Heliyon 10 (2024) e40394

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

Indigenous bio-coagulant assisted electrocoagulation process for the removal of contaminants from brewery wastewater: Performance evaluation and response surface methodology optimization

Firomsa Sufa Garomsa [a], Yenealem Mehari Berhanu [b], Wendesen Mekonin Desta [b], Firomsa Bidira [b,*]

[a] Department of Water Resourse and Irrigation Engineering, Wollega University, P.O. box 38, Ethiopia
[b] School of Civil and Environmental Engineering, Jimma Institute of Technology, Jimma University, P.O. Box 378, Ethiopia

ARTICLE INFO

Keywords:
Custard apple
Brewery wastewater
Electrocoagulation
Operating factors
Response surface methodology

ABSTRACT

Wastewater from human activities, particularly from brewery industries, is a significant source of pollution. Large volumes of biodegradable and non-biodegradable substances found in brewery effluent make them suitable for natural coagulant-assisted electrocoagulation. The treatment options available today are highly harmful and not economical. To solve this problem and provide a simple method of treating brewery wastewater, the biocoagulant (Custard apple)-assisted electrocoagulation process was created. This study presents an environmentally friendly way of treating wastewater by combining electrocoagulation with biocoagulant. The approach treats wastewater from breweries with a high organic load and a variable composition. Bio- and electrocoagulation are used in the process to target certain contaminants and when combined the method has high efficiency and is environmentally also friendly. The performance of bio-coagulant-assisted electrocoagulation was studied, considering parameters such as pH, time, current, and bio-coagulant dosage. In each experiment, operating parameters were adjusted and their removal efficiency was evaluated after treatment. The bio-coagulant-assisted electrocoagulation process removed COD (99.01 %), BOD (99.09 %), TDS (99.02 %), and) at an ideal pH of 7, a current of 0.5 A, a time of 40 min, and power consumed (0.54kwh/m^3) with a constant dose of 0.75 g/l NaCl as electrolytes. The study found that Indigenous bio-coagulant (Custard apple)-assisted electrocoagulation processes were effective and efficient in removing pollutants from brewery wastewater. In the process of treatment operating factors have a high effect on the performance of the method. The parameters were customized using Response Surface Methodology (RSM), and the dependent variable's value was determined through regression analysis with a design expert.

---

* Corresponding author.
E-mail addresses: firosufa1529@gmail.com (F.S. Garomsa), mehariyenealem@yahoo.com (Y.M. Berhanu), wendemekonin27@gmail.com (W.M. Desta), bidiraabdi84@gmail.com, firomsa.bidira@ju.edu.et (F. Bidira).

https://doi.org/10.1016/j.heliyon.2024.e40394
Received 2 August 2024; Received in revised form 4 October 2024; Accepted 12 November 2024

1. Introduction

Water is a scarce natural resource that is frequently inadequately accessible to home and industrial use in acceptable quality [1]. Water is essential for all life forms on Earth, and humans use water bodies for their basic needs [2]. Contaminated water, including lakes, rivers, oceans, aquifers, and groundwater, impairs water quality and affects the entire biosphere of animals and plants that inhabit these bodies. Human and organism health issues are a result of rising environmental pollution brought on by the rate of population growth and industrialization of countries [3,4] The impact harms not only specific species and populations but also broader natural biological communities [5]. The severe effects of water pollution are felt by humans and all living things worldwide [6]. Water pollution is primarily caused by domestic and industrial effluent waste, leaks from tanks, marine dumping, radioactive waste, and atmospheric deposition. Improper disposal of industrial waste and heavy metals can build up in lakes and rivers, posing threats to people and wildlife [7,8]. Hence, there is a need to treat wastewater and wastewater generated from the industries (see Tables 6–12, Fig. 1).

Wastewater treatment methods include advanced oxidation techniques, Biological processes, physicochemical processes, and membrane filtration and adsorption [9]. Advanced oxidation requires strong oxidants, making treatment risky and expensive [10]. Biological processes require tightly controlled conditions, lengthy retention times, and large footprints, causing unnecessary fines for nearby WWT facilities during dewatering due to strict municipal regulations [11]. Conventional methods are rigid, unreliable, and time-consuming due to numerous variables in wastewater treatment processes [12]. Electrochemical technologies, particularly the electrocoagulation (EC) process, are effective and low-cost in treating industrial wastewater to meet effluent discharge regulations [13].

Beer is among the oldest alcoholic drinks in existence. In reality, with an average intake of 9.1 l per person, beer is the fifth most popular beverage in the world, behind tea, carbonates, milk, and coffee [14]. Wastewater is contaminated water that results from human activity and runoff. It is often classified as home sewage, industrial sewage, or storm sewage depending on how it is created [15]. Between all of these One of the primary sources of environmental pollution is the discharge of industrial effluent into water bodies [16]. Brewing the beer and packaging it are the two key processes in the process of making beer. When combined with effluents, the byproducts produced during these processes such as leftover yeast and discarded grains from mashing cause pollution [17]. It is produced in vast quantities and contains a significant number of pollutants that, if improperly treated before disposal, can seriously endanger aquatic life, the environment, and human health.

There are various methods for treating industrial wastewater effluent. Coagulation is one of the many typical unit processes utilized in traditional water treatment systems. Water and wastewater are frequently treated using the flocculation-coagulation process. Three crucial steps in this procedure are taken into account: coagulant formation, colloid particle destabilization, and inter-particle collision and aggregation [18]. Brewery wastewater will become the main problem for the ecology and the environment if it is not treated effectively. This necessitates the development of the most effective wastewater treatment system. Biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), pH, and nutrients (nitrogen and phosphorus) [19]. In recent years, serious environmental and health difficulties have been recognized, including the high cost, post-use handling, and health issues related to inorganic coagulants like alum. According to reports, consuming large amounts of alum causes Alzheimer's disease [20]. So using biocoagulant-assisted electrocoagulation can overcome these problems.

Some brewery industries treat wastewater using chemical coagulants, but it is not economically and environmentally friendly. So, this study presents integrated custard apple seed powder as a coagulant and electrocoagulation to increase the removal efficiency because Custard apple has high protein content and have high absorbance capacity. Due to its simplicity of use and low maintenance

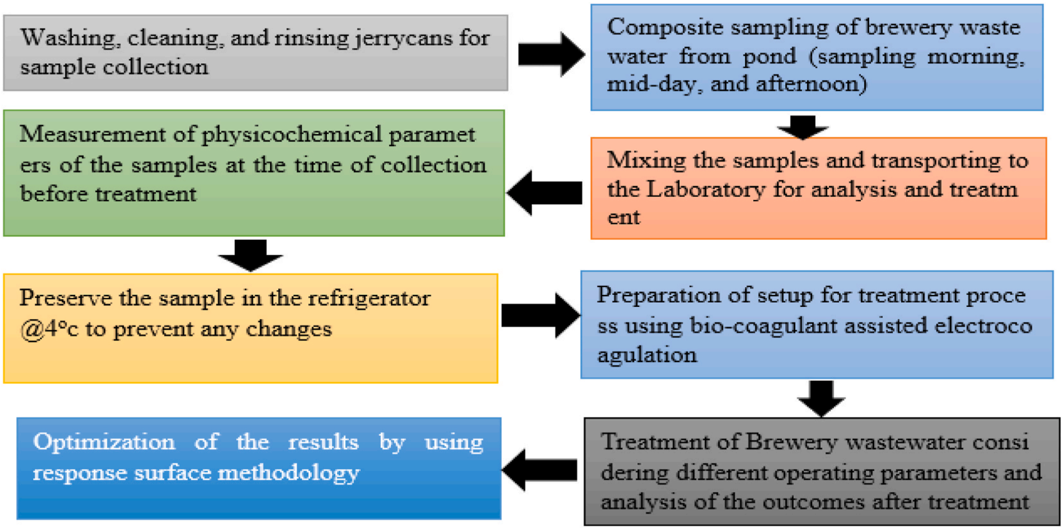


Fig. 1. Sample collection and process of experimental works.

requirements, as well as its adaptability to present systems in many industrial applications, electrocoagulation wastewater treatment has drawn particular interest as a high-performance and dependable technology.

The method blends electrochemical and conventional techniques, employing inexpensive, ecologically sustainable, and biodegradable bio-coagulants obtained locally [21,22]. Among the other electrochemical treatment techniques, electrocoagulation (EC) is a sophisticated, cost-effective approach that has been widely used in practice due to its ability to effectively treat a variety of wastewater [4,8]. This method provides a region-specific wastewater treatment solution while promoting sustainability and utilizing resources that are local to the area [23]. The bio-coagulants improve the floc formation, and the organic pollutants are broken down and impurities are separated using electrolysis (EC process) [24,25]. This approach is economical since natural bio-coagulants are less expensive and more environmentally friendly than synthetic ones. It also lessens the wastewater treatment process's environmental impact by reducing the requirement for toxic substances. The use of chemical coagulants, which have the potential to release secondary contaminants into the environment, is decreased by the hybrid technique [26,27] Overall, combining the two methods proved more efficient than using either method alone for enhancing the removal of contaminants from brewery wastewater [18]. also, the method consumes low energy *(0.54kwh/m^3)* when combined with the bio coagulant and remove the contaminants.

The study aims to investigate the performance of bio-coagulant-assisted electrocoagulation processes for the removal of pollutants from brewery wastewater. Specifically, the study characterizes brewery wastewater, investigating the efficiency of bio-coagulant-assisted electrocoagulation for the removal of COD, BOD, and TDS, and characterizing the effect of operating parameters on pollutant removal efficiency. This approach was novel experimental for treating wastewater using electrocoagulation with custard apple as an assistant coagulant. When used in this manner, it is highly efficient and can address the issue of wastewater released from companies such as breweries.

Electrocoagulation (EC) is an advanced water treatment technique that uses an electric current to destabilize suspended, emulsified, or dissolved contaminants in water [28]. Coagulating agents are produced in situ by electrolytically oxidizing a sacrificial anode during the process. These coagulants, typically metal hydroxides, aggregate the contaminants and facilitate their removal from the water by filtering, sedimentation, or flotation [29]. Electrocoagulation involves several significant electrochemical reactions that occur at the anode and cathode. Electrocoagulation occurs in multiple stages, including the adsorption of soluble or colloidal contaminants on coagulants and the production of coagulants in an aqueous phase [30]. The specific reactions and coagulants that arise are mostly determined by the iron or aluminum composition of the sacrificial electrode [12,22].

$Al \rightarrow Al^{3+} + 3e^-$ (Oxidation reaction) …. (Anode Reaction)

$2H_2O + 2e^- \rightarrow H2(g) + 2OH^-$ …. (Cathode reaction)

$Al^{3+} + 3H_2O \rightarrow Al\,(OH)_3 + 3H^+$ ….(overall reaction) [31].

When the hydroxide ions (OH^-) formed at the cathode interact with the aluminum ions ($Al^{3+)}$ created, they form the aluminum hydroxide, a gelatinous coagulant that neutralizes and adsorbs contaminants.

The electrocoagulation process involves several physical and chemical reactions, such as coagulation, flocculation, adsorption, electrolytic floatation, precipitation, and sedimentation [32]. It is well known for its ability to remove a wide range of contaminants, such as heavy metals, oils, dyes, suspended particles, and some organic pollutants. Compared to chemical coagulation procedures, it is a low-sludge technology that is adaptable inexpensive, and ecologically friendly. EC is widely used to clean drinking water and treat industrial and municipal effluent [31,33].

Custard apple seed powder functions as a bio coagulant that enhances coagulation by forming particle bridges, enhancing adsorption, balancing charges, and binding with metal hydroxide coagulants. Increasing the number of surfaces for pollutant particles to adhere to facilitates floc formation and enhances the elimination of organic and inorganic contaminants. The combined action of metal hydroxides and biocoagulant facilitates the aggregation of small particles into larger flocs for easier removal [22].

$Al \rightarrow Al^{3+} + 3e^-$ … …. (Anode reaction)

$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$ …. (Cathode reaction)

$Al3^+ + 3OH- \rightarrow Al\,(OH)_3(s)$

Organic Pollutants + $Al\,(OH)_3$+Biocoagulant → Flocs↓ . (overall Reaction) [34].

The study's significance lies in its ability to reduce wastewater's negative environmental effects and enhance the overall water quality of the final effluent. Bio-coagulant-assisted electrocoagulation offers an environmentally friendly and cost-effective solution for treating brewery wastewater, as it requires less energy and can lead to significant cost savings for the brewery. The study used a sample from the Bedele Brewery factory and analyzed experimental parameters such as reaction duration, solution pH, electrical current, and natural coagulant dose. The goal was to demonstrate how the EC process can be improved when assisted with natural coagulants as effective treatment strategies for removing COD, BOD, and TDS, from wastewater.

After treatment the results were Optimized by considering the operating parameters of the processes; and statistically by adopting Response Surface Methodology, Composite Design (CCD). Generally, this approach is chosen because biocoagulants are locally available, have high absorption capacity, and are environmentally friendly.

1.1. *Comparison of the method with previously worked research*

Wastewater from diverse production processes poses a serious threat to aquatic environments and animal species due to its high toxicity and numerous pollutants [35,36]. Optimized EC processes in combination with biocoagulant significantly increased the efficacy of wastewater treatment, resulting in removal values for turbidity, color, and chemical oxygen demand of 98.05 %, 95.11 %, and 86.21 % for Al electrodes and 96.89 %, 95.10 %, and 81.78 % for Fe electrodes, respectively [37]. The decolorization and elimination of total organic carbon (TOC) in Acid Brown 14 diazo dye solutions are the subjects of this investigation. After the effluent was treated using electro-Fenton (EF) and photoelectro-Fenton (PEF), the TOC reduction in the chloride and sulfate media was greater, at 90 % and 97 %, respectively [30]. The initial testing of Al and Fe electrodes for COD and color removal showed that Al electrodes outperformed Fe electrodes [38,39]. The study on EC using Al electrodes found that optimal conditions for successful removal of 90 % COD and 92 % residual color from UASB effluent were an initial pH of 5.0, a current density of 15 mA/cm^2, and an electrolysis time of 20 min [40]. Ultrasound-assisted extraction of OFI mucilage showed better yields compared to conventional methods [41]. The extraction yield increased over time at 20 °C and 80 °C, but it took 10 min to achieve the optimal level at 60 % amplitude. By 6.21 %, this increased the extraction yield. The electrocoagulation-electro flotation (EC-EF) method of treating synthetic wastewater with mucilage yielded an ideal concentration of 5 mg/l, which allowed for a maximum turbidity removal effectiveness of 89.47 % at 25 min. When mucilage was present, a 10-min treatment improved the condition by 27 % over the standard procedure. This implies that OFI mucilage can be used as a natural coagulant [41]. Using a stainless-steel electrode at 1816 A/m2, pH 7, and electrode spacing of 10 mm yields the best results for this treatment in 0.55 h The chemical, biochemical, and suspended solid oxygen demands were all lowered by 98.07 %, 98.04 %, and 96.64 %, respectively [42,43].

2. Materials and methods

2.1. *Sample collection*

Using clean, washed plastic jerrycans, wastewater was collected from the Bedele Brewery wastewater collection pond. To ensure a representative sample, samples were taken three times a day using a composite sampling technique. Every collection time's average volume was considered. Before the treatment, the initial physicochemical parameters were measured at the time of collection, and the samples were kept in a laboratory refrigerator at 4 °C to prevent chemical alterations [44]. Thirty liters of wastewater which was the Total sample used for the experimentation collected and transported by plastic containers to the laboratory using appropriate sample preservation protocols for treatment [18]. During the study, chemical analyses were conducted for the samples as it was taken from the Bedele Brewery wastewater treatment collection tank.

The pH of the solutions was adjusted using sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4). Constantly (0.75 g) of Sodium chloride (NaCl) was used as the supporting electrolyte for all runs. All the solutions were prepared by using deionized (distilled water). Chemicals such as manganous sulfate solution, alkaline potassium iodide solution, sodium thiosulfate, Starch solution (indicator), and concentrated sulfuric acid were used for BOD analysis. Mercury sulfate ($HgSO_4$), Ammonium iron (II) sulfate hex hydrate $(NH_4)_2Fe(SO_4)_2$. $6H_2O$, silver sulfate (Ag_2SO_4), ferroin indicator, potassium dichromate ($K_2Cr_2O_7$) and sulfuric acid (H_2SO_4) were used for COD analysis. And, custard seed powder as an indigenous bio coagulant for assisting, Ammonium Molybdate, distilled water, phenolphthalein, sulfuric acid (H_2SO_4), Glycerol, Stannous Chloride ($SnCl_2.2H_2O$), and Stock Solution phosphate (PO_3^-) were used for phosphate analysis.

2.2. *Preparation of indigenous bio coagulant*

Custard apple was bought from the market and its seed was collected from inside. Then the seed was Washed thoroughly to remove dirt and residues. After custard apple was washed it was dried by exposing it to the sunlight and ensuring proper air circulation for properly drying. After it was dried properly by using mortar it was Grinded to very fine particles. The grinded custard apple seed powder was sieved by a smaller diameter sieve. A sieve with a smaller diameter is used for custard apple seed powder, which typically has a particle size of around 100 μm (μm). Then the fine powder was Stored in an airtight container and labeled with the date of preparation. Finer powders, which have a larger surface area, are preferred for more effective treatment. Finally, used as a bio coagulant for Brewery wastewater treatment by measuring it using weight balance depending on the designed coagulant weight or adjusting the dosage of custard apple powder as designed based on Brewery wastewater quality and treatment requirements.

2.3. *Experimental setup*

Tests were performed in a batch reactor such that 1 L of wastewater sample was taken in a beaker for one test. The aluminum electrode was used up for this EC process with a dimension of 15 cm and 5 cm in length and width respectively. Once the wastewater sample was added to the electrocoagulation cell the electrocoagulation cell was placed on a magnetic stirrer. A magnetic stirrer bar was also placed inside the EC containing wastewater samples. An aluminum electrode was connected to an anode and cathode and then inserted into the EC cell containing the wastewater sample. The distance between the electrodes was adjusted to 0.5 cm. Then the electrodes from the anode and cathode are connected to the DC-power supply with electrical wires. By adjusting all operating parameters (pH, current, time, and bio-coagulant dosage) the removal percentage of COD, BOD, TDS, and power consumption were evaluated. The digital DC power supply was used for A-EC (Bio coagulant-assisted electrocoagulation) experiments. A constant-temperature magnetic stirrer was used for solution agitation during the EC process. The Al electrodes were used as Electrode.

2.4. Analysis

The performance of the process was evaluated based on the responses of COD, Color, BOD, TDS, and Phosphate removal efficiencies. RSM (design expert 11) was the software used for modeling and analysis of the data obtained from the laboratory by using the empirical formulas

$$\%\text{Removal} = \frac{\textit{Initial Conc.} - \textit{Final Conc.}}{\textit{Initial conc}} * 100$$

2.5. Experimental design

Response surface methodology (RSM) has been used for modeling and optimizing a variety of water and wastewater treatment processes. RSM is a collection of mathematical and statistical techniques for building models, evaluating the effects of several variables, and obtaining the values of process variables that produce desirable values of the response [45]. In this study, laboratory experiments were carried out using an indigenous bio-coagulant-assisted electrocoagulation process by varying parameters in their interval: pH (3–11), current (0.2–0.8 A), reaction time (20–60min), custard apple seed powder as indigenous bio coagulant (0.5–3.5 g/l) and constantly 0.75 g/l NaCl as an electrolyte to reduce power consumption. As shown in Table 1 these inputs give several experimental runs, range of pH, time, current, and coagulant dosage which was generated by using RSM software (see Table 2).

As shown in Table 1 these inputs give a range of pH, time, current, and coagulant dosage which was generated by using RSM software with a number of experimental runs.

$N = 2^n + 2n + c$ … [12].

where N was the total number of runs, n was several factors and C was the center point.

Totally thirty experiments ($24 + 2*4 + 6 = 30$) using an indigenous bio-coagulant-assisted electrocoagulation process were performed in the laboratory using an aluminum–aluminum electrode combination with an electrode distance of 0.5 cm. Those parameters were to determine the removal efficiency of COD, BOD, and TDS. The order of experiments was arranged randomly.

3. Results and discussion

3.1. Characteristics of Bedele Brewery wastewater

One of the main causes of pollution in the environment is the discharge of industrial wastewater into water bodies [16]. Because a lot of water is needed to produce beer every day, the brewing sector uses a lot of water [46]. Brewery wastewater was characterized in the environmental engineering laboratory at room temperature and pressure. The characteristics of the Bedele Brewery wastewater sample before treatment analyzed in this study were as follows.

3.2. Characterization of indigenous biocoagulant custard apple

3.2.1. X-ray diffraction analysis

The crystalline nature of the as-prepared Custard apple seed was verified by an X-ray diffraction (XRD) pattern. The XRD measurements of the sample were carried out using a Drawell XRD-7000, China, with CuKα radiation ($\lambda = 1.54178$ Å) at the Bragg angle (2 thetas) ranging from 10 to 80° at a scan rate of 0.02 S^{-1} under an X-ray generator having a 450 W tube load at an accelerating voltage of 30 kV and 25 mA. temperature range of 30–550 °C at a rate of 10 °C/min under an inert atmosphere (N_2) (see Fig. 2).

The X-ray diffraction pattern of custard apple seed powder is represented in Fig. 3. It can be seen from the figure, that the Custard apple seed powder shows an amorphous nature as a major portion of the material constitutes of carbon substrate base. Custard apple seed powder's X-ray diffraction (XRD) graph displays a Less crystalline structure. The most noticeable characteristic is a pointed peak that appears at 20.68° (2θ), suggesting that a Small crystalline phase is present. The graph exhibits a broad, lower-intensity signal beyond the acute peak, suggesting a less-ordered or amorphous structure. The peak at 20.68° represents the sample's predominant crystalline characteristic, with the remaining material contributing to the amorphous background. The custard apple seed powder may have an amorphous or less-ordered matrix, according to the XRD graph.

Table 1

Experimental design for bio-coagulant-assisted electrocoagulation.

Factor	Name	Units	Type	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	pH		Numeric	3.00	11.00	−1 ↔ 5.00	+1 ↔ 9.00	7.00	1.82
B	Current	Amp	Numeric	0.2000	0.8000	−1 ↔ 0.35	+1 ↔ 0.65	0.5000	0.1365
C	Time	Min	Numeric	20.00	60.00	−1 ↔ 30.00	+1 ↔ 50.00	40.00	9.10
D	Dose	g/L	Numeric	0.5000	3.50	−1 ↔ 1.25	+1 ↔ 2.75	2.00	0.6823

Table 2
Brewery wastewater characteristics before treatment.

No	Parameters	Quantity Raw sample	Unit
2	COD	4560	mg/l
3	TDS	4430	mg/l
5	pH	4.1	–
6	BOD	3600	mg/l

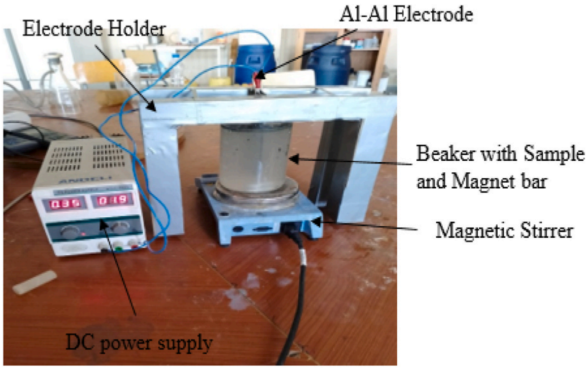


Fig. 2. Experimental setup of EC-Assisted brewery wastewater treatment.

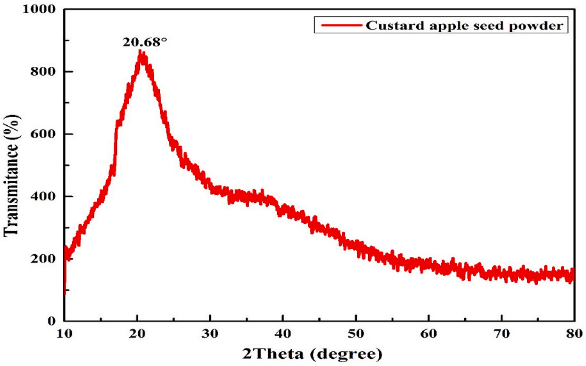


Fig. 3. XRD pattern of custard apple seed powder.

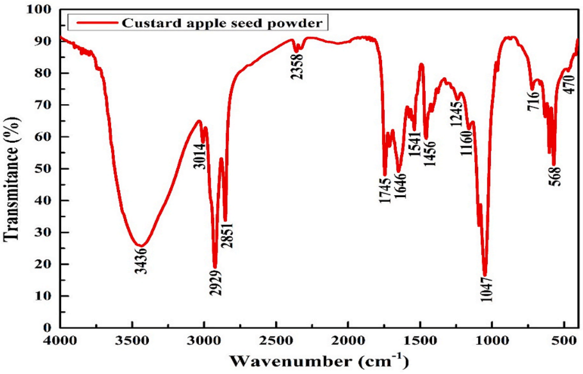


Fig. 4. FTIR spectra of custard apple seed powder.

3.2.2. Fourier transform infrared (FTIR) spectra of custard apple seed powder

Custard apple seed powder's FTIR spectrum indicates the existence of many functional groups, such as hydroxyl (O-H), carbonyl (C=O), aliphatic (C-H), and aromatic (C-H) groups, in addition to potential amine or amide (N-H) signals. As shown in Fig. 4 The peaks provide a thorough understanding of the chemical makeup of the sample by corresponding to various stretching and bending vibrations of these groups.

Fourier transform infrared spectroscopy was used to determine the functional groups present in the synthesized sample. The FT-IR spectra in the range of 400–4000 cm^{-1} for custard apple seed were illustrated in Fig. 3. The peak at 1541 cm^{-1} shows the functional groups that existed in the absorbance which are carboxyl group (C=O) stretching while the peak of 3436 cm^{-1} is due to hydroxyl group (-OH) stretching and transmittance at 2929 cm^{-1} is due to sp3-C-H stretching. This shows that the sample contains a carboxyl group, hydroxyl group, and alkyl group (-CH_3) that are responsible for the adsorption of contaminants. The peak at 2851cm-1 is due to the stretching mode of sp2-C-H groups in hydrocarbon. The peak at 1456 cm^{-1} denotes the methylene group of C-H bending and the peak at 1245 cm^{-1} denotes the C-H bending of the methyl group. The peaks at 1745 cm-1 denote the stretching mode of C=O in amino acids. The peak 1160 cm^{-1} denotes C-O stretching vibration. The peak 716 cm^{-1} denotes the methylene group of CH2 rocking vibration. The characteristic bands in the region of 3014 cm^{-1} revealed = C-H stretch, Dimer OH, aromatic C-H stretch of alkenes, carboxylic acid, and aromatic rings respectively. Transmittance at 2358 cm^{-1} represents the presence of atmospheric CO_2 that the material has adsorbed. The absorption peak at 1646 cm-1 was due to the C=C and C=O stretching vibration of ketones and amides functional groups. The absorption band at 1047 cm^{-1} was due to P-H phosphine, Si-OR organosilicon, and C-O stretching of ester. There are some peaks observed around 470 and 568 cm^{-1} due to the tensile vibration Si-O-Si, Si-OR, =CH out of the plane, R-Cl of alkenes, alkyl halides, aromatic and ester functional group.

3.2.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a sample is heated at a constant rate.

The TGA curve of custard apple seed shows a three-step weight loss as shown in Fig. 5. The first part of the weight loss 13.27 % occurs in the temperature range of 198–273 °C that corresponds to the evaporation of absorbed water molecules. The second part of the weight loss of 4.04 % exists around 273–375 °C which is attributed to the loss of volatile organic compounds and the loss of interlayer water molecules. The third part of weight loss 2.63 % occurs from 373 to 520 °C owing to the removal of oxygen-containing functional groups in the sample.

3.3. Removal efficiency of bio-coagulant assisted electrocoagulation process for brewery wastewater

The removal efficiency of the bio-coagulant-assisted electrocoagulation process to remove brewery wastewater pollutants was investigated in this study. The bio-coagulant-assisted electrocoagulation process was efficient by maximizing pollutant removal and minimizing power consumption during the process. The results investigated were discussed in this section.

In Table 4.2 factors like pH, current time, and coagulant dosage were considered with different ranges, similarly, the removal efficiency for COD, BOD, TDS, and power consumption were determined. Hence using the bio-coagulant-assisted electrocoagulation process the removal efficiency of COD was 99.01 %, BOD 99.09 %, TDS was 99.02 % and power consumption was 0.54 KWh/m^3. So that as Table 3 above shows the pollutant removal efficiency was high and the power consumption was minimal for the bio-coagulant-assisted electrocoagulation.

3.4. Effect of operating parameters on % removal efficiency

The operating parameters that highly affect the electrocoagulation and bio-coagulant-assisted electrocoagulation processes, such as solution pH, electric current, reaction time, and bio-coagulant dosage studied in terms of % COD, BOD, TDS, removal at room temperature.

3.4.1. Effect of pH

The pH of the solution plays a critical role in the elimination of pollutants in the EC and A-EC processes. To evaluate the effect of pH

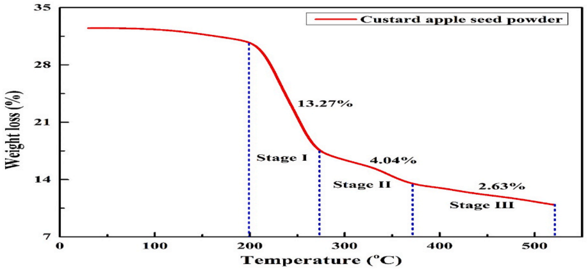


Fig. 5. TGA curve of custard apple seed powder.

Table 3

Removal efficiency by bio-coagulant-assisted electrocoagulation process.

Factors						Response		
Run	A: pH	B:Current	C:Time	D:Dose	COD	TDS	BOD	Power consumed
		(Amp)	(min)	(g)	%	%	%	kwh/m^3
1	7	0.5	40	3.5	92.263	96.251	92.721	0.411
2	11	0.5	40	2	66.926	70.914	67.384	0.512
3	7	0.8	40	2	95.518	99.506	95.754	1.146
4	9	0.65	30	1.25	89.868	93.856	90.326	0.651
5	9	0.65	30	2.75	86.573	90.561	87.031	0.521
6	9	0.35	50	1.25	86.638	90.626	87.096	0.408
7	7	0.5	40	0.5	94.801	98.789	95.259	0.634
8	7	0.5	40	2	95.036	99.024	95.494	0.543
9	5	0.65	30	1.25	87.289	91.277	87.747	0.651
10	7	0.5	20	2	92.253	96.241	92.711	0.267
11	5	0.65	30	2.75	83.763	87.751	84.221	0.521
12	9	0.35	30	2.75	86.729	90.717	87.187	0.227
13	5	0.65	50	1.25	88.279	92.267	88.737	1.083
14	7	0.5	60	2	95.214	99.202	95.353	0.822
15	7	0.5	40	2	94.836	98.224	94.894	0.535
16	7	0.5	40	2	94.476	98.464	94.934	0.567
17	5	0.65	50	2.75	84.569	88.557	85.027	0.978
18	7	0.5	40	2	94.936	98.924	95.394	0.535
19	3	0.5	40	2	62.473	66.461	62.931	0.523
20	9	0.65	50	2.75	87.696	91.684	88.154	0.897
21	7	0.2	40	2	93.565	97.553	94.023	0.246
22	5	0.35	30	1.25	83.468	87.456	83.926	0.315
23	7	0.5	40	2	94.466	98.454	94.924	0.578
24	5	0.35	50	2.75	86.898	90.886	87.356	0.469
25	9	0.35	30	1.25	85.214	89.198	85.668	0.245
26	9	0.65	50	1.25	90.307	94.295	90.765	1.083
27	5	0.35	30	2.75	84.696	88.684	85.154	0.282
28	9	0.35	50	2.75	87.861	91.848	88.318	0.379
29	5	0.35	50	1.25	85.767	89.955	86.225	0.475
30	7	0.5	40	2	94.723	98.311	95.581	0.537

on the process's performance it is altered in the range of 3–11 by integrating NaOH and H_2SO_4 solution [15]. When the pH is appropriate, the dissolved metal ions can produce a variety of coagulated species and metal hydroxides that can either precipitate and adsorb dissolved pollutants or destabilize and agglomerate the suspended particles [47]**.** As shown in Fig. 6 The investigation's highest removal efficiency is found at pH 7, or neutrality. The distribution of products from aluminum hydrolysis is influenced by pH, which is a significant component in electrical coagulation procedures that may negatively impact process efficiency [48]. Removal efficiency rises when pH shifts from acidic to neutral because more metal hydroxide precipitates are formed. Because a pH of 7 creates the perfect environment for steady metal hydroxide floc production, the removal efficiency was enhanced. However, because metal hydroxides become less soluble at higher pH values, removal efficiency declines as pH rises to an alkaline (basic) level. Since metal hydroxide flocs are less stable and dissolve substantially into the solution at a pH of about 7, the best removal effectiveness was achieved during the biocoagulant-assisted electrocoagulation process [49].

3.4.2. Effect of current

The current applied has a direct correlation with the current density, an essential operating variable. Aluminum dissociation was occurring to a great level and there were several metal hydroxide flocs during the current increase. The elimination of pollutants has improved because of this aspect [50]. The current applied for this study was 0.2–0.8 A and the optimum current was 0.5 A. As the current increases voltage also increases as a result, the formation of Al $(OH)_3$ hydroxide is accelerated. The effectiveness of organic oxidation decreases when a higher voltage is applied because oxygen evolution occurs. as concluded in Fig. 7 Extremely high current

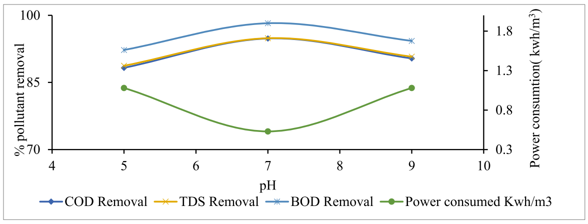


Fig. 6. Effect of pH on % removal efficiency by bio-coagulant assisted electrocoagulation.

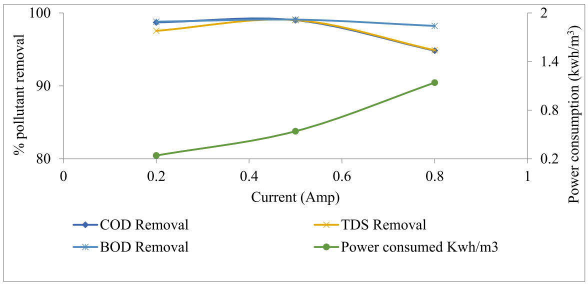


Fig. 7. Effect of current on % removal efficiency by bio-coagulant assisted electrocoagulation.

negatively affects(decreases) on the treatment of wastewater from the brewery wastewater [51]. One important factor that affects the electrochemical treatment process used for purifying wastewater from breweries is current density. The degree to which pollutants are eliminated during the electrocoagulation process depends on the voltage or current employed [52]. Over-potential effects, often referred to as over-potential phenomena, can result from the usage of excessively high voltages or currents. This suggests that the system is being overloaded, which could have unintended consequences and unanticipated negative repercussions. When there is a high voltage or current, gas bubbles can form at the electrode surfaces. The contaminant and electrode may be unable to make contact because of these gas bubbles, which would reduce the removal efficiency overall. Additionally, the formation of gas bubbles can cause electrode erosion, which may lead to the separation of electrode materials and potential fouling of the system [25].

3.4.3. Effect of time

Removal of contaminants increases up to 20–40 min and then starts to decrease after optimum 40 min. Fig. 8 shows COD, BOD, TDS, removal, and power consumption were 99.63 %, 99.01 %, 99.09 %, 99.02 %, and 0.54 KWh/m^3 for bio-coagulant assisted electrocoagulation process at the optimum time of 40 min. In this investigation, very long and short contact times have less efficiency in the removal of contaminants from brewery wastewater (see Fig. 9).

The electrolysis time in electrocoagulation procedures influences the metal ion generation, as per Faraday's law. The removal effectiveness versus time increases with a steep slope at the beginning of the process, resulting in the maximum pollutant removal rate in the experiments [48]. The amount of time needed for the process to produce metal hydroxides and accomplish the impurity coagulation is known as the electrocoagulation time. Current density is maintained constant to investigate the impact of time. The amount of metal hydroxide produced rises as the electrolysis time increases for a certain current density. A longer duration of the electrolysis period leads to a rise in floc formation and an improvement in the efficiency of pollutant removal. The pollutant removal efficiency does not increase for electrolysis times longer than the ideal electrolysis time because there are sufficient flocs available to remove the pollutant [38].

3.4.4. Effect of bio-coagulant dose

Bio coagulant is an alternative gaining increasing attention for its advantages of low cost and abundant availability [53]. In brewery wastewater treatment, indigenous bio-coagulant-assisted electrocoagulation was a very nice technology rather than the electrocoagulation process alone, as the study shows. The bio coagulant used for this study was custard seed powder (0.5–3.5 g/l) for one test. As the figure shows, COD, BOD, TDS, removal, and power consumption are 99.01 %, 99.09 %, 99.02 %, and 0.54 kWh/m^3, respectively, for the bio coagulant-assisted electrocoagulation process. Optimum bio-coagulant dosage of 2 g/l. Maximum and very low dosages have low removal efficiency.

Small dosages contain insufficient bridging and coagulation sites, which leads to limited elimination efficiency. Saturation, overdose, and stability brought on by large doses might result in smaller, colloidal particles that are more challenging to remove from water. The optimal dosage balances these effects to ensure that particles can effectively agglomerate and settle out of the solution. In

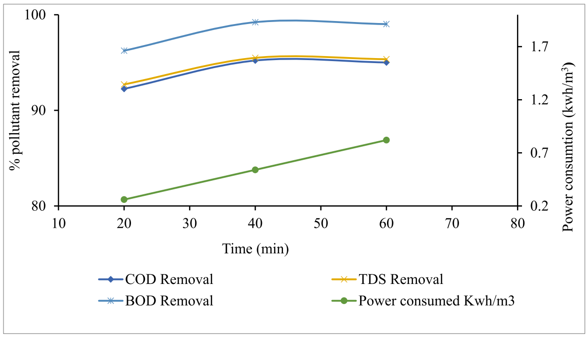


Fig. 8. Effect of time on % removal efficiency by bio-coagulant-assisted electrocoagulation.

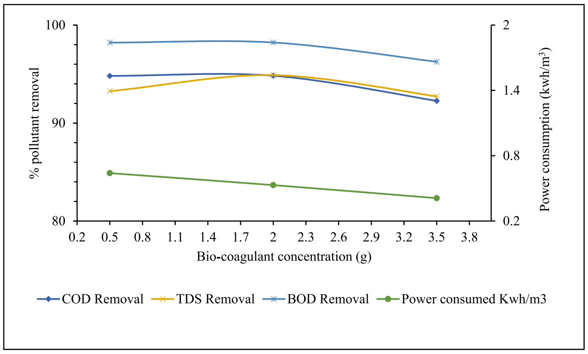


Fig. 9. Effect of coagulant dosage on the efficiency of bio-coagulant-assisted electrocoagulation.

conclusion, extremely small dosages of natural coagulants are insufficient for effective contaminant interaction and floc formation, whereas very large dosages can result in destabilizations and other undesirable effects [54].

3.5. Optimization by response surface methodology based on central composite design

3.5.1. Analysis of variance test

To determine the interaction between the process variables and the response, graphical analyses of the data were performed using analysis of variance (ANOVA). The correlation coefficient (R^2) value represented the fit quality of the polynomial model, and the F test verified its statistical significance. Model terms were assessed using a 95 % confidence level and the P value, or probability [55]. As shown in Table 4 the amounts of P values for the model confirmed that the selected factors are significant ($\leq$0.05) (see Table 5).

I) ANOVA for the % removal of pollutants by bio-coagulant-assisted electrocoagulation

The Model F-value of 1657.31 implies the model is significant. There is only a 0.01 % chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, A, B, C, D, AB, BC, and BD, are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms model reduction may improve the model. The Lack of Fit F-value of 1.44 implies the Lack of Fit is not significant relative to the pure error. There is a 36.15 % chance that a Lack of Fit F-value this large could occur due to noise.

The Model F-value of 1263.62 implies the model is significant. There is only a 0.01 % chance that an F-value this large could occur due to noise. Less than 0.0500 indicates model terms are significant. In this case, A, B, C, D, AB, BC, and BD, are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms model reduction may improve your model. The 0.89 implies the Lack of Fit is not significant relative to the pure error. There is a 59.26 % chance that a Lack of Fit F-value this large could occur due to noise.

The Model F-value of 1320.64 implies the model is significant. There is only a 0.01 % chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, A, B, C, D, AB, BC, and BD, are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms model reduction may improve your model. The Lack of Fit F-value of 0.74 implies the Lack of Fit is not significant relative to the pure error. There is a 67.79 % chance that a Lack of Fit F-value this large could occur due to noise.

Table 4
ANOVA for the % removal of COD by a quadratic model.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	67.14	14	4.80	1657.31	<0.0001	significant
A-pH	1.05	1	1.05	361.80	<0.0001	
B-Current	0.3740	1	0.3740	129.23	<0.0001	
C-Time	0.4448	1	0.4448	153.73	<0.0001	
D-Dose	0.2869	1	0.2869	99.16	<0.0001	
AB	0.0608	1	0.0608	21.01	0.0004	
AC	0.0119	1	0.0119	4.10	0.0610	
AD	0.0073	1	0.0073	2.52	0.1330	
BC	0.0342	1	0.0342	11.82	0.0037	
BD	0.8317	1	0.8317	287.41	<0.0001	
CD	0.0000	1	0.0000	0.0106	0.9192	
Residual	0.0434	15	0.0029			
Lack of Fit	0.0322	10	0.0032	1.44	0.3615	
Pure Error	0.0112	5	0.0022			
Cor Total	67.18	29				

Table 5

ANOVA for the % removal of BOD by a quadratic model.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	66.83	14	4.77	1263.62	<0.0001	significant
A-pH	1.05	1	1.05	277.01	<0.0001	
B-Current	0.3524	1	0.3524	93.27	<0.0001	
C-Time	0.4109	1	0.4109	108.77	<0.0001	
D-Dose	0.2868	1	0.2868	75.92	<0.0001	
AB	0.0609	1	0.0609	16.12	0.0011	
AC	0.0118	1	0.0118	3.13	0.0970	
AD	0.0073	1	0.0073	1.94	0.1840	
BC	0.0343	1	0.0343	9.07	0.0088	
BD	0.8319	1	0.8319	220.21	<0.0001	
CD	0.0000	1	0.0000	0.0074	0.9324	
Residual	0.0567	15	0.0038			
Lack of Fit	0.0363	10	0.0036	0.8897	0.5926	
Pure Error	0.0204	5	0.0041			
Cor Total	66.89	29				

Table 6

ANOVA for the % removal of TDS by a quadratic model.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1664.67	14	118.90	1320.64	<0.0001	significant
A-pH	25.75	1	25.75	285.96	<0.0001	
B-Current	9.11	1	9.11	101.15	<0.0001	
C-Time	11.40	1	11.40	126.60	<0.0001	
D-Dose	7.39	1	7.39	82.08	<0.0001	
AB	1.65	1	1.65	18.31	0.0007	
AC	0.3528	1	0.3528	3.92	0.0664	
AD	0.2285	1	0.2285	2.54	0.1320	
BC	0.9516	1	0.9516	10.57	0.0054	
BD	20.34	1	20.34	225.96	<0.0001	
CD	0.0006	1	0.0006	0.0061	0.9386	
Residual	1.35	15	0.0900			
Lack of Fit	0.8077	10	0.0808	0.7439	0.6779	
Pure Error	0.5429	5	0.1086			
Cor Total	1666.02	29				

Table 7

ANOVA for the % of power consumption by quadratic model.

Source	Sum of square	df	Mean Square	F-value	p-value	
Model	1.89	14	0.1353	277.2	<0.0001	Significant
A-pH	0.0062	1	0.0062	12.65	0.0029	
B-Current	1.21	1	1.21	2474	<0.0001	
C-Time	0.5014	1	0.5014	1027	<0.0001	
D-Dose	0.0489	1	0.0489	100.1	<0.0001	
AB	0.0025	1	0.0025	5.17	0.0381	
AC	0.0008	1	0.0008	1.63	0.2205	
AD	0.0005	1	0.0005	1.01	0.3299	
BC	0.0670	1	0.0670	137.1	<0.0001	
BD	0.0135	1	0.0135	27.68	<0.0001	
CD	0.0000	1	0.0000	0.028	0.8675	
Residual	0.0073	15	0.0005			
Lack of Fit	0.0056	10	0.0006	1.61	0.3129	
Pure Error	0.0017	5	0.0003			
Cor Total	1.90	29				

Table 8

Model summary for removal of COD by bio-coagulant-assisted electrocoagulation.

Std. Dev.	0.0538	R^2	0.9994
Mean	97.65	Adjusted R^2	0.9988
C.V. %	0.0551	Predicted R^2	0.9970
		Adeq Precision	174.4559

Table 9

Model summary for % removal of BOD by electrocoagulation.

Std. Dev.	0.0484	R^2	0.9997
Mean	96.21	Adjusted R^2	0.9994
C.V. %	0.0503	Predicted R^2	0.9987
		Adeq Precision	202.5627

Table 10

Model summary for % removal of BOD by bio-coagulant-assisted electrocoagulation.

Std. Dev.	0.0615	R^2	0.9992
Mean	97.74	Adjusted R^2	0.9984
C.V. %	0.0629	Predicted R^2	0.9964
		Adeq Precision	151.9981

Table 11

Model summary for % removal of TDS by bio-coagulant-assisted electrocoagulation.

Std. Dev.	0.3001	R^2	0.9992
Mean	92.20	Adjusted R^2	0.9984
C.V. %	0.3255	Predicted R^2	0.9967
		Adeq Precision	156.2180

Table 12

Model summary for % of power consumption by bio-coagulant-assisted electrocoagulation.

Std. Dev.	0.0221	R^2	0.9961
Mean	0.5680	Adjusted R^2	0.9926
C.V. %	3.89	Predicted R^2	0.9818
		Adeq Precision	58.9532

The Model F-value of 277.21 implies the model is significant. There is only a 0.01 % chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, A, B, C, D, AB, BC, and BD, are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms model reduction may improve your model. The Lack of Fit F-value of 1.61 implies the Lack of Fit is not significant relative to the pure error. There is a 31.29 % chance that a Lack of Fit F-value this large could occur due to noise.

3.5.2. Fit statistics

The sum of squares regression (SSR) to the total sum of squares (SST) ratio is displayed by the coefficient of determination (R^2), which is the ratio of the total changes in the anticipated response by the model. R^2 should be large and near to 1, and it is required that R^2 and adjusted R^2 (Adj.R^2) coincide. R^2 expresses the second-order polynomial model's fitness quality [56].

The Predicted R^2 of 0.9970 is in reasonable agreement with the Adjusted R^2 of 0.9988; i.e., the difference is less than 0.2. Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 174.456 indicates an adequate signal. This model can be used to navigate the design space.

The Predicted R^2 of 0.9987 is in reasonable agreement with the Adjusted R^2 of 0.9994; i.e., the difference is less than 0.2. Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. Your ratio of 202.563 indicates an adequate signal.

The Predicted R^2 of 0.9964 is in reasonable agreement with the Adjusted R^2 of 0.9984; i.e., the difference is less than 0.2. Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 151.998 indicates an adequate signal.

The Predicted R^2 of 0.9967 is in reasonable agreement with the Adjusted R^2 of 0.9984; i.e., the difference is less than 0.2 Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 156.218 indicates an adequate signal. This model can be used to navigate the design space.

The Predicted R^2 of 0.9818 is in reasonable agreement with the Adjusted R^2 of 0.9926; i.e., the difference is less than 0.2. Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 58.953 indicates an adequate signal. This model can be used to navigate the design space.

3.5.3. Effects of model parameters and their interactions

The most useful way to disclose the conditions of the reaction system is to employ 3D surfaces and 2D contour plots, which are graphical representations of the regression equation for the optimization of reaction conditions. They are also used to see how each variable affects answers. The response functions of two elements are depicted in such quadratic model plots by varying within the experimental ranges while all other factors are kept constant at their values. From the results, it was observed that all the combined process variables showed a significant effect on the COD, TDS, BOD, and removal with their power consumption in the treatment process. The optimal values of the operation parameters were estimated by the three-dimensional response surface analysis of the independent variables and the dependent variable. A series of three-dimensional (3D) response surface graphs were generated and are presented in Figure below which shows the relationship between removal efficiency and factors.

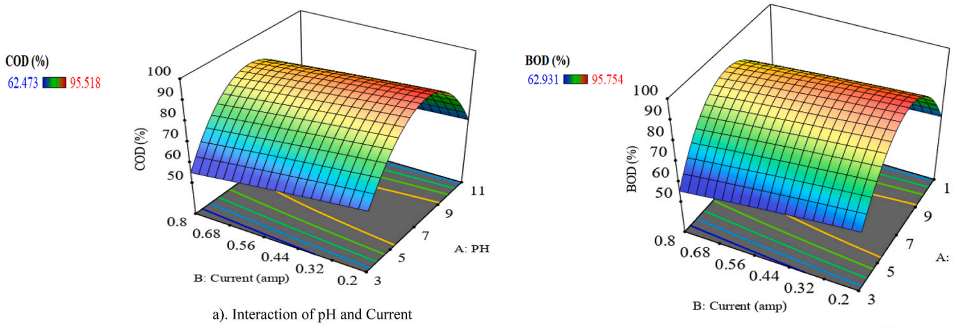
Some interaction effects were shown on 3D graphs as shown below. Fig. 10a the 3D plot reveals the interaction between pH (A) and current (B) on COD (%), indicating the chemical oxygen demand (COD) removal efficiency in a process. The plot shows that higher COD removal percentages occur as the pH moves from acidic to more neutral/basic values, reaching a peak in the pH of 7. As the current increases from 0.2 amps to 0.5 amps, the COD removal efficiency also increases. The COD removal percentage plateaus at a high percentage (96 %) when the pH is above 7 and the current is above 0.5 amps. The interaction plot suggests that for optimal COD removal efficiency, both higher pH (around 7) and higher current levels (about 0.5 amps) are required. As shown in Fig. 10 b) the interaction effect of current and pH as the 3D graph indicated below shows that the BOD removal efficiency was high at current which is indicated by red color and when the current was above 0.5 amp and pH 7. The red color shows high removal efficiency and the green color shows low removal efficiency. So, the interaction effect of current and time was significant. Fig. 10c shows the interaction effect of pH and time it shows that the TDS removal efficiency was high at neutral pH when the time was 40 min at the center of the graph which is red color and terminal points which was indicated by green color show lower removal efficiency. So that the interaction effect of pH and time was significant. Fig. 10d) shows the interaction of pH and bio-coagulant dosage it shows that the TDS removal efficiency was low at the terminal corners of the graph which is indicated by the green color and it was high removal efficiency in the middle at neutral pH which is indicated by red color. So, the interaction effect of pH and bio-coagulant dosage was significant.

3.5.4. Regression equations

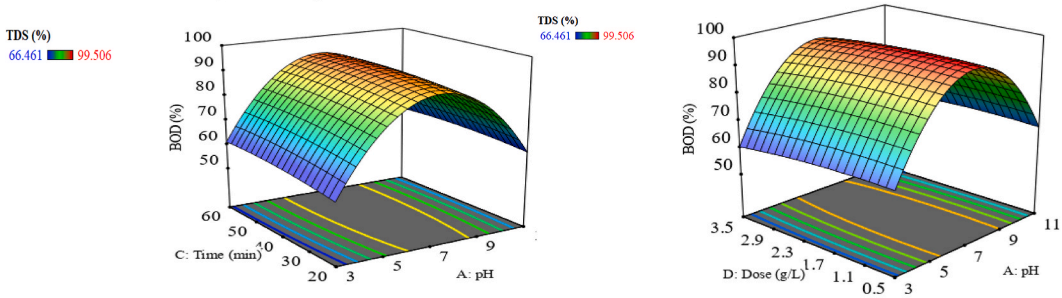
Response Surface Methodology (RSM) is a procedure for analyzing the relationship between the process variables and the responses [23]. These are mathematically fitted by second-order polynomials which enable the evaluation of the parametric effects of the process parameters and their interactions on the investigating the operating factors. Those polynomials can be developed depending on their effect on removal efficiency [57]. Regression analysis reveals the link between a response (dependent) variable and one or more (predictor) independent variables, to the extent that information is present in the data. The response variable is modeled as a function of the predictor factors in regression analysis. The data used determines the duality of the fit as well as the precision of the result. There for the experiment was investigated in terms of selection of pH(A), Current (B), Time(C), and Coagulant dosage(D). To determine optimum operating conditions for maximum removal efficiency of pollutants.

% COD removal $= 98.9491 + 0.2088A + 0.1248B + 0.1361C + 0.1093D + 0.0616\,AB - 0.0272AC + 0.0213AD - 0.0462BC - 0.2279BD + 0.0013CD$

% BOD removal $= 99.0407 + 0.208817\,A + 0.121167\,B + 0.1308C - 0.1093\,D + 0.0617\,AB - 0.0272\,AC + 0.0214\,AD - 0.0462\,BC - 0.2280BD + 0.0013\,CD$



a). Interaction of pH and Current



c. Interaction of pH and time

d. Interaction of time and coagulant dose

Fig. 10. Interactions of operating parameters by bio-coagulant-assisted electrocoagulation.

% TDS removal $= 98.5668 + 1.0357\ A + 0.616\ B + 0.689C - 0.5549\ D + 0.321\ AB - 0.1485\ AC + 0.1195\ AD - 0.2438\ BC - 1.127\ BD - 0.0058\ CD - 7.472$

% Power consumption $= 0.5491 + -0.0160\ A + 0.224\ B + 0.144C - 0.0451\ D + 0.012\ AB - 0.0070AC - 0.0055\ AD + 0.0646\ BC - 0.029\ BD$

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as −1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients [58,59]. According to the results, many of the model terms were significant for responses which include: pH(A), Current ampere(B), time(C), Coagulant dosage(D), Coagulant dosage(D), and interaction terms of AB, AC, AD, BC, BD, CD.

A constant term (98.9491) represents the baseline COD removal, while the unique effects of each component on COD removal are represented by linear terms (A, B, C, and D). The elimination of COD is positively impacted by raising pH, although current has a marginally lesser effect than pH. Positive effects on COD elimination are observed for both time and coagulant dose. The combined effect of two factors is indicated by the interaction terms (AB, AC). For example, improving pH and current simultaneously has a greater effect on COD elimination than combining their independent effects. However, the efficacy of COD elimination is decreased when high current and high coagulant doses are combined. A constant term (98.5668) with a positive interaction between pH and current represents the baseline TDS removal. On the other hand, a considerable negative effect (−1.127) suggests that the TDS removal effectiveness is greatly decreased when high current and high coagulant dosage are used simultaneously. A constant term (0.5491) is used to describe power consumption. A positive coefficient (0.0646) indicates that power consumption is greatly increased when longer operation times are combined with greater currents. A negative value of −0.029 signifies a small reduction in power usage when higher current and coagulant doses are combined.

The terms in the models are organized in a coding system. The ANOVA test was used to determine the model's appropriateness. The lack of fit test was used to confirm model validity, as seen in the tables above. On the regression model, was extremely significant ($P < 0.001$), but the ANOVA for lack of fit was insignificant ($P > 0.05$). All of the results show that this model is a good fit for the experimental data. These findings indicate that the indigenous bio-coagulant-assisted electrocoagulation process was the most effective method for the treatment of brewery wastewater due to the higher percentage of COD, TDS, and BOD removal value and better extraction yield within the shortest time. Means with different letters within the same row indicate significant differences ($P \leq 0.05$).

3.5.5. The optimum condition for responses

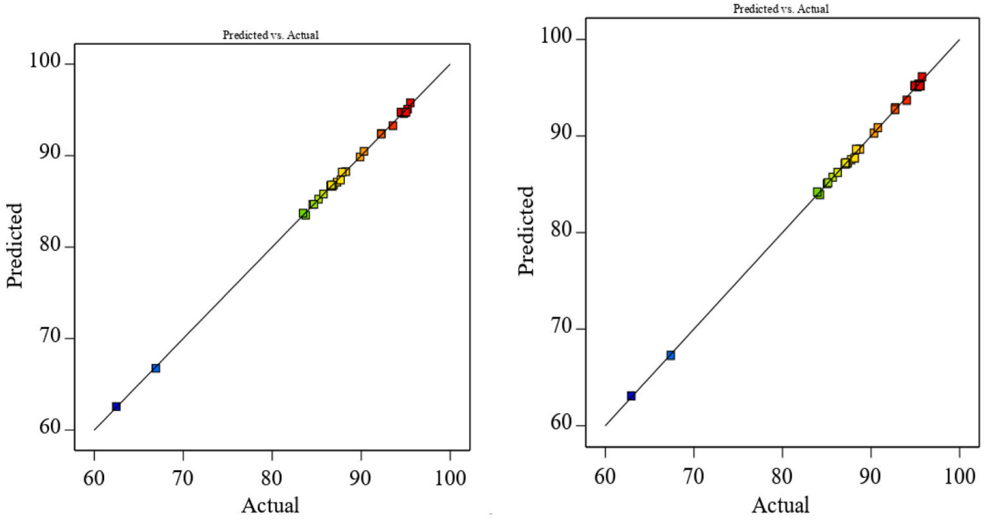
The main advantages of response surface methodology by CCD are to obtain the optimum condition for the removal of pollutants and power consumption based on laboratory experiments. The results were optimized using the regression equation of RSM (design expert 11) based on Central Composite Design. In the optimization of pH(A), Current (B), time(C), and bio-coagulant dosage(D) were selected as within range and the responses such as % removal for Color, COD, BOD, TDS, and power consumption were minimized.

The optimum A-EC conditions were obtained at an electrolysis time of 40 min, pH 7, current 0.5 A, bio-coagulant dosage 2 g/l, and constant electrolytes 0.75 g/l of NaCl. Verification experiments were performed under optimal conditions to further validate the reliability of the theoretical model prediction. The results showed that the experimental results for removal efficiencies were very close to what was predicted, and their difference was less than 0.2. The values were not significantly different ($P > 0.05$), so it could be concluded that the established model in this study was appropriate and valid. Fig. 11 shows that Comparison of the predictive and actual value of COD, BOD, TDS, and power consumption for the bio-coagulant-assisted electrocoagulation process.

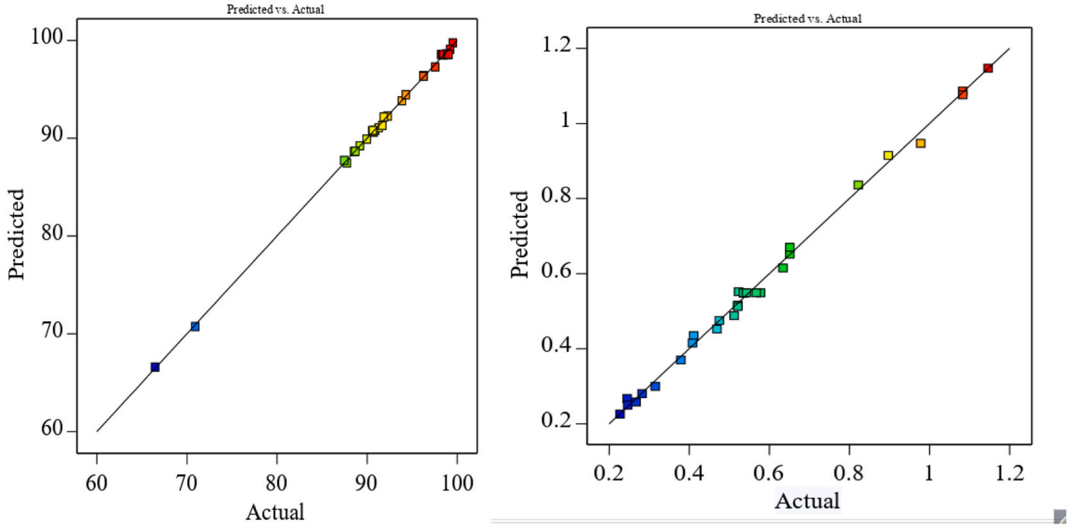
The charts in Fig. 10 display a scatter plot comparing predicted values to actual values, with points color-coded to represent different categories or periods. A 45-degree reference line ($y = x$) is included, indicating perfect prediction accuracy. Points that fall on this line represent cases where predicted values match the actual values, while deviations from the line indicate reduced accuracy. Fig. 10 shows that at optimal levels, the predicted and experimental results align closely with the reference line, demonstrating strong agreement and validating the model's accuracy. To develop a parsimonious model with relevant predictors, the backward elimination method was used. The model's coefficient of determination revealed a quadratic relationship between responses and parameters, along with a strong regression coefficient. In general, most data points are clustered near the reference line, indicating overall accuracy. Upon closer inspection, blue points exhibit greater deviation from the line, reflecting less accurate predictions. As the color transitions from yellow to red, the points become more concentrated near the reference line, suggesting improved prediction accuracy across different dimensions. This plot provides a visual assessment of the model's performance, illustrating how well its predictions align with actual outcomes across various segments, as indicated by the color gradient.

Figs. 11–14 illustrate statistical analysis, particularly that which is concerned with normal probability and residual analysis. The first determines whether a set of data follows a normal distribution by using a normal probability plot. The diagonal line that connects the dots indicates the degree to which the data resembles normality. The residuals are essentially continually distributed if the majority of the points closely resemble the red line. The residuals may have a normal distribution based on the points' good alignment with the diagonal (see Fig. 15).

The second figure is a plot of residuals against fitted values, with errors shown on the y-axis and fitted values that is, values the model predicted on the x-axis. The assumptions of linear regression, particularly homoscedasticity (constant variance of residuals), are evaluated with the aid of this graphic. Although there is not a noticeable trend in the residuals, there might be some minor variance-related difficulties that call for additional research on heteroscedasticity or model fit. In conclusion, the points' exact alignment with



a.) % COD removal b.) % BOD removal



c) % TDS removal d) % power consumption

Fig. 11. Comparison of the predictive and the experimental results for bio coagulant assisted electrocoagulation process.

the line suggests the residuals have a normal distribution.

3.6. *Limitation of the method*

Numerous factors affect the effectiveness of biocoagulant-assisted electrocoagulation in removing contaminants. This method of treatment strongly depends on precise management and modification of operational parameters like pH, current density, reaction time, and solution conductivity. Moreover, Large volume and highly turbid wastewater can obstruct the coagulation process, which could prevent flocs from forming and decrease the effectiveness of pollutant removal. In many situations, initial pollutant concentration has a big impact on how well the treatment works. Also, the method could not be applicable where there was no electric power. Lastly, the treatment plan requires close monitoring and revision due to the complex interactions of these components. To guarantee that the parameters are precisely managed and that the intended treatment outcomes are achieved, this calls for the support of an appropriately trained individual. For large-scale treatment, specially designed compartments and control structures are required to precisely manage and regulate the process, necessitating both adequate funding and skilled manpower.

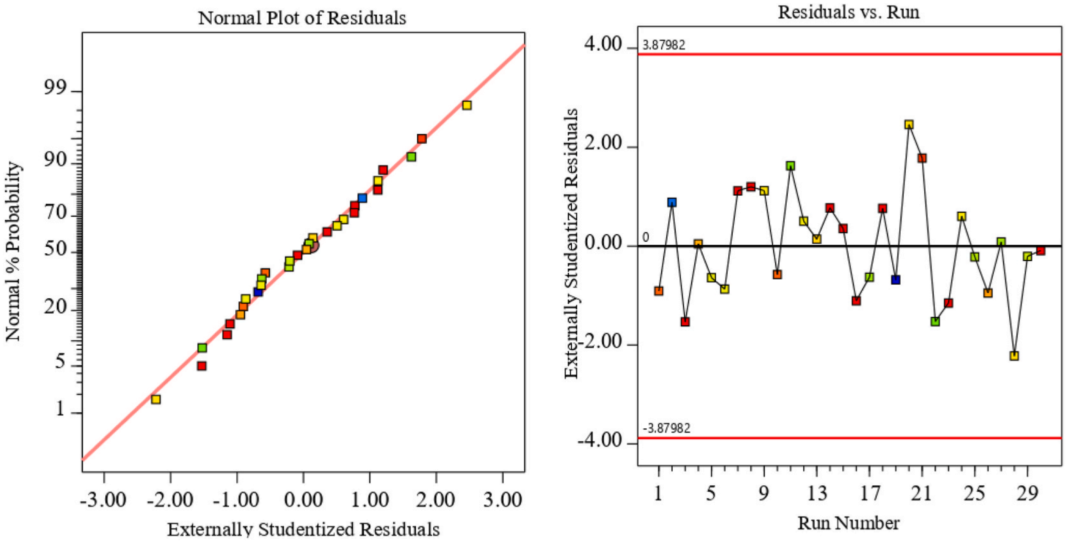


Fig. 12. Distribution of normal probability % and residuals for COD removal.

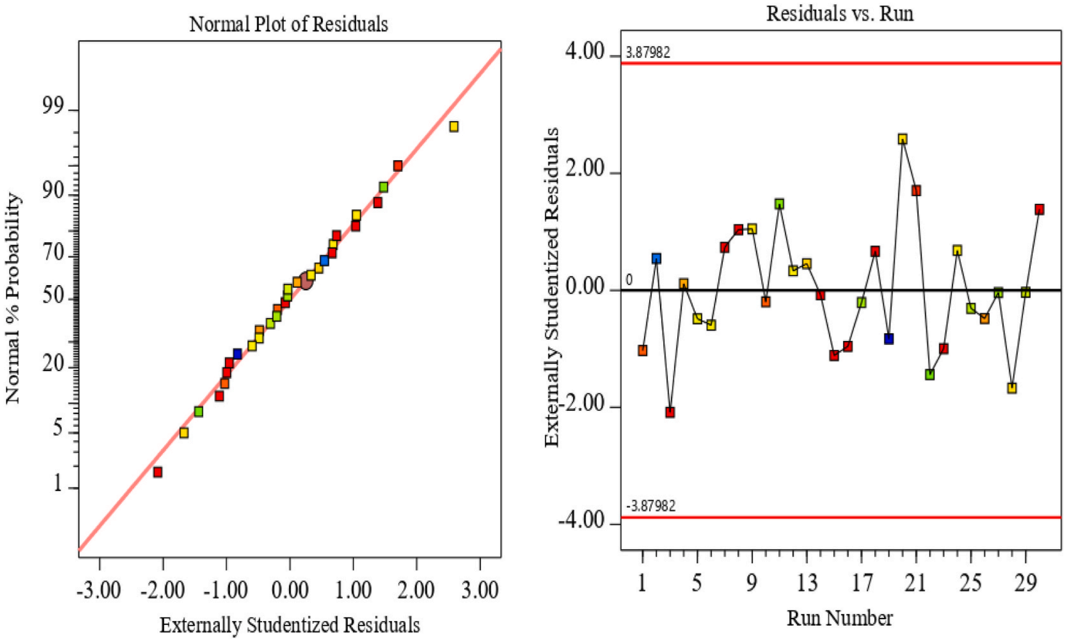


Fig. 13. Distribution of normal probability % and residuals for BOD removal.

4. Conclusions

The method of bio-coagulant-assisted electrocoagulation provides a practical, economical, and ecologically friendly technique to treat wastewater effluent from brewery industries. The results of the study showed that the use of custard apple seed powder as a natural coagulant significantly improved pollutant removal. High efficiencies were achieved under optimal conditions by varying important parameters like pH, length of time, current, and dosage of the biocoagulant. With the least amount of power usage (0.54 kWh/m^3), the method used was able to reach maximum removal efficiency for COD (99.01 %), BOD (99.09 %), and TDS (99.02 %). With a steady 0.75 g/l NaCl electrolyte, 40 min of treatment, 2 g/l of custard seed powder, an ideal pH of 7, and a current of 0.5 A, these outcomes were achieved. The technique is more inexpensive than using conventional approaches because of the decrease in power use. Furthermore, important insights into the influence of factors were obtained by statistical optimization utilizing Response Surface Methodology (RSM), allowing for more accurate control and improving treatment effectiveness. Analysis of variance was used to establish the significance of independent variables and their interactions at a 95 % confidence level. All things considered, this

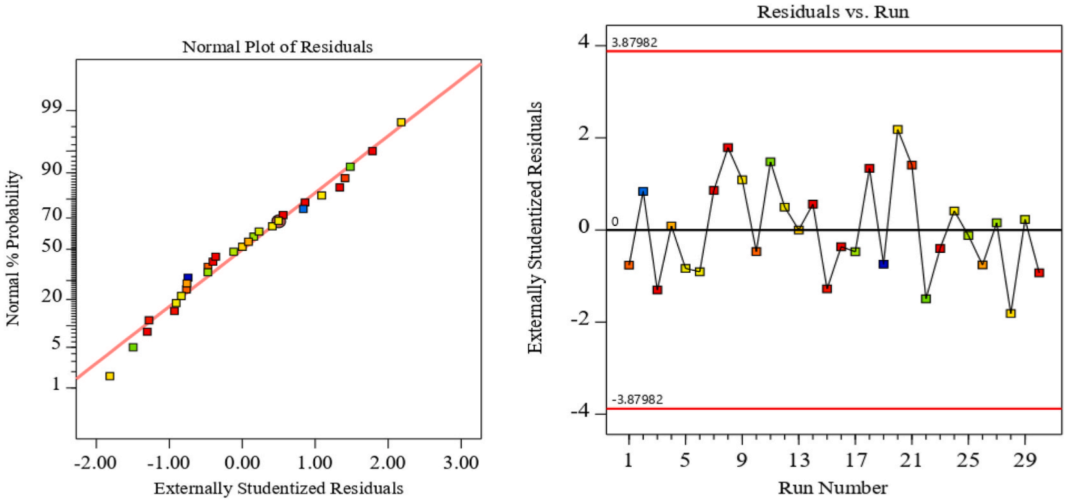


Fig. 14. Distribution of normal probability % and residuals for TDS removal.

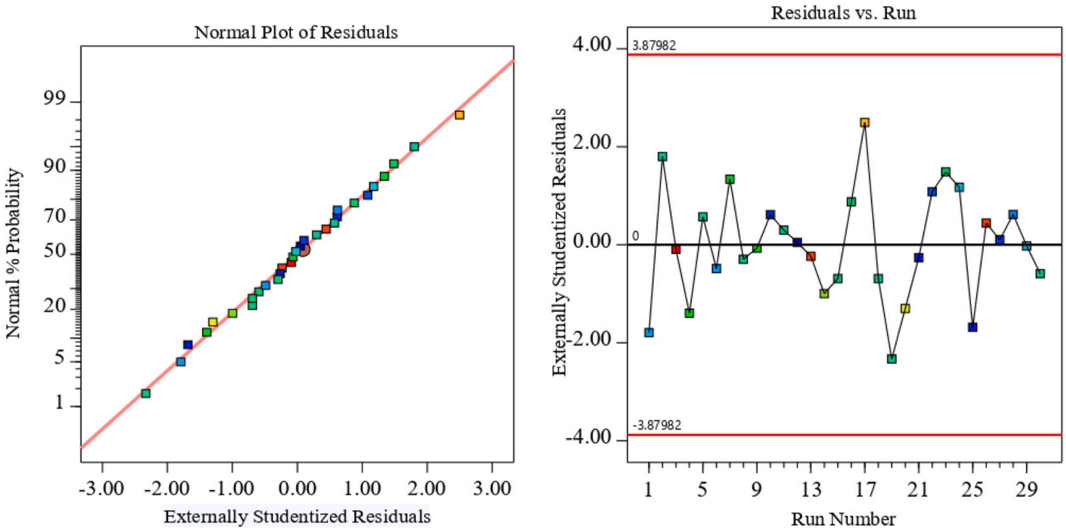


Fig. 15. Distribution of normal probability % and residuals for power consumption.

innovative solution reduces pollution from brewery wastewater, reduces the negative effects on the environment and facilitates the use of sustainable, locally available resources. It also provides a better alternative to more conventional techniques like oxidation ponds, which have lower removal efficiency. The nutrient-rich sludge from breweries can be utilized as a building material, animal feed, compost, biogas production, soil amendment, water recovery, and biochar manufacturing. So, sludge management was not such a problem. It is possible to use it as an additional resource. Lastly, the approach requires specially constructed facilities for the process and power supply, which requires expert labor, to be used for industries and companies.

CRediT authorship contribution statement

Firomsa Sufa Garomsa: Writing – original draft, Methodology, Formal analysis, Data curation. **Yenealem Mehari Berhanu:** Software, Resources, Project administration, Investigation. **Wendesen Mekonin Desta:** Validation, Supervision, Resources, Project administration. **Firomsa Bidira:** Writing – review & editing, Visualization, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Declarations

Ethical approval and consent to participate Not applicable as no human participant and animal experiments were performed in this study. Consent for publication is Not applicable.

Funding

This research did not receive any specific grants from funding agencies in the public, commercial, or not-for-profit sectors.

Declaration of competing interest

There is no conflict of interest between the authors. The authors declare that none of the work reported in this study could have been influenced by any known competing financial interests or personal relationships.

Acknowledgments

The authors would like to express their gratitude to Jimma University, Institute of Technology, Environmental Engineering department for their invaluable assistance during Laboratory work. As well as the Badele brewery industry for Allowing and supporting to investigation of waste effluent from their company.

References

[1] A.K. Chopra, A.K. Sharma, V. Kumar, Scholars research library Overview of Electrolytic treatment : an alternative technology for purification of wastewater 3 (5) (2011) 191–206.
[2] R. Bauer, H. Fallmann, The Photo-Fenton oxidation - a cheap and efficient wastewater treatment method, Res. Chem. Intermed. 23 (4) (1997) 341–354, https://doi.org/10.1163/156856797X00565.
[3] G.D. Noudeh, M. Asdaghi, N.D. Noudeh, M. Dolatabadi, S. Ahmadzadeh, Response surface modeling of ceftriaxone removal from hospital wastewater, Environ. Monit. Assess. 195 (1) (2023) 1–12, https://doi.org/10.1007/s10661-022-10808-z.
[4] A. Mahroudi, M. Aghasi, M. Dolatabadi, S. Ahmadzadeh, Removal of reactive blue 171 dye from aqueous solution and textile industrial wastewater using peroxide-electrocoagulation process by iron electrode: application of response surface methodology, Desalination Water Treat. 272 (2022) 266–276, https://doi.org/10.5004/dwt.2022.28821.
[5] M. Dolatabadi, R. Malekahmadi, A. Ghorbanian, S. Ahmadzadeh, Investigation of electrocoagulation process for efficient removal of bisphenol A from the aqueous environment: promising treatment strategy, Journal of Environmental Health and Sustainable Development 6 (2) (2021) 1275–1283, https://doi.org/10.18502/jihad.v6i2.6539.
[6] L. Issue, S. Ahmed, S. Ismail, A.B. St, R.A. Ct, International Journal of Current Advanced Research 7 (2) (2018).
[7] D.A. Tziouvaras, et al., Mathematical models for current, voltage, and coupling capacitor voltage transformers, IEEE Trans. Power Deliv. 15 (1) (2000) 62–72, https://doi.org/10.1109/61.847230.
[8] M. Dolatabadi, A. Kheirieh, M. Yoosefian, S. Ahmadzadeh, Hydroxyzine removal from the polluted aqueous solution using the hybrid treatment process of electrocoagulation and adsorption; optimization, and modeling, Appl. Water Sci. 12 (11) (2022) 1–9, https://doi.org/10.1007/s13201-022-01780-7.
[9] I. Sirés, E. Brillas, M.A. Oturan, M.A. Rodrigo, M. Panizza, Electrochemical advanced oxidation processes: today and tomorrow. A review, Environ. Sci. Pollut. Control Ser. 21 (14) (2014) 8336–8367, https://doi.org/10.1007/s11356-014-2783-1.
[10] B.N. Malinović, J. Markelj, A. Žgajnar Gotvajn, I. Kralj Cigić, H. Prosen, Electrochemical treatment of wastewater to remove contaminants from the production and disposal of plastics: a review, Environ. Chem. Lett. 20 (6) (2022) 3765–3787, https://doi.org/10.1007/s10311-022-01497-8.
[11] K.P. Shabangu, B.F. Bakare, J.K. Bwapwa, The Treatment Effect of Chemical Coagulation Process in South African Brewery Wastewater : Comparison of Polyamine and (2022).
[12] P. Asaithambi, M. Matheswaran, Electrochemical treatment of simulated sugar industrial effluent: optimization and modeling using a response surface methodology, Arab. J. Chem. 9 (Nov. 2016) S981–S987, https://doi.org/10.1016/j.arabjc.2011.10.004.
[13] G. Asha, B.M. Kumar, Evaluation of electrochemical process for treating coffee processing wastewater using aluminum electrodes 9 (9) (2015) 74–82, https://doi.org/10.9790/2402-09927482.
[14] M. Meshksar, T. Roostaee, M.R. Rahimpour, Membrane Technology for Brewery Wastewater Treatment, Elsevier Inc., 2020, https://doi.org/10.1016/B978-0-12-816823-3.00010-1.
[15] R. Shrestha, et al., Technological trends in heavy metals removal from industrial wastewater: a review, J. Environ. Chem. Eng. 9 (4) (2021), https://doi.org/10.1016/j.jece.2021.105688.
[16] T.E. Aniyikaiye, T. Oluseyi, J.O. Odiyo, J.N. Edokpayi, Physico-Chemical Analysis of Wastewater Discharge from Selected Paint Industries in Lagos, Nigeria (2019) 5, https://doi.org/10.3390/ijerph16071235.
[17] G.S. Simate, et al., The treatment of brewery wastewater for reuse : state of the art, DES 273 (2–3) (2011) 235–247, https://doi.org/10.1016/j.desal.2011.02.035.
[18] B.I. Okolo, M.C. Menkiti, P.C. Nnaji, O.D. Onukwuli, C.C. Agu, The Performance of Okra Seed (Hibiscus Esculentus L .) Extract in Removal of Suspended Particles from Brewery Effluent by Coag-Flocculation Process the Performance of Okra Seed (Hibiscus Esculentus L .) Extract in Removal of Suspended Particles from Bre, 2014, https://doi.org/10.9734/BJAST/2014/9887. January 2016.
[19] T.B. Kebede, Wastewater treatment in brewery industry, Review 6 (1) (2018) 716–722.
[20] T. Oljira, D. Muleta, M. Jida, Potential Applications of Some Indigenous Bacteria Isolated from Polluted Areas in the Treatment of Brewery Effluents, vol. 2018, 2018.
[21] H.G.J. Pacheco, N.Y. Elguera, M. Ancco, A.E.L.F. Castro, M.E.B. Meza, V.C. Almeida, Combined coagulation-electrocoagulation process using biocoagulant from the Opuntia ficus-indica for treatment of cheese whey wastewater, Environ. Monit. Assess. 195 (4) (2023), https://doi.org/10.1007/s10661-023-11095-y.
[22] A. Patchaiyappan, S.P. Devipriya, Application of plant-based natural coagulants in water treatment, Cost Effective Technologies for Solid Waste and Wastewater Treatment (2021) 51–58, https://doi.org/10.1016/B978-0-12-822933-0.00012-7.
[23] P.C. Nnaji, et al., Statistical computation and artificial neural algorithm modeling for the treatment of dye wastewater using mucuna Sloane as coagulant and study of the generated sludge, Results in Engineering 19 (June) (2023) 101216, https://doi.org/10.1016/j.rineng.2023.101216.
[24] Q. Wu, Treatment of Wastewater by Coagulation and Flocculation Using Biomaterials Treatment of Wastewater by Coagulation and Flocculation Using Biomaterials, 2017, https://doi.org/10.1088/1757-899X/263/3/032006.
[25] K. Grenda, Modification of Natural Polymers and Natural By-Products for Coagulation and Flocculation Purposes, 2018, pp. 43–44. August.

[26] R. Nile, The Impact of Some Organic and Inorganic Pollutants on Fresh Water (Rashid the Impact of Some Organic and Inorganic Pollutants on Fresh Water (Rashid Branch, River Nile), Egypt, September 2019, https://doi.org/10.24297/jab.v10i2.6481.

[27] H. Agarwal, D. Sharma, and S. K. Sindhu, "REMOVAL OF MERCURY FROM WASTEWATER USE OF GREEN ADSORBENTS - A REVIEW".

[28] Q.H. Nguyen, et al., COD Removal from Artificial Wastewater by Electrocoagulation Using Aluminum Electrodes, vol. 15, 2020, pp. 39–51, https://doi.org/10.20964/2020.01.42.

[29] M. Susree, P. Asaithambi, R. Saravanathamizhan, M. Matheswaran, Journal of Environmental Chemical Engineering Studies on various mode of electrochemical reactor operation for the treatment of distillery effluent, Biochem. Pharmacol. 1 (3) (2013) 552–558, https://doi.org/10.1016/j.jece.2013.06.021.

[30] Ö. Gökkuş, Y.Ş. Yildiz, Application of electrocoagulation for treatment of medical waste sterilization plant wastewater and optimization of the experimental conditions, Clean Technol. Environ. Policy 17 (6) (2015) 1717–1725, https://doi.org/10.1007/s10098-014-0897-2.

[31] S. Sadeghi, M.R. Alavi Moghaddam, M. Arami, Techno-economical evaluation of hexavalent chromium removal by electrocoagulation process with the aid of poly aluminum chloride as coagulant: optimization through response surface methodology, Environmental Engineering and Management Journal 16 (1) (2017) 93–104, https://doi.org/10.30638/eemj.2017.011.

[32] I. Kabdaşlı, O. Tünay, Electrocoagulation Applications for Industrial Wastewaters : a Critical Review, vol. 2515, 2012, https://doi.org/10.1080/21622515.2012.715390.

[33] E. Keshmirizadeh, S. Yousefi, M.K. Rofouei, An investigation on the new operational parameter effective in Cr(VI) removal efficiency: a study on electrocoagulation by alternating pulse current, J. Hazard Mater. 190 (1–3) (2011) 119–124, https://doi.org/10.1016/j.jhazmat.2011.03.010.

[34] K.T. Asefaw, P. Asaithambi, M. Tegegn, Treatment of wet coffee processing wastewater using a pulsed-electrocoagulation process: optimization using response surface technique, Appl. Water Sci. 14 (3) (2024) 1–17, https://doi.org/10.1007/s13201-024-02118-1.

[35] M.A. Oturan, J.J. Aaron, Advanced oxidation processes in water/wastewater treatment: principles and applications. A review, Crit. Rev. Environ. Sci. Technol. 44 (23) (Dec. 02, 2014) 2577–2641, https://doi.org/10.1080/10643389.2013.829765.

[36] T. Dye, C. Wastewater, S. A. Ishak, M. F. Murshed, H. Akil, and N. Ismail, "The Application of Modified Natural Polymers in".

[37] H.G.J. Pacheco, N.Y.M. Elguera, M.R.A. Mamani, N.P.L. Alvarez, V. de C. Almeida, Treatment of textile wastewater by electrocoagulation process assisted with biocoagulant obtained from the pitahaya peels, Desalination Water Treat. 283 (2023) 1–10, https://doi.org/10.5004/dwt.2023.29186.

[38] A. Shalaby, E. Nassef, A. Mubarak, M. Hussein, Phosphate removal from wastewater by electrocoagulation using aluminum electrodes, American Journal of Environmental Engineering and Science 1 (5) (2014) 90–98.

[39] F. Sher, K. Hanif, S.Z. Iqbal, M. Imran, Implications of advanced wastewater treatment: electrocoagulation and electroflocculation of effluent discharged from a wastewater treatment plant, J. Water Proc. Eng. 33 (0) (2020) 1–40, https://doi.org/10.1016/j.jwpe.2019.101101.

[40] K. Yetilmezsoy, F. Ilhan, Z. Sapci-zengin, S. Sakar, M.T. Gonullu, Decolorization and COD reduction of UASB pretreated poultry manure wastewater by electrocoagulation process : A post-treatment study 162 (2009) 120–132, https://doi.org/10.1016/j.jhazmat.2008.05.015.

[41] N. Adjeroud-Abdellatif, et al., Effect of a natural coagulant extract from Opuntia ficus-indica cladode on electrocoagulation-electroflotation water treatment process, Int. J. Environ. Anal. Chem. 102 (17) (2022) 5822–5846, https://doi.org/10.1080/03067319.2020.1804889.

[42] M. Nasrullah, M.N.I. Siddique, A.W. Zularisam, Effect of high current density in electrocoagulation process for sewage treatment, Asian J. Chem. 26 (14) (2014) 4281–4285, https://doi.org/10.14233/ajchem.2014.16134.

[43] T. Mahamad, A. Shaikh, Adsorption of Pb (II) from wastewater by natural and synthetic adsorbents 10 (5) (2020) 6522–6539.

[44] H.N. Ibarra-Taquez, E. GilPavas, E.R. Blatchley, M.Á. Gómez-García, I. Dobrosz-Gómez, Integrated electrocoagulation-electrooxidation process for the treatment of soluble coffee effluent: optimization of COD degradation and operation time analysis, J. Environ. Manag. 200 (Sep. 2017) 530–538, https://doi.org/10.1016/j.jenvman.2017.05.095.

[45] A.T. Nair, A.R. Makwana, M.M. Ahammed, The use of response surface methodology for modeling and analysis of water and wastewater treatment processes : a review (2014) 464–478, https://doi.org/10.2166/wst.2013.733.

[46] O.A. Afolabi, K.O. Adekalu, D.A. Okunade, Electro-Fenton treatment process for brewery wastewater: effects of oxidant concentration and reaction time on BOD and COD removal efficiency, J. Eng. Appl. Sci. 69 (1) (2022) 1–14, https://doi.org/10.1186/s44147-022-00089-1.

[47] E. Bazrafshan, L. Mohammadi, A. Ansari-Moghaddam, A.H. Mahvi, Heavy metals removal from aqueous environments by electrocoagulation process - a systematic review, Journal of Environmental Health Science and Engineering 13 (1) (2015), https://doi.org/10.1186/s40201-015-0233-8.

[48] G. Hasani, et al., A comparative optimization and performance analysis of four different electrocoagulation-flotation processes for humic acid removal from aqueous solutions, Process Saf. Environ. Protect. 121 (2019) 103–117, https://doi.org/10.1016/j.psep.2018.10.025.

[49] K.T. Asefaw, F. Bidira, W.M. Desta, P. Asaithambi, Sustainable Chemistry for the Environment Investigation on pulsed-electrocoagulation process for the treatment of wet coffee processing wastewater using an aluminum electrode, Sustainable Chemistry for the Environment 6 (March) (2024) 100085, https://doi.org/10.1016/j.scenv.2024.100085.

[50] M.I. Litter, N. Quici, Photochemical advanced oxidation processes for water and wastewater treatment, Recent Pat. Eng. 4 (3) (2011) 217–241, https://doi.org/10.2174/187221210794578574.

[51] S. Vasudevan, Journal of Water Process Engineering an efficient removal of phenol from water by peroxi-electrocoagulation processes, J. Water Proc. Eng. 2 (2014) 53–57, https://doi.org/10.1016/j.jwpe.2014.05.002.

[52] G. Mouedhen, M. Feki, M.D.P. Wery, H.F. Ayedi, Behavior of aluminum electrodes in electrocoagulation process, J. Hazard Mater. 150 (1) (2008) 124–135, https://doi.org/10.1016/j.jhazmat.2007.04.090.

[53] T. Zhuan, et al., Application of central composite design for optimization of the removal of humic substances using coconut copra, International Journal of Industrial Chemistry 6 (3) (2015) 185–191, https://doi.org/10.1007/s40090-015-0041-0.

[54] F. Nyström, I. Herrmann, A. Hedström, M. Viklander, M. Cimbritz, And Luleå tekniska universitet Institutionen för samhällsbyggnad och naturresurser. Coagulation Process Characteristics and Pollutant Removal from Urban Runoff, 2019.

[55] H.M. Bui, Optimization of electrocoagulation of instant coffee production wastewater using the response surface methodology 19 (2) (2017) 67–71.

[56] M. Darvishmotevalli, A. Zarei, MethodsX Optimization of saline wastewater treatment using electrochemical oxidation process : prediction by RSM method, MethodsX 6 (2019) 1101–1113, https://doi.org/10.1016/j.mex.2019.03.015.

[57] D. Bähre, O. Weber, A. Rebschläger, Investigation on pulse electrochemical machining characteristics of lamellar cast iron using a response surface methodology-based approach, Procedia - Social and Behavioral Sciences 6 (2013) 362–367, https://doi.org/10.1016/j.procir.2013.03.028.

[58] A.K. Husen, F. Bidira, W. Mekonin Desta, P. Asaithambi, COD, color, and turbidity reduction from surface water using natural coagulants: investigation and optimization, Progress in Engineering Science 1 (2–3) (2024) 100007, https://doi.org/10.1016/j.pes.2024.100007.

[59] F. Bidira, Z. Asmelash, S. Kebede, A. Bekele, Optimization and evaluation of the process variable's effect on color and turbidity removal from coffee processing wastewater: using a photoelectrochemical oxidation process, Environmental Health Engineering and Management 10 (1) (2023) 1–15, https://doi.org/10.34172/EHEM.2023.01.