

Treatment of Black Liquor Produced From Wheat Straw Pulping Process

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in Partial Fulfilment of the Requirements for the Degree of

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Saskatoon, Saskatchewan

By

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ABSTRACT

With the increasing number of pulp and paper industries, the production of black liquor, which is one of the main by-products of the pulping process, is also being increased simultaneously. The produced black liquor is toxic to human, aquatic life and the environment as a whole because of its high pH and alkalinity, hence, various ways for its treatment and management are being carried out, yet it has been mostly used as energy for fuels only. Furthermore, the black liquor produced, especially, in the wheat straw pulp and paper industry is found to contain high concentrations of lignin, silica, etc., and its poor biodegradability on the other hand hinders the performance of conventional biological degradation methods of wastewater treatment. Hence, this research incorporated the use of an electrocoagulation process as a pretreatment step, where the flocculating agent was generated by electro-oxidation of sacrificial anodes that removed pollutants in black liquor by electrostatic attraction. The study investigated its efficacy for the biological degradation of black liquor under anaerobic conditions with varying concentrations of black liquor.

This study included the optimization of the electrocoagulation process of pretreatment of black liquor with the help of the Response Surface Method in which pH (7-11), voltage (10-30 V), and electrolysis time (10-60 min) were used as the operational parameters and Chemical Oxygen Demand (COD), phenol, Total Solid (TS), Total Dissolved Solid (TDS), color, pH, and Specific Energy Consumption (SEC) were used as the analytical parameters. Proximate analysis, Klason lignin analysis, Thermogravimetric Analysis (TGA), Fourier-Transform Infrared Spectroscopy (FTIR), and X-ray Fluorescence were also carried out to understand the characteristics of black liquor samples. Finally, anaerobic digestion was carried out with both untreated and pretreated black liquor for 36 days with varying concentrations from (10% to 30%) to find out the effectiveness of electrocoagulation for biological degradation. The degradation of the black liquor was evaluated by the reduction of COD, pH, TS, and volatile matter (VM). Along with that, biomethane potential was also assessed during the process of anaerobic digestion of black liquor.

The overall optimum condition for electrocoagulation treatment of black liquor was initial pH 9, 20 V, and 35 min electrolysis time, which led to a successful removal of 49.40% COD, 43.61% phenol, 53.89% TS, 46.50% TDS, and 29.33% color and a reduction in alkalinity of the black liquor by 0.52 pH. The optimized condition of electrocoagulation resulted in a black liquor

with 21,000 mg/L COD, 198 mg/L phenol, 19,690 mg/L TS, 7,000 mg/L TDS, 50.49 whiteness index and 8.48 pH . The operation was conducted with an average current output of 0.87 A and a current density of 33.02 mA/cm². The specific energy consumption was found to be 1.98 kWh/kg of COD removal. Additionally, it helped reduce lignin by 71.85%, and volatile matter by 12.50% (dry basis) and 58.00% (wet basis). Overall, electrocoagulation treatment of black liquor followed by anaerobic digestion reduced the inhibition time and the retention time for gas production. The biogas yield obtained from 30% EC treated BL in 10 days optimal time was 185.14 mL/g of COD loading, which was double in value than that produced from the raw black liquor. When pretreated, gas yield increased by 40.00% and 99.50% for 10% and 30% black liquor concentration, respectively. 25.14% of COD, 13.43% of TS, and 35.34% of VM was reduced when 30% of pretreated black liquor was digested under anaerobic condition. Hence, this study incorporated the ability to treat black liquor produced in wheat straw pulp and paper industry by an integrated approach of electrocoagulation and biological degradation under anaerobic conditions.

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DEDICATIONS

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LIST OF ABBREVIATIONS

AD	Anaerobic Digestion
ANOVA	Analysis of Variance
BL	Black Liquor
BOD	Biological Oxygen Demand
CAGR	Compound Annual Growth Rate
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
DOE	Design of Experiment
EC	Electrocoagulation
FTIR	Fourier-Transform Infrared Spectroscopy
RF	Radio Frequency
RLP	Red Leaf Pulp
R.S.D.	Relative Standard Deviation
RSM	Response Surface Methodology
SEC	Specific Energy Consumption
TDS	Total Dissolved Solid
TGA	Thermogravimetric Analysis
TS	Total Solid
TSS	Total Suspended Solid
UV	Ultraviolet
VM	Volatile Matter
WI	Whiteness Index
XRF	X-ray Fluorescence

CHAPTER 1: INTRODUCTION

1.1 Research Background

The industrial revolution has led to an increase in pulp and paper industries globally. Also, it is undeniable how much importance this industry holds because of the multiple benefits and usage we can get from pulp and paper in our daily lives. A variety of consumer, innovative, and specialty products such as printouts, receipts, paper cups, tissues, cardboard, LCD screens, handbags, food casings, binding agents, etc. are a few of the products and applications we obtain from the pulp and paper industry (Figure. 1.1). In context to Canada’s pulp and paper industry, it was born in the early 1800s and has been booming ever since then (Kuhlberg 2015). Praet (2022) confirms the annual generation of paper production has reached 20.7 million tonnes, and this number is going to increase even more in the future considering the increase of production capacity of existing pulp and paper industries in Canada. Industries, in general, have been using wood as raw material to produce paper creating an enormous influence on global forests. This sector of industries involved in producing mainly office and home products like catalog paper, glossy paper, paper packaging, tissues, etc. accounted for nearly 15% of total wood consumption and used up to 40% of all industrial wood traded globally (Pacheo et al. 2021) In response, this has led to unsustainable deforestation and clearcutting of old-growth forests (Gopal et al. 2018; Haile et al. 2021a). Because of the environmental issues created by the wood-based pulp and paper industries, these industries have been criticized, and the country requires to shift towards sustainable raw materials for pulp and paper production.



Figure 1.1 Various Applications of Pulp and Paper Products

On the other side, responsible pulp and paper operations can help reduce haphazard deforestation and bring benefits to the economy, people, and the environment, as a whole, yet Canada is lagging in incorporating sustainable pulping operations. However, studies have been accelerated to demonstrate leadership in developing, constructing, and operating alternative fibre plants in Canada. Supporting the growth of the agricultural bioeconomy by creating and utilizing bio-based products and investing in cutting-edge research to develop good jobs and a clean economy is of great importance to Canada. To the context, Red Leaf Pulp Ltd. (RLP), being the first entity in Canada, has started a project on the production of cellulose pulp and paper products from wheat straw which helps in upgrading the sustainable pulp and paper industry, along with creating economic benefits to the agricultural sector in Canada (Papnews 2021; RLP 2023). The utilization of wheat straw, which is otherwise burned in open fields, lowers the emissions and overall carbon footprint of the process. The facility is anticipated to utilize approximately 370,000 tonnes of waste straw and will produce 200,000 tonnes of pulp and black liquor (BL) containing lignin, hemicellulose, and nutrients. While the application of cellulose pulp is well established, Red Leaf Pulp is interested in identifying ways to sustainably manage black liquor.

Black liquor is an integral part of the pulp and paper industry, and it needs to be treated or utilized considering the environmental problems, especially related to water resources. It is an aqueous by-product produced in the kraft process, that comprises lignin, hemicellulose, and inorganic chemicals used in the process (Biermann 1996a). It is generated in large volumes in both wood and non-wood pulping processes (Huang et al. 2007; Kamali et al. 2020; Kamali and Khodaparast 2015) The chemical oxygen demand (COD) for this aqueous solution varies generally from 10,000 to 120,000 mg/L, and the pH ranges from 10 to 13, which makes it unfavorable to be discharged directly into the municipal wastewater treatment facilities (Hu et al. 2015; Huang et al. 2007). The wastewater treatment facilities equipped with aerobic and anaerobic systems are not able to treat this range of industrial effluents, and it might hinder their biological activity and the entire performance instead. At the same time, the black liquor is toxic if discharged directly to water resources because higher COD levels account to greater amount of oxidizable organic material resulting in a reduced dissolved oxygen (DO levels). The reduced DO can further lead to an anaerobic condition causing threat to aquatic life (RealTech 2017). Therefore, the black liquor obtained from pulp and paper industries needs to be treated before being discharged to avoid adverse environmental problems on aquatic bodies as well as municipal treatment plants (Adhikari

and Bhattacharyya 2015). The idea of black liquor treatment is not new. Most of the black liquor by-products were being consumed by the kraft industries by the 1990s and the remaining parts were treated using a biological degradation system (Stevan Mufson 2009). Meanwhile, black liquor derived from non-woody materials are poorly biodegradable, highly alkaline and contain high color level and phenolic content (Bajpai 2017a; Doma and Abou-Elela 2003; Ghatak et al. 2008; Pola et al. 2022). Also, due to high silica content and high viscosity in black liquor obtained from straw pulping, the chemical recovery process becomes difficult (Tutus 2016). The inorganic composition, i.e., the higher silica content of 2.5 to 5.5 % in wheat straw interferes with the chemical recovery process and the energy recovery process eventually. The ash content in softwoods and hardwoods is generally less than 1%, hence there is no problem originating from silica with the wood pulping, whereas the ash content in non-wood plants goes up to 20%. The ash produced causes handling and disposal problems along with the decrease in combustion efficiency of the black liquor. affects the combustion efficiency. In addition, it is difficult to obtain sufficient concentrated liquor by evaporation from the black liquor produced from straw because of its viscous property (Fengel Dietrich et al. 2011; Tutus 2016). The plant or broiler tends to consume high energy during black liquor combustion if it is to be burnt instead due to sodium silicate concentrate. The most cost-effective treatment to treat this range of wastewater is biological treatment (Lihong et al. 2009). However, the presence of inhibitory compounds such as lignin derivatives, tannin, resins, etc., in black liquor hinders microbial activity as these are toxic to both aerobic and methanogenic microorganisms, hence pretreatment of black liquor is essential (Buzzini and Pires 2002; Kamali et al. 2020; Villamar et al. 2009; Zheng et al. 2022).

Electrocoagulation (EC) is a pretreatment process opted for black liquor treatment where the flocculating agent is generated by electro-oxidation of sacrificial anodes which removes pollutants by electrostatic attraction. It removes suspended solids to sub-micrometer levels, breaks emulsions (oil, grease, latex), and oxidizes and eradicates heavy metals from water without the use of filters or the addition of separation chemicals. It is efficient and compact, and characterized by easy operational equipment, short operation time, and no chemical use, thus minimizing the generation of secondary pollution(Chen 2004; Mouedhen et al. 2008) The residue obtained from electrocoagulation does not contain sulfur compounds unlike in the ones generated from acid hydrolysis method. This opens pathways for valorization of residue obtained after the electrocoagulation process without the generation of secondary pollution. Therefore, this

research has investigated the feasibility of biological degradation of black liquor under anaerobic conditions with an integrated pretreatment step of electrocoagulation before biological digestion. Furthermore, this research has explained the performance of the electrocoagulation process as a pre-treatment step by exploring and optimizing the effect of operational variables: initial pH, voltage, and electrolysis time. The treatment efficiency of the electrocoagulation process was determined and discussed based on the reduction of Chemical Oxygen Demand (COD), phenol, Total Solid (TS), Total Dissolved Solid (TDS), color intensity, and lignin content and pH change. The optimized electrocoagulation process was compared with the non-treated black liquor based on their biomethane potential, volatile matter (VM) content, COD content, and pH change after biological degradation.

1.2 Rationale

In contrast to the traditional wood-based raw materials for pulp and paper production, RLP is using an alternative fiber plant in Canada, i.e., wheat straw. Likewise, instead of undertaking the commonly used kraft cooking process that uses the solution of sodium hydroxide and sodium sulfide to dissolve the lignin and hemicellulose in the lignocellulosic biomass to produce cellulose pulp, RLP incorporates mild alkali cooking condition (Cheremisinoff and Rosenfeld 2010). The structural difference of lignin in wood and non-wood-based raw materials makes straw lignin soluble in alkali conditions as compared to wood which requires an additional sulfur compound to increase the solubility (Buranov and Mazza 2008a; Sun et al. 1998a). Lignin produced from a mild alkaline process is sulfur-free and can be chemically treated to produce bio-based materials (Kim et al. 2016a). This method of sulfur-free mild alkali cooking conditions opens the pathways for valorization by extraction of lignin and hemicellulose. The option to treat the black liquor in the municipal wastewater treatment plant provides operational flexibility to RLP while the valorization pathways are being developed for the utilization of components in the black liquor. The lignin and other extracts in the black liquor could be toxic to both aerobic (activated sludge treatment) and anaerobic (anaerobic digestion) microorganisms (Morales et al. 2015); therefore, a comprehensive study is needed to understand the loading rate of the black liquor and its effect on the COD, phenol, TS, TDS, color intensity, pH and lignin removal along with its biomethane potential and the properties of digested sludge.

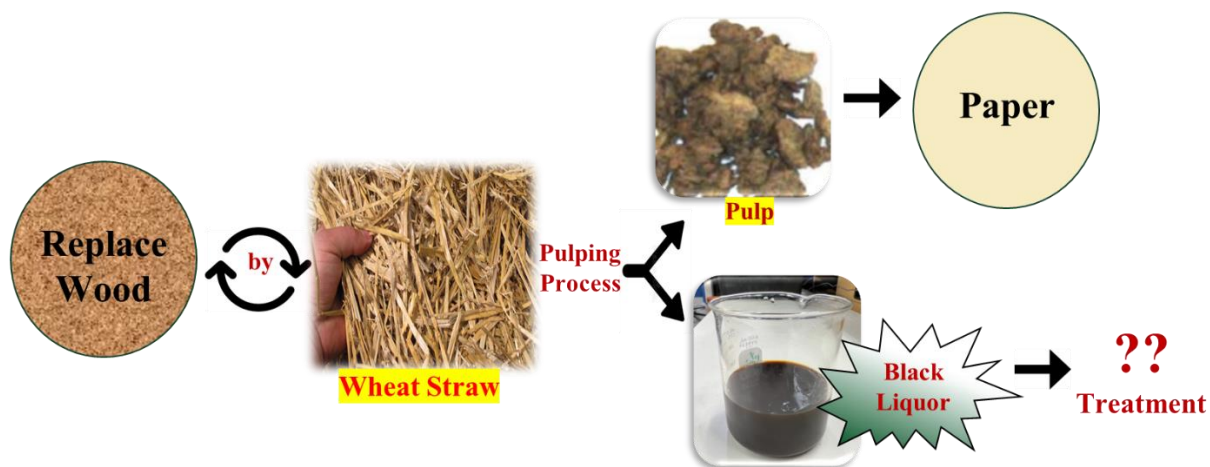


Figure 1.2 An Illustration of the Replacement of Wood by Wheat Straw in Pulp and Paper Industry (The Pulping Process being Well Developed Seeking the Treatment of Black Liquor)

Hence, the research helps to understand the effect of the possibility of treating black liquor obtained from the wheat straw pulping process, i.e., by the process of biological degradation. To make the obtained result more valuable, an optimized pretreatment step was added before anaerobic digestion (AD). The result of this study contributes to identifying a viable way of treatment of black liquor under the given condition (Figure 1.2). This study has both immediate as well as future implications.

1.3 Knowledge Gaps

- The treatment of black liquor produced from non-wood-based pulp and paper industries has not been extensively studied.
- The effect of anaerobic treatment depends on the processes used during pulping and not much study has been carried out with black liquor produced from sulfur-free cooking conditions.
- Electrocoagulation treatment of black liquor is less explored in this field of research.

In summary, this research study aims to cover the research gap in the treatment of black liquor derived from non-woody feedstock by the integrated method of electrocoagulation, and anaerobic digestion.

1.4 Research Objectives

The overall objective of this research is to understand the feasibility of treating black liquor produced from the wheat straw pulping process in the municipal wastewater treatment facility by biological degradation .

The specific objectives are as follows:

- To study the effect of initial pH, voltage and electrolysis time to reduce COD, phenol, TS, TDS, color and pH of black liquor by a pretreatment method called electrocoagulation .
- To study the effect of anaerobic digestion of raw and electrocoagulated black liquor and understand their biomethane potential.

1.5 Hypothesis

- The pretreatment process of electrocoagulation helps in the partial treatment of black liquor produced from the wheat straw pulping process by reducing COD content, phenol content, TS content, TDS content, color intensity, and alkalinity.
- The process of anaerobic digestion helps in the treatment of black liquor by reducing COD content, volatile matter content, and pH.
- The electrocoagulation treatment helps in enhancing the anaerobic digestion of black liquor.

1.6 Scope and Limitations

The research focuses on developing an integrated approach of biological treatment of black liquor obtained from the pulp and paper industry that uses non-wood-based raw materials with the help of electrocoagulation and anaerobic digestion. The results of this research can be tested concerning its feasibility and reliability for similar kinds of industries. The research provides an improved outlook on the biological treatment of black liquor by enhancing anaerobic digestion with the addition of a pretreatment method called electrocoagulation. Electrocoagulation is one of the many pretreatment processes of black liquor that is to be carried out before biological degradation. The data and research findings have both research and industrial applications. Since

this research is dedicated to industries using non-wood-based feed for pulp and paper industries, it has policy-level application considering environmental concerns.

Amongst the various pulp and paper industries using non-wood-based raw materials, such as wheat straw, rice straw, cotton stalks, sugarcane bagasse, etc., this research focuses only on industries using wheat straw. The research is limited to only one pretreatment method, i.e., electrocoagulation, and checks its ability to enhance the biological degradation of black liquor with certain characteristics obtained from the Red Leaf Pulp Industry and doesn't investigate its conversion to higher value bioproducts. Also, the research being focused on the treatment of black liquor from non-woody material, this may not give the desired treatment procedure for the woody feeds.

1.7 Organization of the Thesis

The thesis is written in a traditional style and organized into five chapters, each serving a specific purpose as follows:

Chapter 1 provides a brief introduction to the research including background, rationale, knowledge gaps, objectives, and hypothesis of the research.

Chapter 2 presents a comprehensive literature review on black liquor produced by the pulp and paper industry, its properties, usability, treatment methods, and challenges. The effectiveness and challenges of using biological treatment of black liquor are also incorporated in this part.

Chapter 3 focuses on materials and methods used for carrying out the research including experimental design, laboratory scale experimental setup, chemical analysis, instrumental analysis, and statistical analysis.

Chapter 4 discusses the result of electrocoagulation pretreatment of black liquor and its optimization. The efficacy of biological degradation of black liquor and its biomethane potential is also discussed in the later section of this chapter. The results and discussion section are based mainly on COD, phenol, TS, TDS, color, lignin removal for electrocoagulation, and COD, VM, and pH removal along with biomethane potential for anaerobic digestion of black liquor.

Chapter 5 states the key conclusions drawn from the research, along with recommendations and suggestions for future work.

Chapter 6 provides the details of the contribution of this research thesis.

CHAPTER 2: LITERATURE REVIEW

2.1 Pulp and Paper Industries

The pulp and paper industries predominantly convert woody plant material into a wide variety of cellulose-based products such as pulps, papers, paperboards, etc. Market Research Experts (2023) states and predicts that the global pulp and paper market size was valued at 347.20 billion US dollars in 2022 and will reach 361.40 billion US dollars in 2028. Moreover, the value added in the pulp and paper market is projected to increase from 250 billion US dollars to 309.22 billion US dollars in five years (2023-2028) with a compound annual growth rate (CAGR) of 3.85 (Statista 2023). The Canadian industry began in the 1800s and has undergone revolutionary changes over the years (Kuhlberg 2015). In today's modern days of electronic media, the move from newsprint to social media platforms caused the industry to decline; however, pulp and paper remain a fundamental part of the Canadian economy, especially for remote and northern communities. Besides communication purpose, the demand for paper-based daily consumables and specialty products have been increasing (ImperialDade 2023). This can be justified by the increase of industrial revenue of Canadian paper mills to 6.6 billion US dollars in 2023 with a CAGR of 6.4% over five years (IBISWorld 2023). Also, paper products being biodegradable, have been exceeding in demand as a replacement for plastic products especially in the food and packaging industries (Deshwal et al. 2019).

2.2 Pulping Process, Byproducts and Challenges

In general, the pulping process is aimed at removing lignin without losing the strength of fiber, thereby getting free fibers with impurities and discoloration removed (Pulp and Paper 2023). The lignin and hemicellulose content in black liquor is highly dependent on the pulping process and the cooking conditions. Cooking conditions such as base concentration, sulfur compounds, ratio of solid to liquid, cooking temperature, treatment time, pressure, and biomass used can interfere with the by-product content (Ghaffar and Fan 2014; Oriez et al. 2020).

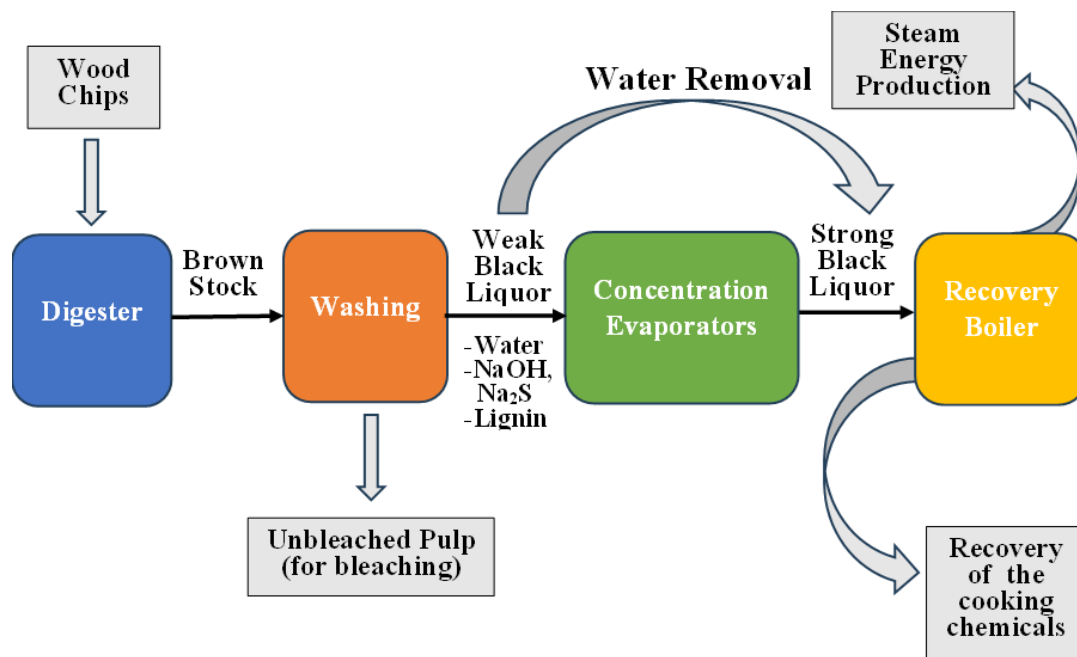


Figure 2.1 Schematic Diagram of Kraft Pulping (Redrawn from (Oliveira et al. 2018))

Oliveira et al. (2019) state that approximately 90% of the chemical pulp is produced by the kraft pulping process in the whole world (Figure 2.1). The wood biomass or agricultural remains are comprised mainly of cellulose, hemicellulose, and lignin. So, in the kraft cooking process, a solution of sodium hydroxide and sodium sulfide is used to dissolve lignin and hemicellulose in the wood chips in the digester which later forms brown stock (Cheremisinoff and Rosenfeld 2010). The process is followed by washing giving rise to unbleached pulp and weak black liquor. Thereafter, the weak black liquor passes through evaporators to form strong black liquor, which then goes through a process of combustion in a recovery boiler for steam and energy generation within the pulp mill (Biermann 1996b; Maniatis et al. 2013; Oliveira et al. 2018; Popa 2013).

The pulp and paper industries have been challenged to manage their by-product, black liquor. The kraft cooking process will induce some structural differences which produce molecules of various ranges from monomeric phenols to high molecular weight polymers (Zhao et al. 2019). Besides its burning in the facility for fuel production, not many efforts have been successful enough to valorize it (Ramezani and Sain 2018). The burning of the black liquor requires a high investment, high operational cost, and possesses risk of explosion. The rate of return is also not in favor of the industries and sometimes small paper mills just avoid this step and discharge the black

liquor directly into the environment because of the operational difficulty and high cost (Mahesh et al. 2006). Despite this issue, one of the main reasons for industries adopting incineration of black liquor in their own paper mills is because of the structure of the lignin component of wood-based pulping raw materials which is unique in comparison to its native one. It requires an additional sulfur compound to increase the solubility hence hindering its opportunity to produce value-added products from black liquor (Buranov and Mazza 2008b; Sun et al. 1998b). Considering these hindrances, studies have been carried out to adopt mild alkali sulfur-free cooking processes, especially targeted to those industries using non-wood-based raw materials (Chen et al. 2016; Kim et al. 2016b). Sulfur-free pulping has an environmental advantage over the traditional kraft cooking process. Likewise, under the same cooking time, the total burning times for the sulfur-free black liquors are higher (15–55%) than those from the conventional kraft black liquors (Chen et al. 2016).

2.3 Wood-Based Raw Materials for Pulping

Wood is considered the primary source of raw material in pulp and paper production (Eugenio et al. 2019; Haile et al. 2021b). The major constituents of wood are cellulose, lignin, and hemicellulose with traces of extractives of different types, as shown in Table 2.1, making it suitable for extracting different kinds of pulp and paper products. Furthermore, wood can be divided into two types: softwood and hardwood comprising 35% and 65% abundance in the world, respectively, respectively (CNBM 2018). Hardwood comes from angiosperm trees whereas softwood comes from gymnosperm trees. Both can be individually or in a combined manner applied to pulp and paper making. Examples of hardwoods include maple, oak, walnut, teak, etc. and softwoods are cypress, pine, fir, etc.

Table 2.1 Composition of Wood (Redrawn from (Haile et al. 2021b))

S.N.	Component	% Composition
1.	Cellulose	40-50%
2.	Hemicellulose	25-30%
3.	Lignin	25-30%
4.	Extractives	Minor

2.4 Non-wood Based Raw Materials for Pulping

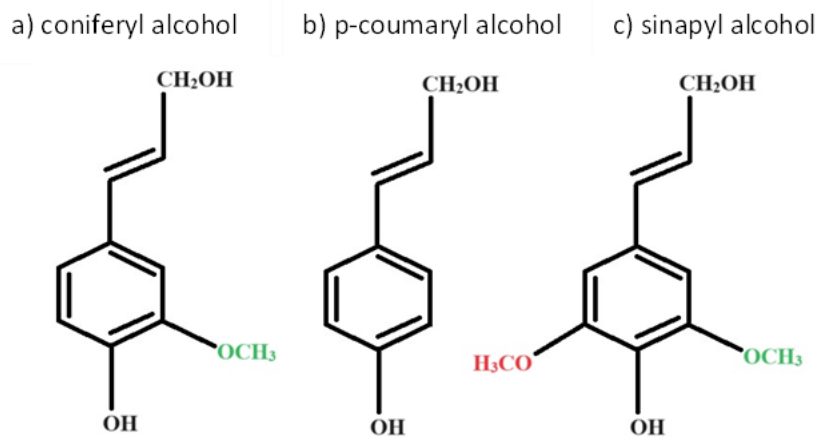


Figure 2.2 Diagram Showing Three monolignols Present in Native Lignin (a) coniferyl alcohol, b) p-coumaryl alcohol and c) sinapyl alcohol) (Redrawn from (Amthor 2003; Whetten et al. 1998))

Due to increasing environmental concerns caused by wood-based pulp and paper industries along with the lack of wood, the need for pulp and paper industries using non-wood plant materials has increased. Besides wood pulp, there are other fiber materials for pulp and paper making, such as bagasse, bamboo, reed, wheat straw, cotton, jute, wastepaper, etc. (CNBM 2018). Amongst others, agricultural residue such as wheat straw has the potential as a raw material for paper industries due to its abundance, availability and the lignin structure similar to that of the native lignin (Rastegarfar et al. 2015). Unlike wood lignin present in wood-based black liquor, straw lignin comprises all three monolignols as that of its native kind, namely, p-coumaryl alcohol (MH), coniferyl alcohol (MG), and sinapyl alcohol (MS), which makes it readily soluble in alkali conditions without additional sulfur requirement (Figure 2.2) (Sun et al. 1998a). This can further give rise to high-value applications of lignin and hemicellulose as there will not be interference of the sulfur compounds. According to RLP (2023) the fiber production from wheat straw uses just 5% of the water and 30% of the energy in comparison to wood pulp production because of the lower moisture content and the higher ratio of cellulose fibre to lignin of wheat straw in comparison to wood. The most important obstacle to the development of its use is the presence of pulping black liquor that contains significant amounts of color and phenol compounds due to its soluble lignin. However, if this kind of problem is solved by some pulping process modification, the future

of non-wood plant fibers as pulping and papermaking raw material looks promising (Abd El-Sayed et al. 2020).

2.5 Black Liquor and its Characteristics

Both wood and non-wood pulping processes produce large quantities of black liquor as a waste by-product (Huang et al. 2007) Being the final concentrated liquid obtained after washing cellulose pulp, it contains all the impurities and toxins. Black liquor is used for incineration in bigger pulp plants, but the small pulp mills generally discharge this harmful liquid directly into the environment due to the lack of a proper recovery system and its exceeded cost of management and treatment (Venkatesh and Nguyen 1992). The lignin and phenol compound in black liquor leads to higher COD content and dark color, so its treatment has become a prerequisite for any pulp and paper industry in the whole world. One of the characteristics of black liquor is that it has a basic value of pH, hindering the biological treatment (Zhang and Chen 2016).

2.6 Treatment of Black Liquor

Pulp and paper industries have been opting for wet oxidation, ozone treatment, biological treatment, adsorption, etc. for the treatment of black liquor generated after pulp extraction (Fox and Noike 2004; Freire et al. 2000; Ortega-Clemente et al. 2004; Shawwa et al. 2001). Although these treatments can be helpful in the reduction of toxicity from the black liquor, they come with high operational costs and comprise the use of huge amounts of chemicals (Nazari et al. 2007). Biological treatment can be considered one of the most cost-effective and popular treatments of industrial wastewater along with black liquor, but still, it has some hindrances in the treatment process due to high silica content and viscosity adversely affecting the microbial growth in the digestion process (Lihong et al. 2009; Zheng et al. 2022). Among the alternative processes that can be used in this field, the electrolysis of black liquor is one of the most promising processes (Ghatak et al. 2008; Oliveira et al. 2016; Royghatak 2006).

2.7 Biological Treatment of Black Liquor

An alternative to the complex process of valorization of black liquor is to biologically treat the black liquor before discharging it to the municipal wastewater treatment facility. It refers to the treatment of wastewater with the help of aerobic or anaerobic microorganisms that results in

decanted effluents and separate sludge containing microbial mass together with pollutants (Nations 1997). This treatment method utilizes the metabolic function of microorganisms to purify wastewater by eliminating soluble organic matter, which is difficult to remove by chemical means (Doma and Abou-Elela 2003).

If COD components and reductive inorganic compounds could be oxidized by bacteria efficiently, the energy and the cost of wastewater treatment would become lower. However, the lignin and other extracts present in black liquor could be toxic to the biological degradation process, i.e., to both aerobic (activated sludge treatment) and anaerobic (anaerobic digestion) microorganisms, meaning the metabolic activity in the microorganisms might be hindered and they might not be able to break down the organic component of the black liquor. Considering this issue, biological treatment method can be integrated with a pretreatment method. An example of pulp and paper industry incorporating aerobic digestion as a post treatment of the black liquor was found capable to eliminate the acute toxicity (Doma and Abou-Elela 2003; Schnell A. et al. 1990).

A high concentration of organic content in black liquor has the properties of high alkalinity. Thus, black liquor possesses distinct features such as high pH value, high temperature, and high COD. So, one of the most cost-effective treatments to treat this range of wastewater is biological treatment (Lihong et al. 2009). There have been treatment systems, such as integrated or hybrid systems, generally comprised of two physiochemical processes, or one physiochemical process and one biological process or two biological processes, which have been introduced lately (Ashrafi et al. 2015).

The two main types of biological processes: aerobic and anaerobic digestion for black liquor treatment, their limitations, and challenges along with preferability are explained in the following subsections.

2.7.1 Aerobic Digestion of Black Liquor

Aerobic digestion is the degradation of organic matter in the presence of oxygen. When the oxygen is introduced as fine bubbles of air into the reactor, the microorganisms present in the sludge convert the organic material to carbon dioxide and water, and the ammonia and amino species to nitrate (Judd 2020). The primary disadvantage of aerobic digestion is that it is energy intensive because this process consumes air and produces carbon dioxide rather than methane or

biogas. Also, the digested sludge that is generated after the process is not as readily dewaterable mechanically unlike in anaerobic digestion (Van Haandel 2012).

Aerobic digestion has been interestingly used in treating black liquor either in a hybrid way or as a secondary step in the past. Morales et al. (2015) studied the effect of black liquor shocks on activated sludge treatment. Activated sludge systems including an aerobic reactor and settling unit were used. Two activated sludge systems were taken, so one could be used as a control and the other as a trial system. Raw wastewater with adjusted flow rate and hydraulic retention time was fed in normal conditions. Likewise, for black liquor trials, the various concentration of black liquor was used, and the pH was also adjusted accordingly to approximate 7. In the final step, raw wastewater was used without the addition of black liquor. The biodegradability in this experiment was tested by the relation of BOD₅/COD, indicating the average value of 0.46, concluding that the effluent was not fully biodegradable, yet this study concluded that good stabilization of the activated sludge system could resist the shock under the condition provided. Vadodaria (1999) studied the effect of black liquor by using various concentrations of black liquor with differential sludge concentrations. In addition, foam fractionation was also used as a pretreatment step which could not improve the kinetics of the activated sludge. It was found that the initial sludge concentration affected the COD removal rate. Another study on the influence of residual black liquor in pulp on wastewater pollution after the bleaching process was carried out, showed that more than 34% of the COD is produced by the residual black liquor (Chen et al. 2016).

2.7.2 Limitation of Aerobic Digestion for Treatment of Black Liquor

Aerobic digestion involves the use of oxygen to break down organic matter and is typically used for the treatment of municipal and industrial wastewater (Demirbas et al. 2017). It can be used to treat certain aspects of black liquor, but it has limitations and is less advantageous as compared to anaerobic digestion (Lab Unlimited 2013).

The process of aerobic digestion can reduce the COD content of the black liquor from the pulp and paper industry, which measures the amount of oxygen required to break down the organic compounds (John and Kumar 2023). Chemical oxygen demand (COD) is the amount of a specified oxidant that reacts with the wastewater under controlled conditions (APHA 2023a). Lowering the COD is important for reducing the environmental impact of discharging black liquor into water

bodies (Irfan et al. 2017). Likewise, the microorganisms involved in aerobic digestion feed on the organic matter in the black liquor, converting it into simpler substances and biomass. This can lead to the partial degradation of lignin and other complex organic compounds. However, there are some challenges and limitations associated with using aerobic digestion for black liquor treatment. Black liquor is typically high in lignin and has a complex chemical composition. Aerobic microorganisms may struggle to efficiently break down these compounds in comparison to anaerobic microorganisms (Kim et al. 2020). The process may require a longer retention time than anaerobic digestion process and a constant supply of oxygen is required throughout the digestion process. Moreover, the aerobic digestion of such kind of waste generates sludge in large volumes, which needs further treatment and disposal along with high energy consumption due to the oxygen requirements (Adriaan 2006; Bokhary 2021). Efficient recovery of chemicals from black liquor, which is a crucial aspect of black liquor treatment, may be more challenging with aerobic digestion.

In summary, the aeration requirement and huge amount of sludge production in aerobic digestion along with the complexity of black liquor composition hinder the applicability of aerobic degradation for black liquor treatment. The use of aerobic digestion is still limited for industrial wastewater treatment.

2.7.3 Anaerobic Digestion and Biomethane Potential

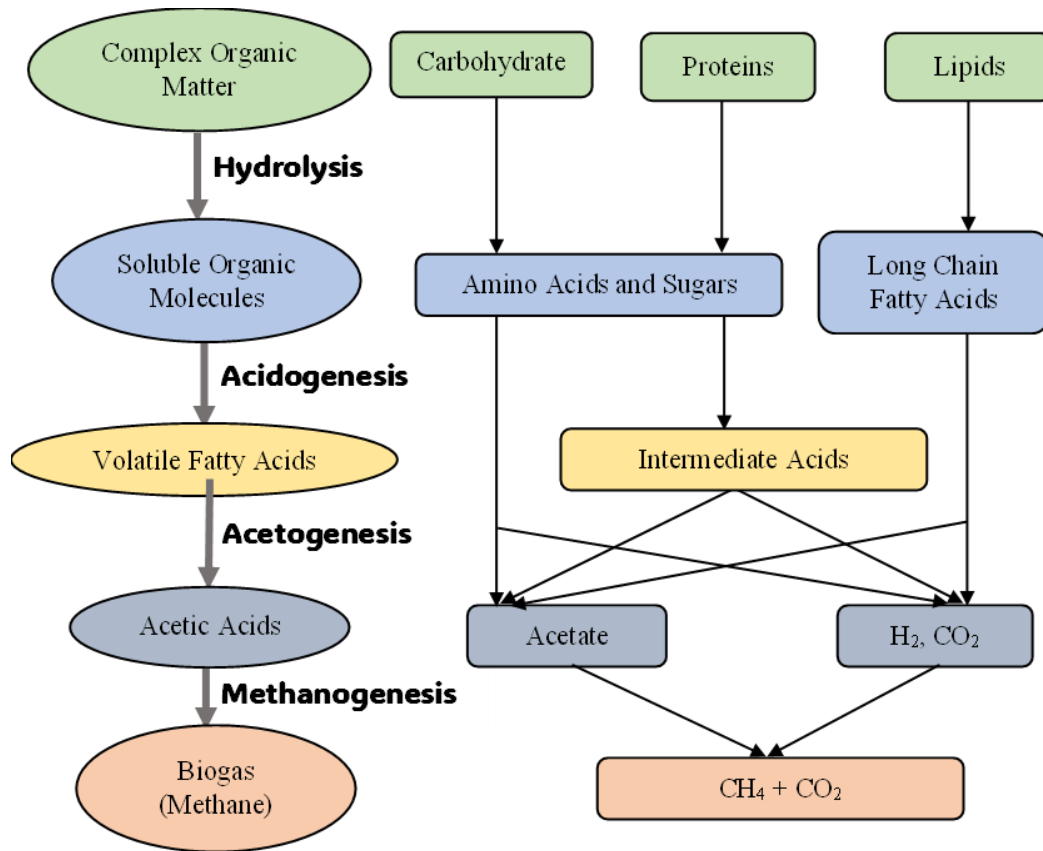


Figure 2.3 Biological Process of Anaerobic Digestion

Anaerobic digestion is a process through which bacteria break down organic matter in the absence of oxygen. Anaerobic digestion for biogas production takes place in a sealed vessel called a reactor or digester that contains complex microbial communities that break down or digest the waste and produce resultant biogas and digestate (EPA 2023).

Figure 2.3 shows the biological process of anaerobic digestion that takes place in four successive stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The digestion process is dependent on the interactions between the diverse microorganisms that are carried out in four stages (Gujer and Zehnder 1983; Meegoda et al. 2018).

First, complex organic molecules are broken down into simpler compounds, such as sugars, amino acids, and fatty acids by hydrolysis, then in the second acidogenesis step, the products of hydrolysis are further metabolized into organic acids (e.g., acetic acid, butyric acid). In the third

step of acetogenesis, organic acids are converted into acetate and hydrogen gas followed by the methanogenesis step, where the methanogenic bacteria use acetate and hydrogen, along with carbon dioxide, to produce biogas which is a mixture of methane (CH₄) up to (50-75%) and carbon dioxide (CO₂) upto (25-50%) and traces of nitrogen up to (2-8%) (Li et al. 2019). Biogas is a green and sustainable form of energy produced during the degradation of organic waste anaerobically resulting in ecological and economic benefit (Kweiyor Tetteh and Rathilal 2021). In the context of a single-stage batch reactor, all wastes are loaded simultaneously, and all four processes take place in the same reactor sequentially, after which the digestate is then emptied at the end of a given retention period or the cessation of biogas yield (Verma 2002).

Anaerobic digestion systems have been successfully deployed for the treatment of industrial wastewaters because of its lower energy requirements as compared to the aerobic digestion systems. Another added benefit is the reduced sludge generation and the savings in nutrient and chemical dosing. Many paper mills have been relying on anaerobic treatment of black liquor for reducing up to 85% of pollution loads along with recovering the biochemical energy potential as biogas for use as fuel (Rao V. V. 1992).

2.7.4 Anaerobic Digestion and Biomethane Potential of Black Liquor

In general, anaerobic digestion has been used for wastewater sludge treatment, agricultural manure management, and food waste management industries (Vutai et al. 2016). In the context of pulp and paper industries, anaerobic digestion has been confined to the treatment of a few selected types of effluent, and the resulting biogas is commonly burned to produce steam and electricity (Meyer and Edwards 2014). However, the increasing energy costs and the decreasing availability of energy resources has raised concerns to industries and consumers about their social activities, environmental and economic impact (Campo et al. 2021; Kweiyor Tetteh and Rathilal 2021; Ning et al. 2013). As a result, experts are reconsidering wastewater treatment plants as an important source for a bio-based circular economy rather than end-of-life treatment options and disposal facilities (Spierling et al. 2018). Anaerobic digestion method of wastewater treatment in return has turned out to be the most effective and sustainable treatment system for reduction, recovery and recycling of resources (Bennich and Belyazid 2017; Casas-Godoy et al. 2020). The black liquor obtained from the pulp and paper industry is a complex mixture of organic compounds, primarily lignin, hemicellulose, and other extractives, and these organic materials are rich in energy source,

so the black liquor can be considered to have high potential as an energy source (Darmawan et al. 2018). The organic content of black liquor can act as a feed to the anaerobic microbes in an anaerobic digestion system, which as a result produces biogas along with the treatment of the black liquor. The produced biogas can be captured, processed and the utilized as a source of renewable energy. Methane is the combustible component of biogas, and it can be utilized for various applications, including heat and power generation. Anaerobic digestion also serves the environment by treating the organic content, reducing COD and mitigating the environmental impact of the black liquor. By utilizing biogas from the black liquor, the pulp and paper industries can reduce their reliance on fossil fuels, thus contributing to a reduction in greenhouse gas emissions.

(Morya et al. 2022) state that 45–75% v/v of methane can be produced by the digestion of black liquor in an anaerobic digester. The gas production in anaerobic digester is highly dependent on pH, organic loading rate, hydraulic retention time, and temperature. The optimum pH range is between 6.8 to 7.5 and the temperature is between 35°C to 37°C (Ceron-Vivas et al. 2019). Besides these, the volatile acid concentration of 50 to 300 mg/L is to be maintained, and the organic loading rate should be in the range of 1.6 to 6.4 kg.m⁻³.d⁻¹ (Grangeiro et al. 2019). Grover et al. (1999) showed that an OLR of more than 6 kg.m⁻³.d⁻¹ of black liquor adversely affected the digestion process and decreased the biogas production in a continuous mode baffled anaerobic reactor.

Jian et al. (2021) assessed the effect of black liquor on sludge solubilization and methane production and found that the addition of black liquor increased the COD content and volatile fatty acids, thus helping in the amount of methane production by 7-30%. A start-up delay occurred due to the addition of black liquor in the hydrolysis step, but the methanogenesis step remained stable with constant production of biomethane. The economic analysis showed that the co-digestion of sludge and black liquor can produce surplus bioenergy, yet the balance between energy output and the residual organic compounds should be analyzed further. Another research on the two-step degradation process, i.e., photocatalytic pretreatment of black liquor followed by anaerobic digestion demonstrated the potential for biogas production. The efficiency of the pretreatment process was increased by adding H₂O₂, which also improved the biomethane potential (Jung 2019). Likewise, the bio-methanation system with an up-flow anaerobic sludge blanket (USAB) has been proven to be technically and economically reliable for the treatment of alkaline sulfite black liquor.

On average, 8000-9000 cubic meters of biogas yield was obtained with a 45-48% reduction of COD and a 72-80% reduction of Biological Oxygen Demand (BOD) (Chatterjee et al. 2002). Another experimental study carried out in India for bio-methanogenesis of black liquor of pulp and paper mill in a continuously stirred tank reactor (CSTR) followed by an activated sludge process (ASP) could have a methane yield of 430 mL/day with COD reduced up to 64% at 7.3 pH, 37 °C temperature and 8 days hydraulic retention time (Bishnoi et al. 2006). Chandra and Abhishek (2011) used two bacterial strains IITRL1 and IITRSU7 known as *Citrobacter freundii* (FJ581022) and *Citrobacter sp.* (FJ581023), respectively in an axenic and a mixed state for the treatment of black liquor in an anaerobic condition. This study concluded that mixed bacterial culture was more efficient in color removal than the use of isolated bacterial culture. Likewise, chlorophenols like 2,4,6-trichlorophenol, 2,3,4,5-tetrachlorophenol, and pentachlorophenol were not detected in mixed culture unlike in the axenic culture, which advocates the efficacy of mixed culture for black liquor treatment.

In summary, the organic content in black liquor, mostly the hemicellulose makes it suitable for the anaerobic digestion and biogas potential. This could be explained by the studies mentioned above on how anaerobic digestion in various stages of black liquor treatment helped treat the black liquor along with the production of biogas.

2.7.5 Challenges in Anaerobic Digestion of Black Liquor

The chemical structure of lignin in black liquor is compromised due to the addition of sulfur in the pulping process. This affects the pretreatment ability of black liquor prior to biological digestion. Likewise, high alkalinity is another factor affecting anaerobic digestion, as the optimum pH range in an anaerobic digester is 6.8 to 7.2 and can tolerate a range of 6.5 up to 8.0 (Cioabla et al. 2012). The already high lignin and phenol content in black liquor acts as vice-versa to the efficacy of biological activity and degradation in the digester (Doma and Abou-Elela 2003). The hindrance of biological activity due to the chemical component, i.e., lignin of black liquor is one of the major challenges to be solved during black liquor treatment. Lignin can have both positive and negative aspects in the biological degradation of black liquor, depending on the specific context and treatment goals. Lignin is a complex organic polymer that contains a significant amount of energy, so during anaerobic digestion, the breakdown of lignin in black liquor can contribute to the production of biogas, primarily methane. Meanwhile, lignin is known for its

recalcitrant nature, meaning it is resistant to microbial degradation, so during biological treatment, the presence of lignin in black liquor may impose challenges, as certain microorganisms may struggle to break it down effectively. This can cause inhibitory effect on microbial activity. Therefore, strategies for optimizing lignin degradation and addressing potential inhibitory effects are key considerations in the effective anaerobic digestion of black liquor for its treatment and biogas potential.

In summary, methane is considered a value-added product from the wastewater stream from the pulp and paper industry. The pulp and paper industry when subjected to anaerobic digestion, produces biogas, which can fuel boilers and paper dryers as a form of renewable energy. However, poor biodegradability nature of black liquor causes limitation to biomethane potential, meaning the overall energy output efficiency is less attractive for full-scale application. Optimizing the anaerobic digestion of the pulp and paper industry is an essential step to harvest energy and economic return from the pulp and paper industry (Jian et al. 2021).

2.7.6 Comparison of Aerobic and Anaerobic Digestion of Black Liquor

The anaerobic digestion of black liquor can reduce the environmental impact by the reutilization of black liquor (Norli et al. 2010). Among aerobic and anaerobic, the aerobic biological treatment process can be more challenging due to its continuous aeration requirement, energy usage, and increasing operational cost. Furthermore, the integrated or hybrid system of biological treatment system exhibited better performance with great efficiency in the removal of organic content and color (Ashrafi et al. 2015).

In summary, the choice between aerobic and anaerobic digestion for black liquor treatment depends on various factors, including energy requirements, chemical recovery goals, environmental considerations, and the specific characteristics of the black liquor. Anaerobic digestion, often used in conjunction with recovery boilers, is more prevalent in the pulp and paper industry due to its efficiency in chemical recovery and renewable energy generation. Anaerobic digestion is more efficient for black liquor treatment than in comparison to aerobic digestion, particularly for chemical recovery and minimizing environmental impact (Nishio and Nakashimada 2007). The pulping process imposes a lot of structural changes, and might result in complex compounds, which is better if treated with the help of anaerobic digestion.

2.8 Pretreatment of Black Liquor

Pretreatment of black liquor can play a crucial role in enhancing the valorization of this liquor. Valorization of black liquor includes chemical recovery, lignin extraction and energy recovery, and pretreatment processes are designed to modify the structure of black liquor components, making them more amenable to further processing and extraction of value. Either of these steps help in the management of black liquor in the pulp and paper industry giving rise to a protected environment. There are various pretreatment methods such as pH reduction to disrupt the lignocellulosic structure for extraction of cellulose, coagulation-flocculation using chemical reagents, electrolysis, or electrocoagulation, and/or mechanical treatment methods (Morya et al. 2022).

As a pretreatment step to biological treatment, electrocoagulation has been a method of interest in black liquor treatment for the reduction of COD, polyphenols, and colors. It is a simple method of generating a flocculating agent by electro-oxidation of a sacrificial anode, generally made up of iron or aluminum. According to Zaied and Bellakhal (2009) the electrocoagulation treatment of black liquor helped remove 98% of COD, 92% of polyphenols, and 99% of color intensity with good repeatability relative standard deviation (R.S.D.) less than 3%. Even in the Soda-AQ pulping process of wheat straw, the electrocoagulation process is found to be a low-cost yet very efficient method to treat black liquor (Rastegarfar et al. 2015).

2.9 Electrocoagulation Treatment of Black Liquor

Electrocoagulation occurs via electrolytic reactions at the electrode surface and the formation of coagulants, which are responsible for the precipitation of suspended particles and the adsorption of dissolved contaminants (Ghosh et al. 2008; Kobya et al. 2003). It is a pretreatment process opted for black liquor treatment where the flocculating agent is generated in situ by electro-oxidation of a sacrificial anode which removes pollutants by electrostatic attraction. Black liquor is poorly biodegradable, viscous, very alkaline and contain high color level, so pretreatment is preferable before biological degradation (Doma and Abou-Elela 2003). Among various other chemical pretreatment methods, electrocoagulation is efficient and compact (Chen 2004). Some of the characteristics of the electrocoagulation method of black liquor treatment includes easy operational equipment, short operation time, and no chemical use, thus minimizing the generation

of secondary pollution (Mouedhen et al. 2008). It removes suspended solids to sub-micrometer levels, breaks emulsions (oil, grease, latex), and oxidizes and eradicates heavy metals from water without the use of filters or the addition of separation chemicals.

Electrocoagulation is a complex process occurring because of electrolytic reactions at the surface of electrodes and the formation of coagulants in the aqueous phase. Coagulant is responsible for the aggregation and precipitation of suspended particles, as well as the adsorption of dissolved contaminants (Ghosh et al. 2008; Kobya et al. 2003). It occurs in three consecutive stages. First, the dissolution of metal ions from reactive electrodes helps in the formation of coagulants. In this step, the electrode acting as an anode gets oxidized to produce metal ions, while water is reduced at the electrode acting as a cathode to produce hydroxide ions. Thereafter, the destabilization of particulate colloidal suspension is the second step followed by aggregation of the destabilized suspension and formation of flocs, which later can be removed is the third step of electrocoagulation (Mollah et al. 2001; Rastegarfar et al. 2015).

When iron and aluminum metal electrodes are used, the generated Fe^{+3} or Al^{+3} ions undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides (Ozyonar and Karagozoglu 2011). The dissolution of anode and cathode takes place giving out aqueous state aluminum ions (Al^{+3}) and OH^- . These ions transform to form $\text{Al}(\text{OH})_3$ in solid form, which prompts the removal of soluble organic compounds and colloidal particles by surface complexation or electrostatic adsorption (Kalyani et al. 2009). Later these flocs can be easily removed from an aqueous solution by precipitation, floatation, or filtration (KOBYA et al. 2006).

This method of electro-oxidation with the help of a sacrificial anode could be successfully deployed for many purposes. In the context of industrial wastewater, this technique was used for the treatment of textile effluents, aircraft industry effluent, and pulp and paper mill effluents (Katal and Pahlavanzadeh 2011; Meas et al. 2010; Sridhar et al. 2011; Zodi et al. 2010). A similar treatment process was applied by the dairy industry to remove 95 % of total suspended solids (TSS) (Tchamango et al. 2010). Likewise, another example of the removal of 87% of color and 55% of COD from wastewater was reported by an olive mill (Belaid et al. 2013). This method as a pretreatment is highly recommended for increasing the effectiveness of biological treatment of pulp and paper industry wastewater.

CHAPTER 3: MATERIALS AND METHODS

This chapter covers a detailed discussion of various aspects, including research methodology, materials and instruments used, experimental design, sample preparation, process optimization, and chemical and mathematical analysis. It provides an overview of analytical techniques and procedures used for black liquor characterization, comparison, and treatment.

3.1 Process Flow Diagram

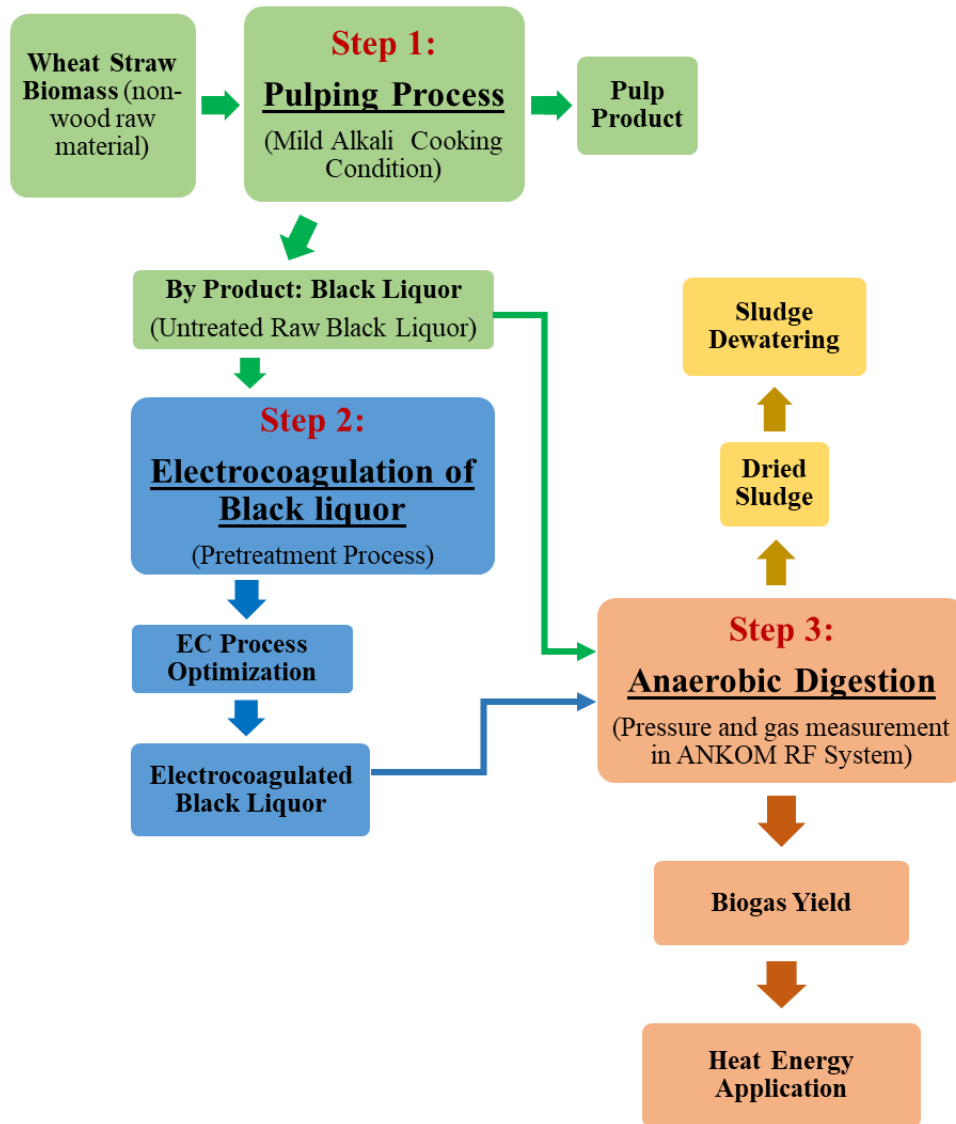


Figure 3.1 Process Flow Diagram of Treatment of Black Liquor

Figure 3.1 represents the entire process involved in the research methodology. In the first step, the non-wood-based raw material, i.e., wheat straw was processed using similar conditions as that in the pulp and paper industry, generating pulp and black liquor as the by-product. The pulp produced having further industrial value, went through washing and bleaching as the requirement of the final product, whereas the toxic black liquor needed to be treated, which was the main aim of this study. This untreated black liquor, termed as raw black liquor in this thesis, did not undergo any treatment steps until then. Moving forward, as a second step, the raw black liquor went through the pretreatment process, and there it passed through the electrocoagulation unit. This process of pretreatment of black liquor was optimized after conducting analysis and characterization of different black liquor samples by calculating and comparing the analytical parameters. Thereafter, the third step was anaerobic digestion. Both the untreated raw black liquor and the electrocoagulated black liquor were digested in gas modules with varying concentrations. The gas modules measured the pressure developed, from which the value of gas production from each type of black liquor sample was interpreted and compared. This process of biological degradation under anaerobic conditions resulted in sludge. The sludge could be further processed according to the need, and biogas on the other hand was generated as a value-added product. This biogas could be utilized for heat energy applications.

3.2 Properties of Black Liquor Used

Table 3.1 Characteristics of Raw Black Liquor

Parameters	Value	Unit
pH	12.10	pH
COD	41,900	mg/L
Phenol	362	mg/L
Total Solid (TS)	41,950	mg/L
Total Dissolved Solid (TDS)	15,800	mg/L
Color	38.58	WI
Lignin impurities	10,256	mg/L
Lignin Content	25	%w/w

The black liquor used for various analyses, comparisons, and treatment methods was prepared in a working reactor in the laboratory by using a mild alkali cooking process. The cooking process was sulfur-free to replicate the similar conditions of Red Leaf Pulp Ltd., Canada. First, the dried wheat straw was chopped and ground and then digested at 160 °C using 15% NaOH for an hour. Soon after the digestion of the biomass, a dark color liquid was produced, which was separated from the solids remaining and collected in jars as black liquor for further treatment analysis. Characteristics of raw black liquor after collection are shown in Table 3.1. This data was taken before pH adjustment and electrocoagulation treatment. According to this data, the black liquor was very alkaline with a pH value of 12.10. Likewise, the values for COD, phenol, TS, TDS, and lignin impurities of the black liquor were 41,900 mg/L, 362 mg/L, 41,950 mg/L, 15,800 mg/L, and 10256 mg/L, respectively. This concluded that the black liquor generated in the lab had 25% w/w lignin content, which was on the lower side as compared to the composition constituents of typical black liquors in wood-based black liquor by-products which contain about 35% to 45% w/w lignin (Speight 2023). It was very dark in color with a lower color intensity of 38.58 Whiteness Index (WI) value indicating the presence of an abundance of lignin in it after the pulping process (Figure 3.2).

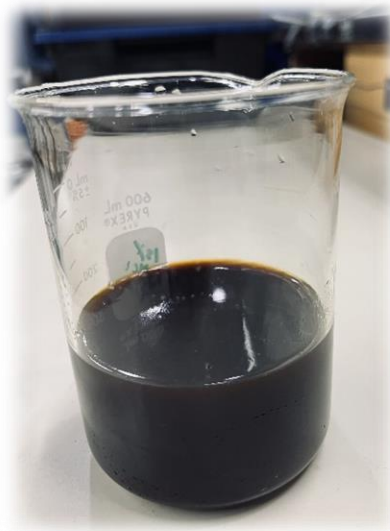


Figure 3.2 Black Liquor used for Study

3.3 Electrocoagulation Treatment of Black Liquor

The obtained black liquor was very dark in color, viscous, highly alkaline with high phenol content of 362 mg/L and high lignin impurities of 10,256 mg/L, which imposed treat to the environment if discharged, hence a proper treatment of the black liquor was required. Electrocoagulation was the primary process of black liquor treatment in this research thesis. This was an intensive process executed systematically with the help of experimental designs and runs in Minitab, followed by delicate handling and timely experimentation of all the sample runs. All of these have been detailed in the following sub-sections.

3.3.1 Experimental Design

Table 3.2 shows the experimental design created for carrying out the electrocoagulation process in the laboratory. As this research study included the optimization of the electrocoagulation process, three operational parameters: initial pH level (7, 9, and 11), voltage (10, 20, and 30) V, and electrolysis time (10, 35, and 60) min were considered. The pH range chosen considering the alkaline nature of the black liquor and its ability to be treated in an alkaline region beyond the neutral range. The voltage and the electrolysis time ranges were taken considering the optimal conditions obtained in the previous electrocoagulation treatment studies for black liquor obtained from kraft cooking process of wood and soda-AQ pulping process of wheat straw (Zaied and Bellakhal 2009). The difference in variation of runs and their comparison gave the best condition thereafter. Hence, for this reason, response surface methodology (RSM) was used to obtain the Box–Behnken experimental design runs for those factors in Minitab. This helped to place each independent variable, at one of three equally spaced values, usually coded as -1, 0, +1, essentially suppressing selected runs to maintain the higher order surface definition (Box and Behnken 1960; Institution of Mechanical Engineers (Great Britain) 2012).

The design contained three factors, fifteen base runs, and one base block with two replicates making it a total of 30 runs and two blocks. Later this design was fitted into the Minitab platform for statistical analysis and process optimization.

Table 3.2 Experimental Design for Electrocoagulation Process

Std Order	Run Order	Pt Type	Blocks	pH Level	Voltage (V)	Electrolysis Time (min)
9	1	2	1	9	10	10
10	2	2	1	9	30	10
8	3	2	1	11	20	60
15	4	0	1	9	20	35
3	5	2	1	7	30	35
2	6	2	1	11	10	35
7	7	2	1	7	20	60
5	8	2	1	7	20	10
13	9	0	1	9	20	35
4	10	2	1	11	30	35
11	11	2	1	9	10	60
14	12	0	1	9	20	35
6	13	2	1	11	20	10
1	14	2	1	7	10	35
12	15	2	1	9	30	60
20	16	2	2	7	20	10
29	17	0	2	9	20	35
17	18	2	2	11	10	35
24	19	2	2	9	10	10
30	20	0	2	9	20	35
25	21	2	2	9	30	10
19	22	2	2	11	30	35
22	23	2	2	7	20	60
26	24	2	2	9	10	60
18	25	2	2	7	30	35
27	26	2	2	9	30	60
16	27	2	2	7	10	35
23	28	2	2	11	20	60
28	29	0	2	9	20	35
21	30	2	2	11	20	10

3.3.2 Experimental Setup

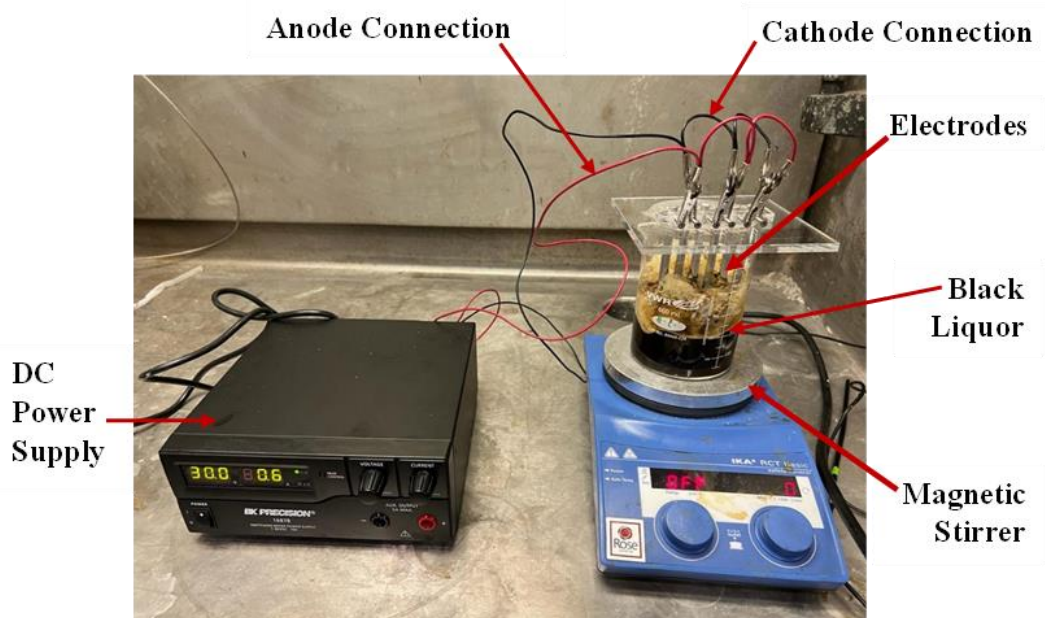


Figure 3.3 Laboratory Setup of Electrocoagulation Process

A beaker filled with black liquor, covered with a special covering of plexiglass supporting a series of six parallel aluminum electrodes, connected to a DC power supply to maintain constant voltage was used for conducting electrocoagulation in the laboratory (Figure 3.3). The experimental set up was considered based on the working principle of electrocoagulation treatment of wastewater. It followed the principle of electrochemistry, according to which when electricity is supplied, the cathode is oxidized and loses electrons, while the water is reduced and gains electrons, thereby making the wastewater treated (Butler et al. 2011). The design was also inspired by the previous study carried out for the electrocoagulation treatment of black liquor produced from kraft pulping process (Zaied and Bellakhal 2009). Three of the electrodes were used as sacrificial anodes and the other three as cathodes, alternatively. Aluminum was used for making the electrodes considering its simplicity, availability, and efficiency in the process of electrolysis (Kalyani et al. 2009; Zaied and Bellakhal 2009). The aluminum electrodes were arranged in such a way that when black liquor was placed in the beaker and covered by the plexiglass, the electrodes would be partially submerged in the liquid. In the experiments conducted, 250 ml of black liquor was used in each test, so that 41.40 mm of the electrodes would be submerged. This consistency

was necessary to maintain experimental accuracy and later could affect the amount of current flow for electrolysis to occur.

3.3.2 Preparation of Sample and Experimentation

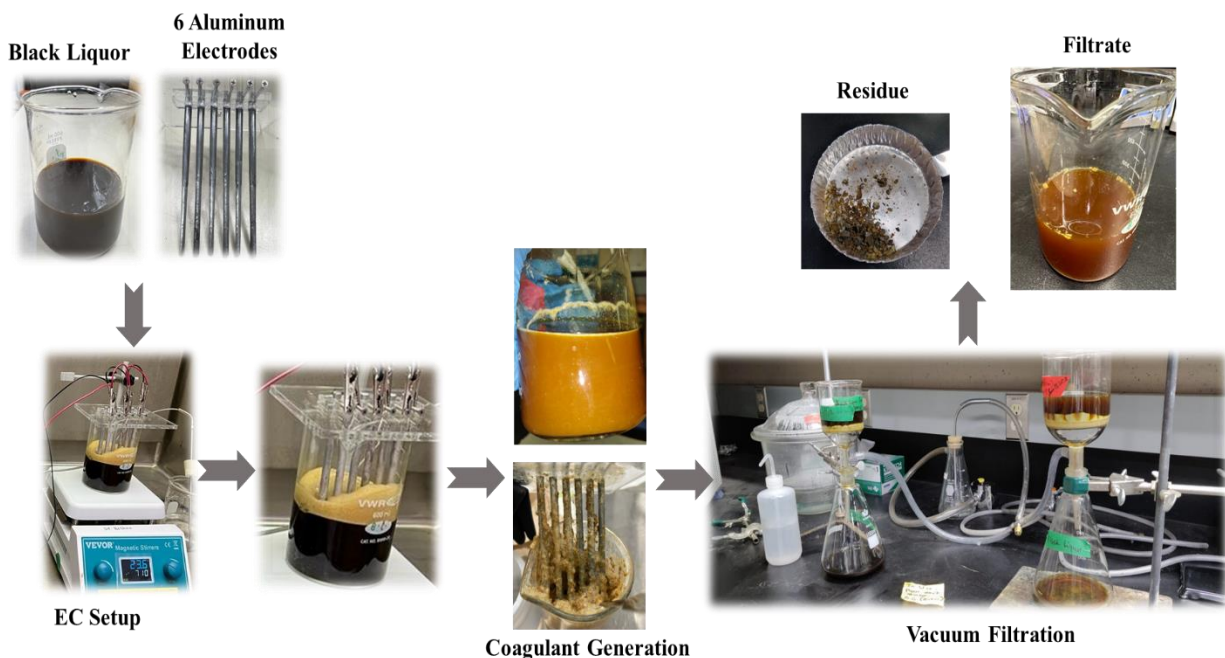


Figure 3.4 The Picturization of Electrocoagulation Process

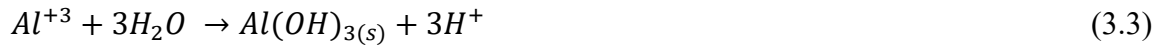
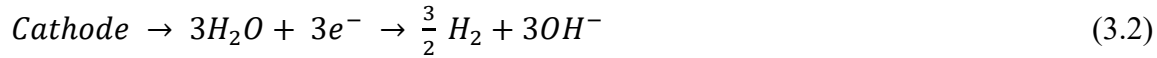
Figure 3.4 visualizes the pretreatment process of electrocoagulation used for black liquor treatment. Considering that every electrocoagulation process specific to a certain type of wastewater varies in terms of initial pH, it was important to consider initial pH as an important operational parameter (BL2F 2020). Hence, thereafter, the pH of black liquor was adjusted with 2M sulfuric acid solution as required and the experimental runs were carried out in order. This created a certain shift in characteristics of the black liquor as presented in Table 3.3. All tests were conducted at 25 °C using 250 mL of black liquor solution stirred continuously with a magnetic stirrer at 280 rpm speed. Simultaneously, the current outputs of all the experimental runs were noted throughout the experiment time and averaged to find out the current density. After each run, the electrodes were treated with 15% hydrochloric acid, polished with sandpaper, washed, and then dried to remove oxides and passivation layers, and prevent precipitation in the electrodes (Mahesh et al. 2006; Rastegarfar et al. 2015). The electrodes were also replaced in case of

excessive abrasion on the surface because the abrasion would have reduced the surface areas of the electrodes resulting in the reduction of current flow and lower rate of floc formation. In this case, one set of electrodes lasted for four runs on average before abrasion started appearing on them, so they were replaced immediately, and this consistency was maintained throughout the 30 experiments to avoid inaccuracy in data interpretation.

Table 3.3 Characteristics of pH-reduced Black Liquors

pH	COD (mg/L)	Phenol (mg/L)	TS (mg/L)	TDS (mg/L)	Color (WI)
7	39200	332	42750	13900	39.42
9	41500	352	42700	14000	39.04
11	45800	362	41500	14100	38.88

The following electrochemical reaction occurred for the formation of coagulating agent and floc using aluminum electrodes (Can et al. 2006; Daneshvar et al. 2006; Kalyani et al. 2009):



The flocks of $Al(OH)_3$ formed during the experiment had larger surface areas, aiding rapid adsorption of soluble organic compounds in black liquor. Furthermore, those flocks were good for trapping colloids present in the black liquor. All these flocks formed were later removed with the help of a vacuum filtration system as shown in Figure 3.4.

3.3.3 Calculation of Analytical Parameters

The obtained solution from the electrocoagulation process was filtrated with the help of a vacuum filtration apparatus, to separate the residue and the filtrate. The filtrates from each run were compared with the pH-adjusted black liquor solution with the help of various analytical parameters like COD, phenol, TS, TDS, color intensity, and pH to find the optimum condition for each parameter. The removal efficiency of the treatment was determined mostly by monitoring the decrease in the value of those parameters. Change in pH on the other hand was considered optimum

by its ability to reside in the zone suitable for anaerobic digestion. All the detailed steps applied to analyze and calculate each parameter are explained in the subsection below.

3.3.3.1 Chemical Oxygen Demand (COD) Analysis



Figure 3.5 Chemical Oxygen Demand (COD) Analyzing Unit

COD was determined by the standard potassium dichromate method or the reactor digestion method using high-range COD vials from Hach (APHA 2023a). COD of all black liquor samples before and after treatment were measured. The COD of raw untreated black liquor, along with pH-adjusted black liquor and all the treated liquors obtained after electrocoagulation followed by vacuum filtration were analyzed.

First, for sample preparation, each black liquor sample was homogenized with the help of a magnetic stirring device, and then consecutive samples with varying dilution factors of 10, 100, and 200 were prepared. After that, 2 mL of the sample was added to a COD vial at a 45-degree angle, capped tightly, rinsed with water, wiped, and then inverted gently several times to ensure proper mixing. Similar steps were undertaken for the blank sample except for one criterion, i.e., deionized water was used instead of the sample. The sample vials were inserted in a preheated reactor, DRB200, for two hours at 150 °C. Then, the vials were cooled down to 120 °C within the reactor, and soon after this they were inverted several times and placed in a rack to cool to room temperature at 25 °C. As the sample vials got cooled, they were analyzed with the help of DR6000 ultraviolet-visible spectrophotometer for the colorimetric determination of COD at 620 nm (Figure 3.5).

After testing with blank samples and their serial dilutions, the desired result was obtained within the range of 20-1500 mg/L. Only the selected samples falling under this value were considered and calculated after multiplying with their dilution factor. All the experimental analysis were repeated two times to avoid any analytical errors.

3.3.3.2 Phenol Analysis

Phenol content was measured by the 4-aminoantipyrine method at room temperature with the help of a phenol measuring kit called Phenols TNTplus Vial Test (5-150 mg/L) from Hach (APHA 1998) (Figure 3.6). First, the sample was homogenized and diluted with dilution factors 10 and 20. Thereafter, 0.40 mL of sample volume was added to the phenol vial, then the cap was closed tightly and inverted several times to ensure proper mixing. Again, 0.40 mL of phenol reagent 'A' was added to the sample vial and closed with a dosicap and inverted several times.

Phenol determination from this method was sensitive to the increasing time, so after a few minutes of reaction time, the vials were cleaned and read under DR6000 ultraviolet-visible spectrophotometer at 510 nm absorbance considering the blank solution with deionized water. Only those reading between 5 to 150 mg/L were considered and multiplied with their respective dilution factors to find out the actual phenol content in each sample. All the samples were replicated to ensure the accuracy of the chemical analysis.



Figure 3.6 Phenol TNTplus Reagent Set

3.3.3.3 Total Solid (TS) Analysis



Figure 3.7 Oven Dried Samples of Black Liquor

Total solid content is the quantity of solids present in a known volume of sample (APHA 2023b; Metcalf & Eddy et al. 2013). So, for the measurement, first, an aluminum dish was weighed, tarred to zero, and then filled with a known volume of black liquor sample. The procedure was duplicated for each sample. Thereafter, each sample with the vessel was kept in an oven at 105 °C for 24 h or more until the dried residue would give a constant weight (Figure 3.7). After complete drying of the samples, their weight was taken again for the calculation. The total solid concentration was the difference between the dry weight of the aluminum dish with the residue and the weight of the dish without it. The obtained weight was expressed in percentage terms by dividing it by the original weight. Also, the obtained weight was expressed in mg/L by dividing it by the volume of the sample used for the analysis purpose. The technique required the sampling containers to be kept in a desiccator, a sealed glass container that contained material able to absorb moisture. This step ensured that the weighing was not biased by water condensing on the sampling container.

3.3.3.4 Total Dissolved Solid (TDS) Analysis

The Extech EC600 Waterproof Conductivity Kit was used for measuring the Total Dissolved Solid (TDS) of all the black liquor samples (Figure 3.8). This 7-in-1 kit had an inbuilt TDS measuring program, and a probe submersed in distilled water, which helped in the measurement of TDS of any liquid sample in the range of 0-100 mg/L.



Figure 3.8 EC600 Waterproof 7-in-1 Conductivity Kit

For measurement, first, the sample black liquor was homogenized well, and then the TDS probe was inserted inside the liquid and kept until a steady reading was observed. After each reading, the probe was wiped with distilled water and dried well. All readings were repeated to maintain the accuracy.

3.3.3.5 Color Analysis



Figure 3.9 Digital Precise Colorimeter

Color intensity was monitored and compared by measuring the whiteness index by using a colorimeter, WR10QC-8 (Shahabi-Ghahfarrokhi et al. 2015; Shahabi-Ghahfarrokhi and Babaei-Ghazvini 2019) (Figure 3.9). The portable colorimeter used the CIE standard illuminant D65 and a pointer from the CIE chromaticity diagram.

To carry out this analysis, first, the samples were homogenized well and 1 mL each was pipetted out on a white square cut filter paper, which was then kept at room temperature for 48 h to completely dry. The dried film specimens were placed on a white standard plate ($L^* = 100$, $a^* = -1$, $b^* = 2$) and the colorimeter then measured the tristimulus color values of L (lightness), a (redness/greenness), and b (yellowness/blueness) at five random points on each film sample. All the measurements were repeated thrice and the shape and size of the specimens for all samples were kept the same. Those readings were then averaged to provide a more precise and accurate depiction of the specimen's color. Colors are described by L values ranging from 0 (black) to 100 (white); negative values of a (greenness) to positive values (redness); and negative values of b (blueness) to positive values (yellowness). Furthermore, the total color difference (ΔE), whiteness index (WI), and yellowness index (YI) were calculated using the following equations:

$$\Delta E = \{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2\}^{0.5} \quad (3.4)$$

$$WI = 100 - \{(100 - L)^2 + (a)^2 + (b)^2\}^{0.5} \quad (3.5)$$

$$YI = \frac{(142.86 \times b)}{L} \quad (3.6)$$

3.3.3.6 pH Analysis

The pH of the black liquor samples was measured using the Extech EC600 Waterproof 7-in-1 Conductivity Kit. The kit contained a pH probe submersed in a 4M Potassium Chloride (KCl) solution. When required, the probe was dipped inside a stirring sample of black liquor. The reading fluctuated for a while, so the one with the steady reading was recorded. The measurement was repeated to maintain the precision of the process. The pH probe was calibrated every 3 months to get accurate readings.

3.3.4 Calculation of Specific Energy Consumption

The specific energy consumption (SEC) was calculated as an important economic function to compare the various optimum conditions obtained concerning COD, phenol, TS, TDS, and color intensity removal. It summarized the total energy requirement under different operating conditions, pH, and time to remove 1 kg of COD during the electrocoagulation process according to the following equation (Rastegarfar et al. 2015; Zaied and Bellakhal 2009):

$$SEC \text{ (kW per kg of COD)} = \frac{V * I * t}{60 * 0.25 (C_0 - C_t)} \quad (3.7)$$

Where: V is the applied voltage (V),

I is the current amount (A),

t is the electrolysis time (min),

C₀ is the initial concentration (g/L),

C_t is the concentration value of COD (g/L),

t is time and

0.25 is the volume of black liquor used for electrocoagulation.

In the end, the optimum condition having the lowest SEC was considered the overall optimal condition for the electrocoagulation method of black liquor treatment.

3.3.5 Process Optimization

The RSM was used to design the experiment and was used for statistical analysis and optimization of the electrocoagulation process, as well. The three operational factors; pH, voltage, and electrolysis time were considered as continuous parameters. The Box–Behnken design was fitted to understand the interaction between the factors on different conditions of the electrocoagulation process. As the response surface analysis has four key output that includes the p-values, the coefficients, R², and the residual plots, the interpretation of the design was done by considering the following steps:

1. A Pareto chart was used to compare the relative magnitude of the statistical significance and interaction effects. It helped in determining the most significant factor and the interactions that contribute most to the variability in the response.
2. The statistical significance between the response and each term in the model was done by comparing the p-value for the term to the significance level. When the p-value was less than or equal to the significance level, it was concluded that there was a statistically significant association between the response variable and the term.
3. Examination of the goodness-of-fit statistics in the Model Summary table was carried out to determine how well the model fitted the data and for this parameters S, R^2 , R^2 (adjusted), and R^2 (predicted) were considered.
4. In addition, the data were analyzed using residual plots, normality plots, and histograms to confirm the assumption of the analysis.
5. The surface contour plot was analyzed to identify the optimum condition for the response.
6. Optimization analysis was carried out and results were presented.

3.3.6 Characterization of Black Liquor

To gain a comprehensive understanding of the properties of raw black liquor, electrocoagulated black liquor, and the residue obtained after filtration of EC BL, a detailed characterization was imperative. The following characterization techniques were employed:

3.3.6.1 Proximate Analysis of Black Liquor

The proximate analysis of black liquor included the determination of ash content, moisture content, volatile matter content and fixed carbon. Before carrying out this experimental analysis, the black liquor samples were oven-dried at 105 °C for 24 h to remove all the moisture content, hence giving rise to dry basis analysis results and wet basis analysis results. Likewise, the residue after electrocoagulation was also dried. The rest of the parameters were determined by the following methods:

1. Volatile matter was determined as the loss in mass, less than due to moisture when a sample was heated at 900 °C for seven minutes. This procedure was undertaken out of contact with air under standardized conditions (EN 2009).

2. The ash test involved taking a known amount of sample, placing the weighed sample into a dried, and pre-weighed porcelain crucible, burning away the polymer in an air atmosphere at a temperature of 600 °C, and weighing the crucible after it had been cooled to room temperature in a desiccator (Sluiter et al. 2008).
3. Fixed carbon content was calculated from 100% reduced by moisture content (MC), ash content, and volatile matter (Anshariah et al. 2020) as follows:

$$FC \% = 100\% - (MC\% + AC \% + VM\%) \quad (3.8)$$

3.3.6.2 Lignin Content Analysis

Analyzing the lignin content of black liquor is an important step in the pulp and paper industry, as it provides valuable information about the recovery of lignin and the efficiency of the pulping process. Here in this research, it was an important step to find out the removal percentage of lignin after electrocoagulation. The most common method for analyzing lignin content in black liquor, i.e., the Klason lignin determination was used (Bajpai 2018). In the first step, 250 mL of black liquor sample was taken, and then acid hydrolysis was carried out by reducing the pH of the black liquor to 3 pH using 72% H₂SO₄. This induced the concentrated sulfuric acid to hydrolyze the cellulose and hemicellulose, leaving the lignin behind as a solid residue. This liquid was kept on the countertop overnight for proper dissolution and sedimentation, and then filtrated, washed 15 times, and dried to get the solid residue (precipitated lignin) from the liquid.

The lignin content was expressed as a percentage based on the weight of the original black liquor sample. This method provided an estimation of the lignin content in the black liquor as there could be precipitation of other unknown impurities as well after the process of acid hydrolysis. The same conditions such as an equal amount of samples, and the same number of washing and timing were considered to maintain uniformity and accuracy in measurement.

3.3.6.3 Thermogravimetric Analysis (TGA)

In this research, TGA analysis was performed using a thermogravimetric analyzer (Perkin-Elmer TGA 8000, Llantrisant, UK). Approximately 10 mg of oven-dried sample of black liquor was subjected to heating from 50 to 900 °C at a heating rate of 20 °C/min, under a constant nitrogen gas flow of 30 cm³/min. The differential form of TGA (DTG) was obtained by differentiating the

TGA values, which helped in identifying the maximum disintegration temperature at each stage of thermal degradation.

3.3.6.4 Fourier Transform Infrared Spectroscopy (FTIR)

The attenuated total reflectance-FTIR spectrophotometer (Spectrum 3 Tri-Range MIR/NIR/FIR Spectrometer, PerkinElmer, USA) was used to examine the Fourier Transform Infrared Spectroscopy (FTIR) spectra of the film samples. The sample was oven-dried for 24 h at 105 °C, cooled, and a very small pinch of it was placed directly on the ATR crystal. The analysis was conducted within the wavenumber ranges of 4000 - 500 cm^{-1} , with a resolution of 4 cm^{-1} .

3.3.6.5 X-ray Fluorescence (XRF) Analysis

X-ray Fluorescence (XRF) analysis is a useful analytical technique for determining the elemental composition of materials, including black liquor. When applied to black liquor, XRF analysis provides information about the concentrations of various elements present in the liquid. To perform XRF analysis, samples of black liquor were oven-dried at 105 °C for 24 h first and then ash-dried at 600 °C for 6 h (Figure 3.10). Thereafter, they were serially exposed to high energy X-ray radiation, which caused the atoms in the sample to become temporarily excited, leading to the emission of characteristic X-ray fluorescence radiation. The emission of characteristic X-ray fluorescence radiation caused it to contain characteristic peaks corresponding to the elements present in the sample and the XRF instrument detected and quantified those X-ray signals, allowing for the identification and quantification of elements.

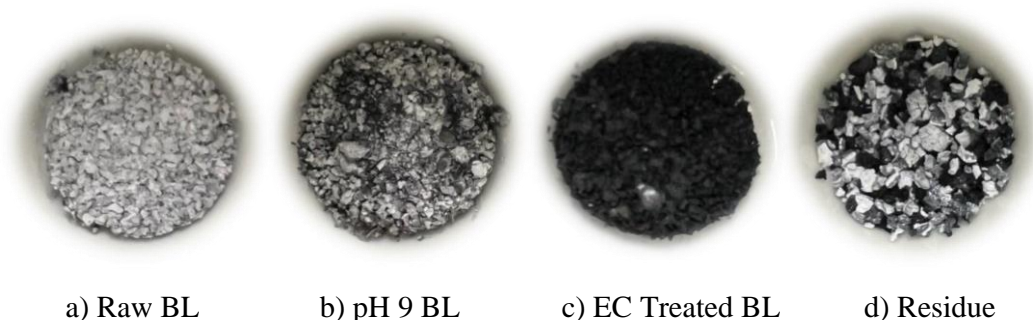


Figure 3.10 Ash of Raw BL, pH 9 BL, EC Treated BL, and Residue

3.4 Anaerobic Digestion and Biomethane Potential of Black Liquor

The anaerobic digestion study was carried out with untreated black liquor and black liquor after the electrocoagulation process. The black liquor and the mixture were analyzed for their pH, total solids, and volatile matter. The aromatic organics in the black liquor are prone to inhibit microbial activity along with an increase in osmotic pressure from high inorganic salts leading to reduced digestion. So, this research study investigated the biomethane production potential from the black liquor and the effect on the process and quality of the digested sludge along with their comparison with the electrocoagulated black liquor.

3.4.1 ANKOM RF Gas Production System Set Up

The biological digestion process under anaerobic conditions was carried out in the ANKOM RF Gas Production System (Figure 3.11). This system is designed to measure the kinetics of microbial fermentation in an automated fashion by monitoring the gas pressure within multiple modules and remotely recording the data in computer spreadsheets. Equipped with a temperature sensor, each Module could also monitor the temperature of its environment and could communicate information to a computer using radio frequency (RF) transmission. From the computer interface, numerous variables such as data recording intervals and the automatic release of pressure through internal valves in each module could be controlled.

To set up the ANKOM system, first GPMx software was installed, and a pathway was created in the data interface to obtain the value of pressure developed because of the production of gas due to anaerobic digestion in modules. The modules, and the vent valves in the modules, all were cleaned and dried completely before use. One reference module was used which provided a default value of 14.5 psi for ambient pressure, which was connected as soon as the GPMx software was run. Likewise, the base coordinator was connected, and each module was checked with purging to verify the vent valve operation for each module.

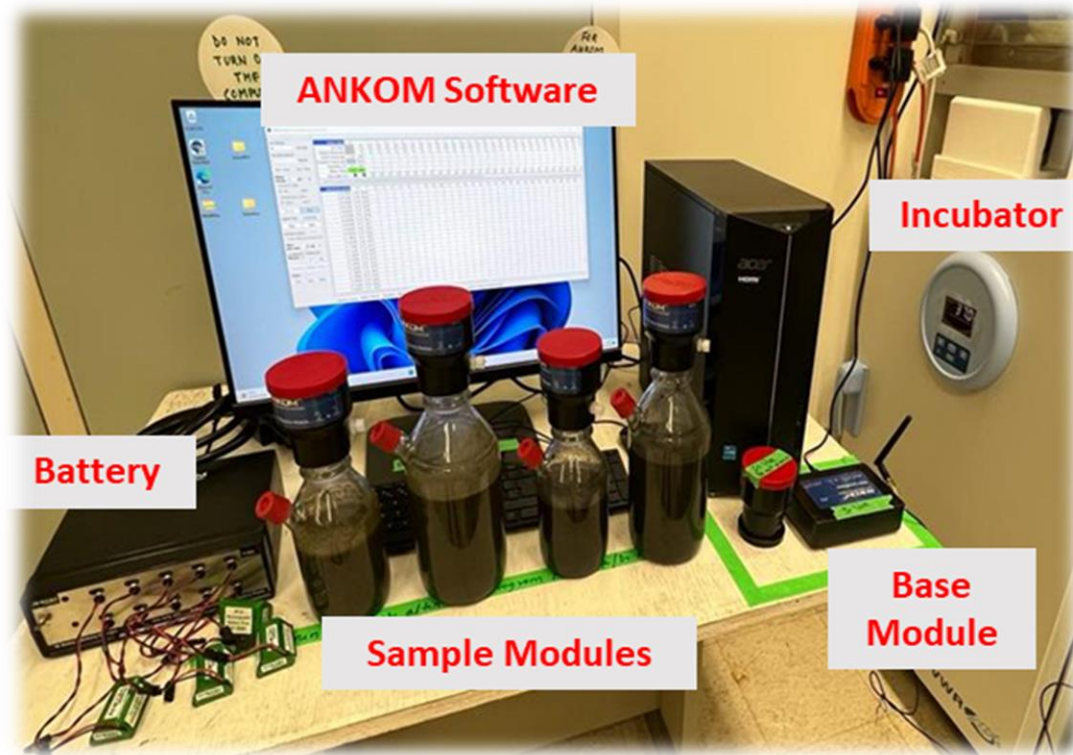


Figure 3.11 Experimental Setup for ANKOM System

3.4.2 Sample Preparation and Experimentation

The inoculum for the study was obtained from the anaerobic digester of the City of Saskatoon wastewater treatment plant. The effluent from the anaerobic digester was used, so that it contained anaerobic microorganisms. Since, the inoculum was an already digested sludge, it had very less traces of biogas potential. This ensured that it could be set as a control for the process and would not interfere with the gas production ability of the black liquor. The black liquor used in the digestion process was varied between 10% and 30% of the total mixture of liquid and in each process, 10% and 30% of distilled water mixed with the inoculum was digested to get the gas production ability of control and create an accurate result. Altogether three modules were analyzed in one batch, one being the control and the other two with varying percentage content of black liquor samples. The batch reactor anaerobic digestion was carried out at 37 °C. It was made sure that the mixture was set outside in the module for a day before conducting the experiment. During the period of digestion, each module was manually shaken for 30 sec every day.

3.4.3 Calculation of Biomethane Potential of Black Liquor

ANKOM system used the help of inbuilt ANKOM Software to provide cumulative pressure translated to gas yield with the help of ‘Ideal Gas Law’ and ‘Avogadro’s Law’. The values were then differentiated with the control (sludge yield) to compare the actual gas yield in each type of straw. The digestion was performed for 36 days till no significant amount of gas was produced. The system was configurable to allow for gas pressure measurements in either psi or mbar units, so the gas pressure measured during the study was converted to moles of gas produced using the ‘Ideal Gas Law’ as follows:

$$n = p \left(\frac{V}{RT} \right) \quad (3.9)$$

Where: n = gas produced in moles (mol)

p = pressure in kilopascal (kPa)

V = head-space volume in the glass bottle in liters (L)

T = temperature in kelvin (K)

R = gas constant (3.314472 L.kPa.K⁻¹mol⁻¹)

This value of ‘n’ was then converted to milliliters (mL) of gas produced using Avogadro’s law. Using Avogadro’s Law, at atmospheric pressure measured in psi (1 psi = 6.894757293 kilopascal), 1 mole will occupy 22.4 L at 273.15°K and 101.325 kPa (standard conditions). Therefore, gas measured in moles was converted to gas measured in mL as follows:

$$\text{gas produced (in ml)} = n * 22.4 * 1000 \quad (3.10)$$

The sludge mixture before and after anaerobic digestion was collected and analyzed to measure pH, TS, COD, and VM.

3.4.4 Calculation of Analytical Parameters

The parameters such as COD, VM, and pH were analyzed to understand the biotoxicity of black liquor produced from the wheat straw pulping process in comparison to the electrocoagulation treated black liquor. Altogether twelve samples including 10% control and 30%

control underwent this analysis. The four samples were Raw BL with 10% and 30% volume constituent before and after anaerobic digestion and the other four were EC treated BL with 10% and 30% volume constituent before and after anaerobic digestion.

3.4.4.1 COD Analysis

COD was determined by the standard potassium dichromate method or the reactor digestion method using high-range COD vials from Hach (APHA 2023b). COD of all sludge mixtures before and after biological degradation were measured.

First, for the sample preparation, each sludge mixture sample was homogenized using a magnetic stirring device, and then transferred to a 15 mL falcon tube for centrifugation. The centrifugation was done on ‘Eppendorf Centrifuge 5804 R’ at 400 rotation per minute (RPM) for 15 min at room temperature. This generated an aliquot, which was again diluted with varying dilution factors of 10 and 100. After that, colorimetric determination of COD at 620 nm was carried out using an ultraviolet-visible spectrophotometer as explained in section 3.3.3.1 of this thesis.

3.3.4.2 Volatile Matter (VM) Content Analysis

Volatile matter in the context of black liquor refers to the organic components of black liquor that have the potential to vaporize or release as gases when subjected to heat or elevated temperatures. Black liquor is a byproduct of the pulp and paper industry, primarily composed of lignin, hemicellulose, and other wood-derived organic compounds and these organic components are what make up the volatile matter in black liquor. In general, black liquor has a high content of volatile organic matter, and a great potential for biogas potential and energy recovery but can be affected by other impurities and toxicity derived during the pulping process. In this study, volatile matter was determined by the standard procedure, as the loss in mass, less than due to moisture, when a sample was heated at 900 °C for a period of 7 min. This procedure was undertaken out of contact with air under standardized conditions (EN 2009).

3.3.4.3 pH Analysis

The pH of the sludge mixture before and after biological degradation was measured using Extech EC600 Waterproof 7-in-1 Conductivity Kit. The reading fluctuated for a while, so the one

with steady reading was recorded. The measurement was repeated to maintain the precision of the process. Also, the pH probe was calibrated every 3 months to get accurate readings.

3.3.4.3 TS Analysis

The total solid content for the sludge samples was measured by following the same procedures mentioned in the 3.3.3.3 section of this thesis. For the sample preparation, the samples after centrifugation were used.

CHAPTER 4: RESULTS AND DISCUSSION

This chapter presents the comprehensive characterization of raw black liquor and electrocoagulated black liquor. It encompasses the use of Minitab Response Surface Methodology for designing experiments for electrocoagulation and finding out the optimum condition considering COD, phenol, TS, TDS, pH, and color. Also, it summarizes the SEC methodology for choosing the best condition to use for anaerobic digestion. Additionally, it presents the results obtained from anaerobic digestion of black liquor, both untreated and pretreated ones, their comparison and preferability with the justification of various parameters such as VM, pH, TS, COD, and analytical methods such as FTIR, TGA, DTGA, and XRF. The findings presented in this chapter provide insights into the significance of electrocoagulation as a pretreatment method to optimize the biological degradation process. Likewise, anaerobic digestion is well explained in terms of black liquor.

4.1 Electrocoagulation

This electrolytic reaction is affected by various operational parameters and might have non-uniform results of coagulant formation and black liquor treatment. Similarly, the experimental runs obtained in Minitab had varying combinations of operational parameters (electrolysis time, initial pH level, and voltage), all resulting in differences in the effect of electrocoagulation. So, to understand the effect of electrocoagulation in the treatment of black liquor produced from the wheat straw pulping process, six analytical parameters (COD, phenol, TS, TDS, color intensity, and pH) were considered. The decrease in the value of those operational parameters helped us understand the treatment efficiency of each run, hence, firstly, the optimum condition concerning each of those parameters is discussed in the following sections:

4.1.1 Effect on COD Removal

Table 4.1 Initial, Final and % Decrease in COD after Electrocoagulation of Black Liquor under Different Operational Conditions of pH, Voltage and Electrolysis Time (Green and red highlights denote the operational conditions with maximum and minimum COD removal efficiency, respectively)

S.N.	pH Level	Voltage (V)	Electrolysis Time (min)	Initial COD (mg/L)	Final COD (mg/L)	Decrease in COD (%)
1	9	10	10	41500	25900	37.59
2	9	30	10	41500	24800	40.24
3	11	20	60	45800	34600	24.45
4	9	20	35	41500	21500	48.19
5	7	30	35	39200	21800	44.39
6	11	10	35	45800	30000	34.50
7	7	20	60	39200	25700	34.44
8	7	20	10	39200	23300	40.56
9	9	20	35	41500	21000	49.40
10	11	30	35	45800	35200	23.14
11	9	10	60	41500	21000	49.40
12	9	20	35	41500	21400	48.43
13	11	20	10	45800	31800	30.57
14	7	10	35	39200	29200	25.51
15	9	30	60	41500	29000	30.12
16	7	20	10	39200	23100	41.07
17	9	20	35	41500	21100	49.16
18	11	10	35	45800	28300	38.21
19	9	10	10	41500	26700	35.66
20	9	20	35	41500	21300	48.67
21	9	30	10	41500	24200	41.69
22	11	30	35	45800	35200	23.14
23	7	20	60	39200	23300	40.56
24	9	10	60	41500	21000	49.40
25	7	30	35	39200	21700	44.64
26	9	30	60	41500	28800	30.60
27	7	10	35	39200	29500	24.74
28	11	20	60	45800	33900	25.98
29	9	20	35	41500	21300	48.67
30	11	20	10	45800	30900	32.53

The removal of organic compounds in black liquor was determined by monitoring the decrease of COD by electrocoagulation process. From a minimum of 23.14% to a maximum of 49.40% COD removal could be achieved during experimental runs. Table 4.1 shows all the runs with their COD % removal after electrocoagulation, where the green color highlighted ones had the maximum COD removal and the red color highlighted one had the least COD removal. The maximum removal efficiency was found at three different experimental runs (9, 11, and 24). Run 9 was performed with black liquor of initial pH 9 at 20 V voltage, 0.87 A current, and 33.02 mA/cm² current density for 35 min, run 11 with initial pH 9 at 10 V voltage, 1.03 A current, and 39.10 mA/cm² current density for 60 min and the other run 24 with initial pH 9 at 10 V voltage, 1.13 A current, and 42.89 mA/cm² current density for 60 min. While comparing those three runs, all the runs had black liquor of initial pH 9, but the first condition could be termed the best one as it ran for less time and with lower current density. Furthermore, it was justified by optimization step in Minitab.

4.1.1.1 Response Surface Method Analysis for COD Removal

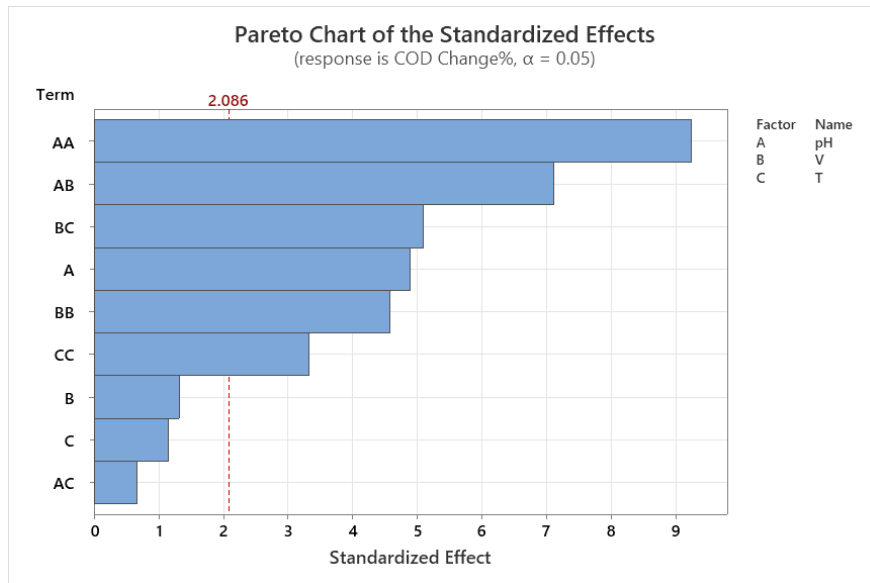


Figure 4.1 Pareto Chart for RSM of COD Removal by Electrocoagulation

Figure 4.1 shows the pareto chart for the removal of COD after electrocoagulation of black liquor under three operational parameters: initial pH level (7, 9, and 11), voltage (10, 20, and 30) V and electrolysis time (10, 35 and 60) min. This chart compared the relative magnitude of the statistical significance and interaction effects between operational parameters for the removal of COD. It helped in determining the most significant factor and the interactions that contribute most to the efficiency in the removal of COD. The result showed that for the removal of COD, the square term for pH (AA), the interaction between pH and voltage (AB), the interaction between voltage and time (BC), the pH term (A), the square term for voltage (BB), and the square term for electrolysis time (CC) were significant.

Table 4.2 Model fit summary for RSM of COD Removal by Electrocoagulation

S	R²	Adjusted R²	Predicted R²
3.23719	91.32%	87.41%	77.82%

The association between the response and each term in the model was compared by the p-value for the term to the significance level of 0.05. The R² of 91.32 % was a considerably good fit of the model with the data. The goodness of the fit was examined in the Model summary presented in Table 4.2.

Further, the assumptions of the analysis were verified by analyzing the residual plots (Figure 4.2). In the residual versus fits plot, the points fell randomly on both sides of 0, with no recognizable patterns in the points. This verified that the residuals were randomly distributed and had constant variance. Similarly, the residuals versus order plot verified that the residuals were independent of one another. Independent residuals showed no trends or patterns when displayed in time order. The normal probability plot of the residuals followed an approximately straight line, hence, was considered normal. We could see certain outliers in the histogram, but we lacked enough evidence to eliminate them. The sample size was small, so each bar on the histogram did not contain enough data points to reliably show skewness or outliers.

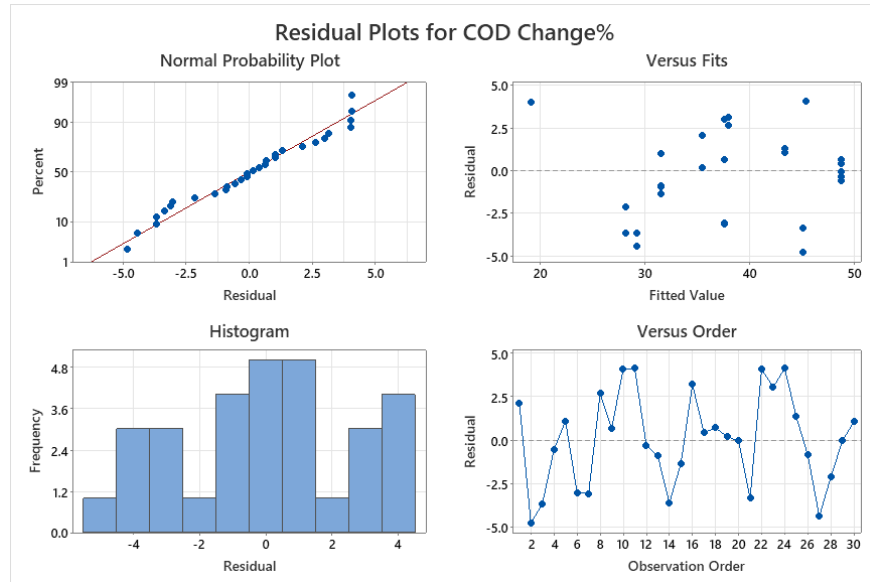


Figure 4.2 Residual plots for RSM of COD Removal by Electrocoagulation

The effects of COD removal efficiencies are shown in contour plots (Figures 4.3, 4.4, and 4.4). A higher COD removal efficiency of above 45% was achieved in the region near pH 9 and 20 V voltage. The efficiency decreased when either pH increased or decreased beyond this point, The efficiency of COD removal was better in pH 9 than in pH 11 as shown in Figure 4.3. Here, the efficiency was less than 30% when pH was 11 and voltage was 30 V.

A higher COD removal efficiency of above 48% was achieved in the region near to pH 9 and at any electrolysis time between 20 to 50 min according to Figure 4.4. The efficiency decreased on either side of the pH 9 and the time was not that significant in that case. The least efficiency was observed at the extreme points.

As shown in figure 4.5, a higher COD removal efficiency of above 48% was achieved when voltage was between 15 to 25 V and electrolysis time was between 20 to 45 min. There, the efficiency was less than 32% when pH was 11 and voltage was 30 V.

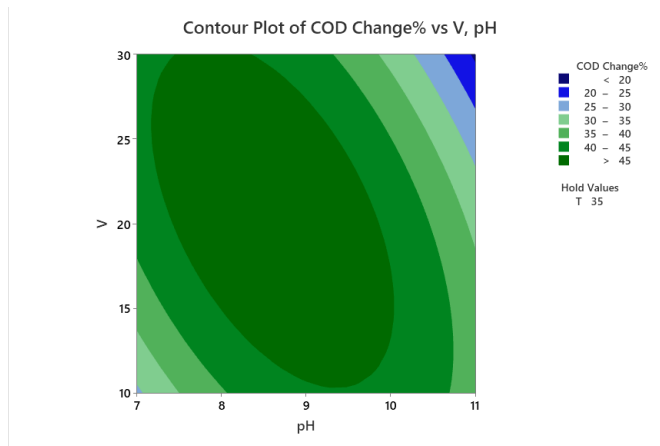


Figure 4.3 Response Surface Contours for COD Removal at 35 min

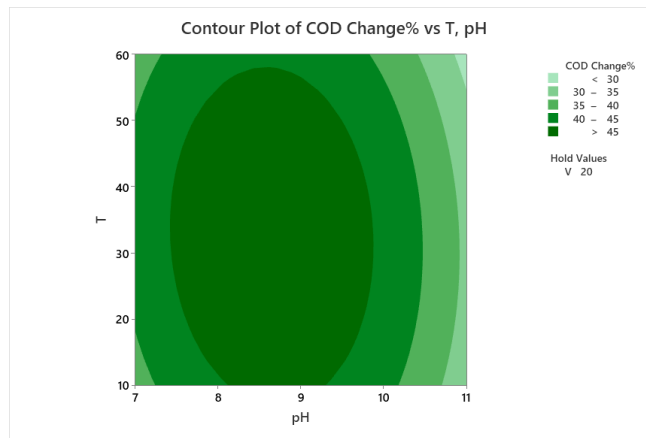


Figure 4.4 Response Surface Contours for COD Removal at 20 V

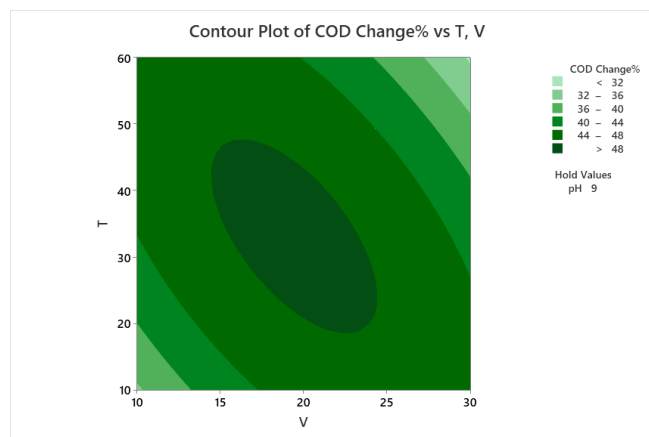


Figure 4.5 Response Surface Contours for COD Removal at pH 9

From the pareto chart and the contour plots, it has been established that the influent pH was the most important operating factor influencing the performance of electrocoagulation process. This condition is same in comparison to the result obtained in electrocoagulation treatment of black liquor from kraft pulping (Zaied and Bellakhal 2009). Additionally, the series of experiments showed that the treatment efficiency in terms of COD removal was better when performed with an initial pH of 9 rather than with pH 7 or 11. The electrocoagulation of black liquor obtained from soda-AQ pulping of wheat straw showed the highest COD removal at the midpoint pH 7. The efficiency decreased when the pH was acidic (pH 3) and alkaline (pH 10.5) (Rastegarfar et al. 2015). Although not at the neutral pH, this research study showed a similar result of maximum removal efficiency of COD at the midpoint, i.e., at 9H and then the decrease in efficiency on either side. This analysis suggested that electrocoagulation could be an effective method for COD reduction.

Similar result was obtained in an electrocoagulation treatment study done on kraft pulping process, where the highest COD removal of 70% was achieved at pH values in the range 5-8 (Zaied and Bellakhal 2009). As metal ions were generated at the anode during the process of electrocoagulation, they reacted with water to form metal hydroxide precipitates. So, the pH at a region of 9 provided the ability to the metal hydroxides to function as coagulants. Lesser than this or higher than this interfered with its solubility and affected COD removal. For electrolysis time, more amount of time helped to form more flocs, but when the current flow was high, the flocs formation increased at first and then later dissolved as the opposite effect. The floc forming pattern was the same for voltage since lower voltage hindered the floc formation, and higher voltage broke off the flocs formed. This confirmed the requirement of an adequate amount of voltage to achieve the maximum COD removal. The electrolysis time and the voltage showed an interaction in the removal efficiency of COD. This study showed that increase in voltage could shorten the electrolysis time and vice-versa just like the relationship between current and electrolysis time in Rastegarfar et al. (Rastegarfar et al. 2015). The only difference was the use of parameter voltage in our case, and the use of parameter current in case of Rastegarfar et al. This was comparable as, according to the Ohm's Law, the current is directly proportional to the voltage.

4.1.1.2 Optimization for COD Removal

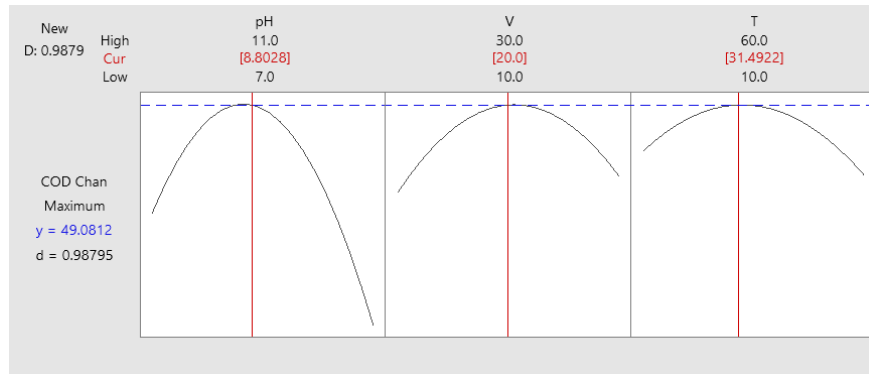


Figure 4.6 Response Optimization for COD Removal by Electrocoagulation

The COD removal process was fed through the response optimization in Minitab to get the graph as shown in Figure 4.6. The optimized pH, voltage and electrolysis time from the diagram were found to be 8.8 pH, 20 V, and 31.5 min, respectively. 8.8 pH was adjusted to pH 9 and 31.5 V voltage was adjusted to 35 min to bring to their nearest operational run adopted in the experiment. Hence, the optimal operation condition for COD removal in the electrocoagulation process was initial pH 9 black liquor, running at 20 V voltage for 35 min time.

4.1.2 Effect on Phenol Removal

Soluble lignin content in black liquor produced from the pulp and paper industry resulting in high phenol compounds is responsible for the dark color and high COD of black liquor making it an important parameter to be treated. Hence, the removal of lignin content in black liquor was determined by monitoring the decrease of phenol by the electrocoagulation process. From a minimum of 19.62% to a maximum 43.61% of phenol removal could be achieved during experimental runs. It seemed the electrocoagulation method was successful enough to reduce phenol as a pretreatment step. The maximum removal efficiency was found at experimental run 9, highlighted by green color and the minimum was found at experimental run 3, highlighted by red color in Table 4.3. Run 9 had an initial pH 9, in which run 9 was running at 20 V voltage, 0.87 A current, 33.02 mA/cm² current density for 35 min. A similar electrocoagulation study of wheat straw showed 81% removal of phenol in acidic medium at 55 min time and 61.81 mA/cm² (Rastegarfar et al. 2015). Rastegarfar et al. could removal nearly double the phenol content as compared to our optimum condition. However, our process of electrocoagulation used just the half of the electrocoagulation time in comparison to the Rastegarfar et al., and also the medium was alkaline in our case, which might have affected the phenol removal efficiency. In addition, the current density in our case was half than in comparison to the Rastegarfar et al. This justified the relationship between time, pH and voltage and/or current density for the removal efficiency of phenol from the black liquor. The optimum condition obtained concerning phenol removal aligned with the optimum condition obtained concerning COD removal. This could happen as phenol content directly affects the COD of black liquor. It was justified by the optimization step in Minitab.

Table 4.3 Initial, Final, and % Decrease in Phenol of after Electrocoagulation Black Liquor under Different Operational Conditions of pH, Voltage and Electrolysis Time (Green and red highlights denote the operational conditions with maximum and minimum Phenol removal efficiency, respectively)

S.N.	pH Level	Voltage (V)	Electrolysis Time (min)	Initial Phenol (mg/L)	Final Phenol (mg/L)	Decrease in Phenol (%)
1	9	10	10	352	241	31.48
2	9	30	10	352	215	38.92
3	11	20	60	362	291	19.62
4	9	20	35	352	203	42.38
5	7	30	35	332	204	38.55
6	11	10	35	362	232	35.94
7	7	20	60	332	221	33.30
8	7	20	10	332	219	33.89
9	9	20	35	352	198	43.61
10	11	30	35	362	291	19.56
11	9	10	60	352	202	42.61
12	9	20	35	352	201	42.93
13	11	20	10	362	265	26.82
14	7	10	35	332	261	21.39
15	9	30	60	352	264	24.88
16	7	20	10	332	216	34.94
17	9	20	35	352	202	42.66
18	11	10	35	362	235	35.18
19	9	10	10	352	239	32.10
20	9	20	35	352	199	43.36
21	9	30	10	352	224	36.36
22	11	30	35	362	292	19.35
23	7	20	60	332	220	33.73
24	9	10	60	352	202	42.61
25	7	30	35	332	204	38.59
26	9	30	60	352	261	25.85
27	7	10	35	332	259	22.12
28	11	20	60	362	286	21.07
29	9	20	35	352	202	42.56
30	11	20	10	362	264	27.07

4.1.2.1 Response Surface Method Analysis for Phenol Removal

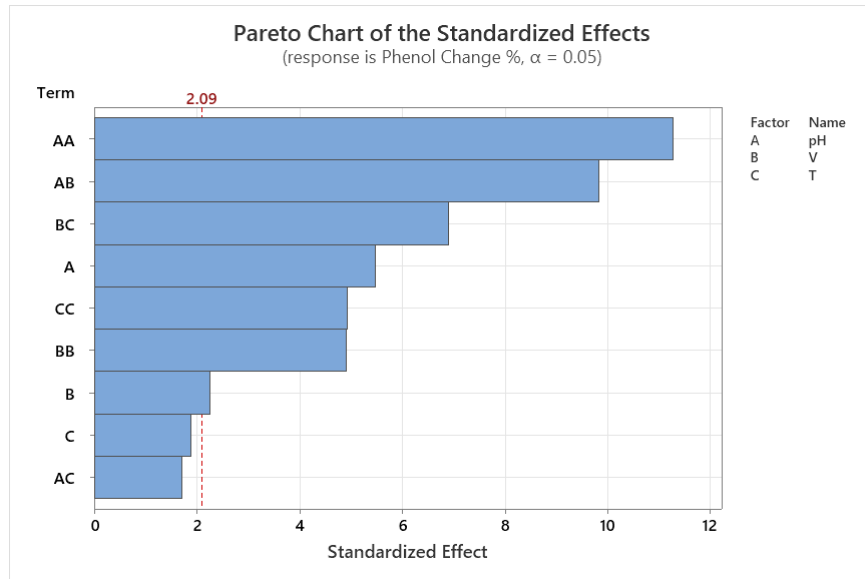


Figure 4.7 Pareto Chart for RSM of Phenol Removal by Electrocoagulation

Figure 4.7 shows the pareto chart for the removal of phenol after electrocoagulation of black liquor under three operational parameters: initial pH level (7, 9 and 11), voltage (10, 20, 30) V and electrolysis time (10, 35 and 60) min. The result showed that for the removal of phenol, the square term for pH (AA), the interaction between pH and voltage (AB), the interaction between voltage and time (BC), the pH term (A), the square term for time (CC), the square term for voltage (BB), and the electrolysis time (C) were significant. This explained how almost all parameters and their interactions were important to induce phenol reduction.

The association between the response and each term in the model could be compared by the p-value for the term to the significance level of 0.05. The goodness of the fit was examined in the Model summary presented in Table 4.4. The R^2 of 94.51% was a considerably good fit of the model with the data.

Table 4.4 Model fit summary for RSM of Phenol Removal by Electrocoagulation

S	R^2	Adjusted R^2	Predicted R^2
2.36562	94.51%	92.03%	86.00%

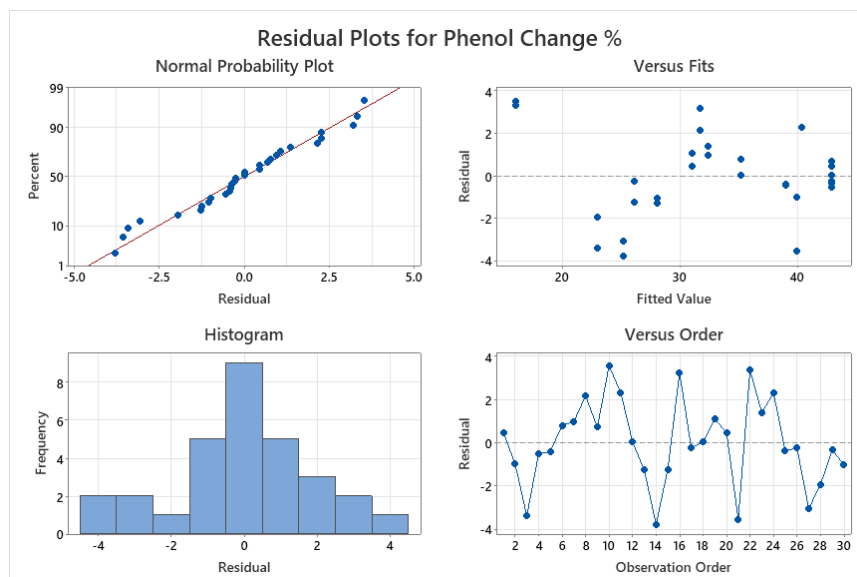


Figure 4.8 Residual plots for RSM of Phenol Removal by Electrocoagulation

The assumptions of the analysis were verified by analyzing the residual plots in Figure 4.8. The residuals versus order plot verified the assumption that the residuals were independent, randomly distributed, and had constant variance. The normal probability plot of the residuals approximately followed a straight line thus verifying the assumption that the residuals were normally distributed.

The effects of phenol removal efficiencies are shown in contour plots (Figure 4.9, 4.10 and 4.11). A higher phenol removal efficiency of above 40% was achieved in the region pH 9 to pH 10 with 20 to 30 V voltage. The efficiency decreased on either side of that pH range, and the efficiency was less than 20% when the pH was 11 and the voltage was 30 V (Figure 4.9).

A higher phenol removal efficiency of above 40% was achieved in the region of pH 9 with time in between 30 to 40 min when 20 V voltage was kept constant according to Figure 4.10. The efficiency decreased on either side of the pH 9. Least efficiency was observed at the extreme points, just like that for the COD removal.

As shown in figure 4.11, a higher phenol removal efficiency of above 42% was achieved when voltage was between 15 to 25 V and electrolysis time was between 20 to 45 min. There, the efficiency was less than 27% when the time was 60 min, and the voltage was 30 V. This indicated that increasing time and voltage simultaneously affected the electrocoagulation process adversely.

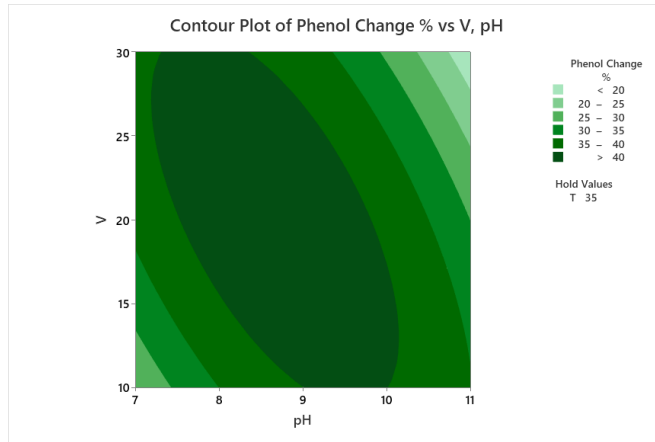


Figure 4.9 Response Surface Contours for Phenol Removal at 35 min

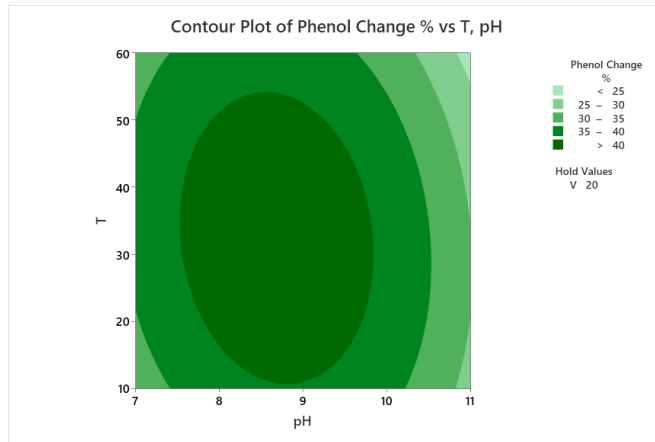


Figure 4.10 Response Surface Contours for Phenol Removal at 20 V

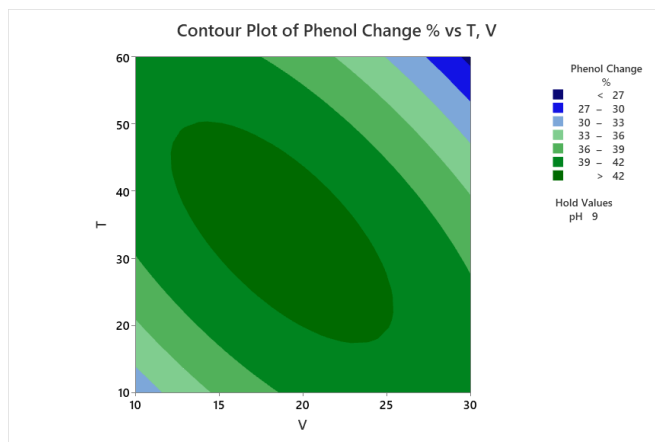


Figure 4.11 Response Surface Contours for Phenol Removal at pH 9

4.1.2.2 Optimization for Phenol Removal

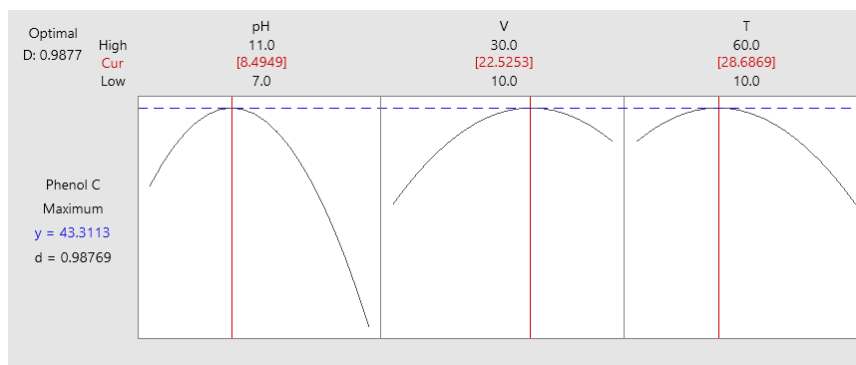


Figure 4.12 Response Optimization for Phenol Removal by Electrocoagulation

The phenol removal process was fed through response optimization in Minitab to get the graph as shown in Figure 4.12. The optimized pH, voltage, and electrolysis time were found to be 8.5 pH, 22.50 V, and 28.70 min, respectively. 8.5 pH was adjusted to pH 9, 22.50 V was adjusted to 20 V, and 28.70 min was adjusted to 35 min to bring to their nearest operational run adopted in the experiment. Hence, the optimal operation condition for COD removal in the electrocoagulation process was the black liquor with initial pH 9, running at 20 V voltage for 35 min time.

In summary, the phenol content in the black liquor was due to the lignin component, as lignin is a complex polymer made up of phenolic compounds and this was added to the COD loading. Like COD removal, the performance of phenolic compound removal could be compared.

4.1.3 Effect on TS Removal

The TS in black liquor is responsible for turbidity and specific conductance, hence its removal efficiency was monitored in the electrocoagulation method. From a minimum of 27.15% to a maximum of 53.89% TS removal was achieved during experimental runs. The run with the lowest TS removal is highlighted in red color and the run with the maximum TS removal is highlighted in green color in Table 4.5. The maximum TS removal was achieved in run 9. It was carried out with black liquor of initial pH 9, 20 V voltage, 0.87 A current, 33.02 mA/cm² current density for 35 min. This indicated that electrocoagulation could be successfully used to treat black liquor by reducing its TS content.

Table 4.5 Initial, Final and % Decrease in TS after Electrocoagulation of Black Liquor under Different Operational Conditions of pH, Voltage and Electrolysis Time (Green and red highlights denote the operational conditions with maximum and minimum TS removal efficiency, respectively)

S.N.	pH Level	Voltage (V)	Electrolysis Time (min)	Initial TS (mg/L)	Final TS (mg/L)	Decrease in TS (%)
1	9	10	10	42700	24960	41.55
2	9	30	10	42700	22800	46.60
3	11	20	60	41500	27380	34.03
4	9	20	35	42700	20160	52.79
5	7	30	35	42750	21920	48.73
6	11	10	35	41500	25040	39.66
7	7	20	60	42750	28800	32.63
8	7	20	10	42750	26720	37.50
9	9	20	35	42700	19690	53.89
10	11	30	35	41500	30080	27.52
11	9	10	60	42700	22000	48.48
12	9	20	35	41500	19880	52.09
13	11	20	10	41500	26560	35.99
14	7	10	35	42750	29280	31.51
15	9	30	60	42700	24480	42.68
16	7	20	10	41700	25690	38.40
17	9	20	35	43100	20130	53.29
18	11	10	35	42200	25570	39.41
19	9	10	10	43100	24910	42.21
20	9	20	35	43100	20670	52.04
21	9	30	10	43100	22600	47.56
22	11	30	35	42200	30740	27.15
23	7	20	60	41700	27930	33.01
24	9	10	60	43100	22050	48.83
25	7	30	35	41700	21000	49.63
26	9	30	60	43100	24490	43.17
27	7	10	35	41700	28360	31.98
28	11	20	60	42200	27660	34.45
29	9	20	35	43100	20270	52.97
30	11	20	10	42200	27040	35.93

The series of experimental runs resulted that TS removal was better achieved when performed with black liquor of initial pH 9 rather than with pH 7 or 11. All the experiments performed with pH 9 black liquor had more than 41% TS removal. The optimum condition obtained with respect to TS removal aligned with that of COD and phenol removal.

4.1.3.1 Response Surface Method Analysis for TS Removal

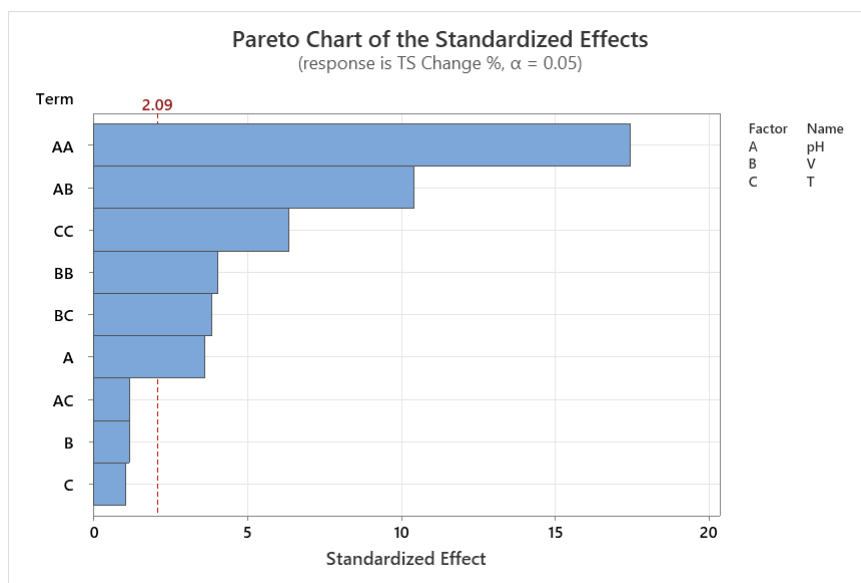


Figure 4.13 Pareto Chart for RSM of TS Removal by Electrocoagulation

Figure 4.13 shows the pareto chart for the removal of TS after electrocoagulation of black liquor under three operational parameters: initial pH level (7, 9 and 11), voltage (10, 20, 30) V and electrolysis time (10, 35 and 60) min. The result showed that for the removal of TS from black liquor, the square term for pH (AA), the interaction between pH and voltage (AB), the square term for electrolysis time (CC), the square term for volage (BB), the interaction with voltage and time (BC) and the pH term (A) were significant. Change in TS was more highly dependent on term pH than on term voltage and term time.

The goodness of the fit was examined in the Model summary presented in Table 4.6, where the R^2 of 95.97%, which was a considerably good fit of the model with the data.

Table 4.6 Model fit summary for TS of Phenol Removal by Electrocoagulation

S	R ²	Adjusted R ²	Predicted R ²
2.00947	95.97%	94.15%	89.81%

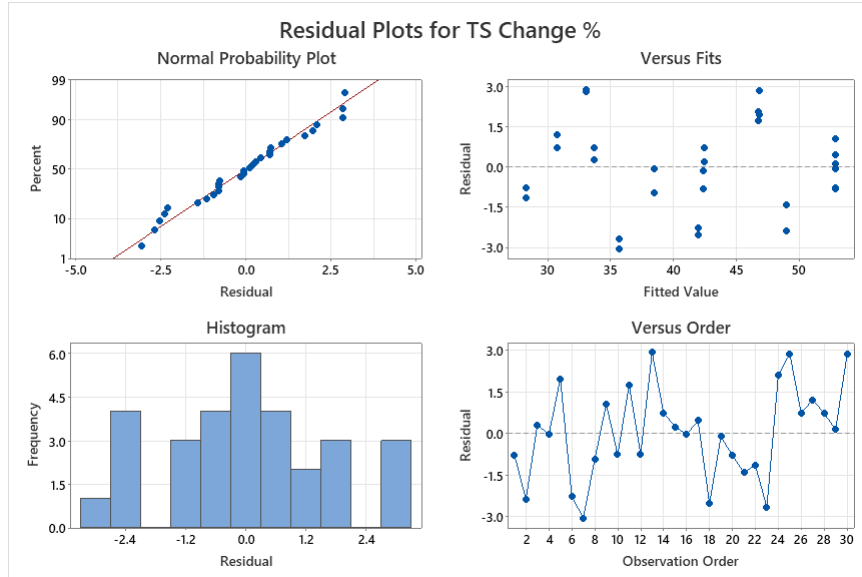


Figure 4.14 Residual plots for RSM of TS Removal by Electrocoagulation

The assumptions used in the analysis were verified by analyzing the residual plots in Figure 4.14. The residuals were independent, randomly distributed and had constant variance. The normal probability plot of the residuals approximately followed a straight line, and this signified the assumption that the residuals were normally distributed.

Response surface contour plots were plotted to determine the region of efficiency for the removal of TS from the black liquor by the process of electrocoagulation. Figure 4.15 shows that a higher TS removal efficiency of above 50% was achieved between pH 9 and 9.5 when the time 35 min was constant. The efficiency due to voltage values was constantly changing.

Likewise, Figure 4.16 shows that pH 9 provided the maximum TS removal efficiency when electrolysis time was maintained between 20 and 50 min and 20 V voltage was held back. As shown in Figure 4.17, the TS removal was greater than 52% at pH 9 and time 35 min. The lowest value of TS removal when pH 9 was constant was 44%, confirming the suitability of pH 9 reduced black liquor for electrocoagulation.

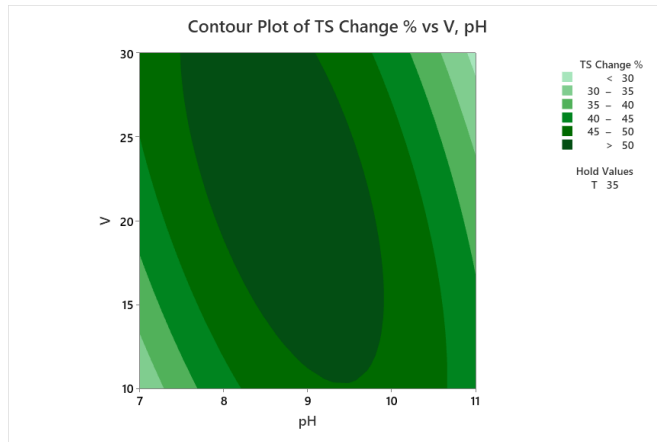


Figure 4.15 Response Surface Contours for TS Removal at 35 min

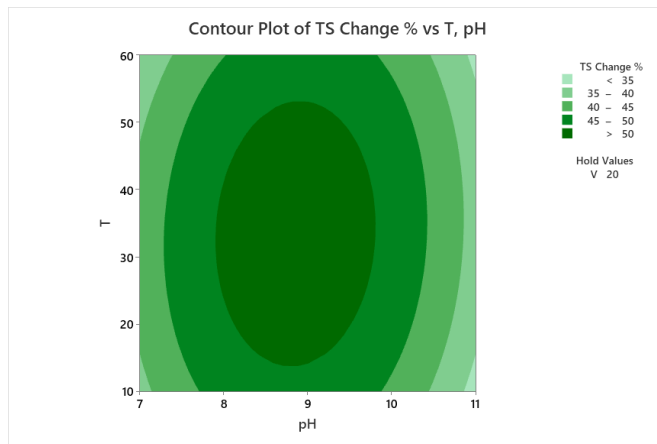


Figure 4.16 Response Surface Contours for TS Removal at 20 V

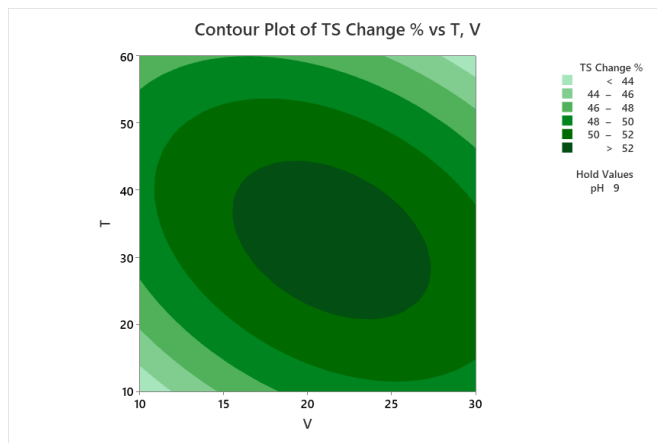


Figure 4.17 Response Surface Contours for TS Removal at pH 9

4.1.3.2 Optimization for TS Removal

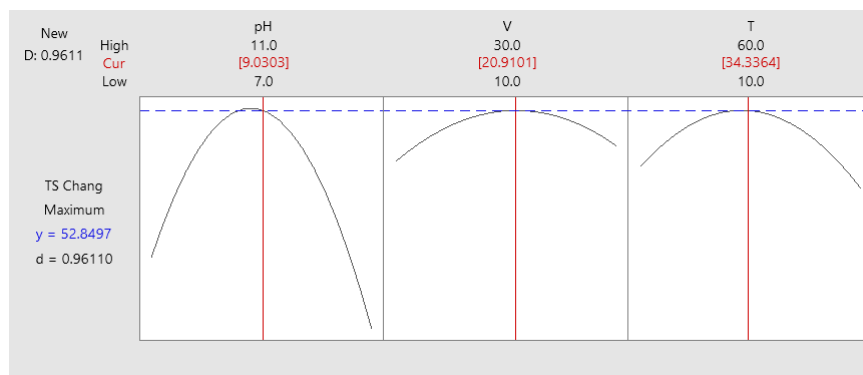


Figure 4.18 Response Optimization for TS Removal by Electrocoagulation

The TS removal process was optimized to obtain the best values for pH, voltage, and electrolysis time (Figure 4.18). The optimized pH, voltage and electrolysis time was found to be 9 pH, 20.91 V and 34.34 min, respectively. 20 V was considered in place of 20.91 V and 35 min was considered in place of 34.34 min to bring their value to the nearest operational conditions applied in the experimental runs. Hence, the optimum condition of TS removal was pH 9, 20V and 35 min. This condition could remove 53.89% TS with 33.02 mA/cm². Rastegarfar et al. could remove 68% TS with 61.81 mA/cm² current density (Rastegarfar et al. 2015). Our method of electrocoagulation was commendable in achieving such as greater amount of TS removal with just half of current density in comparison to the Rastegarfar et al. The black liquor obtained in our case was from mild alkali sulfur free process and that of Rastegarfar was soda-AQ pulping process. The pulping process difference might have impacted the constituents of black liquor, and their TS removal efficiency as well.

4.1.4 Effect on TDS Removal

TDS represents dissolved organic matter and inorganic salts in black liquor, and its removal efficiency was monitored in the electrocoagulation method. A minimum of 22.88 % to a maximum of 46.58% of TDS removal was achieved at experimental run 17 as shown in Table 4.7. The minimum TDS removal run is highlighted in red color and the maximum run is highlighted in green color in the table. Run 17 was carried out with black liquor of initial pH 9 at 20 V voltage, 1.10 A current, 41.75 mA/cm² current density for 35 min.

Table 4.7 Initial, Final and % Decrease in TDS after Electrocoagulation of Black Liquor under Different Operational Conditions of pH, Voltage and Electrolysis Time (Green and red highlights denote the operational conditions with maximum and minimum TDS removal efficiency, respectively)

S.N.	pH Level	Voltage (V)	Electrolysis Time (min)	Initial TDS (mg/L)	Final TDS (mg/L)	Decrease in TDS (%)
1	9	10	10	14000	10000	26.29
2	9	30	10	14000	9000	36.71
3	11	20	60	14100	10000	25.67
4	9	20	35	14000	8000	45.71
5	7	30	35	13900	9000	34.6
6	11	10	35	14100	9000	33.11
7	7	20	60	13900	10000	30
8	7	20	10	13900	9000	31.73
9	9	20	35	14000	7000	46.5
10	11	30	35	14100	11000	24.54
11	9	10	60	14000	8000	41
12	9	20	35	14000	8000	44
13	11	20	10	14100	10000	27.94
14	7	10	35	13900	11000	22.88
15	9	30	60	14000	9000	34.29
16	7	20	10	13900	10000	30.13
17	9	20	35	14000	7000	46.58
18	11	10	35	14100	9000	34.1
19	9	10	10	14000	14000	31.43
20	9	20	35	14000	10000	45.93
21	9	30	10	14000	9000	37.05
22	11	30	35	14100	11000	24.35
23	7	20	60	13900	10000	29.71
24	9	10	60	14000	8000	40.71
25	7	30	35	13900	9000	33.93
26	9	30	60	14000	9000	34.2
27	7	10	35	13900	11000	23.13
28	11	20	60	14100	10000	25.98
29	9	20	35	14000	8000	43.31
30	11	20	10	14100	10000	28.98

Comparing the experimental runs concerning initial pH, the black liquor with pH 9 and 11 showed better TDS removal than with pH 7. Irrespective of the experimental design, all the runs could achieve more than 22% TDS removal with the help of the electrocoagulation method. The optimum condition obtained concerning TDS removal aligned with COD, phenol, and TS removal and could be justified by RSM fit, contour plots, and optimization graph.

4.1.4.1 Response Surface Analysis for TDS Removal

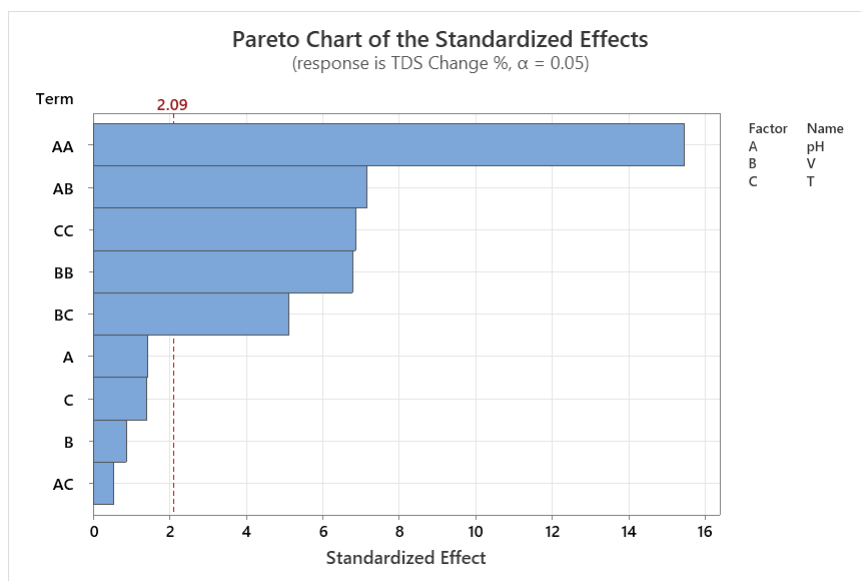


Figure 4.19 Pareto Chart for RSM of TDS Removal by Electrocoagulation

The RSM analysis shown by the pareto chart (Figure 4.19) gives the significant factors affecting the removal of TDS from black liquor with the help of the proper electrocoagulation method. The square term for pH (AA), the interaction between pH and voltage (AB), the square term for time (CC), the square term for voltage (BB), and the interaction between voltage and time (BC) showed the significance to the fit of this analysis by RSM. The square terms were more significant than the single terms according to the result.

The goodness of the fit was examined in the Model summary presented in Table 4.8, where the R^2 was 95.02%, the adjusted R^2 was 92.77%, and the predicted R^2 was 87.88%, which denoted considerably a very good fit of the model with the data and justified the RSM analysis.

Table 4.8 Model fit summary for RSM of TDS Removal by Electrocoagulation

S	R²	Adjusted R²	Predicted R²
2.01678	95.02%	92.77%	87.88%

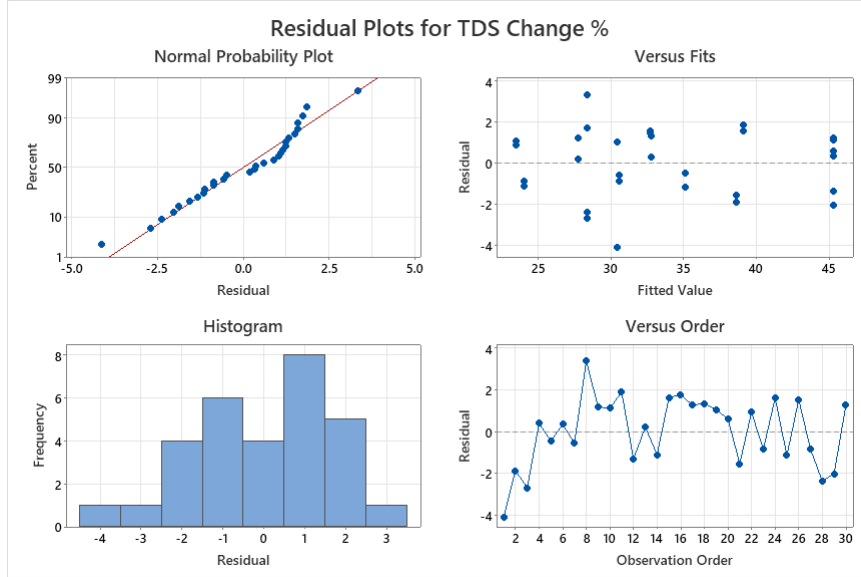


Figure 4.20 Residual plots for RSM of TDS Removal by Electrocoagulation

Figure 20 shows residual plots for RSM of TDS removal by electrocoagulation and all the residuals were independent, randomly distributed, and had constant variance.

Furthermore, three contour plots were created to understand the region of maximum removal of TDS from the black liquor. When time was kept constant at 35 min, the efficiency was greatest at pH 9 and voltage 20 V, as shown in Figure 4.21. When the time was 35 min, the least efficiency of 25% was at the extremes, i.e., in either of those two conditions: one when pH 7 and voltage 10V, and the other when pH 11 and voltage 30V. Similarly, when voltage was kept constant at 20 V, the maximum efficiency above 45% of TDS removal was achieved at pH 9 when the electrolysis time fluctuated between 30 to 40 min (Figure 4.22). Efficiency started to fall as the circle moved towards the extremes, yet a minimum of 30% TDS removal was achieved. When pH 9 was kept constant, the efficiency of TDS removal was more than 44% at 20 V and 35 min (Figure 4.23). All these contour plots and justifications showed that pH 9, 20 V voltage, and 35 min electrolysis time as the ideal operating conditions for electrocoagulation to remove dissolved solids from the black liquor.

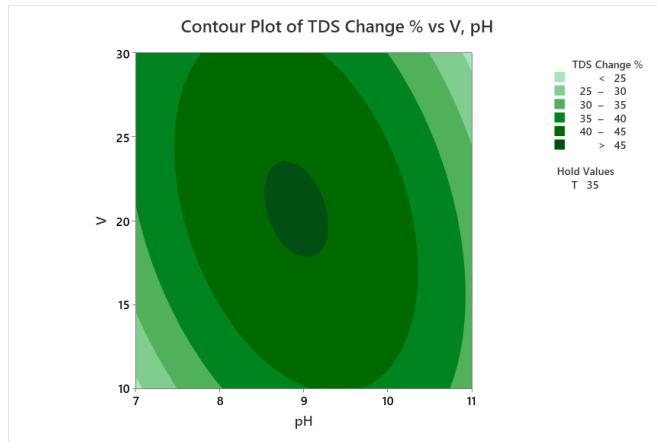


Figure 4.21 Response Surface Contours for TDS Removal at 35 min

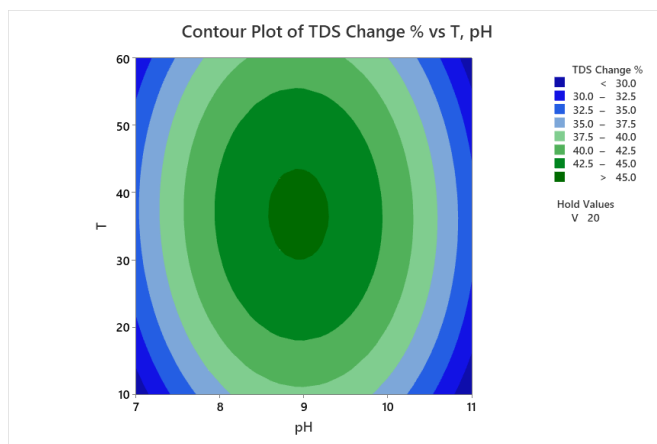


Figure 4.22 Response Surface Contours for TDS Removal at 20 V

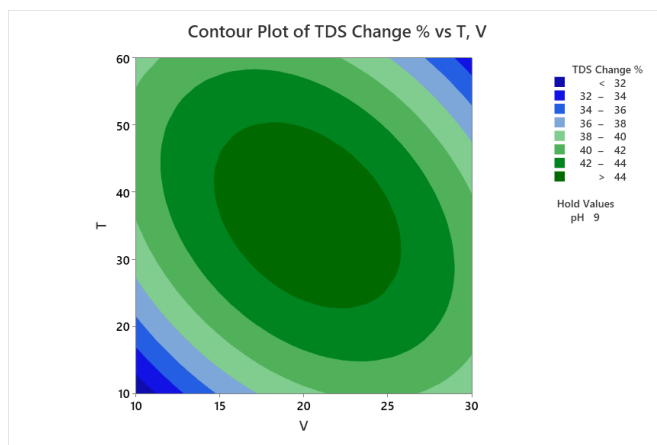


Figure 4.23 Response Surface Contours for TDS Removal at pH 9

4.1.4.2 Optimization for TDS Removal

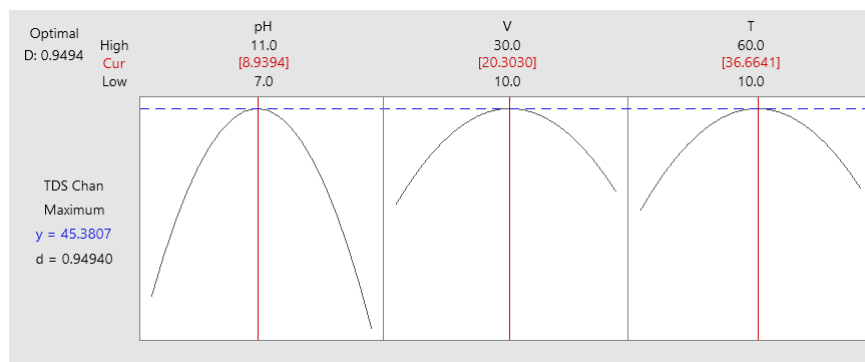


Figure 4.24 Response Optimization for TDS Removal by Electrocoagulation

Figure 4.24 shows the optimization chart for the maximum removal of the total concentration of all dissolved substances in the black liquor, including both inorganic and organic compounds with the help of the electrocoagulation method of pretreatment. This chart shows that pH 8.9, voltage 20.3 V, and electrolysis time 36.6 min favored the best condition for TDS removal. However, 8.9 pH was adjusted to 9 pH, 20.3 V was adjusted to 20 V and 36.6 was adjusted to 35 mins as the optimum operation conditions to bring those values close to their nearest operational runs in the experiment. This condition could remove 46.58% TDS with 41.75 mA/cm². Rastegarfar et al. could remove 61% TDS with 61.81 mA/cm² current density at acidic medium (Rastegarfar et al. 2015). Our method of electrocoagulation was commendable in achieving such as greater amount of TS removal with just two-third of current density in comparison to the Rastegarfar et al. In addition, the electrocoagulation was performed in an alkaline medium in our case, which might be reasonable to lesser TDS removal than in Rastegarfar et al.'s study. The black liquor obtained in our case was from mild alkali sulfur free process and that of Rastegarfar was soda-AQ pulping process. The pulping process difference might have impacted the constituents of black liquor, and their TS removal efficiency as well.

4.1.5 Effect on Color Intensity Removal

The dark brown color of black liquor in the pulp and paper industry is formed by the degradation of lignocelluloses during the bleaching process and is an indirect measurement of lignin content (Irfan et al. 2017; Kovacs et al. 2002). The higher the lignin content, the darker the

effluent and the greater the tendency to produce foam creating a poisonous environment for aquatic life and a threat to the receiving water bodies. So, the color intensity removal with the help of the electrocoagulation process was monitored by comparing the whiteness index.

The dark color in black liquor was associated with the presence of whiteness index (WI) and its increment showed the removal of dark color in black liquor. As shown in Table 4.9, with the help of electrocoagulation, a maximum of 40.04% of color intensity was removed at run 5 when the black liquor of initial pH 7 was run for 35 min at 30 V voltage, 2.74 A current, and 104.01 mA/cm² current density. Previous study on electrocoagulation black liquor from kraft pulping showed 99% color removal, which is more than double in our case (Zaied and Bellakhal 2009). Zaied and Bellakhal would have achieved this because of their black liquor being produced from wood pulping. Another study on electrocoagulation of black liquor from non woody feedstock could remove 98.2% of color in 55 min electrolysis time in acidic medium (Rastegarfar et al. 2015). Black liquor obtained from straw pulping is more viscous, alkaline and dark in color in comparison to the one obtained from wood pulping, which justifies the lesser color removal efficiency in our case (Bajpai 2017b; Doma and Abou-Elela 2003). The current was very high in the condition pertaining to maximum color removal in comparison to other optimum conditions obtained. In addition, the optimum condition obtained concerning color intensity removal did not match with the optimum conditions obtained for any other analytical parameters. To the least, 26.5% of the whiteness index was increased during the electrocoagulation process. The green and red highlights in the table show the runs with maximum and minimum WI index, respectively.

Table 4.9 Initial, Final and % Increase in WI after Electrocoagulation of Black Liquor under Different Operational Conditions of pH, Voltage and Electrolysis Time (Green and red highlights denote the operational conditions with maximum and minimum increase in WI, respectively)

S.N.	pH Level	Voltage (V)	Electrolysis Time (min)	Initial WI	Final WI	% Increase in WI
1	9	10	10	39.04	50.44	29.21
2	9	30	10	39.04	50.50	29.36
3	11	20	60	38.88	49.72	27.87
4	9	20	35	39.04	50.52	29.41
5	7	30	35	39.42	55.20	40.04
6	11	10	35	39.04	50.62	29.66
7	7	20	60	39.42	52.29	32.66
8	7	20	10	39.42	49.97	26.76
9	9	20	35	39.04	50.49	29.33
10	11	30	35	38.88	51.48	32.42
11	9	10	60	39.04	51.51	31.95
12	9	20	35	39.04	50.11	28.35
13	11	20	10	38.88	49.28	26.74
14	7	10	35	39.42	53.24	35.06
15	9	30	60	39.04	51.92	32.98
16	7	20	10	39.42	49.87	26.5
17	9	20	35	39.04	50.03	28.16
18	11	10	35	38.88	50.40	29.64
19	9	10	10	39.04	50.40	29.11
20	9	20	35	39.04	50.01	28.11
21	9	30	10	39.04	50.44	29.21
22	11	30	35	38.88	51.69	32.96
23	7	20	60	39.42	51.98	31.86
24	9	10	60	39.04	51.27	31.32
25	7	30	35	39.42	54.83	39.09
26	9	30	60	39.04	51.78	32.64
27	7	10	35	39.42	53.09	34.68
28	11	20	60	38.88	49.42	27.11
29	9	20	35	39.04	50.34	28.94
30	11	20	10	38.88	49.23	26.61

4.1.5.1 Response Surface Method for Color Intensity Removal

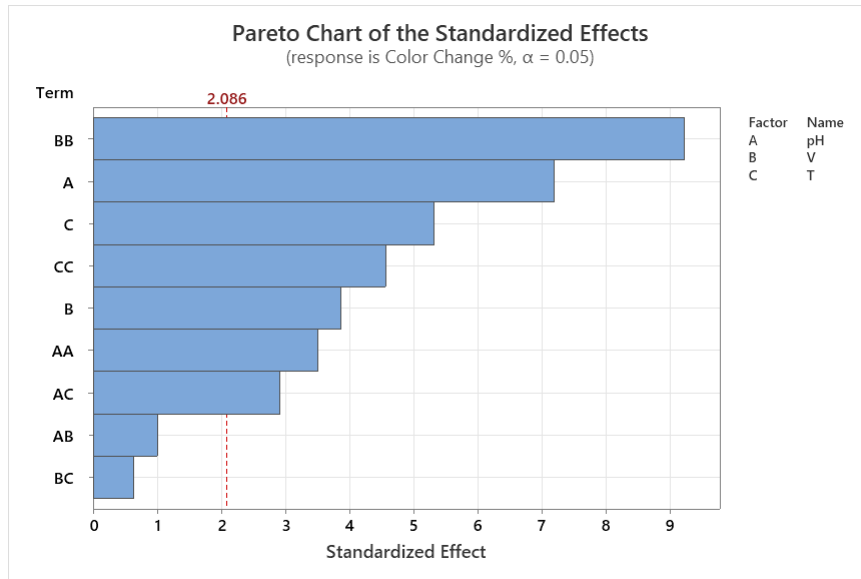


Figure 4.25 Pareto Chart for RSM of Color Removal by Electrocoagulation

The pareto chart in Figure 4.25 shows the significant terms associated with RSM analysis for color removal from the black liquor. The square of the term voltage (BB), the pH term (A), the electrolysis time term (C), the square of electrolysis time (CC), the voltage term (B), the square of the pH term (AA), and the interaction between pH and electrolysis time (AC) were statistically significant to show the most variability in this model, simultaneously.

Once the model was established, we could analyze the fit of the model with the model summary Table 4.10 obtained from the response surface analysis. The R^2 value for the model was 91.95% which was greater than 90% and showed a good fit. The adjusted R^2 value of 88.33% was more than the predicted R^2 value of 79.96%, suggesting that the model was likely overfitting the data. However, they are in a range to justify the goodness of fit of the model.

Table 4.10 Model fit summary for RSM of Color Removal by Electrocoagulation

S	R^2	Adjusted R^2	Predicted R^2
1.16819	91.95%	88.33%	79.96%

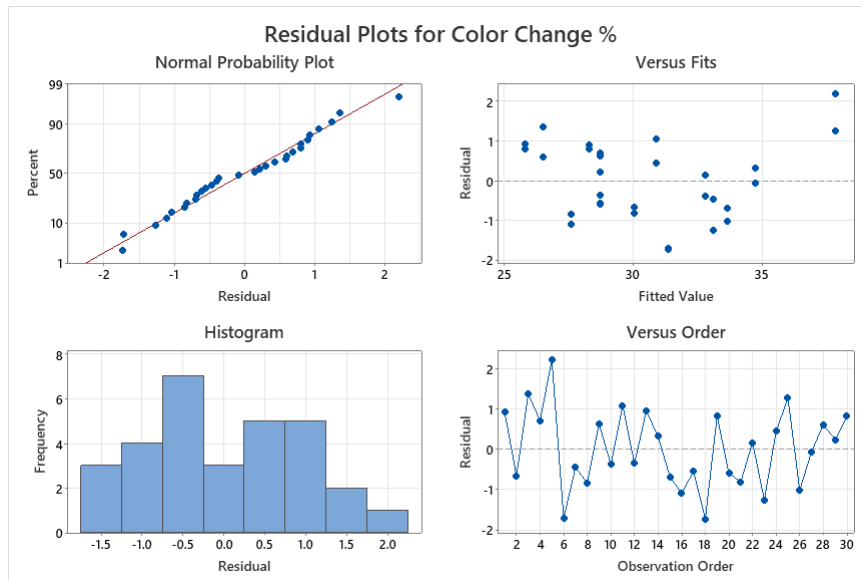


Figure 4.26 Residual plots for RSM of Color Removal by Electrocoagulation

Figure 4.26 shows four residual plots for RSM for color removal. The normality probability plot suggested that the residuals were approximately normally distributed. The versus fits plot showed the relationship between the fitted and the residuals, and it was found that the residuals were randomly scattered around 0 without any discernable pattern. The versus order plot showed the residuals in the order in which the data was collected. The histogram showed a wide distribution indicating higher variability in data.

Figure 4.27 presents a contour plot for color removal at a constant electrolysis time of 35 min. The higher efficiency above 36% was seen at two conditions: one was the run with pH 7 and voltage 10 V and the other run with pH 7 and voltage 30 V. Less than 25% efficiency for color removal was seen at the run conducted with 20 V voltage and pH lying between 10 and 11. Response surface contours for color removal at 20 V indicated that the highest removal of color intensity or the highest increase in whiteness index (WI), i.e., more than 32% was observed at pH 7 and electrolysis time in between 35 to 60 min (Figure 4.28). As the pH increased the color removal intensity decreased. Meanwhile, the response surface contours for color removal at 9 pH showed a higher efficiency of color removal of more than 34% in electrolysis time 35 min, either at 10 or 30 V voltage (Figure 4.29). As the voltage approached in between these two terms and the electrocoagulation was carried out in just 10 min, the color removal intensity dropped to the lowest, i.e., by less than 26%.

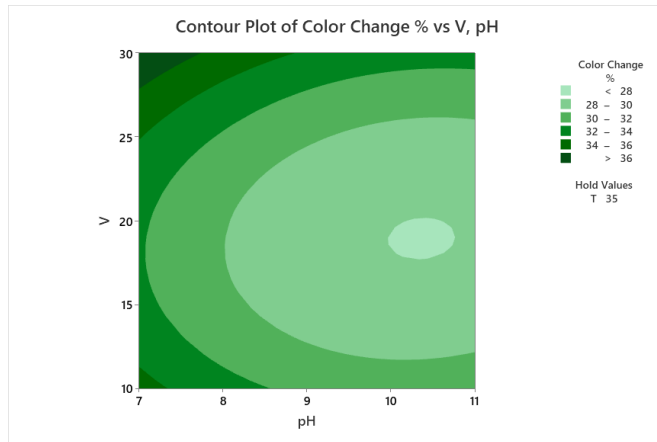


Figure 4.27 Response Surface Contours for Color Removal at 35 min

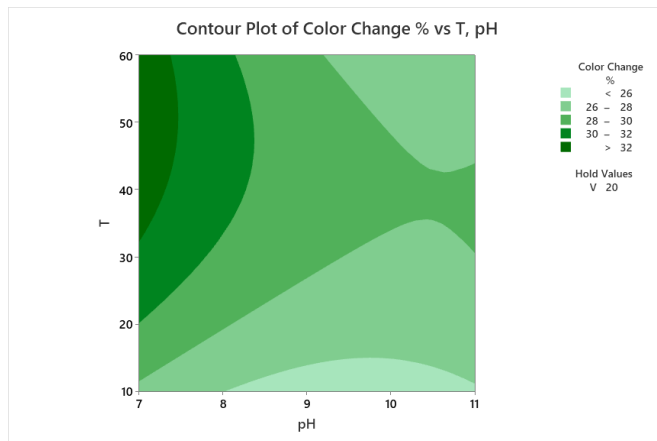


Figure 4.28 Response Surface Contours for Color Removal at 20 V

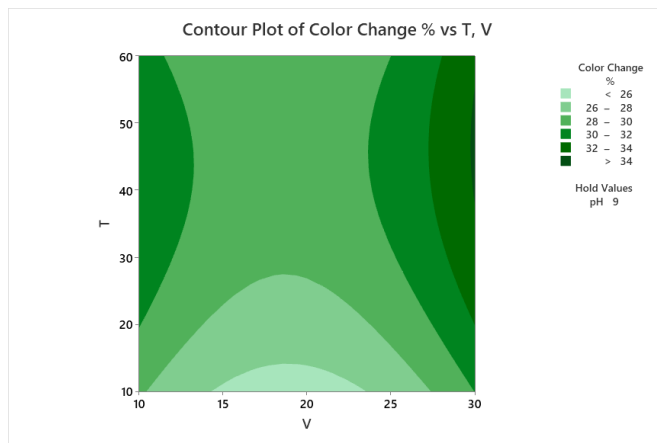


Figure 4.29 Response Surface Contours for Color Removal at pH 9

4.1.5.2 Optimization for Color Intensity Removal

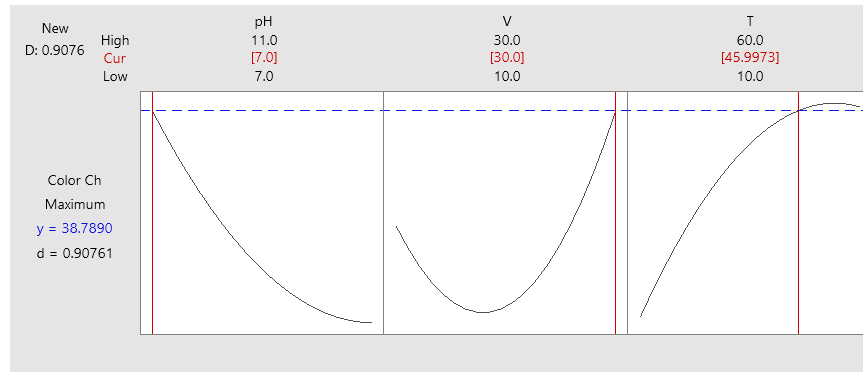


Figure 4.30 Response Optimization for Color Removal by Electrocoagulation

According to Figure 4.30, the optimum condition for maximum color removal from black liquor could be achieved when the pH 7 sample was electrocoagulated at 30 V voltage for 45 min electrolysis time. To simplify and make this result comparable to our obtained experimental design runs, 35 min electrolysis time was considered in place of 45 min.

4.1.6 Effect on pH Change

The pH of either influent or effluent in biological degradation in anaerobic conditions plays a vital role in proper functioning and performance of anaerobic microorganisms. So, considering this, pH removal also plays a significant role in determining the effectiveness of electrocoagulation as the pretreatment step for black liquor. The pH of raw black liquor was adjusted to pH 7, 9, and 11, but the process or electrocoagulation itself induced a lot of chemical reactions to bring out the changes in the final pH. Table 4.11 shows all the experimental runs and the associated change in pH. The highest decrease in alkalinity is shown by red highlight and the highest increase in alkalinity is shown by green highlight. All the samples with initial pH 7 showed an increasing trend whereas, the samples with initial pH 9 and pH 11 showed a decreasing trend.

Table 4.11 Initial, Final and % Change in pH after Electrocoagulation of Black Liquor under Different Operating Conditions of pH, Voltage and Electrolysis Time (Green and red highlights denote the operational conditions with highest decrease in alkalinity and highest increase in alkalinity, respectively)

S.N.	pH Level	Voltage (V)	Electrolysis Time (min)	pH after EC	Change in pH (in %)	Effect in pH
1	9	10	10	8.91	1	Decrease in pH
2	9	30	10	8.88	1.33	Decrease in pH
3	11	20	60	10.79	1.91	Decrease in pH
4	9	20	35	8.77	2.56	Decrease in pH
5	7	30	35	9.58	-36.86	Increase in pH
6	11	10	35	10.4	5.45	Decrease in pH
7	7	20	60	8.6	-22.86	Increase in pH
8	7	20	10	8.33	-19	Increase in pH
9	9	20	35	8.48	5.78	Decrease in pH
10	11	30	35	10.39	5.55	Decrease in pH
11	9	10	60	8.89	1.22	Decrease in pH
12	9	20	35	8.96	0.44	Decrease in pH
13	11	20	10	10.56	4	Decrease in pH
14	7	10	35	8.46	-20.86	Increase in pH
15	9	30	60	8.93	0.78	Decrease in pH
16	7	20	10	8.36	-19.43	Increase in pH
17	9	20	35	8.93	0.78	Decrease in pH
18	11	10	35	10.32	6.18	Decrease in pH
19	9	10	10	8.92	0.89	Decrease in pH
20	9	20	35	8.13	9.67	Decrease in pH
21	9	30	10	8.14	9.56	Decrease in pH
22	11	30	35	10.44	5.09	Decrease in pH
23	7	20	60	8.62	-23.14	Increase in pH
24	9	10	60	8.9	1.11	Decrease in pH
25	7	30	35	9.23	-31.86	Increase in pH
26	9	30	60	8.96	0.44	Decrease in pH
27	7	10	35	8.46	-20.86	Increase in pH
28	11	20	60	10.74	2.36	Decrease in pH
29	9	20	35	8.95	0.56	Decrease in pH
30	11	20	10	10.53	4.27	Decrease in pH

As observed in other studies, a final pH increase occurred when the influent pH was low and when the influent pH was above 9, a pH drop occurred (Adhoum and Monser 2004; Kobya et al. 2003; Zaid and Bellakhal 2009). Run 5, with initial pH 7, 30 V, and 35 min electrolysis time showed the highest increase in pH by 36.86%, whereas run 20, with initial pH 9, 20 V, and 35 min showed the highest decrease in pH by 9.67% at 0.90 A current and 34.16 mA/cm² current density. Here, electrocoagulation also acted as a buffer reaction process to bring out the liquid to the neutral range or up to 8 pH. Additionally, finding out the optimum condition for pH removal by response surface regression method analysis is presented below in sub-sections.

4.1.6.1 Response Surface Method Analysis for pH Change

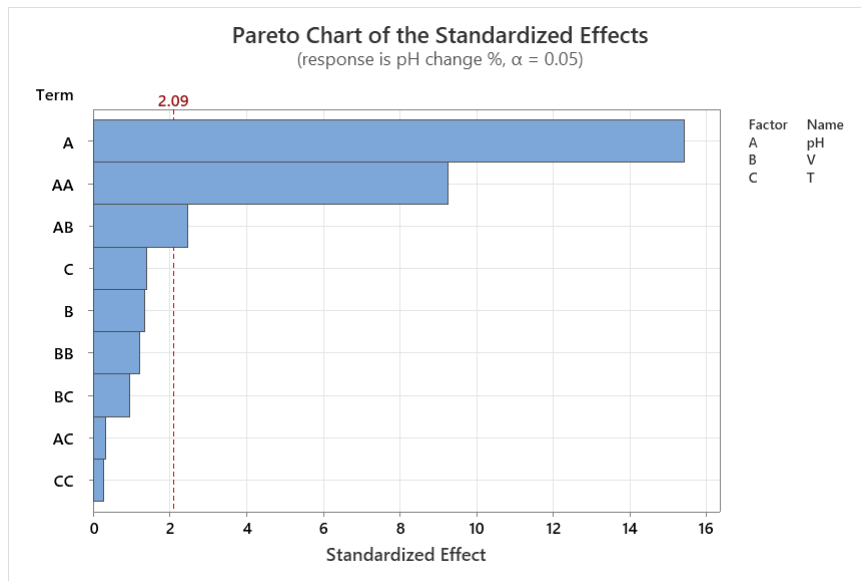


Figure 4.31 Pareto Chart for RSM of pH Removal by Electrocoagulation

The pareto chart in Figure 4.31 shows the statistically significant terms for the model we have developed for pH removal by electrocoagulation of black liquor. The pH term, (A), the square of pH term (AA), and the interaction between pH and electrolysis time (AC) caused the variability in data in this method analyzer. This concluded the significance of the initial pH condition for the change in final pH. Electrolysis time when combined with the initial pH condition affected the pH removal to a certain extent. This chart does not mention any effect by voltage, so voltage was not significant for the model.

Table 4.12 Model fit summary for RSM of pH Removal by Electrocoagulation

S	R ²	Adjusted R ²	Predicted R ²
3.72175	94.38%	91.85%	87.19%

The fit of the model for RSM of pH removal by electrocoagulation is summarized in Table 4.12. It provides R² of 94.38%, adjusted R² of 91.85%, and predicted R² of 87.19%, which attributed to a good fit of the model.

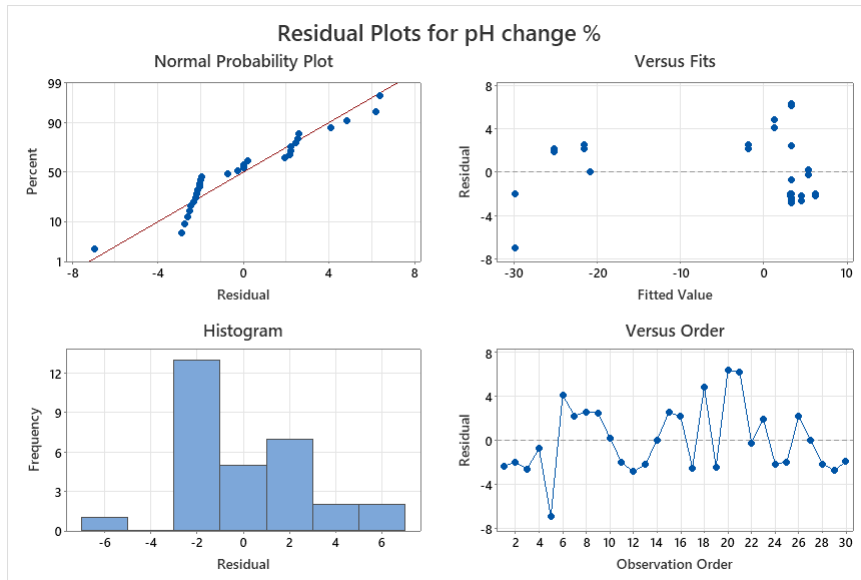


Figure 4.32 Residual plots for RSM of pH Removal by Electrocoagulation

Figure 4.32 presents four residual plots for RSM of pH removal by electrocoagulation. The normality plot showed a normal line with few points as outliers, attributing it still to be a normal distribution with independent variables. The residual versus the fitted value plot showed that the data point was distributed outside the zero point without any pattern giving a unanimous design. The histogram, on the other hand, was spread with a little bit of skewness on the right side and does not still affect the model due to the smaller number of data values.

Now, analyzing the contour plots to understand the optimum condition for pH removal with the help of Figure 4.33, which shows that at a constant electrolysis time of 35 min, black liquor with initial pH 10 could undergo maximum pH removal at any voltage point from 10 V to 30 V. To the opposite, all the sample runs with pH 7 showed increase in pH of the final liquor.

Figure 4.34 justifies, that the maximum pH removal efficiency was obtained with sample runs having an initial pH of 9 or more at a constant voltage. There, the electrolysis time did not play much of a role.

Figure 4.35 shows that the highest pH removal efficiency was obtained when pH 9 was kept constant at 20 V voltage and 10 min electrolysis time and its efficiency went on decreasing with the decrease in the electrolysis time. pH 9 sample at 30 V voltage and 60 min electrolysis time showed the lowest pH removal efficiency.

From these three contour plots, it could be concluded that the black liquor with pH 7 caused an increase in pH, and the ones with initial pH 9 and pH 11 caused a decrease in the pH of the final liquor. Similar results of initial pH acting as a buffering agent was obtained in the previous studies of electrocoagulation (Rastegarfar et al. 2015; Zaided and Bellakhal 2009). Samples with pH 7 irrespective of any other conditions remained unchanged in their property to increase and this could be attributed to the amphoteric property of $\text{Al}(\text{OH})_3$. On one hand, the OH^- radical in $\text{Al}(\text{OH})_3$ neutralized H^+ to make water and an aluminum salt and on the other hand, the $\text{Al}(\text{OH})_3$ solid reacted with excess OH^- to dissolve and form the complex ion $[\text{Al}(\text{OH})_4]^-$. This justified the shift of pH by electrocoagulation using aluminum electrodes due to the initial pH condition of black liquor.

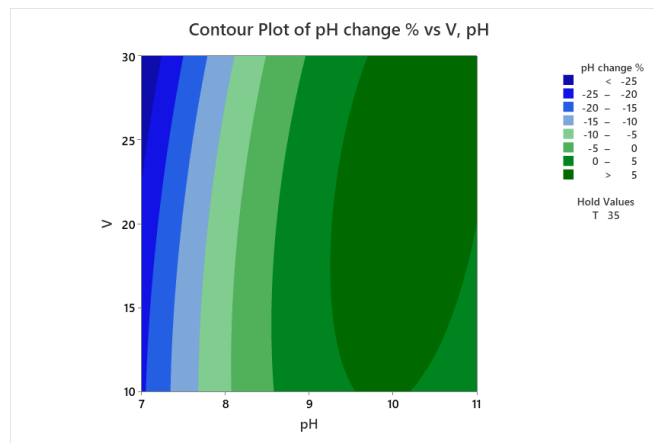


Figure 4.33 Response Surface Contours for pH Removal at 35 min

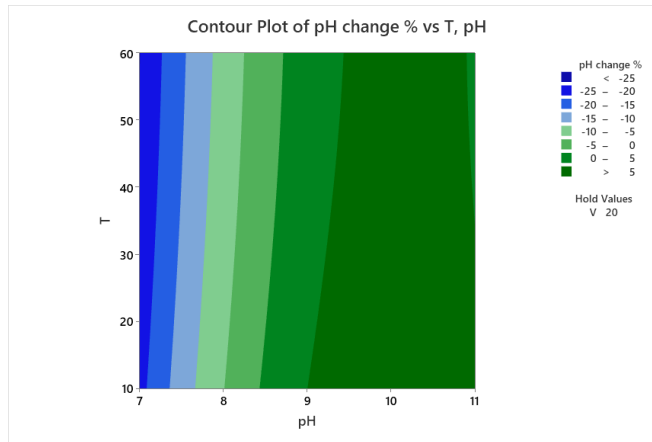


Figure 4.34 Response Surface Contours for pH Removal at 20 V

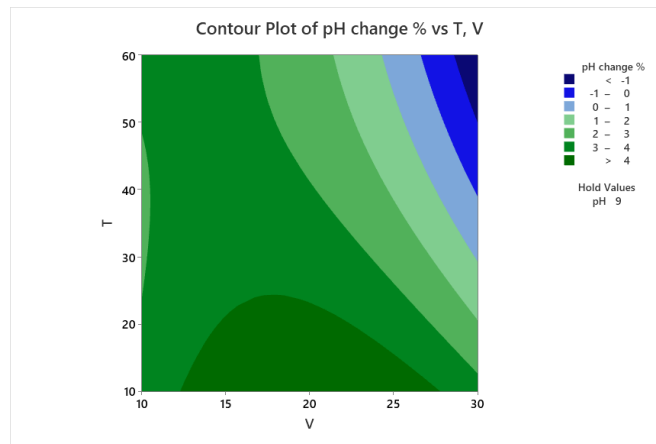


Figure 4.35 Response Surface Contours for pH Removal at pH 9

4.1.6.2 Optimization for pH Change

The RSM model was optimized in Minitab to obtain the maximum pH removal, which is presented in Figure 4.36. It showed that pH 10.42, voltage 20.68 V, and electrolysis time 10 min were the optimal conditions for pH removal, however, to make the chart comparable to our curated experimental design runs, we considered 11 pH with 20 V voltage and 10 min electrolysis time as the best condition.

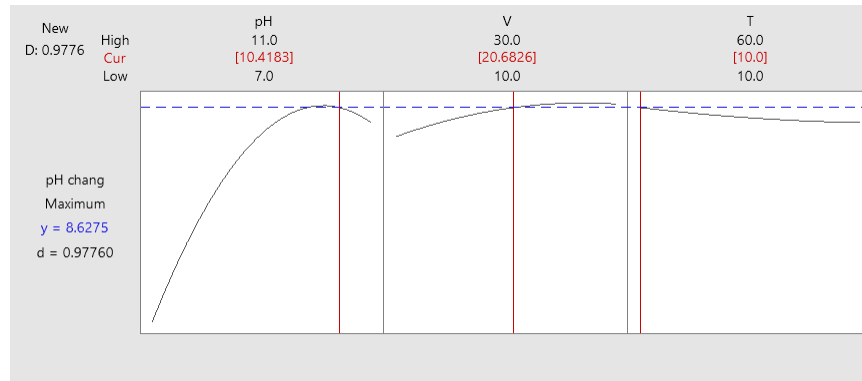


Figure 4.36 Response Optimization for pH Removal by Electrocoagulation

Later, all those values were fed to get the specific energy consumption and the overall optimized condition.

4.1.7 Specific Energy Consumption and Overall Process Optimization

As a final step to get the overall optimum condition for the electrocoagulation treatment process, SEC for all obtained optimum runs (4, 5, 9, 12, 13, 17, 20, 25, 29, and 30) was calculated as shown in Table 4.13. Here, the green highlight denotes the operation conditions with the least SEC value. Comparing all the SEC values of the experimental runs obtained from the optimum conditions with respect to COD, Phenol, TS, TDS, color, and alkalinity removal, run 9 and run 30 were found to be the best ones with the least SEC of 1.98 and 1.46 kWh/kg of COD, respectively. However, as justified by the four analytical parameters: COD, phenol, TS, and TDS, run 9 was more suitable, and run 30 was discarded.

Hence, the overall optimum condition for electrocoagulation was found to be black liquor adjusted to an initial pH 9 running at 20V voltage, with 0.87 A current output, 33.02 mA/cm² current density for 35 min time. This condition, as a result, helped in the removal of 49.4% COD, 43.61% phenol, 53.89% TS, 46.5% TDS, 29.33% color, and 5.78% pH, demonstrating the ability to use electrocoagulation for treatment of black liquor produced from the wheat straw pulping process. This method and condition could be replicated for the treatment of black liquor produced in other non-wood pulp and paper industries.

In comparison the previous studies carried out for electrocoagulation of black liquor, Zaied and Bellakhal and Rastegarfar had also adopted SEC as an economical parameter considering that

the cost of the process depended mainly on the consumption of the sacrificial electrode and the electrical energy (Rastegarfar et al. 2015; Zaied and Bellakhal 2009). The overall optimum condition for Zaied and Bellakhal was obtained at neutral pH, electrolysis time of 55 min, and current density of 14 mA/cm² and the optimum condition for the electrocoagulation study carried out by Rastegarfar et al. was obtained at acidic pH, electrolysis time of 55 minutes and current density of 61.81 mA/cm². Zaied and Bellakhal (2009) carried out electrocoagulation of black liquor obtained from Kraft pulping process of wood, whereas (Rastegarfar et al. 2015) carried out electrocoagulation study for black liquor obtained from soda-AQ pulping process of wheat straw lignin. This could be the reason that our study is more comparable to the result obtained from Rastegarfar et al. The lesser electrolysis time justifies the lesser current density in our case in comparison to the previous studies.

Table 4.13 Specific Energy Consumption of All Optimum Runs Obtained with Respect to COD, Phenol, TS, TDS, Color and Alkalinity Removal (Green highlight denotes the operational conditions with the least SEC value)

S.N.	Runs	pH	Voltage (V)	Electrolysis Time (min)	Specific Energy Consumption				
					Initial COD (mg/L)	Final COD (mg/L)	Current (mA)	Current Density (mA/cm ²)	SEC (KWh/kg of COD)
1.	4	9	20	35	41500	21500	930	35.30	2.17
2.	5	7	30	35	39200	21800	2740	104.01	11.02
3.	9	9	20	35	41500	21000	870.00	33.02	1.98
4.	12	9	20	35	41500	21400	930.00	35.30	2.16
5.	13	11	20	10	45800	31800	1670.00	63.39	1.59
6.	17	9	20	35	41500	21100	1100.00	41.75	2.52
7.	20	9	20	35	41500	21300	900.00	34.16	2.08
8.	25	7	30	35	39200	21700	2700.00	102.49	10.80
9.	29	9	20	35	41500	21300	900.00	34.16	2.08
10.	30	11	20	10	45800	30900	1630.00	61.87	1.46

4.1.8 Characterization of Raw Black Liquor and Electrocoagulated Liquor

The results for the characterization of raw black liquor, pH 9 black liquor, overall optimum condition electrocoagulated black liquor, and the residue obtained after electrocoagulation are discussed below:

4.1.8.1 Proximate Analysis

Proximate analysis of fuel provides the percentage of the material that burns in a gaseous state (volatile matter), in the solid state (fixed carbon), and the percentage of inorganic waste material (ash) (Nunes et al. 2018; Ozbayoglu 2018). The analysis of black liquor helps determine the major components necessary for making combustion calculations. It is simple to perform, requires no complicated equipment, and can estimate black liquor ultimate analysis and combustion properties (Bajpai 2017b). There is a positive relationship between fixed carbon (FC) and charcoal yield whereas the volatile matter (VM) and ash content (AC) relate negatively with charcoal yield. Thus, it is expected that greater biomass volatile content led to greater gas production (Nunes et al. 2018).

Table 4.14 shows the proximate analysis of 24-hour oven-dried samples of black liquor along with the residue of electrocoagulated black liquor obtained after vacuum filtration and Table 4.15 shows the proximate analysis of wet samples.

Table 4.14 Proximate Analysis of Black Liquor Samples (Dry Basis)

For 24-hour Oven Dried Samples				
S.N.	Type of Samples	Ash Content (%)	Volatile Matter (%)	Fixed Carbon (%)
1.	Raw Black Liquor	35.95	51.13	12.92
2.	pH 9 Black Liquor	43.82	53.17	3.01
3.	EC Treated Black Liquor	56.64	46.54	3.56
4.	Residue Optimum Condition	39.26	51.15	9.60

Table 4.15 Proximate Analysis of Black Liquor Samples (Wet Basis)

		For Wet Sample				
S.N.	Type of Samples	TS % Wet Sample (%)	Moisture Content for Wet Sample (%)	Ash Content (%)	Volatile Matter (%)	Fixed Carbon (%)
1.	Raw Black Liquor	4.15	95.85	1.49	2.12	0.54
2.	pH 9 Black Liquor	4.33	95.67	1.90	2.30	0.13
3.	EC Treated Black Liquor	2.08	97.92	1.18	0.97	0.07

The changes in ash content, volatile matter, and fixed carbon are justified by the following explanation:

1. The data showed that, when the pH of raw untreated black liquor was decreased to pH 9, the ash content increased from 35.95% to 43.82%, volatile matter increased from 51.13% to 53.17% and fixed carbon decreased from 12.92% to 3.01%. As both have similar moisture content, their proximate analysis on a dry basis was comparable. In general, black liquor in alkaline conditions had a relatively low ash content to ensure efficient and clean combustion. When it was adjusted to bring it to pH 9, the alkalinity decreased. Likewise, it promoted the formation of solid materials, which were easier to separate from the liquid phase causing an increase in ash content. The volatile matter content in black liquor was primarily composed of organic compounds, and it could be affected by changes in the pH of the black liquor. Lowering the pH of black liquor to 9 led to an increase in the volatile matter content. This was because lowering the pH could make the organic compounds in the liquor more volatile and, therefore, more readily released during combustion or other thermal processes.
2. The data showed that the value of ash content of electrocoagulated black liquor was 56.64%, the volatile matter was 46.54% and fixed carbon was 3.01% on dry basis and 1.18%, 0.97%, and 0.07% simultaneously in wet basis. The effect of electrocoagulation on the ash content of black liquor depended on several factors, including the composition of the black liquor, the efficiency of the electrocoagulation process, and the specific objectives of the treatment. Although electrocoagulation was primarily used to remove suspended solids, colloidal particles, and certain ions from the liquid, it also reduced ash content and volatile matter. This

could be possible because the untreated black liquor contained suspended ash particles or ionic impurities that could be effectively coagulated and separated through the electrocoagulation process. Likewise, it could remove a certain amount of organic compounds and particulate matter from black liquor. As a result, it led to a reduction in the volatile matter content of the treated liquor. The removal of organic contaminants during the process resulted in a decrease in the volatile organic matter. Electrocoagulation did not have much effect on fixed carbon, as fixed carbon primarily consisted of the organic components in black liquor that do not volatilize or burn during combustion, and fixed carbon content was generally more influenced by the pulping process and the composition of the raw materials used, rather than the post-treatment processes like electrocoagulation.

3. The ash content, volatile matter, and fixed carbon in residue obtained after electrocoagulation was found to be 39.26%, 51.15%, and 9.60%, respectively. The value of fixed carbon justified the decrease in fixed carbon content when the pH of black liquor was adjusted to pH 9. The ash content and volatile matter content could not be compared with that of the treated and untreated samples as it was an entirely dried-based analysis. However, those values showed the successful removal of ash and volatile matter from black liquor after electrocoagulation.

4.1.8.2 Lignin Content

Table 4.16 shows the amount of lignin content remaining after acid hydrolysis of 250 mL black liquor samples. Raw black liquor, pH 9 black liquor, and electrocoagulation treated black liquor contained 10256 mg/L, 10544 mg/L, and 2968 mg/L of lignin, respectively. The black liquor generated in the lab had 25% w/w lignin content, which was on the lower side as compared to the composition constituents of typical black liquors in wood-based black liquor by-products which contain about 35% to 45% w/w lignin (Speight 2023). This could be justified from the previous study carried out for the comparison of lignin distribution and structure in wheat straw and wood, which concluded that the straw lignin had a lower lignin content as compared to the wood (Zhang et al. 2022). The study showed that 71.85% of lignin was removed from the black liquor when it went through electrocoagulation treatment. It could be due to the removal of lignin-containing particles or colloids that were effectively coagulated and separated from the black liquor during the electrocoagulation process.

The result was also justified by the result shown by the reduction of COD after electrocoagulation. The relationship between lignin content and COD in black liquor is that lignin is a significant contributor to the organic portion of the COD. Therefore, a decrease in the lignin content of black liquor would lead to a decrease in the COD. However, COD also includes contributions from other organic and inorganic compounds, so it is not solely a measure of lignin. Anyway, this significant amount of decrease in lignin content helps in either the chemical recovery process or the biological degradation process.

Table 4.16 Lignin Content of Black Liquor Samples

S.N.	Particulars	Lignin Content (mg/L)
1.	Raw BL	10256
2.	pH 9 BL	10544
3.	EC Treated BL	2968

4.1.8.3 TGA Analysis

Thermogravimetric Analysis (TGA) of black liquor provided valuable information about its thermal behavior and composition. During TGA, the sample was subjected to a controlled temperature increase, and its weight changes were measured as a function of temperature (Coats and Redfern 1963). The TGA graph shows how the weight of the sample changes as it is heated, and the DTGA curve is the derivative of the TGA curve and provides information about the rate at which the sample is losing weight at specific temperatures (Figure 4.37 and Figure 4.38). Peaks or valleys in the DTGA curve correspond to rapid weight loss events and indicate different decomposition processes.

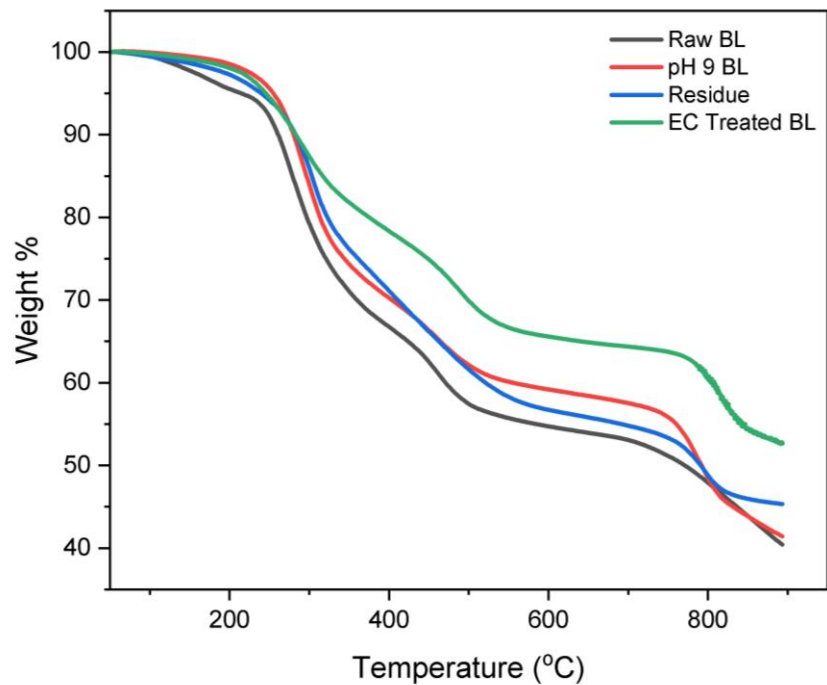


Figure 4.37 TGA Curves of Black Liquor Samples

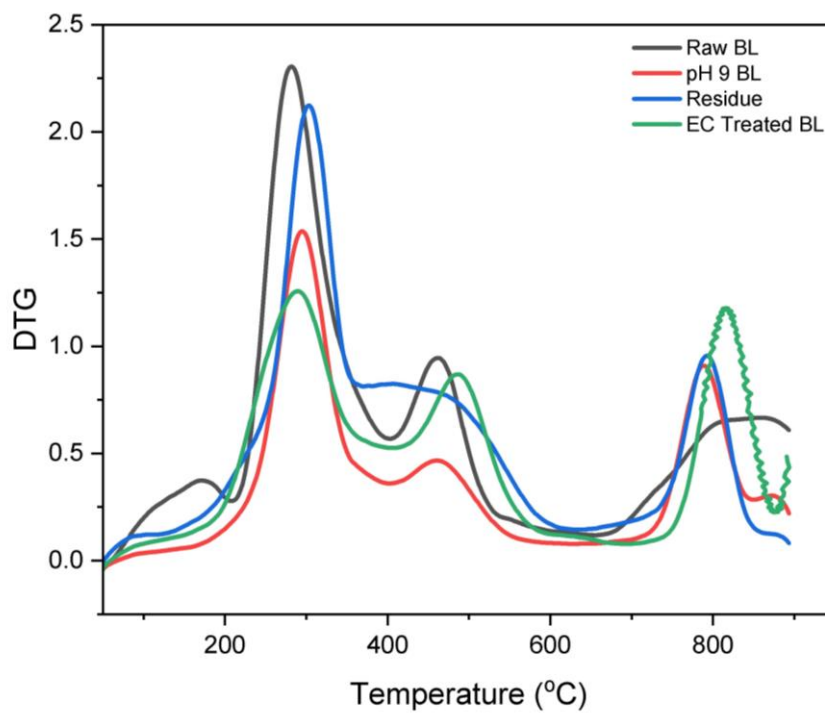


Figure 4.38 DTGA Curve of Black Liquor Samples

Primarily, the curves showed thermal degradation weight between 50 °C and 100 °C because of the evaporation of water from the sample (Tarrés et al. 2022). Up to 200 °C, volatile matter also started to decompose, and the peak was higher in raw BL and pH 9 BL than in comparison to the EC treated BL. This was because the VM was reduced after electrocoagulation. After this step, in the second stage, the weight loss became more apparent between 250 °C and 350 °C. This weight loss could be attributed to the cellulose, hemicellulose, and lignin content (Domínguez et al. 2008). The higher peaks shown by DTGA curves of untreated liquor and residue showed reduction in the remaining cellulose, hemicellulose, and lignin after the electrocoagulation process. This difference could be explained by a 71.85% reduction of Klason lignin in an electrocoagulated sample of black liquor. The degradation experienced above 400 °C was attributed to the decomposition of aromatic rings (Domínguez et al. 2008; Sun et al. 2000). This justified the reduction of phenolic content and lignin in an electrocoagulated sample of black liquor. Finally, there was another pick at around 750 to 800 °C. This was attributed to complex organic compounds, remaining char, and ash content. In contrast, the peak intensity was higher for electrocoagulated black liquor, and this may be due to the formation of other complex organic compounds due to the deposition of aluminum after electrocoagulation. This curve for residue also justified the condition.

Comparing the TGA curve of treated black liquor with that of untreated black liquor, the temperature at which weight loss events occurred and the extent of weight loss differed in those two patterns. Those differences indicated changes in the composition of the black liquor because of the pretreatment by electrocoagulation. There had been a reduction in the organic content or a shift in decomposition temperatures due to the removal of certain impurities through electrocoagulation.

4.1.8.4 FTIR Analysis

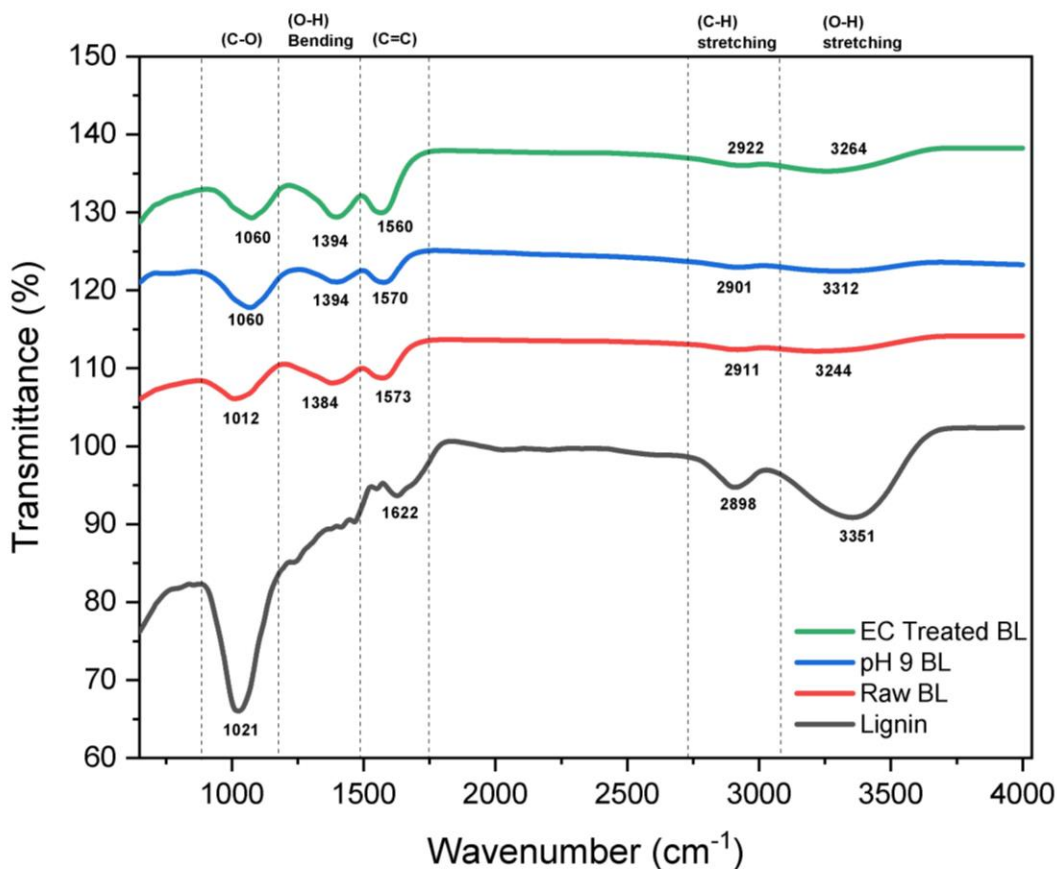


Figure 4.39 FTIR graph of Black Liquor Samples

FTIR analysis of black liquor can provide insights into the functional groups, chemical bonds, and molecular constituents present in the sample and the comparison with FTIR patterns of treated and untreated black liquor helps acknowledge the importance of electrocoagulation for treatment of black liquor (Figure 4.39). To have a more relevant comparison, lignin extracted from non-wood-based biomass was used. A broad peak at around 3400 cm^{-1} was associated with the stretching vibrations of hydroxyl (O-H) groups, indicating the presence of water and alcohol functional groups. This also corresponded to both aromatic and aliphatic hydroxyl groups present in lignin. The peak was the deepest for pure lignin and gradually decreased for the untreated and then the treated black liquor. The band (C-H) observed at around 2900 cm^{-1} indicated the presence of methyl and methylene groups. Bands located at 1600 , 1400 , and 1050 cm^{-1} could be attributed to the vibration of the aromatic rings of the lignin (Tarrés et al. 2022). Moreover, the band located

at 1600 cm^{-1} was assigned to the carbon-carbon double bonds (C=C), which are often found in aromatic compounds. Likewise, the band located at 1030 cm^{-1} was associated with the deformation vibrations of C-H bonds in the aromatic rings and deformation vibrations of C-O bonds in primary alcohols (Cao et al. 2021; Sewring and Theliander 2019). Although not prominent, the peaks and stretchings in electrocoagulated black liquor showed a decrease in lignin, phenol, and organic content justifying its treatability.

4.1.8.5 XRF Analysis

Table 4.17 shows the elemental composition result obtained after XRF analysis of untreated and treated black liquor along with the residue obtained after electrocoagulation.

Table 4.17 Elemental Composition of Black Liquor Samples

Elements	Untreated BL	EC Treated BL	EC Residue
Na (%)	43.80	38.70	9.20
Al (%)	1.40	6.20	19.40
Si (%)	15.50	2.80	13.50
P (%)	0.70	1.50	1
S (%)	18.20	14.50	13.80
Cl (%)	1	0.80	0.70
Zn (%)	0	0	0
Cu (%)	1.10	1.20	0.70
Fe (%)	1	0.90	0.80
Mn (%)	0.20	0.20	0
Cr (%)	0	0	0.20
V (%)	0	0	0
Ti (%)	0	0	0
K (%)	26.40	31.10	19.70
Ca (%)	2.20	2.10	1.70

The elemental decrement after electrocoagulation for Sodium (Na) was from 43.80% to 38.70%, i.e., by 11.64%, Sulphur (S) was from 18.20% to 14.50%, i.e., by 20.33%, Chlorine (Cl) was from 1% to 0.80%, i.e., by 20%, and Silicon (Si) was from 15.50% to 2.80%, i.e., by 81.94%, indicating suspended or colloidal particles in the black liquor that carry sodium, sulfur, chlorine and silicon ions were effectively coagulated and separated during the treatment. This accounted for the decrease of Silica or Silicon dioxide (SiO_2) in black liquor, providing reasons to improve biological degradation. On the other hand, it showed the increase in aluminum (Al) by 77%, and this occurred because of the use of aluminum electrodes for electrocoagulation, which was later precipitated after filtration up to a great extent. Other elements such as Calcium (Ca), Copper (Cu), Iron (Fe), Manganese (Mn), etc. did not show significant differences after electrocoagulation.

4.2 Anaerobic Digestion and Biomethane Potential

Anaerobic digestion is vital for the treatment of black liquor obtained from wheat straw pulping to obtain the effect of its toxicity in the digestion process. At the same time, the biological degradation process with electrocoagulated black liquor provides insights into its importance as a pretreatment method for black liquor.

In this section, the results obtained after anaerobic digestion of 10% and 30% control (sludge inoculum), black liquor, and electrocoagulated black liquor are discussed and compared.

4.2.1 Biogas Potential

Biogas yield or potential is one of the additional benefits obtained alongside the treatment of black liquor under anaerobic conditions. Here, the digester produces biogas which is comprised of around 60% methane (CH_4) and 40% carbon dioxide (CO_2), which can be used to generate heat or electricity purposes (Molino et al. 2013). The obtained biogas yield was subtracted from their respective control yield to get the accurate biogas potential of the black liquor sample and sludge mixtures. The biogas potential of controls as shown in Figure 4.40 shows that 10% control produced 490.43 mL of biogas and 30% control produced 328.54 mL of gas when inoculated in a 500 mL module system for 36 days. The 30% control was more diluted than the 10% control, causing a decrease in organic loading, hence causing the decrease in biogas yield. These values were significant for determining the actual biogas potential of black liquor samples.

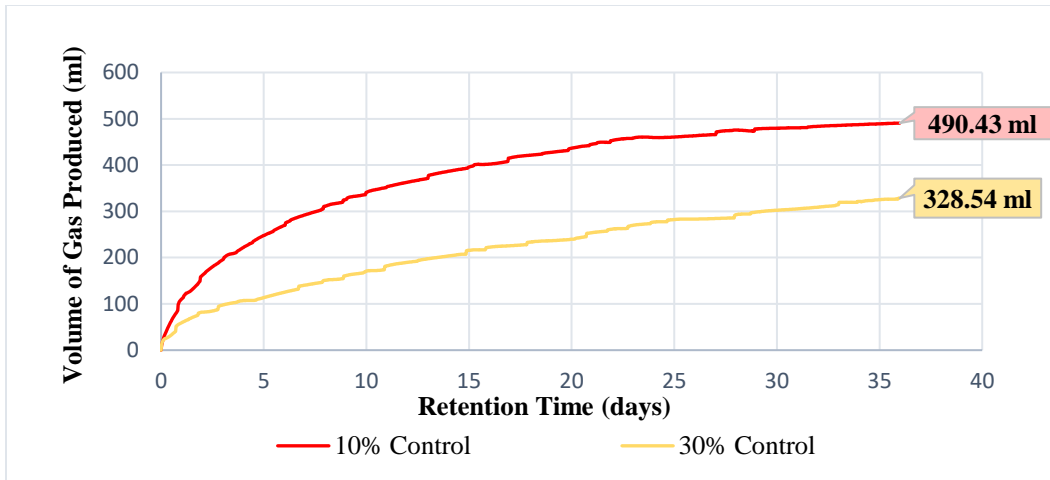


Figure 4.40 Biogas Potential of 10% Control and 30% Control in 36 days Retention Time

4.2.1.1 Biogas Potential of Raw Black Liquor

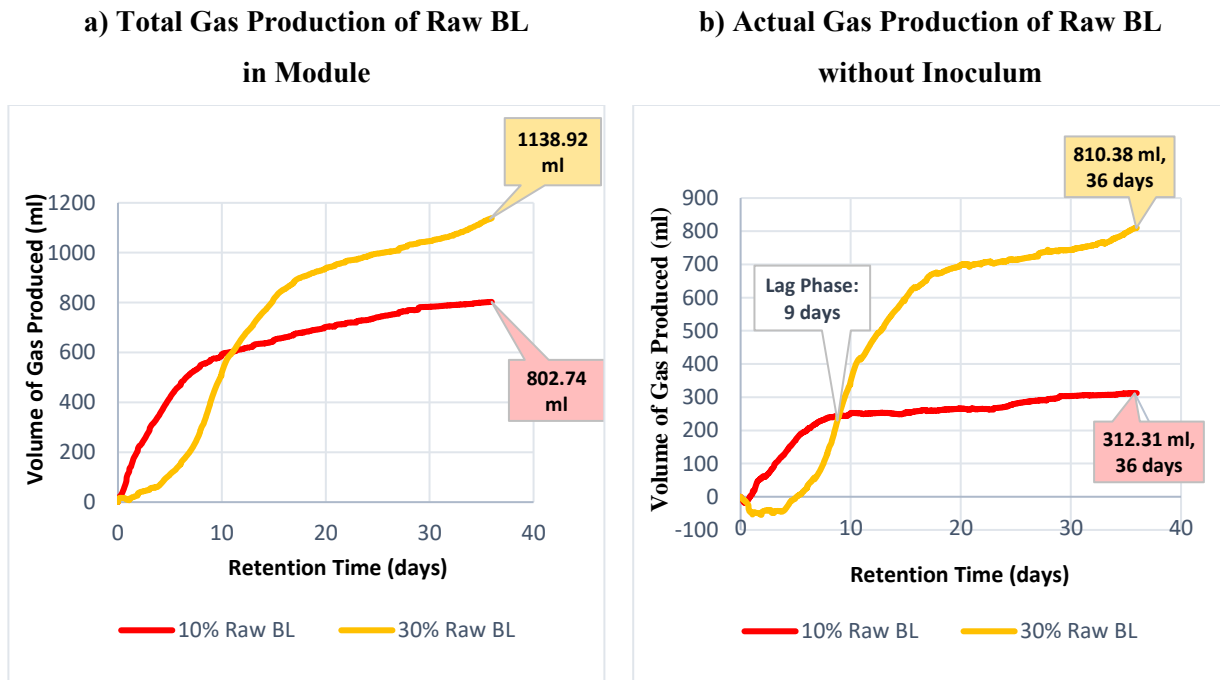


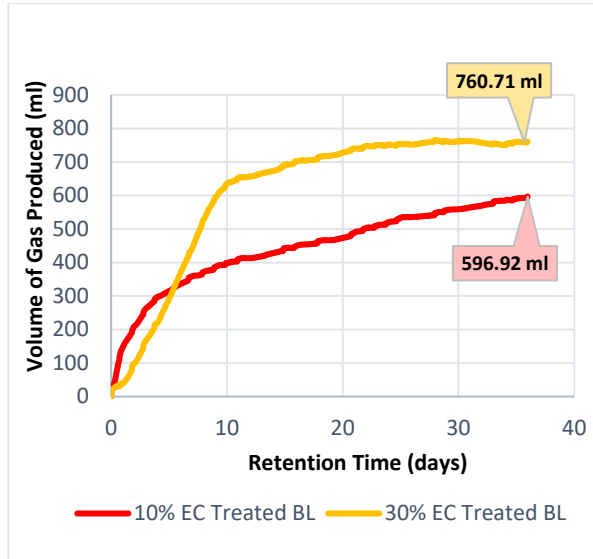
Figure 4.41 Biogas Potential of Raw BL with 10% and 30% Concentrations in 36 days Retention Time, where a) Total Gas Production of Raw BL in Module shows gas potential of BL and Inoculum and b) Actual Gas Production of Raw BL without Inoculum shows gas potential of BL after subtracting the gas yield of control with respective concentrations

Figure 4.41 a) shows the biogas potential of raw black liquor after mixing with the inoculum with varying concentrations in 36 days retention time. Figure 4.41 b) shows the actual biogas production of raw BL after subtracting gas yield of their respective 10% and 30% controls. When 10% of raw BL was used, the total gas production was 312.31 mL and when 30% raw BL was used, it was 810.38 mL in 36 days. The pattern of gas production showed that although the gas production was slow during the first 9 days for 30% raw BL, it escalated afterward showing the potential of black liquor for biogas yield. This result can be compared with the conclusion obtained in previous study on assessment of black liquor on methane production. The study found that the addition of black liquor increased the methane production (Jian et al. 2021). In our case, the increment of black liquor ratio from 10% to 30% resulted in an increase in the gas production. Likewise, another study on valorization of black liquor from pulping industry was focused on the major components present in black liquor (Morya et al. 2022). According to this study, hemicellulose is responsible for the biogas yield from the black liquor.

4.2.1.2 Effect of Electrocoagulation on Biogas Yield

Figure 4.42 a) shows the biogas potential of EC treated black liquor after mixing with inoculum with varying concentrations in 36 days retention time. Figure 4.42 b) shows the actual biogas production of EC treated BL after subtracting gas yield of their respective 10% and 30% controls. When 10% of EC BL was used, the total gas production was 106.49 mL and when 30% raw BL was used, it was 432.17 mL in 36 days. The pattern of gas production showed that although the gas production was slow during the first 3 days for 30% EC BL, it escalated afterwards showing the potential of electrocoagulated black liquor for biogas yield. This could be possible because the organic loading rate increased with the increasing ratio of black liquor in the module reactor, resulting in production of more gas when 30% EC treated BL was used (Ceron-Vivas et al. 2019).

a) Total Gas Production of EC Treated BL in Module



b) Actual Gas Production of EC Treated BL without Inoculum

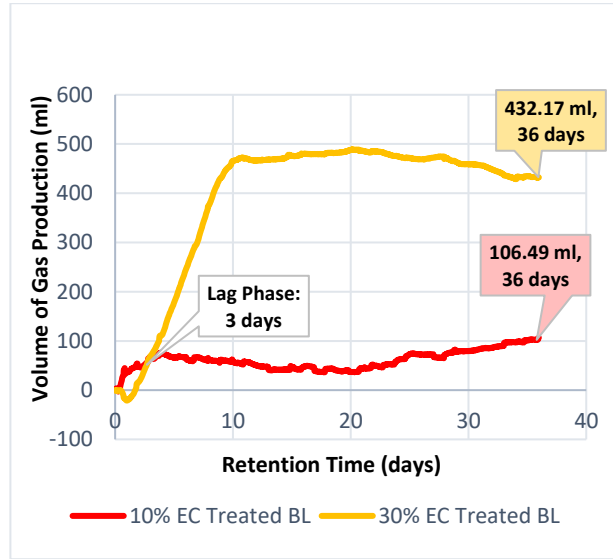


Figure 4.42 Biogas Potential of EC Treated BL with 10% and 30% Concentrations in 36 days Retention Time, where a) Total Gas Production of EC Treated BL in Module shows the gas potential of BL and Inoculum and b) Actual Gas Production of EC Treated BL without Inoculum shows the gas potential of BL after subtracting the gas yield of control with respective concentrations

4.2.1.3 Comparison of Biogas Potential of 10% Raw BL and EC

Figure 4.43 a) shows the total biogas yield when 10% raw BL and 10% EC treated BL in their respective modules including the gas yield from the inoculum and Figure 4.4.3 b) shows the actual biogas yield of 10% raw BL and 10% EC treated BL without considering the inoculum yield. This value was obtained by subtracting 10% control gas yield . When 10% of raw BL was used, the total gas production was 312.31 mL and when 10% of EC treated BL was used, it was 106.49 mL in 36 days. The pattern of gas production showed that the EC treated black liquor was not inhibited unlike the raw black liquor and reached near its maximum potential in just 4 days. This attributed to how electrocoagulation of black liquor helped in improving anaerobic digestion by reducing the residence time.

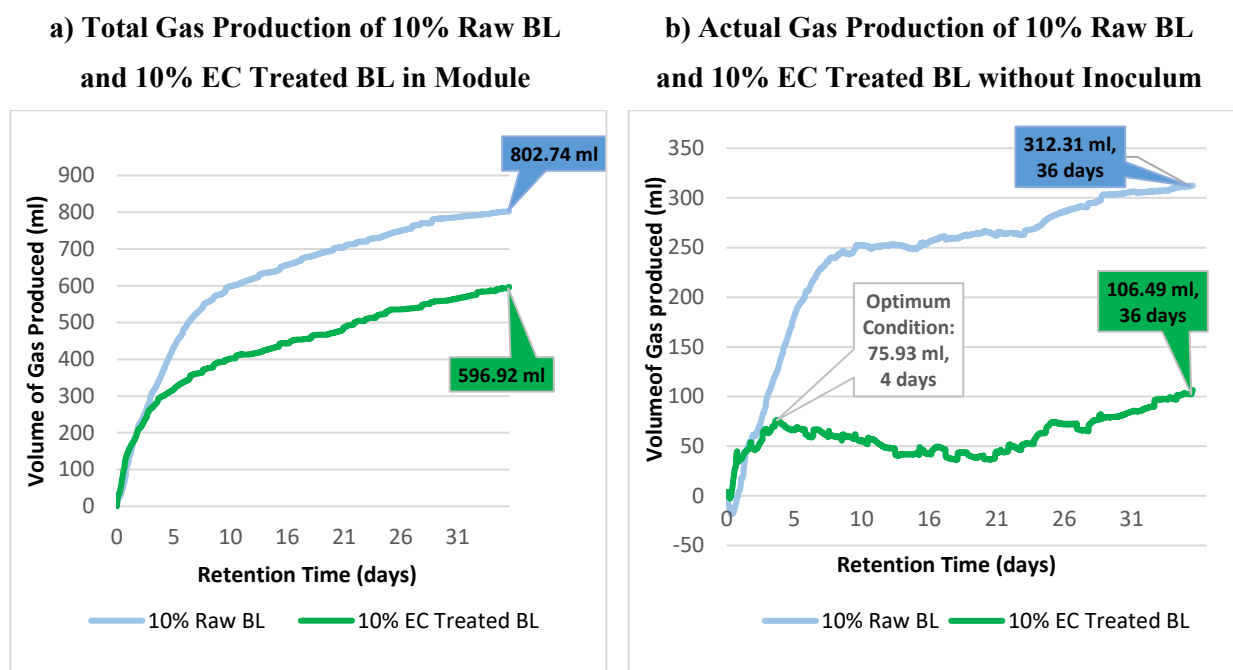


Figure 4.43 Comparison of Biogas Yield of 10% Raw BL and 10% EC Treated BL includes a) Total Gas Production of 10% Raw BL and 10% EC Treated BL in Module and b) Actual Gas Production of 10% Raw BL and 10% EC Treated BL without Inoculum

From Table 4.18, it was found that the gas potential of 10% raw BL was 186.34 mL/g of COD loading, and for EC treated was 126.77 mL/g of COD loading. Nonetheless, the total potential of gas yield was low for EC treated, it had improved anaerobic digestion by preventing inhibition time taken for gas production. Also, when the optimal condition of gas yield with 75.93 mL of gas production by 10% EC treated black liquor was reached in 4 days, the gas yield potential was 40 % more than the 10% raw black liquor as shown in Table 4.18.

Table 4.18 Biogas Potential of 10% Raw BL and 10% EC Treated BL

S.N.	Parameters	Retention Time (days)	Gas Produced (mL)	Volume of sample used (mL)	COD (mg/L)	Gas Potential (mL/g)
1.	10% Raw BL	36	312.31	40	41900	186.34
2.	10% EC BL	36	106.49	40	21000	126.77
3.	10% Raw BL	4	108.40	40	41900	64.68
4.	10% EC BL	4	75.93	40	21000	90.39

4.2.1.4 Comparison of Biogas Potential of 30% Raw BL and EC

Figure 4.44 a) shows the total biogas yield when 30% raw BL and 30% EC treated BL in their respective modules including the gas yield from the inoculum and Figure 4.4.3 b) shows the actual biogas yield of 30% raw BL and 30% EC treated BL without considering the inoculum yield. This value was obtained by subtracting 30% control gas yield. Figure 4.44 shows the biogas potential of 30% raw BL and EC treated BL. When 30% of raw BL was used, the total gas production was 810.38 mL and when 30% of EC treated BL was used, it was 432.17 mL in 36 days. The pattern of gas production shows that the EC treated black liquor was not inhibited unlike raw black liquor and reached near its maximum potential in just 10 days. This attributed how electrocoagulation of black liquor helped in improving anaerobic digestion by reducing the residence time.

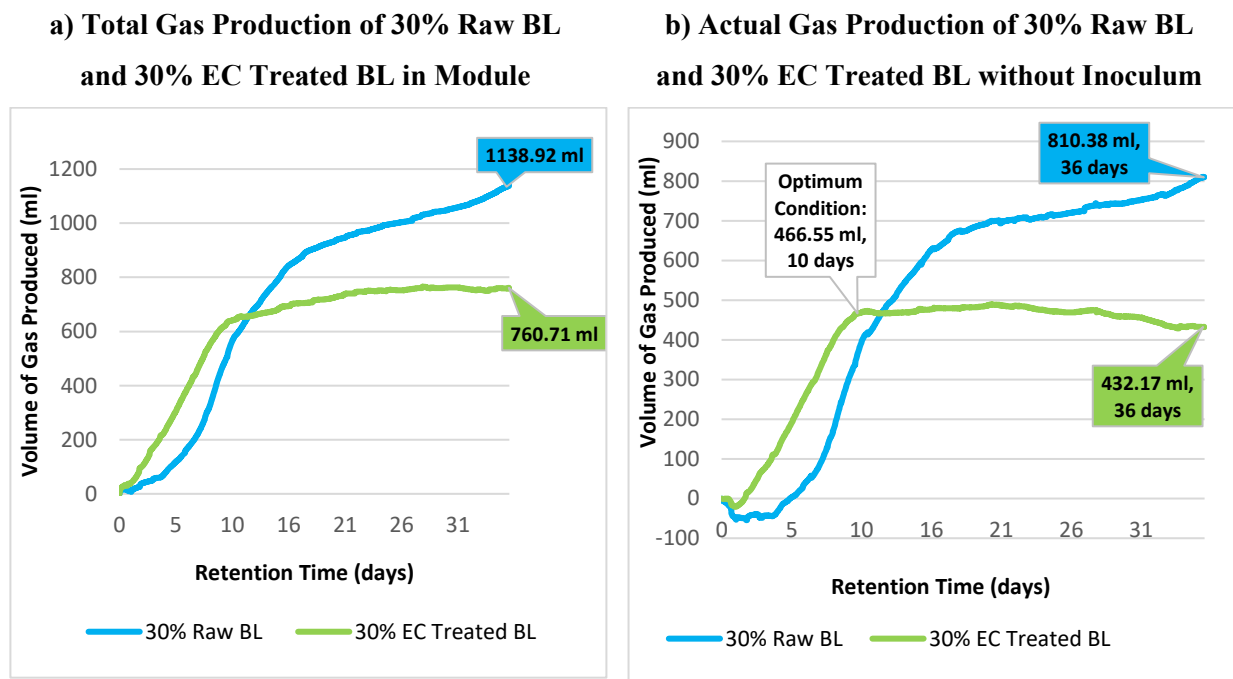


Figure 4. 44 Comparison of Biogas Yield of 30% Raw BL and 30% EC Treated BL includes a) Total Gas Production of 30% Raw BL and 30% EC Treated BL in Module and b) Actual Gas Production of 30% Raw BL and 30% EC Treated BL without Inoculum

Table 4.19 Biogas Potential of 30% Raw BL and 30% EC Treated BL

S.N.	Parameters	Retention Time (days)	Gas Produced (mL)	Volume of sample used (mL)	COD (mg/L)	Gas Potential (mL/g)
1.	30% Raw BL	36	810.38	120	41900	161.17
2.	30% EC BL	36	432.17	120	21000	171.50
3.	30% Raw BL	10	466.55	120	41900	92.79
4.	30% EC BL	10	466.55	120	21000	185.14

From Table 4.19, it was found that the gas potential of 30% raw BL was 161.17 mL/g of COD loading and for EC treated was 171.50 mL/g of COD loading. This showed that the overall gas yield increased by 6.40% when electrocoagulation was done before biological degradation. Nonetheless, when the gas producing pattern was considered and the gas production rate was ceased after 10 days i.e., when 30% EC treated BL reached its maximum potential of 466.55 mL, the gas yield potential was 99.50 % more than the 30% raw black liquor as shown in Table 4.19.

In summary, 30% EC treated BL performed the best in terms of more gas yield in less retention time. This condition also helped reduce the inhibition period in the anaerobic digestion process. This result can be compared with a previous study on improvement of biomethane potential by the addition of photolytic pretreatment step before anaerobic digestion (Jung 2019). The study suggested that decreasing the total organic content in terms of lignin concentration in the pretreatment step improved the biomethane potential. Although not the same, our study also incorporated a pretreatment step, i.e., helped removed the organic content in forms of flocs and improved the anaerobic digestion and biomethane potential. The reduction in phenol, lignin, and pH and silica content using electrocoagulation also helped improved the anaerobic digestion process of black liquor (Ceron-Vivas et al. 2019; Morya et al. 2022).

4.2.2 Reduction in COD after Digestion

Usually, the anaerobic digestion process reduces the COD of black liquor significantly. It does not eliminate all organic compounds due to other factors such as the complex composition of the black liquor, the efficiency of the anaerobic digestion process, and the operational conditions

for biological degradation. There will be some residual COD always remaining in the digestate. A previous study on anaerobic digestion and biogas production resulted that 85 to 90 % of COD could be degraded in an optimized anaerobic digestion system as microbes rely on organic content for their food (Huang et al. 2017). The reduction in COD after anaerobic digestion of black liquor can be justified by this study.

Table 4.20 COD Reduction after Anaerobic Digestion

S.N.	Particulars	Before AD	After AD	COD change (in %)
1	Sludge	2860	-	-
2	10% Control	2160	2120	1.85
3	30% Control	1690	1570	7.10
4	10% Raw BL	3920	3770	5.36
5	30% Raw BL	8440	6450	19.78
6	10% EC Treated BL	3150	2840	9.84
7	30% EC Treated BL	5250	3930	25.14

In this research, the EC treated black liquor was better than the untreated black liquor in the context of COD reduction. The reduction of lignin, phenol and silica content prior to anaerobic digestion with the help of electrocoagulation pretreatment of black liquor, made it more suitable for the anaerobic digestion system (Ceron-Vivas et al. 2019; Morya et al. 2022). Although lignin contains a significant amount of carbon, and rich in energy, it can act as recalcitrant, meaning it is resistant to microbial reduction. So, decreasing lignin content by 71.85% by electrocoagulation process helped improved the anaerobic digestion process. A better anaerobic digestion process involves breaking down of carbon content and a reduction in the COD. Moreover, a sludge mixture with 30% electrocoagulated black liquor was the best in COD reduction up to 25.14% (Table 4.20). This result also attributed that electrocoagulation of black liquor could increase the COD reduction rate by 83.58% and 27.1% for 10% and 30% volumes of black liquor, respectively. When comparing the concentration of black liquor used, the more the black liquor was used for the anaerobic digestion process, the more reduction in COD was observed at the end of the process. Also, as the concentration of black liquor in the sludge mixture increased, the difference in COD reduction potential between untreated and treated black liquor decreased.

4.2.3 Reduction in Volatile Matter Content after Digestion

In general, pre-treatment of feedstocks can increase biogas production and volatile matter reduction, and increased solubilization, so does the electrocoagulation had created in this research when used for the pretreatment of black liquor (Appels et al. 2008; S et al. 2016). Likewise, the reduction of volatile matter in a properly operating digester is 40-60% of the total volatile matter present in raw sludge feed (Kroehn and Mickelson 1992).

This research study showed that the reduction in volatile matter occurred by 14.45%, 9.42%, 16.35%, 16.53%, 29.23%, and 35.34% for 10% control, 30% control, 10% raw BL, 30% raw BL, 10% EC treated BL and 30% EC treated BL, respectively (Table 4.21).

Table 4.21 Reduction in VM after Anaerobic Digestion

S.N.	Particulars	VM% Before AD	VM% After AD	Change in VM% (%)
1	10% Control	61.32	52.46	14.45
2	30% Control	57.44	52.03	9.42
3	10% Raw BL	59.01	49.36	16.35
4	30% Raw BL	57.27	47.80	16.53
5	10% EC Treated BL	57.70	40.84	29.23
6	30% EC Treated BL	58.46	37.80	35.34

There was a significantly higher amount of VM reduction in EC treated BL justifying its higher gas yield due to the breaking down of organic matter or organic compounds by microorganisms in the absence of oxygen to convert into biogas. During biogas production, microorganisms, such as methanogenic bacteria, break down the volatile organic matter in the feedstock, also known as fermentation, which converts it into biogas, primarily methane (CH₄), and carbon dioxide (CO₂). While comparing the EC treated BL with the raw BL, raw BL, due to its biotoxicity was not able to convert its organic content to biogas to the potential of EC treated one. This was attributed to the importance of the pretreatment process in the biological degradation of black liquor for biomethane potential.

4.2.3 Change in pH after Digestion

The change in pH after anaerobic digestion of black liquor can vary depending on several factors, such as the initial pH of the black liquor, the specific composition of the black liquor after pulping, and the conditions under which the anaerobic digestion process is carried out. The pH of raw black liquor obtained after pulping was 12.1 and was reduced to 9. Both were on the alkaline side and during anaerobic digestion, microorganisms broke down the organic matter in black liquor, leading to pH change.

Table 4.22 Reduction in pH after Anaerobic Digestion

S.N.	Particulars	Before AD	After AD	pH reduction (in %)
1	Sludge	7.27	-	-
2	10% Control	7.45	7.75	4.03
3	30% Control	7.41	7.59	2.43
4	10% Raw BL	7.47	7.82	4.69
5	30% Raw BL	7.28	7.93	8.93
6	10% EC Treated BL	7.50	7.67	2.27
7	30% EC Treated BL	7.57	7.86	3.83

In this study, the pH of the mixture liquor was highly influenced by the pH of sludge obtained from the anaerobic digester of the city of Saskatoon, which was 7.17. This caused the overall pH of all mixtures to be within 8 pH. This being on the neutral side (i.e., around pH 7), the pH after digestion remained relatively stable and decreased just by 8.93% to the maximum when the acid was produced by the microbial activity (Table 4.22).

4.2.3 Change in TS after Digestion

Table 4.23 shows the reduction in TS content of sludge mixtures after anaerobic digestion which is justifiable because organic matter content is consumed and broken down for gas formation. The maximum TS reduction was obtained when 30% EC treated black liquor was used, and it showed better performance in comparison to raw black liquor. However, the data presented could not be compared to the actual breakdown of total solid content by the anaerobic microorganisms because TS analysis for the sludge mixtures was carried out for the aliquots obtained after centrifugation. The reduction rate in TS content must be higher after anaerobic digestion.

Table 4.23 Reduction in TS after Anaerobic Digestion

S.N.	Particulars	TS change (in %)
1	10% Control	5.25
2	30% Control	11.10
3	10% Raw BL	8.78
4	30% Raw BL	11.78
5	10% EC Treated BL	7.18
6	30% EC Treated BL	13.84

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

This chapter summarizes the major outcomes of this thesis. In addition, the direction of future studies related to this topic of interest is suggested.

5.1 Conclusion

The main objective of this research was to understand the feasibility of treating black liquor produced from wheat straw pulping process in the municipal wastewater treatment facility by biological degradation. To enhance this process, a pretreatment step was added and its effect on biological processes under anaerobic conditions was assessed with various parameters and analytical methods to conclude as follows:

1. The research has shown the applicability of the electrocoagulation process for the treatment of black liquor produced from the non-wood pulp and paper industry and its possibility of being an effective pretreatment step before biological degradation.
2. The effects of initial pH, voltage, and electrolysis time on the removal efficiency of COD, phenol, TS, TDS, color intensity, and pH were explored and optimized for the electrocoagulation process using RSM. Thereafter, optimized conditions concerning each analytical parameter were calculated and compared with the economic factor, and specific energy consumption (SEC) to get the overall optimum condition. As a result, the overall optimum condition was justified by run 9 with initial pH 9 running at 20V voltage for 35 min electrolysis time with SEC of 1.98 kWh/kg of COD. Consequently, this could help remove 49.4% COD, 43.61% phenol, 53.89% TS, 46.50% TDS, 29.33% color, and a reduction in alkalinity of the black liquor by 0.52 pH.. The optimized condition of electrocoagulation resulted in a black liquor with 21,000 mg/L COD, 198 mg/L phenol, 19,690 mg/L TS, 7,000 mg/L TDS, 50.49 whiteness index and 8.48 pH.
3. The efficacy of electrocoagulation treatment of black liquor was justified with the help of proximate analysis, lignin content, TGA curve, DTGA curve, FTIR analysis, and XRF analysis. It is found that electrocoagulation helps in the reduction of lignin by 71.85%, and VM by 12.5% (dry basis) and 58% (wet basis) resulting in electrocoagulated black liquor with 2968 mg/L lignin, 46.54% VM (dry basis) and 0.97% VM (wet basis). Likewise, the reduction in peak intensity and shift in degradation temperature in TGA and DTGA analysis contributed

to the reduction of organic content and impurities. Likewise, in the FTIR plot, the peaks and stretching in electrocoagulated BL showed decrease in lignin, phenol and organic content justifying its treatability. XRF analysis indicated the reduction in suspended and colloidal particles in BL that carry Na, S, Cl, and Si ions by electrocoagulation.

4. Black liquor, both untreated and pretreated showed promising results for anaerobic digestion and biogas potential. 10% and 30% Raw BL produced 312.31 mL and 810.38 mL of biogas in 36 days, whereas 10% and 30% EC treated BL produced 106.49 mL and 432.17 mL of biogas in 36 days in an ANKOM reactor of 500 mL.
5. Electrocoagulation reduced the retention time of gas production from 36 days to 4 days and 10 days for 10% and 30% BL composition, respectively by preventing the inhibition time of the reaction.
6. The gas yield potential of BL increased by 40% when pretreated with electrocoagulation and digested for 4 days resulting in a biogas yield of 90.39 mL/g of COD loading. Likewise, the gas yield potential of BL increased by 99.50% when pretreated and digested for 10 days, resulting in a biogas yield of 185.14 mL/g of COD loading. Overall, 30% EC treated BL performed the best. The biogas yield obtained from 30% EC treated BL in 10 days optimal time was 185.14 mL/g of COD loading, which was double in value than that produced from the raw black liquor.
7. The efficacy of anaerobic treatment of black liquor for both treated and untreated ones, and the effectiveness of EC treated BL over untreated BL was justified by the reduction parameters like COD, TS, pH, and VM. The maximum of 25.14% COD was reduced when 30% EC treated BL was used, which was 27.1% more than the untreated one. Likewise, the maximum 35.34% of VM was reduced when 30% EC treated BL was used, which was double in comparison to the untreated one. In addition, 13.43 % of TS was reduced when 30% EC treated BL was digested, which was 17% more than that of the untreated one. In the case of pH reduction, it was nearly stable in all conditions.

5.2 Recommendations for Future Work

1. Considering the need to shift the wood-based pulp and paper industries to non-wood-based because of the negative implications it has, this research study can be established and enhanced to apply in real world systems.
2. The optimization of the electrocoagulation process adopted in this research thesis does not include the addition of any electrolyte, hence, the use of sodium chloride as an electrolyte for enhancing the process is suggested.
3. Likewise, electrocoagulation can be enhanced by increasing the surface area of electrodes, so rectangular aluminum plates are suggested in place of cylindrical ones. This would contribute to the generation of more flocs.
4. Techno-economic and life cycle analysis should be conducted to understand the economic feasibility of using electrocoagulation as a pretreatment method for black liquor. This will guarantee its fit in the real industries.
5. In the case of anaerobic digestion, a continuous stirring digester is preferred. This would give the true biomethane potential.

5.3 Contribution of The Thesis

This thesis emphasizes on two environmentally friendly methods of black liquor treatment, namely electrocoagulation and anaerobic digestion. Electrocoagulation method not only helps in the treatment of black liquor without using any chemicals, but it also opens pathways for valorization of residue obtained after the treatment process without the generation of secondary pollution. The black liquor being rich in lignin content, the residue obtained from electrocoagulation of the black liquor does not contain sulfur compounds unlike in the ones generated from acid hydrolysis method of lignin precipitation, hence, the residue can be used to generate lignin powder, that can be used for other various applications such as a plastic biomaterial or in electronics and batteries. Anaerobic digestion method of wastewater treatment itself being one of the most effective and sustainable treatment system for reduction, recovery and recycling of resources, this research thesis contributes to incorporating this system into the treatment of black liquor obtained from wheat straw pulping process. Moreover, this study contributes to one of the very few approaches of using non-wood materials for pulping process and its treatment in the most

easy, sustainable, and environmentally friendly way. This thesis contributes to opening potential of treating black liquor along with the generation of biogas and energy sources.

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APPENDIX A: Supplementary Calculations for Analytical Parameters of Black Liquor

Table A1: Experimental Design Summary for Electrocoagulation

Design Summary			
Factors:	3	Replicates:	2
Base runs:	15	Total runs:	30
Base blocks:	1	Total blocks:	2

Table A2: Randomized Experimental Design Table for Electrocoagulation in Minitab

Runs	Blk	A	B	C
1	1	0	-1	-1
2	1	0	1	-1
3	1	1	0	1
4	1	0	0	0
5	1	-1	1	0
6	1	1	-1	0
7	1	-1	0	1
8	1	-1	0	-1
9	1	0	0	0
10	1	1	1	0
11	1	0	-1	1
12	1	0	0	0
13	1	1	0	-1
14	1	-1	-1	0
15	1	0	1	1
16	2	-1	0	-1
17	2	0	0	0
18	2	1	-1	0
19	2	0	-1	-1
20	2	0	0	0
21	2	0	1	-1
22	2	1	1	0
23	2	-1	0	1
24	2	0	-1	1
25	2	-1	1	0
26	2	0	1	1
27	2	-1	-1	0
28	2	1	0	1
29	2	0	0	0
30	2	1	0	-1

Table A3: Current Flow During Electrocoagulation

Runs	Starting Current (A)	Current at Mid (A)	Ending Current (A)	Average Current (A)
1	0.8	1.2	1.6	1.20
2	7.9	1.5	0.9	3.43
3	2.1	0.3	0.1	0.83
4	1.1	1.4	0.3	0.93
5	6	2	0.23	2.74
6	1.2	0.7	0.9	0.93
7	1.1	2.2	2	1.77
8	1.1	3.6	2	2.23
9	1.1	1.2	0.3	0.87
10	4.4	0.3	0.1	1.60
11	0.8	2	0.3	1.03
12	1.3	1.2	0.3	0.93
13	2.2	1.5	1.3	1.67
14	0.9	1.3	2.6	1.60
15	8	0.2	0.1	2.77
16	1.1	3.7	2	2.27
17	1.4	1.6	0.3	1.10
18	1.5	0.8	0.9	1.07
19	0.8	1.3	1.8	1.30
20	1.1	1.3	0.3	0.90
21	8	1.5	0.9	3.47
22	4.6	0.3	0.1	1.67
23	1.1	2	2	1.70
24	0.8	2	0.6	1.13
25	6	2	0.1	2.70
26	7.7	0.2	0.1	2.67
27	0.9	1.3	2.6	1.60
28	2.2	0.2	0.1	0.83
29	1.1	1.3	0.3	0.90
30	2.2	1.4	1.3	1.63

Table A4: TS Calculation of Black Liquor Samples after Electrocoagulation for Block 1

S.N.	Block No.	Particulars	[B] Vessel Weight (in g)	[S] Sample Weight (in g)	[F] Final Weight after Drying (in g)	[X=F-B] Final Weight of Sample Only (in g)	[V] Volume of Sample (in mL)	[X/V] TS (in mg/L)	Average TS (in mg/L)
1	Block 1	Run 1	1.96	5.023	2.085	0.125	5	25000	24960
2			1.923	4.989	2.048	0.125	5	24920	
3		Run 2	1.97	4.923	2.080	0.110	5	21900	22800
4			1.955	4.906	2.074	0.119	5	23700	
5		Run 3	1.962	4.988	2.099	0.137	5	27300	27380
6			1.96	4.923	2.097	0.137	5	27460	
7		Run 4	1.969	4.699	2.070	0.101	5	20100	20160
8			1.969	4.699	2.070	0.101	5	20220	
9		Run 5	1.953	4.825	2.063	0.110	5	21900	21920
10			1.953	4.825	2.063	0.110	5	21940	
11		Run 6	1.974	4.925	2.094	0.120	5	24000	25040
12			1.977	4.846	2.107	0.130	5	26080	
13		Run 7	1.949	4.913	2.084	0.135	5	27000	28800
14			1.943	4.848	2.096	0.153	5	30600	
15		Run 8	1.902	5.004	2.035	0.133	5	26500	26720
16			1.902	5.004	2.037	0.135	5	26940	
17		Run 9	1.96	4.733	2.055	0.095	5	19020	19690
18			1.96	4.733	2.062	0.102	5	20360	
19		Run 10	1.936	4.704	2.081	0.145	5	29000	30080
20			1.962	4.897	2.118	0.156	5	31160	
21		Run 11	1.935	4.877	2.045	0.110	5	22000	22000
22			1.928	5.009	2.038	0.110	5	22000	
23		Run 12	1.965	4.957	2.060	0.095	5	19000	19880
24			1.943	5.058	2.047	0.104	5	20760	
25		Run 13	1.972	5.041	2.100	0.128	5	25500	26560
26			1.957	4.847	2.095	0.138	5	27620	
27		Run 14	1.99	4.983	2.135	0.145	5	29000	29280
28			1.957	4.933	2.105	0.148	5	29560	
29		Run 15	1.923	4.958	2.043	0.120	5	24000	24480
30			1.923	4.958	2.048	0.125	5	24960	

Table A5: TS Calculation of Black Liquor Samples after Electrocoagulation for Block 2

S.N.	Block No.	Particulars	[B] Vessel Weight (in g)	[S] Sample Weight (in g)	[F] Final Weight after Drying (in g)	[X=F- B] Final Weight of Sample Only (in g)	[V] Volume of Sample (in mL)	[X/V] TS (in mg/L)	Average TS (in mg/L)
1	Block 2	Run 16	0.965	4.641	1.090	0.125	5	25000	25690
2			0.961	4.994	1.093	0.132	5	26380	
3		Run 17	0.981	5.011	1.082	0.101	5	20100	20130
4			0.964	4.913	1.065	0.101	5	20160	
5		Run 18	0.972	5.078	1.095	0.123	5	24500	25570
6			0.974	5.027	1.107	0.133	5	26640	
7		Run 19	0.976	4.956	1.099	0.123	5	24500	24910
8			0.976	4.883	1.103	0.127	5	25320	
9		Run 20	0.96	4.974	1.060	0.100	5	20000	20670
10			0.987	4.916	1.094	0.107	5	21340	
11		Run 21	0.963	5.025	1.071	0.108	5	21600	22600
12			0.975	4.899	1.093	0.118	5	23600	
13		Run 22	0.974	4.889	1.127	0.153	5	30500	30740
14			0.967	4.956	1.122	0.155	5	30980	
15		Run 23	0.953	4.936	1.088	0.135	5	27000	27930
16			0.975	4.907	1.119	0.144	5	28860	
17		Run 24	0.98	5.047	1.090	0.110	5	22000	22050
18			0.978	4.992	1.089	0.111	5	22100	
19		Run 25	0.978	5.005	1.086	0.108	5	21500	21000
20			0.968	4.946	1.071	0.103	5	20500	
21		Run 26	0.977	4.924	1.102	0.125	5	24900	24490
22			0.983	4.922	1.103	0.120	5	24080	
23		Run 27	0.992	4.952	1.137	0.145	5	29000	28360
24			0.964	4.848	1.103	0.139	5	27720	
25		Run 28	0.979	4.903	1.119	0.140	5	28000	27660
26			0.985	4.908	1.122	0.137	5	27320	
27		Run 29	0.977	4.898	1.078	0.101	5	20200	20270
28			0.968	4.879	1.070	0.102	5	20340	
29		Run 30	0.959	4.95	1.096	0.137	5	27400	27040
30			0.985	5.037	1.118	0.133	5	26680	

Table A6: Calculation of WI, ΔE and YI of Black liquor Samples

Color Index Calculation							
S.N.	Particulars	L	a	b	WI Whiteness Index)	ΔE (Total Color Difference)	YI (Yellowness Index)
1	RB	47.42	15.09	27.93	38.58	60.79	84.14
5	pH7	49.81	16.62	29.58	39.42	59.92	84.83
6	pH9	47.54	14.99	27.20	39.04	60.35	81.73
7	pH11	47.12	14.03	27.25	38.88	60.50	82.62
8	Run 1	59.18	11.30	25.72	50.44	48.79	62.09
9	Run 2	60.02	11.52	26.81	50.50	48.69	63.82
10	Run 3	58.73	11.97	26.12	49.72	49.53	63.53
11	Run 4	59.85	11.49	26.54	50.52	48.68	63.35
12	Run 5	65.36	10.70	26.31	55.20	43.91	57.51
13	Run 6	60.08	11.86	26.53	50.62	48.59	63.09
14	Run 7	62.44	12.89	26.43	52.29	46.91	60.48
15	Run 8	61.01	14.24	27.93	49.97	49.24	65.40
16	Run 9	60.25	11.40	27.22	50.49	48.68	64.55
17	Run 10	61.28	11.34	26.94	51.48	47.68	62.81
18	Run 11	62.49	12.14	28.23	51.51	47.62	64.53
19	Run 12	59.97	11.97	27.27	50.11	49.08	64.96
20	Run 13	59.47	13.14	27.52	49.28	49.94	66.11
21	Run 14	62.76	12.52	25.35	53.24	45.99	57.71
22	Run 15	63.61	13.62	28.33	51.92	47.23	63.62
23	Run 16	56.02	6.56	23.16	49.87	49.38	59.06
24	Run 17	57.35	6.89	25.10	50.03	49.14	62.53
25	Run 18	59.27	7.74	27.22	50.40	48.70	65.61
26	Run 19	57.53	7.41	24.51	50.40	48.80	60.87
27	Run 20	58.04	7.65	26.06	50.01	49.14	64.15
28	Run 21	57.32	6.74	24.26	50.44	48.76	60.47
29	Run 22	61.12	8.41	27.40	51.69	47.39	64.05
30	Run 23	59.19	6.27	24.52	51.98	47.17	59.18
31	Run 24	58.33	5.79	24.60	51.27	47.89	60.25
32	Run 25	60.49	4.72	21.38	54.83	44.38	50.49
33	Run 26	58.36	5.44	23.70	51.78	47.39	58.01
34	Run 27	59.99	6.70	23.55	53.09	46.09	56.08
35	Run 28	58.22	8.19	27.31	49.42	49.70	67.01
36	Run 29	58.79	7.55	26.66	50.34	48.78	64.79
37	Run 30	58.12	8.45	27.43	49.23	49.90	67.43

Table A7: TS Calculation of Black Liquor Samples before Electrocoagulation

S.N.	Particulars	[B] Vessel Weight (in g)	[S] Sample Weight (in g)	[F] Final Weight after Drying (in g)	[X=F-B] Final Weight of Sample Only (in g)	[V] Volume of Sample (in mL)	[X/V] TS (in mg/l)	Average TS (in mg/l)
1	RB	1.923	10.044	2.336	0.413	10	41300	41950
2		1.974	10.149	2.4	0.426	10	42600	
3	pH7	1.969	9.991	2.397	0.428	10	42800	42750
4		1.942	9.813	2.369	0.427	10	42700	
5	pH9	1.955	9.894	2.377	0.422	10	42200	42700
6		1.961	9.837	2.393	0.432	10	43200	
7	pH11	1.975	9.747	2.382	0.407	10	40700	41500
8		1.957	9.956	2.38	0.423	10	42300	

APPENDIX B: Minitab Response Surface Method Background Analysis

Table B1: Coded Coefficients for COD Removal after Electrocoagulation

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	48.76	1.32	36.89	0.000	
pH	-3.962	0.809	-4.90	0.000	1.00
V	-1.065	0.809	-1.32	0.203	1.00
T	-0.935	0.809	-1.16	0.262	1.00
pH*pH	-11.02	1.19	-9.25	0.000	1.01
V*V	-5.45	1.19	-4.58	0.000	1.01
T*T	-3.97	1.19	-3.33	0.003	1.01
pH*V	-8.15	1.14	-7.12	0.000	1.00
pH*T	-0.75	1.14	-0.66	0.518	1.00
V*T	-5.84	1.14	-5.11	0.000	1.00

Table B2: Analysis of Variance for COD Removal after Electrocoagulation

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	2204.29	244.921	23.37	0.000
Linear	3	283.24	94.415	9.01	0.001
pH	1	251.11	251.109	23.96	0.000
V	1	18.15	18.150	1.73	0.203
T	1	13.99	13.986	1.33	0.262
Square	3	1112.04	370.681	35.37	0.000
pH*pH	1	896.46	896.464	85.55	0.000
V*V	1	219.49	219.491	20.95	0.000
T*T	1	116.14	116.143	11.08	0.003
2-Way Interaction	3	809.00	269.667	25.73	0.000
pH*V	1	531.29	531.294	50.70	0.000
pH*T	1	4.55	4.547	0.43	0.518
V*T	1	273.16	273.160	26.07	0.000
Error	20	209.59	10.479		
Lack-of-Fit	3	176.38	58.792	30.09	0.000
Pure Error	17	33.21	1.954		
Total	29	2413.88			

Regression Equation in Uncoded Units:

$$\text{COD Change\%} = -277.1 + 56.28 \text{ pH} + 6.560 \text{ V} + 1.010 \text{ T} - 2.754 \text{ pH*pH} - 0.0545 \text{ V*V} \\ - 0.00635 \text{ T*T} - 0.4075 \text{ pH*V} - 0.0151 \text{ pH*T} - 0.02337 \text{ V*T}$$

Parameters:

Response	Goal	Lower	Target	Upper	Weight	Importance
COD Change%	Maximum	23.1441	49.3976		1	1

Solution:

Solution	pH	V	T	COD Change% Fit	Composite Desirability
1	8.49495	22.3232	28.1818	49.2675	0.995047

Multiple Response Prediction:

Variable	Setting			
pH	8.49495			
V	22.3232			
T	28.1818			
Response	Fit	SE Fit	95% CI	95% PI
COD Change%	49.27	1.25	(46.65, 51.88)	(42.03, 56.51)

Table B3: Coded Coefficients for Phenol Removal after Electrocoagulation

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	42.917	0.966	44.44	0.000	
pH	-3.244	0.591	-5.48	0.000	1.00
V	-1.336	0.591	-2.26	0.035	1.00
T	-1.119	0.591	-1.89	0.073	1.00
pH*pH	-9.814	0.871	-11.27	0.000	1.01
V*V	-4.268	0.871	-4.90	0.000	1.01
T*T	-4.298	0.871	-4.94	0.000	1.01
pH*V	-8.230	0.836	-9.84	0.000	1.00
pH*T	-1.425	0.836	-1.70	0.104	1.00
V*T	-5.774	0.836	-6.90	0.000	1.00

Table B4: Analysis of Variance for Phenol Removal after Electrocoagulation

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	1925.56	213.951	38.23	0.000
Linear	3	216.94	72.314	12.92	0.000
pH	1	168.35	168.351	30.08	0.000
V	1	28.54	28.542	5.10	0.035

T	1	20.05	20.048	3.58	0.073
Square	3	883.82	294.606	52.64	0.000
pH*pH	1	711.24	711.240	127.09	0.000
V*V	1	134.50	134.498	24.03	0.000
T*T	1	136.40	136.396	24.37	0.000
2-Way Interaction	3	824.80	274.933	49.13	0.000
pH*V	1	541.86	541.863	96.83	0.000
pH*T	1	16.24	16.245	2.90	0.104
V*T	1	266.69	266.690	47.66	0.000
Error	20	111.92	5.596		
Lack-of-Fit	3	104.52	34.840	80.01	0.000
Pure Error	17	7.40	0.435		
Total	29	2037.48			

Regression Equation in Uncoded Units

$$\text{Phenol Change \%} = -261.7 + 51.77 \text{ pH} + 6.085 \text{ V} + 1.155 \text{ T} - 2.453 \text{ pH*pH} - 0.04268 \text{ V*V} - 0.00688 \text{ T*T} - 0.4115 \text{ pH*V} - 0.0285 \text{ pH*T} - 0.02310 \text{ V*T}$$

Parameters:

Response	Goal	Lower	Target	Upper	Weight	Importance
Phenol Change %	Maximum	19.35	43.61		1	1

Solution:

Solution	pH	V	T	Phenol Change % Fit	Composite Desirability
1	8.49495	22.5253	28.6869	43.3113	0.987687

Multiple Response Prediction:

Variable	Setting			
pH	8.49495			
V	22.5253			
T	28.6869			
Response	Fit	SE Fit	95% CI	95% PI
Phenol Change %	43.311	0.917	(41.399, 45.224)	(38.019, 48.603)

Table B5: Coded Coefficients for TS Removal after Electrocoagulation

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	52.845	0.820	64.42	0.000	
pH	-1.828	0.502	-3.64	0.002	1.00
V	0.588	0.502	1.17	0.255	1.00
T	-0.529	0.502	-1.05	0.305	1.00
pH*pH	-12.894	0.739	-17.44	0.000	1.01
V*V	-3.002	0.739	-4.06	0.001	1.01
T*T	-4.708	0.739	-6.37	0.000	1.01
pH*V	-7.409	0.710	-10.43	0.000	1.00
pH*T	0.852	0.710	1.20	0.244	1.00
V*T	-2.732	0.710	-3.85	0.001	1.00

Table B6: Analysis of Variance for TS Removal after Electrocoagulation

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	1921.26	213.47	52.87	0.000
Linear	3	63.48	21.16	5.24	0.008
pH	1	53.47	53.47	13.24	0.002
V	1	5.53	5.53	1.37	0.255
T	1	4.47	4.47	1.11	0.305
Square	3	1353.12	451.04	111.70	0.000
pH*pH	1	1227.80	1227.80	304.06	0.000
V*V	1	66.54	66.54	16.48	0.001
T*T	1	163.69	163.69	40.54	0.000
2-Way Interaction	3	504.66	168.22	41.66	0.000
pH*V	1	439.12	439.12	108.75	0.000
pH*T	1	5.81	5.81	1.44	0.244
V*T	1	59.73	59.73	14.79	0.001
Error	20	80.76	4.04		
Lack-of-Fit	3	76.19	25.40	94.49	0.000
Pure Error	17	4.57	0.27		
Total	29	2002.02			

Regression Equation in Uncoded Units:

$$\begin{aligned} \text{TS Change} &= -290.7 + 63.92 \text{ pH} + 4.976 \text{ V} + 0.571 \text{ T} - 3.224 \text{ pH}^2 - 0.03002 \text{ V}^2 \\ \% &- 0.00753 \text{ T}^2 \\ &- 0.3704 \text{ pH} \cdot \text{V} + 0.0171 \text{ pH} \cdot \text{T} - 0.01093 \text{ V} \cdot \text{T} \end{aligned}$$

Parameters:

Response	Goal	Lower	Target	Upper	Weight	Importance
TS Change %	Maximum	27.15	53.89		1	1

Solution:

Solution	pH	V	T	TS Change % Fit	Composite Desirability
1	8.61616	24.1414	30.2020	53.2151	0.974762

Multiple Response Prediction:

Variable	Setting
pH	8.61616
V	24.1414
T	30.202

Response	Fit	SE Fit	95% CI	95% PI
TS Change %	53.215	0.772	(51.605, 54.825)	(48.725, 57.705)

Table B7: Coded Coefficients for TDS Removal after Electrocoagulation

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	45.338	0.823	55.07	0.000	
pH	-0.715	0.504	-1.42	0.172	1.00
V	0.439	0.504	0.87	0.395	1.00
T	0.706	0.504	1.40	0.177	1.00
pH*pH	-11.475	0.742	-15.46	0.000	1.01
V*V	-5.033	0.742	-6.78	0.000	1.01
T*T	-5.095	0.742	-6.87	0.000	1.01
pH*V	-5.105	0.713	-7.16	0.000	1.00
pH*T	-0.390	0.713	-0.55	0.590	1.00
V*T	-3.657	0.713	-5.13	0.000	1.00

Table B8: Analysis of Variance for TDS Removal after Electrocoagulation

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	1550.87	172.319	42.37	0.000
Linear	3	19.24	6.413	1.58	0.226
pH	1	8.18	8.180	2.01	0.172
V	1	3.08	3.080	0.76	0.395
T	1	7.98	7.981	1.96	0.177

Square	3	1214.91	404.970	99.57	0.000
pH*pH	1	972.44	972.444	239.08	0.000
V*V	1	187.05	187.054	45.99	0.000
T*T	1	191.73	191.729	47.14	0.000
2-Way Interaction	3	316.72	105.574	25.96	0.000
pH*V	1	208.49	208.488	51.26	0.000
pH*T	1	1.22	1.217	0.30	0.590
V*T	1	107.02	107.018	26.31	0.000
Error	20	81.35	4.067		
Lack-of-Fit	3	56.07	18.692	12.57	0.000
Pure Error	17	25.27	1.487		
Total	29	1632.22			

Regression Equation in Uncoded Units:

$$\text{TDS Change \%} = -274.4 + 56.66 \text{ pH} + 4.866 \text{ V} + 0.962 \text{ T} - 2.869 \text{ pH*pH} - 0.05033 \text{ V*V} \\ - 0.00815 \text{ T*T} - 0.2553 \text{ pH*V} - 0.0078 \text{ pH*T} - 0.01463 \text{ V*T}$$

Fits and Diagnostics for Unusual Observations:

Obs	TDS Change %	Fit	Resid	Std Resid	
1	26.29	30.41	-4.12	-2.58	R
8	31.73	28.39	3.34	2.10	R

Parameters:

Response	Goal	Lower	Target	Upper	Weight	Importance
TDS Change %	Maximum	22.88	46.58		1	1

Solution:

Solution	pH	V	T	TDS Change % Fit	Composite Desirability
1	8.93939	20.3030	36.6641	45.3807	0.949395

Multiple Response Prediction:

Variable	Setting				
pH	8.93939				
V	20.303				
T	36.6641				
Response	Fit	SE Fit	95% CI	95% PI	
TDS Change %	45.381	0.822	(43.667, 47.095)	(40.838, 49.923)	

Table B9: Coded Coefficients for WI Increment after Electrocoagulation

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	28.717	0.477	60.21	0.000	
pH	-2.103	0.292	-7.20	0.000	1.00
V	1.129	0.292	3.87	0.001	1.00
T	1.556	0.292	5.33	0.000	1.00
pH*pH	1.509	0.430	3.51	0.002	1.01
V*V	3.968	0.430	9.23	0.000	1.01
T*T	-1.962	0.430	-4.56	0.000	1.01
pH*V	-0.414	0.413	-1.00	0.328	1.00
pH*T	-1.204	0.413	-2.91	0.009	1.00
V*T	0.262	0.413	0.64	0.532	1.00

Table B10: Analysis of Variance for WI Increment after Electrocoagulation

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	311.753	34.639	25.38	0.000
Linear	3	129.855	43.285	31.72	0.000
pH	1	70.728	70.728	51.83	0.000
V	1	20.408	20.408	14.95	0.001
T	1	38.720	38.720	28.37	0.000
Square	3	168.384	56.128	41.13	0.000
pH*pH	1	16.819	16.819	12.32	0.002
V*V	1	116.266	116.266	85.20	0.000
T*T	1	28.429	28.429	20.83	0.000
2-Way Interaction	3	13.513	4.504	3.30	0.041
pH*V	1	1.370	1.370	1.00	0.328
pH*T	1	11.592	11.592	8.49	0.009
V*T	1	0.551	0.551	0.40	0.532
Error	20	27.293	1.365		
Lack-of-Fit	3	23.981	7.994	41.03	0.000
Pure Error	17	3.312	0.195		
Total	29	339.046			

Regression Equation in Uncoded Units

$$\text{Color Change \%} = 65.8 - 6.59 \text{ pH} - 1.325 \text{ V} + 0.4777 \text{ T} + 0.377 \text{ pH*pH} + 0.03968 \text{ V*V} \\ - 0.003139 \text{ T*T} - 0.0207 \text{ pH*V} - 0.02407 \text{ pH*T} + 0.00105 \text{ V*T}$$

Fits and Diagnostics for Unusual Observations:

Obs	Color Change %	Fit	Resid	Std Resid	
5	40.040	37.839	2.201	2.38	R

Parameters:

Response	Goal	Lower	Target	Upper	Weight	Importance
Color Change %	Maximum	26.5	40.04		1	1

Solution:

Solution	pH	V	T	Color Change % Fit	Composite Desirability
1	7	30	54.4444	39.0028	0.923396

Multiple Response Prediction:

Variable	Setting
pH	7
V	30
T	54.4444

Response	Fit	SE Fit	95% CI	95% PI
Color Change %	39.003	0.857	(37.215, 40.790)	(35.981, 42.025)

Table B11: Coded Coefficients for pH Removal after Electrocoagulation

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	3.30	1.52	2.17	0.042	
pH	14.355	0.930	15.43	0.000	1.00
V	-1.256	0.930	-1.35	0.192	1.00
T	-1.300	0.930	-1.40	0.178	1.00
pH*pH	-12.67	1.37	-9.25	0.000	1.01
V*V	-1.65	1.37	-1.20	0.243	1.01
T*T	0.39	1.37	0.28	0.779	1.01
pH*V	3.25	1.32	2.47	0.023	1.00
pH*T	0.45	1.32	0.34	0.738	1.00
V*T	-1.26	1.32	-0.96	0.348	1.00

Table B12: Analysis of Variance for pH Removal after Electrocoagulation

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	4652.62	516.96	37.32	0.000
Linear	3	3349.35	1116.45	80.60	0.000
pH	1	3297.06	3297.06	238.03	0.000
V	1	25.25	25.25	1.82	0.192
T	1	27.04	27.04	1.95	0.178
Square	3	1204.34	401.45	28.98	0.000
pH*pH	1	1186.11	1186.11	85.63	0.000
V*V	1	20.01	20.01	1.44	0.243
T*T	1	1.12	1.12	0.08	0.779
2-Way Interaction	3	98.93	32.98	2.38	0.100
pH*V	1	84.57	84.57	6.11	0.023
pH*T	1	1.59	1.59	0.12	0.738
V*T	1	12.78	12.78	0.92	0.348
Error	20	277.03	13.85		
Lack-of-Fit	3	160.64	53.55	7.82	0.002
Pure Error	17	116.39	6.85		
Total	29	4929.64			

Regression Equation in Uncoded Units:

$$\begin{aligned} \text{pH change \%} = & -290.9 + 60.64 \text{ pH} - 0.753 \text{ V} - 0.075 \text{ T} - 3.168 \text{ pH*pH} - 0.0165 \text{ V*V} \\ & + 0.00062 \text{ T*T} \\ & + 0.1626 \text{ pH*V} + 0.0089 \text{ pH*T} - 0.00505 \text{ V*T} \end{aligned}$$

Fits and Diagnostics for Unusual Observations:

Obs	pH change %	Fit	Resid	Std Resid	
5	-36.86	-29.88	-6.98	-2.37	R
21	9.56	3.35	6.21	2.11	R

Parameters:

Response	Goal	Lower	Target	Upper	Weight	Importance
pH change %	Maximum	-36.86	9.67		1	1

Solution:

Solution	pH	V	T	pH change % Fit	Composite Desirability
1	10.2727	26.3636	10	9.36087	0.993356

Multiple Response Prediction:

Variable	Setting			
pH	10.2727			
V	26.3636			
T	10			
Response	Fit	SE Fit	95% CI	95% PI
pH change %	9.36	2.04	(5.11, 13.61)	(0.51, 18.21)

APPENDIX C: Laboratory Experiments and Handlings



Figure D1 Cold Room for Sample Storage at 4 °C

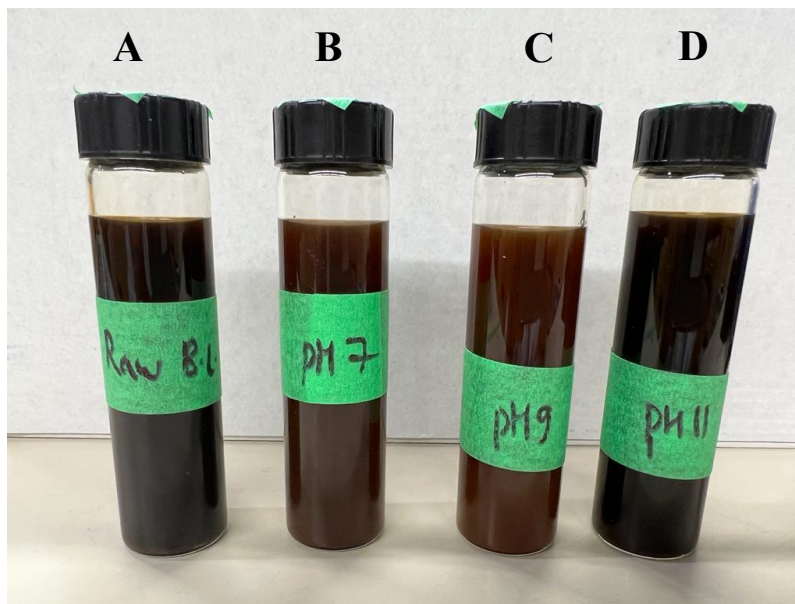


Figure D2 Black Liquor Samples (A: Raw BL, B: pH 7 BL, C: pH 9 BL, D: pH 9=11 BL)

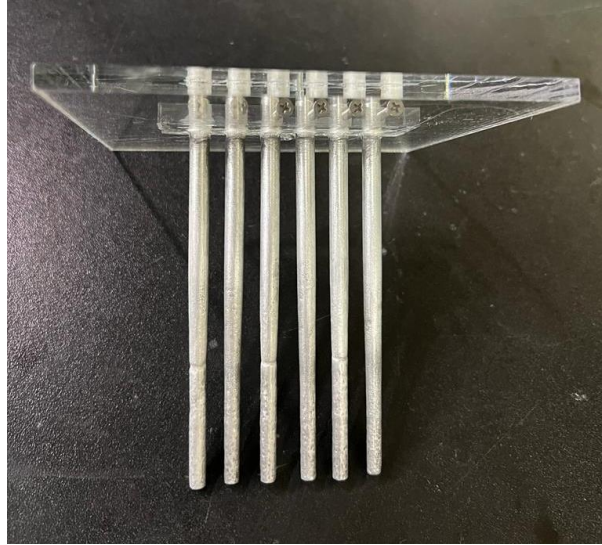


Figure D3 Aluminum Electrodes used for Electrocoagulation



Figure D4 Alternate anode and cathode connection to the Electrodes

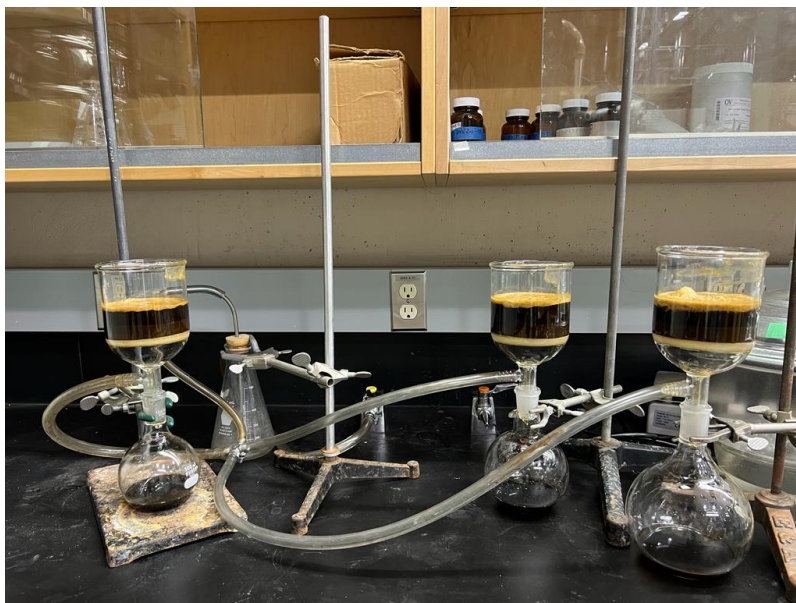


Figure D3 Vacuum Filtration Unit



Figure D4 Lignin Precipitation of BL Samples by Acid Hydrolysis

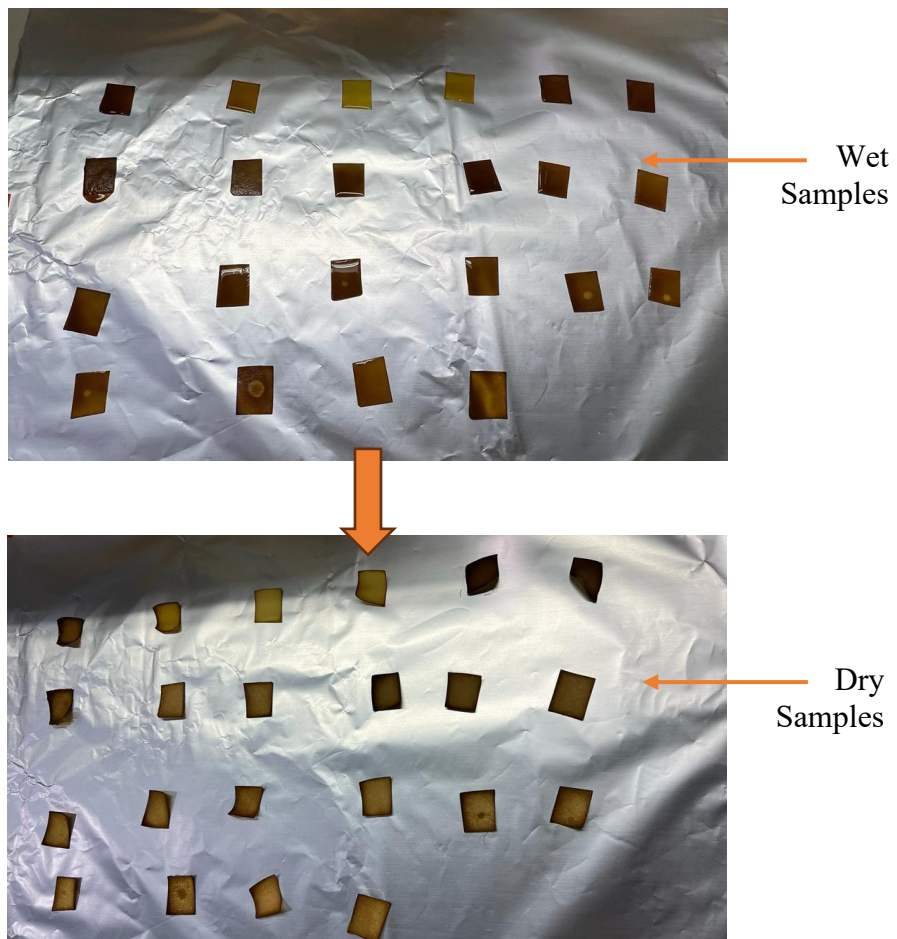


Figure D5 1 mL each of BL Sample Dried on Filter Paper for Color Measurement



Figure D6 Sludge Used for Anaerobic Digestion



Figure D7 ANKOM Modules Cleaned and Dried after Every Run

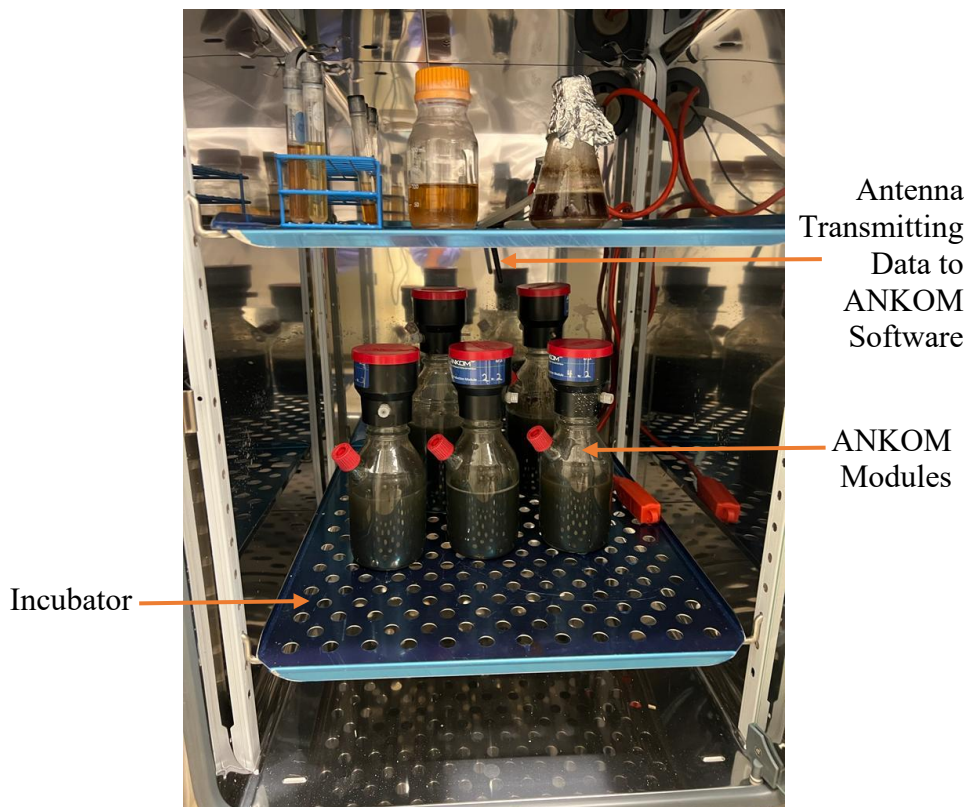


Figure D8 Incubation of ANKOM Modules/Digesters at 37 °C

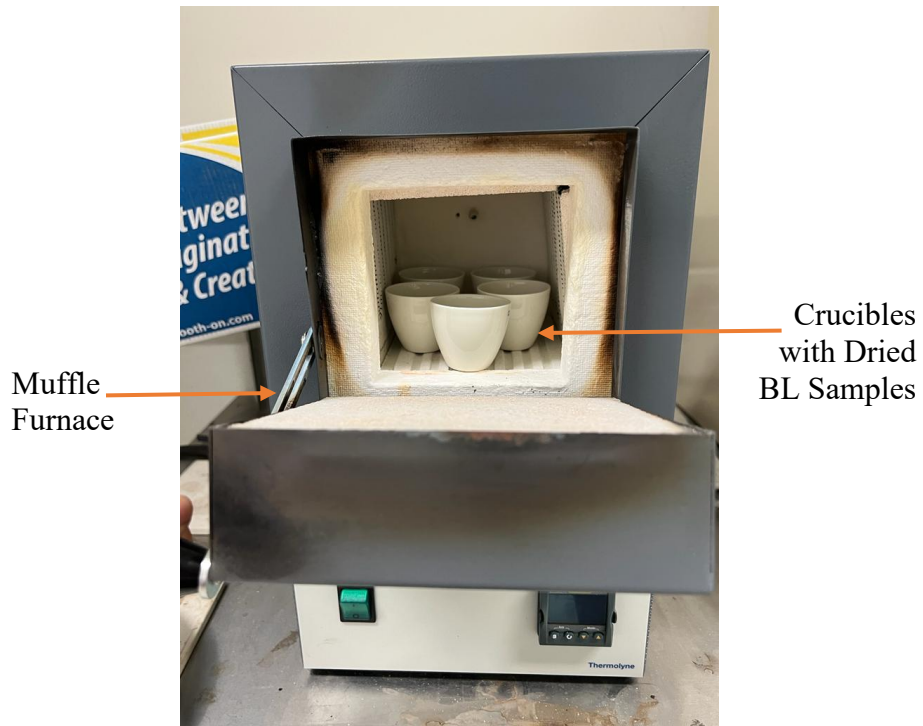


Figure D9 Measuring Ash Content of BL Samples in Muffle Furnace at 600 °C



Figure D10 Centrifugation of Anaerobically Digested BL Samples using Centrifuge 5804 R

