ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY SCHOOL OF CHEMICAL AND BIO ENGINEERING

INVESTIGATION OF THE PERFORMANCE OF MOLYBDENUM-IMPREGNATED ACTIVATED CARBON FOR THE REDUCTION OF VOLATILE ORGANIC COMPOUNDS (VOCS) FROM LEATHER PROCESSING.

By

Tsehay Getachew

Advisors

Dr. Shegaw Ahmed

A thesis submitted to the School of Graduate Studies of Addis Ababa University in partial fulfillment of the Degree of Master of Science in Leather Technology

Addis Ababa, Ethiopia

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Declaration

I, Tsehay Getachew, hereby declare that this research study, titled Investigation of the Performance of Molybdenum-Impregnated Activated Carbon for the Reduction of Volatile Organic Compounds (VOCs) from Leather Processing, is my original work. I affirm that all references have been accurately recorded and acknowledged. Furthermore, I confirm that this thesis has not been submitted, in full or in part, to any university for academic qualification.

This thesis has been submitted for examination with the approval of my advisor, Dr. Shegaw A., from the School of Chemical and Bioengineering at Addis Ababa University, Ethiopia. I certify that I have reviewed this thesis prepared under my guidance and recommend its acceptance as fulfilling the thesis requirement.

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Acknowledgements

First and foremost, I humbly acknowledge the divine blessings and guidance of the Almighty God throughout my research expedition. Without His grace, none of these accomplishments would have been attainable.

I wish to express my profound gratitude to my esteemed mentors, Dr. Shegaw, Dr. S. Swaranleta, and Dr. Prabhakaran from the Environmental Science Lab at CSIR - CLRI. Their invaluable expertise, profound guidance, and unwavering dedication to academic excellence have been pivotal in shaping the trajectory and triumph of this research endeavor.

I am profoundly thankful to Dr. Anteneh.M for his steadfast support and mentorship, which have served as a wellspring of inspiration for me. Furthermore, I extend my deepest appreciation to the Leather Industry Development Institute for granting me the opportunity to conduct this research. Their unwavering support and collaboration have been essential in providing the requisite resources and facilities for the successful culmination of this study.

Additionally, I am grateful to CSIR-CLRI (Central Leather Research Institute) for their profound knowledge and expertise in the leather domain, enabling us to leverage their facilities, thereby significantly enhancing the depth and caliber of this research.

My heartfelt thanks go out to my family and friends for their unwavering support, encouragement, and understanding. Their love, patience, and unwavering belief in my capabilities have been a constant source of motivation. Their presence and encouragement have empowered me to surmount challenges and persist in my quest for knowledge

Abstract

The increasing concerns regarding the adverse effects of volatile organic compound (VOC) emissions on human health and the environment have necessitated the development of effective strategies for VOC reduction. This study aims to investigate the impregnation process and optimize parameters such as hydraulic retention time (HRT), pressure, and pH in order to enhance the catalytic activity and VOC adsorption capacity of activated carbon. The performance evaluation of the optimized composite material, consisting of activated carbon impregnated with a molybdenum catalyst (Mo-ACM) with a 3% loading of Mo, was conducted and the physicochemical characteristics of the composite material were determined and found to be; density (0.386 g/cm^3), moisture content (4.9%), ash content (75.67%), pH (11), and HRT (120 minutes), instrumental analysis; Fourier transform infrared spectroscopy was used to characterize the metal catalysts, revealing peak shifts indicating the presence of molybdenum. X-ray diffraction analysis showed sharp peaks at 26.380° and 44.60°, while scanning electron microscopy with elemental mapping analysis demonstrated a more uniform distribution, slightly rougher morphology, and increased pore connectivity in Mo-ACM, resulting in a contiguous network of voids. Energy-dispersive X-ray spectroscopy (EDAX) confirmed the presence of molybdenum (Mo), and electron paramagnetic resonance (EPR) analysis indicated the presence of free electrons at g=1.9872.The treatment efficiency of VOCs was monitored using chemical oxygen demand (COD), total organic carbon (TOC) analysis, and UV-vis analysis. The initial tannery raw water, after stripping and dissolution, exhibited COD and TOC levels of 35,200 mg/L and 7,200 mg/L, respectively. After treatment, COD levels decreased to 192 mg/L, and TOC levels decreased to156.4 mg/L, indicating a reduction rate of 95%. The catalytic efficiency of Mo-ACM was determined to be 87.2% over 10 treatment cycles, highlighting its effectiveness in VOC treatment and prevention of air pollution. The findings of this study empower these industries to adopt sustainable practices and meet stringent environmental regulations.

Keywords: - Volatile organic compounds, Molybdenum impregnated activated carbon material, catalytic oxidation of VOC's and CETP effluents.

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List of Acronyms

ACM- Activated carbon material

APHA- American Public Health Association

CETP-Common effluent treatment plant

HAP- Hazardous air pollutant

MEK- methyl ethyl ketone

Mo-ACM molybdenum impregnated activated carbon martial

PBCR-Packed bed catalytic reactors

PFCs- per fluorinated compounds

PFOA -perfluorooctanoic acid and

PFOS- perfluorooctanoic sulfonic acid

POM- particulate organic matters

PSA – Pressure Swing Adsorption Processes

R-134a -(Chemical formula: CH_2FCF_3)

R-22 -Chemical formula: $CHClF_2$ (trade name Freon-22)

SVOC- semi volatile organic compounds

TSA-Temperature Swing Adsorption Processes

USEPA - United States Environmental Protection Agency

VOC- volatile organic compounds

VVOC- very volatile organic compounds

WHO- World Health Organization

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CHAPTER ONE

INTRODUCTION

1.1. Background of the study

Leather production is an ancient craft with a long history dating back millennia. Archaeological evidence indicates that by approximately 3000, sophisticated leatherworking techniques had been established [1]. Through a process known as tanning, animal hides are transformed into a durable and versatile material. Tanning involves subjecting collagen-rich animal skins and hides to controlled chemical and mechanical processes. This stabilizes the protein structure against putrefaction while rendering the material supple yet resilient. The production process for leather encompasses range of activities and to produce leather tailored for specific applications, the appropriate animal hide must undergo an optimized sequence of pre-tanning, tanning, and finishing stages. While these three main series are common, the specific processes within each stage, their extent, and type can differ depending on type leather being made, skin type and processing methods used. As a result, there is considerable flexibility in customizing the leather production protocol to achieve desired characteristics.

The overall production process for leather begins with acquisition of raw materials including hide and skins of cattle, sheep, goats and pigs. The hide and skins predominantly obtained from livestock raised for meat consumption but now a day's research also explores alternative material like plant-based options. Once raw materials are procured by the tanner hides and skin undergo pre-treatment process to remove hair, fat, flesh, dirt and other impurities this step typically involves soaking, fleshing and liming. A critical step followed by pre-treatment is tanning; tanning is process that converts the perishable hides and skins to long-lasting durable leather suitable for commercial activities during the tanning process animal skin and hides are treated to remove non structured proteins and fat, leaving an initially pure collagen matrix that is preserve during tanning which involve the impregnation of skins with mineral, synthetic or vegetable tanning agent [2]. Once tanned the leather

Under goes various finishing process to enhance its appearance, texture and performances. These may include dyeing, embossing, buffing and application protective coatings.

The leather industry has played an important economic role globally for centuries. As one of the earliest large-scale manufacturing sectors, it has also long grappled with significant environmental challenges arising from its production processes. Historically, primitive tanning methods involved soaking hides in noxious chemicals in open areas, emitting odors that plagued surrounding communities and earned the reputation as one of the smelliest industries [3]. While modern factories have mechanized operations within closed facilities, the fundamental pollution Issues persist due to the huge volumes and toxic nature of waste streams generated. Tanneries discharge effluents laden with heavy metals, salts, and chemicals used across pre-tanning, tanning and finishing stages. If not properly treated, these pollutants can contaminate the environment and pose risks to public health. Today with the growth of population and strain being put on our world for saving natural resources its is becoming more apparent that the disposal of waste matter of industry's are responsible to the society around it [3] .The expansion of leather production to larger urban-based factories has exacerbated these pollution problems due to greater production scales. At the same time, tightening regulations and a growing global population have heightened sustainability pressures on natural resource and land usage [3]. Therefore addressing waste management responsibly is critical to the industry's long-term social license to operate. The overall production process for leather involves the use of chemicals that can have detrimental effects on the environment and human health. Some of the different types of waste released in the leather industry are solid organic wastes such as un-tanned trimmings, fleshings, splits, and tanned trimmings, splits, and shavings from raw hides and skins [4] These solid wastes can accumulate and cause environmental damage if not properly treated and disposed of, liquid waste as a result of various processes, including Beamhouse operations and wastewater treatment. The effluents generated during the Beamhouse operations, which involve the removal of dirt, hair, epidermis, non-collagenous proteins, and grease from raw skin, can have a high organic load Proper treatment and management of liquid waste are essential to prevent pollution of water bodies [5]and air emissions(gaseous, VOCs).

Volatile organic compounds (VOCs) refer to a class of organic chemicals that readily evaporate under ambient conditions due to their high vapor pressure the leather manufacturing industry

Produces a variety of VOC's that pose environmental and health risks if not properly controlled. Common VOCs emitted during leather production include aldehydes such as formaldehyde, ketones, benzene derivatives, alcohols, acids, and sulfur-containing compounds. When released into the atmosphere, VOCs contribute to ground-level ozone smog formation, greenhouse effect and stratospheric ozone depletion exacerbating air quality issues. Prolonged human exposure to high VOC levels has also been associated with respiratory irritation and organ damage in some cases. Therefore to mitigate these impacts, leather facilities require effective VOC abatement systems meeting regulatory standards. Researchers have explored techniques used for treating VOC-laden exhaust gases in the leather manufacturing process include end-of-pipe treatments such as adsorption, condensation, catalytic oxidation and incineration. Adsorption involves the use of materials like activated carbon or zeolites to capture VOCs through physical or chemical binding on high surface area surfaces. However, activated carbon adsorption alone requires regeneration or disposal of saturated adsorbents, which adds to costs and introduces secondary waste streams. When combined with thermal or catalytic regeneration, it becomes highly effective at removing over 90% of VOCs from leather flue gases.

Condensation techniques use cooling processes to condense VOCs, which can then be collected. However, this process is energy-intensive and the condensate requires further treatment or disposal. Incineration, on the other hand, involves high-temperature combustion to destroy VOCs. Some studies have investigated integrating multiple end-of-pipe methods to enhance VOC removal. For instance, membrane separation followed by non-thermal plasma and activated carbon has achieved removal rates above 95%. Another study integrated a bio-trickling filter with activated carbon adsorption to handle fluctuations in VOC concentrations more effectively. While integrating these methods can optimize overall mitigation, it comes with drawbacks such as increased complexity, the need for sophisticated control systems, and potential reduction in individual treatment efficiencies. Additionally, there are higher initial costs associated withmulti-stage systems. Alternative materials and processes can directly reduce VOC generation. For example, using aliphatic solvents, vegetable tanning agents, and chrome-free techniques can result in fewer emissions. Process modifications like automation and closed vessel operations can minimize fugitive VOC losses. Wastewater treatment also offers opportunities for recovery and reuse within industries. However, alternative materials and processes may require facility renovations and equipment upgrades, resulting in significant transition costs. Availability of non-

hazardous substitutes is limited for certain applications, and alternative processes may be less efficient than conventional methods. Wastewater treatment generates sewage sludge, which requires proper disposal and may have the potential for contaminant leaching. It also requires substantial space and infrastructure. Therefore to address these challenges, this study proposes a dual process involving activated carbon adsorption integrated with catalytic treatment. In the adsorption stage, porous activated carbon with a large surface area is used to physically attract and retain VOC molecules. Simultaneously, a catalyst impregnated with molybdenum within the carbon facilitates the oxidation of adsorbed compounds. By combining adsorption and catalytic oxidation, this hybrid system aims to achieve high removal efficiency for a range of VOCs emitted during leather manufacturing.

This study primarily focuses on the various types of volatile organic compound released during the manufacturing process of leather and it tries to identify and propose better solution to mitigate the environmental pollution caused by VOC's scenes VOC's have not received adequate emphases compared to other type of wastes in the leather industry. In general this research aims to design activated carbon supports impregnated with molybdenum catalyst as an effective method for VOC oxidation this process involves adsorption of VOCs onto activated carbon, followed by oxidation using the molybdenum catalyst. The activated carbon acts as a porous medium that captures the VOCs, while the molybdenum catalyst facilitates their oxidation, leading to the removal of harmful emissions.

1.2. Statement of problem

Uncontrolled release of volatile organic compounds (VOCs) during leather manufacturing poses significant risks to both human health and the environment. Emissions such as benzene, toluene, and formaldehyde, which are recognized carcinogens, can exacerbate respiratory illnesses upon exposure. Despite ongoing efforts to mitigate VOC emissions, the leather industry remains a major contributor to national VOC burdens, accounting for over 25% of industrial emissions in many countries. Conventional strategies for VOC abatement, including thermal oxidation, material substitutions, process modifications, and carbon adsorption, are widely used but have limitations in their effectiveness. Thermal oxidation is associated with high energy costs and generates harmful byproducts. Adsorption onto activated carbon becomes saturated over time, leading to incomplete destruction of VOCs. Implementing process changes also presents technical and economic challenges. To address these limitations; this study proposes evaluating a sustainable alternative that integrates activated carbon with a molybdenum oxide catalyst. By promoting complete oxidative breakdown of VOCs to CO_2 rather than partial oxidation, this study aims to assess the performance of a molybdenum-impregnated activated carbon catalyst and results of this evaluation will contribute to establishing the techno-economic feasibility of this promising end-of-pipe solution.

1.3. Objectives

1.3.1 General objective

The objective of this research is to investigate the performance of molybdenum-impregnated activated carbon for the reduction of volatile organic compounds (VOCs) from leather processing

1.3.2 Specific objectives

- To prepare and analyze the physiochemical properties of activated carbon before and after implementation of molybdenum catalyst.
- To determine the type and level of VOC's in leather processing industry.
- Evaluate the performance of molybdenum-impregnated activated carbon in reducing VOC emissions from leather processing.

- Optimize parameters such as hydraulic retention time (HRT), pressure, dosage of H_20_2 and pH for the impregnation process of activated carbon with molybdenum.
- Determine the treatment efficiency of the molybdenum-impregnated activated carbon material in reducing volatile organic compounds (VOCs) emitted during leather processing.

1.4. Significance of the study

The significance of this research lies in its potential to address a critical environmental issue in the leather industry. By investigating and proposing solutions to reduce VOC emissions, this research can contribute to the sustainable development of the industry therefore by investigating opportunities for integrated adsorption-catalytic treatment systems; several important outcomes may be achieved such as

- Reduction of environmental impact: The investigation of VOC emissions in the leather manufacturing process is of great significance due to the environmental challenges associated with these compounds. By addressing this issue, the study aims to contribute to the reduction of environmental pollution and promote sustainable practices within the leather industry.
- Health and Occupational Safety: VOCs released during leather production pose significant health risks to workers and nearby communities. The study's focus on reducing VOC emissions is crucial in safeguarding the well-being and safety of individuals working in the industry and those residing in its vicinity.
- Regulatory Compliance: The study's findings and recommendations can contribute to the establishment of effective regulatory standards and enforcement mechanisms for VOC emissions in the leather industry. This can ensure that manufacturers prioritize VOC reduction efforts and comply with environmental regulations, promoting responsible and sustainable practices.
- Industry Advancement: The study's focus on proposing innovative solutions and technologies for VOC emission reduction can drive industry development and competitiveness. By adopting these advancements, the leather industry can enhance its environmental performance, embrace sustainability, and stay at the forefront of responsible manufacturing practices.

In conclusion, the significance of this study lies in its potential to mitigate environmental pollution, ensure the health and safety of workers and communities, optimize resource utilization, foster regulatory compliance, and contribute to the overall advancement of the leather industry towards sustainability.

1.5. Hypothesis

Implementing activated carbon adsorption followed by catalytic oxidation of VOCs will result in a significant reduction of VOC emissions during the leather manufacturing process. This approach, due to the high surface area and adsorption capacity of activated carbon, combined with the conversion of VOCs into less harmful compounds through catalytic oxidation, will provide an effective solution for VOC removal in the leather industry.

CHAPTER TWO

2. Literature Review

2.1 Leather processing

The production process for leather is a multi-step procedure that involves various stages, including pre-tanning, tanning, and post-tanning, each contributing to the quality and characteristics of the final leather product. The production process can be broadly divided into the following stages:

2.1.1. Pre-tanning (Beamhouse Operations)

A set of process operations which precede tanning as the name indicates they aim to cleanse leather making materials contained in skin/hide and prepare physic-chemically the skin matrix for permanent stabilization or tanning. During the pre-tanning operations, raw hide or skin is extensively washed of foreign matter, hair is loosened and removed, leather making material is swollen so that it could be consolidated and unwanted flesh could be sheared away using a mixture of lime and sharpening agents and delimed and bated for removing debris, short hair and other non desired materials from the matrix and prepared for mineral tanning by reducing the affinity of skin to the tanning material each step present in pre-tanning can explained as follows.

Curing: Raw hides and skins are first preserved to stop them from deteriorating before it goes to the leather processing, before the raw hides and skins are tanned; they can be attacked by bacteria, etc and become putrefied. So to avoid this damage we use different methods of preservation including salting, chilling, freezing and the use of biocides

Soaking: Hides are soaked in water for 1-3 days to rehydrate the skins. This swells the fibers to relax the hides and allows for easier removal of non-collagenous proteins in later stages [6]. Soaking is carried out in alkaline conditions of a pH of 5.5-10 in this operation some enzymes are used such as proteases and carbohydrases. Proteases work by dissolving inter fibrillary proteins that compact fibers together while carbohydrases break up carbohydrates within the hide and as a result increase water uptake[8]

Liming: Liming is a critical pre-treatment operation in leather manufacturing where in the structural matrix of the raw hide or skin is processed for the subsequent tanning phase. The

objectives of liming includes loosening of hair, assisting of removal of flesh, saponification of fat, opening up of fibre bundles for assisting the flow of fluids to assist further processing and degradation of unwanted matrix components. The overall liming operation involves placing of hides or skin in a liming pit containing water, sodium sulfide, and sodium hydroxide agitated for 12-48 hours depending on thickness this process softens the hides by breaking down fat and other proteins through hydrolysis, allowing them to be stretched without damage of fibers [6].

Fleshing and Trimmings: Fleshing is a critical mechanical pre-treatment operation in leather manufacturing. By utilizing specialized fleshing machinery, excess non-collagenous tissues like subcutaneous fat and remnants of muscle are precisely removed from limed hides/skins in a controlled manner. This yields a material with a more uniform thickness and structural matrix composition optimized for subsequent processing steps. Trimming is also conducted to optimize raw material utilization. Peripheral non-grain areas of larger hides often lack the quality demanded by end applications and may harbour undesirable defects affecting finished leather grades. Therefore, industrial leather producers routinely trim fringe hide/skin regions during liming and fleshing operations. This practice aims to maximize the yield of higher-grade leathers produced from each raw hide. For smaller hides, specialized fleshing knives mechanically carry out tissue debulking and edge trimming.

De-liming: De-liming plays a key "undoing" role in leather production by removing the lime compound and swelling effects introduced during liming. This process allows the hide/skin's dimensional stability and dense collagen matrix structure to partially return to their original pre-liming state. Precisely, de-liming aims to neutralize residual calcium hydroxide and sulfur additives used to induce swelling and separation of the grain layer during liming. Reversing this osmotic impact permits mechanical re-equilibration of the substrate for subsequent tanning tailored for specific end product attribute [7].

Bating and degreasing: Bating plays an important role in imparting flexibility required for many soft leathers [9]. The application of proteolytic enzymes during bating allows for partial breakdown of non-collagenous proteins within hides and skins, promoting swelling and resultant softening of the dermal substrate [10]. Several studies have characterized the kinetics of collagen degradation during bating, consistently showing a positive relationship between duration and achieved pliability. However, overly long exposures risk compromising structural integrity if not

carefully controlled. Optimization of time and concentration variables thus remains main factor to customizing functional properties. Concurrent degreasing proves especially crucial prior to chrome tanning of oily skin types, which commonly exhibit high fat content [11]. Untreated greases are known to catalyze in-solubilization of chromium salts, hindering downstream processing. While cattle hides generally contain minimal lipids, certain species require defined degreasing due to exponentially greater adipose deposits.

Pickling: Pickling represents a pivotal preparatory step prior to chromium tanning by precisely manipulating substrate pH Adjustment to 2.8-3.0 optimizes hide/skin matrix conditions for chrome salt infiltration and subsequent covalent coordination bonding interactions with collagen carboxyl functional groups[12]. Industrially, formulations equating to 100% salt pickling float, 10% sodium chloride, and 1% sulfuric acid per limed weight are routinely applied [12] Salt acts to inhibit excessive fiber swelling that could compromise ordered triple helix structures.

2.1.2. Tanning

This process stabilizes the collagen in the hides through cross linking and makes them durable and less susceptible to decomposition. Tanning is a process that arrests the enzymatic degradation by according stability to skin and introduces new chemical crosslink's and adds to thermal stability. Usually tanning agent perform stability by deactivating collagenase and prevent enzymatic degradation, denaturing collagenase by blocking sites in collagen and render the protein not degradable by collagenase, alter the conformation of the protein and render not recognizable by collagenase or a combination of two or more of the above reasons. There are several tanning methods employed, with chrome and vegetable tanning being the most prevalent globally.

Chrome tanning involves the use of trivalent chromium salts, most commonly chromium (III) sulfate. Hides are submerged in vats containing the chromium liquor solution, which is maintained at pH 3-4 for optimal cross linking to occur [14]. The chromium ions penetrate the collagen fibres and form covalent bonds between and within the peptide chains, stabilizing the triple-helical structure [15]. Agitation aids even penetration and the process typically take 1-3 days depending on hide thickness and desired degree of tanning [7]. The chromium-collagen complexes impart characteristics like strength, stability and resistance to biological degradation

Vegetable tanning relies on tannins extracted from plant sources rich in polyphenolic compounds. Popular sources include quebracho from South America and mimosa from Africa [16]. Hides are stacked in deep vats and soaked in a dilute tannin solution, which is periodically replaced. Tannins slowly penetrate the fibres through diffusion over several weeks, forming complexes with collagen amino acid side chains [17]. This results in highly durable, environmentally-friendly leather but requires a substantially longer processing time than chrome tanning.

Aldehyde tanning employs formaldehyde or glutaraldehyde solutions to rapidly crosslink collagen through methylene bridges between amino and carboxyl groups [18]. The process takes only 1-2 days but yields stiffer, less supple leather due to excessive cross linking density. It finds limited application in specialty leathers where durability outweighs flexibility requirements.

2.1.3. Post-tanning Operations

Once tanning is complete, several additional processes are carried out to produce finished leather. post tanning operation mainly classified into three basic groups' i.e. mechanical operation includes Sammying (for moisture adjustment for facilitating mechanical operations) Splitting/ Shaving (Thickness adjustment and recovery value of splits) , chemical operation includes Neutralization (for neutralizing free acidity and preparing for wet finishing) re-tanning, fat liquoring and dyeing (for wet finishing) finishing for addition of surface properties like gloss, smoothness and drying with texture adjustment Setting and drying (for flattening and area recovery) Staking/ other fibre softening systems (Conditioning)/ and drying, buffing snuffing etc.

Dyeing involves application of color using synthetic dyes or natural dyestuffs to achieve the desired shade [19]. Leather is soaked or sprayed with dye liquors which penetrate and bind to collagen fibers.

Fatliquoring improves suppleness and water resistance through introduction of oils, fats or waxes into the collagen matrix [17]. Neatsfoot oil or synthetic fats are applied and cured into the fibers through heating this enhances fullness and feel of the leather

Finishing operations impart the final characteristics for end-use. Mechanical processes like buffing, staking and ironing tighten the grain and smooth the surface. Chemicals may be applied to enhance properties such as flexibility, softness; water resistance etc. tailored to application. Once finished different type of inspections ensures quality standards are met before dispatch. Leather is checked for defects, durability, colorfastness and conformity to specifications [20]. Non-conforming materials are reworked or discarded.

2.2. Tannery Effluents

The environment is under increasing pressure from solid, liquid wastes and gases emanating from the leather industry. These are inevitable by -products of the leather manufacturing process and cause significant pollution unless treated in some way prior to discharge [21]. Tannery effluent refers to the wastewater generated during the leather production process in tanneries. It contains various pollutants and chemicals that can have significant environmental and health impacts if not properly managed. There are different types of pollutants some of them are

2.2.1 Organic Pollutants:- Tannery effluent contains a wide range of organic pollutants, including:-

- Dissolved and Suspended Solids: Tannery operations produce solid waste, such as hair, flesh, and trimmings, which can result in high levels of suspended solids in the effluent. These solids can clog water bodies, disrupt aquatic ecosystems, and reduce oxygen levels, leading to adverse effects on aquatic life [22].
- Proteins and Fats: Blood, proteins, and fats from animal hides are common components of tannery effluent. They contribute to high levels of organic matter, which, when discharged into water bodies, can lead to oxygen depletion, causing harm to aquatic organisms [23].
- Tannins and Polyphenols: Tannins, naturally occurring compounds used in the tanning process, are present in tannery effluent. They can color water bodies, inhibit photosynthesis, and negatively impact aquatic life by reducing light penetration and altering the pH of the water.
- Organic Solvents: Various organic solvents, such as toluene, xylene, and chlorinated compounds, are used in leather processing.

2.2.2 Inorganic Pollutants: Tannery effluent also contains inorganic pollutants, including:

- Chromium: Chromium, primarily in the form of trivalent (Cr (III)) and hexavalent (Cr (VI)) chromium, is widely used in the tanning process. Cr (III) is less toxic and insoluble, while Cr (VI) is highly toxic and soluble. Discharge of Cr (VI) into water bodies can have severe ecological consequences, including genotoxicity and carcinogenicity [24].
- Sulfides: Sodium sulfide is commonly used in the dehairing process in tanneries. Its presence in effluent can lead to the formation of toxic hydrogen sulfide gas, which poses health risks and has an unpleasant odor.
- Ammonia and Nitrogen Compounds: Tannery effluent contains ammonia and various nitrogen compounds, primarily from the breakdown of proteins and other organic matter. These compounds can contribute to eutrophication, a process that causes excessive algal growth and depletes oxygen levels in aquatic ecosystems, leading to the death of fish and other organisms [25].
- Heavy Metals: Other heavy metals, such as lead, mercury, and cadmium, may be present in tannery effluent due to the use of metal-based dyes and chemicals. These metals can accumulate in sediments and organisms, posing long-term risks to both aquatic ecosystems and human health.

2.2.3 Volatile organic compounds

Volatile organic compounds, or VOCs, are organic chemical compounds whose high vapor pressure results in easy evaporation at room temperature. Many VOCs have short to medium chain carbon structures allowing them to vaporize and enter the gas phase under normal indoor conditions. The common VOCs can be classified into several groups on the basis of their boiling point, the VOCs can be divided into very volatile organic compounds (VVOCs), VOCs, semi-volatile organic compounds (SVOCs) and particulate organic matters (POMs) by WHO.

Table 1. classifications of volatile organic compound according to WHO

VOC's	Based on boiling point	♣ $< 50^0$C very volatile organic compounds (VVOC) e.g. methane, formaldehyde, aldehydes, ♣ 50^0C-260^0C volatile organic compounds (VOC) e.g. ethyl acetate, benzene, ketone, ethylene

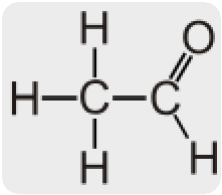
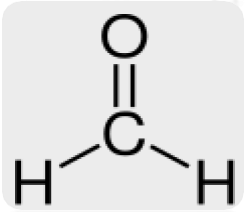
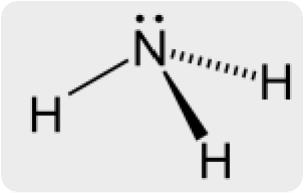
		♣ 260^0C-400^0C semi volatile organic compounds (SVOC) ♣ ≥400^0C particulate organic matters(POM)
VOC's	Molecular structure	Alkanes, aromatic hydrocarbons , halogenated hydrocarbons Alkenes, aldehydes, ketones
	Molecular polarity	Polar and non-polar

The leather industry is known to emit a variety of volatile organic compounds (VOCs), which contribute to environmental pollution. These VOCs encompass a range of chemical substances commonly encountered in leather production. Some of the frequently observed types of VOCs in the leather industry include

- Aldehydes: Aldehydes are a class of VOCs that include formaldehyde, acetaldehyde, and other related compounds. They are primarily emitted during the tanning process in the use of Aldehyde-based tanning agents. Formaldehyde-based tanning agents. Formaldehyde, in particular, is known to be a potent respiratory irritant and a suspected carcinogen [26].
- Solvents: Solvents, such as toluene, xylene, and ethyl benzene, are often used in leather production for various purposes, including degreasing, cleaning, and dyeing. These solvents can readily evaporate and contribute to VOC emissions. Toluene, for example, is a known neurotoxin and can have harmful effects on human health [27].
- Aromatic compounds: Aromatic compounds, including benzene, ethyl benzene, and xylene, are frequently found in the leather industry. These compounds are released during the use of aromatic-based solvents, adhesives, and dyes. Benzene, a known carcinogen, is of particular concern due to its harmful effects on human health and the environment [27].
- Ketones: Ketones, such as acetone and methyl ethyl ketone (MEK), are commonly used as solvents in leather production. These compounds are released during activities like degreasing, cleaning, and adhesive application. Acetone, for instance, is a skin and respiratory irritant with potential adverse effects on human health [27].

- Organic acids: Organic acids, including acetic acid and formic acid, are produced during various stages of leather production, such as tanning and finishing. These acids contribute to the characteristic odor associated with leather and are released as VOCs [26].
- Hydrocarbons: Hydrocarbons, such as hexane and heptanes, are commonly used as solvents in leather production. These compounds can be emitted during degreasing processes and contribute to VOC emissions. Some hydrocarbons have been associated with adverse health effects, including neurological and respiratory issues [27].
- Ester compounds: Ester compounds, including ethyl acetate and butyl acetate, are used as solvents and in the formulation of adhesives and coatings in the leather industry. These compounds can volatilize and contribute to VOC emissions during various production activities [27].

Table 2. Common VOCs released in leather production processes, utilization areas, and potential human health implications

Chemicals	Uses	Structure	Health effect
Acetaldehyde	Used as a degreasing agent during dehairing and bating. Also formed during liming.		Probable carcinogen; linked to respiratory issues like coughing and wheezing. Can damage nasal cavity.
Formaldehyde	Used as a tanning agent and preservative. Also formed during bating and liming.		Known carcinogen causing nasal cancer; toxic if inhaled, swallowed or absorbed through skin. Can damage upper Respiratory tract.
Ammonia	Used during dehairing, liming and de-liming. Also formed during bating.		Severe respiratory irritant; high exposures may damage lungs or cause burns. Associated with respiratory illnesses.

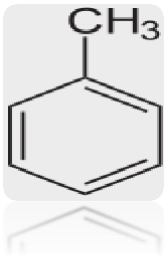
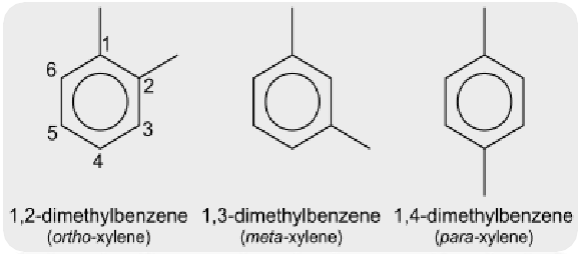
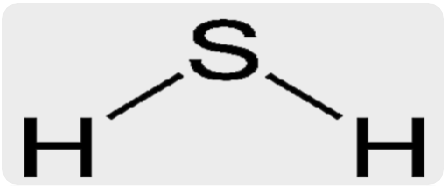
Toluene	Used as a solvent during dyeing and finishing.		Impacts nervous system function; associated with hearing/vision loss, poor birth outcomes
Xylene	Used as solvents during dyeing and finishing.		Neurotoxin, high acute exposures cause headaches and lack of coordination. Chronic exposures linked to anxiety, depression.
Hydrogen sulfide	Formed during bating and reduction processes.		Toxic gas; high concentrations fatal via pulmonary edema. Chronic exposure linked to respiratory disease.

Table3. Comparative analyses of VOCs from various processing stages in leather production [28].

Chemicals	**Classification**
Acetone Cyclohexane Cyclohexanone n-butyl alcohol Ethanol 2-ethoxyethanol Isopropyl alcohol 2-methoxyethanol Napata	Non-HAP VOC's
Benzene Cumene	HAP VOC's

Diethanolamine Ethylene glycol Glycol ethers Formaldehydes Methanol Methyl chloroform Methyl ethyl ketones methyl isobutyl ketones Methylene chloride Tetrchloroethylene Triethylchlooroethylene Triethyl amine Toluene Xylene	HAP VOC's
Chlorine Chromium Chromium compounds Hydrochloric acid Manganese compounds	Non-VOC's HAP

HAP- Hazardous air pollutant

2.2.3.1. Source of VOC's emissions

There are number of source of VOCs emission in leather manufacturing process but the major sources are

- Leather finishing operation;
- Waterproofing operations;
- Solvent degreasing operations and
- Miscellaneous fugitive sources

Leather finishing operation

Leather finishing often utilizes multiple coating layers to achieve the desired aesthetic and performance properties tailored to end use. Most leather pieces receive 3-5 discrete coating

applications [29]. Spray coating, where coatings are atomized and projected onto leather, is the predominant technique due to its efficiency and versatility across varying substrates. However, alternatives like roll, reverse roll and curtain coating offer unique advantages. Roll coating works finished compounds into grain texture through contact with a reverse-patterned roller [30]. This embeds coatings without obscuring natural markings. Curtain coating suspends finishing solutions before leather passes through, imparting an even coating over large areas ideal for upper leathers. Reverse roll coating pulls leather back through contacting rollers to load fibers more thoroughly from the reverse side. The spray coating application technique, widely used in leather finishing introduces volatile organic compound (VOC) emissions at several stages [31]. Upon contact with leather surfaces, solvents in coatings experience rapid evaporation in the "flash zone" between the spray booth and dryer [32]. Overspray bouncing back from leather or flashing off before deposition similarly releases vapors. With spray booths often ventilated directly outside, these evaporating solvents emitted in the initial application area contribute substantially to VOC levels. Dryer's thereafter, frequently partially or fully enclosed further concentrate evaporating solvent as heated leather accelerates the drying process. The accumulated volumes released from finishing booths and dryers comprise a major source of industry VOC output [33].

Waterproofing operations

Waterproofing is a critical finishing step that renders leather impervious to water. It involves application of water-repellent chemicals to the surface. The emission potential of waterproofing process is high because the amount of organic solvent used to dispense the silicon material. Data obtained from industry source indicate VOC emission from waterproofing ranges from 12.3 to 27.8 pounds per 1000 square feet of leather processed [28]. Common waterproofing agents include paraffin and synthetic polymers like Acrylate, polyurethanes and fluorocarbons. Paraffin wax emits alkanes and cyclic hydrocarbons upon application and curing. Fluorocarbons are highly effective but release per fluorinated compounds (PFCs) including PFOA and PFOS - persistent organic pollutants that bioaccumulate, Acrylate and polyurethane finishes emit aromatic and aliphatic hydrocarbon VOCs during curing through thermal decomposition. Compounds like toluene, xylene and formaldehyde are also common and long-term, low-level exposure poses inhalation health risks [34] [35].

Solvent degreasing operations

Solvent degreasing operations are used in small segment of the industry in the wet-end processing of sheep and pig skin. In solvent degreasing, solvent such as perchloroethylene are used to reduce the skin grease content to desired levels and evenly distribute the residual grease prior to tanning. Emissions of VOCs result primarily from evaporation as the degreasing drums are drained and skin uploaded. A study conducted in United Kingdom generated emission estimate for degreasing operation ranges from 600 to 700 mg/m^3 in working areas and airing off cycle (draining and uploading of skin) showed VOC concentration 16000 to 19000mg/ m^3 again from data provides by U.S leather industry show emission resulting from degreasing operation to be about 12.4 pounds of VOC per1000 square feet of leather processing [28].

Miscellaneous fugitive sources

There are number of sources for VOC emission which includes mixing room, coating drum, waste water, cleanup operations, drying operation and hand application of coating materials…etc. each of this operation emits high amount of VOCs which could potently deteriorate the quality of air.

Table 4. Emission of VOCs from leather processing monitored in United Kingdom (1990) [28].

Source		Pollutant	Quantity (mg/m^3)
Crust leather operation	Beam house operation	Hydrogen sulfide, ammonia	Up to 7.1* Up to 35.5*
	Tan yard	Ammonia	Up to 14.2*
Finishing operation	Conveyorised sprayer	VOC	-
	Water –diluted nitrocellulose	VOC	7 to 800**
	Solvent- diluted nitrocellulose	VOC	1200 to 3700**
Finish dryer	Water –diluted nitrocellulose	VOC	Nil to 100**
	Solvent- diluted nitrocellulose	VOC	1200**
* Work place level converted to (mg/m^3) ** Discharge to air vi exhaust system			

2.2.3.2 VOC abatement techniques

Techniques for VOC abatement can be broadly characterized as recovery re-use techniques and destruction techniques. The selection of the appropriate abatement method relies on several factors, including the temperature, composition, and concentration of VOCs in the pollution, the gas flow rate, as well as the installation and operational expenses.

Recovery and re-use techniques

Absorption: - absorption is a technique used for the abatement of Volatile Organic Compounds (VOCs) in which a soluble gas molecule is transferred to a solvent liquid, such as water or low volatility hydrocarbons [40]. This process occurs when the VOCs present in waste gases come into contact with the liquid solvent, and the VOC molecules dissolve into the liquid phase. Absorption systems are particularly effective in treating waste gases that contain high concentrations of VOCs, typically ranging from 500 to 5,000 parts per million (ppm) [39]. These systems are designed to handle such high VOC concentrations and provide an efficient means of removing VOCs from industrial emissions. Classically, absorption is used to remove VOCs from gas streams by bringing the contaminated air into contact with a liquid solvent. Any soluble VOCs transfer to the liquid phase and the air stream is effectively scrubbed. This takes place in an absorber tower designed to provide the gas-liquid contact area necessary to facilitate mass transfer [41]. The absorption process typically involves the following steps:

- Contacting phase: The waste gas stream, which contains high concentrations of VOCs, is brought into contact with the liquid solvent. This contact can occur either through direct contact between the gas and liquid or through the use of packed or tray columns, where the gas and liquid flow counter currently.
- Mass Transfer: During the contact phase, the VOC molecules present in the gas phase transfer into the liquid solvent phase. This transfer occurs due to differences in concentration and affinity between the gas and liquid phases. The VOC molecules dissolve into the solvent, leading to their removal from the gas stream.
- Separation Phase: Once the VOCs have been absorbed into the liquid solvent, the gas and liquid phases are separated. This can be achieved through various separation techniques, such as gravity settling, centrifugation, or filtration. The separated gas can

then be released into the atmosphere, while the liquid solvent containing the absorbed VOCs can undergo further treatment or disposal.

Adsorption: **-** The adsorption method involves the separation of volatile organic compound (VOC) molecules from the atmosphere through the utilization of Van der Waals interactions or chemical bond interactions that occur between the surface of the adsorbent and VOC molecules. This separation process is guided by the adsorption selectivity of the adsorbent, which determines the specific VOC molecules that can be captured and retained on the surface of the adsorbent material. According to its adsorption type; it is divided into physical adsorption and chemical adsorption [42]. Physical and chemical adsorptions are two main mechanisms by which adsorbate molecules bind to an adsorbent surface. The distinction between the two processes lies in the nature of the adsorbate-adsorbent interactions. In physical adsorption, also known as physisorption, the adsorbate molecules are bound to the adsorbent surface by relatively weak van der Waals forces. The process is driven by intermolecular forces between the adsorbate and adsorbent, such as London dispersion forces, and does not require any valence bond formation or breaking. As a result, physical adsorption is a non-specific, exothermic process that is readily reversible with minimal energy input. In contrast, chemical adsorption or chemisorptions involves the formation of chemical bonds such as covalent or ionic bonds between the adsorbate species and functional groups on the adsorbent surface It is a selective, saturable process that requires much higher activation energy compared to physical adsorption.

The bonds formed during chemisorptions are generally stronger and not easily broken, making the process less readily reversible than physical adsorption [43-45]. In comparison to alternative approaches, the adsorption method for treating volatile organic compounds presents notable advantages that include high removal efficiency, low energy consumption, affordability, and a well-established operational framework. Although the effectiveness of adsorption is subject to various influencing factors, it remains one of the most widely employed techniques in VOC treatment. Recognized as a highly promising technology, adsorption stands out for its cost-effectiveness, operational flexibility, and minimal energy requirements well-designed adsorption systems may achieve recovery efficiencies of about 95% - 98%. These favorable attributes, coupled with its extensive application, make adsorption a significant area of research in the field of VOC treatment. A wide variety of porous adsorbent materials have been extensively studied

for applications like pollutant removal owing to properties such as large surface area and structural rigidity that make them suitable for efficient adsorption. Activated carbon continues to be one of the most widely used adsorbents due to its high adsorption capacity resulting from optimized porosity and surface properties imparted by controlled activation/processing techniques [46]. Other adsorbents including porous silica, zeolites, carbon nanotubes and molecular sieves have also shown promise for adsorption-based applications because their pore characteristics can be tailored to specific adsorbate through synthesis methods [45].

The adsorption efficiency depends on factors related to the adsorbent properties as well as process conditions. The adsorbent surface area, pore size distribution and functional groups play an important role in determining the adsorption affinity and capacity since they govern accessibility of binding sites and adsorbate-adsorbent interactions [44-45]. Larger surface area and presence of micro pores enhance contaminant uptake while surface modifications introduce targeted binding sites [47]. Characteristics of the adsorbate like size, shape and concentration also influence the interaction strength with the adsorbent [43]. Process parameters such as temperature, pH and flow rate need optimization for maximum adsorption performance. Among various adsorbents studied carbon materials have emerged as very promising owing to their tunable porosity, high surface area and surface chemistry that can be leveraged through processing techniques. Pre-treatments and doping methods further help enhance their adsorption based on end-use applications. A thorough understanding of influential material-process variables is essential for developing efficient adsorption-based treatment protocols.

Classification of Adsorption Processes

Adsorption separation techniques can be broadly classified based on the operation mode of the adsorption column or vessel. An understanding of different process configurations is crucial for selecting the optimal design for a given adsorption application.

- ♣ *Fixed-Bed Adsorption*

In fixed-bed adsorption systems, the solid adsorbent particles are stationary within a packed bed through which the process stream continuously flows [45]. While simple in design and operation, issues arise due to poor utilization of the bed depth and premature breakthrough of the adsorbate [43]. Optimization of bed dimensions and process conditions is necessary to maximize capacity.

- *Fluidized-Bed Adsorption*

An alternative is fluidized-bed adsorption where the solid adsorbent is kept in continuous motion through the upward flow of gas or liquid. This enhances mass transfer rates and yields higher throughput. However, complex hydrodynamic modeling is required to maintain stable fluidization and prevent fines entrainment [50].

- *Continuous Moving-Bed Adsorption*

A more advanced configuration involves the continuous downward movement of the solid adsorbent counter-current to the ascending process stream in a packed bed [44]. This offers improved capacity with negligible mass transfer limitations. Nevertheless, the energy intensive movement and complex equipment add to costs.

- *Pressure/Temperature Swing Adsorption Processes*

PSA and TSA utilize pressure or temperature changes to modulate the adsorption-desorption equilibrium for continuous regeneration [50]. While enabling high throughput, challenges arise from complex cycling, thermal effects and difficulty achieving high product purity [43].

In summary, no single process is universally suitable. Careful evaluation of adsorbate properties and system constraints aids in selecting the design best balancing performance and economic feasibility. Further research must also develop hybrid configurations to enhance capacity and throughput.

Condensation: - Condensation is an effective thermal separation process widely used for recovering volatile organic compounds (VOCs) from gas streams. The technique relies on lowering the temperature of the contaminated air below the dew point of VOCs, causing them to condense into liquid phase [43, 49]. Saturation (dew point temperature) occurs when the partial pressure of the volatile organic compound is equal to its vapor pressure. Once saturation temperature has been attained, separation via condensation occurs by either increasing the system pressure at constant temperature (known as compression condensation) or by lowering the temperature at constant pressure (known as refrigerated condensation). Refrigerated condensation occurs by means of direct contact between gas and cooling liquid or indirect contact via heat exchanger with a cooling medium [48]. In direct contact condensation, the hot

gas is brought into intimate contact with a cooling medium like water spray to rapidly reduce its temperature; usually indirect condensation is preferred because direct condensation requires an additional separation stage.

The choice of condensation technology depends significantly on the required operating temperature range for effective VOC capture [43, 49]. Coolant condensation systems, utilizing water or glycol as the cooling medium, are suitable when the minimum condensing temperature needs to be approximately 25°C or higher [49]. Refrigerant-based condensation is suitable for applications permitting minimum temperatures as low as 2°C, through direct expansion or indirect cooling of refrigerants like R-22 or R-13a [48].For processes requiring lower condensing temperatures, ammonia brine systems can achieve single-stage minimums of -40°C or two-stage minimums of -60°C through evaporative cooling[47]. The most versatile option is cryogenic condensation, using cryogens such as liquid nitrogen to attain minimum temperatures down to -120°C in a single stage through Joule-Thomson expansion [44].

Membrane separation; - Membrane separation techniques have gained significant importance in various industries due to their ability to provide efficient and cost-effective separation processes. These techniques utilize different types of membranes, which act as barriers to separate components based on their size, charge, or solubility.

- *Reverse Osmosis (RO):*

Reverse osmosis is a membrane process that utilizes a semi permeable membrane to separate solutes from a solvent. It operates by applying pressure to overcome the osmotic pressure and force the solvent through the membrane, leaving behind the solutes. RO is widely used for desalination of seawater, purification of drinking water, and concentration of solutions. Its advantages include high selectivity, removal of a wide range of contaminants, and low energy consumption. However, RO membranes are susceptible to fouling and require regular maintenance [51].

- *Ultrafiltration (UF):*

Ultrafiltration is a membrane process that operates on a similar principle to RO but with larger pore sizes. It effectively removes particles, colloids, and macromolecules, while allowing smaller

molecules and ions to pass through. UF is commonly used in the food and beverage industry, wastewater treatment, and protein purification. Its advantages include high flux rates, low energy requirements, and the ability to retain essential molecules. However, it may not effectively remove small solutes and salts [52].

- *Nanofiltration (NF):*

Nanofiltration is a hybrid process between RO and UF, with a pore size between the two. It is effective in removing divalent ions, organic matter, and color-causing compounds from water. NF is widely used in water treatment, pharmaceuticals, and dairy industries. Its advantages include high selectivity; lower operating pressures compared to RO, and improved flux rates. However, NF membranes are prone to fouling and require careful pretreatment of the feed solution [53].

- *Gas Separation Membranes:*

Gas separation membranes are used to separate mixtures of gases based on their permeability through the membrane. These membranes are commonly employed in applications such as natural gas purification, hydrogen recovery, and carbon dioxide capture. The advantages of gas separation membranes include simplicity, compactness, and energy efficiency. However, their selectivity can be limited, [51] and the presence of impurities in the gas stream can affect membrane performance. Membrane separation techniques offer several advantages over traditional separation methods, including high efficiency, lower energy consumption, and compact system design. They are also environmentally friendly compared to other separation techniques that may require chemicals or produce waste. However, they do have some drawbacks, such as membrane fouling, limited selectivity, and the need for regular maintenance and replacement.

Destruction Techniques

Thermal oxidation; - Thermal oxidation techniques are widely used for the treatment of volatile organic compounds (VOCs) present in waste streams. These techniques involve exposing VOC-containing gases to high temperatures, typically between 800 and 1,200 degrees Celsius, to facilitate the breakdown of pollutants into less harmful compounds. Thermal oxidation

techniques are commonly used in various industries, including chemical manufacturing, pharmaceuticals, and waste management, for the treatment of VOC-containing waste streams. These techniques offer several advantages, such as high destruction efficiency, versatility in handling a wide range of VOCs, and minimal secondary waste generation compared to other methods like adsorption or solvent extraction [55]. They provide an effective means of reducing the emission of hazardous pollutants into the environment.

However, thermal oxidation techniques also have some drawbacks. They consume a significant amount of energy due to the high operating temperatures required, resulting in high operational costs and contributing to greenhouse gas emissions. Additionally, the potential formation of hazardous byproducts, such as NOx and CO, requires careful monitoring and control to ensure compliance with environmental regulations. To optimize the performance of thermal oxidation techniques, factors such as proper waste stream characterization, burner design, temperature control, and gas residence time need to be considered. Ongoing research focuses on developing advanced catalysts, improving energy efficiency, and exploring alternative technologies to minimize the drawbacks associated with thermal oxidation.

- *Thermal Incineration:*

Thermal incineration is a commonly employed technique that involves the complete combustion of VOCs in the presence of excess oxygen. VOC-laden gases are introduced into a combustion chamber and brought to high temperatures. The high heat breaks down the VOCs into carbon dioxide and water vapor. The generated heat can be recovered and used for energy generation [54]. Thermal incineration offers high destruction efficiency and is effective in removing even low concentrations of pollutants. However, it requires significant energy input and may produce hazardous byproducts such as nitrogen oxides (NOx) and carbon monoxide (CO) [55].

Catalytic oxidation; **-** Catalytic oxidation techniques are utilized for the removal of volatile organic compounds (VOCs) from waste streams. These techniques involve the use of catalysts to facilitate the oxidation of VOCs at lower temperatures compared to thermal incineration. Catalytic oxidation operates on the principle of passing VOC-laden gases over a catalyst bed, where the catalyst accelerates the oxidation reaction, converting the VOCs into carbon dioxide and water vapor. The advantages of catalytic oxidation include lower energy consumption,

reduced formation of hazardous byproducts, and the ability to handle a wide range of VOCs. However, careful catalyst selection, potential catalyst deactivation, and limitations in treating certain VOCs are important considerations. Catalytic oxidation techniques are widely employed for the treatment of VOC-laden waste streams, offering effective removal of hazardous pollutants. These techniques utilize catalysts to lower the required operating temperature, making them more energy-efficient compared to thermal oxidation methods such as incineration.

The key process involved in catalytic oxidation is the interaction between the VOCs and the catalyst. VOC-laden gases are passed over a catalyst bed, typically comprised of metals such as platinum, palladium, or rhodium, or metal oxides like manganese or cerium oxides. The catalyst provides a surface for the oxidation reaction to occur, facilitating the conversion of VOCs into carbon dioxide and water vapor. The catalyst itself remains unchanged during the process [54]. The operating principle of catalytic oxidation is based on the ability of the catalyst to lower the activation energy required for the oxidation reaction, thus allowing the reaction to occur at lower temperatures compared to non-catalytic thermal oxidation. The catalyst provides active sites where the VOC molecules can absorb and react with oxygen, leading to their conversion into less harmful compounds [54]. Catalytic oxidation techniques find extensive use in various industries for the removal of VOCs from waste streams. They are particularly employed in chemical manufacturing, pharmaceuticals, and petrochemical industries. These techniques provide an efficient and environmentally sound method for reducing the emission of hazardous pollutants into the atmosphere.

Advantages of catalytic oxidation techniques include:

- ♣ Lower Energy Consumption: Catalytic oxidation operates at lower temperatures compared to thermal incineration, resulting in reduced energy requirements and operational costs.
- ♣ Reduced Formation of Hazardous Byproducts: Catalytic oxidation promotes selective oxidation of VOCs, minimizing the formation of hazardous byproducts such as nitrogen oxides (NOx) and carbon monoxide (CO).
- ♣ Versatility in Handling Different VOCs: Catalytic oxidation is effective in treating a wide range of VOCs, including halogenated compounds and complex mixtures, making it a versatile technique for various industrial applications.

However, there are some drawbacks associated with catalytic oxidation techniques:

- ♣ Catalyst Selection: The choice of catalyst is crucial and depends on the specific VOCs present in the waste stream. Different catalysts have varying degrees of activity and selectivity towards different VOCs, requiring careful consideration during catalyst selection.
- ♣ Catalyst Deactivation: Catalyst deactivation can occur over time due to factors such as fouling, poisoning, or sintering, leading to decreased performance. Regular catalyst maintenance and replacement are necessary to maintain optimal performance.
- ♣ Limitations in Treating Certain VOCs: While catalytic oxidation is effective for a broad range of VOCs, certain compounds, such as highly chlorinated or fluorinated VOCs may be less amenable to oxidation. In these cases, additional treatment steps may be required.

Biofiltrations: **-** Biofiltrations techniques are commonly employed for the removal of volatile organic compounds (VOCs) from waste streams. These techniques utilize microorganisms residing in a biofilm to biodegrade the VOCs into less harmful byproducts. Biofiltrations operates on the principle of passing VOC-laden gases through a bed of organic material, where the microorganisms in the biofilm metabolize the VOCs. The advantages of biofiltrations include high removal efficiencies, low energy consumption, and minimal production of secondary waste. However, factors such as biofilm stability, nutrient availability, and limited applicability to specific VOCs need to be considered. Biofiltrations techniques are widely used for the treatment of VOC-laden waste streams, providing an environmentally friendly and cost-effective approach.

The key process involved in biofiltrations is the interaction between the microorganisms and the VOCs. VOC-laden gases are passed through a bed of granular or porous organic material, such as compost, wood chips, or peat moss. This organic material serves as a support medium for the growth of a biofilm, which consists of microorganisms, including bacteria and fungi. As the VOC-laden gases flow through the biofilter, the microorganisms in the biofilm metabolize the VOCs, breaking them down into simpler, non-toxic compounds, such as carbon dioxide and water[56].The operating principle of biofiltration is based on the ability of the microorganisms in the biofilm to use the VOCs as a carbon and energy source. The microorganisms have enzymes that can transform the VOCs into metabolites through a series of biodegradation reactions. The

VOCs diffuse into the biofilm and are consumed by the microorganisms, resulting in their conversion into harmless end products [56].

Advantages of biofiltration techniques include:

- ♣ High Removal Efficiencies: Biofiltrations can achieve high removal efficiencies, typically above 90%, for a wide range of VOCs.
- ♣ Low Energy Consumption: Compared to other VOC treatment technologies, biofiltration requires minimal energy input, primarily for fan operation to maintain airflow through the bio-filter.
- ♣ Minimal Production of Secondary Waste: Biofiltrations does not produce significant amounts of hazardous byproducts or residues, minimizing the generation of secondary waste streams.

However, there are some drawbacks associated with biofiltration techniques:

- ♣ Biofilm Stability: The stability of the biofilm is crucial for the long-term performance of the biofilter. Factors such as pH, temperature, moisture content, and the presence of toxic compounds can affect the biofilm's stability, requiring careful monitoring and control.
- ♣ Nutrient Availability: The growth and activity of the microorganisms in the biofilm depend on the availability of nutrients, such as carbon, nitrogen, and phosphorus. Adequate nutrient supply is essential to ensure optimal biofilter performance.
- ♣ Limited Applicability to Specific VOCs: Biofiltration may have limitations in treating certain VOCs, such as highly chlorinated compounds or compounds with low water solubility. In such cases, pre-treatment or alternative treatment technologies may be necessary.

2.3. Catalytic activated carbon for VOC control

Catalytic oxidation of VOCs using carbon impregnated with a molybdenum catalyst is an effective method for VOC reduction in various industries, including leather production. This process involves the use of activated carbon, which has a high surface area and adsorption capacity, combined with the catalytic properties of molybdenum to convert VOCs into less harmful compounds through oxidation. Activated carbon, commonly derived from carbonaceous

materials like coal, shells and grain husks this materials possesses a porous structure that provides a large surface area for adsorption. This allows the activated carbon to capture and retain VOC molecules from the surrounding air or gas streams. The impregnation of activated carbon with a molybdenum catalyst enhances its catalytic capabilities, promoting the oxidation of VOCs.

The molybdenum catalyst acts as a facilitator for the oxidation process by providing active sites for the reaction to occur. Molybdenum (Mo) Molybdenum catalysts have gained significant attention in catalytic oxidation processes due to their effectiveness in promoting oxidation reactions. They possess unique properties, including high redox potential, excellent thermal stability, and versatility in accommodating a wide range of organic compounds. The ability of molybdenum to exist in different oxidation states, such as +2, +3, +4, +5, and +6, enables it to participate in redox reactions during catalytic oxidation. This transition between oxidation states allows molybdenum catalysts to actively engage in the oxidation of organic pollutants, enhancing reaction rates and improving selectivity. Additionally, molybdenum catalysts offer advantages over other oxidants, such as cost-effectiveness, lower operating temperatures, and sustainable performance. These characteristics make molybdenum catalysts a promising choice for various applications in waste treatment and environmental remediation is a promising catalyst for this application. Impregnating activated carbon with Mo oxide via wet impregnation enhances the catalytic activity as the VOC-laden air or gas passes through the carbon impregnated with the molybdenum catalyst, the VOC molecules adsorb onto the surface of the activated carbon [38]. The mechanism involves VOCs first adsorbing onto carbon pores via weak van der Waals forces [7]. This brings the pollutants in close contact with dispersed Mo oxide sites. The catalyst then activates oxygen and promotes VOC oxidation even at room temperature [28].The catalytic properties of molybdenum then initiate the oxidation reaction, transforming the VOCs into carbon dioxide (CO_2) and water (H_2O), which are environmentally benign byproducts. The catalytic oxidation process offers several advantages for VOC reduction in the leather industry. Firstly, it provides a cost-effective solution by utilizing activated carbon, which is readily available and relatively inexpensive. Additionally, the use of a molybdenum catalyst enhances the oxidation efficiency, ensuring a high conversion rate of VOCs into harmless compounds. Furthermore, the catalytic oxidation process can be integrated into existing production systems with relative ease.

By incorporating carbon impregnated with a molybdenum catalyst into the ventilation or exhaust systems, VOC emissions can be effectively treated before being released into the atmosphere. This approach minimizes the environmental impact of VOCs and helps the leather industry comply with regulatory standards. It is important to note that the specific conditions and parameters for the catalytic oxidation process, such as temperature, residence time, and catalyst loading, may vary depending on the specific VOCs present in the leather production process. Therefore, optimization of these parameters is necessary to achieve maximum VOC removal efficiency. In conclusion, the catalytic oxidation of VOCs using carbon impregnated with a molybdenum catalyst is a promising method for VOC reduction in the leather industry. By leveraging the adsorption capacity of activated carbon and the catalytic properties of molybdenum, this approach provides an effective and environmentally friendly solution for mitigating VOC.

2.3.1. Comparative Analysis of Catalyst-Impregnated Activated Carbon Systems for VOC Removal

Several studies have made valuable contributions to advancing catalyst-impregnated activated carbons for VOC removal. A 2020 study investigated manganese oxide-impregnated carbon for formaldehyde degradation. Gas chromatography confirmed an 85% formaldehyde reduction compared to non-impregnated carbon. Fourier transform infrared spectroscopy identified the products as CO_2 and H_2O, indicating complete mineralization via catalytic oxidation. While providing mechanistic insights, the study also observed significant manganese leaching under acidic conditions simulated in the lab, which could impact long-term catalyst stability and pose environmental risks if ions are released. Similarly, a 2019 study analyzed titanium dioxide-impregnated carbon for benzene photo-degradation. Gas chromatography-mass spectrometry identified intermediates like phenol and catechol, aided by titanium dioxide's photoelectron generation as evidenced by UV-visible spectroscopy a90% removal efficiency was reported under irradiation. However, reliance on sunlight introduces performance variability. Surface fouling or poisoning over extended usage also warrants investigation to assess efficacy changes.

Another study examined copper oxide-impregnated carbon for nitrobenzene ozonation, achieving 96% reduction as observed via high-performance liquid chromatography. However, inductively

coupled plasma mass spectrometry results revealed extensive copper leaching under acidic conditions mirroring concerns for manganese leaching stability. While these systems demonstrated initial VOC removal successes, long-term reliability depends on mitigating catalyst mobilization issues and characterizing influences of fluctuating wastewater compositions. Subjecting varied formulations to standardized aging protocols could elucidate comparative resilience. Optimizing catalyst design and operational conditions coupled with mitigating identified limitations are critical before full-scale implementation. Continued research is still needed to thoroughly evaluate performance, costs and environmental impacts.

CHAPTER THREE

3. Materials and Methods

3.1. Materials

In the context of advanced research in the field of VOC reduction using molybdenum-catalyzed carbon, a selection of raw materials plays a crucial role in facilitating controlled experimental processes aimed at evaluating the efficacy of this methodology. The fundamental materials employed include activated carbon made from rice husk, high-purity molybdenum V chloride (99.99%), sulphric acid, potassium dichromate, mercury sulfate, ferrous ammonium sulfate, sodium hydroxide, boric acid, hydrogen peroxide, and phosphoric acid. All chemicals utilized in this study were of analytical grade and procured from SD Fine-Chem. Furthermore, essential equipment utilized in the experimental setup encompassed a range of sophisticated instruments and tools such as pH meter, oxidation-reduction potential (ORP) meter, precise analytical weighing balance, glass jars, laboratory ovens, furnaces, COD analyzer, aeration tank, absorption tank, pressure gauge, UV-spectrophotometer, total organic carbon (TOC) analyzer, scanning electron microscope (SEM), X-ray diffraction (XRD) analyzer, Fourier-transform infrared (FTIR) spectrometer, energy-dispersive X-ray spectroscopy (EDAX) system, electron paramagnetic resonance (EPR) spectrometer, and various laboratory apparatus including glassware, sampling tools, vacuum pump, and safety gear. It is noteworthy that all chemicals and equipment mentioned above were sourced from CSI-CLRI.

3.2 Methodology

The process for preparation and utilization of activated carbon impregnated with a molybdenum catalyst involves collection and preservation of sample, preparation of the activated carbon with high surface area, followed by incorporation of molybdenum catalyst onto the activated carbon surface through impregnation, deposition, precipitation, or ion-exchange methods, and evaluation of physical and chemical parameters of the catalyst system. Finally, analytical tests are conducted to assess the efficiency of the catalyst system in adsorbing and removing pollutants, such as measuring chemical oxygen demand (COD) and total organic and analytical tests to assess the efficiency of the activated carbon catalyst system.

3.1.1. Sample Collection and Preservation

The sample collection procedure was carefully designed to ensure the integrity and representativeness of the VOC analysis. First, samples were collected directly from the leather

effluent stream in amber glass jars with air-tight lids to prevent volatilization loss during transport. Immediately after collection, 2 drops of sulfuric acid were added to each jar to acidify the samples and inhibit microbial growth. Upon arrival, the collected samples will be securely placed within the closed flask, undergoes a stripping procedure by varying the pressure of air passing through on our case atmospheric air at 1l/min were purged. This controlled process allows the VOCs to be released from the closed jar and collected in the separate flask, where the environmental conditions, such as pH, are manipulated for further analysis the pH of which could be adjusted between 2-12 using sulfuric acid or sodium hydroxide solutions.

The absorbent trap contained 500mL of distilled water which Solubuilised the VOCs for later analysis. Once purging was complete, as indicated by minimal odors in the off-gas, Additional sample aliquots were analyzed for COD, sulfide, ammonia, TDS and TSS using standard methods.

Fig.1 Apparatus for VOC stripping and condensation

3.1.2. Preparation of Activated Carbon

The raw material selected is rice husk was obtained from CSIR-CLRI environmental laboratory. Rice husk contains favorable properties for activated carbon production due to its high silica (15-25%) this high silica content benefits the formation of activated carbon through various

mechanisms. During the carbonization process, silica acts as a template, influencing the structure of the carbon material which facilitates the creation of pores and provides a framework for the development of a porous network in the activated carbon essential for adsorption applications on the other hand when silica react with the activator phosphoric acid during the activation process, the acid leaches out the silica, creating additional pores in the carbon structure. This reaction not only increases the number of pores but also enhances the surface area of the activated carbon, further improving its adsorption properties. The synergistic effect of silica in rice husk and its reaction with phosphoric acid during the activation process culminates in the formation of activated carbon with optimal porosity, surface area, and adsorption capabilities

Other contents like lignin (15-30%) and cellulose content, give it a highly porous structure upon activation through controlled heating/carbonization. The rice husk is first thoroughly washed and soaked in distilled water overnight to remove any impurities or contaminants. It is then sun-dried for 24 hours to ensure complete moisture removal. The dried rice husk is placed in a sealed container and inserted into a furnace. It undergoes pre-combustion at 400°C for 4 hours to eliminate any residual organic matter resulting in a hard and black, lightweight char material. After pre-combustion, the rice husk char is sieved to obtain a refined, uniform particle size Further activation is done using chemical agents such as $ZnCl_2$, H_3PO_4 or KOH in this case a 150g of rice husk was impregnated in 1500ml of phosphoric acid with mass ratio 1:1 the mixture left overnight to ensure uniform impregnation; once fully impregnated the activated sample was washed with distilled water until the pH reach 6-7 then the washed sample is dried at 110^0c for 12 hr to remove excess moisture. This treatment at elevated temperatures leads to development of porosity within the charred rice husk structure. The activated carbon produced has favorable adsorption properties for pollutants due to its increased surface area and porous characteristics imparted by the carbonization and activation processes. It can then be characterized further for optimized applications.

Rice husk

Rice husk +
phosphoric acid

Activated carbon

Fig.2 preparation of activated carbon from rice husk

3.1.3. Preparation of Molybdenum impregnated rice husk:

A controlled procedure was developed and optimized to prepare molybdenum impregnated activated carbon from rice husk at varying metal loadings. Raw rice husk (600 g) was obtained and divided uniformly into four batches of 150 g each. Molybdenum (V) chloride solutions of defined concentrations, namely 1%, 3%, 5% and 7% w/w, were prepared by precisely weighing 1.4881 g, 4.4643 g, 7.4405 g and 10.3267 g of $MoCl_5$ respectively, and dissolving in 250 ml distilled water to ensure homogenous impregnation of the rice husk batches here; It is crucial to handle the molybdenum catalyst with care, avoiding any contact with the eyes or throat due to its hazardous nature. Each batch was soaked in the respective impregnation solutions for 12 hours with intermittent stirring to facilitate uniform absorption of $MoCl_5$ into the porous rice husk structure. The soaked samples were dried at 110°C for 10-12 hours in a laboratory oven to remove excess moisture. Next, thermal treatment was carried out in a programmable furnace at 400°C for 4 hours with a controlled ramp of 5°C/min under inert nitrogen flow to induce carbonization of the dried precursors. Subsequently, chemical activation was performed at 650°C for 1 hour using 85% phosphoric acid. The activated carbons thus obtained were washed thrice each with hot and cold deionized water to remove residual acid and impurities. Finally, the samples were labeled appropriately based on molybdenum loading as 1%Mo/AC, 3%Mo/AC,

5%Mo/AC and 7%Mo/AC for systematic characterization and evaluation. Plausible interaction of MO with ACM can be represented by

$$RH + MoCl_5 \rightarrow [RH] — MoCl_5$$

$$[RH] — MoCl_5 \rightarrow [PRH — Mo] + H_2O\uparrow + CO_2\uparrow + 5Cl_{2(g)}\uparrow$$

$$2[PRH — Mo] + 2H_3PO_4 \rightarrow 2MO\text{-}ACM + 1/2\ P_2O_5\uparrow + 3H_2O\uparrow$$

3.1.4. VOC Reduction Process:

The following procedure was developed for generating toluene, benzene and formaldehyde contaminated water samples and evaluating their treatment using packed bed reactors containing activated carbon catalysts. Raw contaminated water was prepared by stripping 500mL of the target VOC (toluene, benzene, formaldehyde and leather waste water) from a leather effluent stream using atmospheric air in a sealed reactor with flow controlled at optimized conditions as shown in Fig.1.The stripped gases were bubbled through a condenser to dissolve in 500mL distilled water, producing toluene contaminated water (TCW), benzene contaminated water (BCW) or formaldehyde contaminated water (FCW) respectively. The collected samples from the leather effluent will pass through a bed of the prepared activated carbon impregnated with the molybdenum catalyst i.e. two packed bed catalytic reactors (PBCR) were constructed from acrylic tubes (4.5cm diameter x 50cm height) with a 500mL working volume. Quartz aggregate was packed to 5cm height, followed by finer aggregates to 10cm height to support the catalyst bed. Activated carbon (ACM) or molybdenum-modified activated carbon (Mo-ACM) was separately packed as catalysts to a 35cm bed height, creating the ACM-PBCR or Mo-ACM-PBCR systems. The contaminated water samples were treated individually in the PBCRs by sprinkling onto the catalyst bed at optimized pH, hydraulic retention time and 0.2ml/l hydrogen peroxide dosage which acts as an activator to promote the catalytic degradation of VOCs on the surface of the activated carbon and molybdenum-modified activated carbon.. Treated effluents were collected for analytical characterization. This standardized procedure enables generation of model VOC-contaminated waters and evaluation of novel carbon-based catalysts for water remediation under controlled conditions relevant to real industrial effluents.

Fig.3 model of Mo-ACM-PBCR

3.1.5. Characterization of VOC's from leather Effluent and Activated Carbon-Based Catalytic Systems

Measurement of VOCs from leather effluent using a Portable Gas Detector

Volatile organic compounds (VOCs) present from leather effluent were analyzed using a Tiger SXT gas detector (ION Science, UK). The Tiger SXT is a portable photo ionization detector (PID) equipped with a 10.6eV ultraviolet lamp, allowing detection of a wide range of VOCs. Samples of untreated leather effluent collected were used for VOC analysis. The Tiger SXT was calibrated as per manufacturer instructions using isobutylene calibration gas of known concentration. The detection limit of the instrument for most VOCs is less than 1 part per million (ppm).For sample measurement, the effluent was transferred into 500ml glass bottles sealed and securely placed within the closed flask, undergoes a stripping procedure by varying the pressure of air passing through on our case atmospheric air at 1 l/min were purged lined lids. The Tiger SXT probe, fitted with a 0.2µm PTFE (polytetrafluoroethylene.) filter, was inserted through into the headspace above the glass bottle. VOC concentrations were recorded after allowing sufficient time for equilibration duplicate measurements were taken for each sample and average readings used for quantification. Concurrent measurements of blank deionized water were also made to subtract background readings. This allowed rapid field screening of leather effluent to identify

predominant VOCs present above detection limits, facilitating selection of appropriate treatment methods.

Fig.4. VOC detection using portable photo ionization detector (PID)

3.1.6 Phiso-chemical characteristics of VOCs, ACM and Mo-ACM

Chemical oxygen demand (COD):- COD is a measure of the amount of oxygen required to oxidize organic matter in water. The COD from effluent was measured using laboratory COD digester via the closed reflux titrimetric method (APHA 5220 D). Samples were digested in a sulfuric acid-potassium dichromate solution at 150°C for 2 hours. Remaining dichromate was titrated with ferrous ammonium sulfate using ferroin indicator, calculating COD as milligrams of oxygen consumed per liter the result is measured according to the following.

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

Where A= blank Titrant value

B= titrate value

N= normality of FAS

D.F= dilution factor (if any)

Total 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. USEPA Method 9060A was used to determine the TOC of the samples; Shimadzu TOC-L ROHS instrument used to analyze the VOC contaminated water. This method involves oxidizing the organic carbon in the sample to carbon dioxide using a per-sulfate-based oxidant Determination of Total Organic Carbon using Shimadzu TOC-L ROHS Instrument. Samples are injected into the catalyst combustion tube packed with platinum alumina catalysts. At 680°C, organic carbon compounds are completely oxidized to CO_2, along with inorganic carbon species. Purged carrier gas sweeps combustion gases through a water trap to remove moisture. In the NDIR (non-dispersive infrared) detector, CO_2 absorbs infrared radiation at a characteristic wavelength. Detector response is calibrated using standard solutions and a calibration curve is generated. Sample peak areas are interpolated on this curve to determine TOC concentration. A built-in acid addition unit volatilizes inorganic carbon as CO_2 prior to combustion, allowing separate measurement of total carbon (TC) and inorganic carbon (IC). TOC is calculated as the difference between TC and IC.

pH:- pH is a measure of the acidity or alkalinity of water, indicating the concentration of hydrogen ions. It is an important parameter for water quality characterization. The pH of samples was determined using Standard Method APHA 4500-H+ B. This involves electrometric measurement of pH using a calibrated pH meter. A HI2211 microprocessor-based pH/temperature bench top meter (Hanna Instruments) was used for the analysis. The meter was calibrated daily using standard buffer solutions of pH 4, 7 and 10. Samples were stirred gently and the pH probe was immersed to measure equilibrium pH values at 25°C. Readings were recorded to the nearest 0.01 pH unit.

Oxidation-reduction potential (ORP):- ORP is a measure of the tendency of a solution to undergo oxidation or reduction reactions. It is a measure of the redox potential of a solution. APHA method 2580 B was used to determine the ORP of the samples. A HI2211 microprocessor-based pH/temperature bench top meter (Hanna Instruments) was used for the analysis

Total dissolved solids (TDS):- TDS is a measure of the total amount of dissolved solids in water. It is a measure of the salinity of water. APHA method 2540 C was used to determine the TDS of

the samples. This method involves evaporating a sample of wastewater to dryness and weighing the residue. The residue is the TDS.

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

Total suspended solids (TSS):- TSS is a measure of the total amount of suspended solids in water. It is a measure of the turbidity of water. APHA method 2540 D was used to determine the TSS of the samples. This method involves filtering a sample of wastewater through a pre-weighed filter paper. The filter paper is then dried and weighed. The difference between the weight of the filter paper before and after filtration is the TSS.

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

Density: - Density is a measure of the mass of a substance per unit volume. It is a measure of the compactness of a substance. APHA method 2520 B was used to determine the density of the samples. This meth $\rho = M / V$ ple.

ρ = Density

M= mass

V= volume

Methylene blue: - Methylene blue is a dye that is used to measure the surface area of solids. It is a measure of the porosity of a solid. APHA 2320 B method was use for determining the surface area of a solid by measuring the amount of methylene blue adsorbed onto the solid. Methylene blue is a cationic dye that is adsorbed onto the surface of solids, and the amount of methylene blue adsorbed is proportional to the surface area of the solid. To determine the surface area, a known mass of solid is added to a methylene blue solution and shaken for a period of time. The solution is then filtered and the absorbance of the filtrate is measured at 650 nm using a UV-spectrophotometer. A calibration curve is prepared by plotting the absorbance of a series of methylene blue solutions of known concentrations against the corresponding concentrations. The concentration of methylene blue in the filtrate is determined using the calibration curve, and the surface area of the solid is calculated using the following formula:

$$\text{Methylene blue} = \frac{V * W_{MB} * 100}{W_S\,(100\text{-}M)}$$

Where:

* W_{MB} is the concentration of methylene blue in the filtrate (mg/l)

* V is the volume of methylene blue solution added (ml)

* W_S is the mass of solid used (g)

* M of sample

Ash content: - Ash content determination provides a quantitative measure of inorganic residues remaining after combustion of organic matter. This study performed ash analysis according to the standardized procedure described in APHA 2540 G. Finely powdered samples were weighed into pre-ash and pre-weighed crucibles. The crucibles containing samples were placed in a muffle furnace and heated gradually to 600°C over 2 hours. After cooling in desiccators, the crucibles were reweighed.

This heating process incinerated organic material, leaving only mineral residues. The percentage of ash was then calculated using the following formula:

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

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

3.2. Instrumental analysis of ACM and Mo-ACM

XRD (Powdered X-ray diffraction)

In the characterization of the carbon catalysts derived from rice husk and Mo-ACM, a Rich Siefert 3000 diffractometer model was employed for the XRD analysis. It utilizes X-rays to interact with the sample, causing constructive interference of the X-ray waves that are diffracted by the crystal lattice. By measuring the angles and intensities of the diffracted X-rays, valuable information about the crystal structure and composition of the material can be obtained. During the XRD analysis, the scanning rate of the Rich Siefert 3000 diffractometer model was set at 4 deg min^{-1}. The scanning range covered a wide angular range from 5 to 80 degrees. This range allows for the detection of various diffraction peaks, providing insights into the arrangement of

atoms within the carbon catalysts. To ensure accurate measurements, a step sampling of 0.005 degrees was used. This fine step size allows for detailed analysis of the diffraction pattern, enabling the identification of specific crystallographic phases present in the carbon catalysts.

Fourier Transform Infrared spectroscopy (FTIR)

Fourier Transform Infrared spectroscopy (FTIR) is a widely used technique for analyzing the molecular composition and chemical bonds present in a sample. In the characterization of the carbon catalysts derived from rice husk and Mo-ACM, a Perkin Elmer instrument was utilized for the FTIR analysis. During the FTIR analysis, the samples were prepared in the form of pellets. To achieve this, Merck spectroscopic grade KBr (potassium bromide) was used. KBr is commonly used as a pelletizing agent in FTIR spectroscopy due to its transparency in the infrared region and its ability to form a solid matrix with the sample. The pellets obtained had a thickness of 1mm and a diameter of 13mm. These dimensions were chosen to ensure uniformity and consistency in the sample presentation. The use of standardized pellet sizes allows for reproducible measurements and facilitates comparison between different samples. To create the pellets, a hydraulic pelletizer was employed. The samples, mixed with KBr, were subjected to a pressure of 15 KPa cm^{-2}. This pressure ensures proper compaction of the sample and KBr, resulting in well-formed pellets that are suitable for FTIR analysis. The FTIR spectrum was obtained in the range of 4000 to 400 cm^{-1}. This range represents the wave number values at which the infrared radiation interacts with the sample. By scanning across this range, the FTIR instrument measures the absorption and transmission of infrared light by the sample, providing valuable information about the functional groups and chemical bonds present.

Thermogravimetry Analysis (TGA)

TGA is a technique used to study the thermal stability and decomposition behavior of materials. In the characterization of the carbon catalysts derived from rice husk and Mo-ACM, the Q50 instrument was employed for the TGA analysis. During the TGA analysis, the temperature range for scanning was set from room temperature to 800 °C. This range allows for the investigation of the sample's weight loss or gain as a function of temperature. By subjecting the sample to increasing temperatures, any changes in mass can be observed and analyzed, providing insights

into the thermal properties and decomposition behavior of the carbon catalysts. The heating rate for the TGA analysis was set at 10 °C min^{-1}. This controlled heating rate ensures a gradual and consistent increase in temperature, allowing for accurate measurements of weight changes over time. By maintaining a constant heating rate, the TGA analysis can effectively capture the thermal events and transformations occurring in the carbon catalysts. To prevent any unwanted reactions or oxidation during the analysis, the TGA analysis was performed under a nitrogen atmosphere. Nitrogen gas is commonly used as an inert atmosphere in TGA experiments to minimize the effects of oxygen and moisture on the sample. This ensures that the weight loss or gain observed during the TGA analysis is primarily attributed to thermal decomposition or other relevant processes, rather than external factors.

Differential Scanning Calorimetry (DSC)

In the characterization of the carbon catalysts derived from rice husk and Mo-ACM, the Q200 Thermo Fisher Scientific, Quanta200 (model) instrument was utilized for the DSC analysis. This instrument is known for its high precision and accuracy in measuring the heat flow associated with thermal transitions in materials. It allows for the detection of endothermic and exothermic events, such as phase transitions, crystallization, melting, and chemical reactions, by measuring the heat flow as a function of temperature. During the DSC analysis, the sample and a reference material were placed in separate pans and heated simultaneously. Any heat absorbed or released by the sample is compared to the reference material, allowing for the determination of thermal transitions and energy changes associated with the sample and the scanning range was set from 25 °C to 300 °C. This range indicates that the sample was subjected to a temperature increase from 25 °C to 300 °C.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a powerful technique used to examine the surface morphology of materials at high resolution. The analysis was performed using the Thermo Fisher Scientific Quanta200 model, known for its advanced imaging capabilities. The carbon catalyst samples were prepared for SEM analysis by mounting them onto aluminum stubs using conductive carbon tape. This step ensures proper grounding and stability during the analysis. The samples were then loaded into the SEM chamber of the Quanta200 instrument. The SEM

analysis involved the use of a focused electron beam that scans the surface of the sample. As the beam interacts with the sample, various signals are generated, including secondary electrons. These electrons provide valuable information about the sample's surface morphology. The SEM parameters, including the acceleration voltage (20.00 kV), magnification (1.01Kx), view field (149.34 micrometers), and working distance (16.3220 millimeters), were carefully chosen to capture detailed surface morphology.

Energy Dispersive X-Ray Analysis (EDAX)

Energy Dispersive X-Ray Analysis (EDAX) is a technique used to determine the elemental composition of materials. In this case the analysis was performed using the Thermo Fisher Scientific Quanta200 model. For the EDAX analysis, the energy range used was from 0 to 20 keV. This range allows for the detection of characteristic X-rays emitted by the elements present in the carbon catalyst samples. The carbon catalyst samples, previously prepared for SEM analysis, were used for the EDAX analysis. The samples were mounted onto aluminum stubs using conductive carbon tape and loaded into the SEM chamber of the Quanta200 instrument. During the analysis, the Quanta200 instrument emitted an electron beam onto the sample surface. As the beam interacted with the sample, characteristic X-rays were emitted from the elements present. These X-rays were then collected and analyzed by the EDAX detector, providing information about the elemental composition of the carbon catalysts.

CHAPTER FOUR

4. RESULT AND DISSCUSSTION

4.1. Phiso-chemical characterization of leather effluents, ACM and Mo-ACM

The sample taken from leather effluent containing Volatile Organic Compounds (VOCs) undergoes a stripping (aeration) process in the stripping tank and subsequent condensation in the condensing apparatus. In order to assess the effectiveness of the treatment process and understand the changes in the effluent's properties, various parameters were measured, including COD, pH, TDS, TSS, ORP, and Total Hardness. Additionally, the pH and stripping duration in the condensing apparatus were varied to evaluate their impact on the effluent characteristics.

Table5. Physicochemical Properties of Leather Processing Effluents

Parameters	Stripper (aerated)	Condensed (dissolved)	Dissolved Effluent Treated with Mo-ACM
pH	7.5	11.04	11
ORP	-162	-109.2	156.4
COD(mg/L)	35,200	7200	192
TOC(mg/L)	6454	3227	150.2
TSS(mg/L)	2100	30	ND
TDS(mg/L)	16,400	560	230
Calcium(mg/L) hardness	600	-	-
Ammonia	25.2	16.8	Under detection limit

The above results demonstrate the effectiveness of molybdenum-impregnated activated carbon (Mo-ACM) for treating toxic leather industry effluents in accordance with regulatory discharge limits. As seen in the table, chemical oxygen demand (COD) and total organic carbon (TOC) levels were extremely high in stripping and condensation tanks at 35,200 mg/L and 7,200 mg/L respectively, far exceeding the general discharge limits for the leather industry of 250 mg/L for COD as per the Environmental Protection Agency and 100 mg/L for TOC as per the Central

Pollution control board. The optimized pH of 7.5 in strippers and 11.04 in condensation tanks align with literature extraction kinetics, while prolonged stripping decreased COD over 10 hours as expected. Notably, Mo-ACM treatment under conditions of pH 11.0 and 120 minutes HRT and at rate 18ml/min reduced COD and TOC by over 95% to 192 mg/L and 150.2 mg/L on the other hand we can see the ORP shifting from negative to positive which can indicate that a fundamental change in the redox state of the system, where the substance being oxidized loses electrons to oxygen. A negative ORP indicates a predominance of reducing agents, while a positive ORP suggests a higher concentration of oxidizing agents. The shift from negative to positive during catalytic oxidation implies that the substance is being oxidized, losing electrons to oxygen. Reaction Completion**:** Again shift in ORP can be a strong indicator of complete oxidation. This means that the substance has been fully converted to its oxidized form, often resulting in harmless products like carbon dioxide and water respectively.

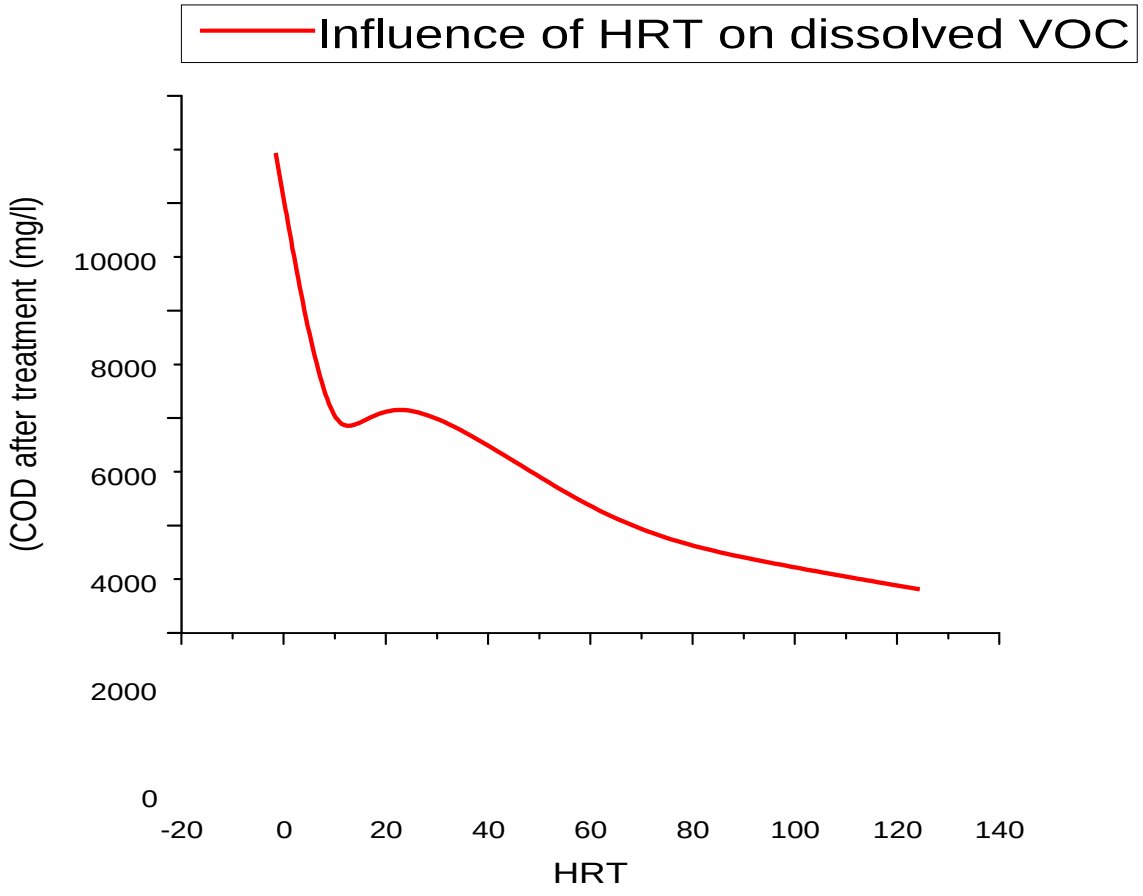


Fig.5. Influence of HRT on dissolve sample being treated with Mo-ACM

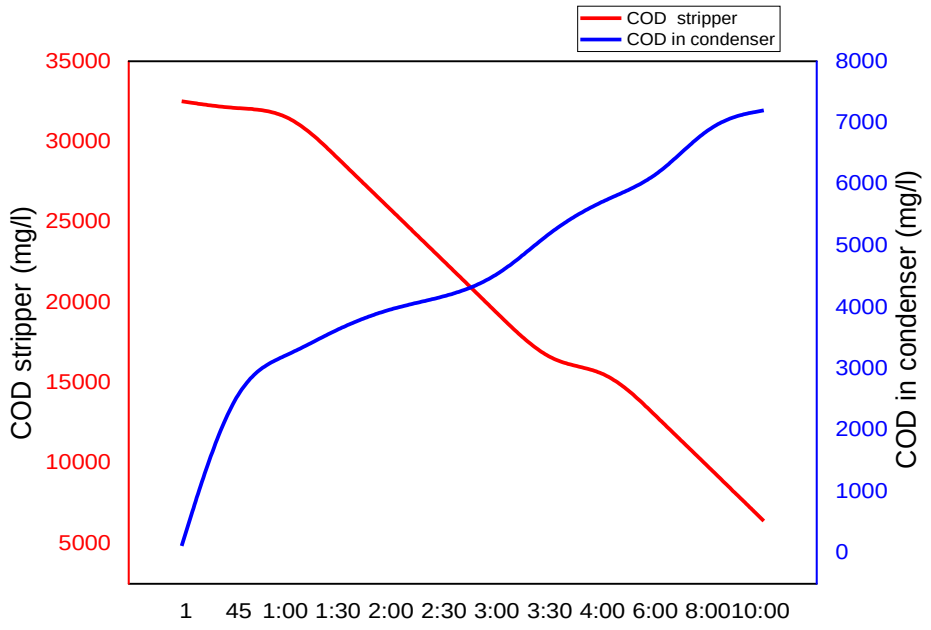


Fig.6 Effect of processing time on COD levels in stripper and condenser

4.1.1 Analysis of VOC using portable photo ionization detector

This section examines the release of volatile organic compounds (VOCs) from tannery effluent samples through air sparging with an aeration rate of 1 L/min was selected to sparge the effluent and strip VOCs. Readings were taken from a portable photo ionization detector (PID) at time intervals ranging from 1 to 15 minutes. The maximum VOC concentration detected by the PID was 120 ppm after the initial 1 minute of aeration. Concentrations then gradually decreased over time, with the minimum of 0.6 ppm recorded after 15 minutes. This trend demonstrates that as the sparging time increased, more VOCs were stripped out of the effluent liquid phase and released into the air stream due to their highly volatile properties. Once in the gas phase, VOCs were rapidly dispersed and their concentrations correspondingly decreased with time. These results provide insight into the volatile nature and ease of stripping hazardous VOCs commonly present in tannery wastewaters. Such characteristics have implications for the design of pretreatment and air pollution control systems to effectively capture and destroy VOCs before discharge or emission.

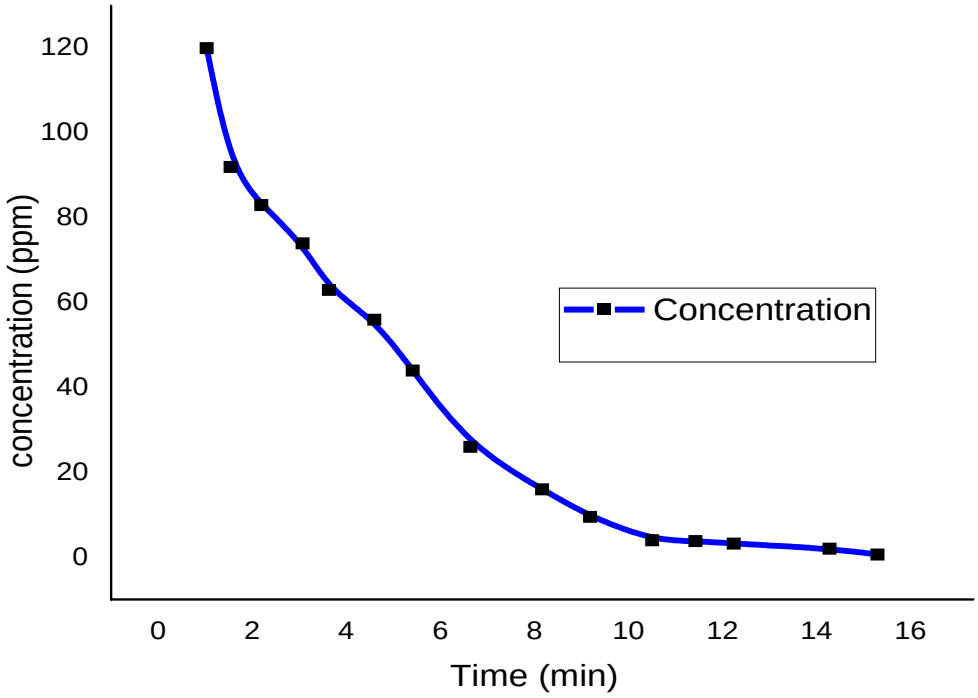


Fig.7 Impact of Processing Duration on VOC Levels in Stripper Effluent

4.1.2. Phiso-chemical characterization of Mo-ACM & ACM

During the physico-chemical characterization of Mo-ACM (Molybdenum-Loaded Activated Carbon Material), various metal loadings were considered, including 1%Mo/AC, 3%Mo/AC, 5%Mo/AC, and 7%Mo/AC. The characterization involved analyzing the ash content, density, moisture content, and methylene blue adsorption. As the percentage of metal loading increased, the ash content and moisture content of Mo-ACM decrease; this phenomenon can be attributed to several factors, such as the interaction between the metal species and the carbon surface, which may lead to the displacement or reduction of ash-forming impurities present in the activated carbon. Additionally, the introduction of metals onto the carbon surface can modify its chemical composition and structure, potentially impacting the ash content of the material. Research studies have explored the effect of metal loading on activated carbon and its influence on ash content. Numerous investigations have been conducted on loading different metals onto activated carbon

for instance silver appears to be widely researched for its antimicrobial properties. Studies show loading silver nanoparticles can significantly decrease ash content by 15-20% through displacement of alkali metals on the carbon surface while copper loading has also been examined considering its effectiveness for removing toxic heavy metals. Ahmad reported copper impregnation reducing ash levels by facilitating the leaching of inorganic impurities during the loading process. Other research indicates metals like nickel may influence ash content depending on factors such as pH and temperature variations (Liao et al., 2015). However, more controlled studies are needed comparing different metal types under diverse conditions. From the above relevant study we can suggest that the presence of molybdenum loading led to a reduction in the inorganic ash content and moisture within the material. The decrease in ash content suggests a higher purity of the Mo-ACM, while the decrease in moisture content indicates improved dryness. However, it is important to note that beyond a 3% metal loading, a decrement in the observed changes was shown. This can be attributed to the presence of excess metal ions, which may have reached a saturation point and no longer contributed to further reductions in ash content and moisture content. Additionally, factors such as saturation of active sites, agglomeration of metal ions, competitive adsorption, and structural changes in the Mo-ACM could also contribute to the observed decrement during metal loading.

On the other hand, the density and methylene blue adsorption of Mo-ACM increased with the percentage of metal loading. The increase in density can be attributed to the incorporation of molybdenum, which adds mass to the material. The higher methylene blue adsorption suggests an enhanced ability of the Mo-ACM to adsorb organic compounds, this can be explained when Mo-ACM is exposed to methylene blue, the dye molecules are attracted to the surface of the activated carbon through electrostatic interactions and other binding forces. The higher adsorption of methylene blue on Mo-ACM indicates the presence of more active sites and enhanced surface properties that facilitate the binding of organic compounds. The increased methylene blue adsorption capacity of Mo-ACM serves as a reliable indicator of its improved ability to adsorb organic compounds. Organic molecules in wastewater or gas streams exhibit similar behavior to methylene blue when interacting with Mo-ACM. The elevated adsorption capacity signifies that Mo-ACM can effectively capture a larger quantity of organic pollutants,

demonstrating its potential for efficient removal of contaminants from various environmental matrices.

Furthermore, the percentage of volatile organic compound (VOC) removal was determined based on the amount of Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) removed. At a molybdenum loading of 3%, the VOC removal was found to be 95%. This indicates that the presence of molybdenum in the Mo-ACM significantly enhanced its ability to remove organic pollutants, as evidenced by the high percentage of VOC removal. Overall, the physico-chemical characterization of Mo-ACM demonstrated that increasing the percentage of molybdenum loading resulted in decreased ash content and moisture content, while increasing density and methylene blue adsorption. However, it is important to consider that beyond a certain metal loading, the observed changes may show a decrement due to the presence of excess metal ions and other factors that affect the material's properties.

Table.6. Phiso- chemical characterization of Mo-ACM

Percentage of metal loading% Mo-ACM	Moister content %	Ash content %	Density(g/cm^3)
1%	4.98	83.1	0.380
3%	4.9	75.67	0.386
5%	4.7	74.87	0.387
7%	4.3	73.45	0.410
ACM -	4.7	85.39	0.305

4.1.3. Characterization of Mo-ACM & ACM Using Analytical Instrumentation

XRD (Powdered X-ray diffraction) analysis

The X-ray diffraction (XRD) analysis reveals significant differences between activated carbon material and molybdenum-impregnated activated carbon. The XRD pattern of ACM shows an amorphous structure, characterized by a broad peak around 22.2°, indicative of a lack of well-defined crystalline phases. In contrast, Mo-ACM displays sharper peaks at21.9^0 26.38° and 44.6°, corresponding to crystallized phases associated with molybdenum and molybdenum carbide (Mo_2C). The presence of these distinct peaks indicates a higher degree of crystallinity in Mo-ACM, shows that metal impregnation can enhance the crystallinity of activated carbon materials, subsequently improving their structural stability.

The sharper peaks in Mo-ACM suggest the formation of well-defined crystalline phases, while the broad peaks characteristic of amorphous materials indicate a disordered structure. The successful incorporation of molybdenum into the activated carbon matrix is substantiated by these crystalline manifestations. This observation aligns with previous studies, such as those by Sevilla and Fuertes, who noted a similar broad peak in the XRD profile of rice husk-derived activated carbon, attributing it to its amorphous nature. Again amorphous structure of ACM suggests a high density of defects and impurities, corroborated by research from Kundu et al. (2020), who indicated that such characteristics limit the material's adsorption capabilities. Conversely, the more crystalline structure of Mo-ACM, facilitated by the presence of molybdenum—a transition metal with a propensity to form strong bonds with carbon—imparts enhanced stability to the carbon framework. This structural distinction may affect performance in various applications; for instance, the crystalline nature of Mo-ACM indicates improved wear resistance compared to ACM. Additionally, the increased degree of crystallinity in Mo-ACM may yield a larger surface area, thereby enhancing its effectiveness in adsorption processes, as supported by studies that show a direct correlation between crystallinity and adsorption capacity in activated carbon

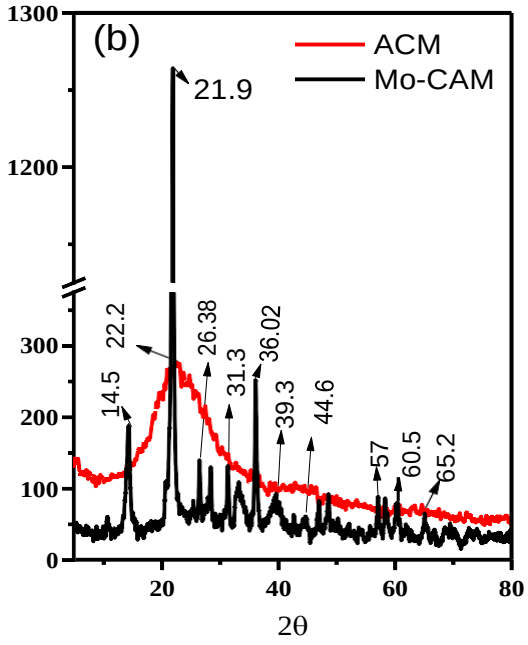


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Fig.8. XRD spectra of ACM and MO-ACM

Fourier Transform Infrared spectroscopy (FTIR)

The Fourier-Transform Infrared (FTIR) spectra of ACM and Mo-ACM showed in Figure8.A exhibits several distinct peaks that provide valuable information about its molecular composition. At approximately 3373cm^{-1} a peak is observed, which can be assigned to the stretching vibrations of hydroxyl (-OH) groups. This indicates the presence of hydroxyl functional groups in the material [62]. Another peak at 1637 cm^{-1} is likely attributed to the stretching vibrations of carbon-oxygen (C-O) groups, suggesting the presence of C-O bonds in the material's structure. [63]. Additionally, a peak at 1095cm^{-1}is observed, which could be the result of the overlapping of the Si-O-Si and C-O-Si bonds [64]. These bonds are derived from the silica component present in ACM, which originates from rice husk, which is rich in amorphous silica (SiO_2). The silica forms the fundamental building blocks of the material, with Si-O-Si bonds and C-O-Si bonds present. Mo-ACM, the addition of molybdenum ions modifies the bonding environment, potentially affecting the Si-O-Si and C-O-Si bonds.

The FTIR spectrum of Mo-ACM shows several notable changes and additional peaks compared to ACM. The peak corresponding to the stretching vibrations of -OH groups, which was observed at 3411cm^{-1} in ACM, is shifted to 3373cm^{-1} in Mo-ACM. This shift suggests a modification in the -OH stretching due to the addition of molybdenum metal ions in the Mo-ACM material. Similarly, the peak at 1637cm^{-1}, associated with the stretching vibrations of C-O groups in ACM, undergoes a shift to 1651cm^{-1} in Mo-ACM. This shift indicates a modification in the C-O stretching, likely due to the bonding of molybdenum with the carbon-silica matrix in Mo-ACM. The peak observed at 1097 cm^{-1} Mo-ACM can be attributed to the Si-O-Si and C-O-Si bonds, similar to ACM. However, the presence of molybdenum ions in Mo-ACM may cause a shift in this peak, indicating a change in the bonding environment. Furthermore, the peak at 798cm^{-1} in Mo-ACM corresponds to the symmetric stretching vibration of Si-O-Si bonds [65].

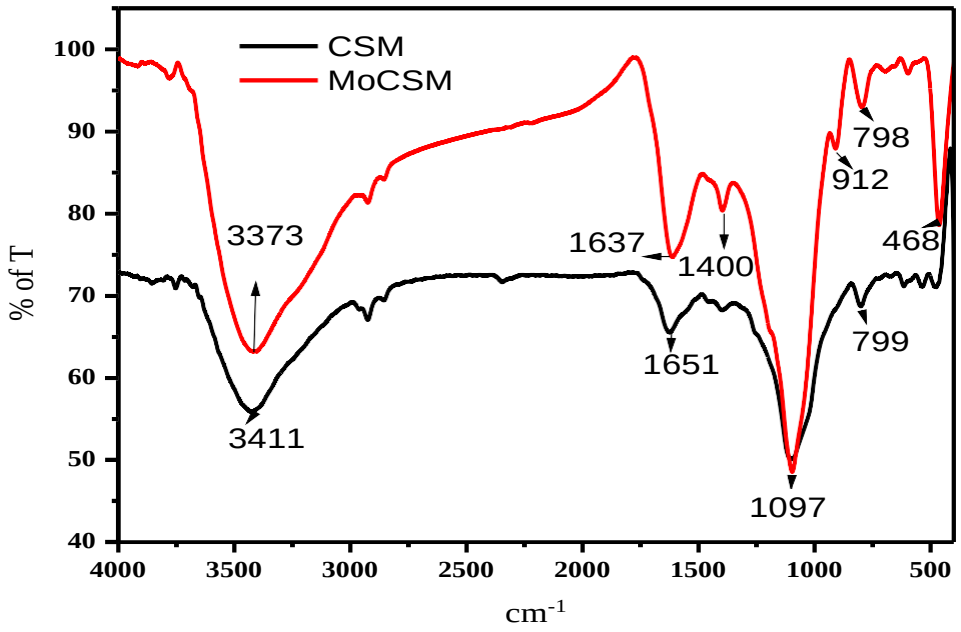


Fig.9. FTIR Spectra of ACM and MO-ACM and XRD spectra of ACM and MO-ACM

Thermogravimetry analysis (TGA)

The Thermogravimetry analysis (TGA) curves presented in the Fig.8 below illustrate the thermal behavior of two distinct materials: Mo-ACM and ACM. The x-axis of the graph represents the temperature, while the y-axis represents the weight loss. Upon analyzing the TGA curves, it becomes apparent that both Mo-ACM and ACM exhibit a gradual reduction in weight as the temperature increases. However, notable distinctions exist between the two materials. In the case of ACM, a substantial weight loss is observed within the temperature range of approximately 600°C to 700°C. This phenomenon can be attributed to the decomposition or combustion of organic constituents within the material, such as the carbon matrix or residual organic matter originating from the rice husk source. Conversely, Mo-ACM displays a similar trend but with noteworthy variations. The initial weight loss of Mo-ACM appears slightly higher compared to ACM, potentially due to the presence of additional organic components or the incorporation of molybdenum species. However, the most significant weight loss for Mo-ACM occurs at a lower temperature range, approximately 400°C to 600°C, indicating a comparatively lower thermal stability when compared to ACM the observed disparities in the TGA curves between Mo-ACM and ACM can be attributed to the introduction of molybdenum species in Mo-ACM. The presence of molybdenum and its interaction with the carbon-silica matrix are likely influential

factors that impact the decomposition behavior and thermal stability of the material. Furthermore, the incorporation of molybdenum may introduce new decomposition pathways or modify existing ones, leading to the observed variations in the TGA profiles.

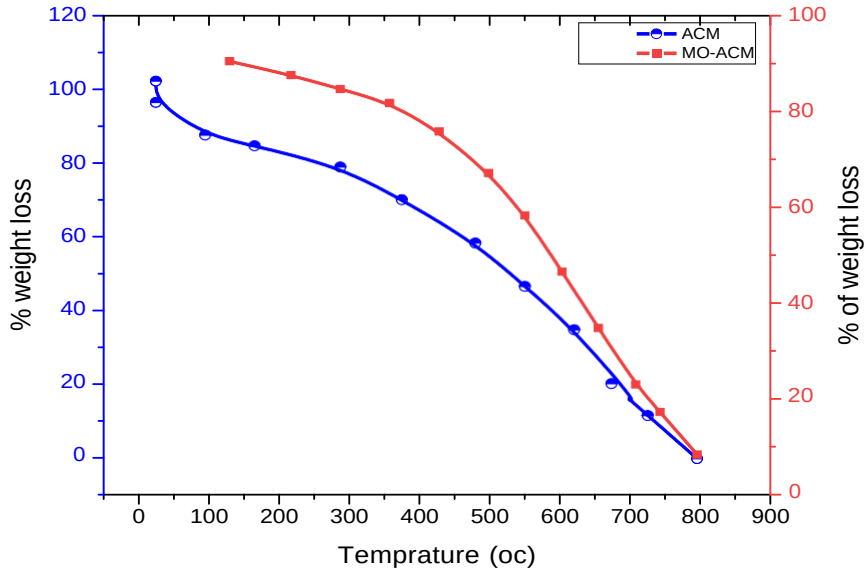


Fig10. TGA analysis of ACM and MO-ACM

Differential Scanning Calorimetry (DSC)

The differential scanning Calorimetry (DSC) curves of two materials, ACM & Mo-ACM are depicted in the provided graph. DSC is a thermal analysis technique employed to measure the heat flow associated with transitions or reactions in materials as a function of temperature. Analyzing the ACM curve a broad endothermic peak centered on 100°C is observed. This peak is commonly linked to the evaporation or removal of adsorbed water molecules or moisture present in the porous silica material. The presence of this peak is anticipated for silica-based materials due to their inherent tendency to adsorbed water from the environment, owing to their high surface area and porosity. As the temperature continues to rise, the ACM curve exhibits an exothermic peak at approximately 335°C. This exothermic peak can be attributed to the decomposition or combustion of residual organic matter or carbon-containing species within the silica material. The release of heat observed during this peak signifies an exothermic process, likely involving the oxidation or thermal degradation of organic components.

On other hand Mo-ACM curve showed a similar broad endothermic peak around 100°C, indicating the removal of adsorbed water or moisture. However, the shape and intensity of this peak differ slightly from the ACM curve, suggesting potential interactions between the molybdenum species and the silica matrix, which may influence the desorption behavior. Significantly, the exothermic peak observed in the ACM curve at around 335°C is either absent or significantly suppressed in the Mo-ACM curve. This observation suggests that the incorporation of molybdenum species into the silica matrix may have altered or inhibited the decomposition or combustion process of the organic components. The presence of molybdenum could potentially stabilize the organic matter or modify the oxidation pathway, resulting in a distinct thermal response in the DSC curve.

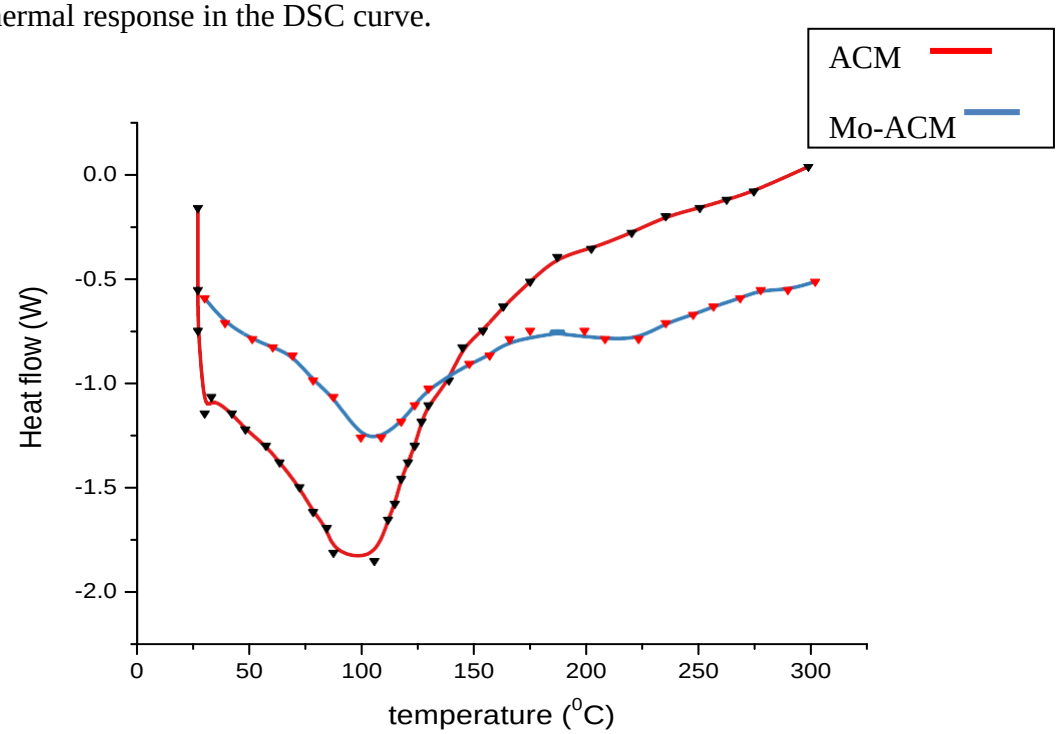


Fig.11 DSC curve for ACM & Mo-ACM

Scanning Electron Microscopy (SEM)

The first SEM image represents the morphology of ACM, while the second image shows the morphology of Mo-ACM. From the first image of the ACM, we observe a highly porous and irregular surface with interconnected particles or grains forming a network of pores and voids. Comparing the two images, we can observe some differences in the surface morphology and pore structure: Pore size and distribution: The pores in the Mo-ACM image appear to be more uniformly distributed and slightly smaller in size compared to those in the ACM image. This

could be attributed to the incorporation of molybdenum species, which may have influenced the pore formation or modification during the impregnation process. Surface texture: The Mo-ACM image exhibits a slightly rougher and more intricate surface texture compared to the ACM image. This could be related to the deposition or interaction of molybdenum species with the activated carbon surface, potentially leading to changes in surface morphology. Pore connectivity: In the Mo-ACM image, the pores appear to be more interconnected, forming a more continuous network of voids. This enhanced pore connectivity could be beneficial for applications involving mass transport or diffusion processes and the more uniform pore distribution and interconnected pore network observed in the Mo-ACM image suggest that the incorporation of molybdenum may have increased the accessible surface area and pore volume. This increase in surface area can potentially enhance the material's ability to adsorb and accommodate more molecules or ions, leading to higher adsorption capacities.

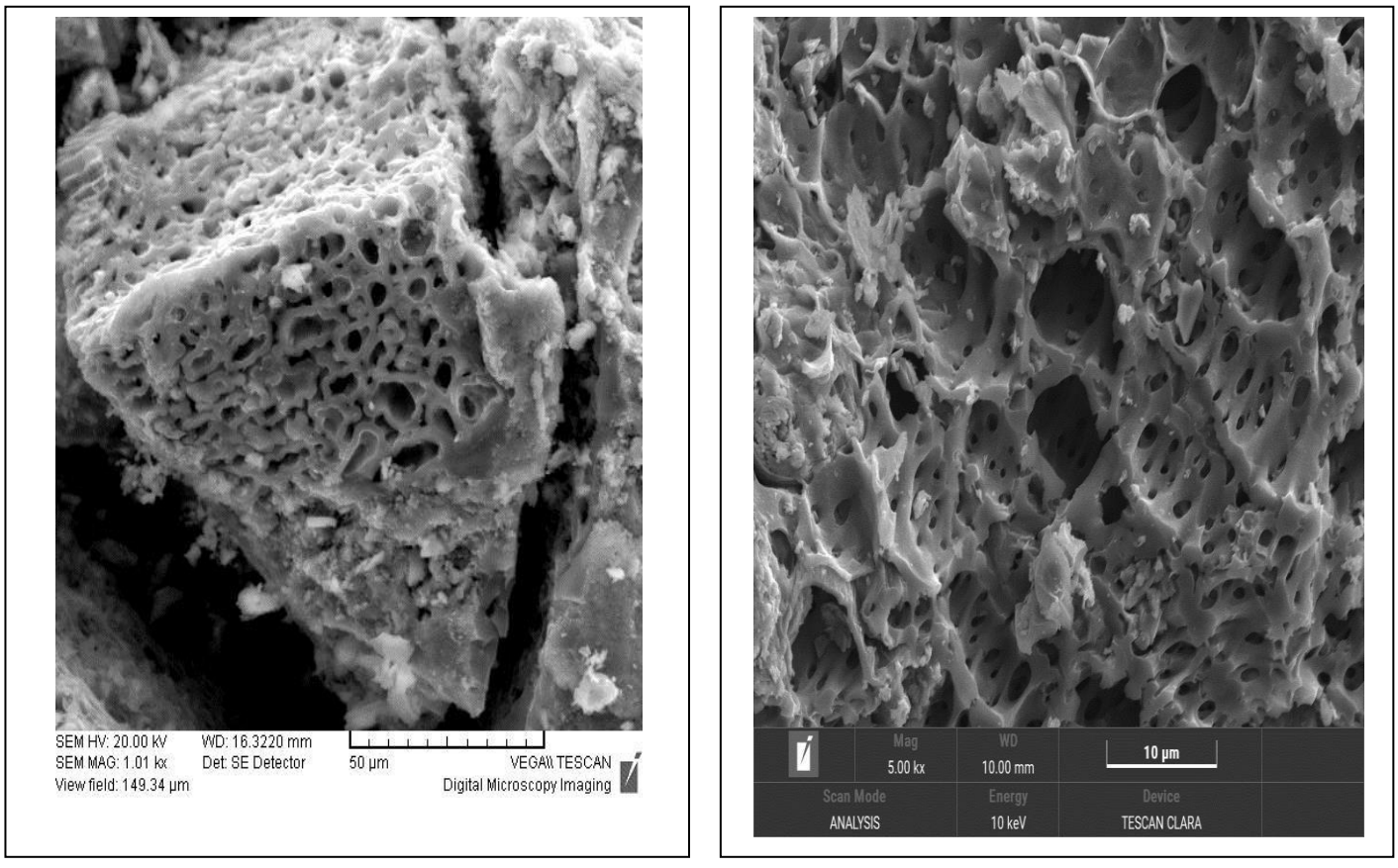


Fig. 12 SEM morphology for ACM and Mo-ACM

Energy Dispersive X-Ray Analysis (EDAX)

EDAX is a powerful analytical technique utilized in conjunction with scanning electron microscopy (SEM) to elucidate the elemental composition of a material. From the figure below we can clearly observe that the spectrum exhibits the energy level in kiloelectron volts (keV) on the x-axis, while the y-axis represents the relative intensity or counts of the detected X-rays. Each peak within the spectrum corresponds to the characteristic X-ray emission line of a specific element present in the sample. The peak at approximately 2.3 keV is indicative of the presence of molybdenum (Mo) within the sample. This peak corresponds to the characteristic X-ray emission line of Mo, affirming the successful impregnation or incorporation of molybdenum into the activated carbon matrix. The smaller peaks at lower energy levels, typically below 1 keV, are

commonly attributed to lighter elements such as carbon (C), oxygen (O), and potentially other elements like nitrogen (N) or sulfur (S) and Si is the third-highest element present next to carbon.

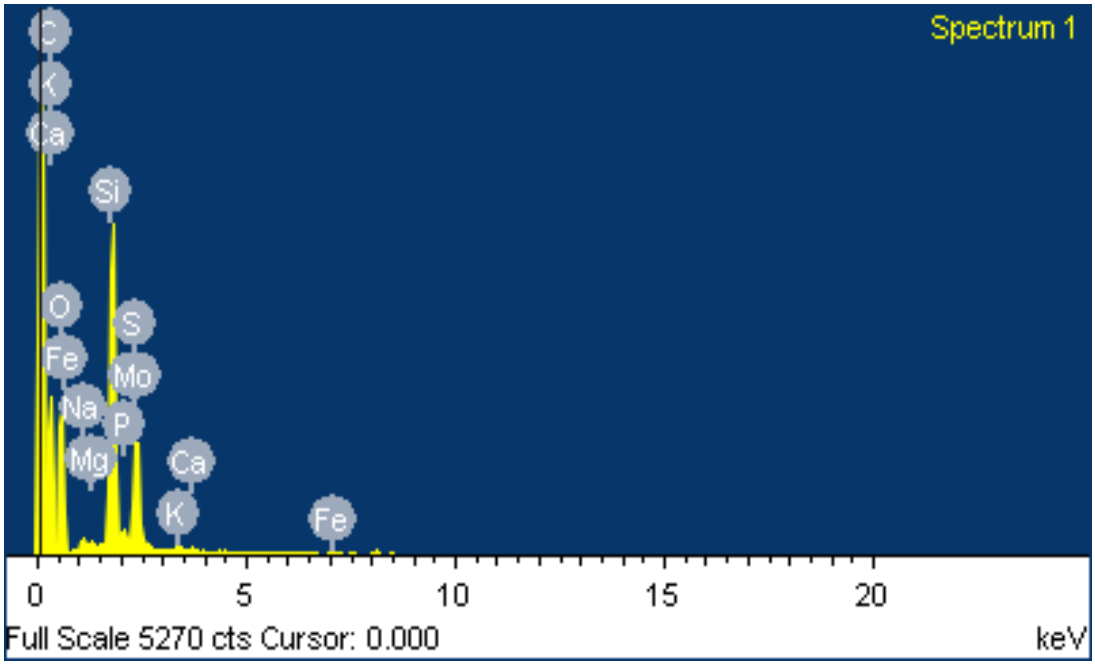
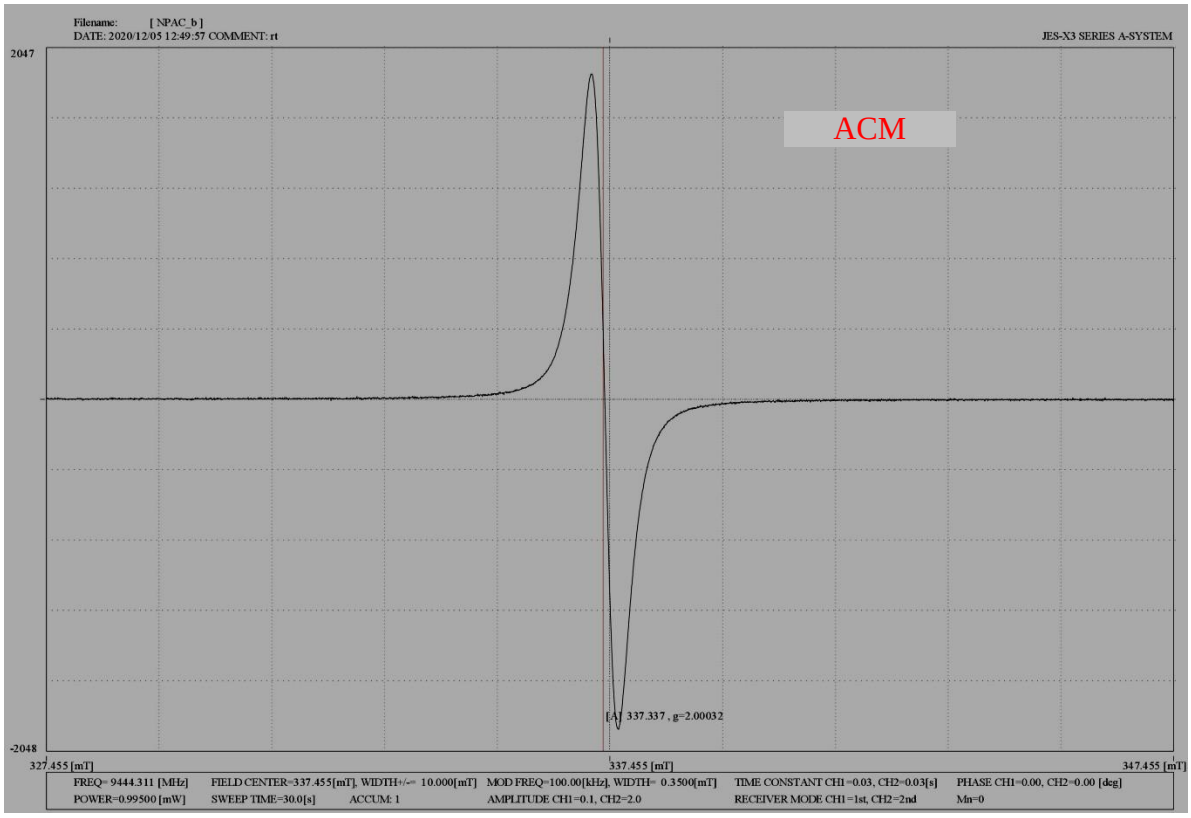


Fig.13 EDAX analysis of Mo-ACM

EPR Analysis of ACM and Mo-ACM

The Electron Paramagnetic Resonance (EPR) results have provided valuable insights into the magnetic properties and chemical behavior of the ACM and Mo-ACM catalyst materials. In the EPR spectrum of ACM, the observation of a single peak at g = 2.00031 can be attributed to the presence of unpaired electrons. These electrons are located at defects or dangling bonds on the surface of the silica material. They play a crucial role in electron transfer processes. With Mo-ACM an additional peak at g = 1.9872 is observed, which corresponds to the incorporation of MoO_3 into the silica matrix during the synthesis process. The presence of this characteristic signal confirms the successful loading of the paramagnetic MoO_3 species in the material. The presence of MoO_3 likely enhances the availability of unpaired electrons for redox reactions due to its intrinsic paramagnetic behavior and interactions with the silica support. This can potentially expand the range of catalytic applications for Mo-ACM. The broadening of peaks in the Mo-ACM spectrum may arise from spin-spin coupling between neighboring paramagnetic centers and interactions with the surrounding lattice, which affect the relaxation times of electrons.



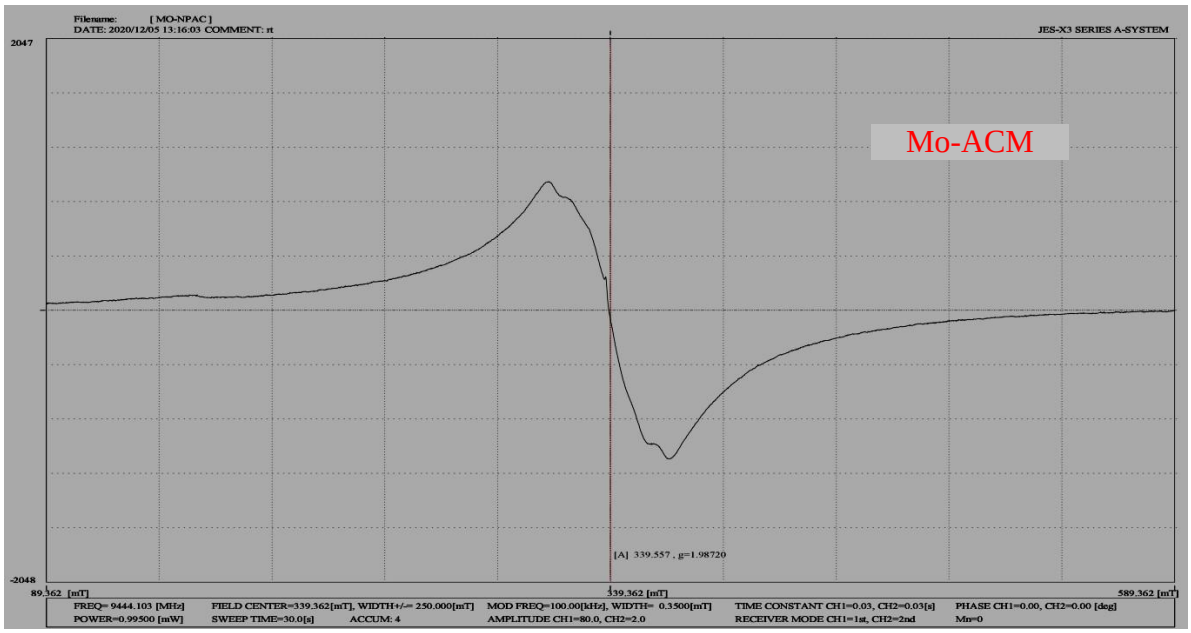


Fig.14.EPR analysis for ACM & Mo-AC

4.1.3. Catalytic Degradation of Volatile Organic Compounds from Tannery Effluent

Catalytic destruction of VOCs using Mo-AC is an effective and environmentally friendly approach for reducing their harmful impact. The catalyst facilitates the oxidation of VOCs through the reaction with hydroxyl radicals generated by hydrogen peroxide. The oxidation process converts VOCs into harmless products such as carbon dioxide and water for instance when we consider benzene oxidation.

Benzene oxidation

1. Benzene adsorption: - C_6H_6 (benzene) from the effluent of the leather industry adsorbs onto the surface of molybdenum-activated carbon (Mo-AC).
2. Benzene Activation:-The adsorbed benzene reacts with hydroxyl radicals ($OH^{\bullet}$) generated from the decomposition of hydrogen peroxide (H_2O_2) in the presence of Mo-AC as a catalyst. This reaction results in the formation of phenol (C_6H_5OH) and a hydroperoxyl radical ($HO_2^{\bullet}$)

$$C_6H_6 + OH^{\bullet} \rightarrow C_6H_5OH + HO_2^{\bullet}$$

3. Benzene Oxidation:-The hydroperoxyl radical (HO2●) further reacts with benzene to produce phenol (C6H5OH) and another hydroperoxyl radical (HO2●):

$$C_6H_6 + HO_2^{\bullet} \rightarrow C_6H_5OH + HO_2^{\bullet}$$

4. Molybdenum Redox Cycle:-During the catalytic process, molybdenum undergoes a redox cycle between different oxidation states. The reactions involved are as follows:

$$Mo^{4+} + H_2O_2 \rightarrow Mo^{5+} + OH\text{-} + HO^{\bullet}$$
$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet}$$
$$Mo^{6+} + HO_2^{\bullet} \rightarrow Mo^{5+} + H^{+} + O_2$$
$$Mo^{5+} + HO_2^{\bullet} \rightarrow Mo^{4+} + H^{+} + O_2$$

5. Hydroperoxyl Radical Decomposition:- Hydroperoxyl radicals ($HO_2^{\bullet}$) decompose to produce molecular oxygen (O_2) and hydroxyl radicals ($OH^{\bullet}$):

$$2\ HO_2^{\bullet} \rightarrow O_2 + 2\ OH^{\bullet}$$

6. Destruction of Benzene:- Hydroxyl radicals ($OH^{\bullet}$) react with benzene and other volatile organic compounds (VOCs) present in the effluent from the leather industry, leading to their conversion into carbon dioxide (CO_2) and water (H_2O):

$$2\ OH^{\bullet} + VOCs \rightarrow CO_2 + H_2O$$

❖ ***Catalytic destruction of tannery effluents***

The catalytic degradation of volatile organic compounds (VOCs) present in tannery effluent, specifically toluene, benzene, formaldehyde, and other tannery VOCs, was investigated through a series of optimization studies. These studies focused on varying the percentage of different metal catalysts, hydraulic retention time (HRT), pH, and hydrogen peroxide dosage to enhance the oxidation of VOCs. The goal was to identify the optimal conditions for efficient VOC removal. In terms of the metal catalyst percentages, the study found that the 3% Mo-ACM catalyst exhibited the highest reduction in VOCs compared to the other concentrations tested (1%, 5%, and 7%). This suggests that a moderate concentration of the catalyst is more effective

in promoting VOC degradation. The investigation into the effect of HRT and pH revealed that a pH of 11 yielded the best results in terms of total organic carbon (TOC) removal efficiency. This finding highlights the importance of maintaining an alkaline environment for efficient VOC degradation. Furthermore, the study examined the impact of hydrogen peroxide dosage on VOC degradation and the results showed that a dosage of 0.2 ml/L hydrogen per oxide provided optimal results, The use of the Mo-ACM catalyst in the catalytic oxidation process significantly enhanced VOC removal efficiency. The Mo-ACSM catalyst achieved a VOC removal efficiency of 95%, while the ACM alone achieved only 20-30 % under the same optimized conditions. This highlights the superior performance of the Mo-ACM catalyst in promoting VOC degradation in tannery effluent.

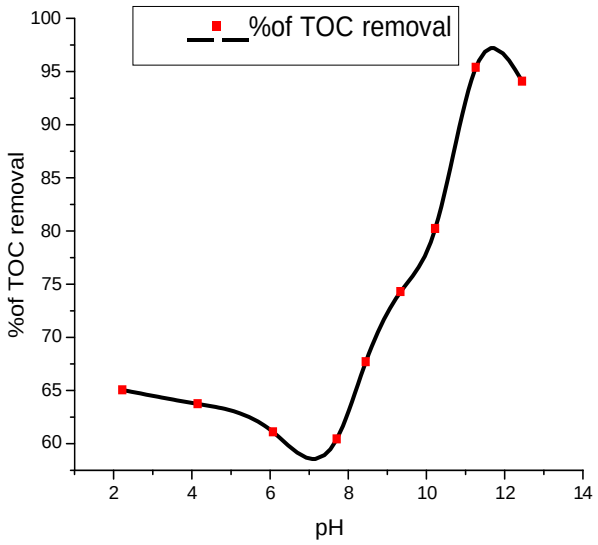


Fig.15.a) Effect of pH on degradation of VOC's

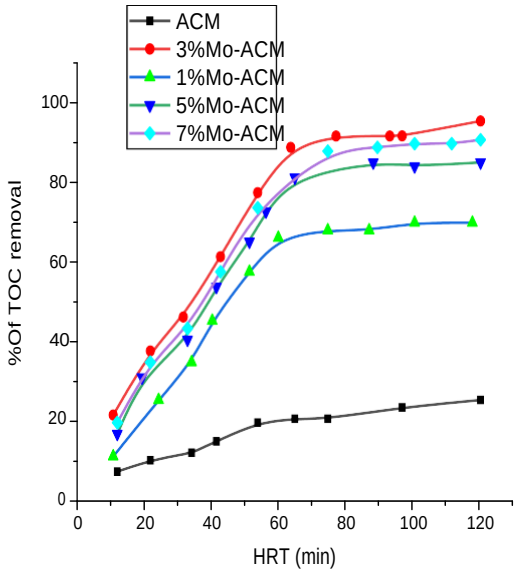


Fig.15.b) Effect of HRT on degradation of VOC's

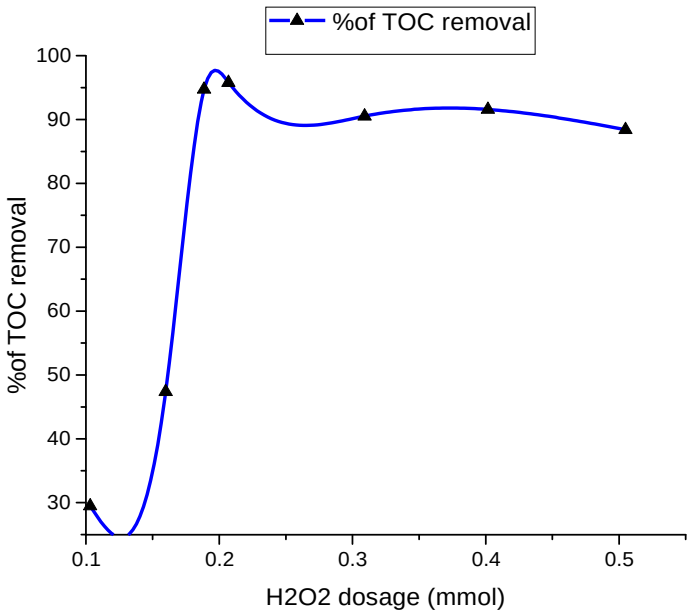


Fig.15. C) Effect of H_20_2 dosage on removal of VOC'S

Characterization of Catalytic VOC Degradation through Ultraviolet-Visible Spectroscopy

Toluene degradation

The degradation of toluene using two different materials: ACM and Mo-ACM was analyzed using Uv-visible instrument. The spectrum of TRW (toluene containing tannery water) exhibited a clear absorption peak at 260 nm, indicating the presence of aromatic compounds, particularly toluene, in the tannery raw wastewater. This confirmed the contamination of the sample with toluene or similar aromatic substances. Moving on to the ACM spectrum, we observed a prominent absorption band centered around 260 nm, which can be attributed to the π-π* electronic transitions within the aromatic carbon framework of the ACM material. This finding suggested that ACM possesses the capability to adsorb toluene and other aromatic compounds from the tannery wastewater. From UV-Vis spectrum of Mo-ACM, we noticed a broad absorption band around 260 nm, similar to the ACM spectrum but with a broader shape and lower intensity. This broadening could be attributed to the incorporation of molybdenum species, which potentially introduce defects or distortions in the aromatic structure of the material. Additionally, we observed a smaller peak or shoulder at longer wavelengths, approximately 320-340 nm. This feature might be associated with charge transfer transitions or d-d transitions involving the molybdenum species integrated into the activated carbon matrix. The disparities between the UV-Vis spectra of ACM and Mo-ACM indicated that the impregnation of

molybdenum onto the activated carbon matrix altered the electronic structure and optical properties of the material. Notably, the absence of the distinct toluene absorption peak at 260 nm in the Mo-ACM spectrum, coupled with the appearance of the longer-wavelength feature, suggested that Mo-ACM has the potential to degrade or transform toluene molecules present in the tannery wastewater. The incorporation of molybdenum species into the activated carbon matrix may facilitate oxidative degradation or transformation of toluene, potentially through catalytic processes or charge transfer mechanisms.

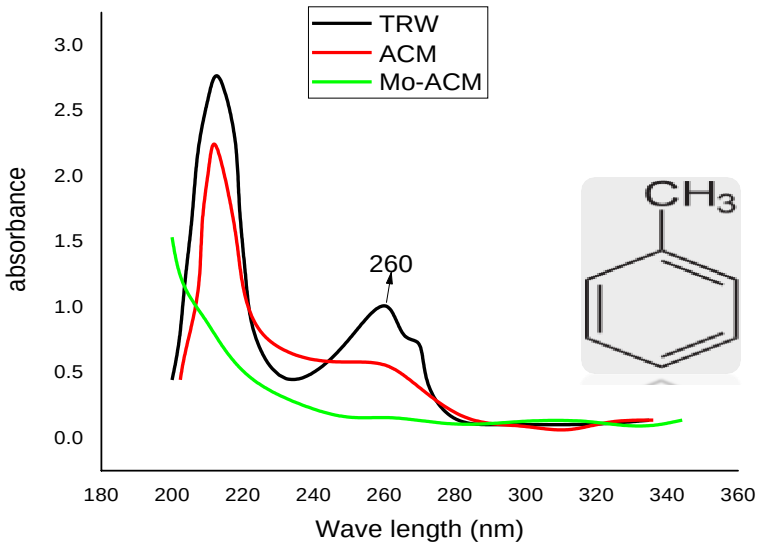


Fig.16 Uv-Vis analysis of toluene containing tannery waste water

Benzene degradation

The benzene-containing tannery wastewater (BCW) spectrum exhibits distinct absorption peaks at 266 nm and 209 nm, characteristic of the aromatic benzene structure. The ACM spectrum displays a prominent absorption band at 266 nm, attributed to the π-π* electronic transitions in the aromatic carbon framework. The decrease in peak intensity at 266 nm compared to the BCW spectrum suggests that ACM effectively adsorbs benzene and other aromatic compounds from the wastewater through physical adsorption processes. Notably, the Mo-ACM spectrum exhibits a significantly different profile, with the absence of the characteristic benzene absorption peaks. Instead, a broad absorption band is observed around 266.8 nm, which could be attributed to the presence of different aromatic or conjugated systems. The absence of the benzene peaks in the

Mo-ACM spectrum indicates that the molybdenum species incorporated into the activated carbon matrix facilitates the oxidative degradation or transformation of benzene molecules. The molybdenum species likely act as catalytic sites, promoting the oxidation of benzene through redox reactions or charge transfer processes. The combination of adsorption by the activated carbon matrix and the catalytic oxidative degradation facilitated by the molybdenum species in the Mo-ACM material provides a synergistic approach for removing benzene from tannery wastewater effluent streams. While ACM effectively removes benzene through physical adsorption, Mo-ACM offers an additional advantage by chemically degrading or transforming the adsorbed benzene molecules.

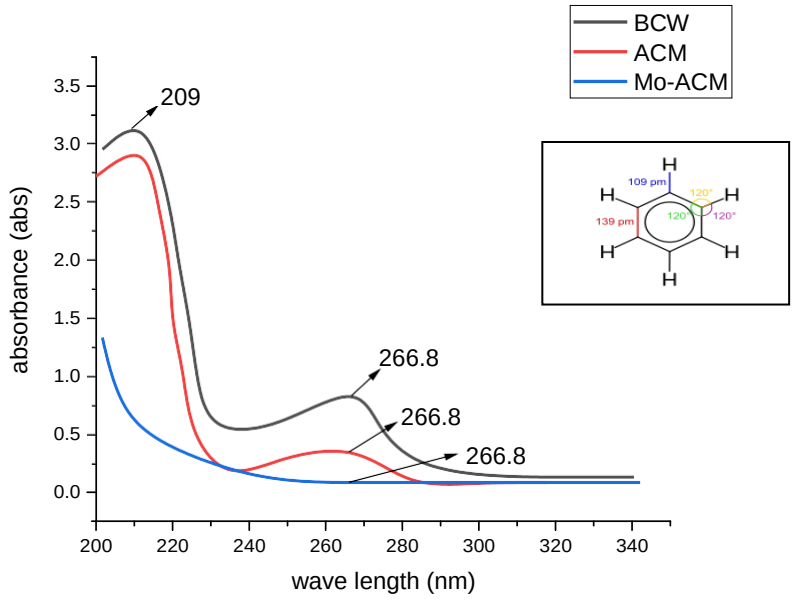


Fig.17. Uv-Vis analysis of benzene containing tannery waste water

❖ ***Catalytic oxidation of VOC's from tannery waste water***

The analysis of volatile organic compounds (VOCs) in tannery wastewater revealed the predominance of toluene, ethylbenzene, benzene, and formaldehyde, which are commonly associated with leather processing operations. The untreated tannery wastewater exhibited remarkably high levels of chemical oxygen demand (COD) and total organic carbon (TOC),

ranging from 35,200 mg/L and 6000-8000 mg/L, respectively. These elevated levels of organic contaminants underscore the urgency for effective treatment strategies to mitigate the environmental impact of tannery effluents. To address this challenge, catalytic treatment employing activated carbon matrix (ACM) and molybdenum-impregnated activated carbon matrix (Mo-ACM) was investigated. The UV-Vis absorption spectrum of the untreated tannery wastewater (TWW) exhibited three distinct peaks, attributable to the presence of VOCs. These peaks are characteristic of aromatic compounds and their conjugated π-systems, typically observed in the UV-Vis spectra of tannery effluents. Upon treatment with ACM, a decrease in peak intensity was observed, indicating the adsorption of VOCs onto the porous activated carbon matrix. However, the Mo-ACM treatment resulted in the removal of these characteristic peaks, suggesting the catalytic degradation or transformation of the VOCs. This observation aligns with findings reported by [68], where molybdenum-based catalysts facilitated the oxidative degradation of aromatic compounds in industrial wastewater.

The superior performance of Mo-ACM in VOC removal can be attributed to the synergistic effect of the porous activated carbon matrix and the dispersed molybdenum active sites. The activated carbon framework facilitates the adsorption and enrichment of VOCs, while the molybdenum species act as catalytic centers, promoting the oxidative degradation or transformation of the adsorbed VOCs. This dual mechanism of adsorption and catalytic degradation renders Mo-ACM an effective treatment strategy for the removal of recalcitrant organic pollutants from tannery wastewater. The results obtained in this study corroborate the findings reported by [69], where molybdenum-impregnated activated carbon catalysts demonstrated enhanced performance in the degradation of organic dyes compared to unmodified activated carbon. Similarly, [70] reported the effective removal of phenolic compounds from industrial wastewater using molybdenum-based catalysts supported on activated carbon.

- ***Enhanced Removal Efficiency of ACM and Mo-ACM through Repeated Cycles***

The study evaluated the repetitive degradation performance of activated carbon matrix (ACM) and molybdenum-impregnated activated carbon matrix (Mo-ACM) for volatile organic compound removal under optimized conditions. The repeatability analysis was conducted over 10 consecutive cycles to assess the catalysts' stability and consistency in pollutant removal. The results demonstrate the remarkable stability and consistent performance of the Mo-ACM catalyst

in VOC degradation. Over the course of 10 cycles, Mo-ACM exhibited an average total organic carbon (TOC) removal efficiency of 87.2%, highlighting its exceptional ability to maintain high catalytic activity and pollutant removal efficiency. This outstanding repetitive performance can be attributed to the synergistic effect of the porous activated carbon matrix and the dispersed molybdenum active sites. In contrast, the unmodified ACM material exhibited a gradual decline in removal efficiency over the cycles, with an average TOC removal efficiency of only 29.3%. This decrease in performance suggests that ACM may be susceptible to deactivation or saturation, limiting its long-term effectiveness in VOC degradation.

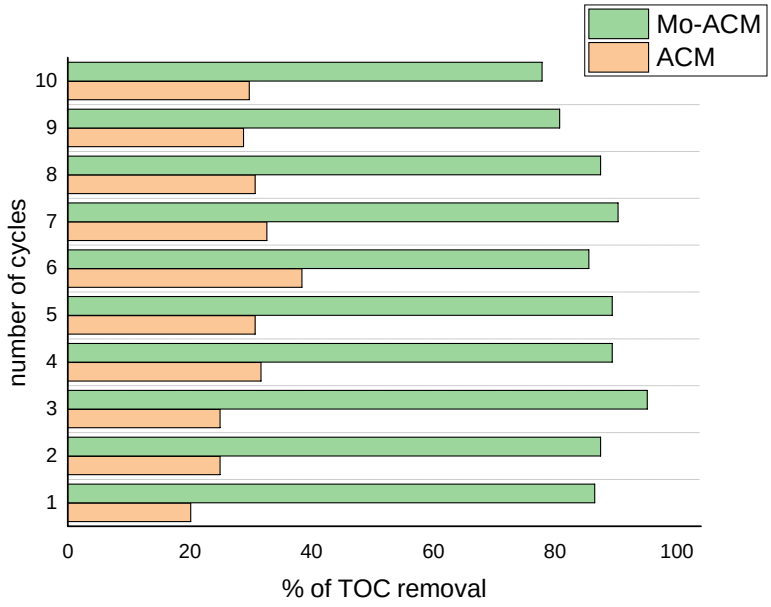


Fig.18. Removal efficiency of ACM and Mo-ACM over repeated cycle

CHAPTER FIVE

5. CONCLUSION AND RECOMANDATION

5.1. Conclusion

Volatile organic compounds (VOCs) emitted from the leather processing industry pose significant environmental and health risks due to their toxic nature, persistence, and ability to form secondary air pollutants. This research study aimed at investigating the catalytic degradation of VOCs in leather industry effluent using molybdenum-impregnated activated carbon material (Mo-ACM). Mo-ACM was synthesized by impregnating activated carbon derived from rice husk with molybdenum V chloride. The successful incorporation of molybdenum oxide species within the carbon matrix was confirmed through various physicochemical characterization techniques such density, ash content, and moister content were determined and found to be 4.9%, 75.67%, 0.386g/cm^3 respectively as at 3%Mo-ACM loading. Instrumental analysis was performed using XRD, FTIR, EPR, SEM-EDX, UV-Vis spectroscopy, TGA, and DSC. The XRD analysis revealed the presence of molybdenum oxide phases on the Mo-ACM, indicating successful impregnation. FTIR spectroscopy demonstrated interactions between molybdenum and the carbon support, further validating the synthesis methodology. SEM-EDX mapping confirmed the uniform dispersion of molybdenum within the material, providing additional evidence of successful synthesis.

To extract the VOCs from tannery wastewater, a stripping and adsorption process was employed, followed by catalytic oxidation using Mo-ACM under optimized conditions. The pH, hydraulic retention time (HRT), and dosage of hydrogen peroxide (H_2O_2) were set at 11, 120 minutes, and 0.2 mmol, respectively. The utilization of Mo-ACM resulted in an average VOC removal efficiency of 87.2% over the course of 10 treatment cycles, demonstrating its effectiveness in VOC treatment. In contrast, unmodified activated carbon showed negligible degradation of VOCs. Further insight into reaction intermediates and pathways was obtained through UV-Vis spectroscopy, total organic carbon (TOC) analysis, and chemical oxygen demand (COD) analysis. These analytical techniques provided valuable information on the reaction mechanisms involved. The improved performance of Mo-ACM can be attributed to the presence of molybdenum oxide sites, which enhance VOC activation through redox reactions. This is

consistent with previous studies that have shown transition metals to enhance catalytic oxidation by facilitating electron transfer processes.

In conclusion, this study has successfully demonstrated the potential of Mo-ACM for the abatement of VOCs in leather industry wastewater. The comprehensive characterization of the material and monitoring of the catalytic reactions have validated the synthesis methodology and provided insights into the catalytic mechanism. With further optimization, this technology holds promise for industrial applications in environmental remediation.

5.2. Recommendation

Based on the findings and analysis conducted in this thesis, it is recommended to further explore the potential of molybdenum-impregnated activated carbon for the reduction of volatile organic compounds (VOCs) in leather processing. The following recommendations are proposed:

- Optimization of Performance: Further research should be conducted to optimize the performance of molybdenum-impregnated activated carbon. This can involve studying the effects of different impregnation methods, varying molybdenum concentrations, and exploring the use of different types of activated carbon. By fine-tuning the parameters, the efficiency and effectiveness of VOC reduction can be enhanced.
- Scale-Up Studies: It is crucial to conduct scale-up studies to assess the feasibility of implementing molybdenum-impregnated activated carbon on an industrial scale. This involves evaluating the performance of the material under realistic operating conditions and considering factors such as cost-effectiveness, system integration, and long-term stability. Collaboration with leather manufacturers and industry stakeholders is essential to ensure successful implementation.
- Long-Term Performance and Regeneration: Investigate the long-term performance and regeneration potential of molybdenum-impregnated activated carbon. Assess the material's durability, stability, and ability to maintain its adsorption capacity over extended periods of operation. Develop effective regeneration methods to restore the adsorption capacity of the material, ensuring its sustainability and cost-effectiveness.

- Comparative Studies: Conduct comparative studies to evaluate the performance of molybdenum-impregnated activated carbon against other VOC reduction techniques commonly used in the leather industry. This will provide a comprehensive understanding of its advantages, limitations, and potential areas of improvement. Comparative data will assist in making informed decisions regarding the adoption of this technology.
- Collaboration and Knowledge Sharing: Foster collaboration between researchers, manufacturers, regulatory bodies, and environmental organizations to facilitate the adoption of molybdenum-impregnated activated carbon. Establish platforms for knowledge sharing, workshops, and conferences to disseminate research findings, exchange ideas, and promote the implementation of sustainable VOC reduction practices in the leather industry.

By implementing these recommendations, the leather industry can make significant strides towards reducing VOC emissions and minimizing its environmental impact. The adoption of molybdenum-impregnated activated carbon as a viable solution holds the potential to transform the industry's practices, promoting sustainability and responsible leather processing.

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