PERFORMANCE EVALUATION OF HYBRID TECHNOLOGIES FOR TREATING TANNERY WASTEWATER

A Thesis

Submitted in partial fulfillment of the requirements

for the award of the degree of

Doctor of Philosophy

by

Sneha Korpe

718007

Department of Civil Engineering

National Institute of Technology

Warangal-506004, India

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Declaration

This is to certify that the work presented in the thesis entitled **“PERFORMANCE EVALUATION OF HYBRID TECHNOLOGIES FOR TREATING TANNERY WASTEWATER”** is a bonafide work done by me under the supervision of **Dr. P. Venkateswara Rao** and was not submitted elsewhere for the award of any degree. I declare that this written submission represents my ideas in my own words and where others' ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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(Dr. P. Venkateswara Rao)
Associate Professor
Department of Civil Engineering
National Institute of Technology
Warangal-506004

Warangal,

Date:

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Abstract

The tanning industry is one of the important industries in India, which earns substantial foreign exchange through leather export. Leather production depends upon the various manufacturing processes that take place in the industry. The tanning industry releases its waste in the form of liquid, solid, and gas. The untreated release of tannery effluents containing high organic carbon, chemical oxygen demand (COD), biochemical oxygen demand (BOD) levels, trivalent chromium, sulphide, chlorides, calcium, magnesium, organics, and other toxic ingredients into the natural water bodies and open lands, affects the flora and fauna of the ecosystem. In recent years, due to stringent water quality regulations, extensive research is focused on upgrading water treatment technologies and developing processes that are economical and to deal with toxic and biologically refractory organic contaminants in wastewater. Research studies have suggested that the tannery wastewater effluent consists of complex compounds requiring a series of treatment processes to meet the desirable effluent discharge standards. Therefore, the research has been conducted on performance of hybrid technologies for the treatment of the tannery wastewater effluent to be able to reach to the desired effluent disposal standards up to the maximum extent.

Objective 1 – Primary study was conducted mainly focussing on the removal of turbidity and total suspended solids from the tannery wastewater effluent using orange peel waste. However, the application of the orange peel waste was done using them as adsorbents. Orange peel waste was used in dehydrated and activated char form termed as orange peel powder and activated orange peel powder respectively. A comparative study was conducted on the degradation efficiencies obtained in terms of turbidity, total suspended solids (TSS) and chemical oxygen demand (COD) removal by using alum as a chemical coagulant, orange peel powder (OPP) and activated orange peel powder (AOPP) as naturally obtained adsorbents respectively. It was observed that the physico-chemical properties of the OPP and AOPP played an important role in the removal of the pollutants from tannery wastewater effluent. Scanning Electron Microscope (SEM) showed that the AOPP consists of a porous structure that leads to adsorption of pollutants over the surface. Brunauer–Emmett–Teller (BET) analysis resulted in surface area reduction of AOPP from 11.663m ^{2}/g to 1.289m ^{2}/g before and after adsorption correlating the experimental results of the study. Moreover, X-Ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Total organic carbon (TOC) proved that the chemical properties also play an important role in degrading the pollutants present in TWE. The experimental analysis showed that AOPP as an adsorbent successfully removed turbidity, Total suspended solids, and COD by 98.43%, 97.65% and 49.85% respectively at optimized conditions of AOPP dosage – 2g/L, pH – 4, contact time – 30 min. Results proved that the application of AOPP as a pre-treatment of tannery wastewater effluent can be recommended for larger-scale implementation.

Objective 2 – Tannery wastewater consists of several complex compounds that have poor biodegradability. The study further conducted experiments on the effluent obtained from previous objective using advanced oxidation processes. A pilot scale study has been conducted on orifice embedded hydrodynamic cavitation reactor for treating real-time TWE. Liquid chromatography-high resolution mass spectrometry (LC-HRMS) has been carried out to identify the specific compounds present in TWE before and after treatment. The common compounds in TWE were found to be phenolic compounds (p-nitrophenol), 4-chloro-m-cresol, polyethylene glycols (PEGs), dibutyl phthalate (DBP), nonyl phenol ethoxylated surfactants and alcohol ethoxylated surfactant. The mass spectra reflected that several intermediate peaks of aromatic compounds, i.e., p-nitrocatechol (m/z=155.1102) and hydroquinone (m/z=110.1123) and acids, i.e., malic acid (m/z=134.0874), the carboxylic acid (m/z=150.150), malonic acid (m/z=104.0615), oxaloacetic acid (m/z= 134.0874) were found in the treated effluent. The spectrum shows that the major peaks found for raw TWE were reduced to less than 30%-50% approximately using a combination of HC+PAA+$FeSO_47H_2O$. Moreover, the experimental analysis done using Response surface methodology (RSM) – Box-Behnken design (BBD) obtained maximum COD, TDS and turbidity removal efficiency of 72.36, 94.54 and 98.89% respectively at cavitation time-97.5 min, inlet pressure-7.5 bar, pH-2, orifice diameter-0.5 mm, PAA dosage-17.5 g/L, and PAA /$FeSO_4.7H_2O$-2:1 ratio using. Kinetic studies resulted in increase of the reaction rate constant from $2.455x10^{-3}$ to $12.75x10^{-3}$ min^{-1} when AOPs were combined with HC and concluded that the combined system shows a synergy. The study concluded that the degradation using HC+PAA+ $FeSO_4.7H_2O$ successfully increased the biodegradability of the TWE without forming any toxic by-products. In addition, the energy and cost requirements for the treatment system have also been discussed in detail to see the significant perspective for scaling – up the system at an industrial scale.

Objective 3 – The increase in the biodegradability of the tannery wastewater using pre-treatment has enhanced the potential of contaminants to produce biogas. The evaluation of biogas production by conducting batch scale study on mono-digestion and co-digestion of tannery wastewater effluent was performed in this study. The effect of influential parameters i.e., C/N and pH on the biogas production and COD reduction was determined. The pre-treatment has shown an increase in biogas yield by 3 times compared to raw TWE using mono-

digestion. However, the co-digestion using chicken manure as a co-substrate resulted in 40.59 ml/g.COD and 104.75 ml/g.COD of biogas production using raw and hydrodynamic cavitation treated wastewater respectively at C/N ratio and pH of 20 and 7.5. Maximum COD removal of 64% at C/N-20 and pH-7.5 was observed for hydrodynamic cavitation treated wastewater. The study proved that the hydrodynamic cavitation as a pre-treatment resulted in significant increase in biogas production for mono-digestion as well as co-digestion. The biogas yield is more in co-digestion with chicken manure when compared to mono digestion.

Objective 4 – This study has been conducted to determine the potential of leather trimmings used as a co-substrate to enhance methane yield. The effect of C/N and pH on the anaerobic digestion of substrates were evaluated to obtain improved biogas yields. The results have clearly shown that the ternary combination of the substrates has increased the methane yield substantially. The maximum of 300.75 ml/g.COD has been produced using leather trimmings as a co-substrate when the HC+PAA+$FeSO_4.7H_2O$ (AOPs) treated wastewater was subjected to anaerobic digestion. However, the ternary combination i.e., AOP treated TWE, CM and LT has resulted in maximum methane yield of 489.81 ml/g.COD at C/N – 20 and pH – 6.5 respectively. In addition, the maximum COD reduction of 72% was obtained for the reactor operating at C/N 20 and pH-6.5. The study proved that the solid waste generated at tanning industry can successfully increase methane production if used as a co-substrate.

Summary –The hybrid treatment system was able to remove suspended solids and degrade complex compounds present in TWE into simpler compounds resulting in increase of biodegradability index. The increase in the biodegradability of the contaminants present in tannery wastewater effluent increased the methane production potential. Moreover, the solid waste generated from the tanning industry successfully increased the methane production potential when used as a co-substrate. The research study concluded that the series of combination of treatment systems was able to treat tannery wastewater up to an extent where it can be further treated aerobically.

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List of Acronyms

Advanced oxidation processes: AOP’s

Activated orange peel powder: AOPP

Activated Sludge Process: ASP

American Public Health Association: APHA

Anaerobic digestion: AD

Analysis of variance: ANOVA

Biochemical oxygen demand: BOD

Biodegradability index: BI

Box Behnken design: BBD

Brunauer–Emmett–Teller: BET

Cavitation number: C_v

Chemical oxygen demand: COD

Chicken manure: CM

Common effluent treatment plant: CETP

Computational fluid dynamics – modelling: CFD

Dibutyl phthalate: DBP

Effluent treatment plant: ETP

Energy dispersive X-ray: EDX

Field Emission Scanning Electron Microscope: FESEM

Fourier Transform Infrared Spectroscopy: FTIR

Hydraulic Retention Time: HRT

Hydrodynamic cavitation: HC

Hydroxyl radical: OH^*

Leather trimmings: LT

Liquid chromatography-high resolution mass spectrometry analysis: LC-HRMS

Low pressure – ultraviolet lamp: LP-UV

Medium pressure – ultraviolet lamp: MP-UV

Monocarboxylate polyethylene glycols: MCPEG

Orange peel powder: OPP

Organic Loading Rate: OLR
Organic peel waste: OPW
Per acetic acid: PAA
polyethylene glycols: PEGs
Response surface methodology: RSM
Solid Retention Time: SRT
Soluble Chemical oxygen demand: sCOD
Tannery wastewater effluent: TWE
Tert-butyl alcohol: TBA
Total Dissolved Solids: TDS
Total Kjeldahl Nitrogen: TKN
Total Organic Carbon: TOC
Total Suspended solids: TSS
Ultrasonication: US
Upflow Anaerobic Sludge Blanket: UASB
Volatile fatty acids: VFA's
Volatile solids: VS
X-Ray Diffraction: XRD

Chapter – 1

Introduction

1.1 Leather production worldwide and India

The rapid growing industrialization is leading lots of environmental issues by its uncontrolled pollutant emission. The destruction of forests, emissions from vehicles, land degradation due to use of poisonous insecticide and pesticide for agriculture, shortage of natural resources, rapid burning of wood fuel and many more contributes to environmental pollution. Pollution is the main reason which leads to lots of diseases, health issues and long-term livelihood impact. Pollution can broadly be classified in four major types of namely Air, Land, Noise and Water Pollution. There are several industries all over the world which are marked for high pollution like Aluminium smelter industries, Cement, Chlorine, Copper smelter, Distillery industries, Fertilizer, Iron and Steel, Oil Refinery, Petrochemicals, Tannery, Pharmaceuticals, Pulp and Paper, Thermal Power Plants and Zinc smelter industries etc (Bosnic et al., 2000).

The Industrialization contributes to the economy of many developed and developing countries. Among various growing industries, tannery industry plays a vital role in bringing up the economy of the country as well as the whole world at a large level. China stands first in leather production followed by Brazil, Italy, India and Russia, South Korea, Argentina, and USA. Figure.1.1 shows the graphical representation of leather production by various countries. All over the world, most of the tannery industries run their operations with good pollution control measures and does not expose local populations to health risk. However, one can find many sites throughout the developing world with abandoned factories that were used for making tanning chemicals or poorly run (usually small) tanneries or legacy contaminated waterways with dangerous levels of chemicals. These places pose significant public health risks to local populations. In India, Tamil Nadu consists of the highest number of tannery units i.e., 900-950, West-Bengal consisting around 600-650, Uttar Pradesh consisting around 350-400, Punjab consisting around 50-100, Maharashtra consisting around 50, Andhra Pradesh consisting around 50 and other states all together consists around 100. Countries like, Saudi Arabia, United States, Hong-Kong, Argentina, Italy, China, Brazil, Pakistan, Nigeria, Turkey and Thailand are the major suppliers of raw materials used for leather production in India (Sindelar, 2016).

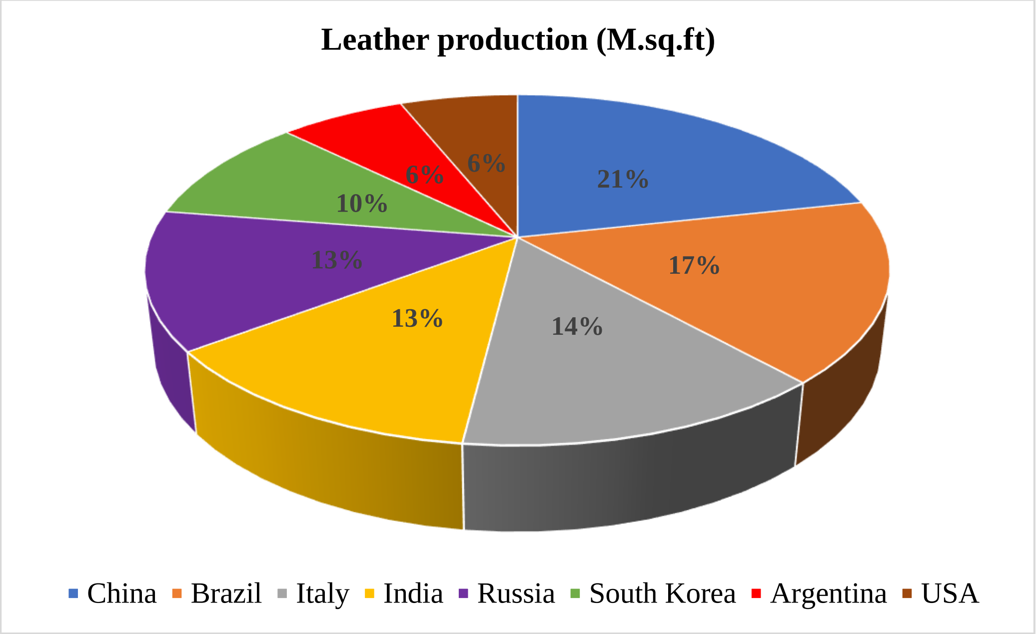

Figure 1.1 Leather production in various countries

The leather manufacturing industry consists of several different processes, with one of the most important activities being the tanning of the raw hides. Tanning involves the processing of raw leather to make it more resilient and stronger for using it in a variety of different products. Tanning is a widespread, global industry that works with both light and heavy types of leather (N. Tapas, R.D. Vyas, L. Szpyrkowicz, 2001). Light leather is generally used for shoes and other soft products such as purses, and heavy leather is used for straps, belts, and even for various machineries. The tanning process itself is made up of three general phases: acquisition and pre-treatment of raw animal hides, treatment of the hides with a tanning agent and drying and shining the hides before sending them to product manufacturers. Though these steps illustrate the general process, there are often many different processes that can be carried out at tanning facilities, and each may provide a variety of other services such as bleaching, dyeing, finishing and weaving of the hides.

Wastes originated from all stages of leather making such as fine leather particles residues from various chemical discharges and reagents from different waste liquors consists of large pieces of leather cuttings trimmings, gross shavings, fleshing residues, solid hair debris and remnants of paper bags. Over 80 per cent of the organic pollution load in terms of bio-chemical oxygen demand comes from the beam house (pre-tanning); much of this comes from degraded hide/skin and hair matter. During the tanning process at least 300 kg of chemicals (lime, salt etc.) are added per ton of hides. Excess of non-used salts will appear in the wastewater because of the changing pH. These compounds can precipitate and contribute to the amount of solid waste or suspended solids. Every tanning process step, except for finishing operations produces wastewater. An average of 35 m^3 is produced per ton of raw hide. The wastewater is made up of high concentration of salts, chromium, ammonia, dye, and solvent chemicals etc., (Kolomaznik et al., 2008).

A large amount of liquid waste generated by tanneries is discharged in open lands and rivers directly or indirectly through open drains with minimal treatment. The surface water and groundwater in the low-lying areas in developing countries like India and Bangladesh is polluted in such a degree that it has become unsuitable for public uses (Boshoff et al., 2004). In summer when the rate of decomposition of the waste is higher, serious air pollution is caused in residential areas by producing intolerable obnoxious odors. Tannery wastewater and solid wastes often find their way into ground as well as surface water, where toxins are carried downstream and contaminate water used for drinking, irrigation, and various other purposes. Chromium waste can also seep into the soil and contaminate groundwater systems that provide drinking water for nearby communities.

In recent years, with an increase in the stringent water quality regulations due to environmental concerns, extensive research has focused on upgrading current wastewater treatment technologies and developing more economical processes that can effectively deal with toxic and biologically refractory organic contaminants in wastewater. In this context, to avoid or mitigate the possible adverse health, environmental impacts and to meet compliance with federal, state and local environmental laws or only to set an example to students, many institutions of higher education have supported research that aims to establish a treatment process for practical and economic disposal of waste chemicals.

1.2 Manufacturing processes in leather industries

The leather production is performed using different types of tanning processes which gives rise to different forms of leather such as chrome-tanned leather, vegetable-tanned leather, aldehyde-tanned leather, synthetic-tanned leather and alum-tawed leather and rawhide across the globe (Dixit et al., 2015). The manufacturing of the leather takes place from the skins/hides of animals such as cow, goat, sheep, buffalo etc. Moreover, industries ranging from cottage to heavy industries carry out different manufacturing processes for the flexibility and durability of the leather material by the tanning of putrescible skin and animal rawhide. The typical processes performed for the manufacturing of leather are shown in the Figure.1.2 (Raghava Rao et al., 2003; Sivakumar et al., 2010).

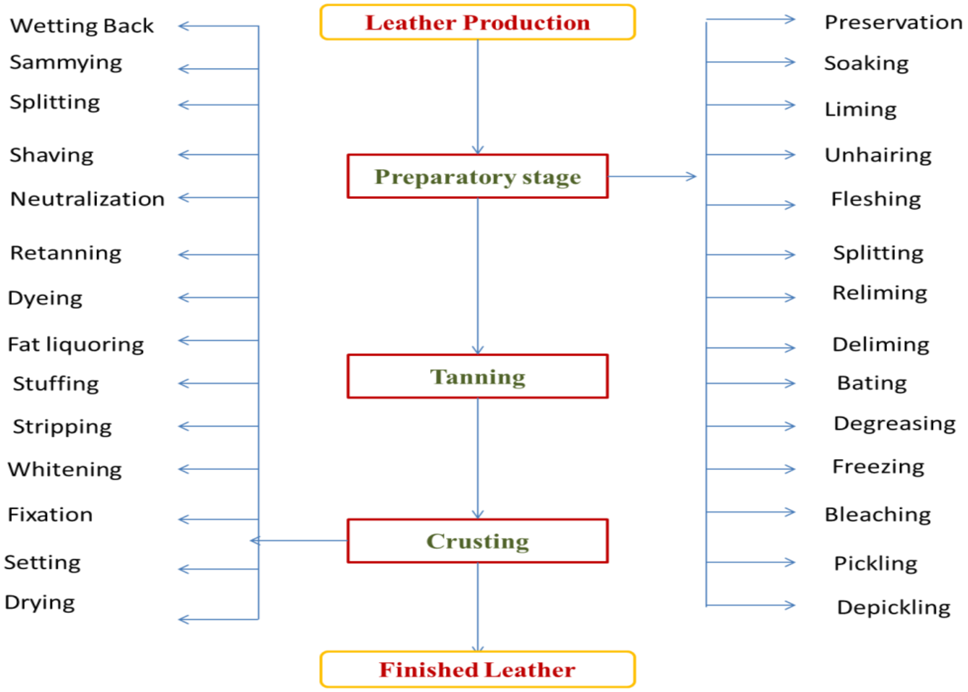

Figure 1.2 Manufacturing processes in leather industry

1.2.1 Preparatory stage

Preservation – The hides or skin are susceptible to bacterial attack due to the presence of proteins in it. Therefore, the preservation of hides or skin is done using different salts such as chlorides and sulphates.

Soaking – The process of removal of the salts from the hides or skin that are soaked in the clean water is termed as soaking. It also helps in increasing the moisture content in the hides or skin.

Liming – The process of treatment of the hides or skin using lime is called as liming. It enables the removal of hair, soluble proteins, grease, and fats present in the hide or skin. It also helps in splitting up of the fibres and bringing the collagen of the hides or skin in a proper condition that can undergo tanning easily.

Unhairing – The process of removal of the extra hair and other extra components from the hides or skin that are not converted into leather such as epidermis and subcutaneous adipose layer.

Fleshing – The process of removal of meat residues presents over the flesh side of the raw hide or skin using sharp blades is called as fleshing.

Splitting – The raw hide or skin is divided into several layers in splitting process.

Deliming – The pH of the hide or skin is adjusted to enable the further enzyme treatment.

Bating – The hides or skin are treated with enzymes to soften them.

Degreasing – The excess amount of fats and greases present over the hides or skin is removed using natural agents such as detergents and solvents in this process.

Pickling – In this process the pH of the hides is further lowered to pH-3 in order make the hides or skin more receptive to the tanning agent.

1.2.2 Tanning

Vegetable-tanning – The naturally obtained tanning agents are used while tanning process such obtained from trees like oak bark, olive leaves rhubarb roots etc.

Chrome-tanning – Chromium is used for tanning the pre-tanned hides to prevent bacterial attack.

1.2.3 Crusting

Wetting back – Rehydration of the semi-processed leather is carried out.

Sammying – Excess amount of water about 45-55% is squeezed out of the semi processed leather.

Splitting – The leather is splitted in various horizontal layers.

Shaving – Cutting of the extra fibres present over the semi processed leather is carried out.

Neutralization – Adjustment of the pH is done between the range of 4.5-6.5.

Re-tanning – Additional chemical agents are added to the semi-processed leather to impart properties.

Dyeing – Colouring of the leather is done.

Fat-liquoring – Fixation of the fats or the oils over the surface of the semi-processed leather is done.

Stuffing – Fixation of the fats or oils in between the leather fibres is done.

Stripping – All the extra tannins left over the semi-processed hides are removed.

Whitening – The process deals with making of the semi-processed hide little lightened in colour.

Fixation – Bonding of the chemicals on the surface of the semi-processed hide is called as fixation.

Setting – Excess amount of water is removed along with imparting flatness to the semi-processed leather.

Drying – The obtained leather is dried up to 14-25% moisture content.

1.3 Composition of Tannery Wastewater

The process of converting the rawhide/skin into well-furnished leather uses lot of chemicals as well as large amount of water, which results into releasing highly contaminated wastewater from the industry (Brandjes et al., 1996). The leather manufacturing in the industry is divided into three different processes: preparatory stage (hide/skin storage and beamhouse operations), tanning stage and finishing stage. Every process result in generation of significant residues into the environment, by using various chemicals. Table no 1.1 shows various operations taking place in a tannery industry, chemicals used, substances removed after every operation and contribution of the removed substances to the TWE characteristics.

Table 1.1 Overview of Leather industries

Sr. no	Name of the process		Chemicals used in the process	Removed Substances and chemical used	Contributing impurities in TWE
Pretanning (Beamhouse operations)					
1	Soaking		Sodium chloride, Bactericides	Removes dirt, manure, blood, and preservatives. Also prevents damage to the skin from halophilic microorganism present in the salt.	- Total Dissolved Solids (TDS)
2	Fleshing, trimming and unhairing		Sulphide Lime	Removal of extraneous tissue is done in this process.	-TDS -Total Suspended solids (TSS) -Biochemical oxygen demand (BOD) -Chemical oxygen demand (COD) -Nutrients
3	Deliming and Bating		Ammonium Salts Enzymes	Ammonium salts are commonly used to lower the pH. Enzymes are used in opening the fibrous structure of the skin and increase the softness. Hair remnants are removed.	- BOD -COD -Total Kjeldahl Nitrogen (TKN) -Ammonia -High conductivity
4	Pickling		Acid liquor and salts	Swelling of hide is prevented. Chromium is allowed to penetrate inside the hide.	-TDS -High conductivity
5	Degreasing		Organic solvents / surfactants	Excess fat is removed to avoid stains and dyeing irregularities	-COD
Tanning					
6	Tanning	Chrome tanning	Chromium (III) Salts are added.	It builds up the resistivity against bacteria and higher temperatures.	-Chromium -COD
		Vegetable tanning	Polyphenols		
Finishing					
7	c) Wet Finishing (Post-Tanning)		Combined tanning agents, dyes and fat liquors	To obtain the proper filling, smoothness and colour. Splitting and shaving enables the hide to get a desired amount of thickness.	-Complex compounds (VOC's)
8	Finishing		Organic solvents / varnish	It makes the hide softer and masks small mistakes.	-Colour -Organic matter -Surfactants -Chromium

The effluent generated from the industry through various processes are treated separately in three different streams as follows:

1.3.1 Soak liquor stream

The preserved raw hides regain their normal water contents and the dirt, manure, blood, preservatives (sodium chloride, bactericides) etc. are removed in the first stage from raw hides, is called as soaking. During fleshing and trimming, the extraneous tissue is removed. Unhairing is done by chemical dissolution of the hair and epidermis with an alkaline medium of sulphide and lime. Moreover, the wastewater released from soaking, fleshing, trimming, and unhairing contributes to the salt line whose treatment is done by collecting the wastewater from these processes and allowing it pass through a Sand Filter followed by evaporation. Salt remained after evaporation is sent to the factory, recovered, and then reused.

1.3.2 Chromium line

The process of chromium tanning is based on the cross-linkage of chromium ions with free carboxyl groups in the collagen and is performed in the drums. It makes the hide resistant to bacteria and high temperature. The chromium-tanned hide contains about 2-3 dry weight percent of Cr^{3+}. Wet blue, i.e., the raw hide after the chrome-tanning process, has about 40 percent of dry matter.

The wastewater generated from chrome tanning is collected in a collection tank and pumped into a tank where lime is added to it followed by precipitation. Thereafter, the supernatant is sent to the solar evaporation tank and the remaining is dried up and sent for recovery to the factory. In addition, the application of biological treatment method for the removal of high percentage of chromium released from tanyard becomes difficult due to the interference of Cr^{3+} and Cr^{6+} in biological activity performed by various micro-organisms. Moreover, the sludge obtained from chrome tanning is found to be highly contaminated with chromium compounds which may lead in hazardous waste contamination in the surrounding area of the industry. Therefore, the tanyard stream is treated separately where chromium is recovered using precipitation method. Although chromium is recovered in the industries, but the quality obtained is too much below the original standards of the chromium used in the tanning process due to the presence of impurities in the form of chromium chlorides and chromium sulphates (Gadlula et al., 2019). Figure. 1.3 shows a flow diagram depicting the effluent from soak liquor to solar evaporation ponds and from chromium line to precipitation tanks.

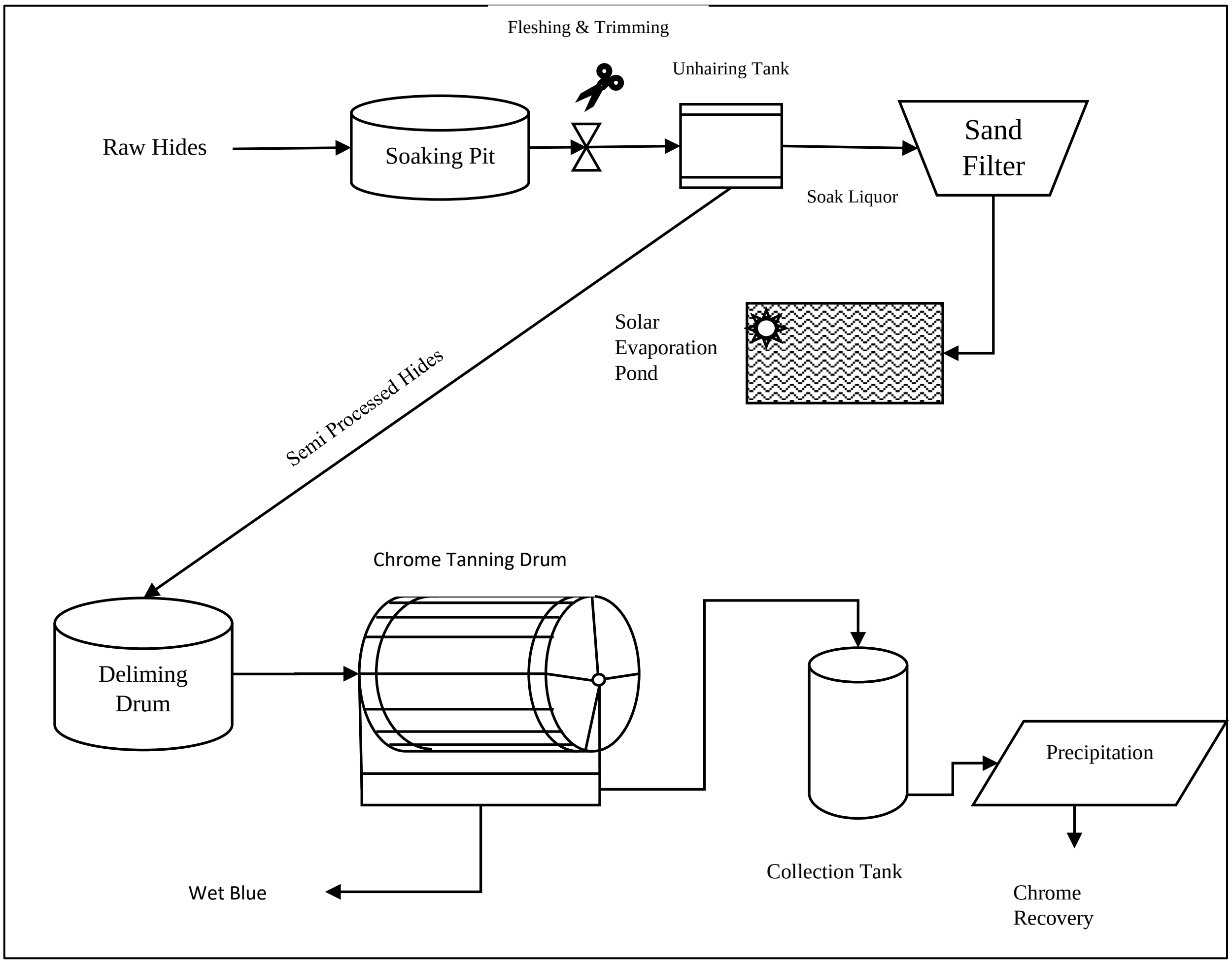

Figure 1.3 Flow diagram depicting fate of soak liquor and chrome line

1.3.3 Wastewater generated from remaining processes

The wastewater releasing from process such as deliming and bating, degreasing, wet-finishing, and finishing is sent to the nearest effluent treatment plant (ETP). The washing out of excess lime is done by putting the skins into the drums or paddling the skin over the pelt by feeding continuous cold water on to the skin which is called as deliming. Sometimes to speed up the process chemical deliming is also done by adding controlled quantity of acids to lower the pH. Mostly weak organic acids such as boric acid, acetic acid lactic acids or even acid salts such as ammonium sulphates or ammonium chloride are used. Bating is done to remove the non-collagenous skin components, several degradation products, elastin, keratin, globular proteins etc. Bating is followed by pickling where the stronger acids are added such as sulphuric acid to bring down the pH to 3 enabling the chromium to penetrate the skin.

The product obtained after chrome tanning is wet blue which further undergoes several finishing stages such as crusting and surface coating. The sub-process involved under crusting such as retanning, dyeing, fat-liquoring using chemicals such as formaldehydes, glutaraldehyde, azo dyes, diesters, polyesters, alkylated benzenes, and phosphate esters imparts high amount of BOD, COD, Total Organic Carbon (TOC) and VOC’s into the effluent wastewater. In addition, the oiling that takes place after wet finishing also contributes to increase of VOC's. In various industries the retanning, dyeing, and fat-liquoring wastewater is treated with iron (II) sulphate to precipitate large amount of protein and organic contaminants (Macchi et al., 1991). The stream generated due to the combination of different manufacturing processes consists of high complex organic pollutant load, high content in terms of the solid substances, large flow variations etc. Most commonly the ETP follows the conventional method as shown in Fig.1.4 to treat the wastewater released from several manufacturing processes.

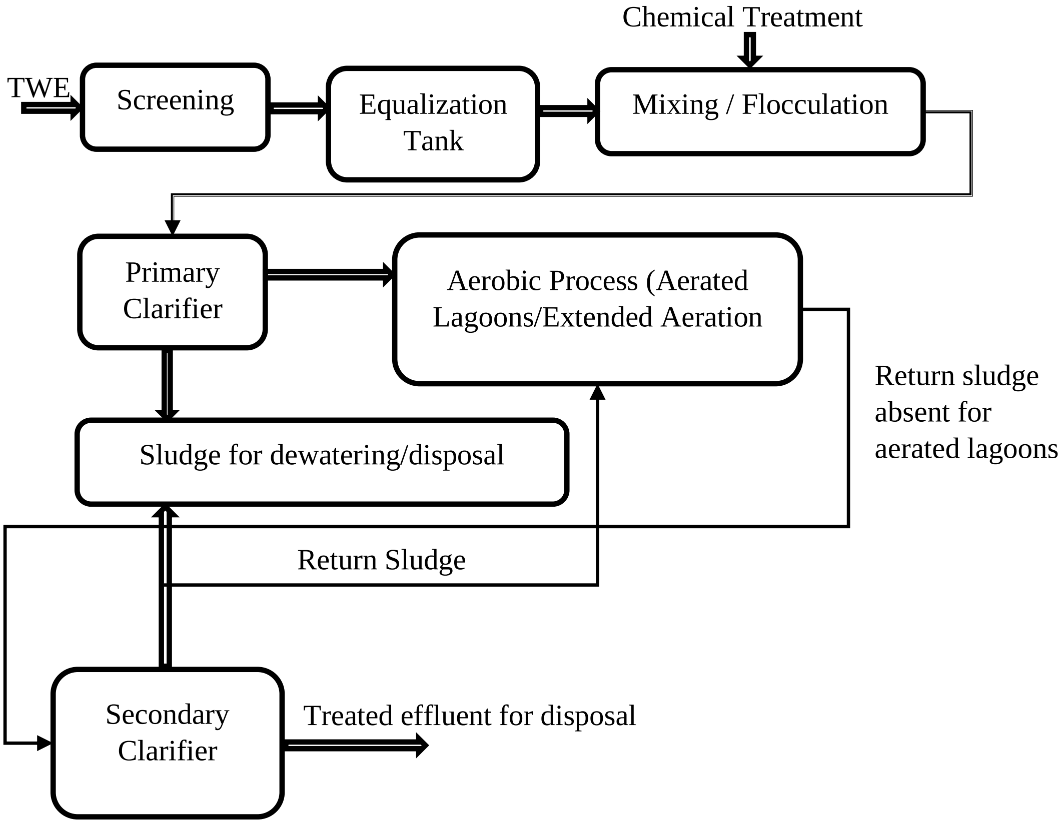

Figure 1.4 Conventional method used for treatment of wastewater released from remaining tanning processes

The wastewater released from the Tanneries is complex in nature having biological and chemical characteristics varying in different ranges. The variation in the values of biological and chemical characteristics is due to the different types of tanning process used, quantity of water utilized, hide preservation process, in-plant activities followed (Tünay et al., 1995). Moreover, the type of treatment process to be applied to treat any type of wastewater depends upon the biodegradability index (BI). BI index can defined as the ratio of BOD/COD of particular wastewater (Saxena, Saharan, et al., 2018b). The BI values ranging between 0.3-0.4 indicates that the wastewater has an ideal biodegradability. The wastewater for which the value of BI lies below 0.3 indicates that the wastewater consists of high amount of non-biodegradable compounds and hence cannot be treated with biological methods alone. Whereas, for BI values greater than or equal to 0.3 and 0.4 indicates that the wastewater can be easily degraded using aerobic processes and anaerobic processes respectively.

1.4 Motivation

The high amount of solid as well as liquid waste production in small clusters producing leather has created an adverse effect on the environment (Sreeram & Ramasami, 2003). TWE contains high amounts of recalcitrant compounds that range from simple halogenated hydrocarbons to complex structured polymers. These compounds are new synthetic compounds that are slowly biodegradable or non-biodegradable in nature and are mostly generated from wet processing activities conducted in the tannery. In addition the presence of these compounds induce toxicity in nature and have become a major problem in meeting the effluent standards either to sewer systems or to any other receiving water bodies (Jochimsen et al., 1997). Excess amount of phenols and formaldehyde present in the water are found toxic to aquatic life as well as to higher plants. Cresols also accumulates in fish or meat if it is in excess quantity (Hohreiter & Rigg, 2001; Tišler & Zagorc-Končan, 1997; X. Wang et al., 2002). The presence of highly organic and inorganic content in the form of phosphates, nitrates etc., in TWE has also been one of the major cause for eutrophication in many of the water bodies (Saxena, Saharan, et al., 2018b). Moreover, due to the presence of excess amount of impurities in water bodies the process of photosynthesis is hindered. This results into low dissolved oxygen level and renders a dark colour to the water body that also has an adverse effect on the aquatic life present inside.

The release of effluent containing high level of COD, BOD , trivalent chromium, sulphides, sodium chloride, Calcium, Magnesium, organics and other toxic ingredients from the tanneries have also created an adverse impact on the human health as well as the flora and fauna of the ecosystem (Kolomaznik et al., 2008; Pal et al., 2018). Most of the health problems are associated with the hexavalent chromium containing compounds. However, many studies have also reported an adverse effect on the agricultural land and livestock surrounding the tanning industry. The residents, especially the workers of tannery industry become the victims of this pollution, which has led to severe ailments such as eye diseases, skin irritations, kidney failure and gastrointestinal problems (Kadam, 1990).

To lower the impact of the contaminants, present in TWE, various treatment technologies are used which reduce the pollutants present in the liquid form and convert them into semi-solid or solid form (sludge). Due to which the pollution threat is shifted from the receiving water bodies to the land. The untreated sludge and the metal salt residues can also affect the quality of soil, affecting the fertility of soil and inhibiting the crop growth further.

Therefore, the treatment of TWE to a level of effluent disposal standards should be maintained prescribed as per various regulatory authorities.

1.5 Aim and objectives of the thesis

The primary objective of the study is to find out the best suitable hybrid technology to treat tannery wastewater. More specifically the objectives of the study are as follows:

1. Studying the effect of natural and chemical coagulants in removing the solids in TWE and optimization of the parameters affecting the removal efficiency.
2. Improving the Biodegradability index (BOD/COD) of TWE by conducting the performance evaluation of AOP’s at various operating parameters.
3. Performance evaluation of biogas production by anaerobic digestion of TWE obtained from physicochemical methods as a post-treatment.
4. Performance evaluation of biogas production using solid waste generated from the Tanning industry as a co-substrate for anaerobic digestion.

1.6 Organisation of the thesis

The thesis is organized as below:

Chapter 1 presents an overview of the leather industry. The manufacturing processes taking place in the industry and types of wastes generated from these manufacturing processes has been discussed. Current scenario for the treatment of tannery wastewater effluent and the environmental impacts have also been discussed in the chapter. The motivation for the research study and the objectives have also been presented in the chapter.

Chapter 2 presents the summary of the research work carried out on treatment of tannery wastewater by various researchers. The gaps identified after the literature survey have also been presented in the chapter.

Chapter 3 presents the materials and methods incorporated to carry out the research study. The procedure followed for carrying out the experimentation and instruments/equipment’s used for analyzing the results have also been described in the chapter.

Chapter 4 presents a comparative analysis between dehydrated orange peel powder, activated orange peel powder and alum used for removal of suspended solids from tannery wastewater effluent. The mechanism involved in removal of pollutants from the wastewater sample has also been discussed in detail.

Chapter 5 presents the performance of the fabricated hydrodynamic cavitation set-up (in-situ) for degradation of tannery wastewater effluent. The effects of various parameters such as cavitation time, pressure, pH, Per acetic acid (PAA) dosage and ratio of PAA to $FeSO_4.7H_2O$ on treatment removal efficiency have been explained in detail. Kinetic studies were also performed to find out the synergy between various treatment systems.

Chapter 6 presents the anaerobic digestion batch scale study adopted to digest the tannery wastewater effluent using mono-digestion and co-digestion. The cumulative biogas and methane yield obtained from co-digestion using chicken manure as co-substrate has been evaluated. The effect of C/N ratio and pH on methane production has been discussed in detail in the chapter. The digestate analysis i.e., volatile fatty acids generated, and chemical oxygen demand reduction has also been presented in the chapter.

Chapter 7 presents the anaerobic digestion batch scale study adopted using leather trimmings (solid waste from leather industry) as a co-substrate to increase the methane production. The effect of C/N ratio and pH on methane production has been discussed in detail in the chapter.

Chapter 8 presents the key findings of the research work inscribed in the thesis. It also includes the scope and recommendations for further research extensions.

Chapter – 2

Review of literature

2.1 Introduction

The increasing population, rising standard of living, and industrialisation have led to the unsustainable exploitation of natural resources. Among various natural resources, water is an essential resource for the survival of living beings; apart from that, water is the leading resource used in multiple industries. The growth of industries in production is majorly dependent on water since most of the manufacturing processes conducted in various industries require a large amount of water, such as textile, sugarcane, tannery, dairy etc. There are, however, various organic and inorganic pollutants in the liquid waste released by these industries. The liquid waste should be appropriately treated and disposed of in the environment by all desired disposal standards to minimize environmental impact. It has been reported that to achieve very high removal efficiencies, a combination of physical, chemical, and biological methods is required to treat highly contaminated wastewater (mainly released from industries) (Sneha Korpe et al., 2019; M. S. Kumar et al., 2018; Lofrano et al., 2013; Módenes et al., 2012; J. Naumczyk & Rusiniak, 2005). Based on the desired effluent standards, a combination of methods implies a pre-treatment step, a conventional step, and a post-treatment step (if necessary).

2.2 Options available for treating tannery wastewater effluent

The treatment of TWE becomes very complex due to the large amount of chemicals used and different methodologies adopted for processing of leather in various industries. Various treatment options consisting of physical, chemical and biological methods can be implemented at industrial scale (Lofrano et al., 2013). Conventional methods available for wastewater treatment include aerobic treatment, anaerobic treatment, chemical precipitation, oxidation, electrochemical methods and physical methods (mechanical treatment) (Gadlula et al., 2019).There are certain circumstances when tanneries may apply these methods in different combinations to achieve the desired effluent quality (Bosnic et al., 2000). Among the various treatment methods mentioned above, the most used biological treatment methods are Activated Sludge Process (ASP) (aerobic treatment) and Upflow Anaerobic Sludge Blanket (UASB) (anaerobic treatment). However, both the treatment methods have their own merits and demerits, where ASP is energy intensive and expensive in terms of operation and maintenance. In addition, the decomposition rate of the pollutants is much faster in ASP than in UASB process. Whereas UASB consumes more time for decomposition and results in less sludge production. To overcome the demerits and enhance the treatment efficiency several studies have been conducted to evaluate the performance of combination of aerobic and anaerobic treatment methods. Moreover, the biological treatment methods are also very sensitive to the fluctuation in the organic loading rates i.e., high COD or TDS concentration which may cause disturbance in the equilibrium of the microbial community and can hinder the operation of the biological treatment plant. However, the treatment of refractory organics present in the TWE makes the implementation of biological treatment methods to be very difficult.

Further, the reagents such as calcium oxide and Calcium hydroxide can also be used in removing chromium, sulphates, and COD present in TWE. However, chemical precipitation method can remove chromium and sulphates present in TWE. It is also to note that the TWE contains variety of contaminants due to which it fails to remove COD to an acceptable extent and resulting into introduction of new compounds as by-products into the system. The treatment of TWE using electrochemical method is also one of the pathways that results in better quality of effluent, but its application at large scale proves to be difficult due to high capital as well as running cost. Other than the application of biological and chemical methods for the treatment of TWE, researchers have also focused on the physical methods such as membrane technology. A combination of biological treatment and reverse osmosis as a pre-treatment incorporating a plane membrane resulted in removing 67% of COD and a complete purification of refractory organic compounds from TWE (De Gisi et al., 2009). From most of the research studies it has been observed that a single treatment method is not efficient enough to treat TWE. Moreover, most of them are also not economically feasible alternatives for implementation at industrial scales. Therefore, research studies on treatment of non-biodegradable TWE using hybrid methods which are economical as well as sustainable should be focussed.

2.3 Natural adsorbents used for pre-treatment

The adsorption method seems more approachable, economical, and easy to handle than other methodologies. Among the different chemical adsorbents, activated carbon has proved to be the most efficient. There is, however, a high cost associated with activated carbon, as well as a high cost associated with the regeneration of these adsorbents (Maria Emilia Fernandez et al., 2014). Therefore, to make the adsorption process comparably efficient in removing the pollutants and more cost-effective, several studies have been carried out on performance evaluation of natural adsorbents such as papaya wood, banana peel, coconut coir pith, orange peel waste etc. (Lata et al., 2015). Various agricultural wastes have also shown a decrease in turbidity, total suspended solids and chemical oxygen demand (COD) by papaya seeds, papaya leaf powder, neem leaf powder and banana peel powder (Maurya & Daverey, 2018). The orange peel biomass and the activated carbon generated from the orange peel biomass have emerged as a promising adsorbent in treating various phenolic compounds, dyes, and heavy metals such as lead, cadmium, chromium etc., present in wastewater (Alwared et al., 2021; Djilani et al., 2012; M. E. Fernandez et al., 2015; Gupta & Nayak, 2012; López-Téllez et al., 2011). However, the preparation procedure of the orange peel powder (OPP) and activated orange peel powder (AOPP) plays a significant role in developing the best physical and chemical properties favourable for higher adsorption rates. The conversion of orange peel waste into activated carbon provides several benefits such as economic viability, reduction in waste disposal cost and usage as an alternative to chemical adsorbent (Rafatullah et al., 2010).

2.3.1 Application of orange peels for water and wastewater treatment

2.3.1.1 Mechanism responsible for removal of pollutants

The removal of the pollutants from the wastewater samples using any chemical or natural coagulant/adsorbent can take place due to four mechanisms:

i) Sweep flocculation
ii) Double layer compression
iii) Adsorption and charge neutralization
iv) Adsorption and inter particle bridging

However, knowing the fact that orange peel powder is porous in nature having large surface area, the removal of the pollutants from the wastewater sample takes place due to adsorption over the surface of the adsorbent.

Majority of the studies have reported that the operating parameters need to be optimized in order to achieve best adsorption results (Alwared et al., 2021; Dhorabe et al., 2017; Gupta & Nayak, 2012). These optimized operating parameters can vary depending on the type of adsorbent and the adsorbate. The adsorption of cadmium was experimented over OPP and nano-adsorbent obtained by co-precipitating OPP with the Fe_3O_4 nanoparticles which reported that the modified OPP showed higher adsorption rates. It also reported that the time and dosage of adsorbent required to achieve maximum adsorption rate using modified OPP was also less as compared to OPP. OPP yielded adsorption capacity of 40mg/g whereas modified OPP resulted in 76.92mg/g yield (Gupta & Nayak, 2012). The adsorption of acid violet-17 was removed from aqueous solution at optimized condition at pH-2 and adsorbent dose of 600mg/50ml of 10mg/L of dye concentration (Sivaraj et al., 2001). It was observed that pH and adsorption rates were inversely proportional whereas the adsorbent dose required was directly proportion to the dye concentration in the aqueous solution. In a study conducted for adsorption of anionic azo dye Congo red cationic modified OPP was used. The modification resulted in increase of the positive charge over the surface of OPP that enables the adsorption of anionic dyes over the adsorbent (Munagapati & Kim, 2016). It is to be noted that if the pollutant to be adsorbed consists of negative charge, then cationic modified OPP is the best alternative to OPP for achieving higher adsorption rates. Moreover, the cationic modified dye can also replace AOPP for achieving higher energy efficiency. The experiments performed on cationic modified OPP resulted in 163 mg/g of adsorption capacity. In addition, the particle size of OPP and AOPP used during adsorption has significant impact on the adsorption capacities. This physical characteristic is analysed using Brunauer–Emmett–Teller (BET) analysis. In a batch study, conducting adsorption of 4-nitrophenol using 300-600 µm size particle of AOPP showed that the unloaded and loaded AOPP surface area to be 540.61 and 84.81 m^2/g which clearly indicates that the particle size and surface are inversely proportional whereas, the adsorption capacity is directly proportional to the surface area (Dhorabe et al., 2017).

A study conducted by Sandhya Maurya and Achlesh Daverey (2018) have used various plant-based materials for the removal of turbidity, TSS and COD from municipal wastewater. However, the plants waste used were banana peel powder, banana stem juice, papaya seed powder and neem leaf powder. But the characterization studies have shown that these plant wastes consist of various functional groups that are also present in OPP and AOPP that implies that the orange peel waste can also be used for municipal wastewater treatment. Moreover, the industries such as textile and tannery use dyes as well as heavy metal such as chromium during manufacturing (Asghar et al., 2015; GilPavas et al., 2019; Saxena, Saharan, et al., 2018b; Vilardi, Di Palma, & Verdone, 2018). Therefore, these adsorbents (OPP and AOPP) can also be used for the treatment of effluent from these industries too.

2.3.1.2 Parameters affecting adsorption process

pH

The pH and the adsorption rates are inversely proportional to each other. From several studies it is evident that the adsorption capacity of the OPP and AOPP decreases at higher pH values. In a study carried out by Munagapati et al., showed a drop of Congo red dye adsorption capacity from 85mg/g to 8mg/g when pH is increased from 3-9 (Munagapati & Kim, 2016). It is due to the presence of higher electrostatic attraction between the positively charged particles over the surface of adsorbent and the negatively charged ions in the dye solution. Moreover, when the pH is increased the quantity of OH^- ions also increases that hinders the adsorption capacity of the adsorbent i.e., the force of repulsion dominates the reaction resulting in lower adsorption rates. Similar type of behaviour is reported by various researchers in their studies for different types of dye removal (Fu & Viraraghavan, 2002; Ho & Chiang, 2001; Torkian et al., 2012; Vijayakumar et al., 2009). It is observed that dye removal extreme acidic conditions are favourable however for removal of few heavy metals such as cadmium the pH favourable is 5-6. This is due to presence of positive charge as well as the dominance of H^+ ions over the surface of OPP. When the pH is increased to 5-6 due to deprotonation of the functional sites cadmium or any positively charge metals can easily get adsorbed (Akinhanmi et al., 2020; Ofudje et al., 2017; Tang et al., 2017).

Contact time

Numerous studies have carried out the adsorption for maximum of 300 min whereas, the optimum contact time required lying between 15-120 min for different forms of adsorbents obtained from OPP and AOPP. In a study carried out for removal of cadmium on comparative analysis between OPP and modified OPP into a nano-adsorbent has shown faster degradation rates for modified OPP than OPP. Various studies have reported that the nano-adsorbents consists of large surface area and a non-porous structure whereas the OPP is porous comparison (Gupta & Nayak, 2012; Nassar, 2010; Nemr et al., 2009; Uheida et al., 2006). The study revealed that the porous structure is destroyed once the OPP is converted into a nano-adsorbent. Therefore, faster adsorption is attributed by non-porous modified OPP-nano-adsorbent as compared to the porous OPP. To acquire all the functional sites, present over OPP takes more time resulting in lower adsorption rates. Moreover, once the optimum contact time is reached the adsorbent surface gets saturated resulting in no further change in adsorption.

Temperature

It is observed in various studies that the increase in temperature has increases the rate of adsorption. The mobility of the molecules is increased due to increase in temperature resulting in higher diffusion rates yielding higher adsorption capacity. At higher temperatures the molecules are more likely to acquire the inner pores of the adsorbent completely hence using all the functional sites due to the decrease in the viscosity of the solution to be treated (Malik, 2003). Moreover, in as study carried out for cadmium removal it is observed that the thickness of the boundary layer of OPP has weakened at higher temperatures resulting in enhancing the adsorption of the metal ions over the surface of the adsorbate (Akinhanmi et al., 2020; Ofudje et al., 2017).

Ionic strength

The ionic strength of the solution and the adsorption capacity are inversely proportional to each other. It was observed that at lower molar concentration of $NaNO_3$ the adsorption was seen too high. The increase in ionic strength influences the reactivity of the metal ions which may result in lower adsorption rates over the adsorbent. (C. Chen et al., 2009; Gupta & Nayak, 2012)

Presence of natural organic matter

The adsorption rates in the presence of natural organic matter depends on the pH of the solution to be treated. It is observed from a study that the humic acid has increased the adsorption rates of OPP and modified OPP into nano-adsorbent in the pH range of 3-6. The surface of adsorbent is covered with more oxygen functional groups in the presence of humic acid that results in adsorption of more cadmium positively charged particles (Gupta & Nayak, 2012)

Adsorbent dosage and initial pollutant concentration

It is observed when the adsorbent dosage is increased it results into higher adsorption capacity. It is because of the presence of more number of functional sites available over the adsorbents (Akinhanmi et al., 2020; Gemeay et al., 2020). However, the dosage of adsorbent and the initial concentration are proportional to each other. The dosage of the adsorbent must be increased when the adsorbate concentration is increased. If the adsorbent is more than the required quantity, it may end up in producing more sludge holding unused adsorbent. Whereas, if the initial concentration of pollutant is more and adsorbent dosage is lesser than the optimized then the maximum uptake of the pollutant over the surface area of adsorbent is not possible. Therefore, both the parameters should be optimized before designing a treatment system using adsorption method.

2.3.1.3 Reusability of adsorbents

The performance of OPP and AOPP for the treatment of variety of pollutants present in wastewater has proved to be a very efficient alternative for costly chemical adsorbents. However, the method used for preparing AOPP consists of involvement of different chemicals as well as energy in the form of heating. Therefore, to make the process more reliable, approachable, eco-friendly, and economical the regeneration and reuse of adsorbent is highly necessary. Several techniques have been used for regenerating the adsorbents such as chemical (using chemical reagents), biological (algal biomass), physical (ultrasonication), physico-chemical (solvent washing), electrochemical and thermal method (Kulkarni & Kaware, 2014; Lata et al., 2015). It is very essential to regenerate the adsorbents to compensate the overall cost of the adsorbents used for the treatment. Moreover, the different types of methods are suitable for various types of adsorbents such as organic and inorganic adsorbents. Therefore, the use of method depends on the capital investment and nature of the adsorbent.

Several studies have been carried for the regeneration of the organic adsorbents such as papaya wood, cellulose containing material, coconut coir pith, magnetic wheat straw, orange peel powder, coffee waste, yeast biomass/waste yeast, red mud etc. (Lata et al., 2015). Papaya wood have successfully removed heavy from the aqueous solution and regenerated using 0.1N Hydrochloric acid (HCl) as a desorbing agent (Saeed et al., 2005). The regenerated papaya wood was able to remove the heavy metals with equal efficiencies up to five repeated usages in removing similar concentration of heavy metal solution. The adsorbent made from coconut coir pith used for arsenic removal was also regenerated using 0.1M HCl solution. However, the adsorption efficiencies of the regenerated adsorbent showed similar removal efficiencies up to 6 more cycles (Anirudhan & Unnithan, 2007). The desorbing agents could also be alkaline in nature and result into comparable desorbing efficiencies. In a study carried out for arsenic removal the magnetic straw adsorbent was regenerated using Sodium hydroxide (NaOH) (Tian et al., 2011). Moreover, the reusing capacity is more as compared to the above inscribed adsorbents i.e., repeatedly around 10 times the regenerated adsorbent could be used efficiently.

The OPP and AOPP adsorbents are organic in nature and thus requires similar implementation of desorbing process as for other studies. In a study carried out for the removal of cadmium the OPP was regenerated by using 0.1 M Nitric acid (HNO_3) was used as desorbing agent (Gupta & Nayak, 2012). The cadmium removal obtained was up to 98% and the regenerated adsorbent was having comparable adsorption efficiency for 5 adsorption-desorption cycles. NaCl solution is also capable of desorbing of the heavy metals or any chemical adsorbed over the surface of OPP (Akinhanmi et al., 2020). However, unlike HNO_3 the reuse of the regenerated adsorbent was recommended to be done for 3 more adsorption-desorption cycles. Moreover, HCl has also been used for regeneration of the OPP adsorbent (Lasheen et al., 2012). The adsorption efficiency decreased from 96.0% to 91.5% from first to fourth adsorption-desorption cycle. From above studies it is very much evident that an adsorbent loses its property of adsorbing after several adsorption-desorption cycles. Therefore, it is necessary to change the adsorbent with a new one after its life cycle is finished to yield better results. Disposal of OPP and AOPP into the neighbouring land area may not create any issue as it is biodegradable. However, it is also to be noted that minimal treatment should be given to the used adsorbent before disposing it into the environment.

2.3.2 Adsorption kinetics and adsorption isotherm

2.3.2.1 Adsorption kinetics

The adsorption capacity (q_e) and removal efficiency were determined using equations 2.1 and 2.2.

$q_e = (C_i - C_e/W)*V$ (2.1)

Adsorption efficiency = $(C_i - C_e/C_i)*100$ (2.2)

The rate constants for the adsorption of COD over AOPP was determined by pseudo-first-order expression and pseudo-second-order kinetic model as given below in equation 2.3 and 2.4.

$\log (q_e - q_t) = \log q_e - (k_f/2.303)*t$ (2.3)

$t/q_t = [1/(k_s*q_e^2)] + (t/q_t)$ (2.4)

where k_f = Lagergren rate constant; k_s [g/(mg min)] = second-order rate constant; q_e and q_t = COD adsorbed (mg/g) at equilibrium and at time t, respectively. The slope and intercept plot of ln (qe – qt) versus t for different concentrations were used to determine the kf and qe values for the first-order kinetic equation. Values of k_s and equilibrium sorption capacity q_e were calculated from the intercept and slope of the plot of t/q_t versus t for the pseudo-second-order kinetic model.

2.3.2.2 Adsorption isotherm

The study has been carried out on real-time wastewater with a single initial concentration of COD input. The experimental data's linear fitting was performed to find the suitable isotherm, i.e., Langmuir and Freundlich isotherm. Synthetic tannery wastewater with initial COD concentrations of 10000-17000 mg/L (interval of 1000 mg/L) was prepared and given as input values (initial concentrations) and underwent a coagulation-flocculation treatment process using AOPP. The Langmuir and Freundlich isotherm were tested to fit the experimental adsorption data. The equilibrium adsorption isotherm equation tested is mentioned below in equations 2.5 and 2.6.

Langmuir adsorption isotherm – $q_e = [q_m *K_L*C_e/1+ K_L*C_e]$ (2.5)

Freundlich adsorption isotherm – $q_e = K_F*C_e^{1/n}$ (2.6)

2.4 Advanced Oxidation Process used for increasing Biodegradability index (BI)

Advanced oxidation processes (AOP's) are chemical methods based upon the mechanism of generating Hydroxyl radical (OH^*), which are highly reactive and can degrade the complex organic pollutants present in different types of industrial wastewater. The reaction of the OH^* and various organic pollutants results into mineral end products, yielding inorganic ions and carbon dioxide (Ledezma Estrada et al., 2012). The physical and chemical properties of the contaminants present in the TWE as well as the generation of reactive radicals mainly, hydroxyl radical determines the efficiency of various AOP's in improving the biodegradability of these pollutants (Stocking et al., 2008). The generation of these reactive radicals can be achieved by several processes, which includes Ozone based processes (Dogruel et al., 2004; Glaze et al., 1987; Preethi et al., 2009; Srinivasan et al., 2009), Fenton and photo-Fenton based reactions (Chakinala et al., 2009; Chamarro et al., 2001; Kurt et al., 2007; Lofrano et al., 2007; Mandal et al., 2010), heterogeneous photocatalysis (Moradi & Moussavi, 2019) and various hybrid technologies (Chamarro et al., 2001; Gottschalk et al., 2009; J. H. Naumczyk & Kucharska, 2017; Sauer et al., 2006; S. G. Schrank et al., 2005; Sivagami et al., 2018). These AOP's can be used as pre-treatment as well as post treatment methods in combination with the other conventional methods to yield desired effluent quality. When AOP is used as pre-treatment, it improves the biodegradability of the wastewater whereas if it is used as post treatment, it tends to remove those contaminants from the wastewater which are not readily biodegradable even after undergoing conventional treatment (Bila et al., 2005; N. J. Karrer, 1997; Poole, 2004; G. Yu et al., 1998).

AOP's consist of several advantages in terms of faster reaction rates, small footprints, it has an ability to treat almost all organic matter as well as several heavy metals, it can also be used for disinfection, it does not create negative impact on the environment and the sludge production is negligible as compared to other chemical and biological treatment methods. In the current study AOPs ($PAA+FeSO_4.7H_2O$) in combination with hydrodynamic cavitation (HC) method has been used in treating TWE.

AOP's can be subdivided into several methods based on their reaction phenomenon i.e., physical phenomenon or chemical phenomenon or combination of both the phenomenon's as shown below in the Figure. 2.1.

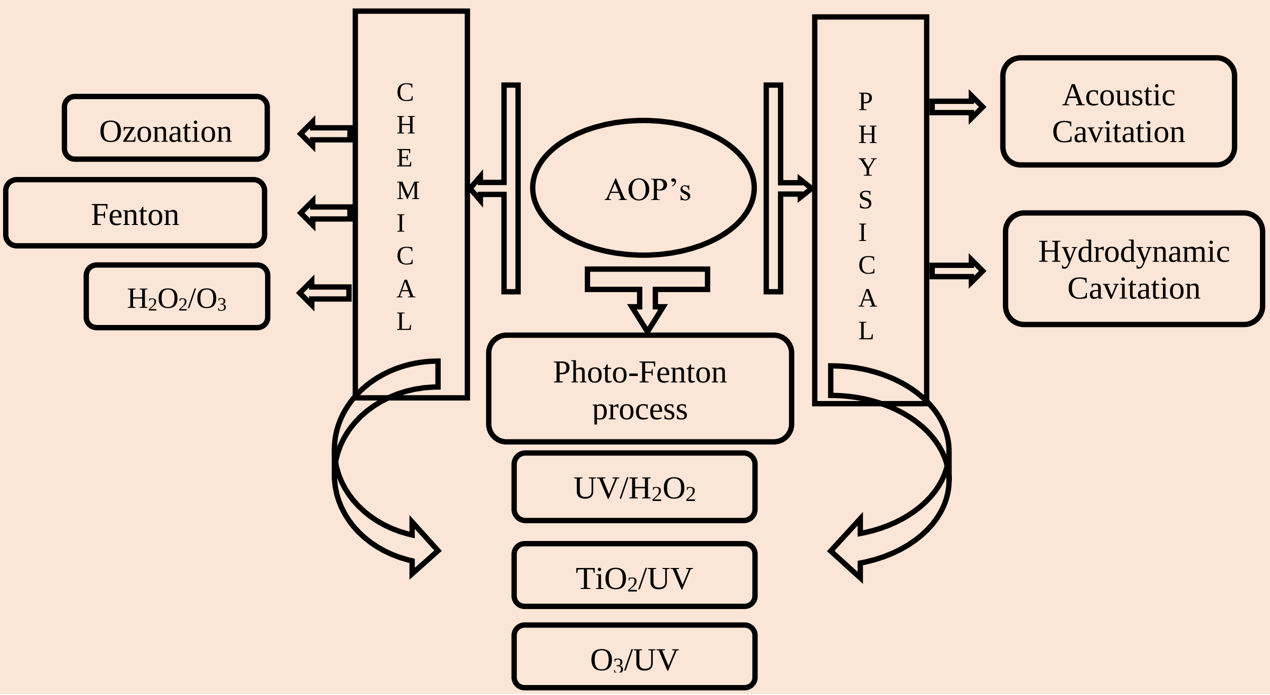

Figure 2.1 Advanced oxidation processes

2.4.1 Ozonation

OH* and ozone are the two strongest chemical oxidants. Ozonation has a capability of converting complex organic compounds into much simpler compounds which can be degraded further using conventional methods. A particular reaction occurs when the contaminants present in TWE comes in contact with the ozone injected inside the sample to be treated. To degrade the contaminants either ozone directly reacts with the complex compounds, or it generates hydroxyl radical which further enables the reaction to take place. The reaction of Ozone with the wastewater or water takes place in two different ways i.e., direct, and indirect pathway. These pathways/reactions result in variety of oxidation products.

2.4.1.1 Application

In general, Ozonation has been applied for the treatment of TWE in combination with several conventional (Physico-chemical and biological) treatment methodologies. However, the use of Ozonation as pre-treatment/post-treatment or simultaneous treatment method depends upon characteristics of the wastewater to be treated and removal efficiencies to be obtained. A study has been conducted to determine the point/phase of application of ozone during the time of biological treatment method (Dogruel et al., 2006). The ozone application was done at four different locations i.e., 1st stage from where the raw wastewater was entering into the biological treatment system, 2nd stage where the readily biodegradable COD was completely depleted, 3rd stage where the wastewater left with only half of its initial hydrolyzable COD content and 4th stage to be the last stage in the biological treatment. From the results it was observed that the application of ozonation after the complete degradation of the readily biodegradable compounds is the better alternative compared to the others.

OH^* generation is the important mechanism involved in degradation of the pollutants present in different types of wastewaters. A review has been conducted to determine the OH^* in different processes such as ozone (O_3), O_3/H_2O_2, O_3/UV and H_2O_2/UV (Glaze et al., 1987). The study stated that the combination of O_3/H_2O_2 had a higher yield of OH^* that would take part in the reactions to degrade the organic pollutants present in TWE. Further, various studies have been carried out to degrade the tannery dye effluent (Preethi et al., 2009; Srinivasan et al., 2009). In a study carried out by S V Srinivasan et al., examined the various parameters affecting the dye and tannery effluent degradation i.e., pH, ozone flow rate and initial concentration of wastewater samples. The results obtained showed that the COD and color removal efficiency was 60-80 % and 90-100% respectively when the influent concentration was 2000 mg/L whereas for influent concentration of 5000 mg/L the COD and colour removal efficiency drastically decreased. Moreover, at optimized conditions the BI is also increased from 0.18 to 0.49. Therefore, there are several research developments in the area of treatment of TWE as well as several specific compounds using ozonation treatment system alone as well as with combination of different AOP's (Dogruel et al., 2004; Sivagami et al., 2018). Therefore, ozonation is one of the effective AOP's in treating most of the highly contaminated industrial wastewater to an extent where it can be used as a pre-treatment method. Moreover, ozone application alone does not introduce any trace metals into the effluent since it decomposes into O_2 and H_2O. But at the same time ozone being a highly toxic gas, a great control is needed while handling.

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2.4.1.2 Process Parameters affecting Ozonation

pH

As explained earlier that ozone reacts with the solute immediately and non-selectively which depends upon the pH of the solution. At lower pH [<4], ozone dominates and initiates the reaction (direct pathway). The molecular ozone is very selective for the destruction of chromophore groups (ethylene, acetylene, carbonyls, acids, esters and nitrile groups etc) but reaction takes place immediately. Whereas, at higher pH[>7], the ozone decomposition takes place generating OH^* (indirect pathway), which helps in degradation of contaminants present in wastewater. In addition, OH^* is less selective in nature and has high oxidation potential than molecular ozone. However, when it comes to TWE the influent pH seems to be more alkaline in nature due to which the indirect pathway predominates. Therefore, while developing a treatment scheme both the pathways should be considered depending upon the nature of contaminants present in the wastewater to be treated.

Initial /Influent concentration

For a given operating condition, the ozone availability is fixed in terms of ozone flow rate. Therefore, the probability of incomplete degradation of the pollutants prevails due to the variation in influent concentrations.

Ozone flow rate

The pollutant degradation removal efficiency has a linear relationship with ozone flow rate with respect to time i.e., for a particular duration if ozone flow rate is increased the removal efficiency will also increase. Several experiments were carried out at various ozone flow rate, ranging from 21.6 mg/min – 93.6 mg/min for different time period in order to reduce COD from TWE (Dogruel et al., 2004). It was observed that the excess of ozone may result into the residual formation of hydrogen peroxide (H_2O_2) generated via. Indirect pathway. In these circumstances the influent concentration could be increased so that the excess amount of H_2O_2 can get consumed by COD present in the wastewater.

2.4.2 Fenton and Photo-Fenton Process

Fenton and photo-Fenton processes are the emerging AOP's used for treating highly contaminated TWE. Iron is a non-toxic element present in the form of Fe^{2+}or Fe^{3+}ions and H_2O_2 is easy to handle and proves to be environmentally friendly method (Safarzadeh-Amiri et al., 1997). To increase the overall treatment efficiency of TWE using this process several process modifications have been done and experiments were also performed. The study of COD, TOC, BOD, color, turbidity, chromium, sulphide and phenolic compounds removal efficiency have been conducted under optimal experimental conditions (Kurt et al., 2007; Mandal et al., 2010; Módenes et al., 2012; S. G. Schrank et al., 2005; Vilardi, Di Palma, & Verdone, 2018). Fenton process takes place when the organic substances present in TWE reacts with hydrogen peroxide in the presence of ferrous sulphate (S. G. Schrank et al., 2005). When pH is dropped down catalytic decomposition of Hydrogen peroxide takes place faster that gives rise to OH° radical generation (Kang & Hwang, 2000).

2.4.2.1 Application

Several studies carried out on Fenton process have explained in detail about its ability to degrade the TWE with higher degradation rates when compared with O_3 and H_2O_2 alone. A study was performed on the comparison of conventional Fenton and heterogeneous Fenton process for the treatment of TWE (Vilardi, Di Palma, Verdone, et al., 2018). The author has used iron nanoparticles for heterogeneous Fenton process and Fe^{2+} for conventional Fenton process during the experiments. The operating parameters were optimized, and final TOC, COD, phenol, and chromium removal efficiency were analysed. Moreover, results also showed that the quantity of sludge formed in heterogeneous Fenton process was almost equal to the conventional Fenton process. A similar kind of experimental work was carried out on synthetic wastewater by using heterogeneous Fenton process (Rodriguez-Rodriguez et al., 2019). The effect of pH was studied in detail on COD and chromium removal efficiencies. The synthetic tannery wastewater was made by $NaHCO_3$ (1 g/L), tannic acid (5 g/L), $K_2Cr_2O_7$ (12.26 g/L), NH_4Cl (1 g/L), CH_2O_2, $Cr_2(SO_4)_3$ (1 g/L), Polyethylene glycol 300, HCOONa (1 g/L) and C_6H_6O (5 g/L). The COD and chromium removal efficiencies were obtained around 70% and 90% respectively using heterogeneous Fenton process.

In a study conducted by Modenes et al., has conducted experiments on TWE using a combination of photo-Fenton process in combination with electrocoagulation process and further the treatment efficiency and cost effectiveness were compared with the conventional process applied in the industrial treatment plant (Filtration, chemical and sedimentation process) (Módenes et al., 2012). The wastewater samples were magnetically stirred and exposed to solar radiation for 5 hours and then the following experiments with Fenton-reagent and electrocoagulation were carried out. A pair of aluminium electrodes were utilized for electrocoagulation process with initial pH of the wastewater sample to be 8.3 and maintaining the distance between the two electrodes to be 4cm. From the results obtained the combined photo-Fenton and electrocoagulation process showed higher removal efficiencies. Moreover, the study also stated that this combination is cheaper as compared to the conventional treatment method.

The combination of Fenton process with biological treatment method have shown increment in treatment removal efficiency. Moreover, the overall time required for the biological treatment process alone have also been decreased from 21days to 72 hours (Mandal et al., 2010). In the study Thiobacillus ferrooxidans were used for the biological treatment whereas for Fenton process the $FeSO_4$ and H_2O_2 chemical were used. COD, BOD_5, sulphide, total chromium and colour removal efficiencies were evaluated after the treatment of Fenton process, biological treatment method and combination of both the processes respectively. The results proved that the combination of Fenton and biological treatment method reduced the amount of chemical dosage required and the time required for the same amount of degradation.

The Fenton process is effective at high temperatures and mostly suitable for batch treatment. Whereas, the introduction of Fe in the treatment of TWE may affect the downstream processes if used as a pre-treatment method, due to the production of $Fe(OH)_3$ sludge. Therefore, the optimization studies are essential to prevent the negative impact of the treatment system over the removal efficiencies.

2.4.2.2 Process parameters affecting Fenton and photo-Fenton reaction

The major parameters that affect the Fenton and photo-Fenton oxidation reaction are the pH of the solution, amount of ferrous ions generated, concentration of H_2O_2, the initial concentration of contaminants and irradiation time (Parag R. Gogate & Pandit, 2004).

pH

The $Fe^{2+}/Fe^{3+}/H_2O_2$ system has its maximum catalytic activity in the pH range of 2.8-3.0 (Lofrano et al., 2010). The pH of the solution is the dominating parameter among all the parameters required for the Fenton reaction to take place. At higher pH [>5], ferric hydroxides are formed due to the precipitation of ferric ion reducing the reactivity of OH^*(Arslan-Alaton & Gurses, 2004). On the other hand, at lower pH [<2], iron complex species which reacts more slowly with H_2O_2 than other species are formed. In addition, hydrogen peroxide becomes more stable and reduces its reactivity with ferrous ions. The oxidation of the pollutants present in the wastewater is also reduced at higher pH (S. G. Schrank et al., 2005). As mentioned in table 1.2, the effluent pH is almost alkaline in nature which has to be dropped down in the pH ranges suitable for Fenton process to give better removal efficiencies.

Concentration of ferrous ion

The studies conducted on the treatment of TWE using Fenton process have proved that the optimization of ferrous ion concentration is very necessary in order get the best removal efficiencies in terms of COD, TOC, BOD, TDS, TSS etc. The application of Fenton reagent ($Fe(II)/H_2O_2$) to remove the above parameters present in TWE was experimented at a range of 0.1-0.2 (Vilardi, Di Palma, & Verdone, 2018).The excess amount of ferrous ions in the solution results in increased TDS due to the formation of precipitates (Sivagami et al., 2018).The application of Fenton process in a proper manner is very important as the amount added in the solution should be totally consumed and no residues should be retained back.

Concentration of Hydrogen peroxide

Hydrogen peroxide is the main source of generation of OH^*. But in the process of producing more reactive species in the form of radicals, the concentration of H_2O_2 in the solution must be optimized. The excess amount of H_2O_2 contributes to the COD of the effluent. The residual H_2O_2 acts as OH^* scavenger which has an adverse effect on the removal efficiency of various parameters analysed after the treatment (S. G. Schrank et al., 2005; Sivagami et al., 2018).

Concentration of contaminants present in TWE

The availability of the Fenton reagent for a specific operating condition is fixed. If the concentration of contaminants is increased, it will result in increase of various biological and chemical characteristics of the TWE. A reduction in removal efficiencies is observed even if a slight change in the ratio of reagent applied for treating TWE (Fenton reagent) to the contaminants available in the TWE is done.

Irradiation time

The time for which the UV-light is exposed to the wastewater undergoing treatment is termed as irradiation time. It should be kept as short as possible to minimize the consumption of electricity. But at the same time, it should not be too short that the treatment process must be compromised. The irradiation time should be optimized to remove the bio-recalcitrant compounds mostly phenols (especially chloro-derivatives) present in the TWE completely otherwise the intermediates may remain in the solution. Moreover, if this treatment method is used as a pre-treatment option, then the residues in the form of oxidants should be completely removed to avoid hindrance occurring in the biological stage.

2.4.3 UV/H_2O_2

UV/H_2O_2 system has several advantages such as no sludge production, significant removal of COD at very short reaction times and very easy to handle (S. G. Schrank et al., 2005). The effectiveness of UV/H_2O_2 process for the degradation of complex compounds present in TWE depends on the several synergistic oxidation mechanisms. The oxidation of the pollutants can occur in two different ways, either, by photolysis or direct reaction with OH^*.

2.4.3.1 Application

The application of combination of UV/H_2O_2 process is a better alternative to Fenton process to avoid sludge formation. However, this process has been used as pre-treatment method to increase the biodegradability of the pollutants present in TWE. A study was carried out using a three-stage process consisting of coagulation/ H_2O_2/UV/ electro-oxidation for the treatment of tannery wastewater. The COD removal efficiency was evaluated by varying the operating parameters such as pH, coagulant dosage, H_2O_2 dosage and current supplied. Among coagulation and electro-oxidation, coagulation showed 57-74 % COD reduction whereas electro-oxidation reduced the COD about 53-73.1%. From the results obtained the author have recommended the three-stage process of coagulation/H_2O_2/UV/ electro-oxidation for the treatment of TWE.

COD, TOC, and toxicity of TWE was evaluated using H_2O_2/UV and Fenton processes (S. G. Schrank et al., 2005). Daphnia magna and Vibrio fischeri were used to evaluate the toxicity present in the wastewater samples collected for the experiments. Operating parameters were also optimized to avoid the accumulation of H_2O_2 which further contributes to COD and Fe^{2+} to avoid formation of iron hydroxides in the effluent. In both the reaction processes Fe^{2+} and UV are used as additional source of generation of OH^* that results in higher degradation rates. UV/H_2O_2 system is one of the most widely used AOP applied for the treatment of hazardous as well as refractory pollutants present in TWE among the others and results in fast treatment (Safarzadeh-Amiri et al., 1997). However, at very high temperatures there is a possibility of deterioration of the lamp performance and the presence of turbidity and colour may also interfere reducing the removal efficiency of the UV/H_2O_2 system. Therefore, the application of this system is not recommended at large scale; however, it can be used as a pre-treatment method in small scale industries consisting of low-moderate contaminated wastewater.

2.4.3.2 Process parameters affecting UV/H_2O_2 process

The effect of H_2O_2 concentration over the removal efficiencies of UV/H_2O_2 system are discussed in detail in Section 2.3.2.2.

pH

The reactivity of the H_2O_2 as well as the generation of the OH^* is little slower in the absence of Fe^{2+} or Fe^{3+} ions. These ions act as catalyst in the reaction which tends to generate more OH° at faster rate. However, the generation of the OH^* has a reciprocal relationship with the pH of the wastewater. Therefore, pH at 3-5 is recommended to implement UV/H_2O_2 process.

UV lamp type

The selection of the lamp generating waves in the wastewater to be treated is the key design parameter for UV/H_2O_2 system. The medium pressure – ultraviolet lamp (MP-UV) and low pressure – ultraviolet lamp (LP-UV) are the two types of lamps which are used for the

UV/H_2O_2 system. MP-UV lamp can emit large spectrum of waves much faster as compared to LP-UV lamp. The dissociation of peroxide radicals is also faster in case of MP-UV lamp. Therefore, MP-UV lamps are exclusively used for UV/H_2O_2 processes due to the fewer and smaller requirements of the lamps and system size respectively. In addition, it also enables direct photolysis that results in faster degradation of contaminants present in TWE.

Temperature

The thermal UV/H_2O_2 system is more efficient in degradation of the contaminants present in TWE at medium temperatures of 40˚C and 60˚ C (Sanz et al., 2013). At ambient temperature the consumption of peroxide by the contaminants is less due to which thermal enhancement is needed. Increase in the temperature increases the generation of OH^* from H_2O_2 and enhances the reactivity of these radicals towards contaminants (Elliot & Simsons, 1984; Jiménez et al., 2003). On the other hand, if temperature is raised beyond an optimum point, due to the recombination of OH^* the scavenging effect (OH^* act as an antioxidant) dominates the thermal decomposition of H_2O_2 present in the TWE.

2.4.4 TiO_2 photocatalysis (TiO_2/UV)

TiO_2 is a semiconductor which consists of a very small energy band width between its valence band and conduction band. When this semiconductor is exposed to visible light or ultraviolet radiation the electron present in the valence band get excited and move on to the conduction band. Generally, the wavelength of UV-light lies between 315-400nm. The TiO_2 surface gains positive or negative charge due to the to and fro movement of the electrons. Moreover, the TiO_2 surface temperature may reach up to 30000℃ when it is exposed to UV light. The degradation of the organic pollutants takes place due to the reactions that occur in the presence of excited state electrons formed due to the contact of TiO_2 catalyst with UV light.

2.4.4.1 Application

The application of TiO_2 in combination with UV and H_2O_2 has been studied for the treatment of tannery wastewater. For the processes TiO_2/H_2O_2 and $TiO_2/UV/H_2O_2$ the effect of H_2O_2 concentration and UV radiation time was studied in detail (Sauer et al., 2006). It was observed that the increase in H_2O_2 concentration increases the degradation rates but after a certain quantity the H_2O_2 had a detrimental effect on the degradation rates. The excess amount of H_2O_2 competed with the active sites of the catalyst and act like OH^* scavenger. All the experiments were carried out in batch reactor. The results obtained showed the COD removal in the order of $TiO_2/UV < TiO_2/H_2O_2 < TiO_2/UV/H_2O_2$.

In a study carried out by Harufumi Suzuki et al., (2015) evaluated the phenol degradation rates by using TiO_2 as a catalyst in combination with O_3 and UV (Suzuki et al., 2015). An AOP reactor was made using TiO_2 as an outer film covering UV lamp and a separate inlet point for O_3. 100% phenol degradation was obtained using the combination of processes whereas O_3 alone gave 21% removal efficiency in 120min reaction time and UV alone could reach 20% of removal efficiency in 180 min. Moreover, the generated OH^* were widely distributed all over the reactor since, TiO_2 was spread all over the outer surface of the quartz glass tube. Therefore, author have recommended the above combined process for complete degradation of phenol.

2.4.4.2 Process parameters affecting TiO_2 photocatalysis

pH

The acidity or the basicity of the wastewater sample to be treated always affects the reaction taking place on the surface of the TiO_2 catalyst. When the medium to be treated is acidic the surface of the catalyst gains a positive charge due to which the electron holes play a dominant role in the degradation reaction. However, when the medium is basic in nature the surface of the catalyst gains negative charge due to which the OH^* are generated that plays a dominant role in degradation reaction further (Gopinath et al., 2020).

Initial influent concentration

The degradation removal efficiencies increase with the increase in the initial concentration. However, initial concentration beyond certain limit shows detrimental effect on the removal efficiencies. The active cites on the surface of the catalyst gets occupied different molecules present in the wastewater and the surface of the catalyst also gets saturated. Therefore, for heavy concentration wastewaters the dilution is recommended.

TiO_2 loading

The TiO_2 loading should also be optimized to obtain higher degradation rates. The active sites on the catalyst surface should be maintained which ultimately depends on the reactor dimensions used for the treatment system.

Light intensity

The rate of degradation increases linearly when the catalyst is exposed to low intensity whereas at moderate values of intensities the rate of degradation is almost equal to the square root of the intensity and last at high intensities it follows zero order degradation rates.

2.5 Cavitation

Cavitation technique is also one of the emerging AOP's based on physical phenomenon of formation, growth, and subsequent collapse of the cavities occurring in an extremely small interval of time (microseconds) and releasing large magnitudes of energy over a very small area generating conditions of local hotpots (temperature = 1000–15,000K; pressures = 500–5000 bar). This phenomenon results in generating highly reactive free radicals, releasing a large amount of energy, and creating intense turbulence in the liquid. Based upon the mode of generation of cavities, the cavitation technique can be distinguished in four different ways i.e., acoustic cavitation, hydrodynamic cavitation, optic cavitation, and particle cavitation. Among the four types of cavitation, acoustic and hydrodynamic cavitation has been proved to be efficient techniques for TWE treatment (Mishra & Gogate, 2010). Although, scaling-up of HC method is more feasible as compared to acoustic cavitation method (Gevari et al., 2020; Sun et al., 2020).

2.5.1 Acoustic cavitation/ Ultrasonication (US)

In the case of acoustic cavitation, the process depends on the chemical changes caused by sound, particularly ultrasound, with a frequency ranging from 16 kHz-2 MHz creating pressure variation in the liquid. When an ultrasound wave propagates through a liquid medium it creates consecutive compression and rarefaction cycles. These cycles are responsible for cavities generation, growth and subsequent collapse dispersing high amount of energy and generating free radicals (Eren & Ince, 2010). The degradation of wastewater using ultrasound alone, for the case of a mixture of pollutants is difficult. To achieve better removal efficiencies, the Ultrasonication is mostly used in combination with other AOP's.

2.5.1.1 Application

Several researchers have utilized the phenomena of cavity collapse for water and wastewater treatment in their studies. Korpe et al., have studied the effect of pH, H_2O_2 concentration and reaction time on the degradation of real tannery wastewater samples using H_2O_2/US and H_2O_2/HC. The US and HC experiments were performed on ultrasound probe sonicator and HC set-up respectively. In US the cavities were generated due to the high frequency waves generated from the probe, whereas, in HC the use of orifice plate was done to generate the cavities inside the wastewater sample. H_2O_2 addition was done to increase the OH^* formation resulting in ultimate degradation of the contaminants present in wastewater sample. Moreover, this study also evaluated the energy dissipated during the cavitation phenomena. The results obtained clearly stated that the treatment and energy efficiency was more for H_2O_2/HC as compared with H_2O_2/US (S. Korpe et al., 2019).

Experiments were performed on TWE using coagulation in combination with US and HC respectively as pre-treatment methods to reduce the COD and TSS along with enhancement of biodegradability of the contaminants (Saxena, Saharan, et al., 2018a). The enhancement of biodegradability was evaluated by calculating the biodegradability index (BI). The volume of wastewater treated using US and HC are 300ml and 8L respectively. In this study, alum was used as a coagulant whereas, US was conducted using an ultrasound probe sonicator however for HC a venturi was used for generation of cavities in HC set-up. The combination of coagulation followed with HC was found to be more efficient in degrading the sample. Moreover, BI index was also raised from 0.1 to 0.57 using the combination of coagulation and HC.

Many researchers have also focused on the degradation of specific compounds using cavitation methodology and evaluated the removal efficiencies. Degradation of specific compounds such as phenol, trichloroethylene and reactive azo dyes have been experimented using US and its combination with UV and H_2O_2 (Mahamuni & Adewuyi, 2010). The rate of degradation of all the three compounds was least for US whereas the cost for applying US as the treatment system was highest of all. Therefore, to make the treatment system more technically and economically feasible the combination of three processes were experimented to treat the wastewater sample which resulted in 40 - 50 times higher degradation rate values.

2.5.1.2 Process parameters affecting acoustic cavitation

Ultrasonic Power

The quantity of OH^* generation and the extent of energy dissipated depend on the ultrasonic power (Sivakumar et al., 2009). The ultrasonic power is directly proportional to the amount of energy released into the sample which enables the degradation of the pollutants present in the wastewater by generating OH^*'s. Moreover, the excessive amount of energy dissipated releases high amount of heat and hence requires further cooling post treatment. In general, the ultrasound probe sonicator is recommended to be operated at lower ultrasonic power to consume less energy. Whereas the continuous increase in the input power allows the generation of OH^* up to a certain extent after which the recombination of OH^* is observed which further results in decrease of the removal efficiency.

Immersion depth of the probe

The propagation of waves through the liquid medium takes place through the probe. The cavities are generated at low pressure cycles as mentioned earlier. It is extremely important that the depth of immersion of the probe to be appropriate for the propagation and dissipation of the wave. The probe should be immersed in the sample to a distance such that the wave travels sufficient distance and get vanished before touching the bottom of the vessel.

2.5.2 Hydrodynamic cavitation (HC)

In the case of HC, the cavities are generated in a flowing liquid by inducing geometric variations. The HC reactor works on Bernoulli principle, where the liquid is allowed to pass through an orifice or a venturi. Cavities are formed when the local pressure of the medium falls below the vapor pressure due to sudden constriction and expansion in a fluid flow. These cavities tend to burst out with intense energy while entering into a larger flow area or high pressure zones i.e. sudden expansion recovering the pressure (Vijayanand S. Moholkar & Pandit, 1997). The intensity of cavitation is expressed in terms of the cavitation number, which is a dimensionless number (P. R. Gogate & Pandit, 2001; Sneha Korpe et al., 2019).

The cavitation number, C_v is at which the inception of cavitation occurs (Kanthale et al., 2005).The cavities are typically generated at $C_v \leq 1$ or at $C_v > 1$. Hence, at very low cavitation number, the cavities generated are much higher and releases high amount of energy. Moreover, the intensity of cavitation can also be escalated by controlling the downstream pressure (Soyama & Hoshino, 2016).

2.5.2.1 Application

To address the problem of high concentration of poorly bio-degradable compounds present in TWE, studies have focused on HC to develop a method that overcomes the disadvantages of US and yield better degradation efficiencies. A study has been carried out to treat the organic pollutants present in TWE using several hybrid methods using HC in combination with O_3, H_2O_2 and Fenton's reagent (Saxena, Rajoriya, et al., 2018). The experiments were performed for 7L wastewater samples and allowed to circulate in HC set-up consisting of venturi as a cavitating device. The results obtained clearly showed that HC in combination with Fenton reagent yielded higher degradation rates as compared to other two processes. It is also observed that the quantity of H_2O_2 required also reduced in HC + Fenton system. Kumar et al., has conducted an experimental work on dye Decolourization using H_2O_2, Fenton reagent, UV, UV/TiO_2 and photo-Fenton process. HC reactor with an orifice plate for cavity generation was used for wastewater treatment. It was observed that the dye degradation rates were intensified when HC was applied in combination with other AOP's. To evaluate the best combination of all the experiments were carried for optimization of the operating parameters. The OH^* generation was observed to be highest for HC/ H_2O_2 due to which the dye degradation rates also increased (Khatri et al., 2018).

The design of the HC reactor can be modified by adding different types of small reactor consisting of various catalyst into it which can accelerate the degradation rates and increase the overall efficiencies. On the similar ground, a study focused on phenol degradation using HC and heterogeneous Fenton oxidation process in combination (Chakinala et al., 2008). Heterogeneous Fenton process was carried out by adding a reactor in the same HC set-up after orifice plate consisting of iron pieces immersed into the ice-bath. These iron pieces act as a source of Fe^{2+} which gives rise to Fenton reaction in the presence of H_2O_2. In this study the experiments were performed to determine the declourization and TOC removal efficiency by evaluating the various operating parameters affecting the overall degradation efficiency. Most importantly the location of the catalyst bed towards the downstream of orifice was determined. It was observed that the Decolourization efficiency was 57% near to the orifice as compared to 53% obtained far from the orifice using iron catalyst bed. Results obtained proved that the continuous flow of wastewater through the bed reactor consisting of iron pieces improves the oxidation phenomena resulting into higher TOC removal efficiencies as well as the decolourization efficiencies when combined with HC.

Further, a similar type of work was carried out on industrial wastewater treatment using combination of HC and heterogeneous Fenton oxidation process (Chakinala et al., 2009). Moreover, in the study copper windings were also used over the iron pieces laid inside the reactor, which resulted into lowering the overall degradation rates. It was observed that in the presence of copper windings the active sites of iron pieces were reduced. Therefore, the results obtained from the study clearly showed that HC + Fenton process proves to be better option to reduce TOC up to 70%.

In a study carried out on methylene blue dye degradation, the combination of HC with photocatalysis and H_2O_2 respectively were used in order to decolourize the dye (Rajoriya et al., 2017). TiO_2 was used as a catalyst along with the visible light illumination inside the HC reactor. HC reactor with 10L capacity was used with a venturi as a cavitating device and positive placement pump was used for pumping the wastewater sample into the reactor. Moreover, the rpm of the pump was also managed using variable frequency drive. It was observed that the dye degradation was higher in the case of HC/ H_2O_2 as compared to HC/photocatalysis.

2.5.2.2 Process parameters affecting Hydrodynamic cavitation

pH

The recombination of generated OH^* takes place at higher pH values. However, for HC reactors the phenomena of corrosion that may occur if the sample moving through the reactor is more acidic. Therefore, the pH of the sample should be optimized before passing through the HC reactor.

Inlet pressure

HC clearly shows the degradation of recalcitrant pollutants present in TWE till the pressure reaches at an optimum point. The removal efficiency decreases or remains constant with further increase in the inlet pressure. The decrease in removal efficiency of various contaminants present in the wastewater is due to occurrence of super-cavitation which tends to reduce the cavitation intensity (Patil et al., 2014).

Temperature

Temperature variation shows incremental as well as detrimental effect on the degradation of the pollutants, due to which optimum temperature must be defined to carry out the experiments in HC reactor. The cavitation intensity increases with the increase in temperature till the temperature reaches at an optimum point. Due to increase in the temperature the kinetic energy of the molecules present in the medium is increased and the probability of undergoing physical or chemical changes also increases. Beyond the optimum temperature the intensity of cavitation is lowered due to the generation of vaporous cavities in the medium resulting into decrease in the degradation efficiency. The temperature of the HC reactor must be maintained at various temperature ranges to carry out the experiments by using an external source which may add up to the additional cost of the whole process implementation at the site. Therefore, the comparison of the benefits in terms of removal efficiencies against the operating costs should also be carried out (Parag R. Gogate & Patil, 2015).

Geometric variations in cavitation device

The utilization of a venturi device for cavitation is used physical transformations, whereas and an orifice is used to undergo chemical reactions (Chakinala et al., 2009). The main aim of the HC reactor is formation of bubbles in the medium, which is carried out by incorporating a cavitating device in the reactor. Generally, orifice and the venturi are the two widely used cavitation devices. In the case of orifice, it consists of a single hole or multiple holes. The holes can be in various combinations as shown in Figure.2.2.

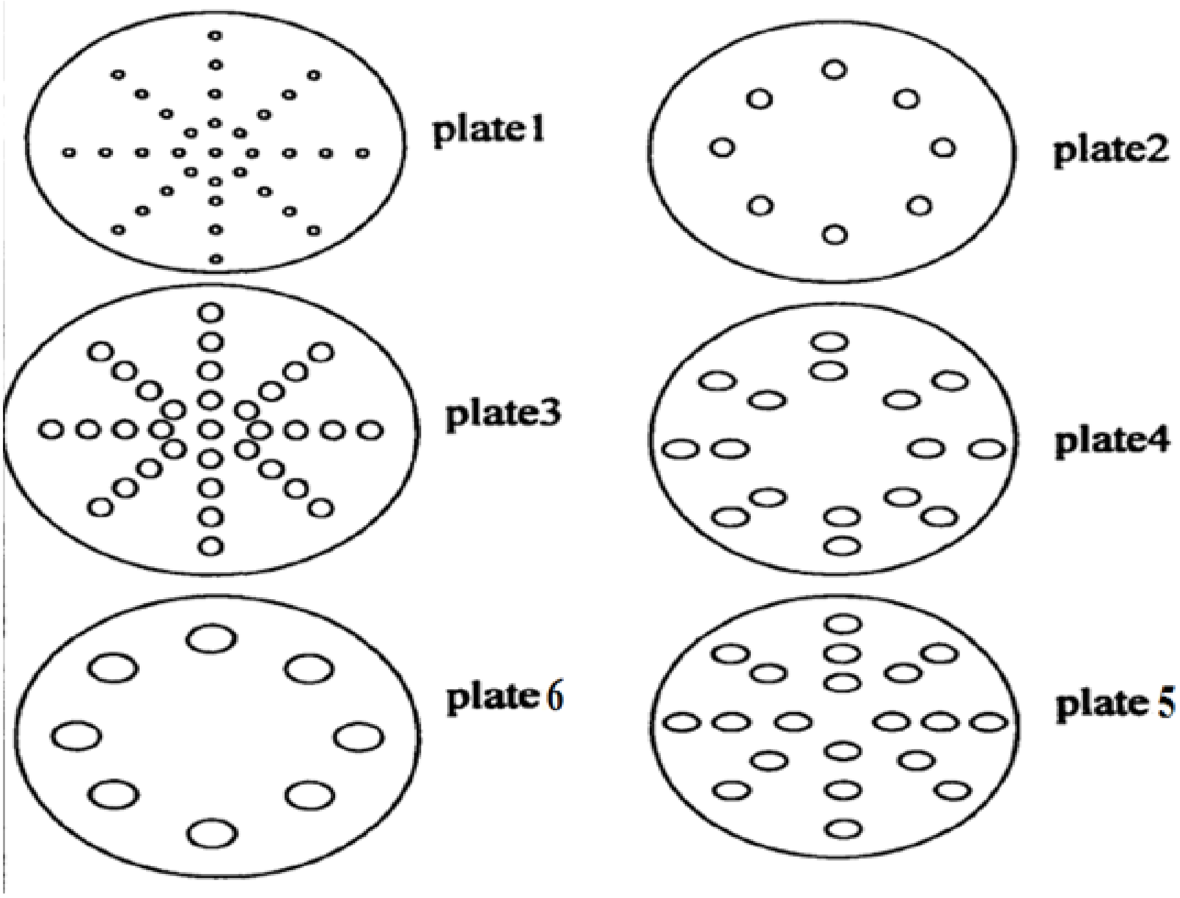


Figure 2.2 Different combinations of multiple orifice plates

The intensity of cavitation depends on the variation in hole geometry as well as ratio of perimeter of the holes present in the orifice to the Cross-sectional area of the orifice (V. S. Moholkar et al., 1999). Therefore, an orifice plate with a perfect combination of holes can control the intensity produced by the fluid inside the reactor. Venturi device consists of converging and diverging sections as shown in the Figure.2.3 those results in generation and collapse of the cavities due to the sudden pressure drop below vapour pressure when a fluid is allowed to pass through the diverging section of the configuration (V. S. Moholkar et al., 1999; Vijayanand S. Moholkar & Pandit, 1997). Venturi devices are mostly used in water treatment whereas the orifice is used for wastewater treatment (Albanese et al., 2015).

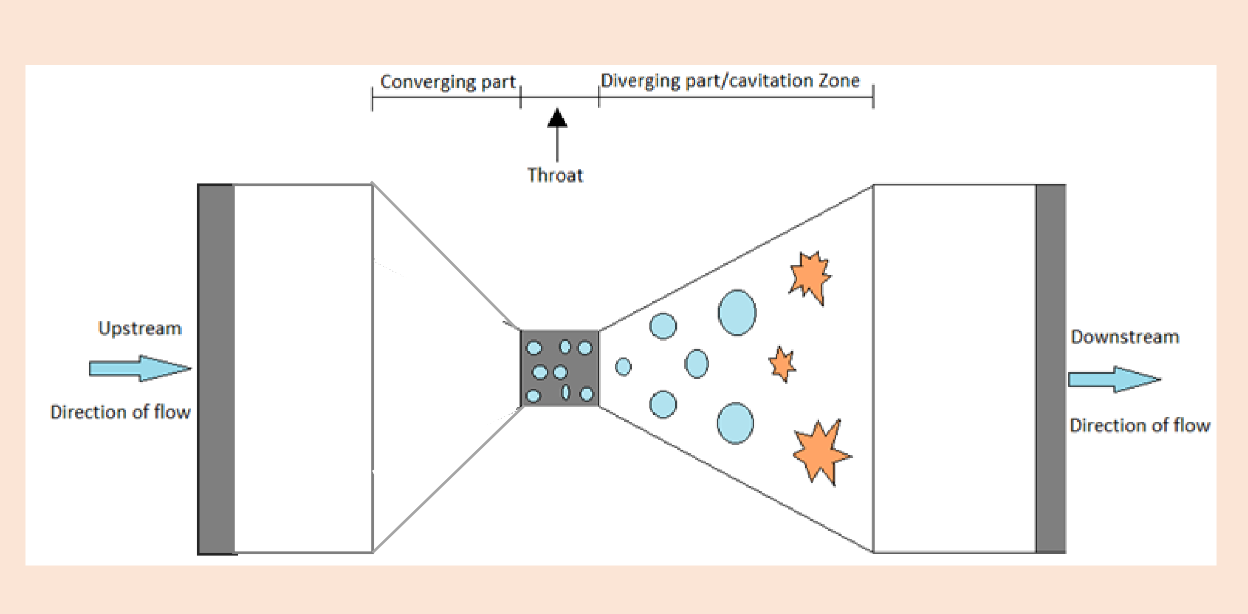


Figure 2.3 Schematic representation of venturi

2.6 Energy recovery from biomass

Anaerobic digestion (AD) is one of the best technologies utilized for converting the organic waste into useful renewable energy. AD consists of four major steps during degradation of organic material i.e., hydrolysis, acidogenesis, acetogenesis and methanogenesis which are carried out in the absence of oxygen conditions (Zhang et al., 2019). The methane gas that is produced from the anaerobic digestion consists of high calorific value due to which it can release heat energy or also can be converted into electricity. There are several countries that practices the industrial application of the biogas generated from several biogas plants. Therefore, application of AD process at tannery wastewater treatment plant can be viable option to produce biogas as well as compensate the initial capital cost of the whole hybrid technology adopted at the treatment plant for achieving desired effluent standards. A study conducted on AD of dairy wastewater resulted in biogas production (Charalambous et al., 2020). In the current study raw and treated TWE has been subjected to anaerobic digestion and chicken manure and leather trimmings have been used as co-substrates to enhance the methane production.

2.6.1. Process parameters affecting anaerobic digestion

Temperature

In anaerobic digestion, temperature is one of the most important parameters for the survival of microorganisms and efficiency of the process. The difference in the temperature range during the decomposition process can be used to distinguish the rate of decomposition. It is considered as one of the important parameter that affects the microbial activity, stability, and reaction rate of the AD process (Desai et al., 1994). If the temperature of the digestion process is under 15°C, then it is called as psychrophilic condition. If it is between 15°C and 45°C then it is termed as mesophilic condition and if the temperature is between 45°C and 60°C, it is called as thermophilic condition. According to the several studies the most suitablecondition would be the thermophilic for AD as it is better option for microbial activity and reduction of volatile solids for treatment of several domestic and industrial wastes than the mesophilic condition. The advantages of thermophilic condition are (i) improves microbial activity (ii) higher rate of reaction. The drawback of the thermophilic condition is that the digester is sensitive to shock loading and accumulation of volatile fatty acids (VFA's) which will lead to the reduction in the biogas yield and causes process instability (Gashaw, 2014).

pH and buffer capacity

The efficiency of the AD process depends on the pH. If optimum pH cannot be maintained during the digestion process, it will cause instability and inhibit the digestion process. The optimal pH range to maintain is 6.5 to 7.5. At the beginning of the digestion process, various organic acids are formed, resulting in a decrease in pH. Later the pH is increased to the optimal range of 7.0-7.5 due to the production of ammonia in the digestion process. When the pH reaches 7.2-8.0, the stabilization of biogas takes place. Generally, a drop in pH is an indicator of the production of large amounts of carbon dioxide. Changes in pH strongly affect the growth rate and rate of reaction. The greater microbial activity was observed at pH 4-7. Clostridium butyricum exists at pH 6, but at pH 8, the propionic acid bacterial community dominates the acid production stage of chemostat culture (Björnsson et al., 2000). There is a relation between hydrolysis and pH as the rate of hydrolysis depends on the pH value. Bacteria having a pH range of 5.5-6.5 are generally acidogenic and 6.5-8.2 are methanogenic. Instead of directly measuring the pH of the system, the buffer capacity is regarded as one of the indicators to measure the stability of the AD process. As acid accumulates, the buffering capacity drops considerably before the pH drop is observed. The buffering capacity is directly proportional to the amount of bicarbonate ions, which is called as alkalinity. Some steps, such as reducing OLR can also help in maintaining the buffering capacity of the system and can lead to improving biogas production.

C/N Ratio

C and N are the important nutrients for the anaerobic microorganisms for its metabolism and cell synthesis. In AD, nitrogen acts as source of energy for the cell synthesis and cell regeneration where the carbon is used for the new cells formation. Depending on the bacterial cell mass the preferred range of C/N ratio is between 20 and 65 for the AD process. Both the high and low ratios of C/N will lead to the problems in the digestion process as the higher C/N ratio will lead to inhibit the rate of the degradation as the available nitrogen content is low which is essential for the cell synthesis (Yan et al., 2015). Lower C/N ratio states that the available N content is higher and in turn formation of the ammonia takes place which will lead to the disturbance in the microbial inactivity as it is toxic and lead to the failure of the digestion process. The initial C/N ratio is a key factor affecting the distribution of VFAs, biogas yield and biotransformation.

Organic Loading Rate (OLR)

OLR is generally defined as the quantity of Volatile solids (VS) that is continuously used in the digester during the AD process. As the OLR increases, the biogas yield increases to a certain level, but for any value higher than the optimal OLR, the yield of biogas will decrease, and the volatile solids will degrade constantly due to overload (Ferguson et al., 2016). During the starting stages of the digestion process, the continuous addition of many new materials every day will cause significant changes in the digester's environment and leads to the inhibition of the microbial activity temporarily. Due to the acidification of the excess substrate in a short period of time, the bacteria produce excess VFA, which in turn reduces the ability of the methanogenic bacteria to convert acid to methane and reduces the pH value in the digester. The optimum dosage is considered as 5 g VS/l. If the organic load is high, the fermentation tank will be blocked due to the increase of butyric acid and valeric acids. Several studies have mentioned that it was observed at a low OLR i.e., about 0.7 VS/l has improved digestion and the biogas yield.

Hydraulic Retention Time (HRT)

The time required for the complete decomposition of organic matter is called retention time.It depends on the growth rate of microorganisms and the temperature of the digester. The average HRT for treating solid wastes at mesophilic temperature in anaerobic digesters is 15 to 30 days, while it is slightly shorter under high temperature conditions. Any deviation from the ideal range will cause problems. The use of digester components is inefficient, if hydraulic retention time lasts longer than optimal and if HRT is less, volatile fatty acids (VFA) will accumulate. If the bacterial loss is greater than the bacterial growth rate and the HRT is less, this may cause failure of the process (Desai et al., 1994). The decomposition time is a key factor affecting the rate of biogas production. Considering the algae biomass, when the HRT is less than 10 days, the biogas production rate is low. If the process is runwith a longer hydraulic retention time and a lower OLR, the performance of the digester will be effective and increases the biogas yield.

Solid Retention Time (SRT)

To ensure a stable state, a small fraction ofthe microbial community will be removed every time during the removal of the sludge from the digester, so that cell growth must compensate for the removed bacterial cells, such that process failure can also be prevented. Many studies stated that at different range of solid retention time, the digestion at mesophilic condition with a longer SRT of 25 days reduces volatile solids more, and in the thermophilic condition with a shorter SRT of 15 days 10 days the reduction of volatile solids more (Yan et al., 2015). The efficiency of the VS reduction is more in mesophilic temperature when compared with thermophilic temperature. To increase biogas production, the best conditions are to maintain a short solid retention time for the effective digestion process.

Mixing/agitation condition

The mixing can be continuous or intermediate depending on the substrates used in the digestion process. Slow mixing helps the system to absorb shocks, and rapid mixing can reduce biogas production (Lindmark et al., 2014). The lower yield of the biogas is because of the formation of the granules of anaerobic particles. Hydrodynamic testing studies are used for the mixing efficiency measurement in the digester, which states that the digester is fully functional or not. Li^+ is used as a visible detector in AD for the measuring the mixing condition. The detector is non-toxic to low-concentration systems and can be present in most of the feeds. Therefore, to ensure suitable mixing condition, the biogas produced in the digester must be recirculated through the bottom of the digester.

Toxicity

The decomposition of the substrate can produce toxic substances, or they may already be present in the system. The H_2S concentration in the non- dissociated form is toxic for the activity of the methanogens during methanogenesis. This is because H_2S in such form can easily diffuse through the cell membrane. This causes protein breakdown and disrupts the metabolism of the microbes. From the literature studies it is stated that the toxicity is relatedto the combined concentration of H_2S at the pH range of 6.9-7.3. The rate of bacterial growth in the digester is inhibited by the toxic substances like mineral ions etc. cleaners are some toxic substances that inhibit the bacterial growth in the digester. When the concentration of these toxic substances is high, they inhibit the growth of microorganisms.

2.7 Summary of the literature

Conventional biological methods alone are found to be not effective in treating TWE. From the literature studies it can be summarized that, to obtain the desired effluent standards, a combination of treatment methods may be used to treat the TWE. Use of more than one process is required for TWE to meet the desired effluent with the disposal standards. TWE consists of a high concentration of poorly biodegradable compounds as well as metals which may inhibit the conventional biological treatment. Therefore, the adoption of pre-treatment processes may address the problem. Coagulation process is one of the majorly used pre-treatment methods to reduce the concentration of the contaminants specifically the solids which are present as colloids in TWE. It has been observed from the studies that several AOPs have been successfully used to increase the biodegradability of the complex compounds present in TWE. Hydroxyl radical generated through AOPs and HC proves to be a better alternative for oxidizing the complex compounds in TWE, resulting in increasing the biodegradability of the effluent. Moreover, among various types of cavitation methods, the hydrodynamic cavitation method has scaling up possibilities and proves to be energy efficient when compared to other cavitation methods. The increase in the biodegradability of the TWE has also paved the way for post-treatment using anaerobic digestion that may result in recovering gas in terms of methane yield which can be useful in the form of fuel etc.

Chapter – 3

Material and methods

This chapter is presented to discuss the various materials used and physico chemical methods followed in the study for the treatment of the tannery wastewater effluent (TWE). The wastewater characterization such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solids (TSS), total dissolved solids (TDS) and turbidity was done using analytical methods as mentioned by the American Public Health Association (APHA). The instruments involved in determining the physico-chemical characteristics of the adsorbent/coagulant have also been inscribed in the following chapter.

3.1 Study area

Real-time wastewater was collected from a small-scale tanning industry located in Desaipet, Warangal urban district (Telangana). The samples were collected weekly, and the experiments were performed to understand the variations in the physicochemical characteristics and preserved for further use. They were collected at the inlet of the effluent treatment plant (ETP) and at the outlet point of sedimentation tank. The collection of samples was carried once a week from the industry, and experimental runs were performed on the fresh sample. The samples were preserved at temperatures below 4°C and were added with H_2SO_4 to prevent bacterial inhibition and avoid forming precipitates (APHA, 1999).

3.2 Adsorbent preparation

3.2.1 Preparation of natural coagulant from orange peel

Orange peels were collected from the nearest juice center and washed with double distilled water. The type of oranges used by the juice center were navel oranges, one of the most obtained varieties of oranges. The washed peels were then sun-dried, followed by oven drying at 70°C for 8 hours. The dried orange peels were further crushed and grinded using a mixer grinder. Sieve analysis was performed for the crushed peel powder, and particles size varying between 50-150µ were used for the experiments. The OPP production process has been adopted from various studies using organic peel waste (OPW) to remove pollutants from wastewater (Alwared et al., 2021; Amin et al., 2019). Picture depicting the procedure to obtain OPP has been shown in Figure.3.1. The collected peel powder was cleaned, and oven dried at 105°C for 24 hours to remove the moisture. Half of the oven-dried samples were stored in an airtight container and named OPP, whereas the other half was used further to prepare activated orange peel powder.

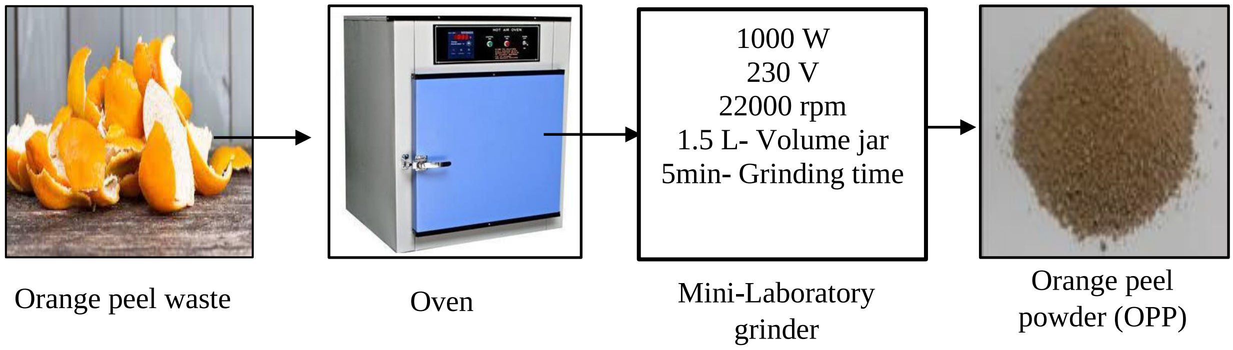


Figure 3.1 Procedure for deriving orange peel powder (OPP)

3.2.2 Preparation of activated orange peel powder (AOPP)

The biochar's chemical activation is done before its use as an adsorbent/coagulant to improve its surface properties. However, several chemical agents can be used for activated carbon impregnation to increase its surface properties. A study has been carried out to evaluate the performance of different chemical agents used for impregnation, such as $ZnCl_2$, KOH, NaOH, H_2SO_4 and H_3PO_4 to activate orange peel-activated carbon. The dye uptake efficiency for KOH and NaOH were almost similar; however, lesser than $ZnCl_2$ (Bediako et al., 2020). However, the cost of $ZnCl_2$ and KOH is comparatively more than NaOH, which might restrict its application on larger scales. Therefore, for the current study, NaOH chemical activation was used.

After preparing activated carbon, the oven-dried OPP was heated in a tubular furnace for 1 hour at 400°C in the presence of a continuous N_2 supply. The sample was cooled down and then chemically activated using 1M NaOH solution and kept in the oven at 105°C for 24 hours. The chemically activated samples were heated further in a tubular furnace for one hour at 800°C and allowed to cool down. The cooled sample was collected from the furnace and washed with double distilled water until the pH of the sample reached neutral. The pH of the sample was adjusted using 0.1N HCl solution. This sample was then kept in the oven at 105°C for 24 hours, and the dried sample was then sieved through a 75µ sieve, allowing it to retain at 50µ sieve, which was named AOPP. Several methods can be adopted for the preparation of activated char. The chemical activation can also be done prior to conversion of OPP to char or after conversion (Bediako et al., 2020; Dhorabe et al., 2017). Moreover, some studies have also been done on biochar obtained after heating without chemical activation (Adeniyi et al., 2020). However, for this study, the chemical activation was done on the char obtained after heating at 400°C. Since OPP and AOPP tend to absorb moisture from the surroundings, they were stored in desiccators for further experimentation. Picture depicting procedure to obtain AOPP has been shown in Figure.3.2.

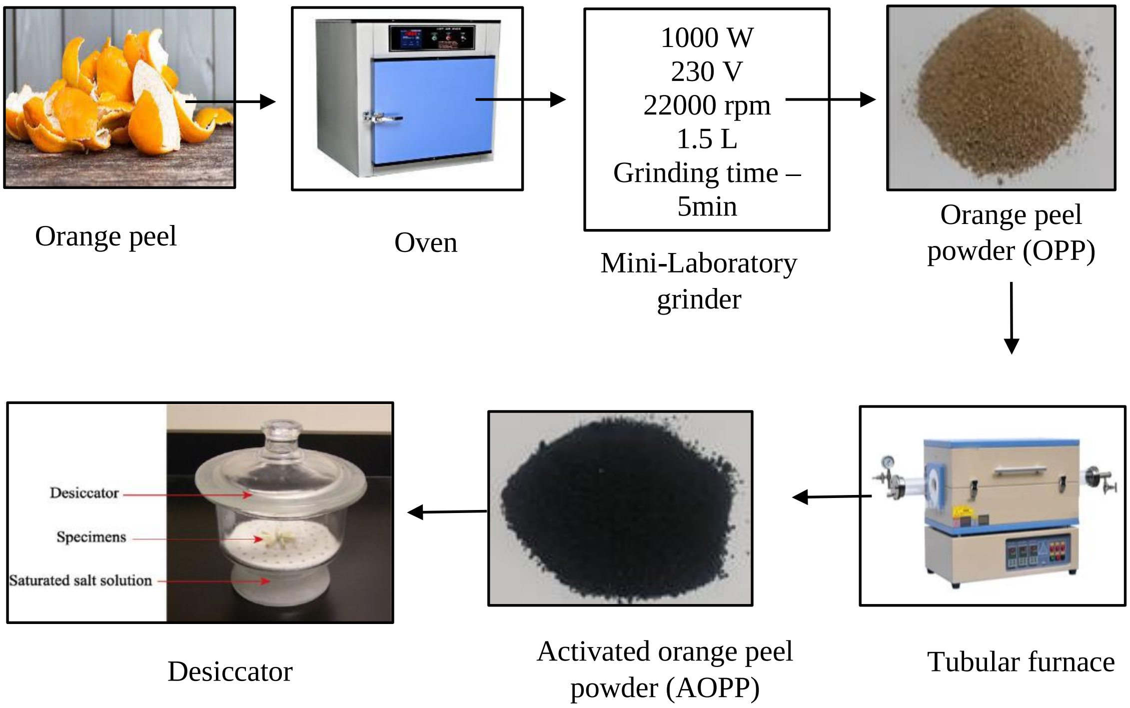


Figure 3.2 Procedure for deriving activated orange peel powder

3.3 Adsorbent physico-chemical characterization

The obtained OPP and AOPP can be characterized using different analysis such as X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Total Organic Carbon (TOC), Scanning Electron Microscope (SEM), Field Emission Scanning Electron Microscope (FESEM), Brunauer–Emmett–Teller (BET) etc for determining the chemical composition and physical properties, functional groups present in the material, evaluating the carbon present in the sample, information about the morphology of the surface of the sample, determining the specific surface area (SSA) respectively.

- XRD works on the principle of absorption and re-emission of the beam of X-rays that falls on the sample to be analysed.
- The working mechanism of FTIR depends on the Infrared source that generates the beam which passes through interferometer box and finally falls on the sample to be analysed.
- The carbon content in a sample can be determined by TOC as well as using Energy dispersive X-ray (EDX) instrument. However, the quantity of sample tested at a time by both the instruments are different. EDX is performed by changing mode in FESEM/SEM instrument where the sample evaluated is < 0.25mg which may account like a tiny particle. Therefore, it may happen that the carbon content

obtained by both the instruments vary. For TOC the quantity of sample taken for analysis is around 10-20g. The values for carbon content obtained through TOC analysis are more representative.

- SEM is used for obtaining high resolution images providing detailed information about the morphology of the surface of the sample. FESEM can provide high resolution images than the SEM analysis along with higher energy range.
- BET is an equipment used for determining the specific surface area (SSA) by allowing adsorption and desorption of N_2 gas over the surface of the samples to determine the SSA of sample.

3.4 Hydrodynamic cavitation set-up

The pilot scale HC set-up was fabricated in the laboratory. The schematic diagram of the HC set-up is shown in Figure.3.3. The set-up was made up of stainless steel supported by a square-shaped iron frame. The capacity of the tank used for wastewater samples was a maximum of 30L. The set-up is designed so that the wastewater samples are rotated in a closed loop using a DC motor of 3kW-HP and a plunger pump of 3HP. The pressure gauge is used to maintain inlet pressure, and valves for controlling the flow and set-up are mounted with an orifice between two pressure gauges that serves the purpose of cavitation. The inlet and outlet are provided below the feed tank. Sample suction is followed by bifurcation into the cavitation and by-pass lines. A manually controlled valve at the by-pass line controls the inlet pressure at the orifice. The provision of changing the orifice diameter i.e., 0.5, 1.0 and 1.5 mm respectively was also possible to increase the intensity of cavitation in the system. The fabricated set-up is shown below in the Figure.3.4. The energy required for the HC system has been calculated using equation.1(Sneha Korpe et al., 2019).

The energy required for the system (J) = $\Delta P * V_o * T$ (3.1)

where,

ΔP = Pressure drop across the orifice

V_o = Volumetric flow rate

T = Reaction time

The occurrence of the cavitation phenomenon depends upon the cavitation number, which can be calculated in equation 2 (Sneha Korpe et al., 2019).

Cavitation number (C_v) = $\frac{P_2 - P_v}{\frac{1}{2} * \rho * v^2}$ (3.2)

P_2 = pressure downstream of the orifice

P_v = Vapor pressure

ρ = density of the liquid

v = velocity of the liquid at the throat of the orifice

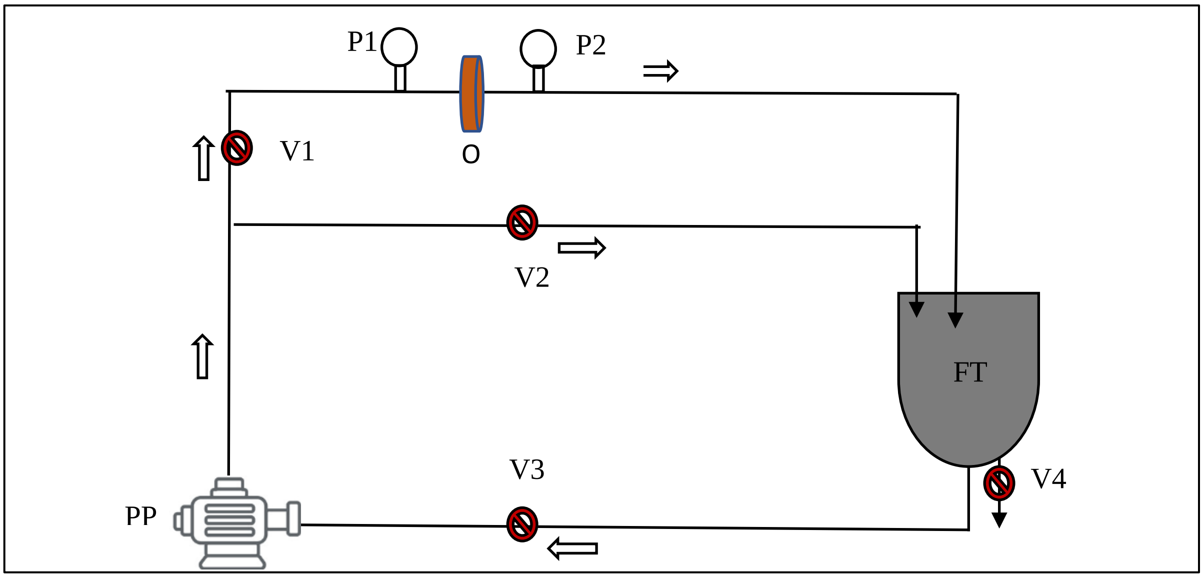


Figure 3.3 Pilot scale Hydrodynamic cavitation set-up

Where,

P – Pressure gauge

V – Valves

PP – Plunger pump

FT – Feed Tank

O – Orifice

Figure 3.4 Fabricated Hydrodynamic cavitation set-up

3.5 Batch scale study for anaerobic digestion

To determine the anaerobic degradability and the biogas yield of TWW the BMP experiments were performed by using 120 ml reagent glass bottles. The bottle is sealed with rubber cork to create anaerobic conditions. The glass bottles are kept in the incubator (37°C). The daily biogas production was quantified using graduated glass syringe of 50 ml with a least count of 1 ml. The experiments were carried out individually with chicken manure as co-substrate in the first set and using acclimatized inoculum taken from the biogas plant of NITW campus along with leather trimmings in the second set. Different C/N ratios and pH were maintained for the digesters based on the operating parameters. All the samples were run in duplicate to obtain more reliable results. It also helps in keeping control over the external factors affecting the anaerobic digestion process. Figure. 3.5 has shown the digester bottles that have been used in the study and the method used for measuring the biogas generated.

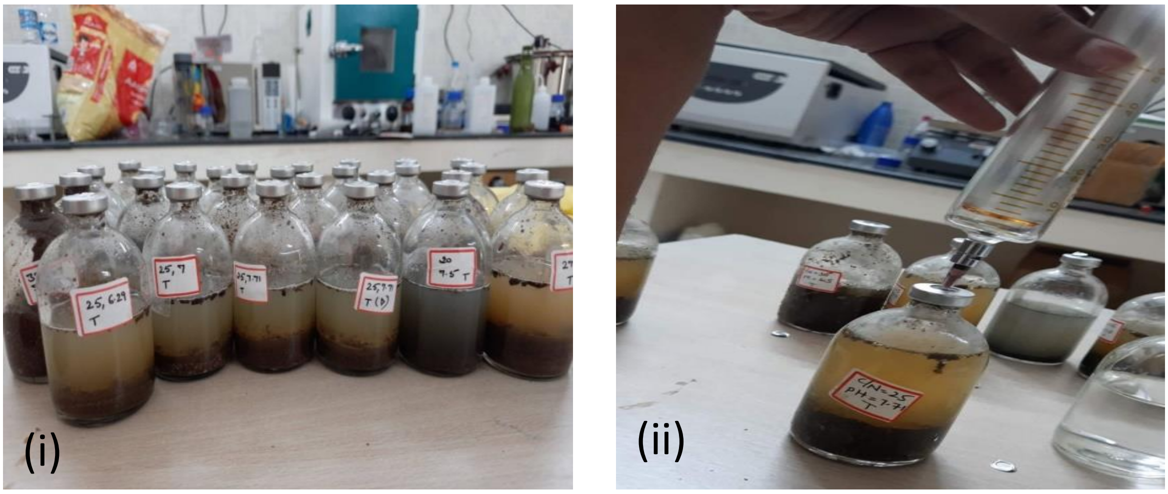


Figure 3.5 (i) Digester bottles (ii) Biogas measurement

3.5.1 Acclimatization of micro-organisms

The anaerobic digestate was collected from the biogas plant located at National Institute of Technology, Warangal and mixed with tannery wastewater in different mix ratios in 2 L jars to acclimatize the microorganisms to the with the contaminants present in the wastewater. The replicas of the mix ratios were taken in serum bottles and the biogas was collected for 30 days to determine the optimum mix ration. The anaerobic digestate which gave the maximum biogas was used as an inoculum.

3.6 Design of experiments, statistical analysis, and optimization

Three-level box-Behnken response surface design was used to reduce the number of experiments conducted and optimize the parameters influencing the removal efficiencies.

Response surface methodologies are commonly used to study the effect of influential parameters on the treatment results. Stat-Ease Design Expert 11.1.2.0 version was used in this study. Analysis of variance (ANOVA) was used to know the relationship between the different variables, followed by optimization.

3.7 Methodology adopted

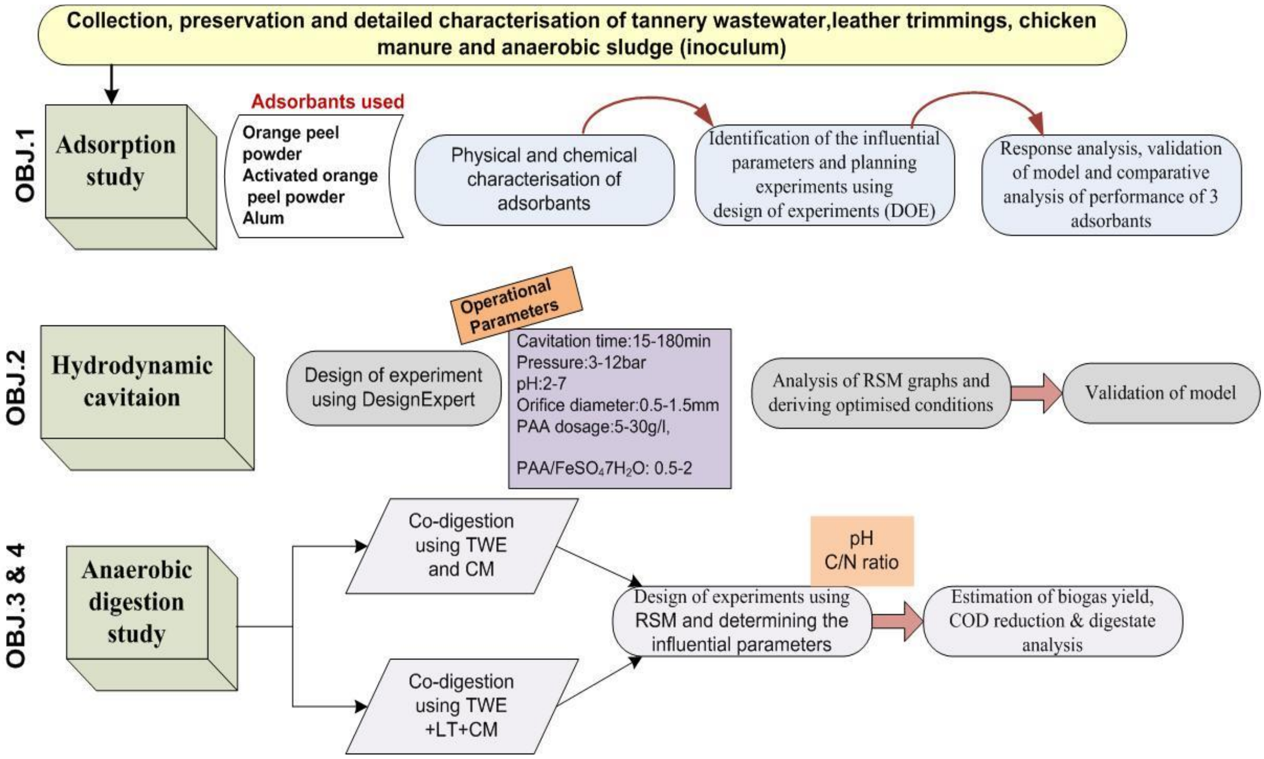


Figure 3.6 Methodology adopted for the research study

3.8 Wastewater sample characterization using analytical methods

All the physico-chemical wastewater characterization of the TWE was carried out to determine chemical oxygen demand (COD), bio-chemical oxygen demand (BOD), total nitrogen, turbidity, total suspended solids, total dissolved solids, pH and turbidity using APHA. In purified form, all the chemicals were procured from SDFCL – S.D fine chemical limited, Industrial estate, Mumbai.

Chapter – 4

Adsorption using Orange Peel Waste

The tannery wastewater effluent (TWE) consists high quantity of total suspended solids (TSS) which contributes to chemical oxygen demand (COD) and interferes the subsequent treatment systems. Therefore, the lab-scale study has been done to remove the TSS using jar-test apparatus. Turbidity, TSS and COD removal efficiencies of treatment using natural and chemical coagulant/adsorbents has been experimented. Parameters affecting the treatment removal efficiencies has also been discussed in detail in the chapter.

4.1 Results and Discussions

Coagulation and flocculation were performed on TWE using AOPP, OPP and alum, respectively, using a jar test apparatus. Hydrated aluminium sulphate $Al_2(SO_4)_3.18H_2O$ (98%) was used as a coagulant. Sodium hydroxide was also used during the preparation of AOPP, and (HCl) was used in diluted form to adjust the pH during the experiments. The characterization of TWE samples collected from effluent treatment plant (ETP) has been analysed and inscribed below in Table.4.1. Similar TWE characteristics were observed in various research studies (Sneha Korpe & Rao, 2021).

Table 4.1 Initial wastewater characteristics of TWE

S.no	**TWE characteristics**	**Observed values (in mg/L except pH)**	
		Initial tannery wastewater effluent characteristics	**Samples collected at the outlet of the sedimentation tank**
1	pH	11.5 ± 0.5	11.5 ± 0.5
2	Total Dissolved Solids	13250 ± 150	12980 ± 150
3	Total Suspended Solids	4490 ± 200	1567 ± 200
4	Turbidity (NTU)	510 ± 20	163 ± 20
5	Biochemical Oxygen Demand	3350 ± 100	2146 ± 100
6	Chemical Oxygen Demand	17782 ± 200	17564 ± 200
7	Soluble Chemical Oxygen Demand (sCOD)	6542 ± 200mg/L	6433 ± 200

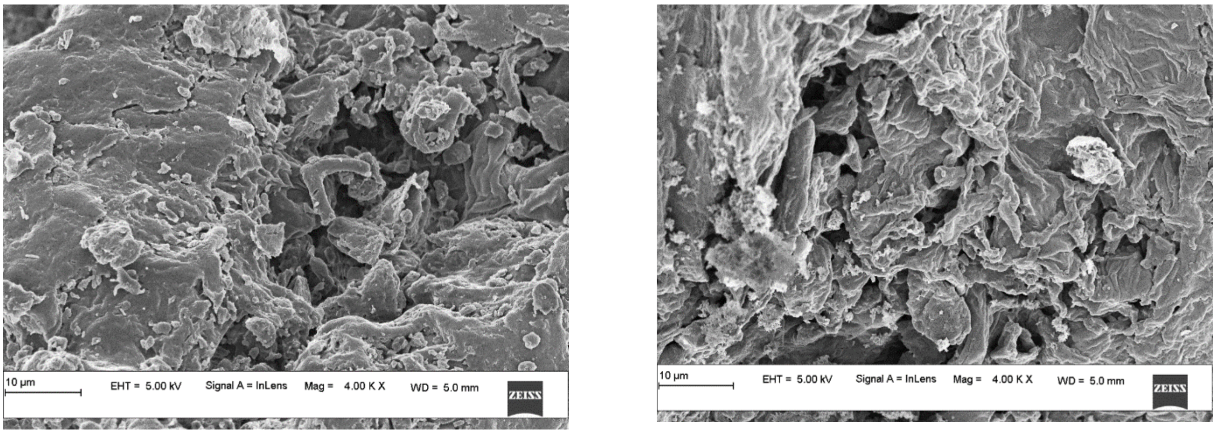
4.2 Physico-chemical characterization of coagulants/adsorbents

4.2.1 Total organic carbon

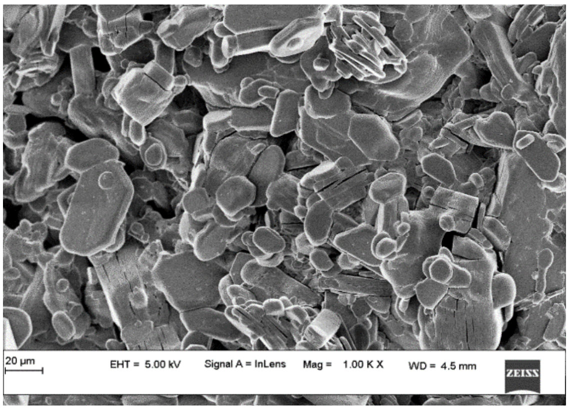
The methodology adopted for preparing OPP and AOPP has resulted in a difference in TOC content in both the prepared adsorbents from OPW. It was observed that the heating of OPP at 800°C has increased carbon content. The initial percentages of TOC for OPP and AOPP are obtained as 39.69% and 74.85%, respectively. The OPP consists of lignocellulose material having high water content and low carbon content. An alum, a chemical coagulant, consists of 1.23% of carbon content, which is almost negligible. Therefore, heating at 800°C dehydrates the compounds and thus results in increased carbon yield. It has also been proved from XRD results mentioned below in the section 4.2.4 that OPP and AOPP are amorphous, indicating presence of more carbon content.

4.2.2 Surface morphology

The surface morphology of all three materials shows that the adsorbents obtained from OPW are porous, unlike alum with cubic morphology. The SEM analysis results for all three different coagulants/adsorbents are demonstrated in appendix document Figure.4.1. The AOPP surface consists of larger diameter holes compared to OPP resulting in more porosity, also confirmed by BET result analysis. Therefore, it can be stated that the turbidity, TSS and COD reduction from TWE may have taken place due to the adsorption of pollutants over the surface. Researchers have experienced similar removal of different contaminants from aqueous solutions (Adeniyi et al., 2020; Amin et al., 2019; Dhorabe et al., 2017). For alum particles, it was observed that the coagulant surface is not porous like OPP and AOPP. The images clearly show the presence of spherical, plated, rod-shaped and cubical-shaped particles [Figure. 4.1]. Therefore, it can be attributed that in the case of alum, the turbidity, TSS and COD reduction may occur due to the charge neutralization phenomenon.



(ii) OPP **(i) AOPP**



(iii) Alum

Figure 4.1 Initial SEM analysis results (i)OPP, (ii) AOPP and (iii) Alum

4.2.3 Surface area

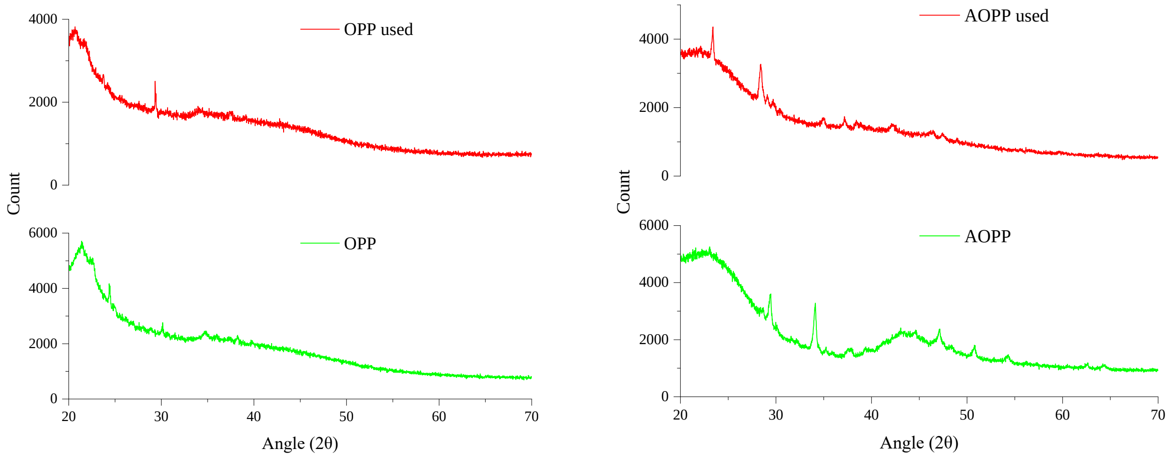
The surface area (SA) of OPP, AOPP and alum before and after coagulation-flocculation treatment has been inscribed in the appendix document in Table.4.2 The SA reduction of 64.4%, 89% and 79.7% has taken the place of OPP, AOPP and alum respectively [Table.4.2]. It shows that the pollutant removal takes place by adsorption mechanism using OPP and AOPP. Although results show that the SA of alum also reduces, indicating that pollutants have accumulated over the surface. However, charge neutralization is a predominant mechanism during alum coagulation flocculation treatment (Xue et al., 2021). The turbidity, TSS and COD removal efficiency increase after the coagulation-flocculation treatment can be best correlated with the SA reduction. It can be attributed that the more the surface area of OPP and AOPP, the more is the availability of functional sites for pollutants to get adsorbed. AOPP has the highest surface area resulting in higher turbidity and COD removal efficiency. Whereas TSS removal efficiencies for alum and AOPP have negligible variance. Similar results have been obtained in a study on removing reactive red dyes using OPW-activated carbon (Alwared et al., 2021).

Table 4.2 BET analysis for OPP, AOPP and alum

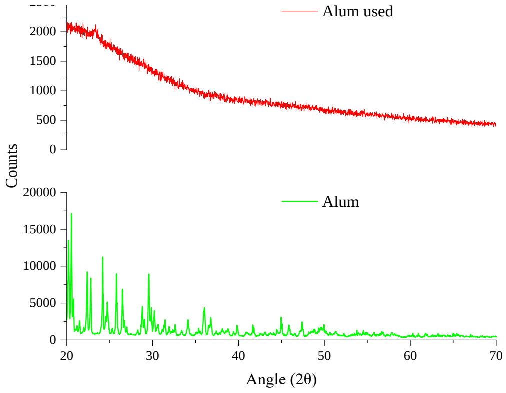
Sample	Surface Area (Initial)	Surface Area (Final)
OPP	4.474 m^2/g	1.593 m^2/g
AOPP	11.663 m^2/g	1.289 m^2/g
Alum	7.226 m^2/g	1.462 m^2/g

4.2.4 Chemical composition

Figure.4.2 in shows the graphical representation of XRD patterns obtained after the analysis of the coagulant/adsorbent. The XRD patterns observed for OPP showed that the compound is amorphous, indicating the presence of cellulose structure and carbon framework at 2θ values of 21.39º and 24.37º, respectively (Bediako et al., 2020; W. Chen et al., 2010). However, after the treatment of the TWE compound, $C_{12}.H_{36}.N_{8}.O_{8}$ was observed at 2θ values of 21.08, 22.91, 24.83 and 35.21, and $O_8.C_{72}.H_{136}$ was observed at 2θ value of 21.79. The analysis of AOPP using XRD attributed that the compound is amorphous with the presence of carbon at 2θ value of 29.45°, dehydrated hemicellulose at 2θ value of 34.1°, 50.76° and 72.68°, graphite structure at 2θ value of 47.15° and calcium carbonate at 2θ value of 88.46° respectively (Bouchelta et al., 2008; Djilani et al., 2012). However, after treating TWE compound guanidinium nitrate ($C_4.N_{16}.H_{24}.O_{12}$) at 2θ value of 29.46 was obtained over the surface of AOPP. Alum XRD patterns indicated that it was crystalline in nature, consisting of $S_6.Al_4.O_{58}.H_{68}$ at 2θ value ranging between 20-39 and the presence of Ammonium tetraoxoiodate ($I_4.O_{16}.N_4.H_{16}$) at 2θ value ranging between 45-50 (Tan et al., 2020). However, after treating TWE, the alum completely changed its structure into amorphous, indicating that pollutants accumulated over the alum's surface. Moreover, it also indicates that the TWE is rich in carbonaceous compounds. The XRD patterns of OPP, AOPP, and alum after the coagulation-flocculation treatment process indicate that the adsorption has taken place that resulted in an increase in the turbidity, TSS and COD removal efficiencies.



(i) OPP **(ii) AOPP**



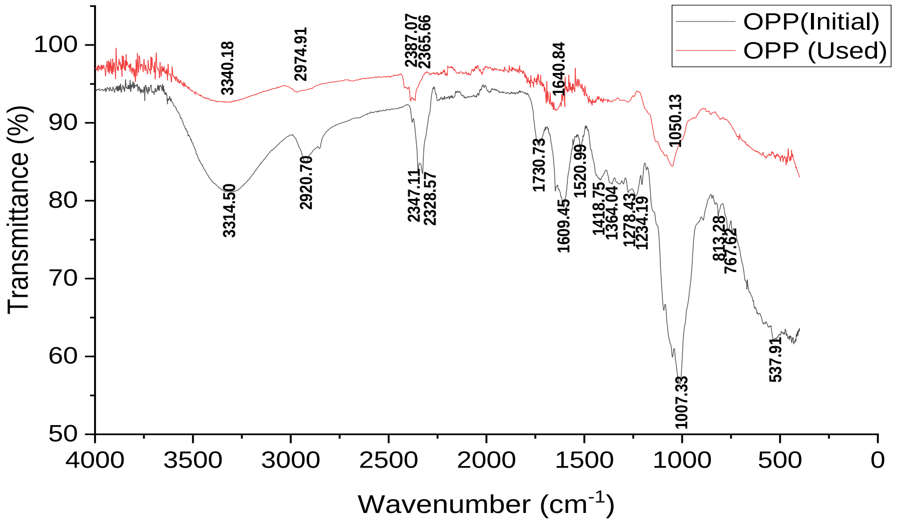
(iii)Alum

Figure 4.2 XRD analysis for (i) OPP, (ii) AOPP and (iii)Alum

4.2.5 Functional groups

The graphical spectrum obtained for OPP, AOPP and alum using FTIR has determined the functional groups present over their surface. It is observed that the spectrum obtained for OPP and AOPP are almost similar. However, several peaks have been shifted from their wavenumbers, and some of them have also been omitted in the AOPP spectrum [Figure.4.3]. The shifting and loss of peaks of AOPP in comparison with the spectrum obtained for OPP are due to the extensive heating of OPP at 800℃, which resulted in dehydration of some of the functional groups. The functional groups obtained over the surface of OPP and AOPP are similarly obtained in several studies (Abdelhafez & Li, 2016; B. Chen et al., 2011; Feng et al., 2011; Guiza, 2017; Pandiarajan et al., 2018). Moreover, alum being a chemical coagulant has shown a higher quantity of inorganic groups present over its surface along with stretching of the –OH group (Tan et al., 2020).

The spectrum of the used adsorbent has resulted in shifting the peaks towards the higher wavenumbers for OPP and AOPP, implying that the molecule's mass has been reduced. The reduction in mass of the molecule implies that interactions have taken place between the adsorbent and the complex compounds present in the wastewater sample. Whereas, for alum, the shifting of the peaks is at the lower side, implying that the formation of complex compounds may have occurred. For OPP, AOPP and alum, the shifting of the peaks and the transmittance percentage indicates the interactions of the wastewater pollutants with the coagulants. These interactions can be attributed to the increase in the turbidity, TSS and COD removal efficiencies. The graphical spectrum showing functional groups present on OPP, AOPP and alum before and after coagulation has been shown in the appendix document in Figure.4.3. Additionally, the functional groups present over the surface of all the coagulant/adsorbent have also been inscribed in Table.4.3.



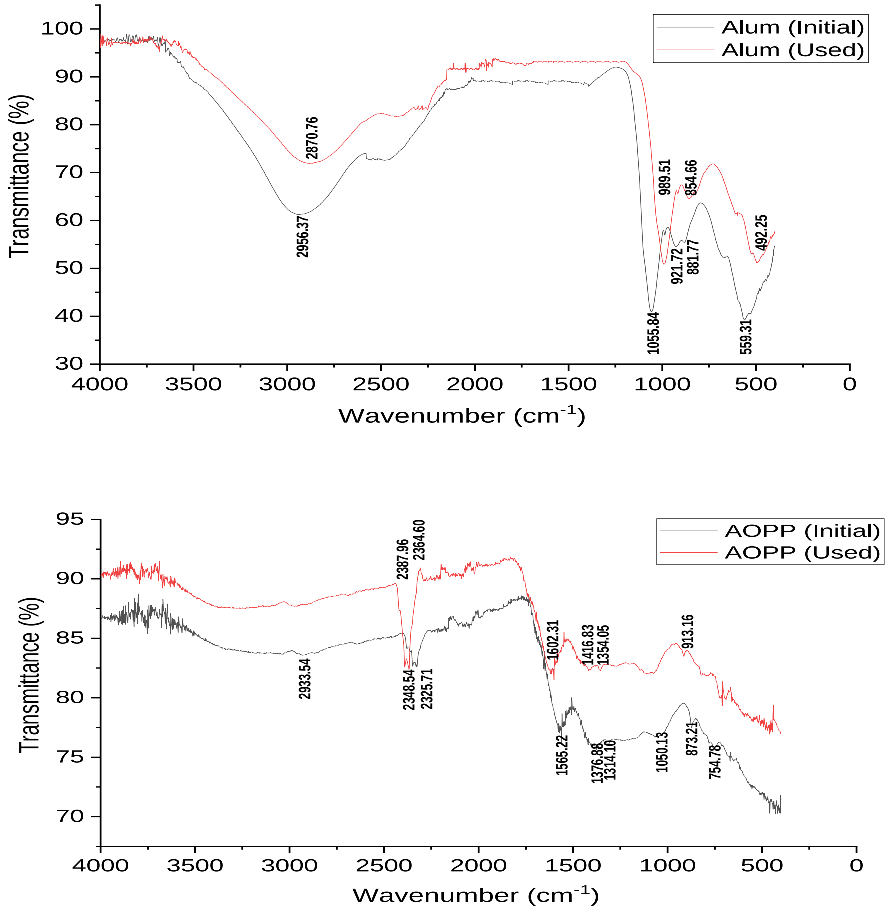


Figure 4.3 FTIR result analysis for OPP, AOPP and Alum before and after experimentation

Table 4.3 FTIR analysis results for OPP, AOPP and alum

S. no	Observed Peaks	OPP	AOPP	ALUM
1	3314.50	Presence of –OH groups consisting of carbohydrates and lignin		
2	2956.37			Presence of –OH stretching
3	2933.54		Presence of asymmetric and symmetric methyl i.e. –CH group	
4	2920.70	Presence of asymmetric and symmetric methyl i.e. –CH group		
5	2479.81			Presence of –OH stretching
6	2348.54		Presence of ketone i.e., =C=O group	
7	2347.11	Presence of ketone i.e., =C=O group		
8	2328.57	Presence of ketone i.e., =C=O group		
9	2325.71		Presence of ketone i.e., =C=O group	

10	1730.73	Presence of carbonyl i.e., C=O group		
11	1609.45	Presence of carbonyl i.e., C=O group		
12	1565.22		Presence of Nitro i.e., N–O group	
13	1520.99	Presence of Nitro i.e., N–O group		
14	1418.25	Presence of –OH group		
15	1364.04	Presence of C=C stretching vibrations		
16	1376.88		Presence of C=C stretching vibrations	
17	1314.10		Presence of C=C stretching vibrations	
18	1278.43	Presence of aliphatic chains such as $-CH_2$ and $-CH_3$		
19	1234.19	Presence of C–N stretching vibrations		
20	1055.84			Presence of sulphates
21	1050.13		Presence of carboxylic acids and esters i.e., C–O group	
22	1007.33	Presence of carboxylic acids and esters i.e., C–O group		
23	921.72			Presence of sulphates
24	881.77			Presence of sulphates
25	873.21		Presence of stretching vibrations of carbonates	
26	813.28	Presence of stretching vibrations of carbonates		
27	767.62	Presence of aromatic compounds		
28	754.78		Presence of aromatic compounds	
29	559.31			Presence of alumina oxide
30	537.91	Presence of deformations of amines i.e., N–H		

4.3 Statistical analysis, ANOVA, and optimization results

The design matrix of three variables obtained from the Box-Behnken response surface design method and the responses in terms of turbidity, TSS and COD removal efficiencies for OPP, AOPP, and alum have been shown appendix document in Tables 4.4, 4.5 and 4.6 respectively.

Table 4.4 Treatment of TWE using OPP

Run	Adsorbent dosage (g/L)	pH	Contact time (min)	Turbidity removal efficiency (%)	TSS removal efficiency (%)	COD removal efficiency (%)
1	3	2	35	51.49	44.67	13.34
2	3	5	10	43.87	38.78	12.89
3	3	8	35	57.86	52.56	13.23
4	2	5	35	73.89	69.8	31.20
5	2	5	35	72.95	68.56	31.42
6	1	5	10	39.70	32.77	11.89
7	2	2	60	60.10	52.90	17.86
8	3	5	60	62.39	57.68	16.65
9	2	2	10	35.98	30.98	8.87
10	2	8	60	50.87	43.98	11.89
11	2	5	35	73.11	69.10	30.87
12	2	5	35	73.46	69.81	30.98
13	2	5	35	72.88	69.73	30.65
14	2	8	10	38.98	33.77	8.79
15	1	2	35	44.13	38.89	14.76
16	1	8	35	44.89	40.76	6.66
17	1	5	60	53.00	48.99	10.00

Table 4.5 Treatment of TWE using AOPP

Run	Adsorbent dosage (g/L)	pH	Contact time (min)	Turbidity removal efficiency (%)	TSS removal efficiency (%)	COD removal efficiency (%)
1	3	8	35	70.76	66.61	21.12
2	2	8	10	59.88	53.26	17.87
3	1	5	60	71.84	62.36	17.32
4	2	5	35	93.86	91.90	40.66
5	2	5	35	93.18	92.00	41.32
6	3	5	10	64.67	60.99	20.98
7	2	5	35	93.62	92.21	41.65
8	1	8	35	62.18	52.32	14.10
9	1	5	10	57.88	46.77	9.89
10	2	5	35	93.43	92.33	41.18
11	2	2	60	78.90	76.33	25.98
12	3	5	60	85.51	80.90	25.87
13	2	2	10	57.84	55.66	18.90
14	2	5	35	93.90	92.53	40.98
15	1	2	35	66.89	61.54	22.00
16	2	8	60	68.92	63.87	19.87
17	3	2	35	75.68	67.89	22.44

Table 4.6 Treatment of TWE using Alum

Run	Adsorbent dosage (g/L)	pH	Contact time (min)	Turbidity removal efficiency (%)	TSS removal efficiency (%)	COD removal efficiency (%)
1	2	2	60	31.09	33.2	19.34
2	2	5	35	72.32	68.77	27.88
3	2	2	10	39.8	36.76	12.19
4	2	8	60	65.56	62.18	14.98
5	2	5	35	71.88	70.9	27.14
6	1	5	10	75.43	74	32.18
7	2	5	35	72.2	70.12	26.94
8	1	5	60	76.56	77.67	22.65
9	3	8	35	59.87	46.98	16.68
10	3	2	35	49.77	48.99	18.23
11	3	5	60	70.86	68.45	25.49
12	3	5	10	54.12	52.1	16.54
13	2	5	35	72.89	69.32	26.88
14	1	2	35	48.89	45.65	17.34
15	2	5	35	72.8	70.6	27.32
16	1	8	35	72.87	66	24.78
17	2	8	10	38.12	30.18	23.12

4.2.1 Turbidity removal efficiency

The curve fitting of the input data to the variable model and ANOVA has shown that the quadratic model was best suited for the turbidity removal efficiency using OPP, AOPP, and alum. The equation obtained through the quadratic model are given below in eq. 4.1, 4.2 and 4.3.

$$\text{Turbidity (\%) for OPP} = 73.26+4.24A+0.1125B+8.48C+1.40AB+1.31AC-3.06BC-10.20A^2-13.46B^2-13.31C^2 \quad (4.1)$$

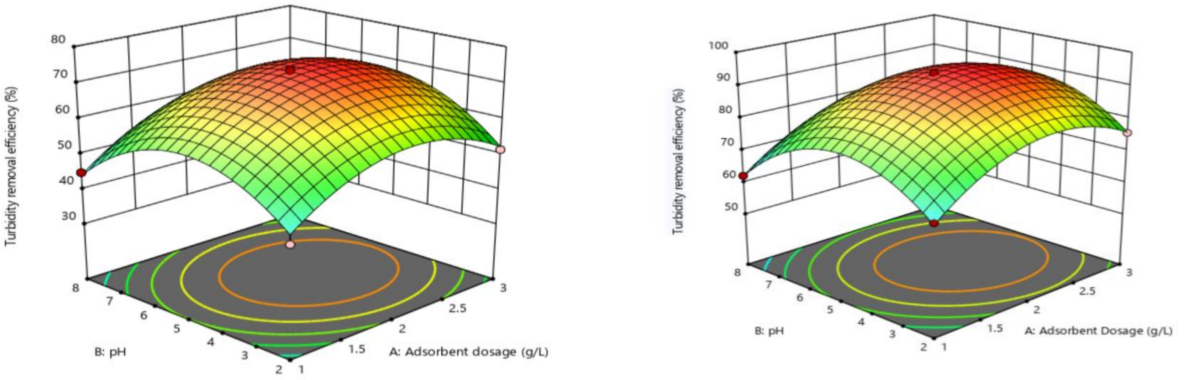
$$\text{Turbidity (\%) for AOPP} = 93.60+4.73A-2.20B+8.11C-0.0525AB+1.72AC-3.00BC-10.57A^2-14.16B^2-13.06C^2 \quad (4.2)$$

$$\text{Turbidity (\%) for Alum} = 72.42-4.89A+8.36B+4.58C-3.47AB+3.90AC+9.04BC+5.52A^2-20.08B^2-8.69C^2 \quad (4.3)$$

where A- coagulant/adsorbent dosage, B-pH, and C-Contact time.

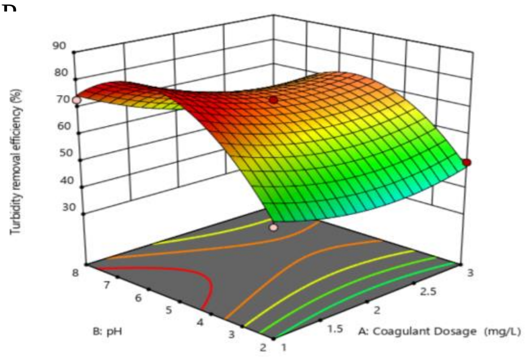
Regarding turbidity removal efficiency, F values of the model 73.99, 508.71 and 95.25 with a P-value <0.0001 showed that the quadratic model is significant. Very small p-value and R^2 values of 0.9762, 0.9965 and 0.9815, respectively, for OPP, AOPP and alum, also showed the significance of the model suggested. The adequate precision value obtained was 23.832, 57.650 and 28.308, respectively, for OPP, AOPP and alum, which is greater than 4, showing that the model can be used to navigate the design space. Moreover, from Equations 4.1, 4.2, and 4.3 the negative coefficient values imply that these factors negatively impact the response. According to ANOVA results, the contact time is the most significant parameter for turbidity removal using OPP (F value =130.14) and AOPP (F value = 788.33). However, for alum treatment, pH is the most significant factor (F value =136.19).

Figure.4.4 shows the 3-D response surface plots regarding the effect of pH and coagulant/adsorbent dosage and their interaction on the turbidity removal efficiency at a contact time of 35 min. The contact time of 35 min is the center point obtained from the design of experiments. The figure depicts that contact time is the predominant factor for turbidity removal efficiencies obtained using OPP and AOPP, which also can be confirmed through ANOVA F-value obtained. However, alum treatment is pH dependent having lower values at the center. The optimized solution obtained for OPP is at an adsorbent dosage of 2.28g/L, pH-4.6 and contact time – 54.54 min.



(a)Turbidity removal efficiency using OP

(b)Turbidity removal efficiency using AOPP



(c) Turbidity removal efficiency using Alum

Figure 4.4 3-D response surface plots for turbidity removal efficiency using OPP, AOPP and Alum

4.3.2 TSS removal efficiency

The curve fitting of the input data to the variable model and ANOVA has shown that the quadratic model was best suited for the TSS removal efficiency using OPP, AOPP, and alum. The equation obtained through the quadratic model is given below in eq. 4.4, 4.5 and 4.6.

TSS (%) for OPP = $69.40+4.04A+0.4538B+8.41C+1.50AB+0.67AC-2.93BC-10.52A^2-14.66B^2-14.33C^2$ *(4.4)*

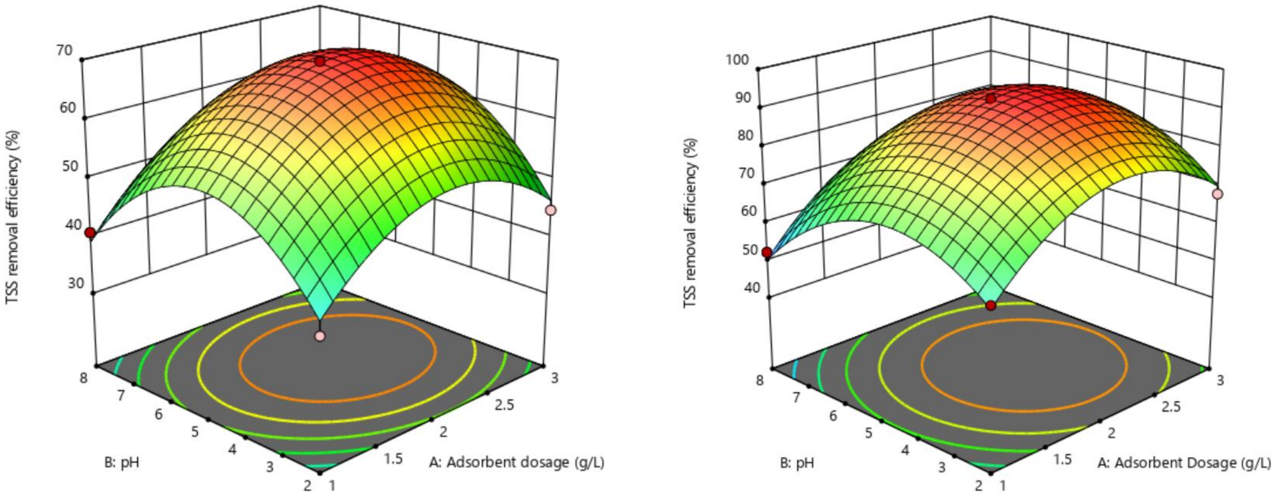
TSS (%) for AOPP = $92.19+6.68A-3.17B+8.35C+1.98AB+1.08AC-2.52BC-14.81A^2-15.29B^2-14.62C^2$ *(4.5)*

TSS (%) for Alum = $69.94-5.85A+5.09B+6.06C-5.59AB+3.17AC+8.89BC+4.72A^2-22.76B^2-6.61C^2$ *(4.6)*

where A- coagulant/adsorbent dosage, B-pH, and C-Flocculation time.

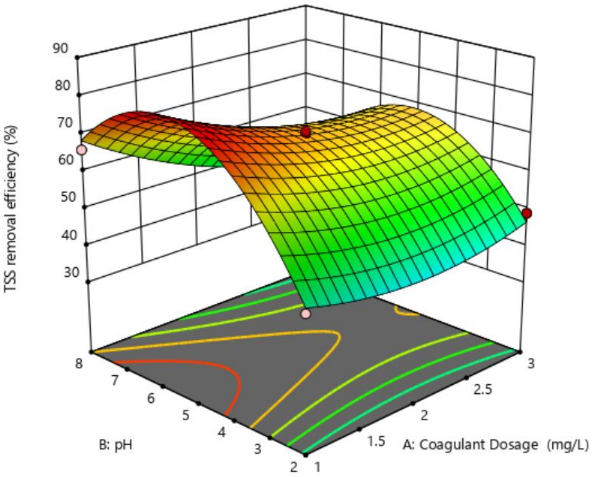
Regarding TSS removal efficiency, the F value of the model 71.96, 131.99 and 66.21 with a P-value <0.0001 showed that the quadratic model is significant. Very small p-value and R^2 values of 0.9756, 0.9874 and 0.9735, respectively, for OPP, AOPP and alum also showed the significance of the model suggested. The adequate precision value obtained was 23.7962, 31.0563 and 23.9945, respectively, for OPP, AOPP and alum, which is greater than 4, showing that the model can be used to navigate the design space. Moreover, from Equations 4.4, 4.5 and 4.6 the negative coefficient values imply that these factors negatively impact the response. According to ANOVA results, the contact time is the most significant parameter for TSS removal using OPP (F value =113.23) and AOPP (F value = 168.05). However, for alum treatment, pH is the most significant factor (F value = 46.84).

Figure.4.5 shows the 3-D response surface plots regarding the effect of pH and coagulant/adsorbent dosage and their interaction on the turbidity removal efficiency at a contact time of 35 min. The contact time of 35 min is the center point obtained from the design of experiments. The figure depicts that contact time is the predominant factor for TSS removal efficiencies obtained using OPP and AOPP, which also can be confirmed through ANOVA F-value obtained. However, alum treatment is pH dependent having lower values at the center.



(a) TSS removal efficiency using OPP

(b) TSS removal efficiency using AOPP



(c) TSS removal efficiency using Alum

Figure 4.5 3-D response surface plots for TSS removal efficiency using OPP, AOPP and Alum

4.3.3 COD removal efficiency

The curve fitting of the input data to the variable model and ANOVA has shown that the quadratic model was best suited for the COD removal efficiency using OPP, AOPP, and alum. The equation obtained through the quadratic model is given below in eq. 4.7, 4.8 and 4.9.

$$COD\ (\%)\ for\ OPP = 31.02+1.60A-1.78B+1.75C+2AB+1.41AC-1.47BC-9.01A^2-10.02B^2-9.16C^2 \quad (4.7)$$

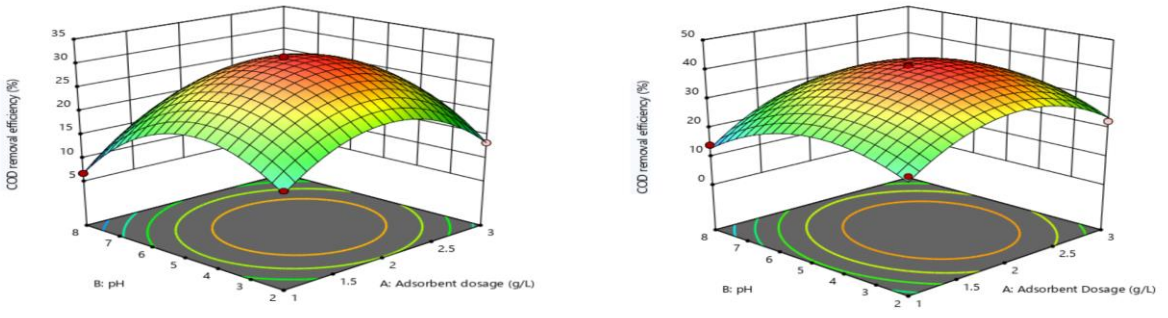
$$COD\ (\%)\ for\ AOPP = 41.16+3.39A-2.05B+2.68C+1.65AB-0.6350AC-1.27BC-11.69A^2-9.55B^2-10.95C^2 \quad (4.8)$$

$$COD\ (\%)\ for\ Alum = 27.23-2.50A+1.56B-0.1963C-2.25AB+4.62AC-3.82BC-0.5835A^2-7.39B^2-2.43C^2 \quad (4.9)$$

where A- coagulant/adsorbent dosage, B-pH, and C-Flocculation time.

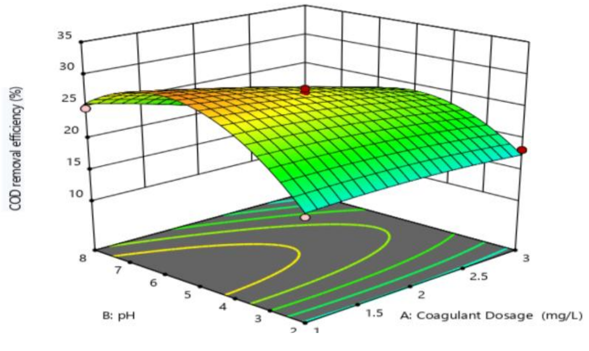
Regarding COD removal efficiency, the F value of the model 71.13, 68.20 and 84.47 with a P-value <0.0001 showed that the quadratic model is significant. Very small p-value and R^2 values of 0.9753, 0.9742 and 0.9791, respectively, for OPP, AOPP and alum, also showed the significance of the model suggested. The adequate precision value obtained was 21.9045, 22.1154 and 30.9551, respectively, for OPP, AOPP and alum, which is greater than 4, showing that the model can be used to navigate the design space. Moreover, from Equations 4.7, 4.8 and 4.9 the negative coefficient values imply that these factors negatively impact the response. According to ANOVA results, the contact time is the most significant parameter for COD removal using OPP (F value =12.04) and AOPP (F value = 19.13). However, for alum treatment, pH is the most significant factor (F value = 75.67).

Figure.4.6 shows the 3-D response surface plots regarding the effect of pH and coagulant/adsorbent dosage and their interaction on the turbidity removal efficiency at a contact time of 35 min. The contact time of 35 min is the center point obtained from the design of experiments. The figure depicts that contact time is the predominant factor for COD removal efficiencies obtained using OPP and AOPP, which also can be confirmed through ANOVA F-value obtained. However, alum treatment is pH dependent having lower values at the center.



COD removal efficiency using OPP

COD removal efficiency using AOPP



COD removal efficiency using Alum

Figure 4.6 3-D response surface plots for COD removal efficiency using OPP, AOPP and Alum

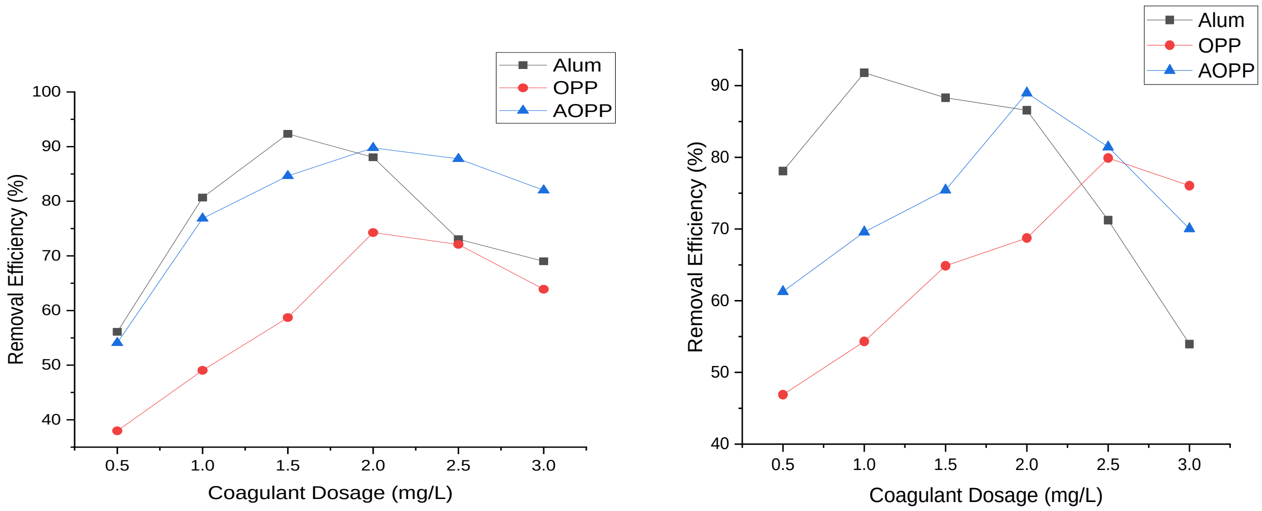
The optimized solution obtained for OPP is at an adsorbent dosage of 2.28g/L, pH-4.6 and contact time – 54.54. The optimized solution obtained for AOPP is at an adsorbent dosage of 2.11g/L, pH-4.37 and contact time – 35.01. However, alum optimized solution obtained through the software is at a coagulant dosage of 1.16 g/L, pH-5.48 and contact time of 20.46 min.

4.4 Experimental analysis performed for validation

The experimental runs were performed to validate the results obtained from the statistical analysis using RSM-BBD. Validation of the model was done by performing set of experiments at operating conditions coagulant/adsorbent dosage – 0.5-3.0 mg/L (@ interval of 0.5 mg/L), pH- 2-8 (@ interval of 1), and contact time – 0-60 min (@ interval of 10 min). Effect of all the influential parameters have been also discussed in detail in the following sections.

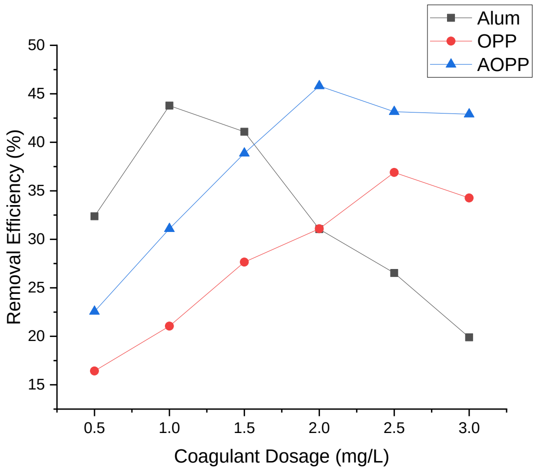
4.4.1 Effect of coagulant/adsorbent dosage

The results indicate a drop in removal efficiencies after a specific coagulant/adsorbent dosage. The decrease in removal efficiencies using OPP and AOPP can be attributed due to the aggregation of the particles. The aggregation leads to decreased overall functional sites present over the surface of the OPP and AOPP for adsorption of pollutants. However, the reduction in removal efficiencies using alum coagulant with an increase of dosage is due to charge reversal taking place during the process. The reversal of charge over the coagulants leads to stabilizing the particles that do not allow the pollutants to settle. Moreover, excess alum dosage also results in the formation of new complex compounds that increase COD in the wastewater sample. Alum treatment resulted in 92.33% and 91.79% removal compared to 74.26% and 79.9% using OPP and 89.78% and 88.98% removal of turbidity and TSS, respectively. However, AOPP resulted in 45.81% of COD removal efficiency, higher than the alum and OPP. The graphical representation has been shown in the Figure. 4.7.



(i)Turbidity removal efficiency (%)

(ii)TSS removal efficiency (%)



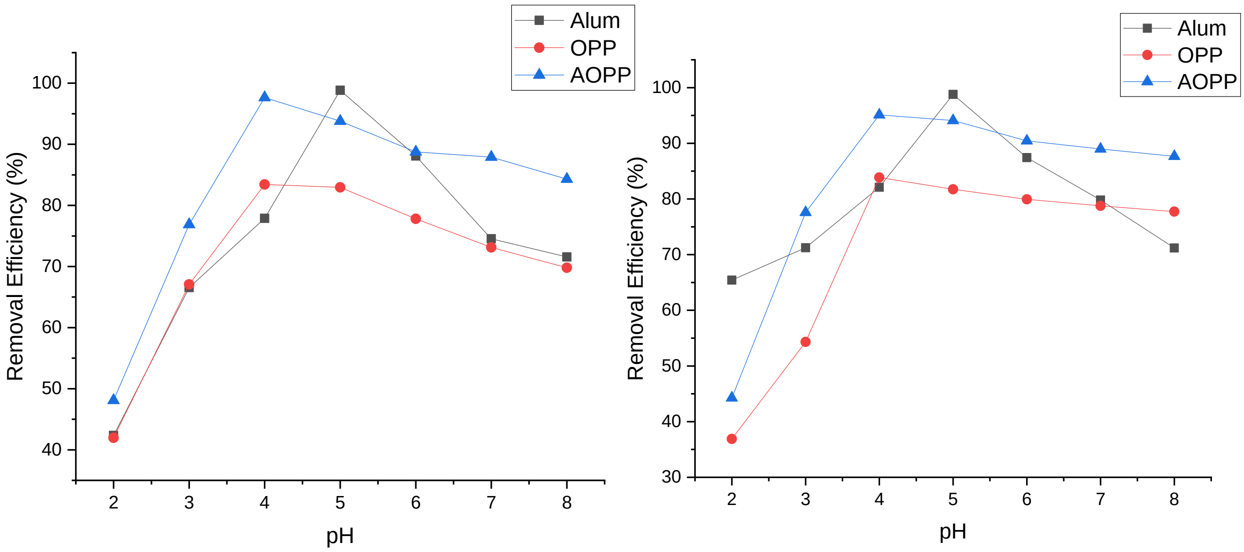
(iii)COD removal efficiency (%)

[Operating conditions: pH-7; contact time – 20min]

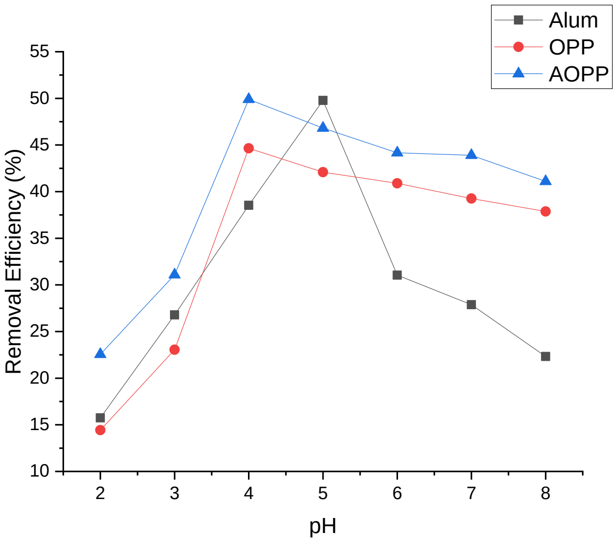
Figure 4.7 (i), (ii), (iii) Effect of coagulant dosage on turbidity, TSS and COD

4.4.2 Effect of pH

The pH of the sample plays a vital role in removing pollutants from TWE. At lower pH values or in the acidic medium, the OPP and AOPP showed maximum removal efficiency in turbidity, TSS and COD. It can be attributed that at lower pH values, the surface of OPP and AOPP gets positively charged and can entrap the negatively charged particles in the wastewater samples. Moreover, in an acidic medium, the coagulant/adsorbent surface protonation takes place while the pollutants present in the samples are deprotonated, resulting in the degradation of the TWE sample. A study by Maria Ververi and Athanasia M. Goula has also inscribed the effect of pH on removing organic pollutants using OPW (Ververi & Goula, 2019). The results clearly stated that the OPP and AOPP were more effective in an acidic medium. The alum coagulation treatment process depends on the charge neutralization phenomenon, which takes place to remove turbidity and TSS along with a reduction in COD of the TWE sample. The graphs below show that the alum removal efficiency drops drastically beyond optimum pH. The drop in removal efficiencies can be attributed to charge reversal at higher pH and adds up to the measured turbidity, TSS and COD quantity. The maximum removal efficiency obtained was at pH 4 for OPP, AOPP, and alum at pH 5.



(i)Turbidity removal efficiency (%) (ii)TSS removal efficiency (%)



(iii) COD removal efficiency (%)

[Optimum dosage – 2.5g/L(OPP); 2g/L (AOPP); 1g/L (alum); contact time – 20min]

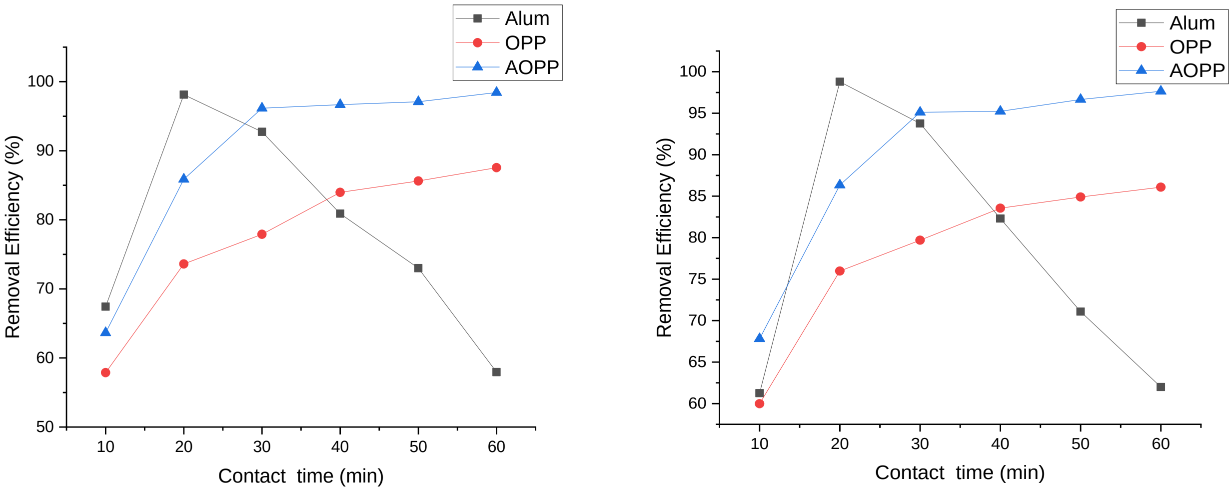
Figure 4.8 (i), (ii), (iii) Effect of pH on turbidity, TSS and COD

4.4.3 Effect of contact time

In the coagulation-flocculation process, it is essential to optimize the contact time to make the treatment system energy efficient. Figure. 4.9 shows the effect of contact time over the treatment removal efficiencies. The experimental analysis showed that removal efficiencies reached equilibrium after a certain period. It was observed that the maximum removal occurred in the first 20-30 min for all three coagulants. Alum took less time compared to OPP and AOPP which may be attributed to the difference in treatment mechanisms.

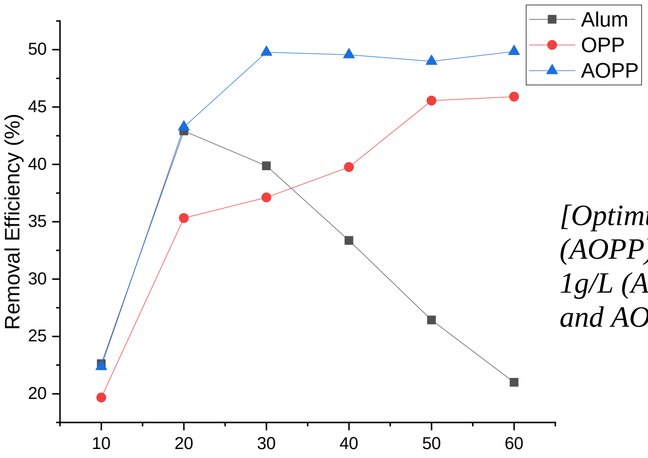
Moreover, the flocs built get disturbed after an optimum duration for alum coagulation. However, for OPP and AOPP, it can be attributed that the outer surface responsible for interactions gets occupied by the pollutants and thus reaches an equilibrium stage avoiding further removal. Similar results have also been obtained in the studies conducted for the removal of phenols and several dyes using OPW (Alwared et al., 2021; Dhorabe et al., 2017).

Figure.4.10 below shows a collective treatment removal efficiency obtained through all the coagulants. The AOPP is more efficient in removing COD from the TWE. However, the difference in TSS and turbidity removal is almost identical for AOPP and alum. But the COD removal efficiency is more for AOPP. Moreover, almost all types of industrial wastewater have high COD levels, which must be treated up to the desired effluent standards without negatively impacting the environment. Since AOPP produces very minimum sludge and can also be reused, therefore, use of AOPP can be recommended for higher-scale applications.



(i)Turbidity removal efficiency (%)

(ii)TSS removal efficiency (%)



[Optimum dosage - 2.5g/L (OPP);2g/L (AOPP);
1g/L (Alum); pH – 5 (Alum),4 (OPP and AOPP)]

(iii)COD removal efficiency (%)

Figure 4.9 Effect of contact time on turbidity, TSS and COD

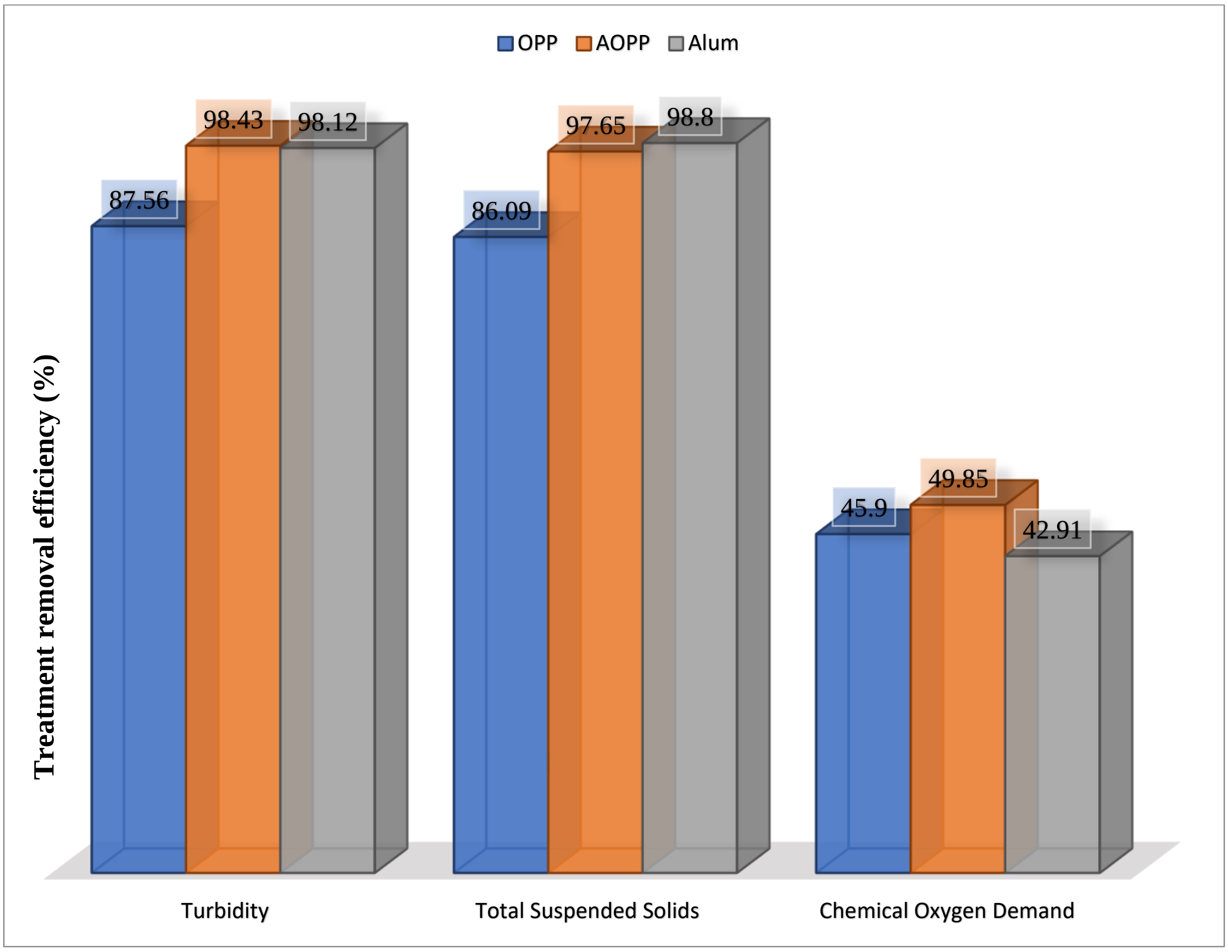


Figure 4.10 Comparative removal efficiency analysis of OPP, AOPP and alum

The bar graph shows the results at optimum operating parameters, i.e., coagulant/adsorbent dosage, pH and flocculation time. OPP at an adsorbent dosage of 2.5g/L, pH-4 and flocculation time – 50min, AOPP at an adsorbent dosage of 2g/L, pH-4 and flocculation time – 30 min and alum coagulant dosage at 1g/L, pH-5 and flocculation time – 20min respectively. The optimized conditions obtained from the experimental analysis are almost like those obtained by statistical analysis. The final effluent characteristics are inscribed in Table 4.7. The final effluent characteristics were analysed at optimum conditions through experimental analysis. It was observed that BOD levels increased after the treatment using OPP and AOPP. However, OPP and AOPP are evaluated for their performance as pre-treatment for TWE as an alternative to alum coagulant. Therefore, post-treatment methods can handle the BOD load. Moreover, from FTIR analysis, it is also clear that the OPP and AOPP do not form into complex compounds from which it can be inferred that the BOD removal can be achieved easily.

Table 4.7 Tannery wastewater influent and effluent characteristics

S.no	Final effluent Characteristics	Observed values (in mg/L except pH)			
		Initial tannery wastewater effluent characteristics	**OPP treated effluent**	**AOPP treated effluent**	**Alum treated effluent**
1	pH	11.5 ± 0.5	6	6.5	7.5
2	Total Dissolved Solids	13250 ± 150	11128	9987	10143
3	Total Suspended Solids	4490 ± 200	624	105.5	53.88
4	Turbidity (NTU)	510 ± 20	63.4	8	9.58
5	Biochemical Oxygen Demand	3350 ± 100	3615	3515	2234
6	Chemical Oxygen Demand	17782 ± 200	9620	8917	10150
7	Soluble Chemical Oxygen Demand (sCOD)	6542 ± 200mg/L	6553	6547	6618

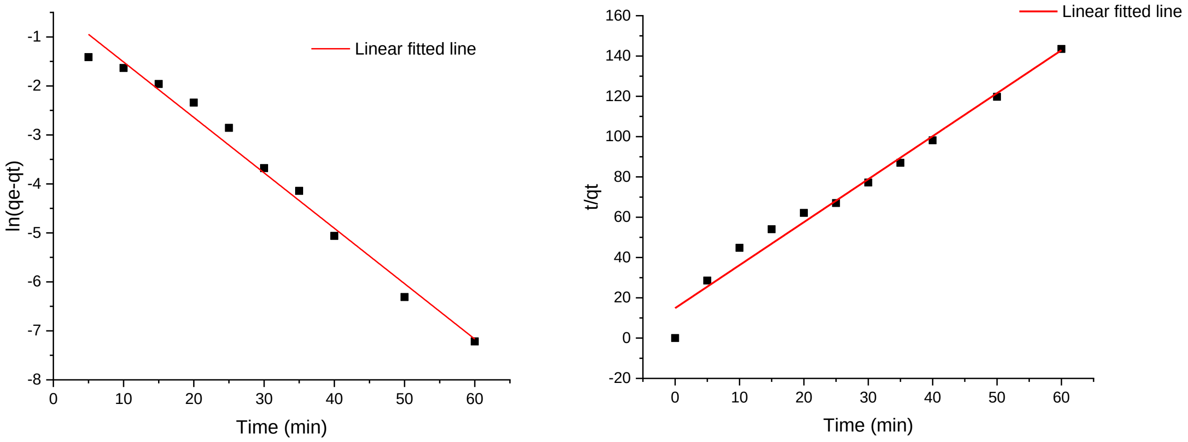
4.5 Adsorption kinetics and adsorption isotherms

To carry out the adsorption isotherm study, the synthetic tannery wastewater was prepared using tannic acid, sodium chlorate, ammonium chloride, sodium dodecyl sulphate and sodium sulphate in 1 liter of tap water (Zouboulis et al., 2019). It was performed for AOPP treatment system since, it has shown better results in terms of all the three contaminants removal.

4.5.1 Adsorption kinetics

The adsorption kinetics curves are shown in Figure.4.11 below, and the kinetic parameter values are shown in Table.4.3. AOPP resulted in higher treatment removal efficiency resulting in higher adsorption capacity. Moreover, the removal of pollutants has taken place due to the adsorption mechanism for which adsorption kinetics were performed. The adsorption capacity was also calculated for AOPP, and kinetic modelling was done for curve fitting.

- *Adsorption capacity using AOPP = 418.37 mg/g of COD*



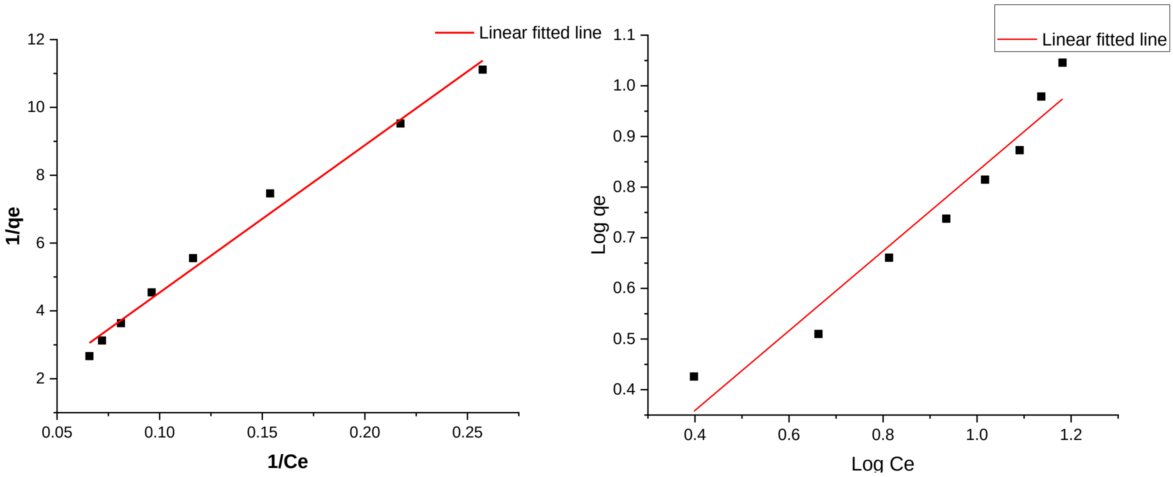
Pseudo first order kinetic model **Pseudo second order kinetic model**

Figure 4.11 Adsorption kinetics curve obtained for AOPP

Pseudo-first-order kinetics was the best-fitted model resulting in a higher linear regression coefficient of R^2=0.981. The results show that the kinetic rate constant depends on the concentration of COD and adsorbent. This also suggests that the adsorption has taken place over the surface of AOPP, resulting in treatment removal efficiencies in terms of turbidity, TSS and COD.

4.5.2 Adsorption isotherm

Figure.4.12 shows the isotherm model best suited for the experimental data observed and Table 4.8 inscribes the adsorption isotherm parameters. Based on the R^2 value obtained, the Langmuir isotherm was found to be best fitted with the experimental data. For Langmuir isotherm assumes that the monolayer adsorption occurs however, for Freundlich isotherm assumes that the multilayer adsorption has taken place. The intercept value and the adsorption capacity are inversely proportional to each other, indicating that the Freundlich isotherm having greater intercept value consists of lesser adsorption sites. Hence, the Langmuir isotherm is best fitted for the experimental data. The slope value lesser than unity also indicates that the adsorption process is favourable for the experimental data. The K_L is Langmuir rate constant that indicates the adsorption strength of a particular adsorbent to bind the pollutants present in the effluent. R_L indicates the separation factor which should be always less than 1 to provide favourable conditions for the adsorbent to adsorb the pollutants. The K_f is Freundlich rate constant that indicates adsorption capacity, intensity and the surface heterogeneity of the adsorbent.



(i) Langmuir adsorption isotherm

(ii) Freundlich adsorption isotherm

Figure 4.12 Adsorption isotherms

Table 4.8 Adsorption kinetics and isotherm parameters

S.no	**Intercept**	**Slope**	**1/n**	**q_e (mg/g**	**q_e^2**	K_1	K_2	**$q_{e\,max}$ (mg/g**	**K_f**	**K_L**	**R_L**	**R^2**
Pseudo first order kinetic model	-0.381	-0.113		683.2		-0.0019						**0.981**
Pseudo second order kinetic model	14.862	2.133		468.7	219679.69		0.015					0.973
Langmuir isotherm	0.0167	0.447						5081.56		0.117	0.4609	**0.987**
Freundlich isotherm	0.0444	0.786	1.271						1.045			0.934

4.6 Sludge production

At optimized experimental conditions, the quantity of sludge produced was observed to be more for alum coagulation than AOPP and OPP. For 1L of TWE sample, 33ml, 18.5ml and 12ml of sludge layer were formed after alum, OPP and AOPP coagulation, respectively. Removal of water content showed that the sludge obtained after alum coagulation was gelatinous in nature. In contrast, sludge obtained after OPP and AOPP coagulation-flocculation was still in a similar powder form as in the initial stage. The regeneration of the alum becomes difficult dues to gelatinous nature of the sludge obtained after the treatment unlike, sludge obtained after OPP and AOPP coagulation-flocculation.

The efficiency of regenerated coagulant/adsorbent to remove TSS from the raw TWE has been shown in Table. 4.9 below. The adsorption capacity of OPP and AOPP was almost similar for the first three cycles, however, it drastically decreased after the fourth cycle. The decrease in the adsorption capacity indicates that the adsorbent may have reached its saturation point where, it further cannot adsorb anymore pollutants. However, for alum the adsorption capacity decreased after the first cycle.

Table 4.9 Turbidity, TSS and COD removed using regenerated coagulants

Sr.no	Parameter	Observed Value			
		1st Coagulation-flocculation cycle – Efficiency (%)	2nd Coagulation-flocculation cycle- Efficiency (%)	3rd Coagulation-flocculation cycle - Efficiency (%)	4th Coagulation-flocculation cycle - Efficiency (%)
1	ALUM	98.8	88.63	--	--
2	OPP	86.09	85.87	84.83	74.50
3	AOPP	97.65	97.34	96.71	89.01

4.7 Economic and technical feasibility of natural coagulants derived from OPW

4.7.1 Economic feasibility

For obtaining OPP, the processing steps include i) Collection of raw orange peels, ii) Washing, iii) Drying and iv) Grinding, whereas, for obtaining AOPP, one additional step to be incorporated after grinding is carbonization at a higher temperature. The economic feasibility of biochar obtained from fruit peel used as an adsorbent for ammonium removal was also calculated similarly (Hu et al., 2020). Therefore, according to the lab scale study, the cost required for obtaining OPP and AOPP from 1 Kg of orange peels is calculated as follows:

Operational cost for OPP preparation = 144 INR/Kg of orange peels [1.84 USD]
Operational cost for AOPP preparation = 362 INR/kg of orange peels [4.65 USD]
Cost of alum procured [Aluminium sulphate [$Al_2(SO_4)_3.18H_2O$]] = 432 INR/kg [5.82 USD]

4.7.2 Technical feasibility

The application of OPP and AOPP for treating TWE samples has proven efficient in removing turbidity, TSS and COD from TWE. The OPP and AOPP treatment process implementation depends on various factors such as the availability of OPW in bulk, required equipment for char production and activated biochar. To implement at the industrial scale, the initial step is the segregation of OPW from various juice centres or from the industry producing juice generating OPW. After segregation, proper drying, grinding, and carbonization should be done in the industry before use. The experimental results have resulted in higher treatment removal efficiencies using AOPP. Therefore, the application of AOPP will be more suitable for treating wastewater at an industrial scale.

4.8 Important findings

- The adsorbents obtained from OPW are porous in nature unlike, alum having cubic morphology.
- The SA reduction of 64.4%, 89% and 79.7% has taken place of OPP, AOPP and alum respectively.
- OPP and AOPP are amorphous unlike alum being crystalline.
- Organic functional groups (ketones, carbonyl, aromatic compounds etc,.) are present on OPP and AOPP unlike inorganic groups (sulphates, alumina oxide etc,.) on alum
- The optimized solution obtained through statistical analysis for OPP is at 2.28g/L, 4.6 and 54.54 min, for AOPP is at 2.11g/L, 4.37 and 35.01 min and for alum is at 1.16 g/L, 5.48 and 20.46 min of coagulant/adsorbent dosage, pH and contact time respectively.
- Maximum turbidity, TSS and COD removal efficiencies obtained using AOPP at optimized conditions of AOPP dosage – 2g/L, pH – 4, contact time – 30min was 98.43%, 97.65% and 49.85% respectively.
- Activated char from orange peel waste resulted in suspended solids and turbidity removal up to 98%.
- Adsorption capacity of 418.31 mg/g of COD was obtained for AOPP treatment of TWE.
- For treating 1L of TWE, about 33ml, 18.5ml and 12ml of sludge was formed after alum, OPP and AOPP coagulation process respectively.
- The sludge obtained after alum coagulation was gelatinous in nature unlike OPP and AOPP were in powder form as in the initial stage.
- Sludge generated using alum coagulation treatment was almost 3 times more that generated by AOPP treatment.
- Pseudo first order kinetics was observed to be best fitted model resulting into higher linear regression coefficient of R^2=0.981 for AOPP treatment.
- Based on the R^2 value obtained, Langmuir isotherm was found to be best fitted with the experimental data for AOPP treatment.

4.9 Conclusions

The physicochemical characteristics of OPP, AOPP and alum are essential in removing pollutants from TWE. Higher surface area and the porous structure of OPP and AOPP have resulted in the removal of the pollutants by the adsorption mechanism. However, alum having cubical morphology resulted in removing pollutants by charge neutralization phenomenon. The broad peaks of carbon-containing compounds have been obtained through XRD plots, whereas alum turned amorphous after the treatment indicating the accumulation of pollutants over its surface. The formation of complex compounds after alum treatment was found using FTIR analysis, unlike OPP and AOPP. Moreover, the regenerated OPP and AOPP have delivered better removal efficiencies compared to alum without compromising the overall treatment removal efficiency. Therefore, applying AOPP treatment for pre-treatment of TWE can be recommended for larger-scale implementation.

Chapter – 5
Application of Advanced oxidation processes

The pre-treatment with AOPP as an adsorbent has been successful in removing the TSS from TWE. The treatment of TWE using AOPs in combination with HC has been conducted over the fabricated hydrodynamic cavitation set-up. The pre-treated wastewater using adsorption enabled smooth running of TWE with minimum solids that might clog the orifice mounted on HC set-up. The chapter deals with the treatment of TWE obtained after sedimentation tank from the industry using AOPs in combination with HC to increase the biodegradability index (BI). Further, experimentation was also carried out on the effluent obtained after AOPP pre-treatment to determine the difference between subjecting of the sedimented and pre-treated wastewater on removal efficiencies respectively. The kinetic studies and isotherms were also performed on the experimental data to find out the best suited kinetic model and isotherm respectively.

5.1 General

The TWE characteristics are shown in the Table.5.1 below. The values clearly indicate that the pH of the TWE is alkaline, and it is rich in solids (TDS and TSS). Moreover, the BOD/COD ratio, i.e., the biodegradability index (BI), is 0.188 and 0.122 for raw and sedimented TWE, respectively. BI clearly shows that the TWE is highly non-biodegradable and toxic in nature. A trial experiment on the raw TWE in a hydrodynamic cavitation set-up resulted in clogging of the orifice due to the presence of suspended solids. The solid particles having a size $\geq$ 1.5mm restricted the flow of wastewater through the orifice. Therefore, all the experiments were performed on the effluent collected after sedimentation in a common effluent treatment plant (CETP) to avoid clogging and enable cavitation phenomenon to occur. Moreover, a series connection of orifice was used in the HC set-up which resulted to be a design failure and therefore, only a single orifice HC set-up was used for the further experimental runs. Many research studies on wastewater treatment have also recommended pre-treated wastewater as input for HC systems to increase the overall degradation efficiency (P. R. Gogate & Pandit, 2001; Saxena, Rajoriya, et al., 2018; B. Wang et al., 2021).

Table 5.1 Tannery wastewater effluent characteristics

S.no	Parameters	Raw TWE characteristics	TWE characteristics of the collected samples at the outlet of the sedimentation tank
1	pH	11.5 ± 0.5	11.5
2	TDS	11250 ± 150 mg/L	10980 mg/L
3	TSS	4490 ± 200 mg/L	1567 mg/L
4	Turbidity	510 ± 20 NTU	163.45 NTU
5	BOD	3350 ± 100 mg/L	2146 mg/L
6	COD	17782 ± 200 mg/L	17564 mg/L
7	sCOD (soluble COD)	6542 ± 200mg/L	6433 ± 200mg/L

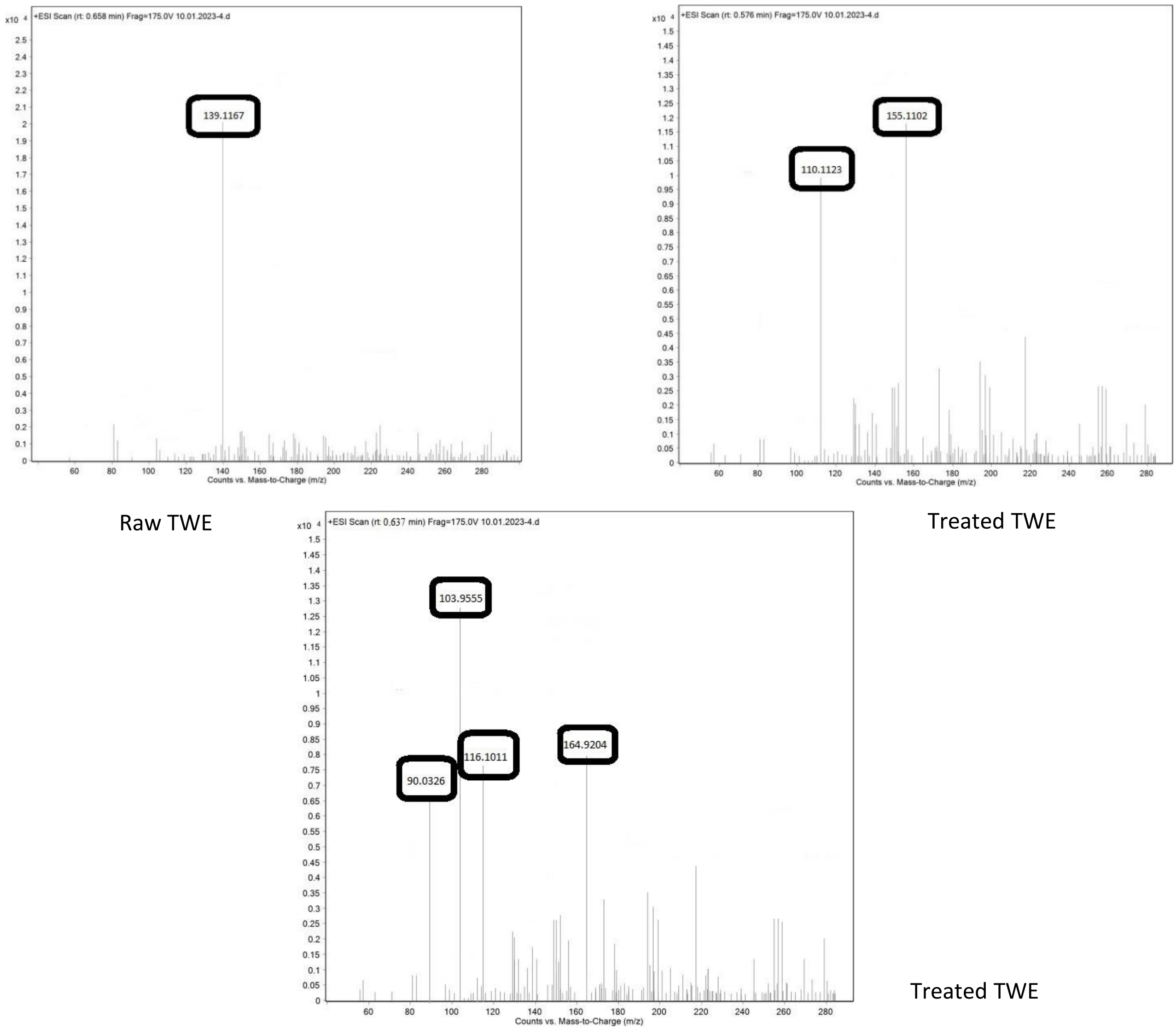
5.2 Liquid chromatography-high resolution mass spectrometry analysis (LC-HRMS)

LC-HRMS analysis of raw TWE and treated effluent enabled us to find out the organic compounds and their intermediate compounds in the treated effluent by matching their MS spectra from the standard data. Table.5.2 shows the compounds, and their respective mass numbers present in TWE before and after the treatment. The common compounds in TWE were found to be phenolic compounds (p-nitrophenol), 4-chloro-m-cresol, polyethylene glycols (PEGs), dibutyl phthalate (DBP), nonyl phenol ethoxylated surfactants and alcohol ethoxylated surfactant. The PEGs and their related acidic forms i.e., Monocarboxylate polyethylene glycols (MCPEGs) with varying numbers of carbon atoms in the carbon chain, were found. Nonyl-phenol ethoxylated surfactant and alcohol ethoxylated surfactants have a very slow bio-degradation rates (S. G. Schrank et al., 2004; Silvia G. Schrank et al., 2017). Figure.5.1- 5.8 shows the comparison of MS spectra at various retention times for raw TWE and treated effluent. However, several intermediate peaks of aromatic compounds, i.e., p-nitrocatechol (m/z=155.1102) and hydroquinone (m/z=110.1123) and acids, i.e., malic acid (m/z=134.0874), the carboxylic acid (m/z=150.150), malonic acid (m/z=104.0615), oxaloacetic acid (m/z= 134.0874) were found in the treated effluent. The spectrum shows that the major peaks found for raw TWE were reduced to less than 30%-50% approximately using a combination of HC+PAA+$FeSO_47H_2O$. The reduction in the intensities of several peaks, the introduction of new peaks and disappearance of peaks shows that the combined system resulted in the degradation of larger carbon chain compounds in smaller molecular chain compounds.

Table 5.2 Identified compounds in raw TWE and treated effluent

S.no	Chemical compounds	m/z	
		Raw TWE	*Treated effluent*
1	p-Nitrophenol	139.1167	155.1102,110.1123,116.1011,90.0326
2	4-chloro-m-cresol	164.9206	164.9204
3	Polyethylene glycols (PEGs)	702.5367, 614.4840, 658.5107	702.5364, 658.5107, 614.4834
4	Dibutyl phthalate	256.8709	256.8210
5	Nonyl-phenol ethoxylated surfactant	222.8794	--
6	Alcohol ethoxylate surfactant	178.1229	178.1228
7	(MCPEG)	878.6412	103.9555, 103.9561

p-Nitrophenol:



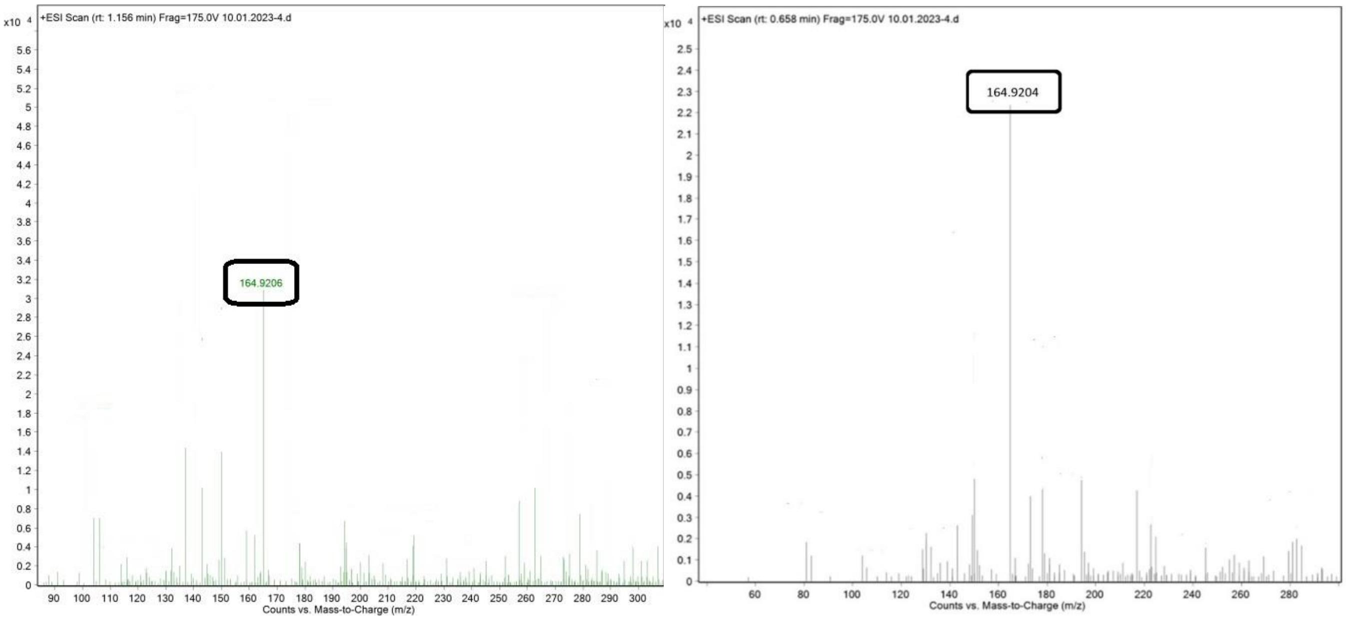
Raw TWE

Treated TWE

Treated TWE

Figure 5.1 Mass spectra of p-nitrophenol present in TWE before and after treatment at various retention time

4 Chloro-m-cresol:

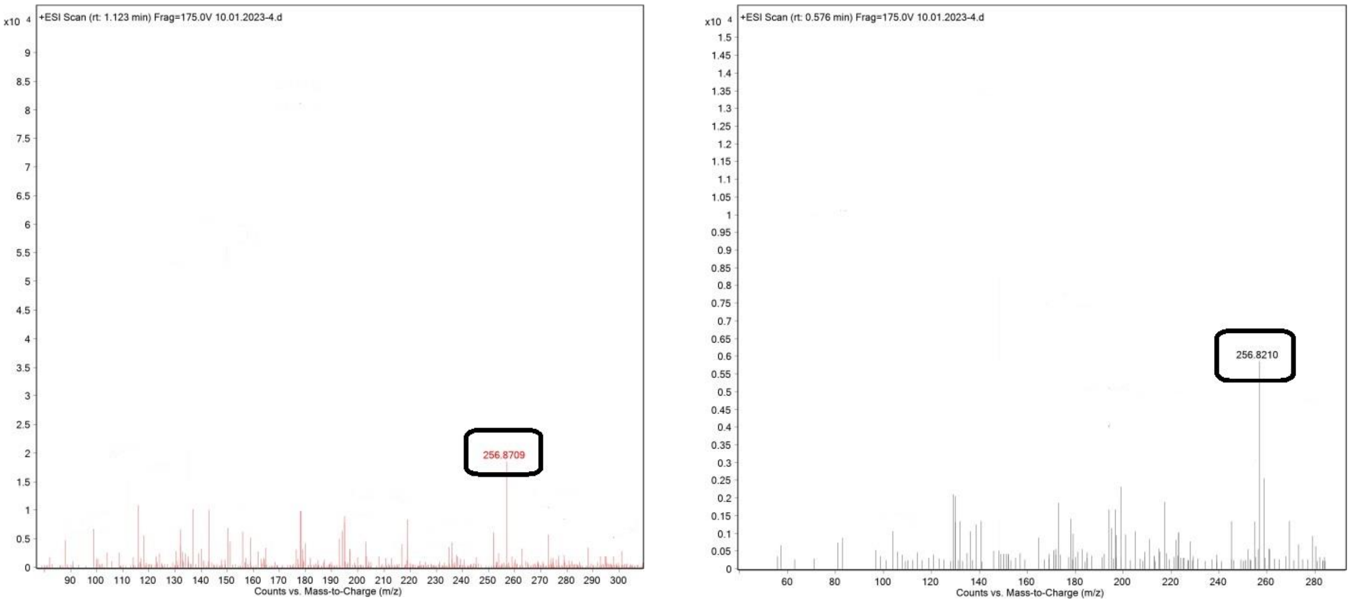


Raw TWE

Treated TWE

Figure 5.2 Mass spectra of 4chloro-m-cresol present in TWE before and after treatment at various retention time

Dibutylphthalate:

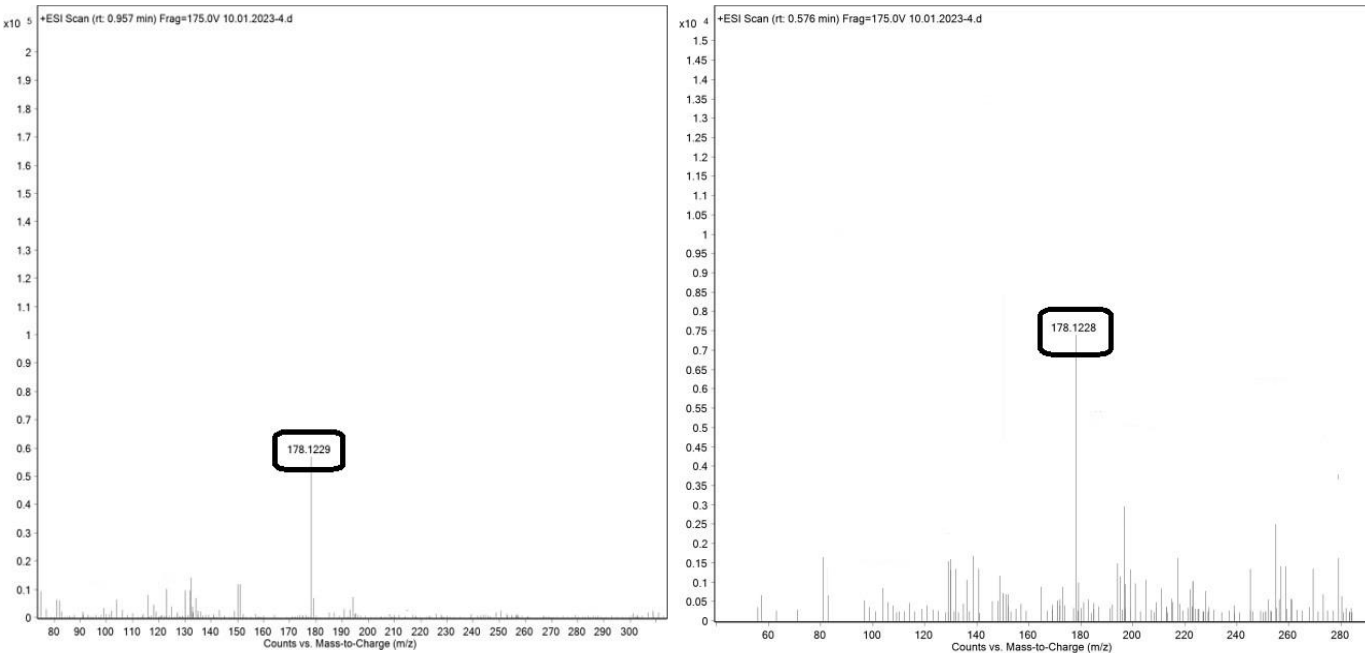


Raw TWE

Treated TWE

Figure 5.3 Mass spectra of Dibutyl phthalate present in TWE before and after treatment at various retention time

Alcohol ethoxylated Surfactant:

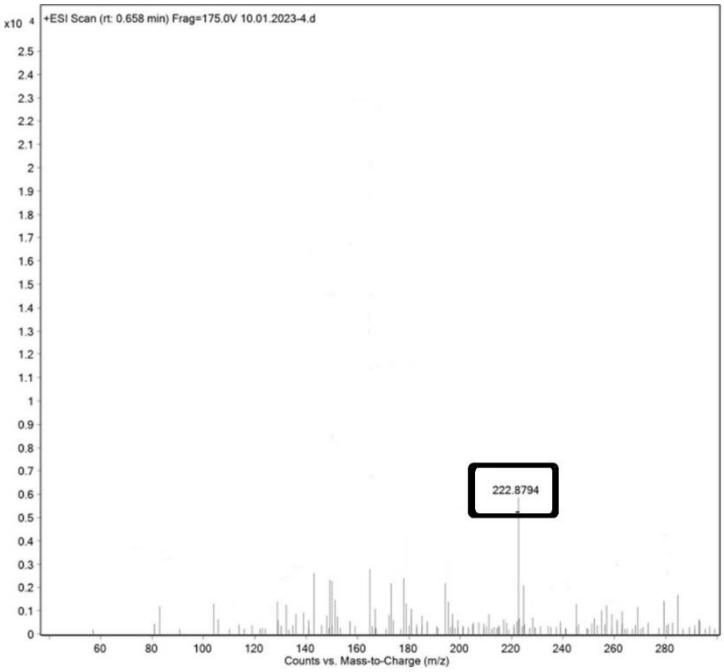


Raw TWE

Treated TWE

Figure 5.4 Mass spectra of alcohol ethoxylated surfactant present in TWE before and after treatment at various retention time

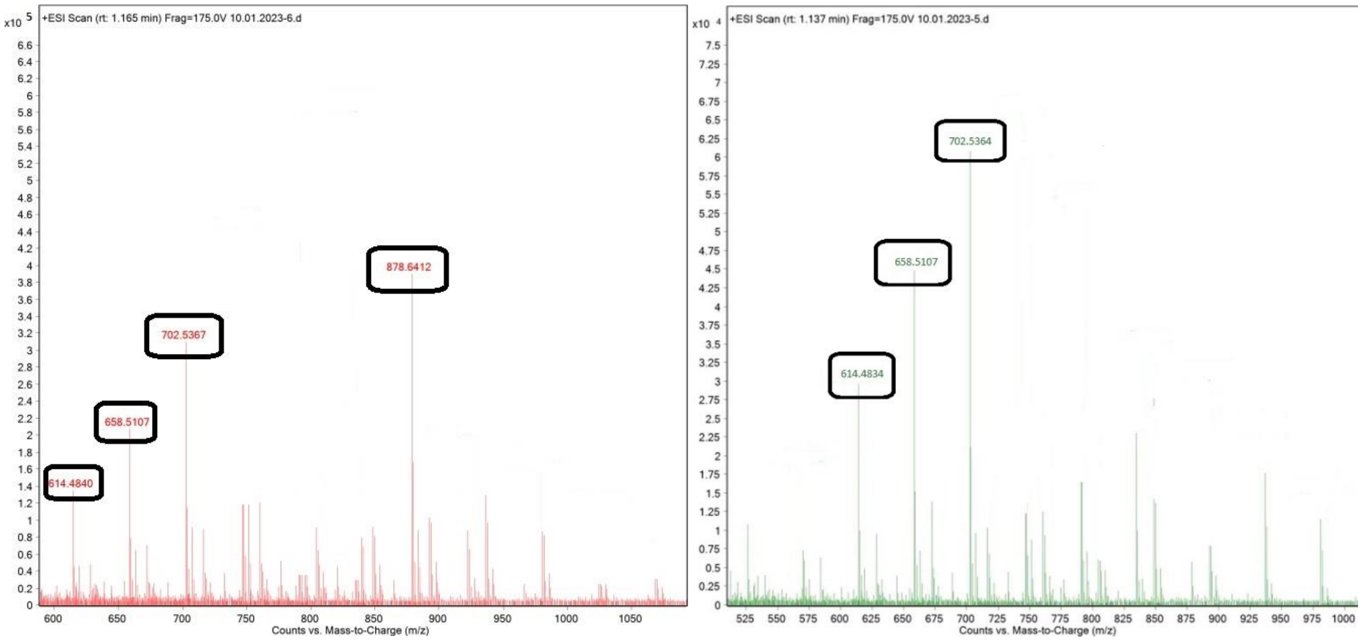
Nonly-phenol Ethoxylated Surfactant:



RawTWE

Figure 5.5 Mass spectra of nonyl-phenol ethoxylated surfactant present in raw TWE treatment

Polyethylene glycols (PEGs):

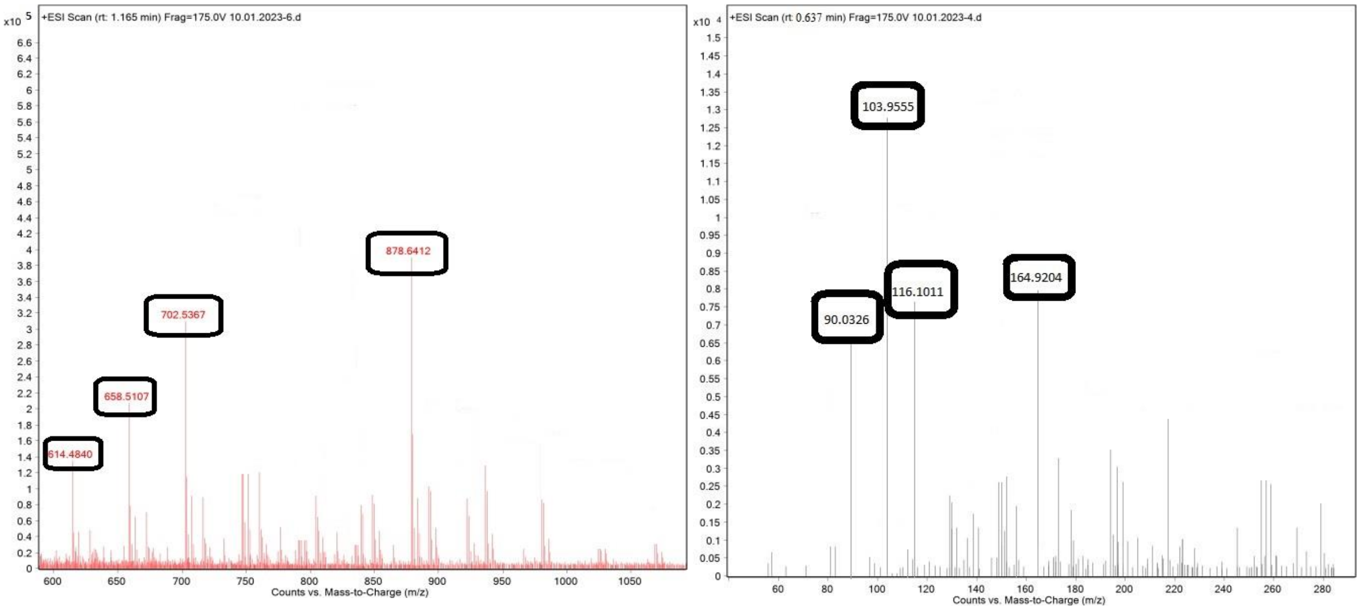


Raw TWE

Treated TWE

Figure 5.6 Mass spectra of polyethylene glycols (PEGs) present in TWE before and after treatment at various retention time

Monocarboxylated polyethylene glycols:

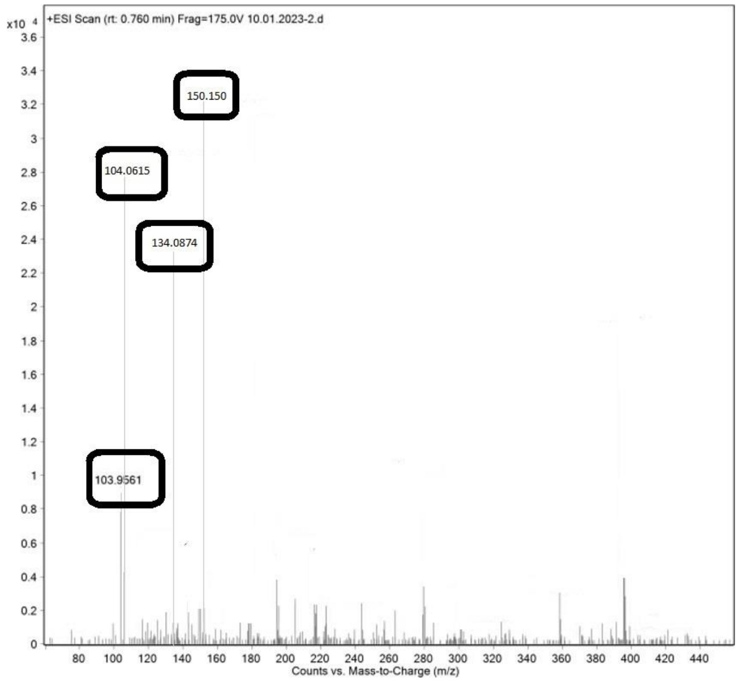


Raw TWE

Treated TWE

Figure 5.7 Mass spectra of monocarboxylate polyethylene glycols (MCPEGs) present in TWE before and after treatment at various retention time

Acids obtained in treated effluent.



Treated TWE

Figure 5.8 Mass spectra of several intermediate compounds present in TWE after treatment

5.3 Reaction mechanism

The dissociation of PAA in the presence of ferrous ions in the wastewater sample is given below in equations 5.1, 5.2 and 5.3 (Kim & Huang, 2021)**:**

$$\mathrm{CH_3COO\text{-}OH + Fe^{2+} \longrightarrow CH_3C(O)O^{o} + Fe^{3+} + OH^{-}} \quad (5.1)$$
$$\mathrm{CH_3COO\text{-}OH + Fe^{2+} \longrightarrow CH_3C(O)O^{-} + Fe^{3+} + OH^{o}} \quad (5.2)$$
$$\mathrm{CH_3COO\text{-}OH + Fe^{2+} \longrightarrow CH_3C(O)OH + Fe^{IV}O^{2+}} \quad (5.3)$$

The dissociated radicals participate in the reaction with the pollutants present in the TWE and decompose the complex compounds into simpler compounds. LC-HRMS has shown a couple of complex compounds present in raw TWE. Therefore, the degradation mechanism for the p-nitrophenol present in raw TWE has been proposed below in Figure.5.9:

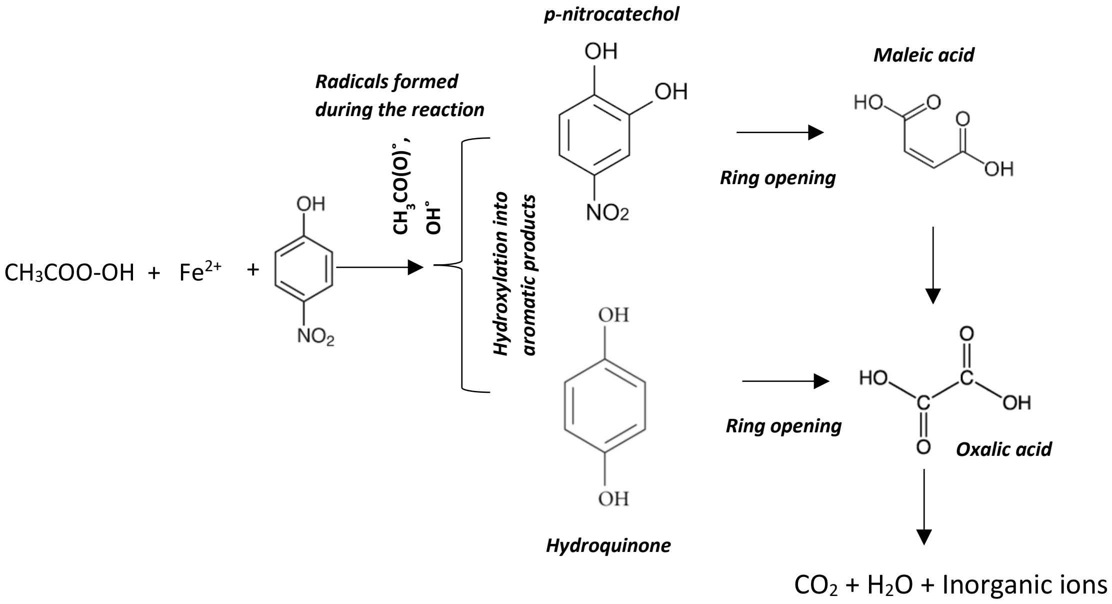


Figure 5.9 Mechanistic pathway involved in the degradation of the p-nitrophenol present in TWE using HC+PAA+Fe^{2+}

It is evident from the m/z values found in the treated effluent at retention times, i.e., 0.576 and 0.637 min, that p-nitophenol has undergone hydroxylation converting to an aromatic compound. Constant free radical attack enabled the ring compounds to open and form simpler compounds such as acids. Therefore, the degradation of p-nitrophenol in TWE has taken place through the radical pathway. Moreover, it can be attributed from LC-HRMS mass spectra showing several intermediate compounds (aromatic ring compounds and acids) that the degradation of compounds would have taken place through the radical pathway. Similar results showing the degradation of several organic compounds using radicals have been communicated in research studies (Fedorov et al., 2022; Rayaroth et al., 2022; Rodrigues & Madeira, 2021). The peroxyl radicals and hydroxyl radicals are primary radicals that are generated in PAA-based AOPs (Kim et al., 2019; Z. Wang et al., 2021; S. Yu et al., 2008; Zhou et al., 2015).

5.4 Radical scavenging test results

Scavenging results are shown in Figure 5.10 by comparing the C_t/ C_0 vs time for HC+PAA/Fe^{2+}, HC+PAA/Fe^{2+} with tert-butyl alcohol (TBA) and HC+PAA/Fe^{2+} with Methanol (MeOH). Overall COD removal in absence of scavengers was observed to be approximately 71%. On adding TBA, COD removal declined up to 45% in overall degradation which indicates peroxyl radicals (CH_3COO^o) plays important role in degradation. Adding MeOH in excess results in inhibition of degradation of (p-nitrophenol, Phenol) compounds in terms of COD removal decrease up to 21%, since it reacts with CH_3COO^o, which indicates presence of both peroxyl radicals and hydroxyl radicals, but it cannot entirely inhibit the COD removal which indicates $Fe^{IV}O^{2+}$ and carbon cantered radicals also takes part in pollutants degradation.

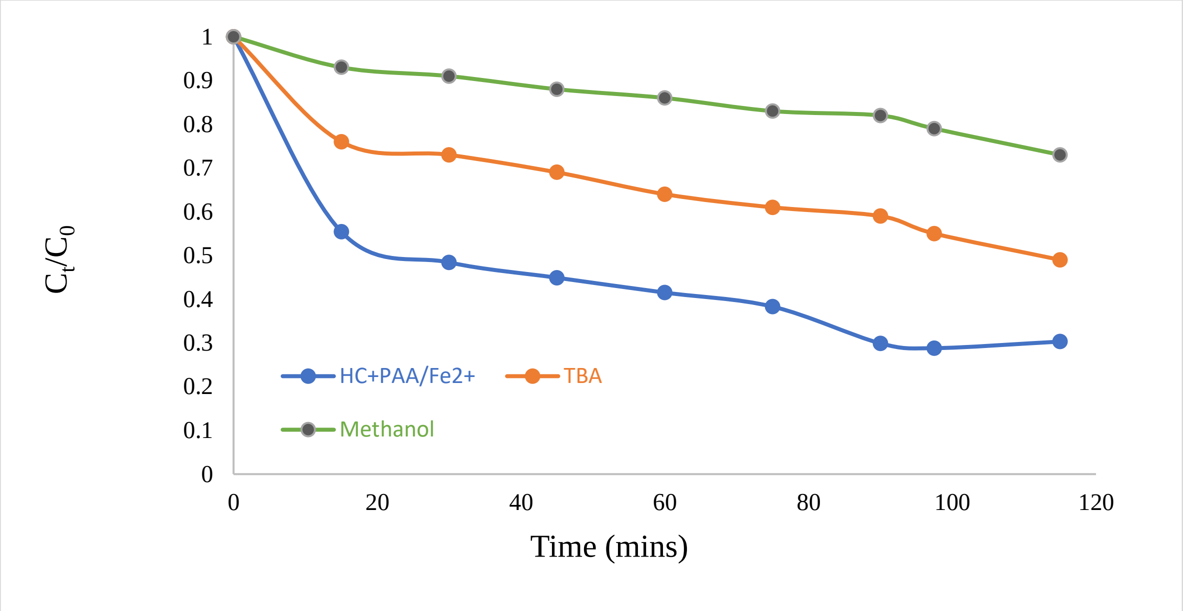


Figure 5.10 Effect of presence of TBA and methanol in HC+PAA/Fe2+ process

5.5 Flow characteristics of the cavitating device

Energy dissipated into the system = $(5.5*10^5)$ Pa x $(320*10^{-3}/3600)$ m^3/s x (97.5*60) sec (5.4)

= 316134J = 316 kJ

The hydraulic characteristics of the orifice have been studied by varying the pressure from 3-12 bar and the flow rate at 300, 320 and 400 LPH. The cavitation number has been calculated using equation.3.2. However, increasing the pressure beyond a certain limit has resulted in a decrease of overall COD removal efficiency. The optimum pressure of 7.5 bar has been used for all further experiments. A lower cavitation number or higher inlet pressure is needed for effective degradation of COD since at higher inlet pressure generation of cavities would be more, the collapse of the cavities would be more violent, and number of passes through the cavitating zone would increase for the same length of operation. This condition could lead to higher-generation hydroxyl radicals and their effective utilization. Violent collapse of cavities may also provide the necessary shock wave required to initiate the dissociation of complex compounds present in TWE. A higher number of passes through the cavitating device ensures the sufficient residence time of wastewater effluent within the cavitating zone and also increases the availability of pollutants at the cavity of the water interface (Šarc et al., 2017). Increasing the inlet pressure beyond 7.5 bar has marginally reduced the extent of degradation of COD due to the choked cavitation (Raut-Jadhav et al., 2013). Table. 5.3 has inscribed the flow characteristics of the cavitating device. The cavitation occurs when

$C_v<1$. Since the cavitation number is much lesser than 1 for the optimised conditions, it can be attributed that the cavities generated are high with a high amount of energy released, resulting in the degradation of the pollutants in TWE.

Table 5.3 Flow characteristics of cavitating device and energy dissipated

S.no	*Upstream pressure (Bar)*	*Downstream pressure (Bar)*	*Flow rate (LPH)*	*Velocity (m/s)*	*Cavitation number (C_v)*	*Number of passes*	*Energy dissipated (kJ)*
1	3	1	300	425	0.001	25	148.16
2	7.5	2	320	453	**0.0063**	26	395.16
3	12	5	400	496	0.0043	32	461.04

5.6 Effect of independent variables on COD removal efficiency

Figures 5.11, 5.12, 5.13, 5.14 and 5.15 show the 3-D RSM plots depicting the interaction between all the operating parameters and their effect on the COD removal efficiency. RSM-BBD has assisted in reducing the experimental runs to be performed, making the HC + AOP process to be more efficient. Table. 5.4 has inscribed the design of experiments for experimental analysis.

Table 5.4 Design of experiments for treatment of TWE

Run	**A: Cavitation time (min)**	**B: Pressure (bar)**	**C:pH**	**D: Orifice diameter (mm)**	**E: PAA dosage (mg/L)**	**F: PAA $/FeSO_4.7H_2O$**	**Response COD (mg/L)**
1	180	12	4.5	1.5	17.5	1.25	1.17
2	180	7.5	2	1	17.5	2	41.92
3	15	3	4.5	1.5	17.5	1.25	1.11
4	97.5	7.5	7	0.5	17.5	0.5	67.45
5	97.5	7.5	2	0.5	17.5	2	70.89
6	15	7.5	4.5	0.5	30	1.25	39.98
7	97.5	3	2	1	5	1.25	11.01
8	180	7.5	4.5	0.5	5	1.25	34.05
9	97.5	12	7	1	30	1.25	16.2
10	15	7.5	4.5	1.5	30	1.25	22
11	15	7.5	2	1	17.5	0.5	38
12	97.5	12	7	1	5	1.25	11.26
13	180	12	4.5	0.5	17.5	1.25	19.89
14	97.5	3	4.5	1	5	2	11.87
15	15	7.5	4.5	0.5	5	1.25	44.66
16	97.5	7.5	2	0.5	17.5	0.5	64.1
17	97.5	3	4.5	1	30	2	12.9
18	97.5	12	2	1	30	1.25	19.08
19	97.5	7.5	4.5	1	17.5	1.25	71.85
20	180	7.5	7	1	17.5	2	34.65
21	15	7.5	4.5	1.5	5	1.25	25.54
22	15	3	4.5	0.5	17.5	1.25	14.87
23	97.5	7.5	7	0.5	17.5	2	70

24	97.5	7.5	4.5	1	17.5	1.25	72.98
25	97.5	3	4.5	1	30	0.5	8.1
26	15	12	4.5	1.5	17.5	1.25	2.56
27	97.5	7.5	2	1.5	17.5	2	60.9
28	180	7.5	4.5	1.5	30	1.25	24.18
29	97.5	7.5	7	1.5	17.5	0.5	40.7
30	97.5	3	7	1	5	1.25	5.87
31	97.5	12	4.5	1	5	2	18.07
32	180	7.5	7	1	17.5	0.5	29.88
33	97.5	3	7	1	30	1.25	10.32
34	15	7.5	7	1	17.5	2	39.13
35	97.5	7.5	2	1.5	17.5	0.5	48.78
36	97.5	3	2	1	30	1.25	11.09
37	15	7.5	7	1	17.5	0.5	36.12
38	97.5	3	4.5	1	5	0.5	4.46
39	97.5	7.5	4.5	1	17.5	1.25	65.44
40	180	3	4.5	1.5	17.5	1.25	2
41	97.5	12	4.5	1	5	0.5	9.78
42	97.5	7.5	4.5	1	17.5	1.25	69.83
43	15	12	4.5	0.5	17.5	1.25	24.8
44	15	7.5	2	1	17.5	2	47.66
45	180	7.5	2	1	17.5	0.5	30.56
46	97.5	12	2	1	5	1.25	16.65
47	97.5	12	4.5	1	30	2	15.15
48	97.5	7.5	7	1.5	17.5	2	44.99
49	180	7.5	4.5	0.5	30	1.25	44.23
50	97.5	7.5	4.5	1	17.5	1.25	71.09
51	97.5	7.5	4.5	1	17.5	1.25	72.87
52	97.5	12	4.5	1	30	0.5	13
53	180	7.5	4.5	1.5	5	1.25	14.88
54	180	3	4.5	0.5	17.5	1.25	10.54

5.6.1 Effect of cavitation time

3-D RSM plots in Figure.5.11 show the interaction of other parameters with respect to cavitation time and their effect on COD removal efficiency. Figure.5.11(i) shows that the maximum COD was removed at an optimized pressure value of 7.5 bar. Lower inlet pressure fails to generate cavities leading to OH^{o} generation whereas, at higher pressure values the probability of super cavitation results in reducing the cavitation intensity. Pressure and cavitation time shows direct proportion with COD removal efficiency till it reaches an optimum point. Whereas, after the optimum point there is decrease in COD removal efficiency due to super cavitation. From Figure.5.11(ii) it can be inferred that pH does not have significant impact on COD removal efficiency. Whereas, Figure.5.11(iii) clearly indicate that at the a given time orifice diameter plays a prominent role in COD removal. The COD removal efficiency is inversely proportional to orifice diameter at optimized cavitation time. However, Figure.5.11(iv) and (v) shows that the PAA dosage and ratio of PAA/Fe^{2+} has significant impact on COD removal efficiency. PAA dosage and ratio of PAA/Fe^{2+} along with the cavitation time are directly proportional to COD removal efficiency up to an optimum point. Excess amount of chemical oxidant i.e., PAA result in auto decomposition of radicals whereas, excess ferrous ions lead to formation of precipitates contributing to COD. Moreover, at higher cavitation time, the system becomes energy inefficient. Due to a more significant number of cavities collapsing, high energy is released, resulting in an increase in the wastewater's temperature that may have a detrimental effect on the COD removal efficiency. Maximum COD removal efficiency occurred at 97.5 min of cavitation time. Similar results have also been observed in a study carried out for enhancing the biodegradability of tannery wastewater effluent using combination of ultrasonic and hydrodynamic cavitation (Saxena, Rajoriya, et al., 2018).

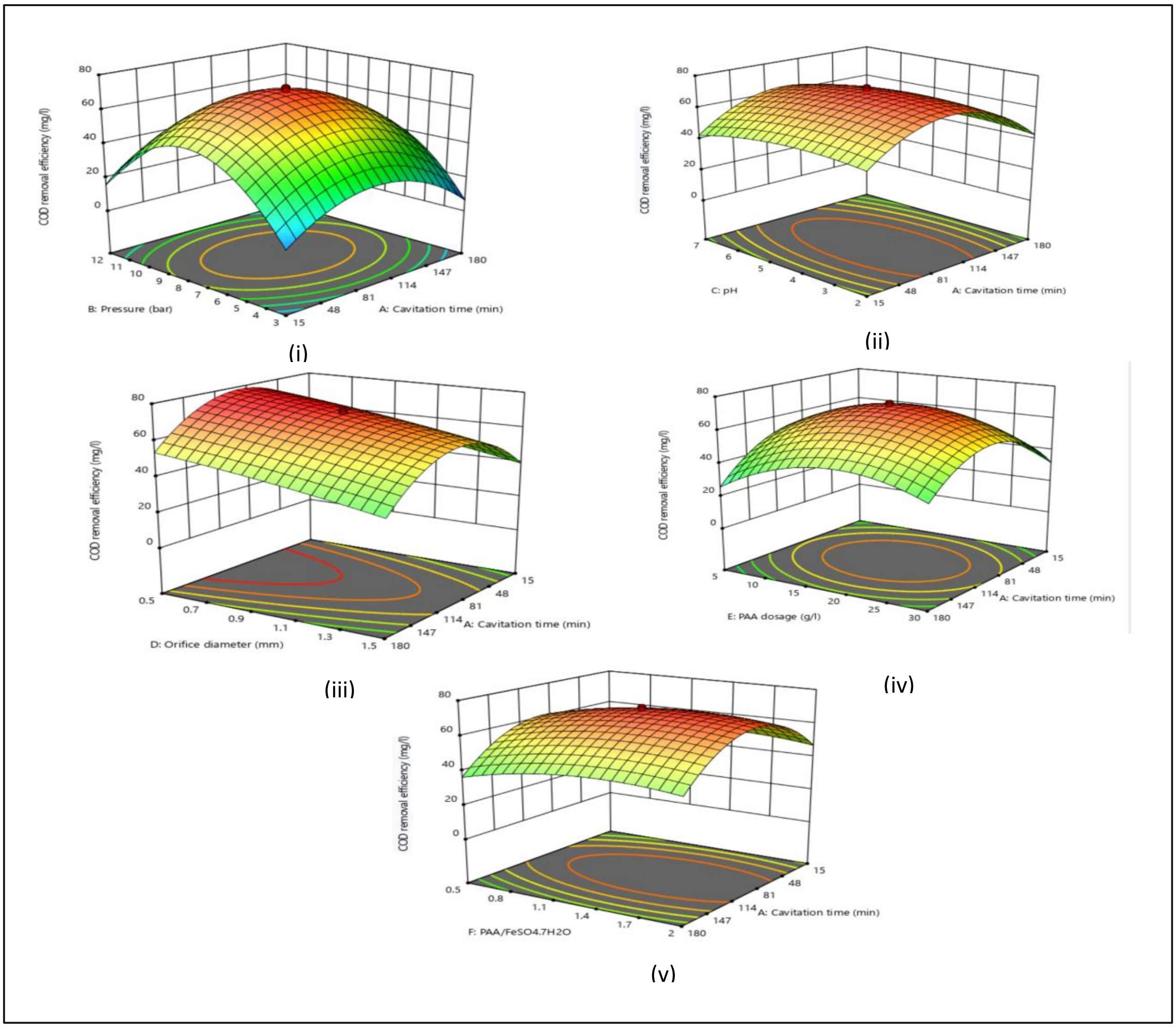
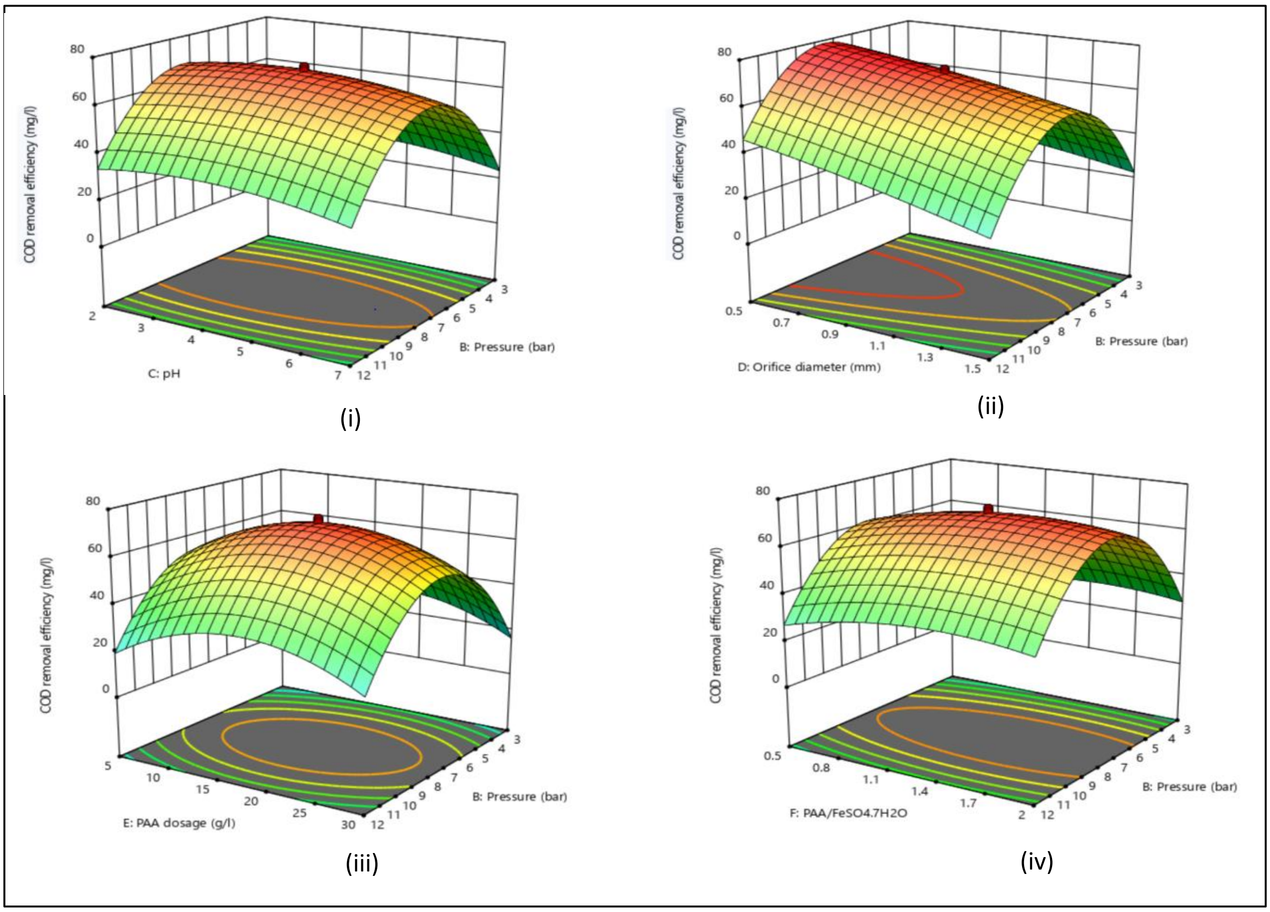


Figure 5.11 3-D RSM results showing interaction of operating parameters with cavitation time over COD removal efficiency

5.6.2 Effect of pressure

The 3-D plots in Figure.5.12 shows the interaction of other parameters with respect to pressure and its effect on COD removal efficiency. Fig.5.12 (i) shows that pH and pressure are directly in proportion with COD removal efficiency till an optimum point. However, it is very clear that pH is not having a major impact on COD removal efficiency. Almost at all pH values at a given pressure, the COD removal efficiency is approximately similar. There is a slight decrease in COD removal efficiency at higher pH values which may be because of the reciprocal relation of pH with OH° radical generation (Boczkaj & Fernandes, 2017). From Figure.5.12.(ii) it is clear that with increase of pressure and decrease in orifice diameter till an optimum point COD removal increases. However, further increase in pressure results in super cavitation. Generation of cavities are more with lesser orifice diameter hole. Figure.5.12. (iii) and (iv) shows that COD removal efficiency increases till an optimum PAA dosage and PAA/Fe^{2+} dosage with respect to pressure. Maximum COD removal efficiency has been obtained at a pressure value of 7.5 bar. Pressure optimization is necessary to obtain high cavitation intensity resulting in generating more OH° has been discussed in a review conducted on hydrodynamic cavitation used for wastewater treatment (Gągol et al., 2018).



(i)

(ii)

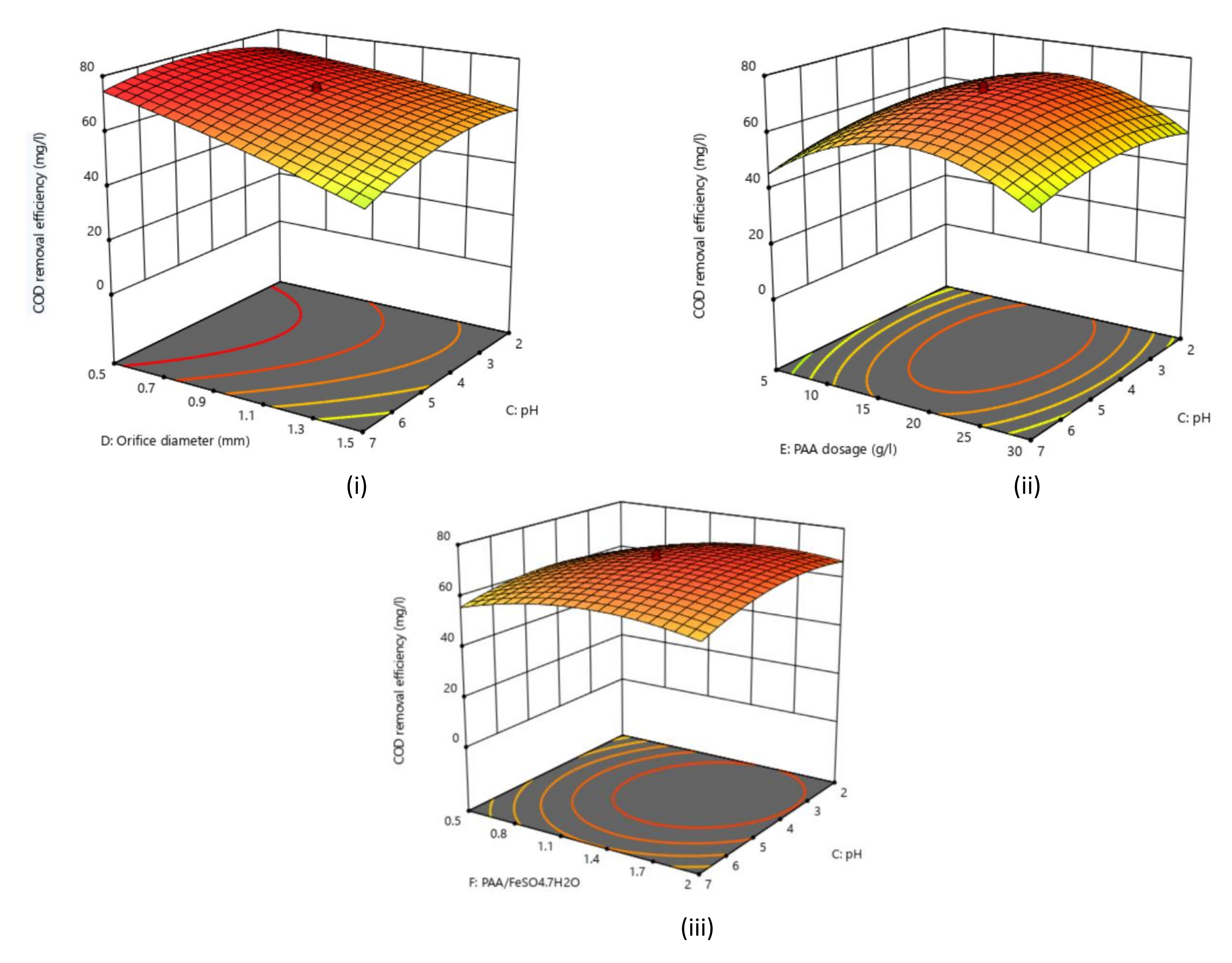
(iii)

(iv)

Figure 5.12 3-D RSM results showing the interaction of operating parameters with pressure over COD removal efficiency

5.6.3 Effect of pH

The interaction between pH and other influential parameters have been shown in Figure.5.13. The pH of the wastewater sample should be maintained to avoid corrosion of the HC system made up of stainless steel. The 3-D plots in Figure.5.13 are almost flat which clearly indicate that pH does not have significant effect on COD removal efficiency. The maximum COD removal efficiency has been obtained at pH-2. However, Figure.5.13 (i), (ii), and (iii) indicates that the slight difference in COD removal efficiency at different pH. The OH^{o} generation and pH are inversely proportional to each other there is a slight decrease in COD removal efficiency at higher pH values. Moreover, it might be due to the variation in orifice diameter, PAA dosage and PAA/Fe^{2+} dosage ratio. At higher pH values, the COD values may have been increased due to the auto-decomposition of the reactive radicals (Boczkaj & Fernandes, 2017). The removal of organic dyes from the textile wastewater was also observed to be the highest at pH-2 (Badmus et al., 2020).



(i)

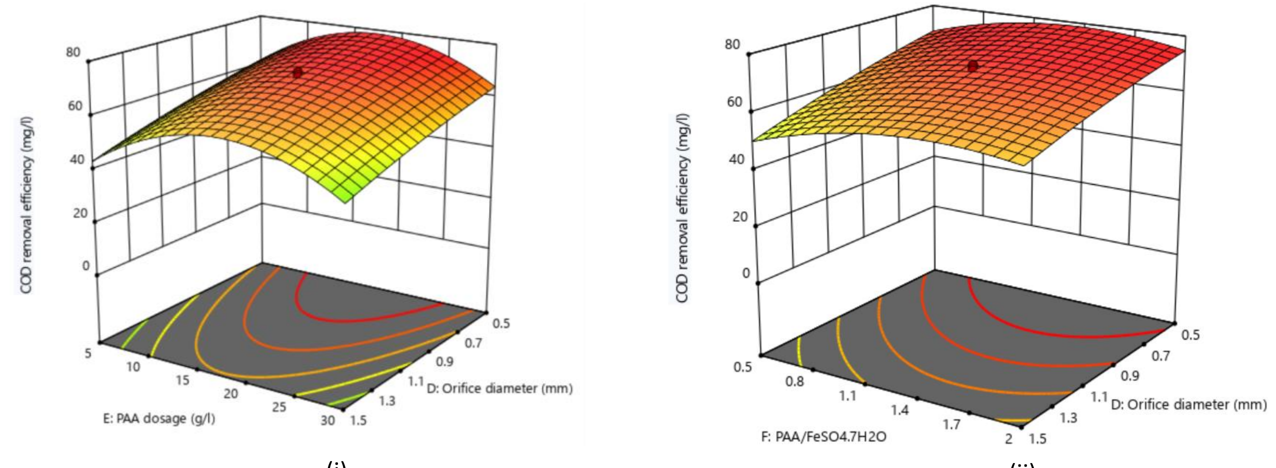
(ii)

(iii)

Figure 5.13 3-D RSM results showing the interaction of operating parameters with pH over COD removal efficiency

5.6.4 Effect of orifice diameter

The cavitation intensity depends upon the cavitation number (C_v). To generate a more significant number of cavities, C_v should be ≤ 1. According to the equation. 2, the diameter of the orifice and C_v have an inverse relationship. Therefore, more the diameter of the orifice lesser is the C_v resulting in lesser cavitation intensity. Moreover, a study conducted on bubble behaviour in the hydrodynamic cavitation system has observed that more cavities are generated only when $C_v \leq 1$ (Vijayanand S. Moholkar & Pandit, 1997). 3-D RSM plots in Figure.5.14 have also shown higher COD removal efficiency for orifice diameter of 0.5mm. Figure.5.14.(i) shows that PAA dosage should be optimized since it has an inverse relation with orifice diameter. The COD removal efficiency increases with increase of PAA dosage upto a certain limit. After an optimum dosage, using orifice of lowest diameter, the COD removal efficiency decreases due to auto-decomposition of the free radicals generated. However, Figure.5.14 (ii) indicates that the ferrous ions have resulted in slight increase in the COD removal efficiency.

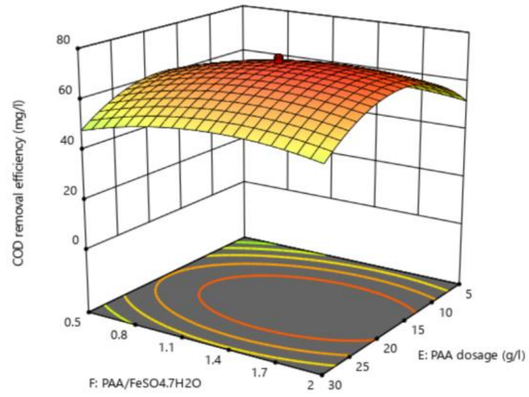


(i) (ii)

Figure 5.14 3-D RSM results showing the interaction of operating parameters with orifice diameter over COD removal efficiency

5.6.5 Effect of PAA dosage

The reaction mechanism has been mentioned in section 5.3. However, maximum COD removal efficiency will occur at a specific dosage and a particular ratio of PAA/ $FeSO_4.7H_2O$. At lower dosage, the amount of OH^{o} generated is insufficient for the complete degradation of the pollutants in the TWE. Excess amount of chemical oxidant i.e., PAA result in the auto decomposition of radicals whereas, an excess amount of ferrous ions leads to the formation of precipitates contributing to COD. The overall TDS in the sample increases due to the formation of ferrous ion precipitates. Figure.5.15 shows that the maximum COD removal is obtained at 17.5g/L dosage of PAA and PAA/ $FeSO_4.7H_2O$ of 2:1. A study on tannery wastewater effluent using Fenton reagents having similar reaction mechanism as PAA has also shown a similar phenomenon of recombination of OH° and precipitation of the salts (S. G. Schrank et al., 2005; Vilardi, Di Palma, Verdone, et al., 2018). A similar phenomenon was observed while treating paper and pulp industry wastewater as well as oil recovery industry wastewater where the excess of OH° recombined to form H_2O_2 resulting in a decrease of COD removal efficiencies (Gunes, 2008; V. Kumar et al., 2019).



(i)

Figure 5.15 3-D RSM results showing the interaction of operating parameters with PAA dosage over COD removal efficiency

5.7 Fitting the model

The curve fitting of the experimental results shows that the quadratic model was the best suited for COD removal efficiency. Equation 5.4 obtained through the model is given below:

$$\text{COD removal efficiency (\%)} = 70.68-2.02A+2.64B-2.25C-9.03D+1.17E+3.22F\ 0.35AB+0.30AC+0.41AD+3.46AE+0.43AF-0.29BC-2.33BD-0.09BE-0.22BF-3.31CD+0.86CE-1.58+0.03DE+0.88DF-1.09EF-22.50A^2-37.30B^2-4.96C^2-1.26D^2-15.73E^2-5.38F^2 \quad (5.4)$$

where,

A = Cavitation time (min)
B = Pressure (bar)
C = pH
D = Orifice diameter (mm)
E = PAA dosage (g/L)
F = PAA/ $FeSO_4.7H_2O$

The statistical analysis results revealed that the quadratic model fits the experimental data. R^2 value of 0.987 also proved that the quadratic model is significant. Moreover, the adequate precision of 52.1 showed that the model could be used to navigate the design space. The F-value obtained through analysis of variance (ANOVA) is 283.86 for the model, which shows that the quadratic model is significant as shown in Table.5.5. The p-value <0.0001 indicates that the terms used in the equation for obtaining COD removal efficiency are significant. Furthermore, the F-value obtained for the operating parameters were 26.78, 45.91, 33.32, 534.87, 9.02, and 67.92 for cavitation time, pressure, pH, orifice diameter, PAA dosage and

PAA/$FeSO_4.7H_2O$ respectively show that orifice diameter is the most significant parameter followed by PAA/$FeSO_4.7H_2O$ and pressure. The F-value obtained through ANOVA agrees with 3-D plots obtained through RSM-BBD.

Table 5.5 Analysis of Variance (ANOVA) for quadratic model

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	**Remarks**
Model	28023.42	27	1037.90	283.86	< 0.0001	significant
A-Cavitation time	97.93	1	97.93	26.78	< 0.0001	
B-Pressure	167.85	1	167.85	45.91	< 0.0001	
C-pH	121.82	1	121.82	33.32	< 0.0001	
D-Orifice diameter	1955.72	1	1955.72	534.87	< 0.0001	
E-PAA dosage	32.97	1	32.97	9.02	0.0058	
F-PAA/FeSO4.7H2O	248.33	1	248.33	67.92	< 0.0001	
AB	1.02	1	1.02	0.2796	0.6014	
AC	0.7565	1	0.7565	0.2069	0.6530	
AD	2.74	1	2.74	0.7491	0.3947	
AE	95.91	1	95.91	26.23	< 0.0001	
AF	1.50	1	1.50	0.4093	0.5279	
BC	0.6962	1	0.6962	0.1904	0.6662	
BD	43.52	1	43.52	11.90	0.0019	
BE	0.1463	1	0.1463	0.0400	0.8430	
BF	0.3916	1	0.3916	0.1071	0.7461	
CD	87.45	1	87.45	23.92	< 0.0001	
CE	5.92	1	5.92	1.62	0.2146	
CF	40.04	1	40.04	10.95	0.0027	
DE	0.0085	1	0.0085	0.0023	0.9620	
DF	6.25	1	6.25	1.71	0.2026	
EF	9.57	1	9.57	2.62	0.1178	
A^2	5205.66	1	5205.66	1423.70	< 0.0001	
B^2	14311.80	1	14311.80	3914.15	< 0.0001	
C^2	253.10	1	253.10	69.22	< 0.0001	
D^2	16.34	1	16.34	4.47	0.0442	
E^2	2544.80	1	2544.80	695.98	< 0.0001	
F^2	367.74	1	367.74	100.57	< 0.0001	
Residual	95.07	26	3.66			
Lack of Fit	55.26	21	2.63	0.3306	0.9672	not significant
Pure Error	39.80	5	7.96			
Cor Total	28118.49	53				

5.8 Optimization of the parameters using desirability analysis

The desirability analysis evaluates the experimental conditions that result in optimal value for all the independent variables simultaneously (Bella et al., 2022). Figure 5.16 shows the desirability plots of the numerical analysis carried out using RSM-BBD. The objective of the desirability analysis is to obtain the maximum desirability function at a particular point. The desirability estimation value closer to 1 show that the response is desirable. However, values closer to 0 indicate the estimated value to be most undesirable. The study has shown the combined objective desirability value 0.9606, very close to 1, indicating it be a good measure. The results show that the maximum COD removal efficiency of 70.36% was obtained at cavitation time 97.5 min, pressure – 7.5 bar, pH – 2, orifice diameter – 0.5mm, PAA dosage – 17.5g/L, and PAA/ $FeSO_4.7H_2O$ – 2:1 ratio using hydrodynamic cavitation set-up. The interaction of influential variables has been shown through RSM-BBD 3-D plots in section 3.3. More number of free radicals, more is the degradation of the pollutants resulting in reduction of COD. However, using any single treatment system i.e., HC alone (physical treatment) or chemical oxidants (chemical treatment) results in lower COD removal efficiencies. Therefore, combination of physical and chemical treatment having similar reaction mechanism can treat the effluent efficiently yielding with higher COD removal efficiencies.

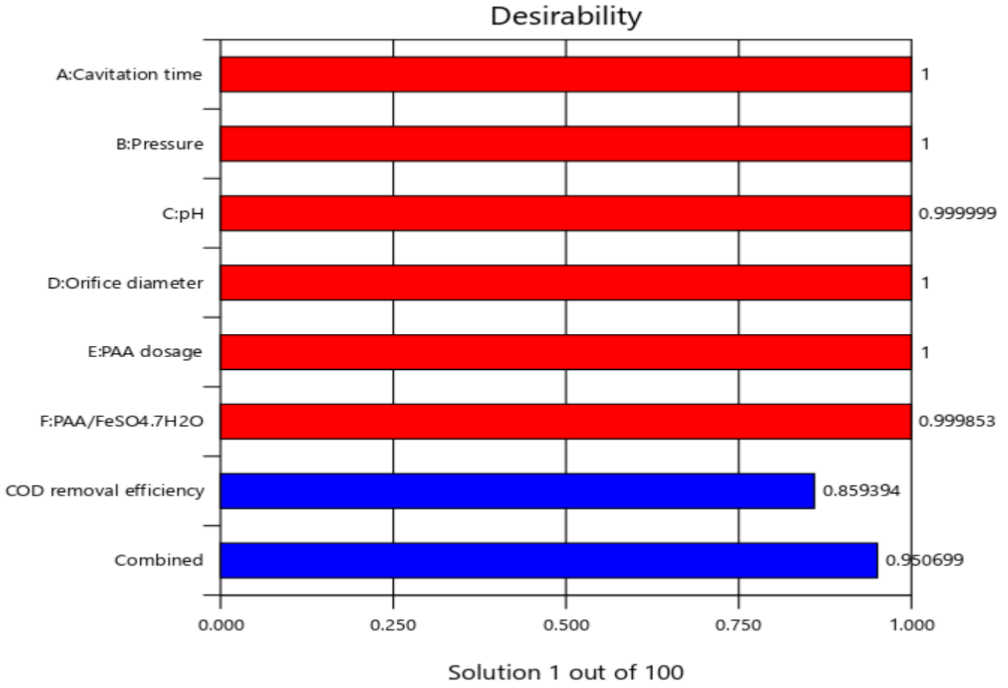


Figure 5.16 Desirability bar graph

5.9 Validation of the model

An experimental run was performed on HC set-up at optimized conditions obtained from response surface methodology (RSM)- Box Behnken design (BBD) to validate the model results. The results obtained are shown below in Table. 5.6. The COD removal efficiency has been maximum at pH-2. However, there is no substantial difference in COD removal efficiency at pH values 2-5. To maintain the overall pH of the treated effluent to be less acidic, the experiments can also be performed at pH-5. Moreover, at pH>7 the solid particles become stable and tend to form precipitates increasing the turbidity and solids percentage in the sample. The reduction in BOD, and COD is due to the OH^o radicals formed during HC reacting with compounds present in TWE. The sCOD has increased after the treatment upto 49% approximately, which shows that the biodegradability of the TWE has increased. Moreover, BI has also increased from 0.122 – 0.269. Therefore, the results obtained by RSM-BBD are in agreement with the experimental run performed for validation. Therefore, maximum COD removal efficiency of 71.30% was obtained at cavitation time 97.5 min, pressure – 7.5 bar, pH – 2, orifice diameter – 0.5mm, PAA dosage – 17.5g/L, and PAA/$FeSO_4.7H_2O$ – 2:1 ratio as per the experimental run performed for validation. The experimental results can also be analysed with respect to the molar ratio of oxidant to the pollutant load. However, TWE consists of mixture of compounds whose degradation has been evaluated in terms of COD reduction. According to the calculations it was found that 0.2301mol/L of PAA and 0.0314 mol/L of $FeSO_4.7H_2O$ is required to degrade 12.470 g/L of COD in TWE.

Table 5.6 Tannery wastewater characteristics after treatment

S.no	Parameters	Treated effluent wastewater characteristics obtained from RSM-BBD	Treated effluent wastewater characteristics for validation at optimized conditions
1	pH	5.3	5.2
2	TDS	614 mg/L	603 mg/L
3	TSS	90 mg/L	84 mg/L
4	Turbidity	6 NTU	4 NTU
5	BOD	1373 mg/L	1366 mg/L
6	COD	5094 mg/L	5065 mg/L
7	sCOD	9683 mg/L	9675 mg/L

The radicals formed in the combined system are highly reactive that oxidises the insoluble organic matter into soluble form, thereby, enhancing the sCOD solubilization. The soluble COD is increasing after the treatment attributing that the treated effluent has been converted into simpler forms/compounds increasing biodegradability. The biodegradability index has also been increased from 0.122 to 0.279.

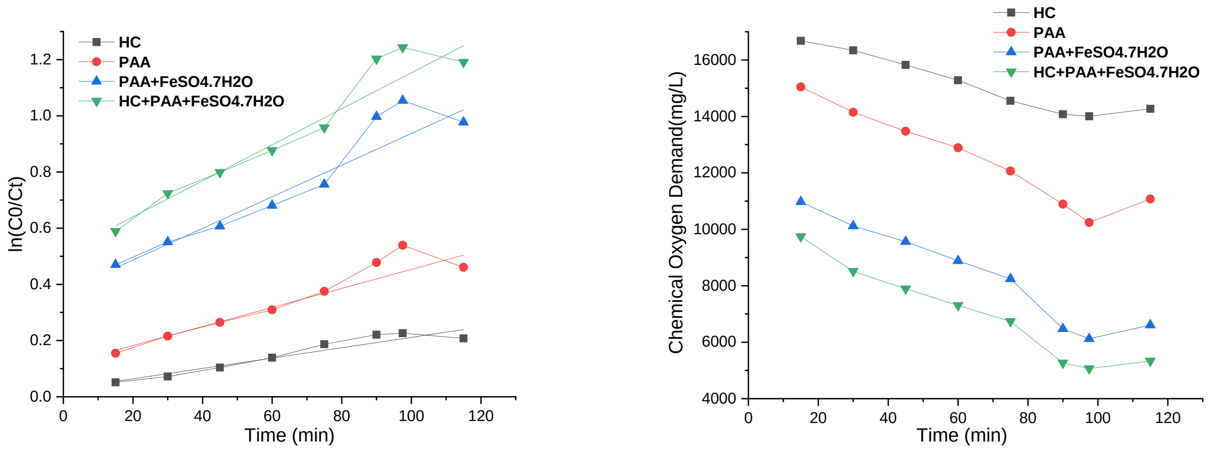
5.10 Kinetic study

The kinetic analysis results indicated that the experimental COD removal values obtained using HC, PAA, PAA+$FeSO_4.7H_2O$ and combination of HC+ PAA+$FeSO_4.7H_2O$ fits into pseudo-first order kinetic model. The reaction rate constant can be calculated using the following equation.5.5 (Fedorov et al., 2020; Saharan et al., 2012; Tao et al., 2016). Since, the OH^o radical formation was continuous having high reactivity and non-selective in nature, so its concentration impact was neglected in order to calculate the rate constant (Saharan et al., 2011). It was observed that the reaction rate constant was increased from $2.455x10^{-3}$ to $12.75x10^{-3}$ min^{-1} when AOPs (PAA+ $FeSO_4.7H_2O$) were combined with HC. The R^2 values for the individual systems obtained through the model were 0.94, 0.91, 094 and 0.92 for HC, PAA, PAA+$FeSO_4.7H_2O$ and combination of HC+ PAA+$FeSO_4.7H_2O$ respectively. The rate constants attributed that the COD has been reduced resulting in conversion of complex and toxic compounds to be low toxic and even non-toxic in nature. Figure.5.17 shows the degradation kinetics and COD removal for TWE with respect to time.

Pseudo first order kinetic equation

$$\ln\frac{Co}{Ct} = k * t + a \qquad (5.5)$$

C_0 = initial concentration
C_t = concentration at specific time
k = reaction rate constant
t = time (min)
a = y-intercept



(i) Degradation kinetics

(ii) COD obtained using different treatment systems

Figure 5.17 Graphical representation of degradation kinetics and COD removal w.r.t time

[Operating conditions - pressure – 7.5 Bar, pH – 2, orifice diameter – 0.5mm, PAA dosage – 17.5g/L, and PAA/$FeSO_4.7H_2O$ – 2:1]

5.10.1 Synergistic effect

The synergistic effect on COD degradation from TWE was evaluated using equation.5.6. This effect is the result of two or more treatment systems to produce an effect over the degradation of pollutants from effluent (COD removal) which tends to be greater than the cumulative effect of these treatment system when used individually. In these combined systems, it can be proposed that the mechanical effect of HC intensifies the generation of highly reactive OH^o radicals. Moreover, the ferrous ions result in increasing the reaction rate. HC also prevents the agglomeration of the ferrous ions and providing a better contact with the contaminants present in TWE. The degradation occurs due to the shear stress developed between the oxidants and microstreaming induced into the system by cavitation. As a result, when these cavities were combined with PAA and $FeSO_4.7H_2O$, the degradation of COD was increased from 19.85 to 72% in 97.5 min of cavitation time. However, $FeSO_4.7H_2O$ alone has shown very low degradation rates attributing that it serves as a catalyst for generating more radicals when used in combination with PAA under HC conditions (Sneha Korpe et al., 2019). Therefore, it is recommended to use $FeSO_4.7H_2O$ in combination with PAA to obtain better removal efficiencies. A comparison of COD removal for all the treatment systems have been shown in Figure.5.20. The synergy effect results are in agreement with the work carried out on degradation of variety of pollutants having similar characteristics (Cako et al., 2020; Fedorov et al., 2022). Table 5.7 shows the Kinetic rate constants for individual treatment system and the synergy rate constants for the combination of the treatment system.

Table 5.7 Kinetic rate constants for individual treatment system

Treatment system	Rate constant (k) ($x10^{-3}$)
HC	2.32
PAA	5.53
$FeSO_4.7H_2O$	1.0612
PAA+$FeSO_4.7H_2O$	10.8
HC+PAA+$FeSO_4.7H_2O$	12.75

Synergy (ξ) = $k_{(HC+PAA+\ FeSO4.7H2O)} / k_{HC} + k_{PAA} + k_{FeSO4.7H2O}$ (5.6)

= 0.01275/ (2.3208+5.5305+1.0612) x 10^{-3}]

= 1.4305

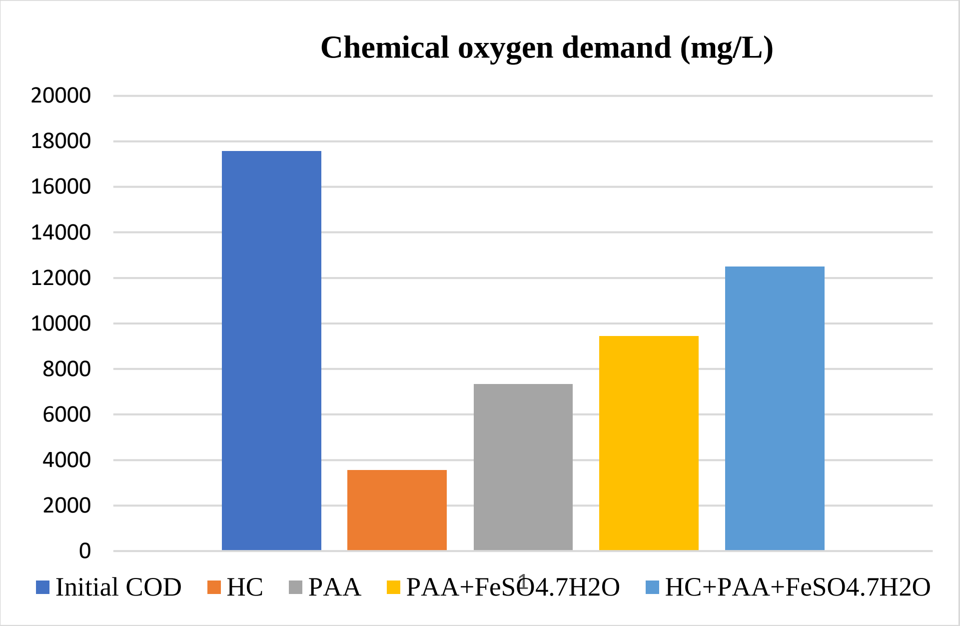


Figure 5.18 Comparison of individual treatment system with Combined AOP+HC

It is evident that the combined system resulted in higher COD removal. Compared to several experimental studies used for treatment of TWE as shown in Table.1 the combination of HC+PAA+ $FeSO_4.7H_2O$ has shown better results. Moreover, the overall degradation for an industrial wastewater such as TWE, depends upon the influent wastewater characteristics which may vary depending upon the manufacturing process adopted to produce leather.

5.11 Energy requirement and cost analysis for the treatment system

Energy requirement

Power consumption = 243.75 kWh/ m^3

- The inlet pressure = 7.5 Bar = 759937.5 Pa
- Downstream pressure = 2 bar = 202650 Pa
- Vapour pressure of water at room temperature = 4242.14 Pa
- Diameter of the orifice = 0.5mm
- Flow area (a) = 0.196 x $10^{-6}m^2$
- Velocity at the throat of the orifice = 457.14 m/s

Cavitation number (C_v) = $\frac{P2 - Pv}{\frac{1}{2}*\rho*v2}$ = 0.0063

The capital cost for the equipment = Rs. 1.0 lakh (Approx.)

Operational costs were calculated for lab-scale hydrodynamic cavitation set-up

- The cost of the electricity required = Rs.1219/m^3
- The cost of chemical reagents required = Rs. 1100

The overall cost for the system = Rs. 4500 (Approx.)/m^3

5.12 Important findings

- Series connection of the orifice was found to be a design failure and further experimental runs were conducted using a single orifice.
- RSM study indicate that the orifice diameter, pressure and cavitation time are the most significant factors whereas, the PAA dosage and pH is the least significant factor affecting the COD removal efficiencies.
- LC-HRMS showed the reduction in the intensities of several peaks, introduction of new peaks and disappearance of peaks.
- Intermediate peaks of aromatic compounds i.e., p-nitrocatechol (m/z=155.1102) and hydroquinone (m/z=110.1123) and acids i.e., malic acid (m/z=134.0874), carboxylic acid (m/z=150.150), malonic acid (m/z=104.0615), oxaloacetic acid (m/z= 134.0874) were found in treated effluent.
- Maximum COD removal efficiencies were obtained at operating conditions - pressure – 7.5 Bar, pH – 5, orifice diameter – 0.5mm, PAA dosage – 17.5g/L, and PAA/$FeSO_4.7H_2O$ – 2:1.
- The curve fitting of the experimental results shows that the linear model having R^2 value of 0.9877. was the best suited for COD removal efficiency.
- The reaction rate constant was increased from $2.455x10^{-3}$ to $12.75x10^{-3}$ min^{-1} when AOPs (PAA+ $FeSO_4.7H_2O$) were combined with HC.

5.13 Conclusions

The cavitation number obtained for 0.5mm diameter orifice less than 1 indicated a large number of cavities generated in the system resulting in degradation of the TWE. The degradation of the pollutants from TWE follows the radical pathway mechanism using HC+PAA+$FeSO_47H_2O$ same as hydrogen peroxide (H_2O_2) aided with Fe^{2+} ions. The study has established that PAA aided with Fe^{2+} ions in combination with hydrodynamic cavitation was able to reduce 72.36, 94.54 and 98.89% of COD, TDS and turbidity respectively in 97.5 minutes. The radicals formed in the combined system are highly reactive that oxidises the insoluble organic matter into soluble form, thereby, enhancing the sCOD solubilization. The soluble COD is increasing after the treatment attributing that the treated effluent has been converted into simpler forms/compounds increasing biodegradability. The biodegradability index has also been increased from 0.122 to 0.279. Moreover, the presence of several intermediates such as aromatic compounds and acids in the treated effluent has proved that the complex compounds has been converted into simpler compounds with lower molecular weights and less toxic compared to their parent compounds. The optimization studies done using RSM-

BBD have suggested that the experimental results were best suited using the quadratic model. The F-value of 283.86 and R^2 value of 0.9877 obtained through ANOVA have shown that the model suggested is significant. The energy and cost requirements for the treatment system have also been discussed in detail to see the significant perspective for scaling – up the system at an industrial scale.

Chapter – 6

Anaerobic digestion of Tannery wastewater

The adsorption and hydrodynamic cavitation experiments on TWW has resulted in the significant removal of the pollutants. However, the treated effluent is not meeting the discharge criteria. Moreover, the effluent obtained from the process is found to be having improved biodegradability. In order to use the natural processes, anaerobic digestion is used to convert into renewable energy. To determine the effect of pre-treatment on the biogas yield a comparative study on anaerobic digestion of treated and raw TWE using chicken manure (CM) as a co-substrate has been undertaken. HC treated wastewater was subjected to anaerobic digestion to determine the effect of pre-treatment on the biogas yield. Batch scale studies were undertaken in 120ml serum bottles to maintain anaerobic conditions keeping 70ml as working volume.

Next set of experiments were carried out to enhance the overall biogas yield using leather trimmings as a co-substrate. Leather trimmings (LT) are rich in organic content that can serve as source of energy for the microbes during anaerobic digestion. Before using, these trimmings were cleaned using water to remove impurities such as dirt and salts from its surface that may hinder process of anaerobic digestion. Comparison of biogas yield using leather trimmings as a co-substrate individually and in combination with chicken manure (ternary combination) for digestion of raw and pre-treated TWE has been incorporated. The efficacy of different pre-treatment methods i.e., HC, HC+PAA, HC+PAA+$FeSO_4.7H_2O$, and coagulation+ HC+PAA+$FeSO_4.7H_2O$ in methane production potential has been evaluated.

6.1 Physicochemical characterization

The physico-chemical characteristics of raw TWE, HC treated TWE, Coagulation + HC + AOPs treated TWE, chicken manure, leather trimmings, and inoculum were determined. The substrates to be used in anaerobic digestion were fixed depending upon the C/N ratio of the TWE. Since, raw TWE and the pre-treated TWE consists of higher C/N value, the substrate consisting of lower C/N were taken for the study to maintain healthy environment for the anaerobic microbial activity. Anaerobic digestion was conducted on various C/N and pH to determine the effect of these parameters on biogas yield. The operating conditions were fixed by using Response surface methodology – Central composite design (RSM-CCD) and digestor reactors were kept at incubation at 37°C for 45 days. The input variables were C/N – 20-30 and pH – 6.5 -7.5 and the response variables were biogas yield and COD reduction. Table. 6.1 and

6.2 shows the design of experiments used for anaerobic digestion and the initial physico-chemical characterization of the samples collected for further use in anaerobic digestion study respectively.

Table 6.1 Experimental conditions used for anaerobic digestion

Run	C/N ratio	pH
1	25	7.71
2	17.93	7
3	20	7.5
4	25	7
5	20	6.5
6	25	7
7	25	7
8	25	7
9	30	7.5
10	25	7
11	32.07	7
12	30	6.5
13	25	7
14	25	6.29

Table 6.2 Physico-chemical characterization of substrates and inoculum

S.no	Parameter	Raw TWE	HC treated TWE	Pre-treated TWE (Coagulation + HC + AOPs)	Chicken manure	Leather trimmings (LT)	Inoculum
1	pH	7.82	5.2	5.2	-	-	-
2	COD (mg/l)	17830	10130	2487	6400	6789	16000
3	BOD (mg/l)	3861	3250	1366	-	-	-
5	Total solids (mg/l)	18676	627	597	-	-	-
6	TOC (mg/l)	4291	2756	2256	248 g/Kg	248 g/Kg	1367 g/Kg
7	TN (mg/l)	104	73	64	33 g/Kg	48 g/Kg	113 g/Kg
8	Volatile solids (mg/l)	5856	573	523	-	-	-
9	BI	0.21	0.32	0.54	-	-	-
10	C/N	41	38	36	7.8	8	12.1

6.2 Acclimatization study

Acclimatization of the microbes is essential to maintain a stability in the anaerobic digestion digestor (Li et al., 2011). The ratio of inoculum to TWE of 3:1 resulted in higher biogas yield which indicated that the food to microorganism’s ratio was maintained between 0.2-0.5. The biogas yield was seen to be minimal for the ratio of inoculum to TWE 2:1 which indicated that the sudden exposure of microbes present in TWE to the inoculum would have created change in the environment (temperature). Moreover, TWE is highly contaminated industrial wastewater consisting of higher percentage of microbes in it which could not have survived due to insufficient food supply. Similarly, for the TWE to the inoculum 8:1 the minimum biogas yield is the result of presence of higher organic fraction and less microbes to consume the organic portion present. Inoculum to TWE ratio of 4:1 has also resulted in comparable results as 3:1 ratio. However, the ratio giving higher biogas yield was further used as inoculum for the batch scale study. Figure.6.1 has shown biogas generation for different inoculum to tannery wastewater effluent.

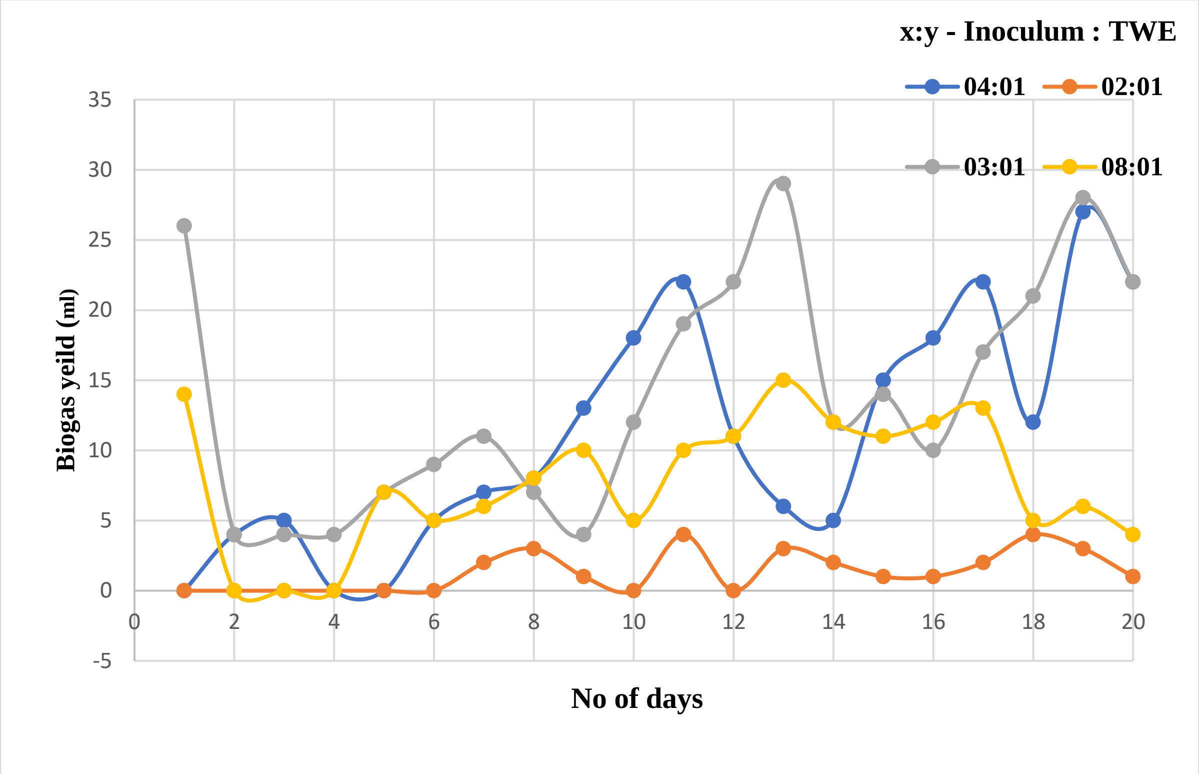


Figure 6.1 Biogas generation for different inoculum to tannery wastewater effluent ratios

6.3 Mono-digestion of raw and pre-treated tannery wastewater effluent

To obtain maximum biogas yield the digestors should always maintain favourable conditions for breakdown of organic fraction by the microbes (Zhang et al., 2019). However, anaerobic digestion of highly contaminated TWE is poorly bio-degradable and results in minimum biogas production. Figure.6.2 shows the cumulative biogas yield from raw TWE and HC treated TWE in 45 days. HC treated TWE resulted in yielding more biogas due to the enhancement of biodegradability index. The increase in biodegradability index result in breakdown of organic fractions more easily resulting in generation of biogas. However, the pollutants present in raw TWE are poorly biodegradable and inhibits the biological process taking place during anaerobic digestion. The pre-treatment has shown an increase in biogas yield by 3 times compared to raw TWE. However, the anaerobic digestion of HC treated TWE has shown negligible biogas yield attributing that the microbes need certain time for adaptation to the environment. Since the HC treated TWE consists of radicals that might have some impact on the microbial growth and therefore, initial lag phase is observed.

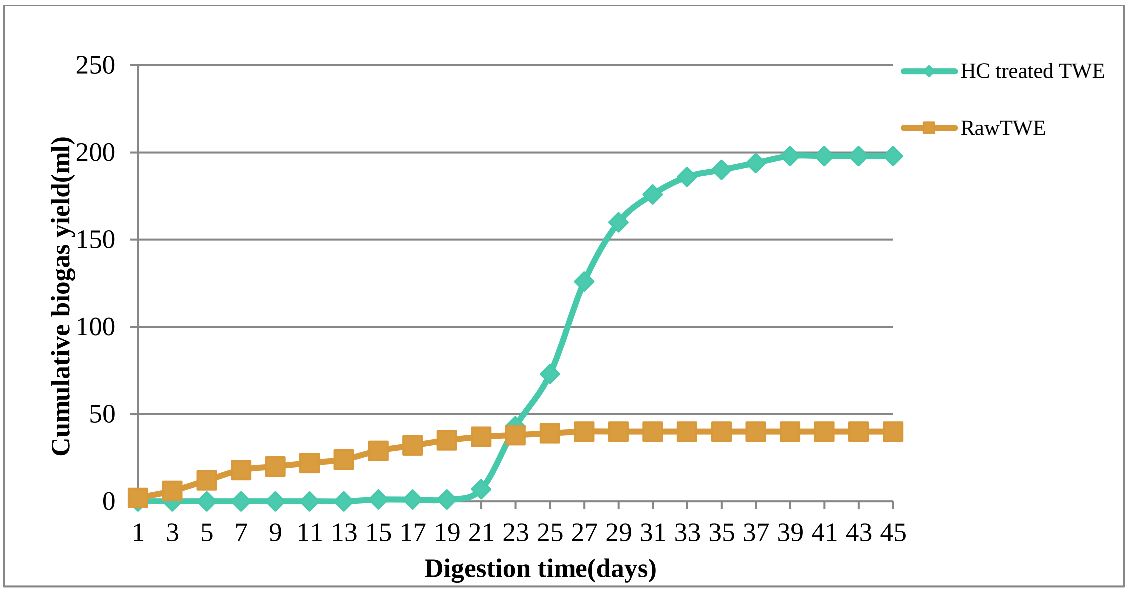


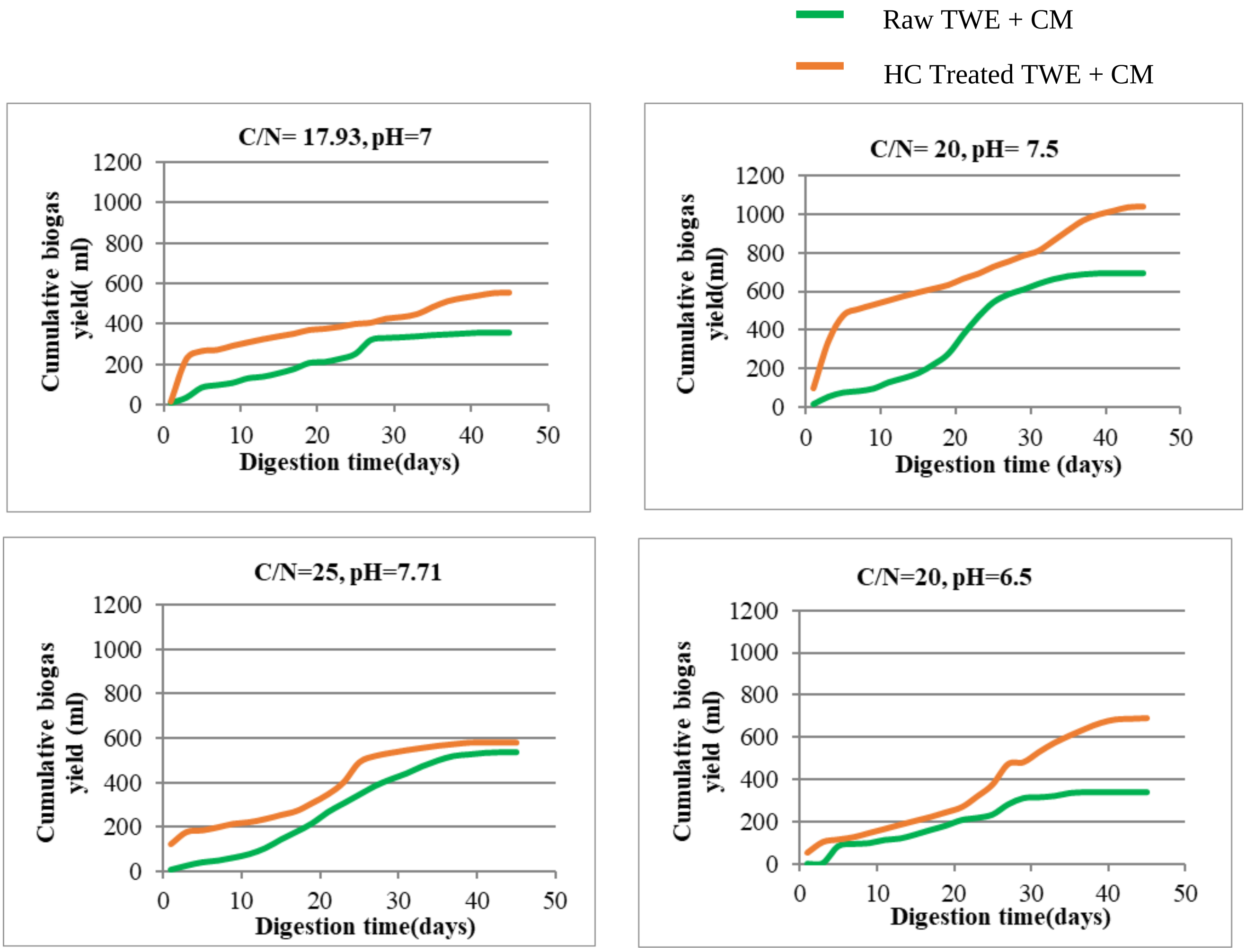
Figure 6.2 Cumulative biogas yield for raw and HC treated wastewater samples

6.4 Biogas production from raw and pre-treated tannery wastewater effluent using co-digestion

It has been observed in the above section that the anaerobic digestion of raw TWE resulted in very less biogas yield of 2.882 ml/g.COD. However, the pre-treatment of the TWE has resulted in enhancement of the biogas yield up to 80.41 ml/g.COD which is very less for a carbon rich wastewater. However, a standard methane yield obtained from per gram of COD is approximately 380 - 400ml. Therefore, CM has been added as a co-substrate to give rise to co-digestion that may result in enhancement of biogas. The co-digestion of TWE using CM has enhanced the overall biogas production. The nutrient rich CM enables favourable conditions for healthy microbial growth leading to biogas production. The operating parameters C/N and pH played an important role in enhancement of biogas production.

It is very essential to optimize the C/N and pH of the reactor to perform the digestion at stable conditions and obtain higher biogas yields. From the results it can be attributed that at higher C/N the nutrients available in terms of nitrogen is scarce and hence hinders the microbial growth. The scarcity of the nitrogen in the reactors leads to inactivation of the methane producing bacteria leading to decrease in methane yield. However, lower C/N ratio indicates carbon scarcity leading to VFA accumulation. Moreover, at lower C/N ratios the ammonium ion concentration is high resulting in inhibition of the microbial growth in the reactor (Yan et al., 2015). Therefore, optimization of the C/N ratio for maintaining favourable conditions in the reactor is important.

pH plays an important role in maintaining the favourable conditions in the reactor. However, it should be optimized to yield better biogas production. For an ideal anaerobic reactor, the pH ranges from 6.5-7.5 (Kainthola et al., 2020). Experimental results have also been in agreement with the ideal range of pH. It can be attributed that at lower pH values accumulation of VFAs takes place hindering the methanogenic activity. However, at higher pH values solids get accumulated and sludge thickening occurs that reduces the biogas yield. From the graphs presented below in the Figure. 6.3 it can be seen at C/N – 20 and pH – 7.5 the biogas production is maximum for raw, and HC treated wastewater.



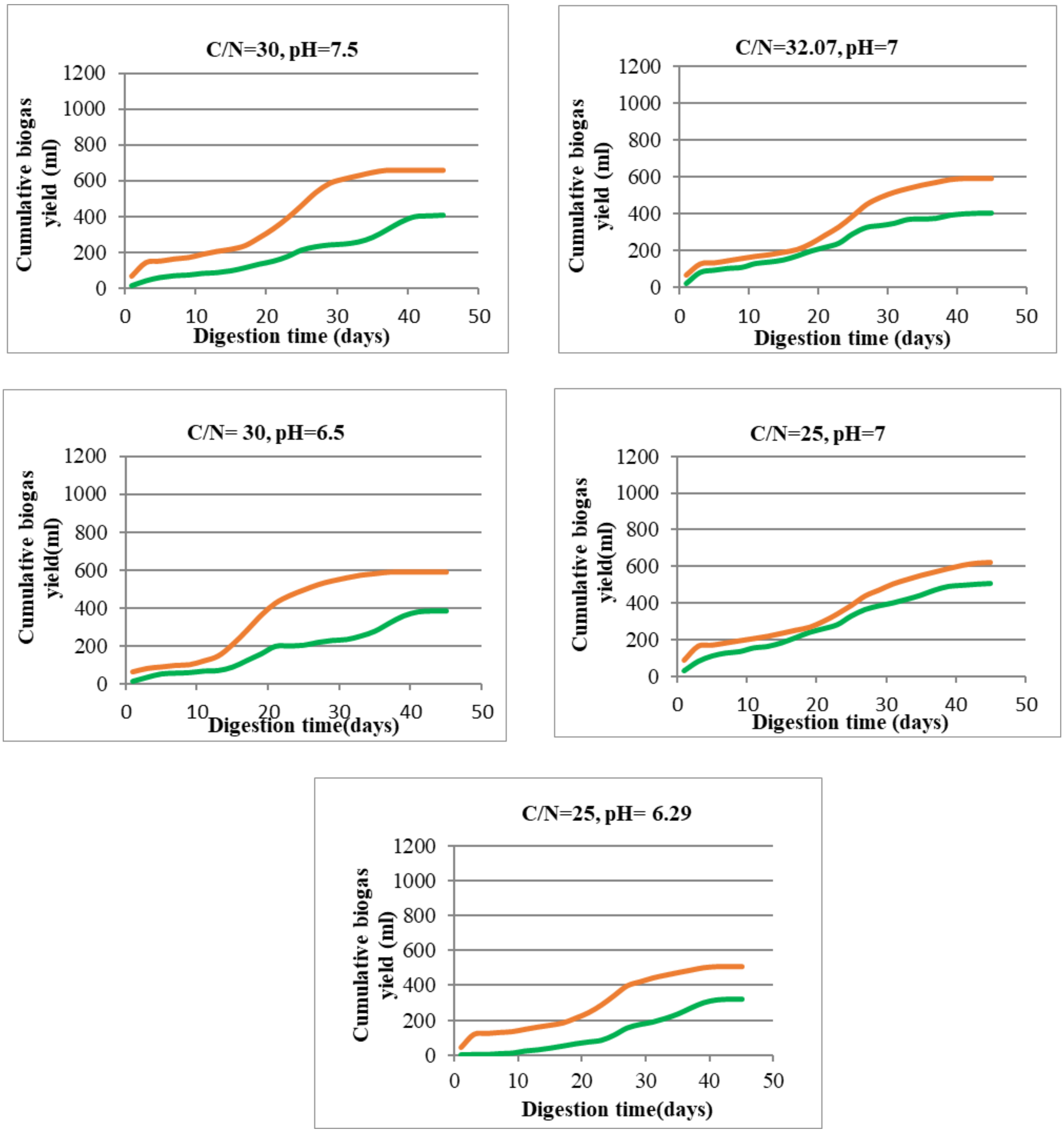


Figure 6.3 Comparison of biogas yield of raw and HC treated tannery wastewater effluent

Figure. 6.4 and 6.5 has shown the cumulative biogas yields for anaerobic digestion of raw and HC treated wastewater at various C/N and pH. The graphs clearly indicates that the C/N and pH of the reactors affects the biogas production. Therefore, these are the most influential parameters that should be balanced in order to maintain reactor stability resulting into enhancement of the biogas. The HC treated wastewater is biodegradable in nature that enables the anaerobic bacteria to convert the organic matter into carbon – dioxide (CO_2) and methane (CH_4) comparatively faster than raw wastewater. The poorly bio-degradable compounds present in raw TWE may affect the microbial growth resulting into less biogas production. Therefore, it is recommended to pre-treat the highly contaminated wastewater before subjecting to anaerobic digestion.

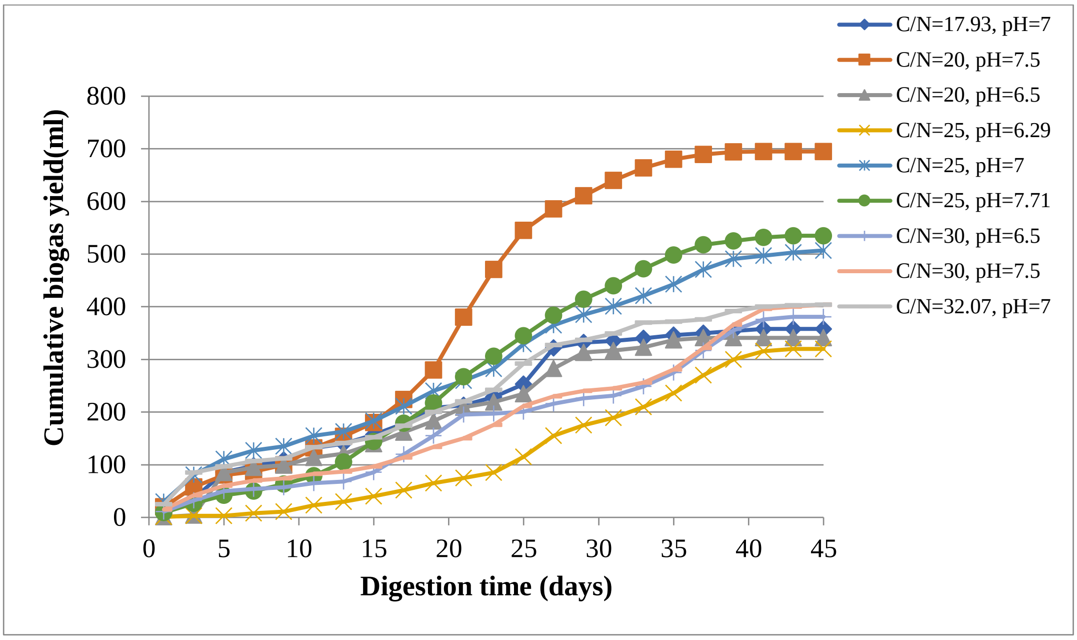


Figure 6.4 Comparison of biogas yield at different C/N and pH for raw tannery wastewater effluent

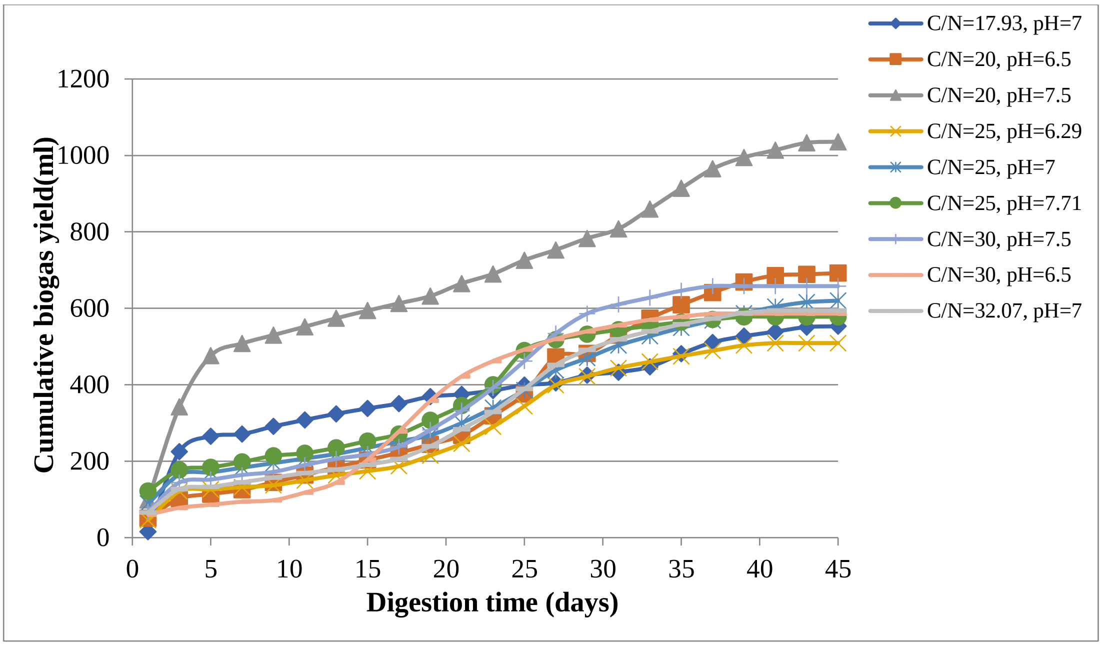


Figure 6.5 Comparison of biogas yield at different C/N and pH for HC treated tannery wastewater effluent

Figure. 6.6 clearly depicts that the co-digestion of the TWE has resulted in better biogas yields. The use of CM as a co-substrate enables balancing and maintaining the C/N ratio of the reactor which is very important for the microbial growth of the bacteria present in the reactor. The C/N ratio of CM is 7.8 which is very less compared to TWE which indicates that the addition of CM provides more nutrients which act as a source of energy for the anaerobic bacteria that are involved in the anaerobic digestion process. Moreover, CM has high biogas production potential due to its organic composition which can be proved from the results shown in Figure. 6.6 shown below. The maximum biogas production observed from raw, and HC treated wastewater without any co-substrate was 2.882 ml/g. COD and 80.41ml/g. COD respectively. However, co-digestion with chicken manure as a co-substrate was able to produce 40.59 ml/g. COD and 104.75 ml/g. COD of cumulative biogas yield for raw and HC treated TWE respectively. The methane yield enhanced to 58% using co-digestion with CM at C/N – 20 and pH – 7.5. Table. 6.2 has shown the methane production for co-digestion of raw and HC treated TWE using chicken manure as a co-substrate at various C/N and pH.

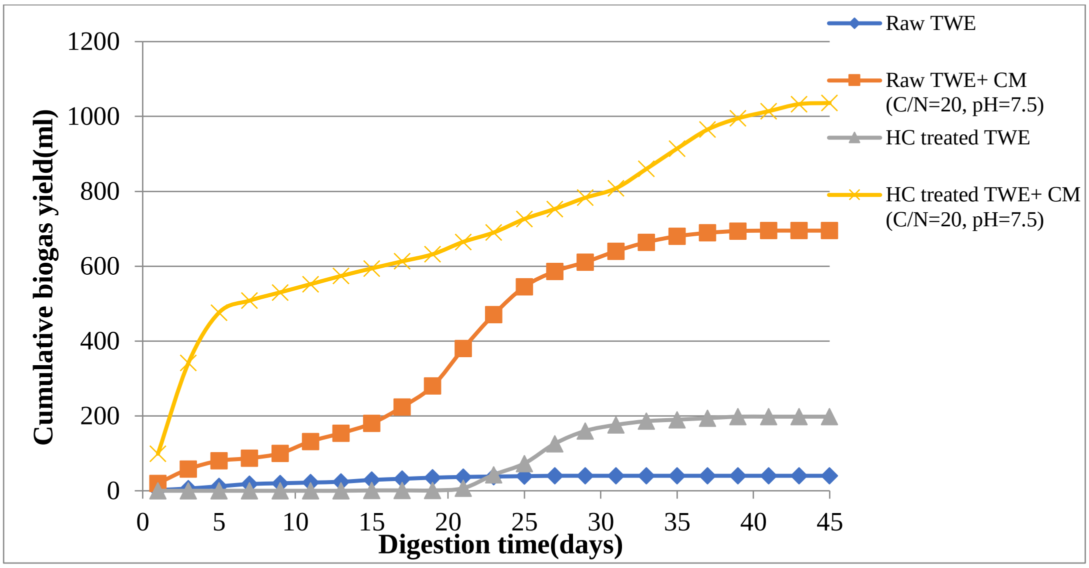


Figure 6.6 Comparison of biogas yield of raw and HC treated tannery wastewater effluent

Table 6.3 Methane production for co-digestion of raw and HC treated TWE using chicken manure as a co-substrate

	Raw tannery wastewater			Hydrodynamic cavitation treated tannery wastewater		
C/N, pH	**Cu. Biogas (ml/g.COD)**	**Cu. Methane (ml/g.COD)**	**Methane (%)**	**Cu. Biogas (ml/g.COD)**	**Cu. Methane (ml/g.COD)**	**Methane (%)**
17.93, 7	22.11	8.70	39.54	57.66	31.43	54.51
20, 6.5	19.91	7.88	39.57	69.97	38.41	54.91
20,7.5	40.59	16.58	40.84	104.75	60.56	57.81
25, 6.29	19.18	7.37	38.42	52.20	29.01	55.59
25, 7	30.39	11.57	38.07	63.59	30.35	47.74
25, 7.71	32.07	10.37	32.33	60.20	33.0	54.83
30, 6.5	29.79	11.43	38.36	75.46	40.55	53.74
30, 7.5	28.09	10.91	38.83	67.21	35.09	52.21
32.07, 7	35.19	10.71	30.43	73.78	33.28	45.11

6.4.1 COD reduction for HC treated wastewater

The anaerobic digested samples were centrifuged at 4500 rpm for 10 min and the supernatant sample was collected to determine the COD reduction of digested samples. Table.6.3 the COD reduction after the anaerobic digestion for all the reactors maintained at different C/N and pH. The characteristics of the substrates used for the anaerobic digestion affecting overall C/N ratio of the reactor results in COD reduction (Cheng et al., 2016). The substrates that are easily biodegradable results in higher COD reduction. Maximum COD removal of 64% at C/N-20 and pH-7.5 was observed since the reactor was at stable conditions. Experimental results are in agreement as at C/N – 20 and pH 7.5, higher methane production was observed for HC treated wastewater attributing that the substrates with the higher biodegradability result in higher COD reduction. pH affects the microbial activity and COD reduction which necessitates optimization of the pH. Several buffers have been used in research studies in order to maintain pH levels in range of 6.5-8. COD reduction in the samples can also be described due to the breakdown of organic matter by the microbes. Moreover, solid-liquid separation also takes place during anaerobic digestion which enables removing organic contaminants and the solid content that contributes to the COD of the sample. Therefore, the concentration of organic matter and the microbes availability in the reactors are the important factors affecting the COD reduction.

Table 6.4 COD reduction for pre-treated samples

S.no	C/N	pH	COD_{mix} of reactor (initial) (mg/L)	COD_{mix} of reactor (final) (mg/L)	% COD reduction
1	17.93	7	9590	4986	48
2	20	6.5	9890	3857	61
3	20	7.5	9890	3540	64.2
4	25	6.29	9750	5070	48
5	25	7	9750	4680	52
6	25	7.71	9750	4923	49.5
7	30	6.5	8710	3832	56
8	30	7.5	8710	4111	52.8
9	32.07	7	8050	3831	52.4

6.4.2 Digestate analysis

Optimizing C/N and pH of the reactor is important to maintain the reactor at stable conditions. The digestate analysis results in Table.6.4 also shows that the reactor operating at C/N-20 and pH-7.5 resulted in VFA/Alkalinity ratio lying between 0.25 to 0.35 which indicates that the reactor was maintained at stable conditions yielding higher methane production. From the results it can be attributed that increase in the VFAs indicates acid accumulation that inhibits the methane production in the reactor. Moreover, alkalinity should also be monitored to maintain a specific pH range for microbial activity to take place. If the alkalinity is very low, it can also lead to acidification and instability of the reactors. Therefore, it is recommended to operate the digestor reactor at VFA/Alkalinity ratio of 0.25-0.35 to maintain a proper microbial environment in the reactors.

Table 6.5 Digestate analysis for anaerobic digestion reactors subjected to HC treated TWE using chicken manure as a co-substrate

S.no	C/N ratio	Initial pH	Final pH	VFA(mg/l)	Alkalinity (mg/l)	VFA/Alkalinity
1	17.93	7	8.2	3920	8000	0.36
2	20	6.5	8.5	8820	9800	0.53
3	20	7.5	8.5	3772	9200	0.32
4	25	6.29	8.2	4410	7200	0.56
5	25	7	8.4	2952	5900	0.5
6	25	7.71	8.6	8720	10900	0.61
7	30	6.5	7.6	3328	6400	0.42
8	30	7.5	8.4	3540	4900	0.41
9	32.07	7	8.4	4914	9100	0.51

6.5 Methane yield for raw and treated TWE using leather trimmings

The bar graph shown in the Figure.6.7 below shows that various pre-treatment methods affect the overall methane yield. Since, the raw wastewater is poorly biodegradable a minimal pre-treatment i.e., HC resulted in increasing the biodegradability which enhanced the methane yield. However, when the TWE pre-treated with HC+PAA was subjected to anaerobic digestion enhanced the methane yield. PAA is one of the strongest oxidizing agents also used as a disinfectant at various industries. It can be attributed that, the presence of PAA in the reactor helped in eliminating harmful microbes that may hinder the performance of useful microbes leading to methane production.

Among all the pre-treatment methods applied before anaerobic digestion, application of HC+PAA+$FeSO_4.7H_2O$ (AOPs) has resulted in maximum methane yields. Iron (Fe^{2+}) serves as a micro-nutrient for several microbes that takes part in degradation of the organic matter resulting in biogas production. Moreover, iron also stimulates the methanogenesis enabling the methanogens to perform better and produce higher methane yield that can be proved from the results shown below. Although coagulation+ HC+PAA+$FeSO_4.7H_2O$ (AOPs) has increased the biodegradability index of the TWE before subjecting to anaerobic digestion but yielded in lower methane production. It can be attributed that there might be presence of residual coagulant that might result in solid liquid phase separation due to which the interaction between organic matter and the microbes is very less. The minimum contact or unavailability of the organic matter for microbial growth might result into lesser production of methane. Therefore, from the results shown below, it is evident that the HC+PAA+$FeSO_4.7H_2O$ (AOPs) treated TWE yield maximum methane production and can be recommended as pre-treatment method for TWE before undergoing anaerobic digestion. The methane yield obtained by anaerobic digestion of HC treated TWE using CM as co-substrate resulted in 60.46 ml/g.COD of methane production at optimized conditions as mentioned in the previous chapter. However, for HC treated TWE using LT as co-substrate resulted in 50.92 ml/g.COD of methane production at optimized conditions. Therefore, further batch scale study was conducted to see the combined effect of CM and LT as co-substrates over the methane yield using the treated TWE (HC+PAA+$FeSO_4.7H_2O$) that yielded maximum biogas yield during co-digestion.

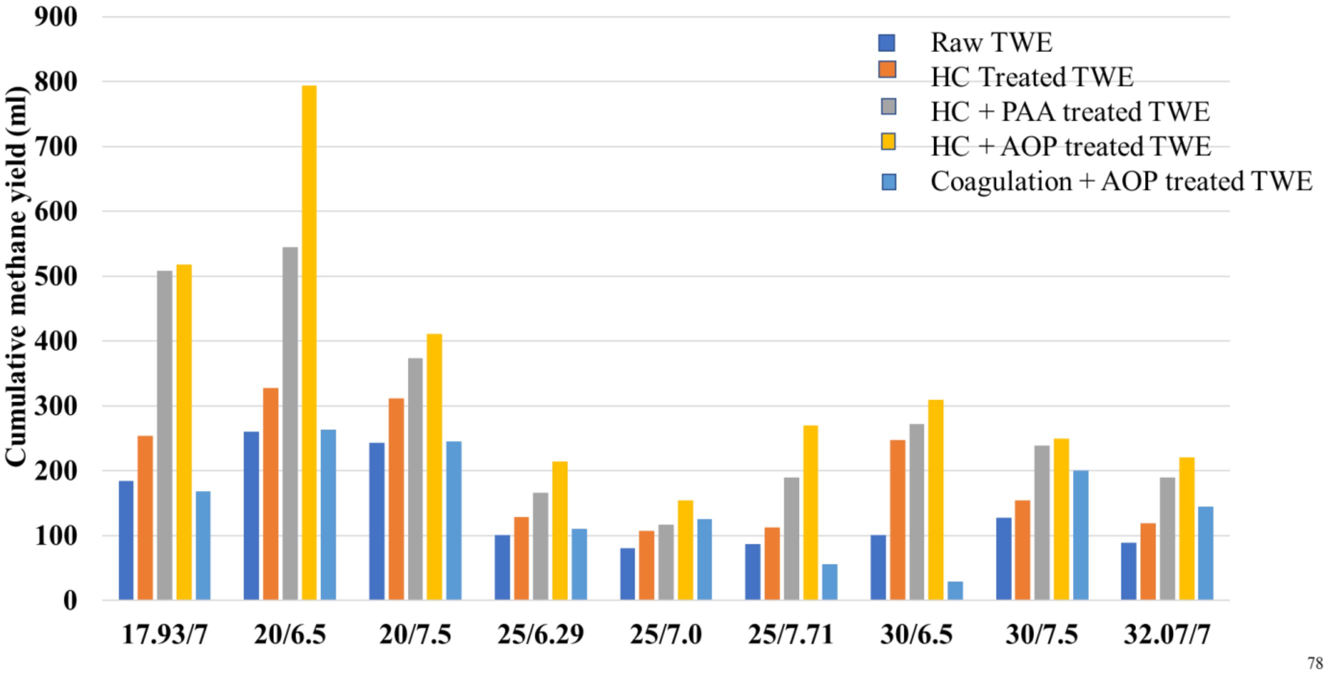


Figure 6.7 Comparison of methane yield using leather trimmings as co-substrate

6.6 Effect of binary and ternary combination

To test the ternary combination for methane yield potential, the HC+PAA+$FeSO_4.7H_2O$ (AOPs) treated wastewater was subjected to anaerobic digestion using CM+LT as co-substrates. Mostly the ternary combinations are used during anaerobic digestion to enhance the biogas yield by utilizing the synergistic effect of all the substrates. The addition of the combination of substrates provides a carbon and nutrient rich environment for the microbes responsible for the biogas production. The leather trimmings being a waste product of the tanning industry can be utilized as a supplement source of energy to microbes in addition with

CM to enhance the overall yield. It can be seen from the results as shown in the Figure. 6.8 and 6.9 that the ternary combinations have resulted in higher methane production for raw as well as treated TWE (HC+PAA+$FeSO_4.7H_2O$ (AOPs)). Methane production increased from 59% to 66% using LT in combination with CM as co-substrate as mentioned below in Table 6.5. Table has also inscribed the methane yield at various C/N ratio and pH values using binary and ternary combination of substrate.

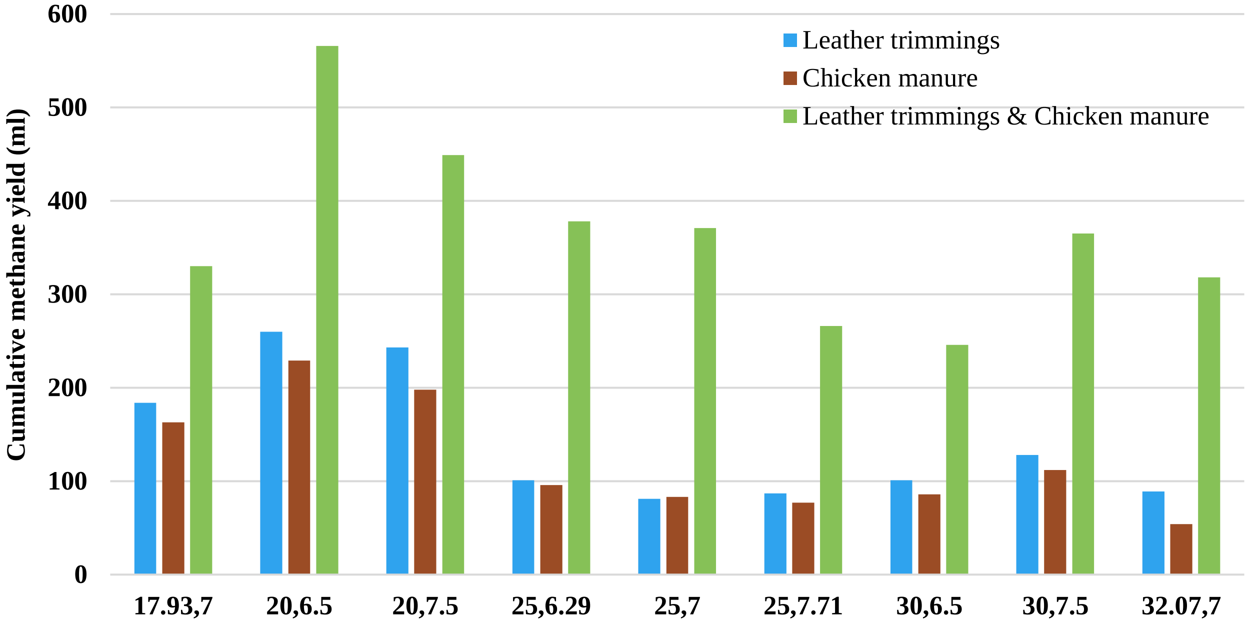


Figure 6.8 Comparison of methane yield using binary and ternary combinations for raw TWE

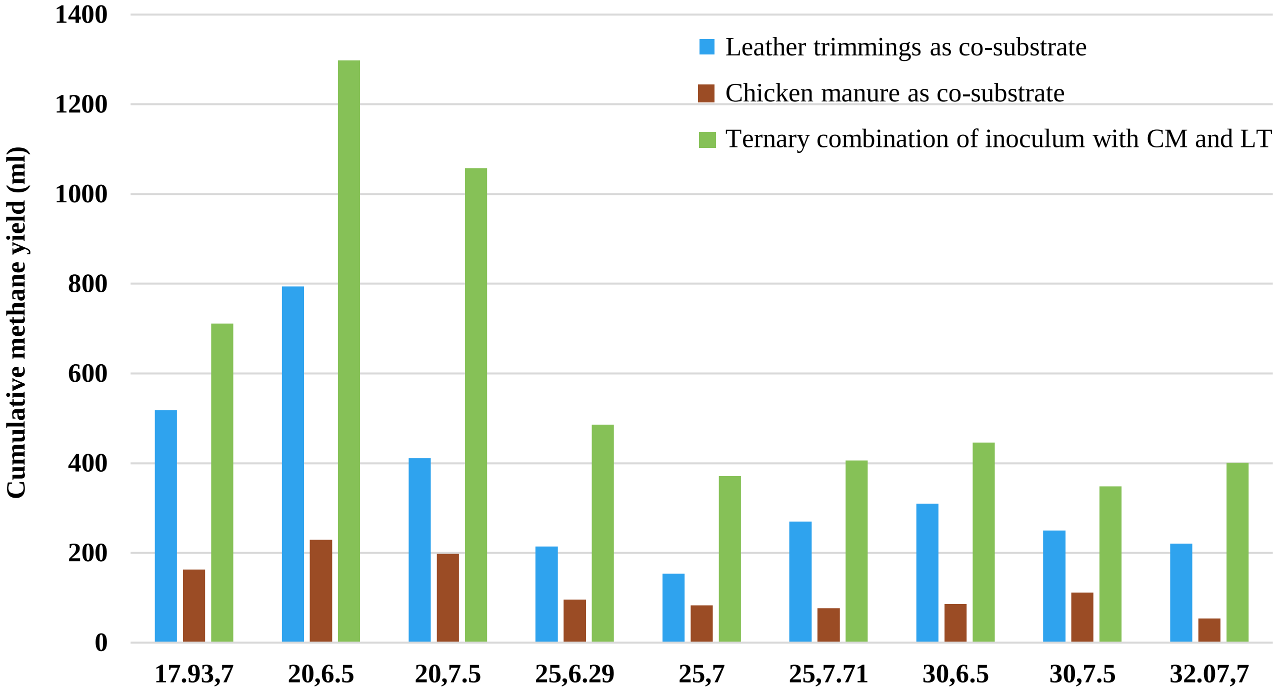


Figure 6.9 Comparison of methane yield using binary and ternary combinations for treated TWE

Table 6.6 Methane production HC+PAA+FeSO4.7H2O treated TWE using binary and ternary combination

	Treated tannery wastewater using LT as co-substrate			**Treated tannery wastewater using CM+LT as co-substrate**		
C/N, pH	**Cu. Biogas (ml/g.COD)**	**Cu. Methane (ml/g.COD)**	**Methane (%)**	**Cu. Biogas (ml/g.COD)**	**Cu. Methane (ml/g.COD)**	**Methane (%)**
17.93, 7	336.49	181.75	54	422.71	241.01	57
20,6.5	509.46	300.75	59	741.88	489.81	66
20, 7.5	293.56	155.68	53	633.58	399.24	63
25, 6.29	169.70	78.10	46	332.38	172.95	52
25, 7	140.51	56.21	40	306.76	132.02	43
25, 7.71	205.10	98.54	48	313.87	144.48	46
30, 6.5	173.62	85.16	49	234.12	117.06	50
30, 7.5	145.87	68.68	57	217.32	91.33	42
32.07, 7	111.55	49.11	44	186.40	83.89	45

6.6.1 COD reduction

The digested samples were centrifuged at 4500 rpm and the supernatant was evaluated to determine the reduction in COD. From the results it was observed that COD reduction was maximum for the reactor operating at C/N – 20 and pH – 6.5 for which methane production was also maximum. It can be attributed from the results that the reactor containing a balance of nutrients and organic matter will result in maximum methane yield which revealed that the reactor contains more biodegradable compounds resulting in degradation of COD also. Moreover, the ternary combination has resulted in 72% of COD reduction due to the addition of LT as a co-substrate. The addition of LT has increased the availability of more biodegradable compounds that can be converted by the microbes in the digestor and result into COD reduction. Moreover, the LT will also have an impact on overall C/N ratio of the reactor that will also result in maintaining favourable environment for the microbial growth in the reactor that results in higher methane production and greater COD reduction. Table. 6.6 below has shown the COD reduction for all the reactors operating at various C/N and pH values for the pre-treated TWE (HC+PAA+$FeSO_4.7H_2O$) subjected to anaerobic digestion.

Table 6.7 COD reduction for pre-treated samples (HC+PAA+FeSO4.7H2O)

S.no	C/N	pH	COD_{mix} of reactor (initial)	COD_{mix} of reactor (final)	% COD reduction
1	17.93	7	2950	1194	59.5
2	20	6.5	2650	750	71
3	20	7.5	2650	848	68
4	25	6.29	2810	1433	49
5	25	7	2810	1559	44.5
6	25	7.71	2810	1545	45
7	30	6.5	3810	2038	46.5
8	30	7.5	3810	2133	44
9	32.07	7	4780	2605	45.5

6.6.2 Digestate analysis

The digestate of the reactors containing ternary combination and producing more methane has been evaluated. The analysis shows that the reactors producing more methane yield has VFA/Alkalinity ratio lying between 0.25-0.35. The addition of the LT as a co-substrate has an impact on the overall C/N ratio of the reactor which is an important factor for methane production and COD reduction in the reactor. However, pH also plays an important role in process stability of the digestion reactors. The initial pH for the previous study at optimized operating parameter was evaluated to be 7, however, for the reactor operating using ternary combination showed initial pH of 6.5. During the anaerobic digestion, the release of alkaline compounds takes place, therefore, it can be attributed from the results that reactor with ternary combination of substrate tends to produce more methane yield before reaching its alkaline pH that will further hinder the microbial activity. However, for binary combination using CM at operating condition of C/N -20 and pH – 7 will reach the alkaline pH faster due to which the microbial activity will be affected. Therefore, it is recommended to maintain suitable pH in the range of 6.5-8.5 to yield better performance in terms of methane yield. Table. 6.7 has shown the digestate analysis for the reactor operating using ternary combinations.

Table 6.8 Digestate analysis for anaerobic digestion reactors using ternary combinations ($HC+PAA+FeSO4.7H2O$)

S.no	**C/N ratio**	**Initial pH**	**Final pH**	**VFA (mg/l)**	**Alkalinity (mg/l) as $CaCO_3$**	**VFA/Alkalinity**
1	17.93	7	8.4	3920	10051	0.39
2	20	6.5	8.2	3020	9989	0.30
3	20	7.5	8.4	3772	10200	0.37
4	25	6.29	8.5	3120	7200	0.43
5	25	7	8.4	8765	11530	0.7
6	25	7.71	8.6	5520	10295	0.53
7	30	6.5	7.6	4350	9255	0.47
8	30	7.5	8.4	7654	12441	0.61
9	32.07	7	8.4	4914	9100	0.54

6.7 Important findings

- Major proportion of the biodegradability substances were found to be converted into biogas during the anaerobic digestion of TWW with other co substrates.
- The optimum C/N ratio and pH for maximum biogas yield and maximum COD reduction are 20 and 7.5 respectively for raw and HC treated TWE.
- The maximum biogas production observed from raw, and HC treated wastewater without any co-substrate was 2.882 ml/g. COD and 80.41ml/g. COD respectively.
- The co-digestion with chicken manure as a co-substrate was able to produce 40.59 ml/g. COD and 380.88 ml/g. COD of cumulative biogas yield for raw and HC treated TWE respectively.
- The maximum methane yield obtained through co-digestion is 58% approximately.

- The cumulative methane yield was increased by 18% when pre-treated TWE was subjected to co-digestion using chicken manure.
- The conditions were appropriate in the digestors as the VFA/Alkalinity ratio obtained was < 0.35 resulting in maximum methane yield.
- The optimum C/N ratio and pH for maximum methane yield and maximum COD reduction are 20 and 6.5 respectively for binary and ternary combinations of co-substrates.
- The maximum methane yield using LT as a co-substrate for pre-treated TWE (HC+PAA+$FeSO_4.7H_2O$) evaluated to be 300 ml/g.COD at C/N – 20 and pH – 6.5.
- The ternary combination i.e., AOP treated TWE, CM and LT has resulted in maximum methane yield of 489.81 ml/g.COD.
- The ternary combination of pre-treated TWE (HC+PAA+$FeSO_4.7H_2O$)+CM+LT increased the cumulative methane yield by 7% as compared to co-digestion using LT.
- Maximum COD reduction of 72% was obtained for the reactor operating at C/N 20 and pH-6.5.
- HC+PAA+$FeSO_4.7H_2O$ treated TWE resulted in the highest methane yield among all the other pre-treatment methods adopted for anaerobic digestion.

6.8 Conclusions

The biodegradability of the compounds present in anaerobic digestor plays an important role in biogas production. The study revealed that the hydrodynamic cavitation as a pre-treatment resulted in significant increase in biogas production for mono-digestion as well as co-digestion. The biogas yield is more in co-digestion with chicken manure when compared to mono digestion.

The leather trimmings obtained from the tanning industry can be used efficiently for anaerobic digestion as a co-substrate for methane production. The LT has been proved to be a good source of energy for microbial growth leading to higher methane production. However, when these are added with CM, and served as co-substrates result into enhancement of methane yield. These trimmings have enabled in maintaining proper C/N and pH of the reactor. However, a proper pre-treatment method also plays an important role in enhancing the overall methane yield. The results have clearly shown that the HC+PAA+$FeSO_4.7H_2O$ treated TWE when subjected to anaerobic digestion has resulted in maximum methane production as compared with the other pre-treatment methods. It has also been observed that, although, the coagulation+ HC+PAA+$FeSO_4.7H_2O$ treated TWE has resulted in maximum increase in BI as shown in table 6.2 but when subjected to anaerobic co-digestion (LT as co-substrate) resulted in lesser methane yield compared to HC+PAA+$FeSO_4.7H_2O$ treated TWE. Anaerobic digestion with appropriate pre-treatment can be a cheaper and efficient option for tannery wastewater treatment and thereby reducing the load on post treatment prior to disposal. Therefore, it is recommended that the pre-treatment method should be selected appropriately that does not create any adverse effects on the anaerobic digestion process.

Chapter – 7

Conclusions and recommendations

7.1 Conclusions

Tannery wastewater effluent consists of different complex compounds such as phenolics, surfactants, phthalates, and polyethylene glycols (PEGs), having very low bio-degradation rates. Moreover, degradation of these pollutants is also not possible using the separation process since, these pollutants cannot be changed from one phase to other. Coagulation of the TWE using OPW i.e., OPP and AOPP in the primary stage of the study helped in removing suspended solids present in the wastewater. The degradation of complex structured compounds present in other phases were converted into simpler compounds using hydroxyl radicals (OH^o). Removal of the suspended solids during the coagulation studies had helped hydrodynamic cavitation experimentation otherwise clogging phenomenon would have occurred. The catalyst such as ferrous sulphate heptahydrate have been used along with advanced oxidation processes (AOPs) and cavitation methods to increase the degradation efficiency and reduce the effective time required for the treatment system. The application of HC in combination with AOPs enhanced the BI of the TWE. The increase in the biodegradability of TWE resulted in higher biogas yield using anaerobic digestion method as a post-treatment. The chicken manure as a co-substrate has resulted in biogas production when TWE was subjected to anaerobic digestion. However, the use of solid wastes (leather trimmings) generated from leather industry as a co-substrate with chicken manure for anaerobic digestion also resulted in enhancement of the biogas yield. The study on treatment of TWE using a hybrid methodology has been successfully performed and evaluated. The significant conclusions made from the study has been inscribed below.

The application of OPW for treatment of TWE proved that the physicochemical characteristics of OPP, AOPP and alum are essential in removing pollutants from TWE. Higher surface area and the porous structure of OPP and AOPP have resulted in the removal of the pollutants by the adsorption mechanism. The statistical and experimental results indicate that the biochar obtained from orange peel biomass has successfully removed TSS, turbidity and COD to an extent, respectively, from TWE. The optimized solution obtained through statistical analysis for OPP is at 2.28g/L, 4.6 and 54.54 min, for AOPP is at 2.11g/L, 4.37 and 35.01 min and for alum is at 1.16 g/L, 5.48 and 20.46 min of coagulant/adsorbent dosage, pH and contact time respectively. However, experimental analysis has obtained maximum removal efficiencies at coagulant/adsorbent dosage, pH, and contact time of 2.5g/L, 4 and 50 min for OPP, 2g/L, 4 and 30 min for AOPP and 1g/L, 5 and 20min for alum respectively. The adsorption kinetics showed that the pseudo-first-order mode is the best-suited model having a higher regression coefficient of R^2 0.981. The adsorption capacity of 418.31 mg/g of COD was obtained for AOPP treatment of TWE, which correlated with the statistical and experimental analysis giving higher removal efficiencies for the AOPP treatment process. For 1L of TWE sample, 33ml, 18.5ml and 12ml of sludge layer were formed after alum, OPP and AOPP coagulation-flocculation process, respectively. Moreover, the regenerated OPP and AOPP have delivered better removal efficiencies compared to alum without compromising the overall treatment removal efficiency. Therefore, AOPP treatment can be given to TWE to remove the suspended solids and turbidity in the initial stages at the treatment plants.

As the suspended solids were removed using coagulation studies, It was observed that the clogging of the orifice plate mounted on HC set-up was prevented during the experiments. The cavitation number obtained for 0.5mm diameter orifice was less than 1 which indicated that a large number of cavities were generated in the system resulting in degradation of the TWE. The degradation of the pollutants from TWE follows the radical pathway mechanism using HC+PAA+$FeSO_4.7H_2O$ same as hydrogen peroxide (H_2O_2) aided with Fe^{2+} ions. The optimization studies done using RSM-BBD have suggested that the experimental results were best suited using the quadratic model. The F-value of 283.86 and R^2 value of 0.9877 obtained through ANOVA have shown that the model suggested is significant. The study has established that PAA aided with Fe^{2+} ions in combination with hydrodynamic cavitation was able to reduce 72.36, 94.54 and 98.89% of COD, TDS, and turbidity respectively in about 97.5 minutes. Moreover, the radicals formed in the combined system are highly reactive that oxidises the insoluble organic matter into soluble form, thereby, enhancing the sCOD solubilization. The soluble COD is increasing after the treatment attributing that the treated effluent has been converted into simpler forms/compounds increasing the biodegradability. Increase in the biodegradability of the TWE paved way to energy recovery using anaerobic digestion method as a post-treatment.

The improved biodegradability of the TWE using HC + AOPs treatment system has resulted in higher biogas production using anaerobic digestion as post-treatment method. The results obtained have revealed that the C/N ratio and the pH of the digestor plays an important role in biogas production. The CM and LT has been proven to be better energy sources for anaerobic digestion of TWE. The maximum methane production 489.81 ml/g.COD was obtained using ternary combination i.e., [HC+AOP treated TWE] + CM +LT which accounts to be around 6.5 and 1.6 times as compared to co-digestion of raw TWE with CM and LT respectively. Therefore, the proposed scheme in the research study consisting of series of treatment systems has been successful in degrading the TWE to a remarkable extent. However, the effluent obtained after the anaerobic digestion should be treated aerobically (aeration method) that could enable the safe disposal of the effluent into the environment.

7.1.1 Significant findings of the study

- The orange peel waste can be used as an alternative to alum for tannery wastewater effluent.
- An adsorption capacity of 418.31 mg/g of COD was obtained for AOPP treatment of TWE.
- The combination of physical chemical phenomenon was responsible for the formation of radicals in the TWE.
- The HC+AOPs resulted in increase of biodegradability index of TWE.
- Pre-treatment of wastewater is required before using the HC system to achieve better removal efficiencies and avoiding clogging of the orifice.
- The radicals generated due to the hydrodynamic cavitation enabled the conversion of complex compounds into easily bio-degradable simpler compounds.
- The reaction rate constant was increased from 2.455×10^{-3} to 12.75×10^{-3} min^{-1} when AOPs (PAA+ $FeSO_4.7H_2O$) were combined with HC.
- Hydrodynamic cavitation as a pre-treatment has shown significant increase in the biodegradability of wastewater which consequently yielded better biogas production using co-digestion with chicken manure as compared to mono digestion.
- The cumulative methane yield was increased by 18% when pre-treated TWE was subjected to co-digestion using chicken manure.
- Mixture of chicken manure and leather trimmings resulted in increase of biogas production and methane recovery.
- The Leather trimmings generated at the tanneries can be utilised for anaerobic digestion of TWE as a source for biogas production.
- The ternary combination of [HC+AOP treated TWE] + CM +LT increased the cumulative methane yield by 6.5 and 1.6 times as compared to co-digestion of raw TWE with CM and LT respectively.
- The hybrid technology consisting of series of treatment processes can efficiently treat highly contaminated industrial wastewaters.

7.2 Scope for the study

- Evaluate the fate of the harmful pollutants that may be trapped on the surface of OPW.
- To improve the removal efficiency of the system, OPW can also be used in a mixture with other agricultural wastes depending upon the type of wastewater to be treated.
- The process intensification can be carried out by improving the HC set-up by varying the arrangements of orifice in a series or parallel arrangement.
- Modelling studies such as computational fluid dynamics – modelling (CFD) would allow understanding the hydrodynamic cavitation set-up design better and improvising accordingly for further implementation at larger scales.
- Techno-economic analysis can be done for the hybrid treatment system.
- Post aerobic treatment may be carried out on the effluent obtained from the anaerobic co-digestion studies.

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Publications based on research work

Publications from the thesis

Korpe S, Rao PV. Application of advanced oxidation processes and cavitation techniques for treatment of tannery wastewater - A review. J Environ Chem Eng [Internet]. 2021;9(3):105234. https://doi.org/10.1016/j.jece.2021.105234 (SCI) [Impact factor-7.9]

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Under review

Sneha Korpe, Polisetty Venkateswara Rao, Pilli Sridhar,"Orange Peel Waste as a Potential Adsorbent for the Treatment of Organic and Inorganic Pollutants" (under review) ENVIRONMENTAL QUALTITY MANANGEMENT (SCOPUS)

Submitted to the journal

Sneha Korpe, Polisetty Venkateswara Rao, "Comparative study on anaerobic digestion to determine the methane potential of chicken manure and leather trimmings as co-substrate". (submitted to the journal) BIORESORCE TECHNOLOGY (SCIE and SCOPUS)

Book chapter

Sneha A. Korpe, Vividha Landge, Vikas S. Hakke, P. Venkateswara Rao [a], Shirish Hari Sonawane, Shriram S. Sonawane, "Advanced Oxidation Processes for Tannery industry wastewater treatment" published in SUSTAINABLE ENERGY TECHNOLOGIES AND ASSESSMENTS (SCI) [Impact factor-7.6]

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Korpe Sneha, P.V. Rao International Conference on Innovative Trends in Civil Engineering for Sustainable Development (ITCSD - 2019) on "Treatment Technologies Used for Treating Tannery Wastewater Effluent- A Review", National Institute of technology, Warangal, India.

Sneha Korpe and P.Venkateswara Rao RECYCLE 2020 Indian Institute of Technology, Guwahati, Assam, India.

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