Brewery Wastewater Treatment using Biocoagulants from Cassava Leaves

H.[1] Mahmud, J. O. [2], Ezeugo, D. O.[3] Onukwuli,

[1,]Department of Chemical Engineering Technology, Auchi Polytechnic, Auchi, Nigeria
2 Department of Chemical Engineering, Chukwuemeka Odumegwu Ojukwu University Uli, Anambra State
[3]Department of Chemical Engineering, Nnamdi Azikiwe University, Awka Anambra State.
Correspondence e-mail: lekebafe@unilag.edu.ng

ABSTRACT

Concerns over the use of traditional metal-based coagulants and flocculants to remove suspended particles from wastewater and drinking water are growing now. Concerning themes these days include the created non-biodegradable sludge's continued impact on human health and further degradation of aquatic habitats. Using the right treatment techniques to lower the pollutant level in receiving waters is essential to achieving coagulation. Using cassava leaf as a bio-coagulant, this study examines the coagulative decrease of turbidity, COD, BOD, and color from brewery wastewater. A Fourier Transform Infrared Spectrophotometer (FTIR) and a scanning electron microscope (SEM) were used to acquire and study these bio-coagulants for their spectrum and morphological properties. The physical-chemical characteristics of the wastewater from the brewery were examined both before and following treatment. The outcome exhibited a natural pH of 7.7 at 300 degrees Celsius. pH (5-8), coagulant dose (0.2–1.0g), temperature (400–700C), settling time (10–70mins), and particle size (0.212, 0.315, 0.5, 1.0, 2.0mm) were the factors evaluated on the coagulation–flocculation process of the brewery wastewater. The factors examined in relation to reduction efficiency revealed that as pH increased, color intensities fell from 75.64% to 70.48%. The Total Suspended Solids (TSS) drop as pH rises, from 81.89% to 79.67%. With an increase in pH, turbidity rises from 38.8% to 41.06%. At 0.3g/L of cassava leaf, the maximum decrease in turbidity was 51.22%, COD was 39.79%, BOD was 100.62%, and color was 4.7%. R2 = 0.95 was obtained by fitting the data using a pseudo first order coagulation kinetics model. At greater R^2 shows that the model matches the data the best. Using the kinetic parameter (R_2), PFO and PSO have respective values of 0.95 and 1.

Keywords: Brewery waste, Coagulation, Cassava leaves, Flocculation, Treatment

INTRODUCTION

Water is a vital part of human life and plays a crucial role in daily survival. People rely on it for a wide range of activities, such as bathing, cleaning, flushing toilets, and maintaining hydration. Many of these uses result in the production of wastewater. To maintain a consistent and safe water supply, proper treatment is necessary. The cycle of water use in human life greatly depends on both the purification of drinking water and the processing of wastewater.[1] Several techniques are used to transform wastewater into treated water and to make raw sources suitable for drinking before being returned to the environment[2]. These methods range from standard traditional approaches to more advanced technologies. One common element in most treatment systems is the process of coagulation followed by flocculation. These stages play a central role in eliminating particles suspended in the water, helping to produce cleaner, clearer results. In many treatment systems, whether for drinking water or wastewater, coagulation and flocculation are part of the initial treatment steps and are essential for ensuring the water is free from visible impurities.

Coagulants and flocculants are materials added during water treatment processes to help in the removal of suspended particles. These substances are often made up of chemical compounds that carry two positive charges, which are commonly used in both wastewater and drinking water purification. In addition, negatively charged polymers with large molecular structures are widely applied, particularly for their flocculating abilities. Some commonly used examples include aluminum chlorohydrate, polyaluminum chloride, polyaluminum sulfate chloride, polyferric sulfate, hydrated lime, magnesium carbonate, various iron salts like ferric chloride and ferric sulfate, as well as aluminum salts such as aluminum sulfate. These compounds are effective at significantly lowering the amount of suspended material in water.[3]

There is increasing global concern about the environmental consequences linked to the long term use of these chemical substances. Several studies have been conducted to explore how such treatments may impact the environment. These effects include increased corrosion of metallic surfaces, changes in water pH, reduced root growth in plants, and interference with seed germination. Conventional water treatment methods have raised awareness about these risks and suggest that the use of naturally sourced alternatives, such as biocoagulants and bioflocculants, could offer a safer solution[3]. These natural agents are biodegradable and derived from living organisms or their byproducts, making them environmentally friendly and safe for human health. The purpose of this study is to evaluate how effective certain waste materials can be when used as bioflocculants for treating wastewater generated by breweries.

MATERIALS AND METHODS

Materials

The wastewater sample from a brewery in Ibadan, Southwest Nigeria, was utilized in this investigation. Before and after treatment, the effluent was kept and subjected to established techniques of analysis for a variety of wastewater parameters.

Processing of the Waste Materials into Bio-flocculants

Cassava leaves were collected from a farm located along Warake Road in Warake, Edo State, Nigeria. Due to their high moisture content, the leaves were thoroughly washed with water and sun-dried for 3 weeks. After drying, the leaves were trimmed with scissors to reduce their size and then ground using a mechanical grinder. To remove any remaining moisture, the ground material was air-dried for another 3 days.

The dried samples were then sieved using a laboratory sieve to separate particles based on size.

An electric blender was used to further blend the material into finer and more uniform granules. The sieved samples were classified into particle sizes of 2 mm to 1 mm, 0.5 mm to 0.351 mm, and 0.212 mm. These processed samples were stored in airtight polyethylene containers until needed.

Coagulation – Flocculation Processing of the Brewery Waste

The pH, coagulant dose, settling duration, particle size, temperature, and flocculation-coagulation studies were conducted in the Unit Operation laboratory.

Effect of settling time: At constant coagulant dose, particle size, temperature, pH, and waste water volume, the impact of settling time was investigated within the range of 10 to 70 minutes. Twenty seven beakers were filled with thirty milliliters of wastewater. At the same time, 0.3 grams of cassava leaves, the coagulant with the smallest particle size (0.212 mm), was concurrently poured into each of the beakers holding the wastewater. Using a stop watch, the liquids were combined and agitated for five minutes at a time. After that, they were given time to settle in each beaker. Following the completion of every test, the mixtures were filtered, and the filtrates were then transferred into distinct sample bottles for additional examination.

Effect of Coagulant Dosage: Using a weighing scale, the coagulant particle with the smallest size (0.212 mm) was divided into different mass (0.2 g, 0.4 g, 0.6 g, 0.8 g, and 1.0 g) and concurrently poured into five (5) beakers holding 30 ml of wastewater. Subsequently, the solutions were concurrently mixed for five minutes, let to settle for eighty minutes, filtered, and the filtrates were then transferred into other sample bottles for additional examination.

Effect of particle size: 0.3g of the coagulant (cassava leaves) for each of the four particle sizes (2 mm, 1 mm, 0.5 mm, and 0.351 mm) was simultaneously poured into four beakers holding 30 ml of wastewater; the mixtures were then stirred for five minutes, let to settle for eighty minutes, filtered, and the filtrates were then poured into individual sample bottles.

Effect of pH: The pH of the wastewater was tested using a pH meter and it was discovered that the wastewater was slightly basic with pH reading of 7.7.

Effect of Temperature: Four (4) beakers containing 30 milliliters of effluent were measured. A water bath was used to raise the temperature of one of the beakers holding the effluent to 400 degrees Celsius. This was verified by checking to see if the temperature was 400C with a thermometer. In the beaker set in the water bath at 400C, 0.3g of the coagulant—cassava leaves—with the smallest particle size was poured. After a few minutes of stirring, the mixture was given eighty minutes to settle. A sample bottle was filled with the filtrate after it had been filtered. After repeating this process for temperature readings of 500C, 600C, and 700C, the filtrates were put into sample vials for additional examination.

Physico-chemical Properties of Brewery Wastewater before and after Coagulation

The physical and chemical characteristics were assessed utilizing the suggested techniques[4]. . The pH was ascertained with an Oakion pH meter, the color was measured calorimetrically with a Jenway PCO1 model colorimeter calibrated with a set of potassium chloroplatinate-cobalt solutions as Pt, the turbidity was assessed with a standardized Hanna H198703 turbidimeter, and the electrical conductivity was assessed by submerging a portable conductimeter model MC METTLER TOLEDO into a beaker container holding 20 mL of each sample. Whole Solids: Gravimetric analysis was performed on the materials.

Total Dissolved Solids: We made use of a handheld TDS meter. The total solids minus the total dissolved solids was used to compute the total suspended solids (TSS). Using mercurimetric titration, the chloride content of the water sample was determined. By employing the phenoldisulfonic acid technique, the nitrate level of the water sample was ascertained[5] . Using absorption spectrophotometry, the amount of sulphate in the sample was ascertained turbidimetrically. Ammonium molybdate spectrophotometric technique was used to quantify the amount of phosphate in the sample.

Dissolved oxygen (DO) was ascertained on-site utilizing a battery-powered HANNA H19142 dissolved oxygen test. The dissolved oxygen concentration (mg/L) was read and recorded on the spot as soon as the meter's probe was carefully lowered into the water body without disturbing it.

Biochemical oxygen demand (BOD) was ascertained by taking a sample's dissolved oxygen content on a particular day, letting it sit for a few days, and then taking another look at the DO value five days later. A measurement of the BOD is the difference. A known quantity of acidified potassium dichromate is used to oxidize the chemically oxidizable organic matter content of a particular sample. Redox titration using ferrous sulphate is then used to quantify the amount of unreacted dichromate.

A round-bottom flask containing 5mL of material was filled with 0.2g of mercuric sulphate and firmly shaken. Cold running water was used to submerge the flask. After adding 5 mL of 0.0625 M potassium dichromate solution, 10 mL of concentrated sulfuric acid, and 1 mL of saturated silver sulphate solution, the mixture was well mixed and allowed to cool in a container of cold water.

A few anti-bumping grains were added, and the flask was attached to a condenser. The remaining dichromate was titrated with 0.0625M ferrous sulphate after one drop of ferrous 1:10 phenanthroline indicator was added. The same process utilized for the sample was likewise followed for the blank determination. The COD content of the water sample was computed using the following formula.

$$\text{COD (mg/L)} = \frac{(A-B)\times M \times 8000}{Volume\ of\ sample\ (mL)}$$

Where,

A = volume (mL) of standard ferrous sulphate used for blank

B = volume (mL) of standard sulphate used for sample M = molarity of standardized ferrous sulphate

Determination of Total Hardness

A conical flask containing 50 milliliters of the sample was set on a tile. Before measuring, a water sample with suspended elements was filtered. Thereafter, 1 mL of ethanolamine buffer solution was added. 1 milliliter of sodium sulfide (0.05%) was added as a masking agent. A two-drop indication (0.005% eriochrome black T) was added. The ensuing solution's color changed to wine-red, indicating the presence of magnesium and calcium ions. This was quickly titrated using a typical 0.01M EDTA solution while being continuously stirred, resulting in a light blue color at the end.

Total Hardness (mg/L) = $\frac{\text{Volume of 0.01 M EDTA} \times 1000}{Volume\ of\ sample\ (mL)}$

Determination of Calcium

A conical flask was filled with 50 mL of the sample. The material was mixed with 2.0 mL of 0.05M HCl and brought to a boil for three minutes. Room temperature was reached for this. Then, for masking, 1 mL of sodium sulfide inhibitor was added. This was combined with 2.0 mL of 0.05M NaOH. After the solution was spread out on a white tile, 3.5 milliliters of glyoxalbix-2-hydroxoanil indicator was added. The mixture was then agitated for a minute and titrated with 0.01 milliliters of EDTA until the solution's color changed from orange-red to lemon-yellow.

Conc. of Calcium (mg/L) = $\frac{\text{Volume of 0.01 M EDTA} \times 1000}{Volume\ of\ sample\ (mL)}$

Determination of Magnesium

The magnesium titre of the sample was determined by subtracting titre value obtained for calcium determination from the titre value for hardness determination.

Conc. of Mg (mg/L) = $\frac{\text{Titre for hardness (mL)} - \text{Titre for Ca} \times 1000}{\text{Volume of sample (mL)}}$

Determination of Sodium and Potassium Using a Flame Photometric Technique

A flame photometer was used to analyze the samples' sodium and potassium spectroscopically[4]. Using a standard stock solution of potassium and sodium with a 30 ppm concentration, the flame photometer was calibrated.

FTIR characterization of the cassava leaves coagulant

The surface chemistry (surface functional groups) of the cassava leaves coagulant sample was revealed by the FTIR spectra, which covered a frequency range of 500 to 4000 cm^{-1}.

Scanning Electron Microscopy SEM Analysis

The form of the product samples was ascertained using scanning electron microscopy (SEM; Hitachi SU 3500 scanning microscope, Tokyo, Japan). Prior to SEM, particles were vacuum-coated with gold.

The surface must be cleaned, the sample must be stabilized, rinsed, dried, dehydrated, mounted, and coated. A tiny coating of gold, about 20 nm in thickness, is applied to the samples. The primary aim of coating the specimen is to enhance its conductivity and facilitate the accumulation of high voltage charges on it.

Energy Dispersive X-ray Spectroscopy (SEM-EDX) The physical morphology of the sample surfaces was observed, and element compositions—including those of visible light elements like carbon, nitrogen, and oxygen—were analyzed.

Determination of Heavy Metals

Nitric acid digestion was used to identify the presence of heavy metals in water samples. After that, the digests were examined using flame atomic absorption spectrophotometry.

RESULTS AND AND DISCUSSIONS

Characterization of brewery wastewater before and after coagulation

The characteristics of the brewery wastewater before and after coagulation process are presented in Table 1.

Table 1: Characteristics of brewery wastewater

Parameters	Pre-coagulation	Post-coagulation
pH	7.14	7.03
Colour (Pt Co scale)	9.69	4.7
Turbidity (NTU)	357	51.22
Elect conductivity (µs/cm)	540.49	30.2
Total solid (TS) (mg/L)	544.09	120.64
Total dissolved solid (TDS) (mg/L)	211.59	44.2
Total suspended solid (TSS) (mg/L)	332.19	76.44
Total hardness (mg/L)	90.63	52.89
Total alkalinity (mg/L)	367	97.51
dissolved oxygen (DO) (mg/L)	4.21	2.52
Biochemical oxygen demand (BOD) (mg/L)	431.03	100.62
Chemical oxygen demand (COD) (mg/L)	674.52	39.79
Lead (mg/L)	0.02	Nill

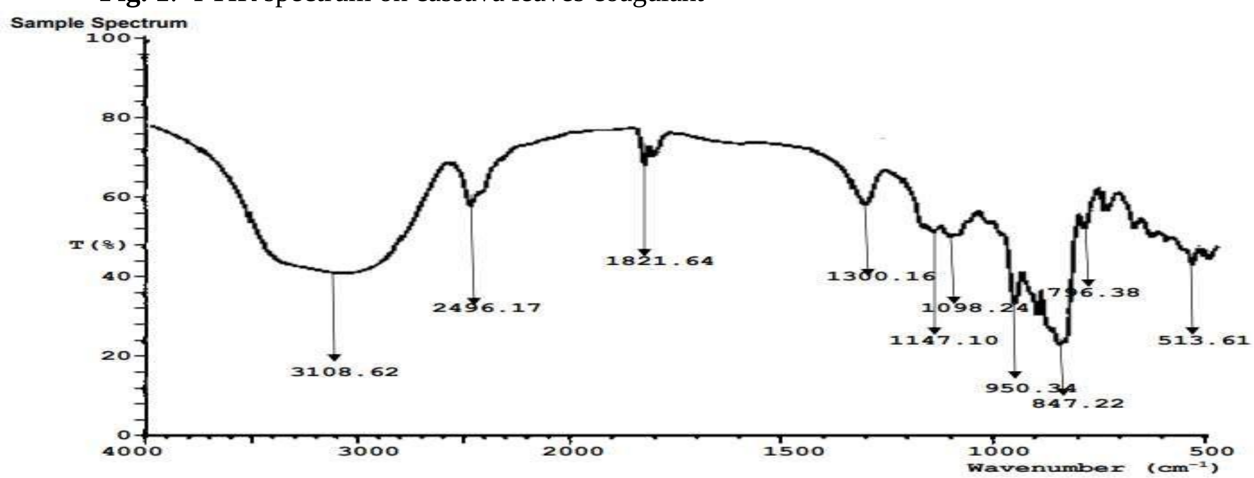
Copper (mg/L)	0.041	0.01
Chromium (mg/L)	0.022	0.01
Manganese (mg/L)	0.053	0.01
Nickel (mg/L)	0.014	Nill
Zinc (mg/L)	0.025	Nill
Iron (mg/L)	2.186	0.1

As demonstrated by the results, the coagulation treatment significantly decreased the pre-treatment values of the pollution parameters, including color, BOD, turbidity, and TSS, among others. This indicated that the treatment method was effective.

FTIR characterization of the cassava leaves coagulant

The FTIR spectra displayed a number of absorption peaks which indicate the presence of different types of functional groups on the sample as shown in Fig. 1.

Fig. 1: FTIR spectrum on cassava leaves coagulant



The standard signature in the FTIR library was compared with the FTIR results[6]. Significant peaks were seen in the sample images; the most common peak was discovered to be at 3108.62 cm-1, which is the O-H stretching of the hydroxyl group. Additionally, 2496.17 cm-1 is ascribed to the carboxylic acid's C=O stretching vibration. Additionally, 1147.10 cm-1 is attributed to the Carbonyl group's –O–C stretching vibration[7]. The coagulant's ability to bind was verified by the existence of these functional groups.

SEM/EDX characterization

SEM/EDX image was used to depict the morphology and texture at x 500 magnification of the cassava leaves coagulant as shown in Fig. 2.

With a bulk density of 1.42 g/cm^3 and a particle size of 35.64 µm, the SEM picture (Fig. 2) was found to display a cluster of particles that are relatively smooth and have dispersed pores. In the meantime, the coagulant's elemental makeup was displayed by the EDX in Figure 2. The coagulant's ability to clot was further elucidated by the EDX, which verified the dominance of iron, phosphorus, and oxygen.

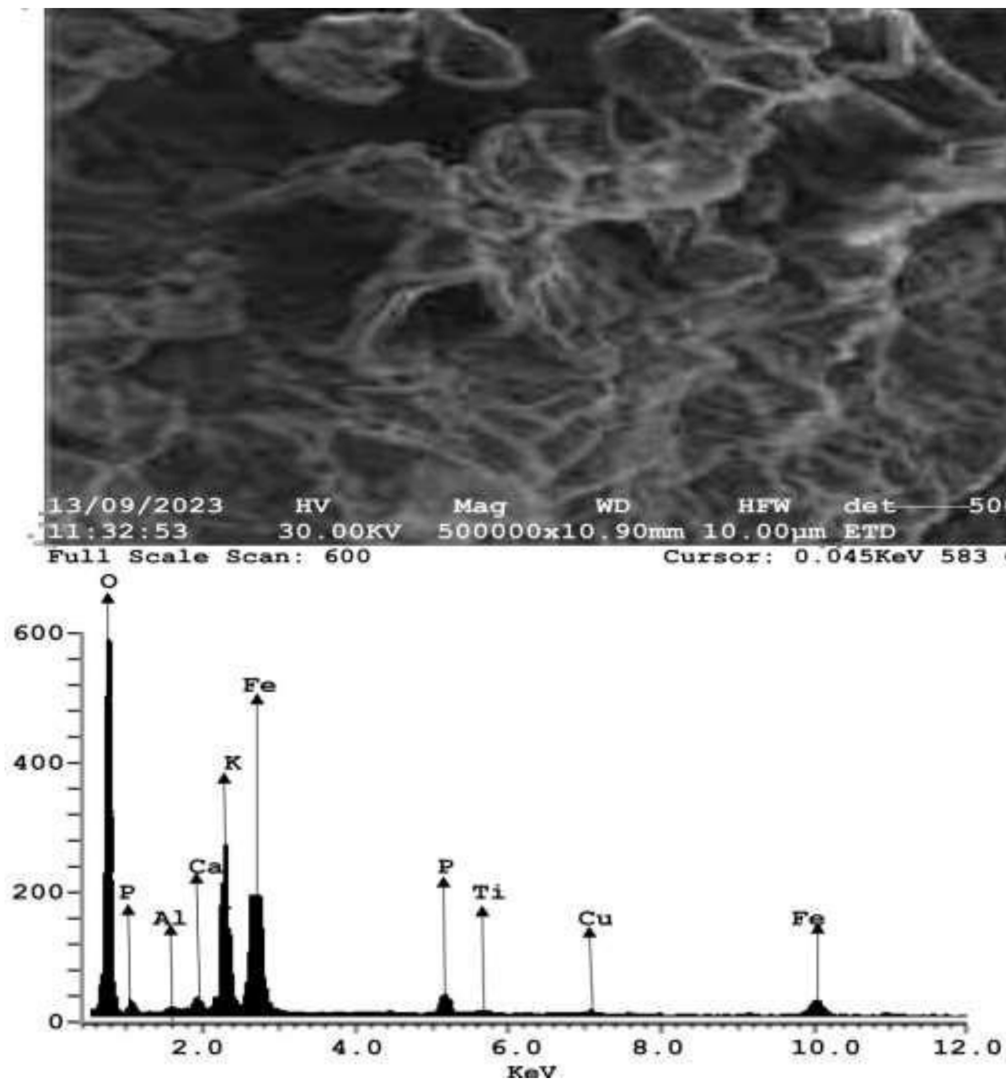


Fig. 2: SEM/EDX image of cassava leaves coagulant at 500× magnification

Effects of the process variables on the reduction Efficiency

Effect of pH on the reduction Efficiency

By varying the pH of the brewery wastewater from 5 to 9 over the course of a 70-minute settling period and using a coagulant dose of 0.3

g/L, as indicated in Fig. 3, the effectiveness of cassava leaves coagulant for color, turbidity, and a decrease of total suspended solids (TSS) in wastewater was examined.

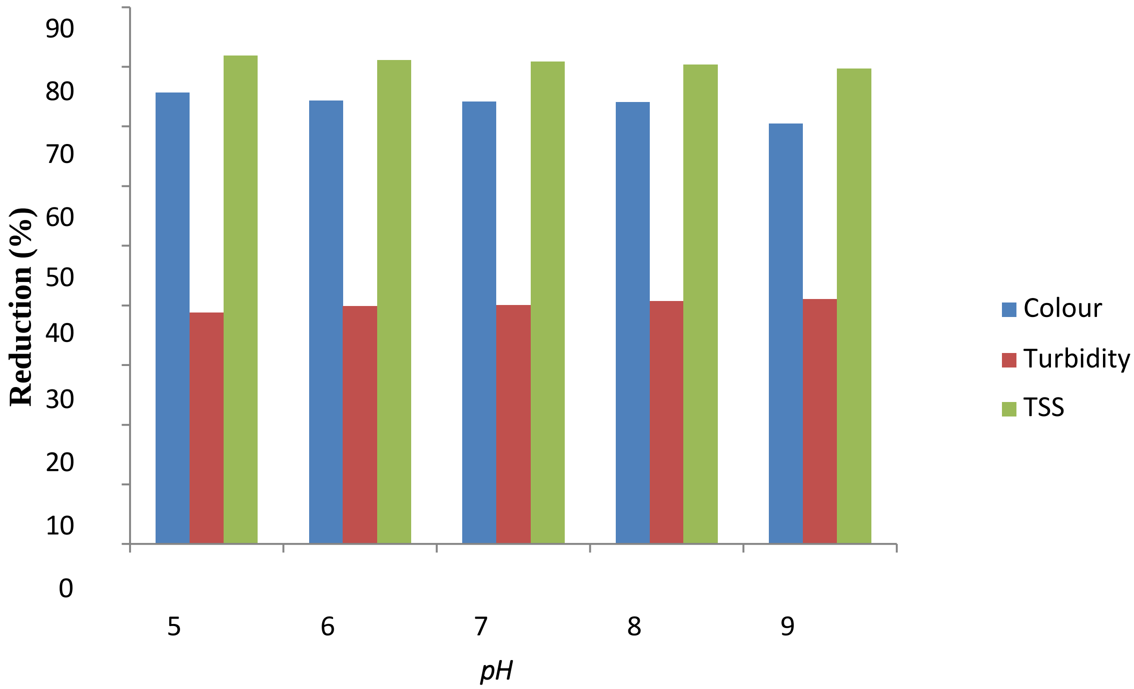


Fig. 3: Effect of pH on the reduction efficiency

With a rise in pH, the color intensity falls by 75.64% to 70.48%. Parallel to this, a rise in pH causes the TSS to drop from 81.89 to 79.67%. But from 38.8 to 41.06 percent, turbidity rises. Thus, due to charges with increased availability of OH-, raising the pH increased the electrostatic repulsion of the particles in the brewery wastewater and the coagulant, which decreased and reduced the stability of the suspended pollutants[7]

Effect of coagulant dosage

The batch experiments were carried out by varying the dosage in concentration (0.2–1.0 mg/L) as shown in Fig. 4.

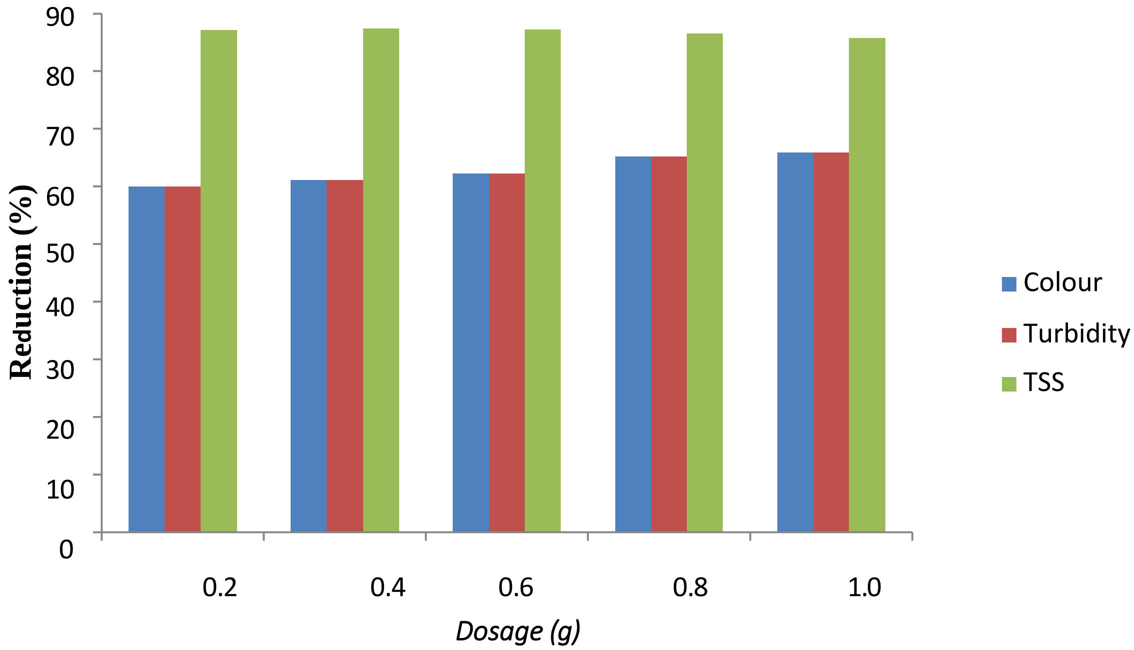


Fig. 4: Effect of dosage on the reduction efficiency

The TSS, turbidity, and color values of the supernatants were measured after they were decanted. The findings of the study on the impact of coagulant dose on the removal of contaminants by the use of cassava leaves are shown in Figure 4. An increase in dose from 0.2–1.0 g was seen to improve the flocculation and instability of colloids. This is consistent with findings from earlier research showing that the efficacy of pollutant removal rises with coagulant dose[8].

Effect of Temperature

The results from the investigation of the effect of brewery wastewater temperature in the range of 3030C to 3430C on the reduction efficiency are presented in Fig. 5. Fig. 5 revealed that the increase in temperature resulted in higher reduction efficiency of turbidity, lower reduction efficiency of colour, and lower reduction efficiency TSS. This is because, at an increased temperature, the molecules of the wastewater solution gain more kinetic energy. This will result in an increase in the rate at which collision between the colloidal particles and the coagulating agent occurs. These will decrease the surface tension and the viscosity of the wastewater; thus, decreasing the settling kinetics of the colloidal particles.

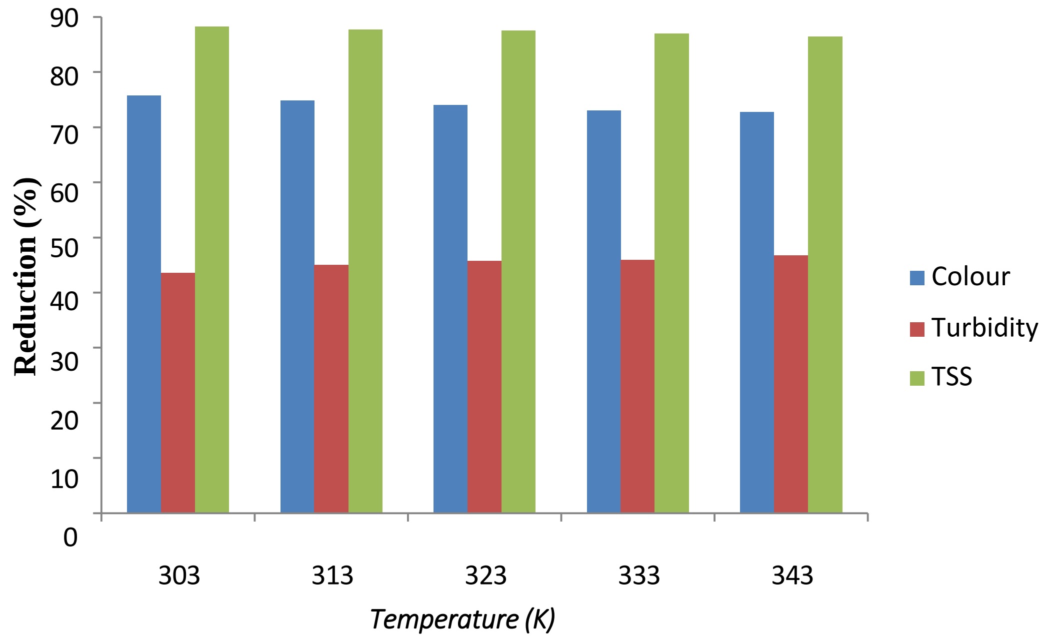


Fig. 5: Effect of temperature on the reduction efficiency

Effect of particle size

Figure 6 shows that the percentage reduction of turbidity increases but the percentage reduction of color and TSS of the wastewater falls as the particle size increases from 0.212 to 2 mm. This is explained by the fact that the coagulant's surface regions that are accessible to flocs have decreased[9].

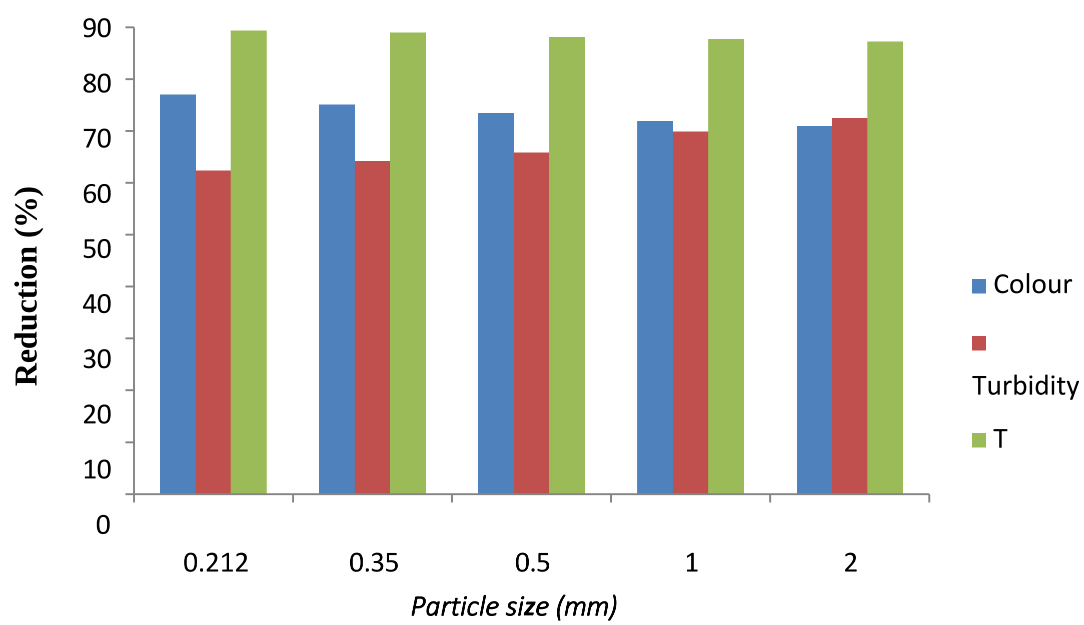


Fig. 6: Effect of particle size on the reduction efficiency

Effect of settling time

Time for the settling of the coagulated flocs, termed _settling time‘, was analyzed at a constant pH, dosage, temperature, particle size, and the results are presented in Fig. 7.

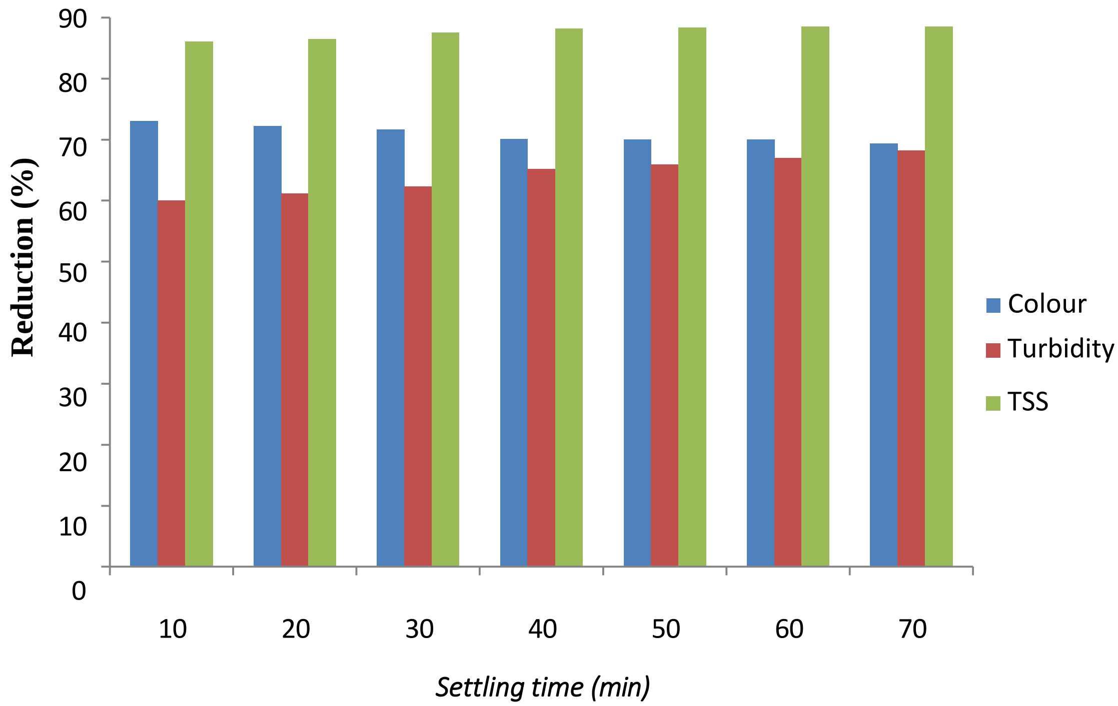


Fig. 7: Effect of settling time on the reduction efficiency

For the coagulant under consideration, turbidity and TSS reduction efficiency were found to rise with settling time, but color reduction efficiency was found to fall. According to Smoluchowski's theory of coagulation[10], longer settling times give settleable particles with slower settling speeds more opportunities for flocculation.

Coagulation-adsorption kinetics studies

Adsorption is known to be more efficient for reducing total suspended solids from effluents, thus the total suspended solid (TSS) was taken into consideration for the investigation of the adsorptive ingredient of the bio coagulation-flocculation process[11,12]. Coagulation events may be theoretically described as processes akin to adsorption[11]. Pseudo-first order coagulation kinetics (PFO) and pseudo-second order coagulation kinetics (PSO), which are depicted in Figs. 8 and 9, respectively, were fitted using experimental data.

$$\frac{1}{Ct} - \frac{1}{CO} = KCt \qquad (1)$$

(When a = 1)

$$\ln ci = kct + \ln Co \qquad (2)$$

(When a = 2) where
Co and C are the
initial turbidity (in
mg/c)

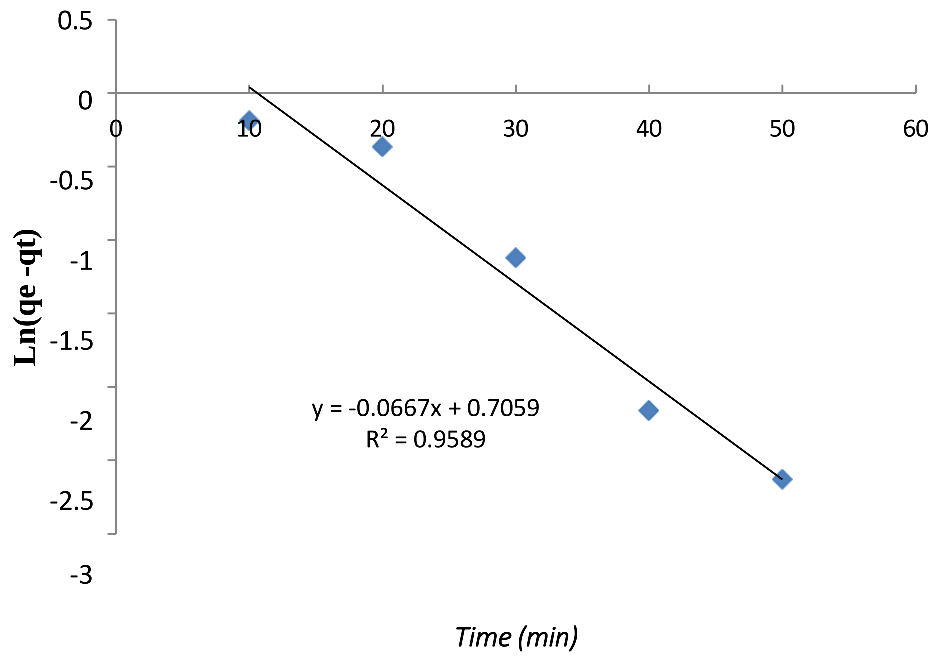


Fig. 8: Pseudo-first order (PFO) coagulation kinetics model fitting

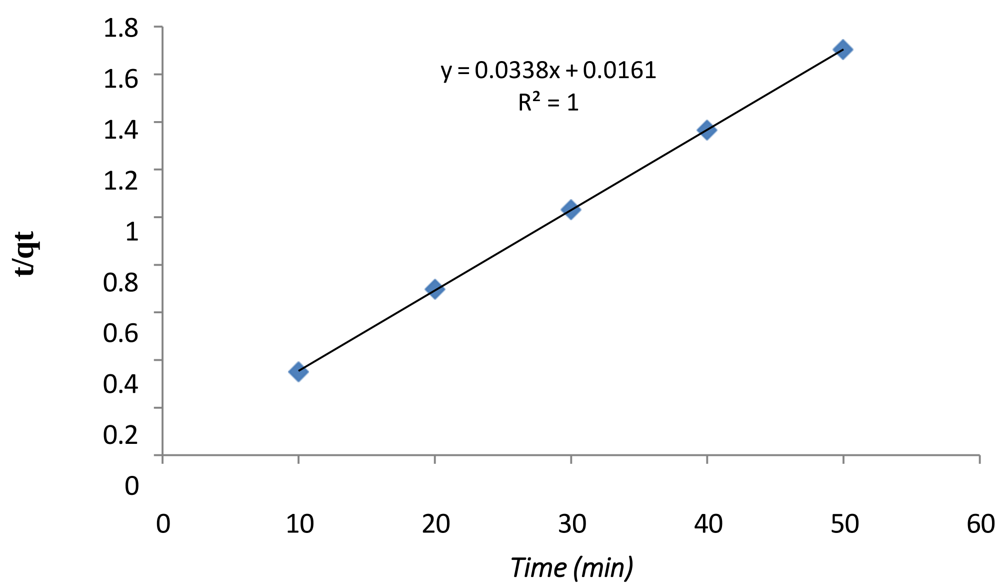


Fig. 9: Pseudo-second order (PSO) coagulation kinetics model fitting

To choose the model that best matches the data, the correlation coefficient, or R^2, was utilized. A model that has a higher R^2 value is the most suitable for the data[13]. In contrast to the first-order kinetic model, the kinetic data followed the second-order kinetic model, as shown by the kinetic parameter (R^2), which was 0.958 and 1 for PFO and PSO, respectively. Based on the linearly regression model equations, the rate constants k_1 and k_2 for PFO and PSO were found to be 0.046 min-1 and 0.115 min^{-1}, respectively.

CONCLUSION

Currently, a number of laboratory-scale research are being carried out on the use of bioflocculants and bio coagolants. Research on the use, however, demonstrates that bio coagulant has a significant advantage over chemical coagulant. Chemical coagulants are extremely harmful to both the environment and the human body. Bio coagulant is biodegradable, which makes it better. With this benefit in mind, there is hope for the future of bio coagulant development as a wastewater treatment procedure.

The coagulation treatment significantly reduced the values of the measured pollution parameters, such as color, BOD, turbidity, TSS, etc., after it was applied, indicating the efficacy of the treatment process. This was based on the results of the analysis. It displays efficacy in eliminating TSS, BOD, and turbidity color. The FTIR study reveals that the carboxylic acid, hydroxyl group, and carbonyl group are the functional groups present. Its bulk density is 1.42 glcms and particle size is 35.64µm for the SEM investigation.

REFERENCES

1. Duan, Jinming John Gregory, (2003) Coagulation by hydrolysing metal salts, Advances in Colloid and Interface Science, Volumes 100–102,Pages 475-502,

2. Ebeling J.M., Sibrell P.L., Ogden S.R., Summerfelt S.T. (2003). Evaluation of chemical coagulation-flocculation aids for the removal of suspended solids and phosphorus from intensive recirculating aquaculture effluent discharge. Aquac. Eng. 23-42

3. Edzwald J.K. (1993). Coagulation in drinking water treatment: Particles, organics and coagulants. Water Sci. Technol. 27 (11): 21–35

4. Moran S. (2018). An Applied Guide to Water and Effluent Treatment Plant Design.

5. Rizkiy Amaliyah Barakwan, Yulinah Trihadiningrum, Arseto Yekti Bagastyo (2019) Characterization of Alum Sludge from Surabaya Water Treatment Plant, Indonesia. J. Ecol. Eng. 20(5):7-13

6. Mohd-Zin N. S. Othman N. (2019) A review of wastewater treatment using natural material and its potential as aid and composite coagulant. Sains Malaysiana 48 (1), 155–164.

7. Mageshkumar, M.; Karthikeyan, R. (2016) Modelling the kinetics of coagulation process for tannery industry effluent treatment using Moringa oleifera seeds protein. Desalination Water Treat. 57, 14954–14964

8. Tetteh, E.K. and Rathilal, S. (2020) Application of Magnetized Nanomaterial for Textile Effluent Remediation Using Response Surface Methodology. Materials Today: Proceedings, 38, 700-711.

9. Igwegbe, C. A., Onukwuli, O. D., Ighalo, J. O., & Menkiti, M. C. (2021). Bio-coagulation- flocculation (BCF) of municipal solid waste leachate using Picralima nitida extract: RSM and ANN modelling. Current Research in Green and Sustainable

Chemistry, 4, 100078. doi:10.1016/j.crgsc.2021.100078

10. Smoluchowski, M. Verscuheiner Mathematischen (1917) Theory der coagulations kinetic kolloiderlousungen, Z. Phys. Chem., 92,129-168.

11. Balarak, D.; Zafariyan, M.; Igwegbe, C.A.; Onyechi, K.K.; Ighalo, J.O. (2021) Adsorption of Acid Blue 92 Dye from Aqueous Solutions by Single-Walled Carbon Nanotubes: Isothermal, Kinetic, and Thermodynamic Studies. Environ. Process.8, 869–888.

12. Phalakornkule, C.; Mangmeemak, J.; Intrachod, K.; Nuntakumjorn, B. (2010) Pretreatment of palm oil mill effluent by electrocoagulation and coagulation. Sci. Asia 36, 142–149

13. Madaki Y.S., Seng L. (2013). Palm Oil Mill Effluent (Pome) from Malaysia Palm Oil Mills: Waste or Resource. Int. J. Sci. Environ. Technol.