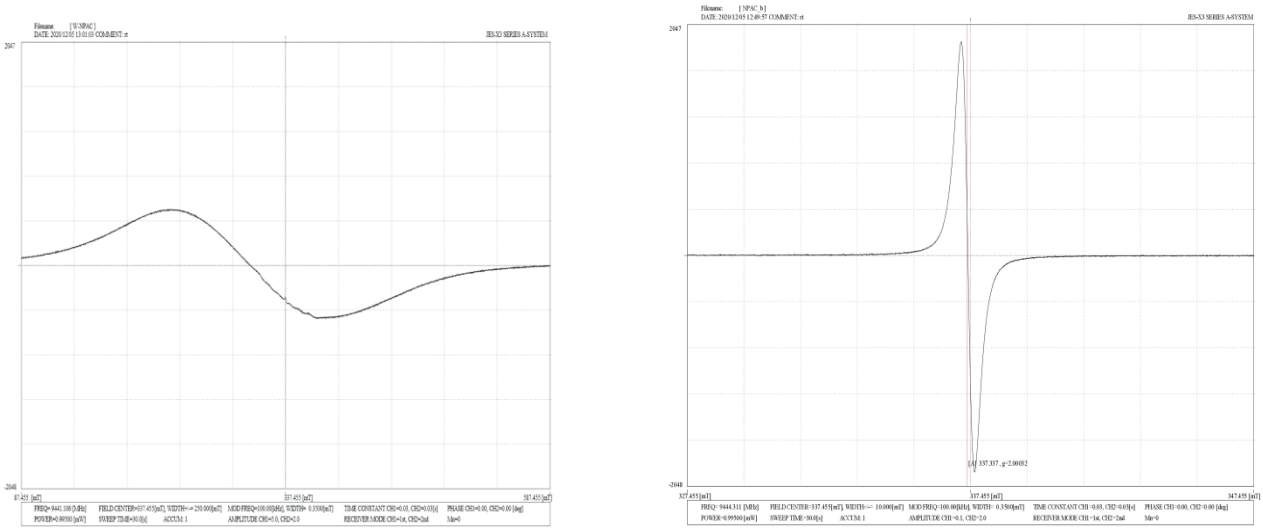


Figure4. 2c & d: EPR Analysis of ACM and WACM

DSC Analysis

The elimination of water molecules in both ACM and WACM caused energy absorption, which is why the DSC displayed an endothermic peak close to 100^{O}C. The breakdown of chemical compounds caused by the W ion's introduction into the matrix resulted in the creation of a new endothermic peak at 220 ^{O}C in WACM as opposed to ACM.

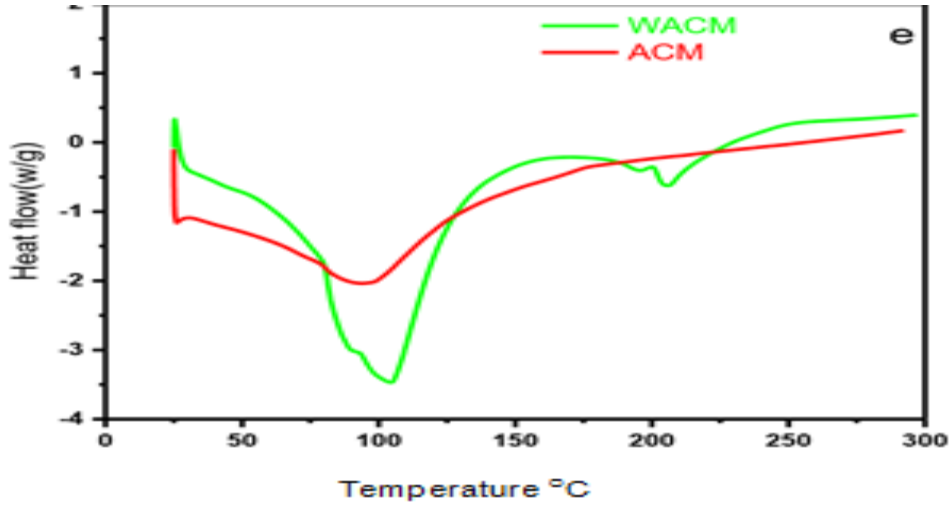


Figure 4.1e: DSC Analysis

TGA Analysis

A drop in mass was seen with an increase in temperature using thermogravimetry analysis (TGA), which may have been caused by the volatile chemicals included in the matrices. It displayed four weight loss segments, each of which represented a mass loss caused by water and surface-bound water molecules between 50 and 225 OC. The organic compounds' volatility is the cause of the mass loss at 225–400 OC. The instability of organic compounds containing nitrogen and the breakdown of the carbon network structure were the causes of the weight loss in the 400–600 OC range. The breakdown of inorganic and oxide chemicals was the cause of the weight loss reported in the 600–800 ^{O}C range. When comparing the two thermograms, it was possible to see that WACM lost less weight at the 800^{O}C because of the matrix's 3% tungsten content, which provides thermal stability and resistance.

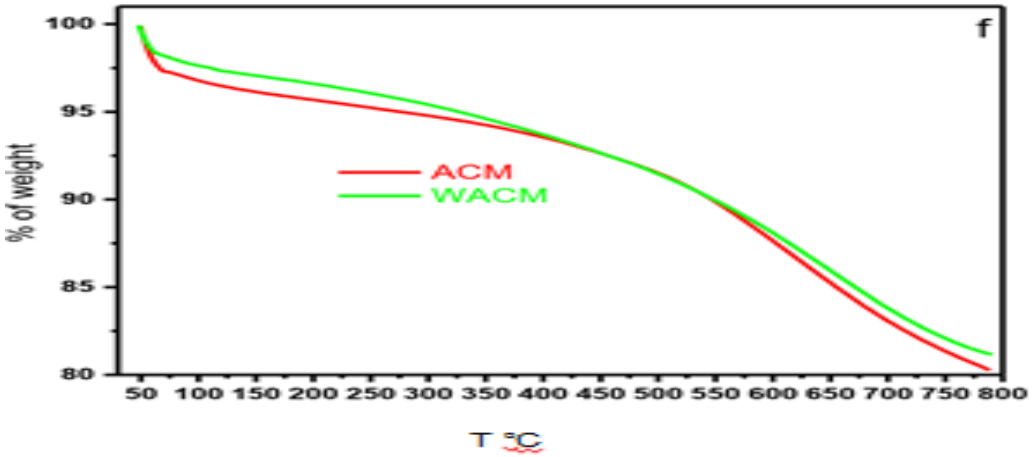


Figure 4.1 f: TGA Analysis

Scanning Electron Microscope (SEM) Analysis

Fig 4.1d displays the scanning electron microscopy (SEM) picture of ACM and WACM. The structure of the pores of both catalysts was discovered to be mesoporous, and the impregnation of tungsten ions filled the active sites that were present in the ACM in the WACM.

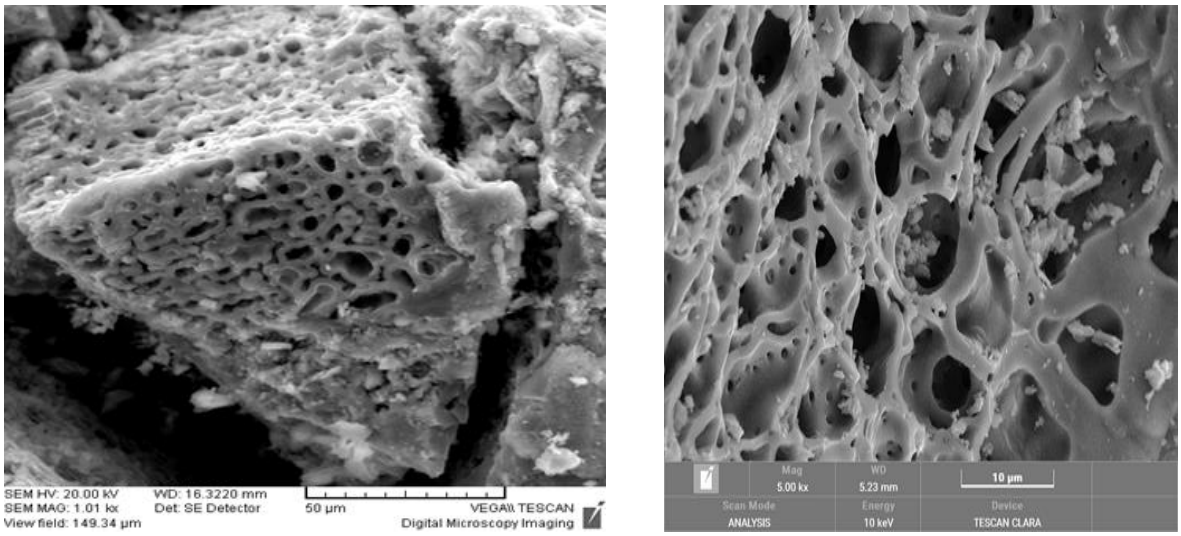


Figure 4.1g: SEM image of ACM and WACM

4.4 Catalytic degradation for Volatile organic compound (Toluene,ethyl benzene,Chlorobenzene and leather VOC)

Parameter	*Toluene contaminated water (TCW)*	*Ethylbenzene contaminated water (ECW)*	*Chlorobenzene contaminated water (CCW)*	*Leather waste weter (lcw)*
pH	10	10	11	7.5
HRT(hrs)	2	24	2	2
Stripping rate(LPM)	1	1	0.5	1
COD(mg/L)	800-850	350-470	608-704	33000-35000
TOC(mg/L)	450-490	100-140	180-210	9000-10000
Toluene(mg/L)	460-510	-	-	-
ethyl benzene(mg/L)	-	110-150		-
Chloro benzene(mg/L)	-	-	285-330	-

Table4. 3: Catalytic degradation of VOCs

Optimized pH 10, HRT for two hours, and a stripping rate of one LPM were used to prepare the TCW. The TCW was found to have 800-850 mg/L of COD, 450–490 mg/L of TOC, and 460–510 mg/L of toluene (Fig. 4.2 a). The optimal pH, duration, and stripping rate for the ECW preparation were 10 LPM and 24 hours. The results showed that the ECW had 350–470 mg/L of COD, 100–140 mg/L of TOC, and 110–150 mg/L of ethylbenzene (Fig. 4.2 b).

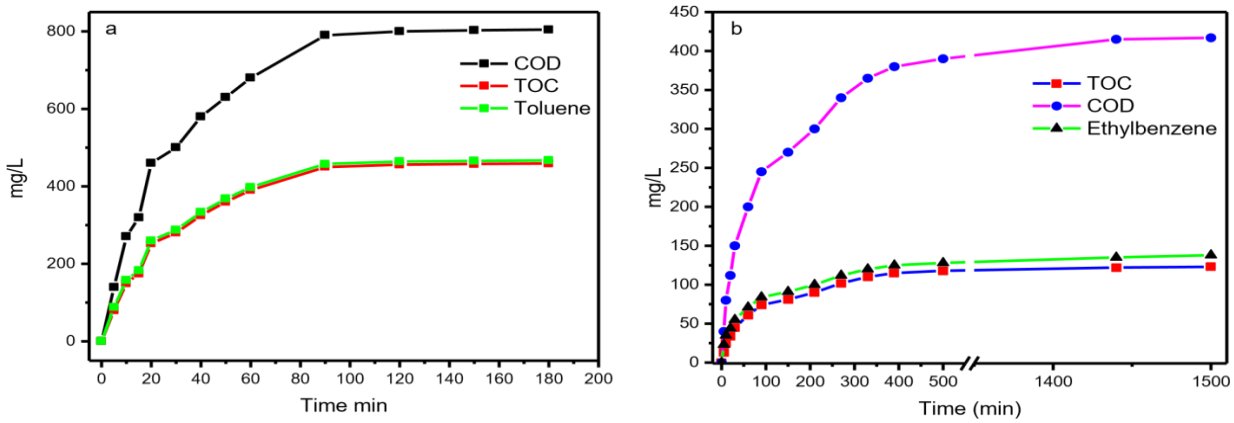


Figure 4.2 a & b: COD, TOC and VOCs concentrations of toluene (a) and ethylbenzene (b) at optimized condition

The direct relationship between COD, TOC, and toluene in waste water was covered in the preceding graph. This suggests that over the specified time, the toluene concentration increases along with the COD value, and vice versa for the TOC. In a similar vein, as ethyl benzene concentration rises, COD and TOC also rise. This suggests that COD contribute significantly to the overall increase in VOCs.

Under optimum conditions, a pH of 11 and a volume of 0.5L of chlorobenzene were used to make the CCW. The results show that the CCW has a COD of 608–704 mg/L, a TOC of 180–210 mg/Lb, and a chlorobenzene level of 285–330 mg/L (Figure 4.2c). Only a slight difference was seen 120 minutes later between the 3%WACM and removal efficiencies of 80.9%, 85.5%, and 80.5% for TCW, ECW, and CCW, respectively. It was observed that the greatest elimination was 30-45% at 120 minutes when compared to water that had been treated with ACM and hydrogen peroxide. It was also studied how both catalysts (3% WACM-H and ACM-H) would function without the presence of hydrogen peroxide. When hydrogen peroxide was not present, the efficiency for 3% WACM-H was found to be lower at 50–62% and for ACM-H, it was found to be lower at 20–30% after 120 minutes. We can now see how the addition of hydrogen peroxide and metal impregnation affect the matrix.

In the LVOCS, TOC was 9000–10,000 mg/L and COD was 33000–35000 mg/L Using W-PBCR and A-PBCR as benchmarks, it was catalytically treated. H_2O_2 was used as an external oxidant (0.2 ml/L) when catalytically oxidizing the LVOCS at varied HRT using different metal concentrations of WACM ranging from 1 to 5%. The results were compared with ACM.

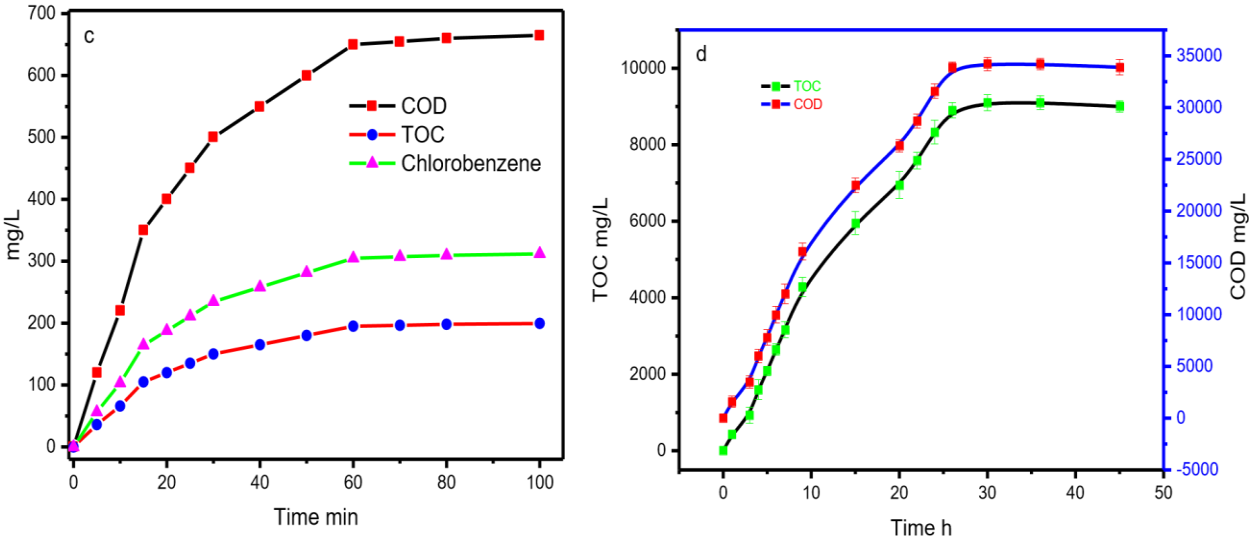


Figure 4.2 c & d: COD, TOC and VOCs concentrations of chlorobenzene(c) and LVOCs (d) at optimized condition.

The graph above illustrated the direct relationship between waste water's COD, TOC, and chlorobenzene levels. This suggests that, during the allotted time, the concentration of chlorobenzene increases with an increase in COD value, and vice versa for TOC. Likewise, when it comes to LVOCs, COD and TOC rise in tandem with LVOC levels. This suggests that COD play a significant part in raising overall VOCs.

4.4.2 Optimization studies for the catalytic oxidation of leather VOCs

The most common VOCs were discovered to be toluene, ethylbenzene and chlorobenzene. The COD and TOC levels in the leather waste were 33000–35000 mg/L and 9000–10,000 mg/L, respectively. For comparative analysis, it was catalytically treated with W-PBCR and A-PBCR. Using varied metal percentages of WACM ranging from 1 to 5% at varying HRT and H2O2 as an external oxidant (0.2 ml/L), the LW was catalytically oxidized and compared with ACM.

4. 5 Stability of catalysts

By examining its phases using XRD analysis, the stability of the WACM matrix after ten treatment cycles (WACM-AU) was validated. The outcome demonstrated that after 10 cycles of LCW treatment, there were no phase changes and the XRD diffraction pattern resembled the

catalyst before usage. The consistency of TOC removal (average of 85.5%) after treating the LCW for ten treatment cycles further supported its stability. Consequently, these findings demonstrated that even after ten treatment cycles, the catalyst WACM remains extremely stable.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The effluent from tanneries is enriched with both organic and inorganic chemical compounds found in leather waste water. The organic components found in leather waste water include VOCs. VOCs are harmful to people, animals, and plants. Numerous detrimental health consequences have been demonstrated to be caused by these substances.

Nowadays, cleaning leather waste water before releasing it into the environment is a crucial problem because to the VOCs present in it. Using an activated carbon matrix based on tungsten, the study's goal was to treat VOCs through catalytic oxidation. Using a metal-impregnated WACM catalyst, the toluene, ethylbenzene, and chlorobenzene-contaminated water was produced under ideal conditions for catalytic oxidation. FTIR, XRD, SEM, , TGA, DSC, and EPR analysis were used to characterize the ACM and WACM. Tungsten is present in tungsten oxide (WO3, WO2), as shown by XRD and FTIR. The impregnation of tungsten metal with the carbon matrix was also validated by the physicochemical characterization. Additionally, the LVOCs found in leather effluent were processed and contrasted with ACM. UV and TOC were used to track the treatability of the VOCs. Regarding TOC, the VOC removal efficiency in 10–15 treatment cycles for toluene, ethylbenzene, chlorobenzene, and LVOCs was 80.5%, 85.5%, 80.9%, and 85.4%, respectively. This treatment approach created a new avenue for air pollution since it used liquid phase oxidation rather than gas phase oxidation. The purpose of this study was to examine the effectiveness of tungsten in the catalytic oxidation of volatile organic compounds (VOCs) in leather waste water. As a result, the performance of tungsten in this process was successfully examined, and additional research may enhance the method's suitability for large-scale applications.

5.2 Recommendation

As this study concludes, tungsten based activated carbon matrix have the potential to degrade VOCs in leather waste water. These performances of tungsten based activated carbon matrix have to be transformed in a higher level in terms of efficiency, sustainability and using advanced technologies. Developing environment-friendly technologies after a careful study and targeting the status of green environmental policies, directed the interest of researchers in getting a supportive engineering measures.

To have a sustainable reduction of VOCs, policies and strategies have to be executed and stakeholders have to be involved. Promoting cost-effective and environmentally friendly wastewater treatment systems can be facilitated by collaborative endeavors, including tanneries, government organizations, and research institutes.

The need to enhance the understanding of tannery operators regarding the adverse environmental ramifications stemming from inadequate wastewater management and the advantages associated with adopting sustainable practices is the other scope of tannery wastewater treatment.

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