Development of Aluminium nanoparticle supported natural coagulant from neem (Azadirachta indica) seed for treatment of detergent effluents

Kedir Geleti Abdi

Thesis Paper is submitted to the Department of Chemical Engineering
School of Mechanical, Chemical, and Material Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Chemical Engineering (Extension program)

Office of Graduate Studies
Adama Science and Technology University

Adama, Ethiopia
June 2023

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DECLARATION

I declare that this master thesis entitled "**Development of Aluminium nanoparticle supported natural coagulant from neem (Azadirachta indica) seed for treatment of detergent effluents "**: is my own original work and has not been presented for a degree in any other university, and that all the sources of material used for the thesis proposal have been duly acknowledged through citation.

Name: Kedir Geleti

Signature: _____

Date: 18/7/2023

RECOMMENDATION OF ADVISOR

I the advisor of this thesis, hereby certify that I have read the revised version of the thesis entitled "**Development of Aluminium nanoparticle supported natural coagulant from neem (Azadirachta indica) seed for treatment of detergent effluents"**: prepared under my guidance by Kedir Geleti and is submitted in partial fulfillment of the requirements for the degree of Masters of Science in Chemical Engineering (Specialization Process Engineering). Therefore, I recommend the submission of a revised version of the thesis to the department following the applicable procedures.

Advisor: Tatek Temesgen (PhD)

Signature:_____

Date: 18/7/2023

ADVISOR APPROVAL SHEET

I hereby certify that the recommendation and suggestion given by the proposal reviewer committee are appropriately incorporated into the final thesis proposal entitled "**Development of Aluminium nanoparticle supported natural coagulant from neem (Azadirachta indica) seed for treatment of detergent effluents"** by Kedir Geleti

Tatek Temesgen (PhD)

Signature: _____

Date: 18/7/2023

APPROVAL OF BOARD REVIEWER

We, the undersigned, members of the Board of Reviewers of the thesis by Kedir Geleti have read and evaluated the thesis entitled **"Development of Aluminium nanoparticle supported natural coagulant from neem (Azadirachta indica) seed for treatment of detergent effluents** " and examined the candidate during the open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Chemical Engineering (Specialization in process engineering).

Chairperson	Signature	Date
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Dr.Wondalem Misganaw External examiner	Signature	Date

Final approval and acceptance of the thesis is contingent upon submission of its final copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

Mr.Hunagnaw Bayle Department Head	Signature	Date
School Dean	Signature	Date
Office of Postgraduate Studies, Dean	Signature	Date

ACKNOWLEDGEMENT

First of all, I would like to praise my almighty ALLAH for the successful completion of my thesis research work.

I would like to express my gratitude to my advisors Dr. Tatek Temesgen for his support, guidance, and valuable criticism. This thesis would not have been accomplished without his outstanding supervision, scientific knowledge, and experience.

I would like to thank, my staff members Mr. Solomon Tsegaye, Miss Alemtsehay and Mr.Tesfaye Girma, as well as Alemu Gizaw (PhD) for their valuable support

With respect, honor, and appreciation I dually acknowledge all lab technicians at Chemical Engineering Laboratory especially Mr. Bundi Roba and my friends.

I wish to extend my warm thanks to my beloved wife Hayat Mohammed for always being there for me when I needed her support.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
COD	Chemical Oxygen Demand
FTIR	Fourier transform infrared spectroscopy
PH	potential of Hydrogen
RSM	Response surface methodology
FPR	Foaming power removal
DSL	Dynamic scattering light
TLC	Thin layer chromatography

Executive summary

Detergent waste water is one of the most difficult environmental issues because it contains high dissolved solids, high suspended solids, chemical oxygen demand (COD), turbidity, and toxic chemicals. The direct discharge of this wastewater without proper treatment into the water bodies (i.e. lakes, rivers, etc.) pollutes the water system directly or indirectly. This indicates the need to develop efficient treatment methods which are environmentally viable. This research focuses on, solving the problem by using coagulation-flocculation methods to remove foam using coagulant formulated from neem (Azadirachta indica) seed and functionalized with aluminium nano particle. Neem seed extraction using Soxhelet extraction was done with operation parameters of (i.e. particle size (350μm), Extraction temperature (45^{o}C), solvent to solid ratio (6:1v/w) and extraction time (4hr) and then characterized using TLC and FTIR. Aluminum nanoparticles were synthesized from aluminum nitrate and the extract and then characterized by FTIR, UV-vis spectrophotometry and DLS.Experimental study on coagulation- flocculation was performed as batch process in conventional jar-test apparatus equipped with six spindle steel paddles in a beaker of 400 mL volume each. Coagulation-flocculation was performed using extract of neem (Azadirachta indica) seed, ferric chloride and Neem extract meditate aluminum nano particle. The treatment process was carried out at different settling time (1.30-12.30hr), coagulant dose (1-4.5g/l) and initial detergent concentration (1g/l) for all three coagulant used. The foaming power removal efficiency of the three coagulants was tested. Response surface method of Box-Behnken was used for experimental data analysis to optimize the parameters. The extraction result of neem was 11.1gram from 100g of grounded seed. The TLC and FTIR result was conforms the presence of Azadirachta indica in the seed. Characterization of aluminum meditate nano particle result was show there was formation of nano particle. Coagulation-flocculation result shows as coagulant dose increases foaming power removal also increases for all coagulant up to 3.5 g for Neem extract, 3.2g for ferric chloride and 3g for aluminum meditate nano particle and then there was no significant change. As settling time increase the foam removal efficiency was increased for all coagulant used. The foaming power removal efficiency of Neem extract was low with the comparison of ferric chloride. From the result of Coagulation-flocculation aluminum meditate nano particle was the best coagulant to remove foam. Experimental data analysis results indicate the optimum foam removal efficiency of Neem was (77.65% % at time= 10.77 hr, initial concentration =1.372 g/l and coagulant dose 2.87 g/l. the optimum removal efficiency of aluminium nano particle was obtained 98.5 % % at time= 12.3 hr, initial concentration =1.46 g/l, and coagulant dose 4.42 g/l. The interaction effect of those parameters had a significant effect on the removal process. Aluminum meditate nanoparticle increase the treatment process

Keywords: *Neem seed, aluminum meditate nano particle, RMS, FTIR, DSL, Uv and treatment*

1. Introduction

1.1. Background

Natural soap was one of the earliest chemicals produced by human beings. Historically, its first use as a cleaning compound dates back to Ancient Egypt. Currently, the detergent industry produces comparatively small volumes of liquid wastes directly. Conversely, it causes pronounced public concern when its products are discharged after use in homes, service establishments, and factories (PatinSA, 1985).

The main danger of detergent contamination lays in their effect on water ecosystems as a whole. In the first case, surfactants may adversely affect microalgae at the lowest trophic level and impact on their function as major suppliers of oxygen to water bodies (PatinSA, 1985).
Detergents affect receiving aquatic environments by causing foaming, limiting oxygen production, causing eutrophication and presenting a hazard to waters used for potable supply (Sanderson H et al. 2006). Surface foams may block aeration of water bodies and their decomposition may increase biochemical oxygen demand and in that way use up dissolved oxygen levels (Karapars R ,1976).Furthermore, detergent concentrations greater than 0.1 g m/l are toxic to some marine organisms.

Consequently, the combined effects of excessive concentrations of detergents in natural waters may be reduced oxygen concentrations, a change in water colour, increased turbidity, sedimentation, and a decrease in biological activity (Egemen Ö, 2000).

1.2 Statement of the problem

Among the different contaminants, detergent as an important pollutant has serious risks to natural ecosystems. Furthermore, detergents can pass into the wastewater treatment plants and have bad effect on their performance. They are part of human life and consumed for different aims especially hygienic purposes. Therefore, detergent components can enter to soil and water bodies from different sources. Detergents affect fauna and flora, and they have direct and indirect effects on ecosystems. Eutrophication, foaming, and altering parameters such as temperature, salinity, turbidity, and pH are more important, and their effects need to be managed and controlled. Eutrophication is the process by which a body of water acquires a high concentration of nutrients, such as phosphates. These typically promote excessive growth of algae. As the algae die and de-compose, high levels of organic matter and the decomposing organisms deplete the water of available oxygen, causing the death of other organisms, such as fish as shown in figure 1.1.

Fig 1.1 Water pollution in lowa (my site japanhs.weehly.com)

This research focuses on characterizing and treating detergent wastewater by development of Al nanoparticle supported natural coagulant prepared from neem (Azadirachta indica) seed to minimize environmental pollution caused by detergent wastewater.

1.3. Objectives

1.3.1 General objective

The main objective of this research is development of Aluminium nanoparticle supported natural coagulant from neem (Azadirachta indica) seed for treatment of detergent effluents to reduce foaming power.

1.3.2 Specific objectives

- Develop and characterize coagulant based on natural product, neem (*Azadirachta indica*) seed extract.
- Modify the neem extracted coagulant with Aluminum nanoparticle to enhance efficiency.
- Compare the removal efficiency of the developed neem extract based coagulants, aluminum meditate nano particle with conventional coagulant, ferric chloride.
- Optimize and investigate the effect of initial foaming power, settling time and dose of the coagulant on the removal efficiency.

1.4. Research question

This proposal will make an attempt to address the following questions:-

1. Does Neem extract reduce foaming power of detergent wastewater by coagulation-flocculation process?
2. Can the extract based coagulant have a feasible potential for detergent containing waste water treatment over conventional (ferric chloride)?
3. Can Neem extract coagulant be modified by aluminium nitrate to form aluminium meditate nanoparticle?
4. Can aluminum meditate nanoparticle improve the efficiency of foaming power removal of detergent waste water?

1.5. Research hypothesis

Treating detergent wastewater with natural coagulant which will be extracted from neem seed (*Azadirachta indica*) will result in reduction of waste load.

2. Literature review

2.1 Classification of Surfactants

Soaps and detergents are articulated products designed to meet different cost and performance Standards (Lawrence K et al. 2013). The formulated products contain many components, such as surfactants to tie up unwanted materials (commercial detergents usually contain only 10–30% surfactants), builders or polyphosphate salts to increase surfactant processes and remove calcium and magnesium ions, and bleaches to increase reflectance of visible light (Lawrence K et al. 20135). They also contain various additives designed to remove stains (enzymes), prevent soil re-deposition, regulate foam, reduce washing machine corrosion, brighten colors, give an agreeable odor, prevent caking, and help processing of the formulated detergent (Greek B.F,1990).

The classification of surfactants in common usage depends on their electrolytic dissociation, which allows the determination of the nature of the hydrophilic polar group, for instance, anionic, cationic, non-ionic, and amphoteric (Chiang et al.1983).

2.1.1 Anionic Surfactants

Anionic surfactants produce a negatively charged surfactant ion in aqueous solution, usually derived from a sulfate, carboxylate, or sulfonate grouping (Chiang et al. 1983). The usual types of these compounds are carboxylic acids and derivatives (largely based on natural oils), sulfonic acid derivatives (alkyl benzene sulfonate LAS and other sulfonate), and sulfuric acid esters and salts (largely sulfated alcohols and ethers)(Chiang et al.1983). Alkyl sulfates are readily biodegradable, often disappearing within 24 hours in river water or sewage plants. Because of their instability in acidic conditions, they were to a considerable extent replaced by ABS and LAS, which have been the most widely used of the surfactants because of their excellent cleaning properties, chemical stability, and low cost. Their biodegradation has been the subject of numerous investigations (Swisher R.D, 1970).

2.1.2 Non-ionic Surfactants

Non-ionic surfactants are mainly carboxylic acid amides and esters and their derivatives, and ethers (alkoxylated alcohols), and they have been gradually replacing LAS in detergent formulations (especially as an increasingly popular active ingredient of automatic washing

machine formulations) since the 1960s. Therefore, their removal in wastewater treatment is of great significance, but although it is known that they readily biodegrade, many facts about their metabolism are unclear (Osburn O.W, 1966).

In non-ionic surfactants, both the hydrophilic and hydrophobic groups are organic, so the cumulative effect of the multiple weak organic hydrophils is the cause of their surface-active qualities. These products are effective in hard water and are very low foamers (Lawrence K.et al.20135).

2.1.3 Amphoteric

As previously mentioned, amphoteric surfactants presently represent a minor fraction of the total surfactants production with only specialty uses (Payne, 1963). They are compounds with both anionic and cationic properties in aqueous solutions, depending on the pH of the system in which they work (Payne, 1963).

The main types of these compounds are essentially analogs of linear alkane sulfonate, which provide numerous points for the initiation of biodegradation, and pyridinium compounds that also have a positively charged N-atom (but in the ring) and they are very resistant to biodegradation(Wright,1972).

2.2. Sources of Detergents Wastewaters

The concentrations of detergent that actually find their way into wastewaters and surface water bodies have quite diverse origins:-

- Soaps and detergents factory

The additional industrial origin of detergent pollution particularly results from the use of surfactants in different industries, such as textiles, cosmetics, leather tanning and products, paper, metals, dyes and paints, production of domestic soaps and detergents, and from the use of detergents in commercial/industrial laundries and dry cleaners (Lawrence K. et al. 20135).

The contribution from agricultural activities is due to the surface runoff transporting of surfactants that are included in the formulation of insecticides and fungicides (Prat, 1964).

Surfactants hold their foaming properties in natural waters in concentrations as low as 1 mg/L, and though such concentrations are nontoxic to humans (Swisher R.D, 1970), the presence of surfactants in drinking water is esthetically detrimental. Extra important, conversely, is the generation of large volumes of foam in activated sludge plants and below weirs and dams on rivers.

2.2.2 Impacts in Rivers

The major factors that influence the formation and stability of foams in rivers are the presence of LABS-type detergents, the concentration of more or less degraded proteins and colloidal particles, the presence and concentration of mineral salts, the temperature and pH of the water (Swisher R.D, 1970).

The formation of foam also creates anxiety and uncertainties for river navigation. For example, in the areas of dams and river locks, the turbulence caused by the intensive traffic of barges and by the incessant opening and closing of the lock gates results in foam formation that may cover entire boats and leave a sticky deposit on the decks of barges and piers(Osburn O.W, 1966). This renders them extremely slippery and may be the cause of injuries. Finally, crowds of foam floating on river waters represent an esthetically intolerable nuisance and a problem for the tourism industry (Prat, 1964).

2.2.3 Toxicity of Detergents

There is an upper boundary of surfactant concentration in natural waters above which the existence of aquatic life, particularly higher animal life, is endangered. Trout are particularly sensitive to concentrations as low as 1 ppm and show symptoms similar to asphyxia (Callely 1976). In another way, numerous studies, which extended over a period of months and required test animals to drink significantly high doses of surfactants, showed absolutely no apparent ill effects due to digested detergents. Also, there are no instances in which the trace amounts of detergents present in drinking water were directly connected to adverse effects on human health (Callely 1976).

River pollution from anionic surfactants, the primarily toxic ones, is of two types: (a) acute toxic pollution due to, for example, an accidental spill from a container of full-strength surfactant products, and (b) chronic pollution due to the daily discharges of municipal and industrial wastewaters. The international literature contains the result of numerous studies that have

established dosages for both types of pollution toxicity due to detergents, for most types of aquatic life such as species of fish (Dhouib et al. 2003).

2.3. Manufacture and Formulation

Detergent industry produces liquid and solid cleaning agents for domestic and industrial use, including laundry, dishwashing, bar soaps, specialty cleaners, and industrial cleaning products (Dhouib et al. 2003).

Numerous processing steps exist between basic raw materials for surfactants and other components that are used to improve performance and desirability, and the finished marketable products of the soap and detergent industry. Inorganic and organic compounds such as ethylene, propylene, ether, LABS, ammonia, dolomite, soda ash, caustic soda, peroxides, and silicates are among the various basic raw materials being used by detergent industry (Babu R et al. 2005).

2.3.1 Liquid Detergents

Detergent actives are pumped into mixing tanks where they are mixed with several ingredients, ranging from perfumes to dyes. Then, the fully formulated liquid detergent is run down to the filling line for filling, capping, labeling, and so on. Whenever the filling line is to change to a different product, the filling system must be thoroughly cleaned out to avoid cross contamination.

2.3.2 Detergent wastewater Characteristics

The wastewater streams are usually expected to contain trace or larger concentrations of all raw materials used in the plant, all intermediate compounds produced during manufacture, all final products, co products, and byproducts, and the auxiliary or processing chemicals employed.

2.4 Waste water treatment methods

Waste waters have been treated with different techniques with the aims of decreasing the generation of these waste waters and also to improve the quality of the treated effluent.

It has been reported that foam separation has been able to remove 70–80% of synthetic detergents, at a wide range of costs. Gibbs reported the successful use of fine bubble flotation and 40 mm

detention in treating soap manufacture wastes, where the skimmed sludge was periodically returned to the soap factory for reprocessing.

According to Wang, the dissolved air flotation process is both technically and economically feasible for the removal of detergents and soaps (i.e. surfactants) from water (Lawrence K. et al, 2013).

From literature review, Treatment of surfactant wastewaters by biological processes such as activated sludge is problematic due to the low kinetics of degradation and foam production (Lawrence K. et al. 2013).

Hence, among the currently employed chemical unit processes in wastewater treatment, coagulation/flocculation has received considerable attention because of high impurity removal efficiency. Coagulation/ flocculation with iron, alum or solid phase (bentonite) is best removal of with the addition of chemical 90% up to 95% of free oils but not environmentally friendly.so natural coagulant which is environmentally friendly is expected to be developed(Chiang et al.1983).

Table 2.1 Waste water treatment method (Lawrence K. et al. 2013, Chiang et al. 1983).

Pollutant and Methods	**Results (efficiency),% of removal**	**Referen**
Oil and grease ✓ API-type separation ✓ Carbon adsorption ✓ Flotation ✓ Mixed media filtration ✓ Coagulation/sedimentation with iron, alum or solid phase(bentonite)	✓ Up to 90% of free oil and ✓ Grease, variable on emulsified oil. ✓ Up to 95% of both free and emulsified ✓ Without the addition of solid phase, alum, iron 70-80% of both free and emulsified oil. With the addition of chemical 90%. ✓ Up to 95% of free oils. Emulsified unknown. ✓ Up to 95% of free oils. Up to 90% of emulsified oils.	(Lawrence K. et al. 2013, Chiang et al.1983)
Suspended solid ✓ Mixed media filtration ✓ Coagulation/sedimentation BOD and COD ✓ Bio conversion (with final clarifier) ✓ Carbon adsorption Residual suspended solid ✓ Sand or mixed media Dissolved solids ✓ Ion exchange or reverse osmosis	✓ 70-80% ✓ 50-80% ✓ 60-95% or more ✓ Up to 90%. ✓ 50-95% ✓ Up to 90%	(Chiang and et.al ,1983)

2.4.1. Coagulation/flocculation process

Coagulation-flocculation is the process by which solids are physically separated from liquid phases through mixing, flocculation, and the application of chemical reagents to destabilize and enlarge the particle size. Sedimentation, flotation, or filtration are frequently used to accomplish this separation. By lowering the repellent potential of the electrical double layer, the process of coagulation causes the instability of particles (Divakaran et al. 2001). As a result, particles in suspension aggregate. The process of flocculation, on the other hand, involves bringing destabilized particles together to create aggregates called flocks that are large enough and heavy enough to sediment. This results in the separation of the created flocks and the water (Divakaran et al. 2001).

Particle sedimentation in water can happen naturally, for example when there are huge particles present. However, some particles won't settle due to their chemical interaction with water, as is the case when hydrophilic chemicals are present in the water (Divakaran et al. 2001).

In order to diminish the influence of the repellent force electrical potential in the solution and achieve coagulation of the particles, which in turn aggregate and settle, mechanical agitation can also be employed to enhance the velocity of big particles of a colloidal solution. But if particles are too tiny to coagulate readily (Taulis M., 2005).

Different substances like suspended, colloidal, and dissolved solids are present in industrial effluent. Colloidal solids between 10-9 mm and 10-6 mm in diameter, suspended solids bigger than 10-6 mm, and dissolved solids less than 10-9 mm. This substance needs to be eliminated before discharge (Metcalf E., 2003).

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One of the most common unit procedures in the treatment of water and wastewater is coagulation. This physicochemical procedure makes it easier to separate suspended and colloidal materials from

wastewater. Destabilized particles aggregate as micro floc, then grows into large floccules that can be settled and are referred to as floc (Freitas et al. 2018).

The coagulation-flocculation process typically involves destabilizing colloids, aggregating, and binding them together into flocculates. The resulting flocs can then be removed by settling or flotation. The essential procedures in wastewater treatment systems are coagulation, flocculation, and clarifying, followed by filtration (Freitas et al. 2018).

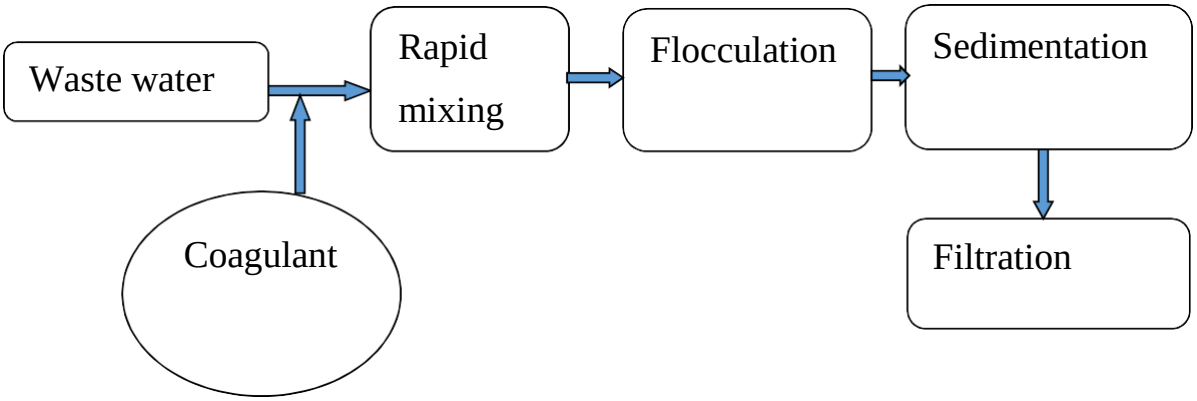

Fig 2.1 Steps of the coagulation process (Freitas et al. 2018).

A coagulant is dosed into the water during the coagulation process, which causes the water to become unstable. It happens in a series of stages designed to counteract the forces that keep the suspended particles stable, enabling particle collision and floc development. Destabilizing the particle charges in the water is the initial step in the coagulation process. To balance the negative charge on the dispersed non-settable solids, a coagulant of opposing charges was introduced. The smaller particles are capable of adhering to produce somewhat larger particles once the charge has been neutralized (Metcalf E., 2003). After the coagulant dose, mixing speed is a design parameter. Rapid mixing ensures that the coagulant is evenly distributed throughout the water and encourages particle collision, both of which are necessary for effective coagulation. By increasing particle impacts, slower mixing encouraged floc development and produced larger flocs (Metcalf E., 2003).

Different destabilization strategies can be used depending on the type of colloidal suspension that needs to go through coagulation, including repression of the double layer, neutralization of colloid charge by adsorption of counter ions on the colloid surface, bridging of colloidal particles via polymer addition, and entrapment of colloidal particles by sweeping floc. When specific chemicals

are added to raw water, the particles become less stable, which allows for floc development and agglomeration. In general, these terminologies are used for this purpose (Freitas et al. 2018):

- Coagulants, which assist the destabilization of particles (particularly colloidal sizes).
- Flocculants (also known as flocculent aids or coagulant aids), assist in the joining and enmeshing of the particles together.

Coagulation and flocculation are treatment techniques that can be used in soap wastewater treatment to minimize color effluent as well as the overall load of contaminants. These techniques' primary benefit is that they offer treatment options that are affordable, easy to use, and energy-efficient (Zhang X et al. 2003). This technique has the inherent drawback of producing significant amounts of chemical sludge, which is classified as hazardous waste and calls for the disposal of hazardous solid waste in protected landfills (Zhang X et al. 2003). For environmental applications, substitute natural materials have been taken into consideration.

In keeping with the general tendency, the term "coagulation" was employed in this study to refer to the entire process, from introducing the coagulant to the wastewater up until their settlement.

Table 2.2 Difference between Coagulation and Flocculation in Water Treatment

Coagulation	**Flocculation**
Coagulation is an important step in water treatment and it involves the addition of a coagulant to enhance the clotting of suspended particles in water.	Flocculation is another important step in water treatment and it involves the formation of visible flocculation by mechanical or physical mixing.
Coagulation is a chemical process.	Flocculation is a physical process.
Coagulation such as inorganic salts of aluminum or iron that neutralizes the suspended particles is added during coagulation.	Flocculants such as an organic polymer that involves bridging and strengthening the flocks are added. It also increases the weight of the flocks and increases the rate of settling.
Coagulation does not involve a physical mixing process	Flocculation involves physical mixing

2.4.2 Types of coagulant

Inorganic and organic coagulants are the two main types that are employed. Among the inorganic coagulants are calcium chloride, ferric chloride, and aluminum sulfate (Zhang, X and et.al, 2003). Inorganic coagulants including poly-aluminum chloride, ferric chloride, and alum (aluminum sulfate) are widely used in wastewater treatment due to their effectiveness and simplicity of use (Zhang X et al. 2003).

The United States, the second-largest country in the world after China, is said to have employed metal coagulants since the 18th century. While China had been employing alum as an efficient coagulant for water clarity during their reign and had since become one of the first pioneers. These synthetic coagulants have been employed in the drinking water sector in addition to wastewater treatment. The most popular conventional metal coagulants, such as Fe (III) and Al (III), offer greater benefits but are nevertheless limited by several limitations, most notably a lack of green chemistry. The widespread and familiar use of this chemical-based technology is preferable, but there are a few lists of drawbacks that should not be overlooked in earlier literature (Zhang X et.al. 2003). When a treatment method is related to neurological disorders like Alzheimer's, particularly when aluminum residue permeates the body and builds up in the brain, there is a small negative perception of the procedure's sustainability. Other risks to human health and the health of other living things have also been identified, most notably energy loss, intestinal constipation, convulsions, and stomach colic (Rasool et al. 2016).

These inorganic salts and synthetic metals also have a somber past related to their physical characteristics. The price will be obviously greater when it enters the commercial market, influencing the social factor in rural communities, even though the cost of raw materials to make the items is said to be relatively efficient (Rasool et al. 2016). There is controversy around the post-treatment following coagulation because it produced a significant amount of toxic sludge that made disposal difficult (Rasool et al. 2016), Teixeira 2019) has been a topic of discussion. Usually, unreacted chemical residues and the interaction of polymer leftovers in treated water are what because the toxic sludge. (Hesami, 2014; Subramonian W et al. 2014). Since larger flocks are generated by smaller ones approaching one another during the coagulation process, the resulting sludge cannot be avoided (Douillard et al. 2013). Since coagulation is only intended to be used as

a pre- and primary treatment, the produced sludge needs to go through another stage of the treatment process. Furthermore, as effective coagulation only functions under specific pH and environmental conditions, the pH of the effluent must also be changed before it can be processed. Low temperatures make it difficult for them to work effectively (Teixeira 20197). More advances in natural polymers and organic coagulants have been made in recent years as a result of a review of the shortcomings of these hydrolysable cations. It is constantly advised to look for environmentally friendly and sustainable treatment methods because they assist so many people. While preventing the chemical and physical aftereffects in the treated medium, the decrease or substitution of these controversial coagulating substances will increase the value of the sources of origin (Essig Jr, 2013).

Sustainable water management has received a lot of focus, but it can be difficult to create effective procedures, particularly in the wastewater business. Current research always looks forward to natural materials again for effective approaches to wastewater treatment, starting from natural ingredients to the laboratory-produced synthetic chemical-based. Natural coagulants, particularly those derived from biological sources, are widely recognized as being free of toxins (Awang, N. A and et.al, 2012). The use of natural coagulants or coagulant aids derived from plants, animals, or agricultural wastes, such as Moringa oleifera (MO) seeds, chitosan, and cassava peel, has been the subject of numerous investigations (Choy, L. T. ,2014; Mohd-Asharuddin 2017). These organic coagulants, such (MO) seeds and chitosan have been the most popular types of bio-based coagulants over the years (Zehir A et al.2017) Since they can be produced from renewable resources and are practical, especially in remote places, the trending application of these coagulants is generally speaking in favor of environmentally beneficial technology (Hossain M. A et al. 2010). Before the invention of chemical salts to clarify wastewater, natural coagulants with biodegradable properties that are believed to be harmless for ecological systems and living things already existed.

Initially, it was discovered that the primary cause of less effective coagulation was the decreased molecular weight of natural polymers. As a result, it is typically used as a coagulant aid rather than as a first choice. When used as a coagulant aid, natural polymer facilitates the creation of the chemical bridge with the suspended solids during the coagulation process (Zehir A et al.2017). The growing amounts of organic matter from coagulants, which may lead to steric problems

between polymer molecules at high concentrations, are the only cause of the performance drawbacks documented. Additionally, this promotes further study into the use of natural materials as alternatives to synthetic coagulants. The growing interest in using natural materials has prompted in-depth research into the features and behavior of these materials during the coagulation process, including the widely used MO seed coagulant. According to the Food and Agricultural Organization of the United Nations (FAO), it comes from a tropical tree with many health benefits that are widely distributed, especially in the sub-Himalayan valleys, Asia, Africa, and Latin America. According to earlier research, the seed can be utilized to produce coagulants as well as edible oils that are used in health and beauty products due to their nutrient content. The remaining residual rind can be used as fertilizer, animal feed, and activated carbon (Ghebremichael, K. A., 2005).

Additionally, it is claimed to produce less sludge by volume and have similar effects to alum in the coagulation of highly turbid water. It has been discovered that the MO seed extract includes the cationic protein of polymerization, which aids in the low-cost techniques for clarity and is frequently utilized in rural communities to clear hazy water. Another example is chitosan, a natural polyelectrolyte that has attracted significant interest due to its high molecular weight, charged density, and origin as a biodegradable polymer. Arthropods, insects, crustaceans, fungus, and other marine organisms all include chitosan, which is produced when chitin is DE acetylated Chitosan is chosen when employed as a coagulant because, upon contact with an acidic solution, it emits positively charged particles that interact with the anionic suspended colloidal (Mohd-Asharuddin 2017). Due to the presence of amine functional groups in nature, chitosan has a positive charge along its chain (Mohd-Salleh, 2019). Coagulants' natural components may also be obtained from organic waste, such as agricultural waste. Agricultural wastes are among the waste types that contribute the most to landfill volume because of their lack of economic value and barriers to commercialization. For instance, cassava peel is a readily available waste-derived coagulant. Since only its cassava starch is used for further commercialization, the usage of cassava peel raises serious concerns because the industries involved in cassava processing produce a tremendous amount of waste (Howeler R. H.et al. 2001). A cassava starch processing machine produces 100 tons of fresh by-products every day, or roughly 47 tons, which, if improperly disposed of, could have a significant influence on the environment (Howeler R. H. et al. 2001).

Cassava peels contain a significant amount of cyanogenic glycosides, in addition to having the potential to release carbon dioxide and a potent odor of rotting trash. Cassava peel has the potential to be chosen as a waste-based coagulant because of its capacity to remove nutrients and heavy metals. This potential is supported by the presence of Si, Ca, Mg, and Fe, as well as by the abundance of functional groups and surface porosity of the media. Considering its bio-polymers, which are made up of proteins and polysaccharides, this natural-polymer coagulant appears to be a viable option for water coagulants (Mohd-Asharuddin 2017; Othman, N.et al. 2016).

2.4.3 Factors Affecting the Effectiveness of Coagulation

The kind of wastewater, the initial concentration of the waste, the amount and type of coagulants/flocculants used, the temperature, the physical and chemical properties of the coagulant, the pH of the solution, the rate of mixing, and other parameters all affect how well the coagulation works (Rozainee M,2008).

One of the most crucial factors taken into account while figuring out the ideal circumstances for the coagulation-flocculation process performance is the coagulant dose. Essentially, a dosage that is either low or too high will lead to subpar performance. There are a number of optimum doses for coagulants at which maximum settling and the most efficient elimination of contaminants are accomplished. Below this point, the amount of coagulant injected is insufficient to cause the particles to become unstable. The coagulant effectively acts as a chemical coating that re-stabilizes the particle above this threshold (Patel H., 2013).

Therefore, it is crucial to establish the ideal dose in order to reduce dosing costs and sludge formation as well as to achieve the best results possible during the treatment process. This research focused on the dose because the spectrum of coagulant doses differs depending on the type of coagulant. The pH is a second crucial factor that has been taken into account while determining the ideal setting for the administration of medication (Singh R et al. 1970).

The degree of stabilization of the suspension will also be impacted by the pH of the coagulation process, in addition to the surface charge of the coagulants. Additionally, pH appears to be a fascinating factor that has a higher impact on the effectiveness of removing contaminants. In order to reduce the production of sludge and get the best treatment results, one of the elements essential to determine the ideal level was pH influence. Thus, to provide the ideal environment for the

coagulation process, pH must be regulated by adding either strong acid or basic. In the coagulation-flocculation process, mixing time has a significant impact on flocs' creation and proliferation in addition to coagulant dose and ph. (Sabur M.et al. 2012).

In any water and wastewater treatment facility that uses coagulation, one of the operating factors that are given careful consideration is the time of macro floc development (flocculation time). Therefore, it's crucial to establish the treatment system's ideal mixing time. In a coagulation process, there are normally three phases of mixing: quick mix, gradual mix, and no mix. A brief period of extremely turbulent mixing known as the quick mixing phase permits coagulants to come into contact with suspended particles (Sabur M. et al. 2012).

The following stage is flocculation time, which is characterized by sluggish mixing and enables destabilized particles to coalesce into bigger particles (Majure L. C et al. 2012). This period of mixing is crucial for the production of flocs. Due to flocs' extreme fragility, abrupt motions cause floc breakup, which reduces their effectiveness. The last phase doesn't involve any mixing. It enables flocculated particles to leave the system by settling. Poor particle agglomeration results from insufficient slow mixing times. However, prolonged durations of agitation form floc fragments to rupture and cause the de agglomeration of particles. The effectiveness and efficiency of coagulation are generally greatly increased by optimizing the coagulant dose, mixing duration, and ph (Sabur M. et al. 2012).

2.4.4 Plant-based coagulants

The Plant based coagulants are broadly utilized for the purification of contaminated water that is in less urbanized, because they seems to be less carrying cost treated coagulates as compared to artificial. PBC coagulants are assumed to treat water showing low-to-medium turbidity range (50–500) NTU) (R.Rajendran et al. 2015).It is surprizing that a complete decisive analysis of existing plant based coagulant is still imaginary in this 21st century. The significance of plant based coagulant to ecosystem in the end yield to an instant area for researcher in strengthening the investigation to find inherent resources (M.J. Pearse, 2003).Among plant based coagulant described namely are Dolichas lablab, Azadirachta Indica, Moringa Oleifera, Hibiscus Rosa Sinensis which are locally available from vegetables, seed sand flowers (Babu R, 2005).The natural coagulants used for this research will extracted from neem seed (*Azadirachta indica*).

2.4.5 Neem seed

Seed kernels of Neem are the source of Azadiracthin and related Liminoids, which has been investigated as natural insecticides (Babu R, 2005).

2.5 Extraction Methods of azadiracthin

There are various technologies available to extract the active ingredients of Neem seed. The technique to be used depends mainly on the quality required of the final product, productions cost and extraction application (Babu R, 2005).

By considering the solubility of the leading component azadiracthin, it is clear that only polar solvents should be used for extraction. Still, the cold pressed Neem oil could contain up to 0.6% azadiracthin. Water and alcohol are the best solvents. Often methanol is the preferred alcohol because of the availability and price, but its environmental toxicity of it headed to see another solvent as a choice. The major three types of extraction technologies that are available are

- Extraction with alcohol(called one-step extraction)
- Refined or enriched extraction method(fluid/fluid extraction)
- Soxhelet extraction (solid liquid extraction).

Chapter three

3. Materials and methods

3.1. Equipment and apparatus

The major equipment and apparatus that were used in this study are, temperature controlled oven, grinding machine, Soxhelet extractor, measuring cylinder, filter paper, chiller, separatory funnel, round bottom flask, analytical balance, beakers, heater, pH meter, Rotary vacuum evaporator (RVO 400, INGOS), Vacuum pump with funnel and beaker, Centrifuge machine, TLC paper with aluminum stand, Filter paper, 0.22μm of diameter 90mm, Fourier transform infrared spectroscopy (FTIR), Uv vis spectroscopy and Dynamic light scattering(DLS).

3.2 Chemicals and reagents

The chemicals that were used in this study are matured neem seed, Ethanol 95%, Potassium hydroxide, Ethyl acetate 99.9%, Isopropyl alcohol, aluminium nitrate (laboratory grade), ferric chloride, Iodine and TLC cellulose.

3.2 Methodology

3.2.1 Raw material preparation

Measured 1.2 kg of matured kernels in a light-yellow color stage was collected from Adama science and Technology University. After the sample was collected and packed in a polyethylene bag, it delivered to ASTU Chemical Engineering Department laboratory. The sample should be stored at room temperature open air before use.

3.2.2 Moisture content of Neem seed

After the sample was decorticated its stem moisture content was analysed. The sample was placed in an oven (Clifton) at 45^{o}C for ten days until its weight become constant. Then the moisture content of the sample was determined using Eq. 1. (M.J. Pearse, 2003).

Fig 3.1 Neem seed preparation

Moisture content (%) = $\left(\frac{W1-W2}{W1}\right)*100$..... (1)(Babu R, 2005)

Where

W_1- initial weight of sample

W_2-final weight of sample

3.2.3 Ash content of Neem seed

Ash content of **Neem seed** sample was determined by igniting the oven dried sample used for the moisture content determination in a box resistance type furnace (SX-2.5-12) at 750^{o}C. The substance remaining after ignition was the ash. It was determined according to equation 2(Babu R, 2005).

Ash content (%) = $\frac{W3}{W2}*100$ ..... (2)(Babu R, 2005).

Where

W_2=ash (g)

W_3=oven dried specimen (g)

Organic matter (%) =100-ash content%

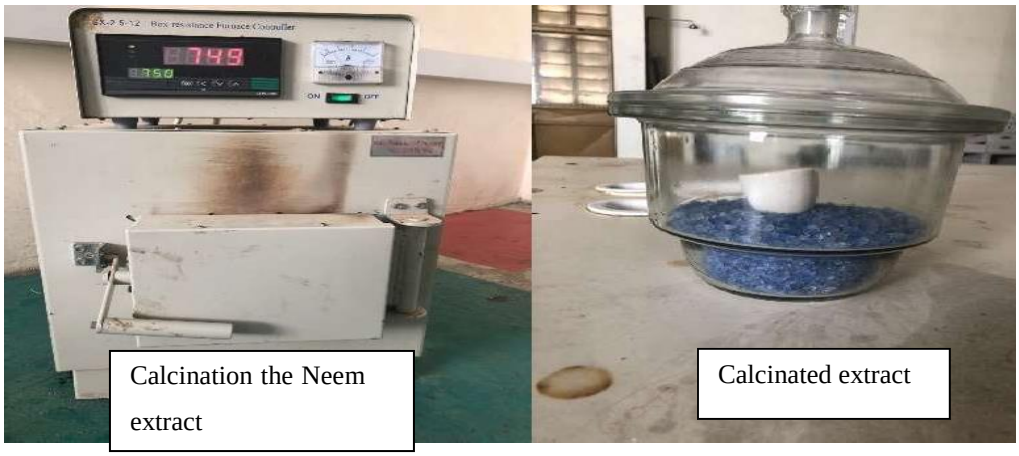

Fig 3.2 Box resistance type furnace and desiccator with crucible

Lastly, the dried sample that was grinded using grinder, and analyzed for its moisture and ash content, was sealed in 1000 mL beaker and made ready for further extraction process.

3.2.4 Neem seed extraction procedure

The optimal operational conditions for Neem seed extraction were 350µm, 45^{o}C, 6:1 v/w and 4 hr of particle size, extraction temperature, solvent to solid ratio and extraction time, respectively (Aklilu Gebrehawaria ,2017). This optimum condition was adopted for this study. Hence, the milled seed was sorted by its particulate size of (350µm) in a 1000ml beaker. A proportionate solvent (ethanol) to solid (seed) ratio (6:1v/w) was prepared (Aklilu Gebrehawaria, 20176). The conventional water chiller as a hot circulates was adjusted. Then, simultaneously the grinded seed were added to an overhead of Soxhelet extractor and the solvent at the bottom of three neck flask for extraction (Aklilu Gebrehawaria, 2017). After adding the solvent and the seed in to the extraction vessel, the extraction lasts for (4hr) (Aklilu Gebrehawaria, 2017).

Then after, the extract was made ready for rotary vacuum evaporation process. Rotary vacuum evaporator made the supernatant to concentrate with an operation condition of 40 rpm rotation and recovery of ethanol at 83 ^{o}C, to yield a dark brownish semi-solid material. The concentrated extract was de-oiled by a means of density difference using separatory funnel.

Finally, the brownish heavy slurry will dried in an oven drier for 48 hrs to solidify the extract for the ease of handling (Aklilu Gebrehawaria, 2017).

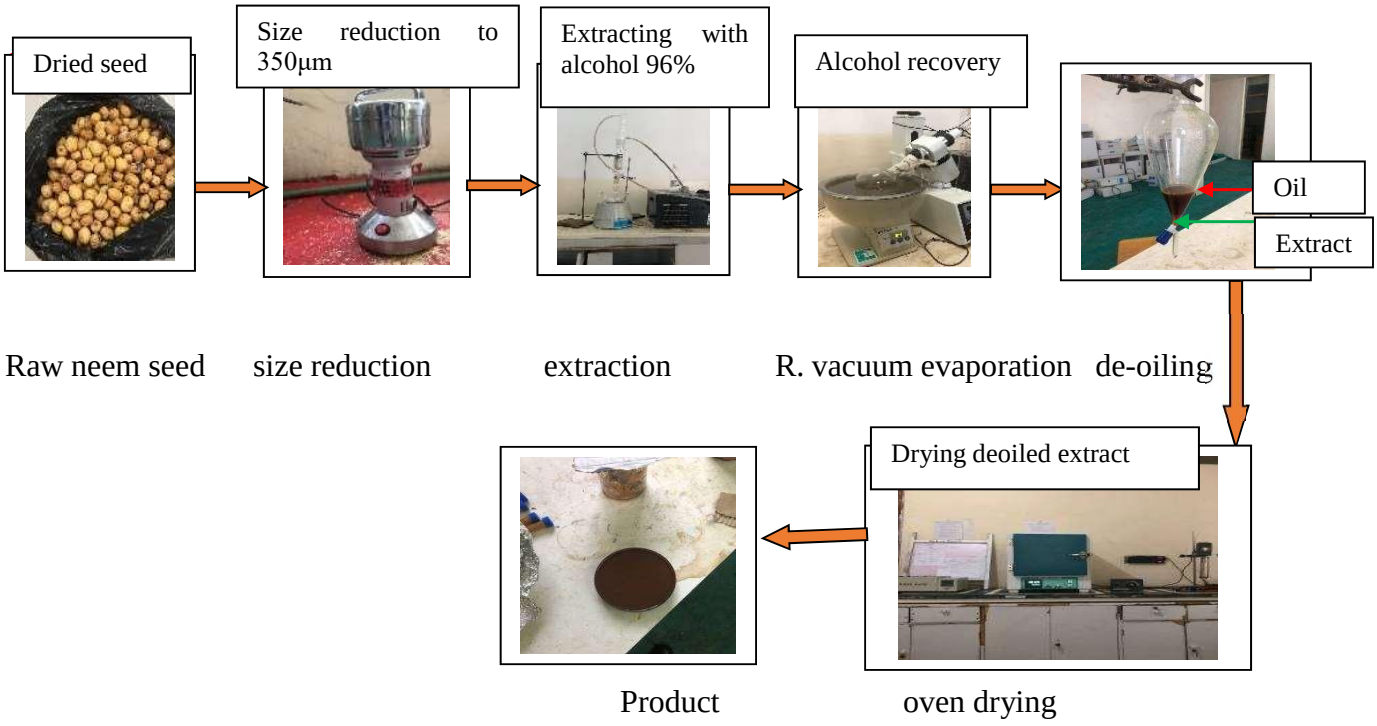

Fig.3.3 The extraction process of neem seed (Babu R, 2005).

3.2.5 Characterization of the Extract

3.2.5.1 Thin Layer Chromatography (TLC) Analysis

This characterization analysis simply indicates the qualitative characteristics of the compound that is azadiracthin with respect to other compounds or elements extracted together and present simultaneously (Supriya Dubhashi, 2013). The test was undertaken by a small amount of extract dissolved in ethanol (96%). Then, the sample was spotted on a TLC plate and placed it in a beaker consisting Iso- propyl alcohol and hexane ratio (2.5:17.5) as mobile phase. It was run till 3/4th of the plate distance, and then placed it in Iodine chamber. The test was given two pale yellow colored spots (Supriya Dubhashi, 20130). The upper spot indicated azadiracthin and the below spot indicated nimbin. This was because of the density difference of nimbin and azadiracthin. The R*f* (Retention factor) of azadiracthin was calculated by dividing the distance traveled by azadiracthin to the mobile phase (isopropyl alcohol and hexane) distance travelled. The value of R*f* was indicate the presence of Azadiracthin in the extract. The R*f* value was calculated using equation (Supriya Dubhashi, 2013).

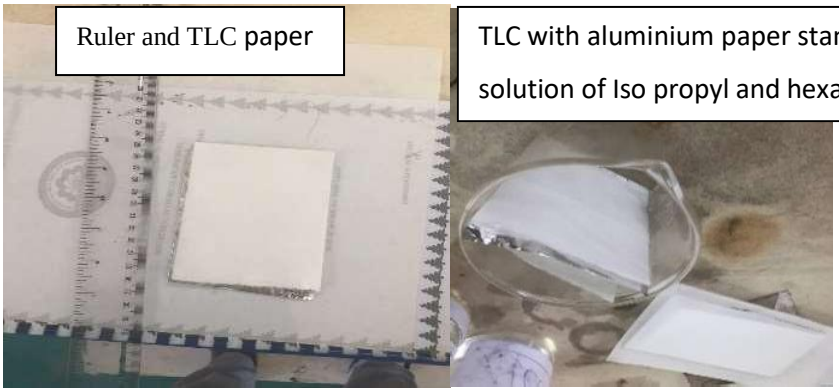

Fig.3.4 Thin layer chromatography measurement

$$Rf = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent}} \quad \ldots\ldots\ldots\ldots \quad (3)$$ (Aklilu Gebrehawaria, 2017)

3.2.5.2 Fourier transformed infrared analysis (FTIR)

The FTIR analysis was used to identify the organic functional groups involved in the extracted Neem. The FTIR spectrum was taken in the mid IR region of 500–4000 cm^{-1} using attenuated total reflectance technique. The dried sample was directly injected to instrument and the spectrum was recorded in transmittance mode.

4.3 Biosynthesis of aluminum Nanoparticle

Aluminum nitrate is the precursor for this biosynthesis with a molecular weight of 375.13 g/mol, which was taken for 2 molar concentrations and was allowed to mix with distilled water. In this step plant (Neem) extract was mixed with aluminum nitrate in 4:1 ratio and were allowed to rotate in batch spindle stirrer with 250 rpm. After 30 min a yellowish brown precipitate was produced, this indicates the presence of alumina Nano powder (Liu C et al. 2017). This was undergoing with a centrifugal process, using methanol and distilled water for the cleaning process (Liu C et al. 2017).

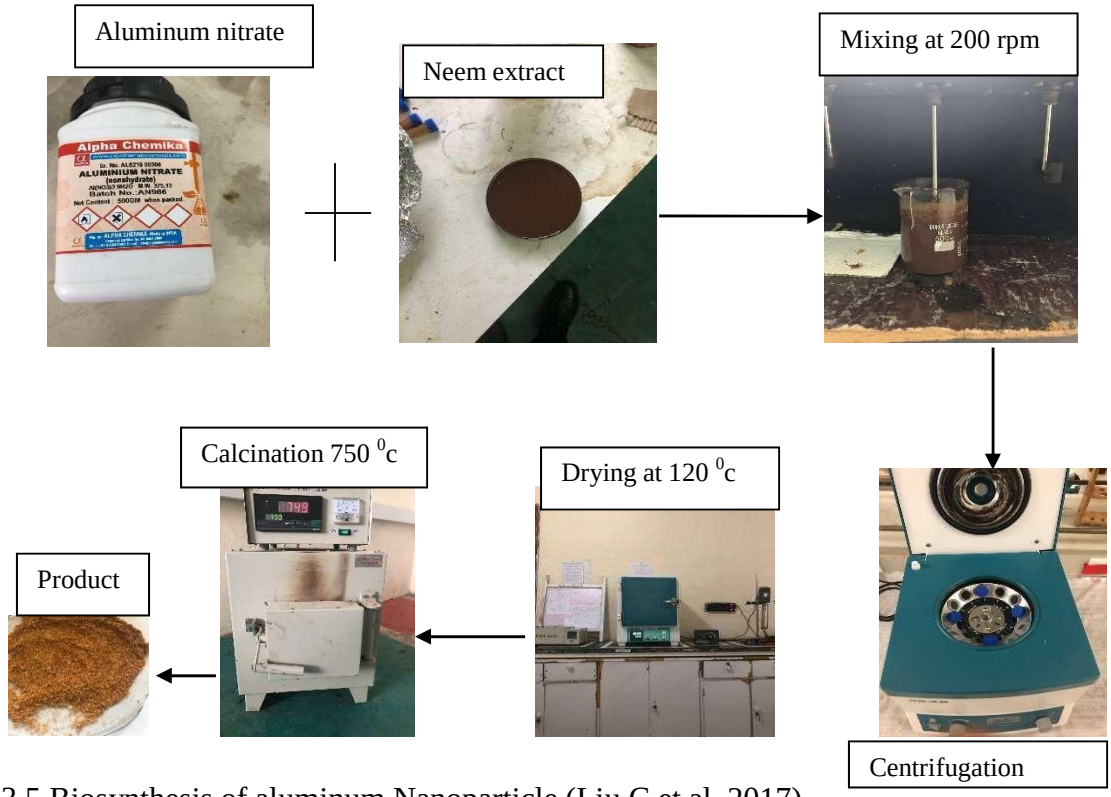

Fig.3.5 Biosynthesis of aluminum Nanoparticle (Liu C et al. 2017).

3.3.1 Purification of Synthesized Aluminium Nano material

Centrifugation process was carried out with 1000 rpm and with time duration of 15 min. Then powder was cleaned using distilled water for removing the non-reacted molecules. Centrifugation process was repeated 3 times for best Nano powder separation. Finally, purified powders was heated in oven at 105 °C for 4 h and then stored in dry bottle. FTIR, UV spectrometer and DSL testing was taken for confirming the alumina Nano powder.

3.4 Coagulation experimental procedure

Coagulation-flocculation and precipitation studies were performed in batch mode conventional jar-test apparatus with six spindle steel paddles in a jar test apparatus equipped with 5 beakers of 400 mL volume. Before Coagulation-flocculation process, wastewater sample was synthesized under controlled parameter and comprehensively mixed to avoid possibility of settling solids. Their initial pH was corrected by adding either acid (LABSA) or base (NaOH) and measured amount of wastewater was added to each beaker (Payne, W.J., 1963)].

The addition of the synthesised coagulant doses (1–4.5 g/l) was followed; and the beakers conducted at constant speed quick mixing (250 rpm) for 30 minutes. The coagulant was evenly

distributed across the beakers due to the quick mixing. The suspension was allowed to settle for various times (1.30 hr - 12.30 hr.) after the agitation ended. The supernatant was filtered using filter papers after settlement. The removal of foaming power was then determined for the samples of the supernatant obtained from each beaker (Choy, L. T., 2014).

The ultimate concentration results of the wastewater sample were compared to the beginning concentration values. In this study, the experimental setup was carried out by changing some operating parameters, namely coagulant dose, settling time, and initial concentration, while holding other parameters constant to study their impact on the coagulation-flocculation process. This also helped to achieve the optimal condition of parameters. As indicated, coagulation-flocculation was performed using extract of Neem (Azadirachta indica) seed and optimum dosage was investigated. In the second step, modification of the natural coagulant using Nano particles was done to improve the process performance of coagulation-flocculation. The same procedure was followed for comparison of results with ferric chloride as coagulant. Lastly, the treated water was characterized for it's as if the foaming power reduced.

Fig .3.6 Experimental setup of jar test

3.5 Characterization of waste water

Detergent wastewater samples was characterised to determine the physical and chemical parameters. The parameters under study include pH, Chemical Oxygen Demand (COD), soap matter and foaming power. All the parameters was analysed in accordance with Standard Methods for the Examination of Water and Wastewater. The pH value was measured by digital pH meter.

3.5.1 Determination of chemical oxygen demand (COD)

The chemical oxygen demand (COD) was determined using the open reflux method. Accordingly, most types of organic matter was oxidize by boiling in a mixture of chromium and sulfuric acids. Thus, the wastewater soap sample was re-flux in a strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). The oxidation reaction time has been 2 hours, and it was held under standard conditions. At the end of the reaction, the remaining unreacted $K_2Cr_2O_7$ was treated with ferrous ammonium sulfate to determine the consumed amount of $K_2Cr_2O_7$. Thereafter, the oxidizable organic and inorganic matter amount in the wastewater sample was calculated in terms of oxygen equivalent.

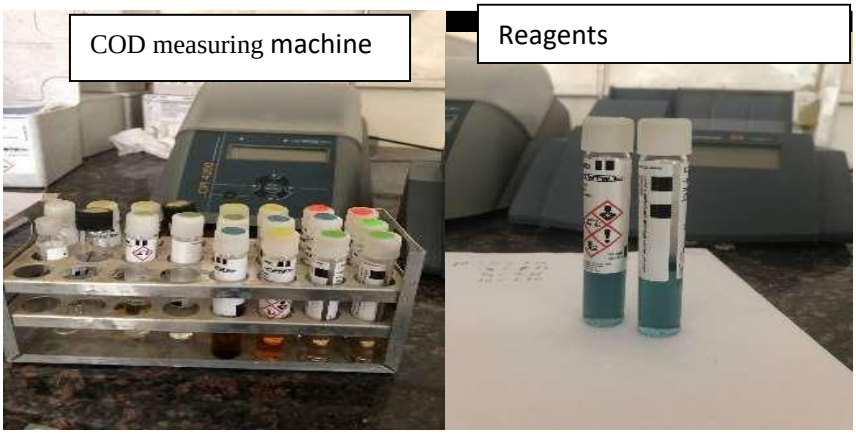

Fig 3.7 COD measurement

3.5.2 Determination of soap matter (active matter)

The prepared wastewater sample was weighed (5 gm in 50mL of beaker). Then, the weighed sample was dissolved in 5 mL of ethanol (96 %) and heated until it boiled. After that the solution was filtered by filter funnel in a dry beaker of 250 mL with recording the weight of the beaker. Filter paper and beaker was washed with 60 mL hot ethanol (96 %). The filtrate solution was taken and distilled to off the ethanol in the solution. Finally, the remaining matter was recorded for calculation of active matter (Eq. 4).

$$\text{Active matter (\%)} = \frac{M2-M1}{S} * 100 \quad \text{.....(4)[16].}$$

Where M1= mass of dry empty beaker

M_2= mass of beaker with sample
S= the amount of sample taken.

3.5.3 Determination of foaming power

Measured 20 mL of prepared wastewater sample was taken and shaken for 20 times manually. Let it stand erectly. Then, it stayed for 30 second and the result was recorded.

3.6 Design experiments and optimization of process variables

Response surface methods were used to evaluate how the primary parameter affects foaming power removal efficiency as well as to optimize all of the affecting parameters collectively through statistical experimental design. The experiments have been carried out using the Box-Behnken statistical experiment design (BBD) of the RSM, which includes a three-factor and three-level for coagulation-flocculation the process. The experimental results were studied and interpreted according to the design. Statistical program Expert.13.0.1 is used to estimate the responses of the dependent variables.

3.6.1 Design experiments for the coagulation process

i. Selection of response variable: foaming power removal

ii. Choice of factors, levels, and range: The potential design factors that have a major effect on the coagulation of detergent wastewater are:-

a) Coagulant dose
b) Settling time
c) Initial detergent concentration

The variables and their levels in the coagulation process were depicted in Table 3.2

Table 3.1 The variables and their levels in the coagulation process

no	Parameters	Unit	Range and level		
			-1	0	1
1	Coagulant dose	g/l	1.5	3	4.5
2	Settling time	hr	1.30	7	12.3
3	Initial detergent concentration	g/l	0.5	1	1.5

Utilizing the Response surface (Box-Behnken) design with the factors of time, coagulant dose, and initial concentration with three levels of each factor was selected to see the treatment's effect on the response (foaming power), and analysis of variance (ANOVA) was used for statistical significance, the data collected from the treatment of soap wastewater at various times, doses, and initial concentration values were analyzed. Total runs conducted are given in Table 3.2.

Table 3.2 Experimental run of the coagulation process

Std	Run	Factor 1A:co.doseg/l	Factor 2B:timehr	Factor 3C:inialconcg/l	Response 1FPR %
13	1	3	7	1	
14	2	3	7	1	
11	3	3	1.5	1.5	
9	4	3	1.5	0.5	
8	5	4.5	7	1.5	
5	6	1.5	7	0.5	
1	7	1.5	1.5	1	
2	8	4.5	1.5	1	
17	9	3	7	1	
3	10	1.5	12.5	1	
10	11	3	12.5	0.5	
7	12	1.5	7	1.5	
4	13	4.5	12.5	1	
16	14	3	7	1	
12	15	3	12.5	1.5	
15	16	3	7	1	
6	17	4.5	7	0.5	

4. Results and Discussion

4.1. Pre-extraction of Neem seed characterization results

4.1.1. Moisture content of Neem seeds

The data collected from the analysis is listed in Table 4.1. From this result, the amount of moisture content removed was calculated using Equation 1. This result indicates that the amount of moisture removed from the seed was about 6.4% of its initial weight (Table 4.1). Basically, the amount of moisture present in the seed blocks the diffusivity of the solvent towards the seed surface and prohibits extraction kinetics

Table .4.1 Neem weight analysis

No of day	Weight (g)
Day 1	1200
Day 2	1162.74
Day 3	1151.29
Day 4	1142.29
Day 5	1136.89
Day 6	1129.09
Day 7	1126.59
Day 8	1124.68
Day 9	1123.28
Day 10	1123.27

Neem Seed with higher moisture content yields less bioactive extract as compared to those with lower moisture content (Orhevba. O., 2013). Generally, as it was shown from the data above the first 24 hrs moisture content removed was about 3.1 %. Since, the amount of moisture content was

decreased consequently and left in small quantity of not aggressively affects the process i.e. less than 0.1%. In addition, drying of the sample beyond this might cause degradation of bioactive component and burning.

4.1.2. Ash contents of Neem seeds

The amount of ash content in a sample designates the total amount of non-organic maters or compounds present in a sample (mostly metallic oxides). Applicably, these compounds are harmful by leaving non-volatile and non-decomposable metallic compounds on the environment. These can causes different health problems on different floral and faunas. For this reason, the amount of ash content should be less as much as possible. From the laboratory result of a replicated seed sample, the ash content calculated was 0.84 %. This indicates that the neem seed has significant organic matter and insignificant non-organic matters. An organic matter is anything that contains carbon compounds that were formed by living organisms. Organic matters are biodegradable and environmental sustainable. So, the need for high amount of organic matter is very important environmentally and applicably. From this, the amount of organic matter in Neem seed calculated was 99.16 %.

The seed has mainly contained organic compounds that are easily decomposable and harmless to the environment. Hence, it can be recommended to be used for the flocculation-coagulation purposes.

4.2. Physico – chemical characteristics of Extract

4.2.1. Thin Layer Chromatography (TLC) Analysis

TLC measurement is a qualitative test used to define the presence of a certain compound or element with respect to another elements or compounds found simultaneously by dissolving in a mobile phase. The standard R*f* value of Azadiracthin is 0.70 (Mukunda, V. P., 2016). The result shown below was found from TLC analysis of extract in with a cellulose coated aluminum stand stationary phase and hexane and isopropyl defined ratio mobile phase.

The result of five randomly selected samples was simply indicating the presence of azadiracthin with an Rf value of 0.693 ± 0.007. This observed result was in good convenience Table 4.2 TLC analysis results of azadiracthin with reported value in the literatures. Here, there is also a trace

amount of nimbin present mixing with azadiracthin. This can be simply shown in the TLC plate by spotting the dark yellow color below azadiracthin (i.e. light yellow) spot.

Table 4.2 TLC analysis results of azadiracthin

Sample no	Concentration(g/ml)	Distance covered(cm)	$Rf = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent}}$	mean ± SD of Rf value
1	0.05	SD=12.095	0.686	0.693±0.007
		CD=8.3		
2	0.045	SD=11.95	0.6778	
		CD=8.1		
3	0.04	SD=11.3	0.699	
		CD=7.9		
4	0.035	SD=11.05	0.71	
		CD=7.85		
5	0.03	SD=10.4	0.692	
		CD=7.2		

4.2.2. FTIR analysis of Neem Extract

The FTIR is an important tool in understanding the involvement of functional groups (Ahmed S. Ikram, 2015). The FTIR spectra peaks of Neem seed extract were recorded in the present study. The peak present at 3270 cm^{-1} indicates (N-H stretching vibrations) primary and secondary amines; 1740 and; 1640 cm^{-1} (C-C stretching vibrations) the aromatics; 1370 cm^{-1} (C-H bend stretching vibration) the alkanes; 1220 cm^{-1} (C-N stretching vibration) the aliphatic amines in (Fig. 4.1).This observation was comparable with the previous findings (Ahmed S. Saifullah, 2016).

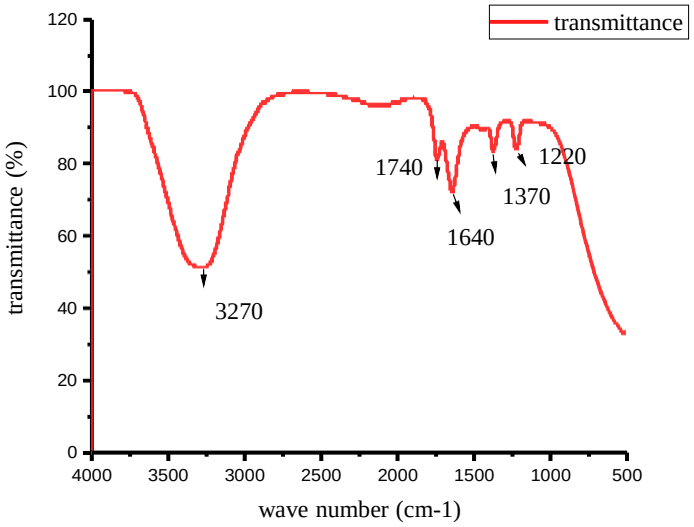

Fig 4.1 FTIR spectra showing the functional groups Neem seed extract.

4.2.3. Azadiracthin Extraction Result

The yield of azadiracthin from Neem seed using Soxhelet extraction with further enrichment process steps and defined operation parameters (i.e. particle size(350µm), Extraction temperature(45^{o}C), solvent to solid ratio(6:1v/w) and extraction time (4hr)) was found 11.123gm from 100gm of grounded Neem seed. The yield was 11.1 %.

4.3. Aluminum Nano Particle analysis

4.3.1. FTIR analysis of aluminum Nano material

The Synthesis of Al Nanoparticles produces clear yellowish colored Nano particle. The formation of this material upon the heating of an aqueous mixture of Al $(NO_3)_3$ and Neem extract. The infrared spectra of synthetic Nano material product was shown in Fig 4.2. The FTIR spectra peaks of Neem seed extract mediated AlNPs were observed at 3270 and 2920 cm^{-1} indicates (=C-H stretching vibrations) alkenes; 1640 and 1410 cm^{-1} indicates (C=O stretching vibrations) carbonyls; 1340 cm^{-1} indicates (C-H rock stretching vibration) alkanes; 1260 cm^{-1} indicates (C-O stretching vibration) carboxylic acids. Band appearing at 1030 cm^{-1} is typically for alumina due to Al–O vibration mode (Jun-Cheng L et al, 2006). The valley between 926 $cm^{-1}$and 773 cm^{-1}confirms the Al oxide form, and the one at 862 cm^{-1} is assigned to the bending vibrations of Al-O bond. Al-O-Al bond of alumina generates the band at 773 cm^{-1}(Xu B.et al. 2017).

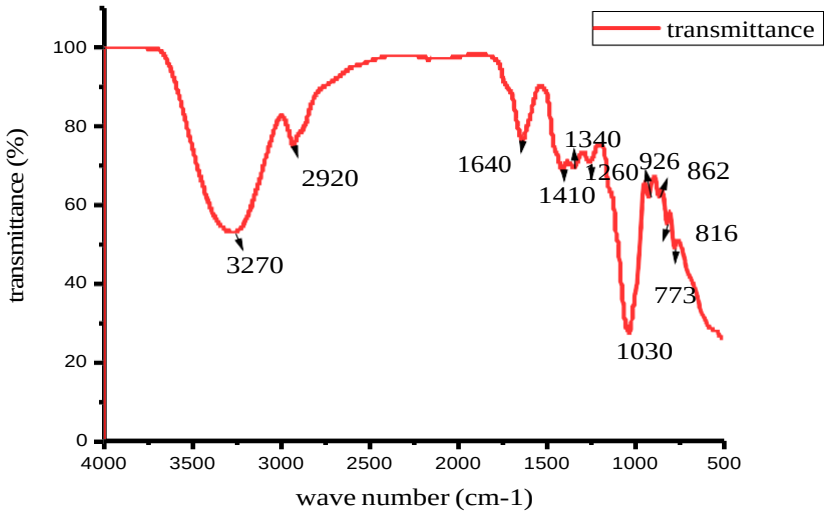

Fig.4.2 FTIR analysis of AlNPs

The FTIR analysis the green synthesised Al NPs confirmed that, the bio-reduction of Aloxide to Al NPs. This is due to the reduction of capping material of plant extract. In the present study, the FTIR analysis also showed the involvement of amines, alkanes, alkenes, aromatics, aldehydes and carboxylic acids of AlNPs, which is similar to other reports (Shankar S.S, 2004; Xu B.et al. 2017). Further, the FTIR studies confirmed that, the carboxylic groups of the amino acid residues and

proteins has the strong ability to bind the metals indicating that, the proteins could play a vital role in capping of AlNPs and preventing agglomeration and thereby stabilises the nanoparticles. This strongly suggests that, the biological molecules could possibly perform the dual functions of formation and stabilisation of Al NPs.

4.3.2UV-Vis spectroscopy aluminum Nano material

The UV-Vis spectroscopy could be used to examine the size and shape-controlled nanoparticles in aqueous suspensions (Ahmed S. Ikram, 2015). The UV-Vis spectroscopy was employed to record the localised surface Plasmon resonance of aqueous Neem extract mediated Al_2o_3 NPs and the peak absorbance was recorded at 312 nm, which confirms the formation of green Al_2o_3 NPs (Fig.4.4). The present findings demonstrated that the reduction of Al nitrate into Al_2o_3 NPs during the exposure to plant extracts was observed. The change in colour was noted and is due to the localised surface Plasmon resonance phenomenon of the formed Al_2o_3 NPs. The metal nanoparticles have free electrons, which give the Plasmon resonance peak absorption band, due to the combined vibration of electrons of metal nanoparticles in resonance with light wave (Prasad T.N.V.K.V., 2011).

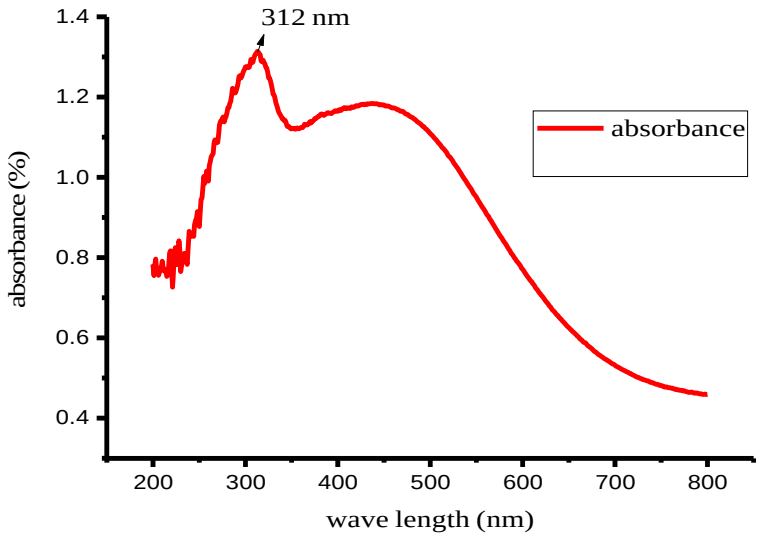

Fig. 4.4| Al_2o_3NPs UV analysis.

Earlier research findings also explained that, the Al NPs showed a surface Plasmon resonance peak in a range of 400-450 nm (Prasad T.N.V.K.V., 20110). Based on the characteristic Al NPs surface

Plasmon resonance range, it was confirmed that *A. indica* has huge potential to reduce $Al_2O_3$to Al NPs. The present observation (312 nm) was differed from the previous results (Lalitha A., 2013; Saini J. 2013) who noted a Plasmon band at 351 and 370 nm, respectively. This lower absorbance may be influenced by several factors such as concentration and combination of plant extract, pH, incubation temperature and reaction time. The variation in the values of absorbance confirms the changes in the particle size (Ahmed S. Ikram, 2015).

4.3.3. DLS analysis of aluminum Nano material

The DLS technique has been used to measure the hydrodynamic diameter (HDD) of the hydrosol in a solution of sodium hydro oxide. The HDD of the aqueous of Neem mediated Al NPs, was 18.7 nm.

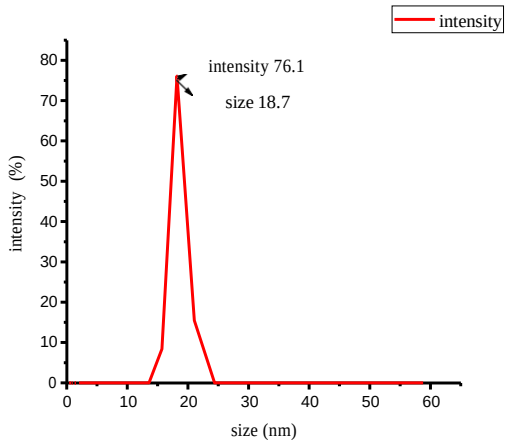

Fig. 4.5| DSL analysis of AlNPs.

The size measurements using the DLS technique for synthesised Al NPs were comparable to other findings (Lalitha A., 2013; Saini J. 2013). The size measurements (18.4 nm) and zeta potentials of 23 Al NPs indicates the good stability of the synthesised Al NPs. This clearly shows that if the hydrosol has the large negative or a positive zeta potential ≥30 mV, then the particles tend to repel with each other and show no tendency to agglomerate resulted in polydispersed particles (Saini J. 2013).

4.4. Characteristics of Raw Detergent Wastewater

4.4.1pH value analysis

The first steps was to determine the physic-chemical composition of the detergent wastewater (pH, COD, soap matter, and foaming power).

The wastewater from the factory (Bekas chemicals) appears to be more alkaline as a result of the average pH of the sample effluent wastewater reported above 9.7.

4.4.2. Chemical oxygen demand (COD) analysis

The intent of the pre-treatment standard is to control the discharge of pollutants to publicly owned treatment works, which pollutant may interfere with, pass through or otherwise be incompatible with such works. In this study the average values for COD in the effluent was 1500 mg/l which was exceed maximum allowable. Hence it need treatment.

4.4.3 Soap matter (active matter) analysis

Detergent concentrations greater than 0.1 g m/l are toxic to some marine organisms. Following the mentioned procedure in methodology the active matter of the waste was measured and the result was 0.8g/. This indicates the waste discharged from detergent plant should be treated

4.4.4 Foaming power analysis

The result of foaming power was 10.g/l which is equal to some detergent.so this should be lowered to standard.

As shown in the above analysis, the physical-chemical characterization of the wastewater effluent (Ph., active matter, COD, and foaming power) results indicates that treatment is essential to prevent environmental pollution degradation of groundwater and surface water resources. This is done by using the synthesized coagulant, which significantly reduces the values of pH, COD, active matter, and foaming power.

4.5. Effect of coagulation parameters on removal of foaming power

4.5.1 Effect of coagulant dose

Coagulant dose is one of the most important constraints that should be taken into consideration to estimate the performance of coagulants in coagulation -flocculation. As shown in Figure 4.6, the influence of coagulant dose on the percentage removal of foaming power is visible. In principle, a dosage that is either minimal or excessive will lead to weak performance. Therefore, it is important to determine the optimum dose in order to reduce dosing costs and sludge formation as well as to achieve the best results possible during the treatment process. The experiments to test the effect of coagulant dose was ranging from 1.5 – 4.5g for all coagulant used in this thesis, while mixing time of 30 minutes at 250 rpm, constant initial detergent concentration, which is 1 g/L, and settling time (12hr). Accordingly, there was continuous removal of foaming power with increases in coagulant doses up to 3.5 g for Neem extract, 3.2 g for ferric chloride and 3 g for aluminum Nano material. After that insignificant increase was observed because of two reasons. First, at low coagulant doses the detergent uptake capacity is high because of the better utilization of the available active sites and at high coagulant dose; too many sites are available for a limited quantity of detergent. Second, at a high coagulant dose, there was lower equilibrium concentration of the detergent.

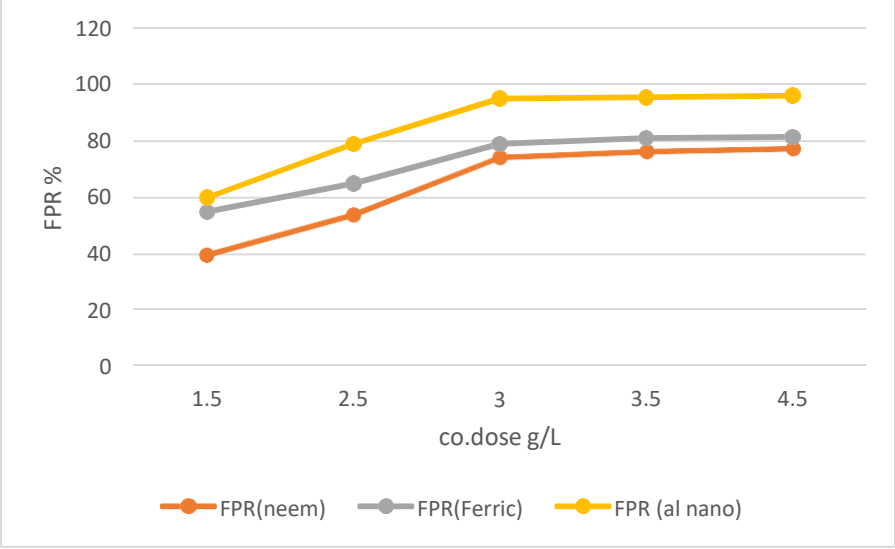

Fig. 4.6| Effect of coagulant dose on FPR

4.5.2. Effect of Settling Time

In the coagulation process, the settling time is an important factor that can influence the overall removal efficiencies of foaming power in wastewater treatment. To determine the effective settling time, experiments were done at different settling times of 1.30 hr-15.30 hr for all coagulant used, while other parameters such as agitation time (30 min), agitation speed (250 rpm), temperature(25^0cC), initial soap concentration (1 g/L), and coagulant dose (3 g/L) were kept constant. The results indicated that the percentage of foaming power removal was increased 15.30 hr. This is because as the settling time increases the contact surface between the coagulant and pollutant was high due to this reason the floc formation over the system was increased. For all coagulant (Neem extract, alum modified and ferric chloride) with increasing settling time up to 15.30 hr. This is because as the settling time increases the contact surface between the coagulant and pollutant was high due to this reason the floc formation over the system was increased.

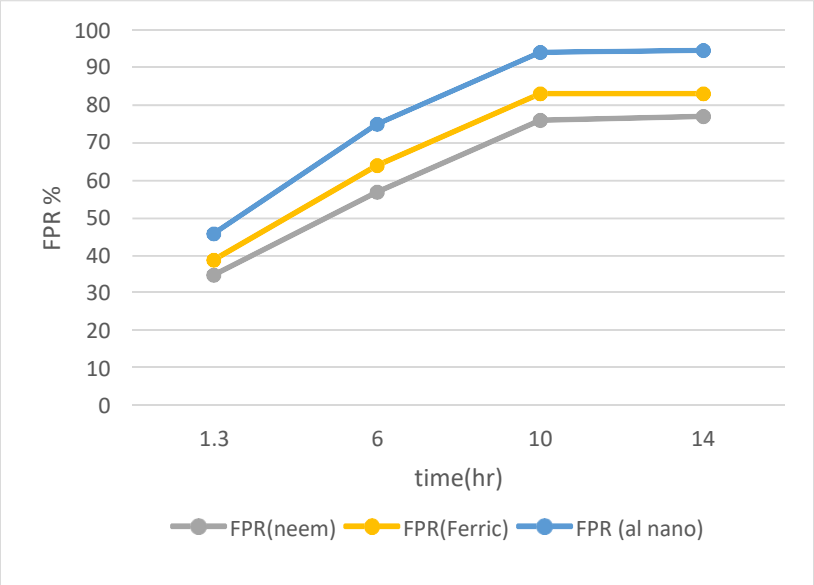

Fig 4.7| Effect of settling time.

4.5.3. Effect of initial concentration of detergent

The effect of initial concentration on the removal of the foam was studied at different initial concentrations of detergent by keeping other parameters constant. The effect of initial concentration on the removal of the foaming power is shown in Fig 4.8 was found that with the

increase in initial concentration of detergent for all three coagulant from 0.5 g/L to 1 g/L, the removal capacity of foaming power also increases. The observation is obvious due to the availability of a higher number of active matter ions resulting in a higher concentration gradient. With the increase of the concentration of detergent in solution, the availability of active matter ions also increases at the interface of the coagulant, increasing removal performance, and the maximum removal efficiency was about 90 % for Neem extract 92 % for ferric chloride and 98 % for aluminium nano material. Then after, the removal of foaming power was decreased as observed in below graph.

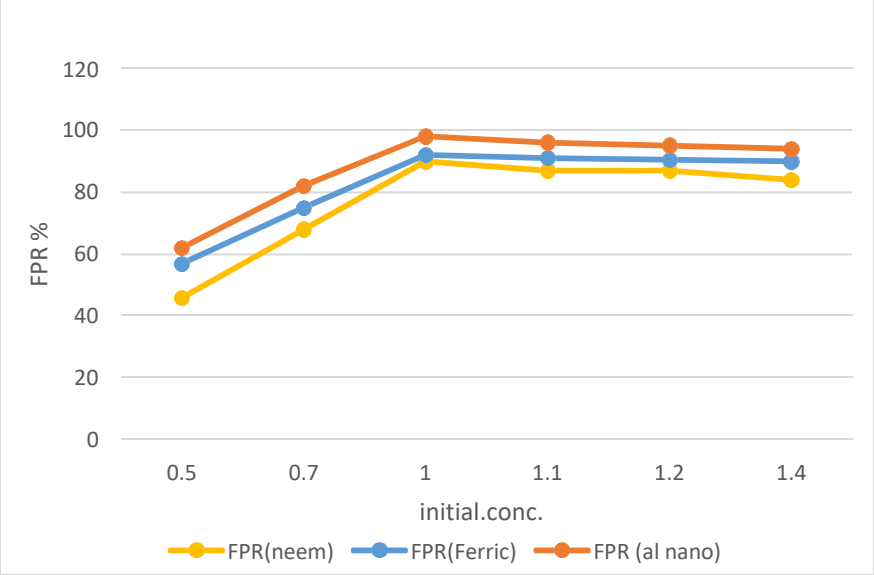

Fig 4.8| Initial concentration.

3.5.4 FTIR result before and after treatment

From the FTIR results as shown in the figure below there is an O-H stretching within the 3250 cm-1 wave number. It shows that as the O-H broadness and intensity increase the interaction (bond) of the coagulant (AlNPs) and pollutant is low in strength because as the O-H peak intensity of the conjugate increase the product is more hydrophilic and easily dissolve in water and easily break the bond between the coagulant and pollutant. The coagulant (AlNPs) increase their effectiveness as the hydrophobicity of the product decrease.

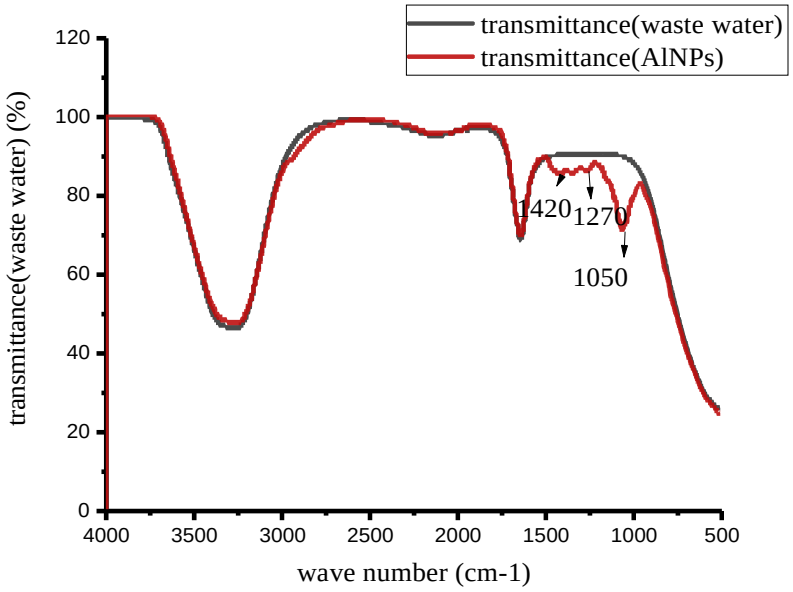

Fig 4.9| FTIR graph of the synthesized AlNPs coagulant conjugates.

4.5.5. Foaming power removal of real wastewater

Batch mode experimental studies for real wastewater by selecting Bekas chemicals detergent industry as a wastewater source were conducted. The result investigated showed that the foaming power of the waste water become 85 % for AlNPs after treatment which is better but not as much as synthetic waste due to a large number of competing pollutants within the waste.

Table 4.3| Real waste water treatment results

Time (hr)	FPR(NEEM)	FPR(FERRIC)	FPR(AlNPs)
1.5	25	30	35.2
5	68	70	65
9	70	75	78
12.5	74	79	85

4.6. Statistical Analysis of the Experimental Results for foaming power removal using biosynthesised coagulant (Neem extract).

The process contains three main factors: coagulant dose, time and initial concentration of soap with one response (foaming power). After following the above sequences of procedures, the experimental outcomes of those particular results were measured for foaming power removal. The result obtained from the Experiment was indicated in the following table.

Table 4.4| Results obtained from the experiment of coagulation of Neem extract

Std	Run	Factor 1A:co.dose g/l	Factor 2B:timeh r	Factor 3C:inial concg/l	Response 1FPR %
13	1	3	7	1	68.8
14	2	3	7	1	80
11	3	3	1.5	1.5	46
9	4	3	1.5	0.5	50
8	5	4.5	7	1.5	88
5	6	1.5	7	0.5	35
1	7	1.5	1.5	1	25
2	8	4.5	1.5	1	45
17	9	3	7	1	81
3	10	1.5	12.5	1	50
10	11	3	12.5	0.5	87
7	12	1.5	7	1.5	35
4	13	4.5	12.5	1	90
16	14	3	7	1	81
12	15	3	12.5	1.5	77
15	16	3	7	1	80
6	17	4.5	7	0.5	85

The removal was performed by using Neem extract as a coagulant at different aspects: Coagulant dose, Time and initial detergent Concentration with a constant mixing time of 30 min stirring Speed of 250 rpm, and 298k temperature.

Using Design Expert version 13.0.1 Software, the data shown in Table 4.4 were examined to determine the impact of the operating parameters of coagulant dose, time, and initial detergent concentration. The percentage of removal of foam was the dependent variable employed as a response parameter. To reduce the impact of unexpected variability in the observed response due to outside variables, all tests were conducted in random order. Summary of the design for the percentage removal with the three levels and three components. Using Design Expert 13 software, the experiments' design model is a quadratic polynomial with five centers for each block.

4.6.1. Effects of Experimental Variables for removal of foaming power (Neem extract)

Table 4.5 Analysis of variance (ANOVA) for the removal of foaming power (neem extract)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	6736.38	9	748.49	31.05	< 0.0001	significant
A-co. Dose	2415.13	1	2415.13	100.19	< 0.0001	
B-time	2380.50	1	2380.50	98.75	< 0.0001	
C-initial conc	153.13	1	153.13	6.35	0.0398	
AB	100.00	1	100.00	4.15	0.0811	
AC	182.25	1	182.25	7.56	0.0285	
BC	9.00	1	9.00	0.3734	0.5605	
A^2	611.89	1	611.89	25.38	0.0015	
B^2	802.43	1	802.43	33.29	0.0007	
C^2	0.8338	1	0.8338	0.0346	0.8577	
Residual	168.74	7	24.11			
Lack of Fit	51.75	3	17.25	0.5898	0.6535	not significant
Pure Error	116.99	4	29.25			
Cor Total	6905.12	16				

From the ANOVA (Analysis of Variance) Table, 4.5 results the higher F-Value and the lower P-value (<0.0001) indicate significance for the regression model. The result demonstrates that the Model F-value of 31.05 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, AC, A^2, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. They are extremely essential to understanding the interaction among the independent variables. The result presented that coagulant dose (Factor A), time (Factor B), and initial concentration of detergent (Factor C) are the main important variables in the coagulation process with P-values < 0.0001< 0.0001 and 0.0398 respectively. Based on the value coagulant dose and time are the best important factor. From the second polynomial model, A^2 and B^2 are significant models with P-values <0.0015 and<0.0007 respectively. In the case of interaction effects, AB (coagulant dose and time) and AC (coagulant dose and initial concentration) are significant model terms for foam removal where the p-value is 0.0811 and 0.0285 orderly. The Lack of Fit F-value of 0.59 implies the Lack of Fit is not significant relative to the pure error. There is a 65.35% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good.

As shown from the ANOVA result, initial detergent concentration indicates insignificant when compared with the other factors. This result confirmed that its contribution to foam removal was the lowest. In addition, the interaction effects of time and initial concentration of detergent (BC) as well as initial concentration square (C^2) did not influence the coagulation process due to their highest P-value. Their P- values were 0.5605 and 0.8577respectively which is greater than 0.1 and indicates the model terms are not significant.

The model equations from the ANOVA result can be used to relatively compare the removal efficiency of foaming within factors and levels. The equation in terms of coded factors can be used to make predictions about foaming power removal efficiency for the given levels of each factor. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. The highest coefficients from the equation indicate the most influential factor

that affects the coagulation process of foam removal. On the other side, the equation in terms of actual factors can be used to make predictions about the Removal efficiency of foam removal for given levels of each factor. The levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

The Final Coded Equations for fatty matter removal from ANOVA result:

Foaming Power Removal Efficiency (FPR) = +78.36+17.38* A +17.25*B -4.38*C +5.00*AB +6.75*AC –1.50*BC -12.06*A^2-13.81*B^2+0.4450*C^2 ……. (6)

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.

Final Equation of Actual Factors

Foaming Power Removal Efficiency (FPR) = -2.48727+ +30.48758 *co. Dose+8.25273*time-35.49182 *initial conc+ +0.606061*co. Dose * time + +9.00000* co. Dose * initial conc – 0.545455*time * initial conc – 5.35778*co.dose² -0.456364*time² +1.78000 *initial conc²…. (7)

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

4.6.2. Model Adequacy

The regression model was found to be significant with the correlation coefficients of determination of R-Squared, adjusted R-Squared, and predicted R-Squared having a value of 0.9756, 0.9441, and 0.8536 respectively as shown in table 10. The goodness fitness of the model was measured by a coefficient of determination R^2, which measured how well the real experimental data points have been approximated together with the regression model. As the result in a table, 4.10 expressed the value of $R^2 = 0.9756$ indicates the better fit of experimental data to that of the predicted one. The value of the larger Regression coefficient (R^2) approach to 1 illustrates, the validity of the model in which it implies an acceptable agreement among the actual and predicted data. It implies that 97.56% of the experimental variable studied attributed to the removal of foam. The Predicted R^2 of 0.9441is in reasonable agreement with the Adjusted R^2 of 0.8536; i.e. the difference is less than 0.2. Therefore, this demonstrates that the measured data is very well fitted with a quadratic model of the predicted value. Model Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 18.390 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.6 Model adequacy measures for FPR

Std. Dev.	4.91		**R^2**	0.9756
Mean	66.40		**Adjusted R^2**	0.9441
C.V. %	7.39		**Predicted R^2**	0.8536
Press	80.1		**Adeq Precision**	18.3900

Generally, the smaller the value of the Predicted residual sum of squares (PRESS) static obtained 80.1 indicates, the better the experimental data points fit the model. Moreover, the high R^2 value and p-value as well as not significant fit indicate the best prediction of the experiment solution. Therefore, the result in both tables 4.4 and 4.5 proved that, the best performance of the fitness of the model equations.

Figure 4.10 indicates the relationship between Actual and predicted values, which can be introduced from the regression model equations of a Design Expert chart based on predicted and actual percent foam removal. The straight line shows the predicted values and the small rectangles represent the actual experimental values. The straight line is very close to the actual values and has a correlation coefficient R^2 equal to 0.9756, which confirms the accuracy of the model. The result confirmed that all the actual and predicted values are close to the line of a perfect fit. Both of them showed good agreement between them.

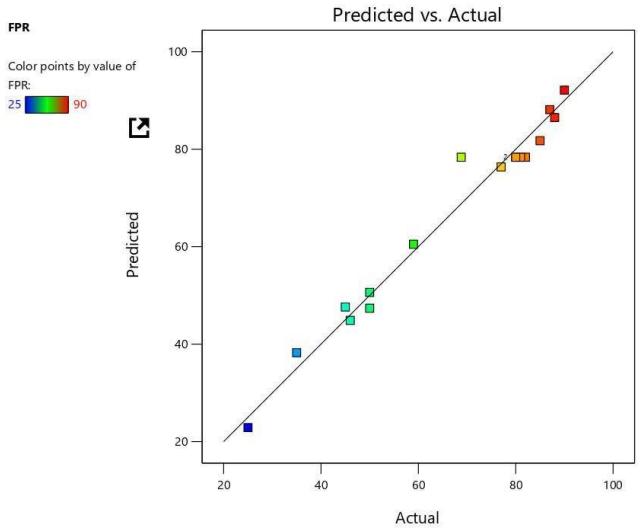

Figure 4. 10 Predicted vs Actual value foam removal plot

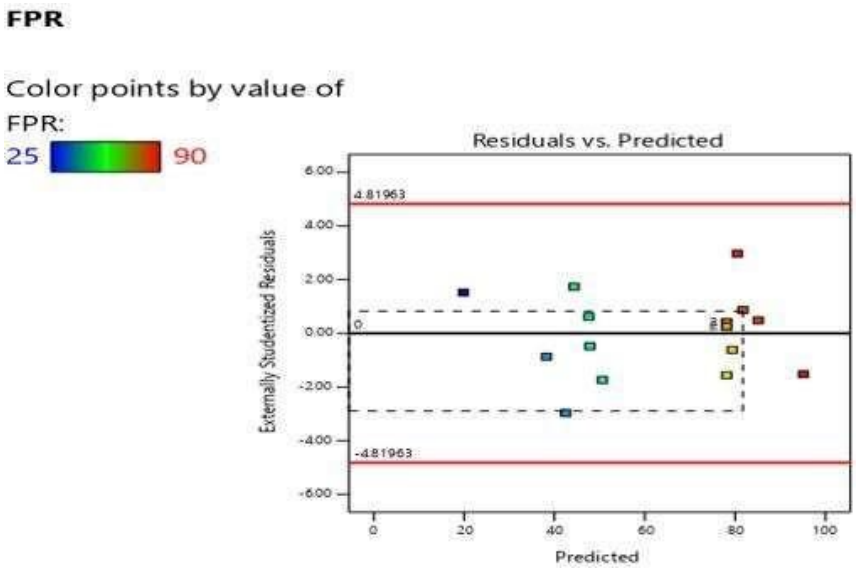

Figure 4. 11 Residual versus predicted values for foam removal

A simple check is to plot the residuals versus the fitted (predicted) values. A plot of the residuals versus the rising predicted response values tests the assumption of constant variance. The plot shows random scatter which justifies no need for an alteration to minimize personal error. The effects of the parameters for the percentage of fatty matter removal are to generate one-factor response and surface plots of the equation.

If the model is correct and the assumptions are satisfied, the residuals should be structured less; in particular, they should be unrelated to any other variable including the predicted response.

4.6.3. Optimization of the Response

To find the optimum value of each independent variable, four statistical metrics such as the larger regression coefficient (R^2), smaller lack of fit F-value, lower p-value, and higher sum squares have been used. The response optimization was used to identify the combination of independent variables particularly, time, initial concentration, and coagulant dose within the response of foam power removal efficiency using neem extract. The goal of the process was to obtain high foam power removal percentage. Therefore it has been set as a maximum while the process parameters such as initial detergent concentration and coagulant dose have been set as "within the range", while the time target to minimize the response surface method was used to optimize the process versus process parameters. According to the result obtained from optimizer Design-Expert version 13 software the maximum optimum removal efficiency of the foam removal was achieved at 77.65% % % at time =10.77 hr, initial detergent concentration =1.372 g/l , and coagulant dose of 2.87 g/l.

4.6.4. Response Surface plots Interaction Effects

The effect of the interactions between the three independent input and output variables and their interactions on the dependent variables can be seen using three-dimensional (3D) response surface plots. As observed from Figure 4.10 - 4.12 indicates the Plots of three-dimensional response surfaces of the function of two variables with the response and the remaining variables at the central level of the other variables.

Figure 4.12 illustrates the 3D interaction effect of coagulant dose and time on foaming power removal efficiency at constant initial detergent concentration and mixing rate and time. As the coagulant dose increased, there was an increment in foaming power removal efficiency. However, the percentage of foam removal did not increase with increasing time at any coagulant dosage. The

coagulant has reached the maximum removal capacity within or before 11 hours. In other word, the surface coverage of the coagulant was already saturated with the foam in less than 11 hours. Therefore, it can be concluded that the percentage of foam removal was highly dependent on the coagulant dose and time but foam removal did not more depend on the contact initial concentration of detergent.

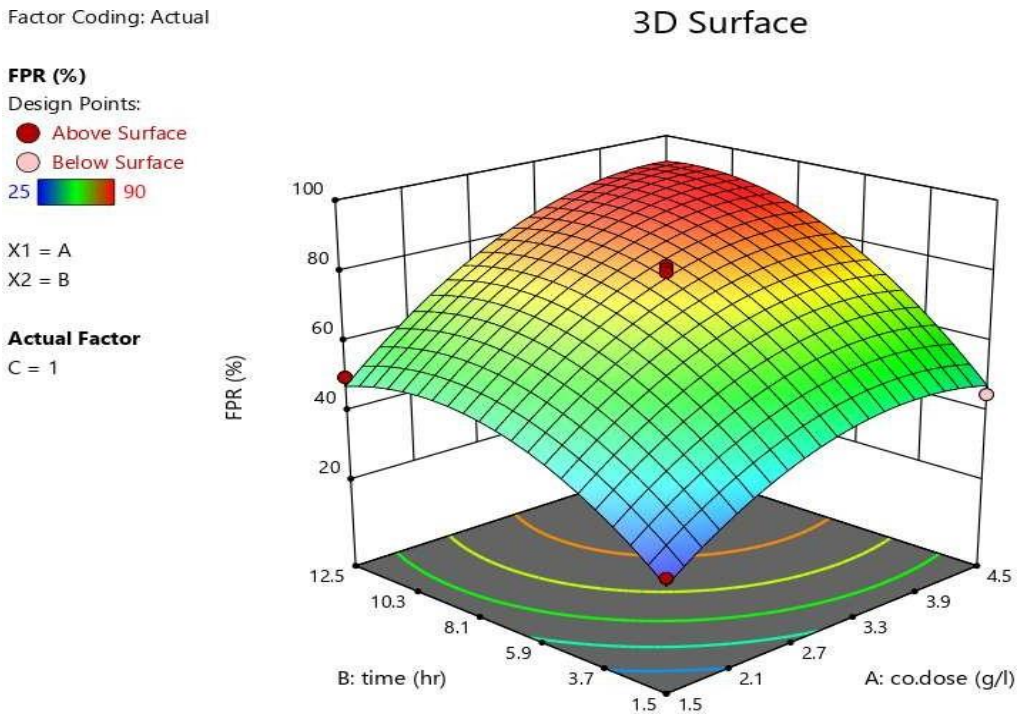

Figure 4. 12. 3D interaction effect of time and coagulant dose

Figure 4.13 indicates the interaction effects of time and initial detergent concentration on foam power removal at a fixed coagulant dose and mixing rate and time. Initially, as initial concentration increases, the removal efficiency of foam also increases. The rise of initial soap concentration leads to increments in the removal of foam from the solution due to the occurrences of large vacant places in the neem extract coagulant. As the initial concentration beyond 1 g/l increases, the removal efficiency decreases because the vacant sites of the coagulant are occupied by the pollutant. In the other case as the time increases leads to an increase in the removal efficiency of foam and reached an optimum of 77.65 at 10.774 hr. The rise of time leads to increments in the

removal of foam from the solution due to the high surface contact of the pollutant and the coagulant.

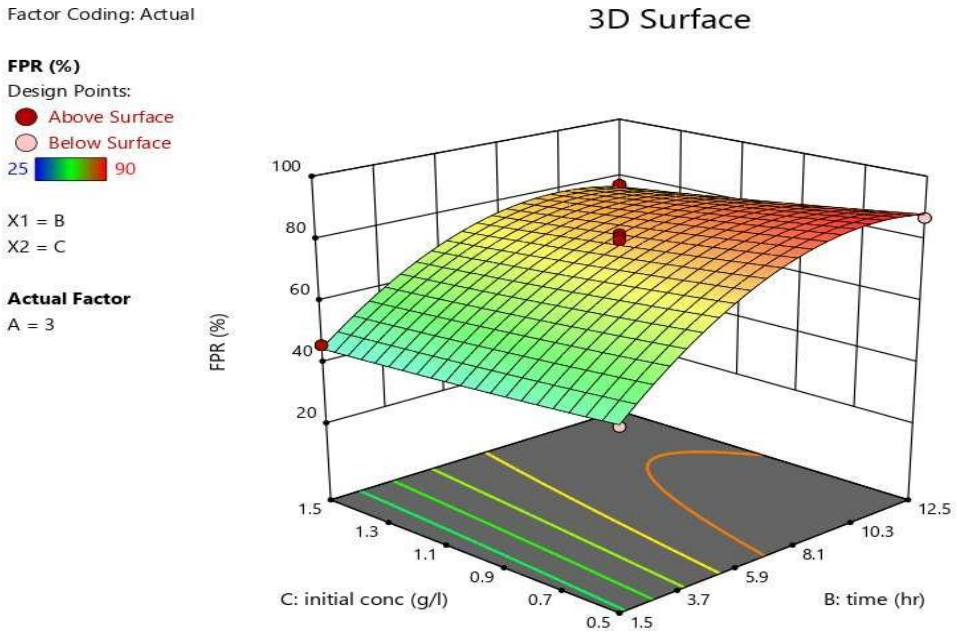

Figure 4. 13 3D interaction effect of time and initial detergent concentration

Figure 4.14 showed the interaction between initial detergent concentration and coagulant dose. As demonstrated by increasing the initial detergent concentration, the percentage removal of foam removal increased proportionally. The process happened due to a higher concentration gradient that was performed as a driving force to conquer the mass transfer between the bulk solution of active ion and coagulant surfaces of neem extract. The coagulant dose has no more effect on foam removal at a lower value of initial detergent concentration. As the initial detergent concentration increased, the percentage of foam removal also increased as a result of the coagulant dose increased. Therefore, the coagulant dose was the main independent variable that affects the removal of foam from the solution.

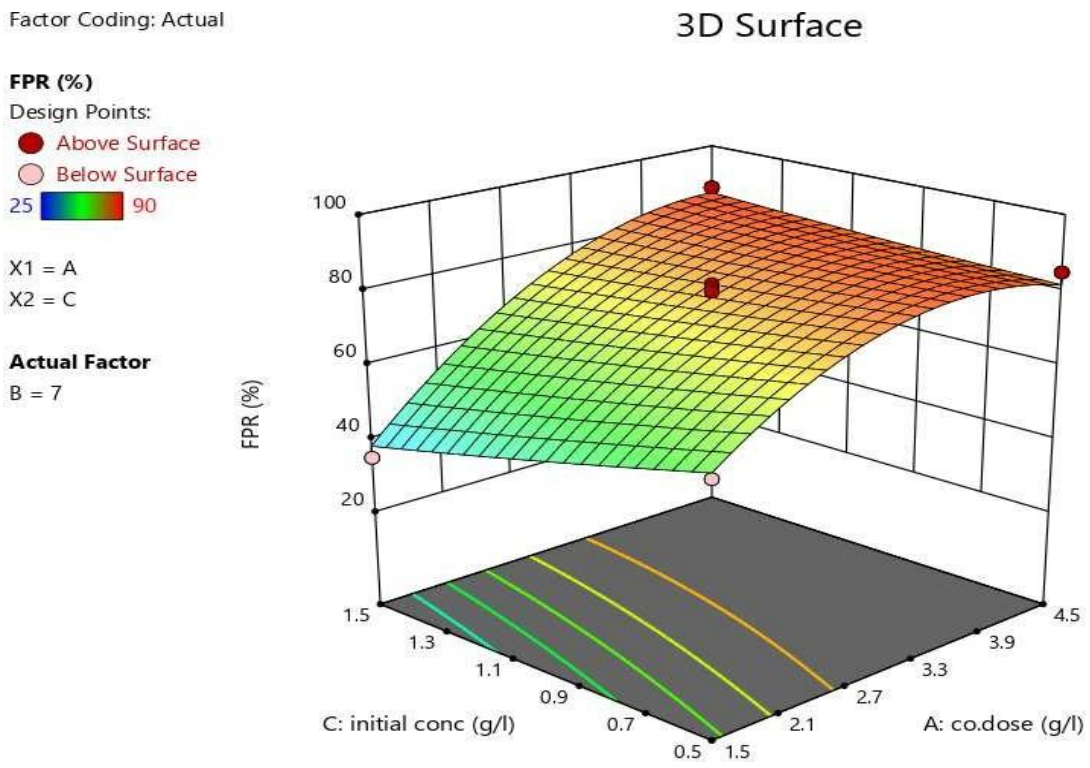

Figure 4. 14 3D interaction effect of coagulant dose and initial detergent concentration

4.7. Statistical Analysis of the Experimental Results for foaming power removal using modified coagulant (Aluminium nano particle).

The process contains three main factors like Neem extract: coagulant dose, time and initial concentration of soap with one response (foaming power). After following the above sequences of procedures, the experimental outcomes of those particular results were measured for foaming power removal. The result obtained from the Experiment was indicated as follows.

Table 4.7 Results obtained from the experiment of coagulation of aluminium nano particle

Std	Run	Factor 1 A:co.dose g/l	Factor 2 B:time hr	Factor 3 C:initialconc g/l	Response1 FPR %
3	1	3	7	1	75
10	2	3	12.5	1.5	80
9	3	1.5	12.5	1	77
8	4	3	7	1	75.5
15	5	4.5	7	1.5	68
4	6	3	1.5	1.5	55
1	7	3	7	1	75
6	8	4.5	7	0.5	78
11	9	1.5	1.5	1	47
14	10	3	7	1	75
7	11	4.5	1.5	1	79
12	12	4.5	12.5	1	98
5	13	1.5	7	0.5	82
13	14	3	12.5	0.5	84
17	15	3	7	1	75
16	16	3	1.5	0.5	62
2	17	1.5	7	1.5	76

The removal was performed by using aluminium nano particle as a coagulant at different aspects: Coagulant dose, Time and initial detergent Concentration with a constant mixing time of 30 min stirring Speed of 250 rpm, and 298k temperature.

Using Design Expert 13. Software, the data shown in Table 4.7 were examined to determine the impact of the operating parameters of coagulant dose, time, and initial detergent concentration. The percentage of removal of foam was the dependent variable employed as a response parameter. To reduce the impact of unexpected variability in the observed response due to outside variables, all tests were conducted in random order. Summary of the design for the percentage removal with

the three levels and three components. Using Design Expert 13 software, the experiments' design model is a quadratic polynomial with five centers for each block.

4.7.1. Effects of Experimental Variables for removal of foaming power (aluminium nano particle)

Table 4. 8 Analysis of variance (ANOVA) for the removal of foaming power

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	9589.36	9	1065.48	62.83	< 0.0001	significant
co. Dose	3612.50	1	3612.50	213.04	< 0.0001	
B-time	2888.00	1	2888.00	170.31	< 0.0001	
C-initial conc	112.50	1	112.50	6.63	0.0367	
AB	870.25	1	870.25	51.32	0.0002	
AC	30.25	1	30.25	1.78	0.2235	
BC	30.25	1	30.25	1.78	0.2235	
A^2	1191.92	1	1191.92	70.29	< 0.0001	
B^2	747.60	1	747.60	44.09	0.0003	
C^2	5.81	1	5.81	0.3428	0.5766	
Residual	118.70	7	16.96			
Lack of Fit	98.50	3	32.83	6.50	0.0511	not significant
Pure Error	20.20	4	5.05			
Cor Total	9708.06	16				

From the ANOVA (Analysis of Variance) Table, 4.10 results the higher F-Value and the lower P-value (<0.0001) indicate significance for the regression model. The result demonstrates that the Model F-value of 62.83 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, AB, A^2 and $B^2$are significant model terms. Values greater than 0.1000 indicate the model terms are not

significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. They are extremely essential to understanding the interaction among the independent variables. The result presented that coagulant dose (Factor A), time (Factor B), and initial concentration (C) are the main important variables in the coagulation process with P-values of < 0.0001< 0.0001 and 0.0367. Based on the value coagulant dose and time are the best important factor. From the second polynomial model, A^2 and B^2 are significant models with P-values 0.0001, 0.0003 respectively. In the case of interaction effects, AB (coagulant dose and time) is significant model terms for foam removal where the p-value is 0.0002. The Lack of Fit F-value of 1.47 implies the Lack of Fit is not significant relative to the pure error. There is a 34.95% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good.

As shown from the ANOVA result, initial detergent concentration indicates insignificant when compared with the other factors. This result confirmed that its contribution to foam removal was the lowest. In addition, the interaction effects of coagulant dose and initial concentration (AC), time and initial concentration of detergent (BC), as well as initial concentration square (C^2) did not influence the coagulation process due to their highest P-value. Their P- values were 0.2235, 0.2235 and 0.5766 respectively which is greater than 0.1 and indicates the model terms are not significant.

As shown from the ANOVA result, initial detergent concentration indicates insignificant when compared with the other factors. This result confirmed that its contribution to foam removal was the lowest. In addition, the interaction effects of time and initial concentration of detergent (BC) as well as initial concentration square (C^2) did not influence the coagulation process due to their highest P-value.

The model equations from the ANOVA result can be used to relatively compare the removal efficiency of foaming within factors and levels. The equation in terms of coded factors can be used to make predictions about foaming power removal efficiency for the given levels of each factor. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. The highest coefficients from the equation indicate the most influential factor that affects the coagulation process of foam removal. On the other side, the equation in terms of actual factors can be used to make predictions about the Removal efficiency of foam removal for given levels of each factor. The levels should be specified in the original units for each factor. This

equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

The Final Coded Equations for fatty matter removal from ANOVA result:

Foaming Power Removal Efficiency (FPR) = +77.9 +21.25* A +19.00*B +3.75*C +14.75*AB -2.75*AC -2.75*BC -18.63*A^2-13.33*B^2+1.17*C^2… (10)

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.

Final Equation of Actual Factors

Foaming Power Removal Efficiency (FPR) = -60.920+ 50.18485*co. Dose+5.25784*time-+16.1000*initial conc+1.78788*co. Dose * time -3.66667* co. Dose * initial conc -1.00*time * initial conc – 7.47778*co.dose² -0.440496*time² +4.7000*initial conc²… (11).

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

4.7.2. Model Adequacy

The regression model was found to be significant with the correlation coefficients of determination of R-Squared, adjusted R-Squared, and predicted R-Squared having a value of 0.9878, 0.9721, and0.8344 respectively as shown in table 4.11 The goodness fitness of the model was measured by a coefficient of determination R^2, which measured how well the real experimental data points have been approximated together with the regression model. As the result in a table, 4.10 expressed the value of R^2 = 0.9878 indicates the better fit of experimental data to that of the predicted one. The value of the larger Regression coefficient (R^2) approach to that of the predicted one. The value of the larger Regression coefficient (R^2) approach to 1 illustrates, the validity of the model in which it implies an acceptable agreement among the actual and predicted data. It implies that 98.78% of

the experimental variable studied attributed to the removal of foam. The Predicted R^2 of 0.9721 is in reasonable agreement with the Adjusted R^2 of 0.8344; i.e. the difference is less than 0.2. Therefore, this demonstrates that the measured data is very well fitted with a quadratic model of the predicted value. Model Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 25.488 indicates an adequate signal. This model can be used to navigate the design space.

Table 4. 9 Model adequacy measures for FPR.

Std. Dev.	4.12	**R^2**	0.9878
Mean	64.26	**Adjusted R^2**	0.9721
C.V. %	6.41	**Predicted R^2**	0.8344
Press	1607	**Adeq Precision**	25.4885

Generally, the smaller the value of the Predicted residual sum of squares (PRESS) static obtained 1607 indicates, the better the experimental data points fit the model. Moreover, the high R^2 value and p-value as well as not significant fit indicate the best prediction of the experiment solution. Therefore, the result in both tables 4.7 and 4.8 proved that, the best performance of the fitness of the model equations.

Figure 4.19 indicates the relationship between Actual and predicted values, which can be introduced from the regression model equations of a Design Expert chart based on predicted and actual percent foam removal. The straight line shows the predicted values and the small rectangles represent the actual experimental values. The straight line is very close to the actual values and has a correlation coefficient R^2 equal to 0.9878, which confirms the accuracy of the model. The result confirmed that all the actual and predicted values are close to the line of a perfect fit. Both of them showed good agreement between them.

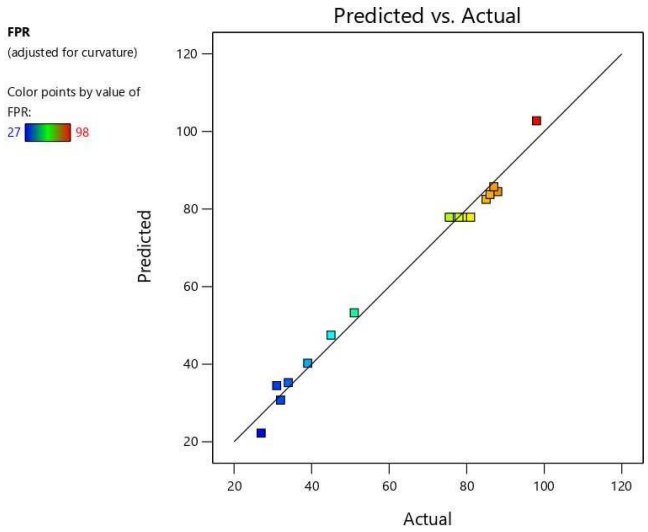

Figure 4. 15 Predicted vs Actual value foam removal plot

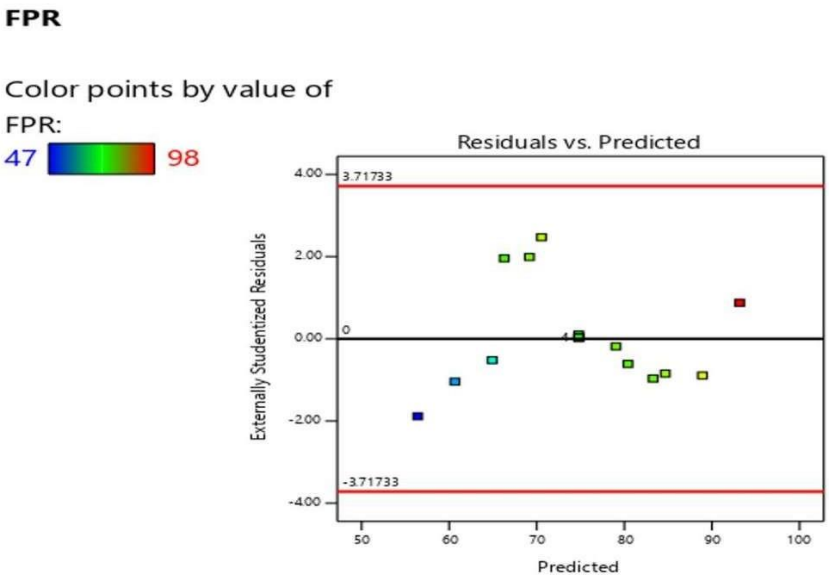

Figure 4. 16 Predicted vs Actual value of foam removal plot

If the model is correct and the assumptions are satisfied, the residuals should be structured less; in particular, they should be unrelated to any other variable including the predicted response. A simple check is to plot the residuals versus the fitted (predicted) values. A plot of the residuals versus the rising predicted response values tests the assumption of constant variance. The plot shows random scatter which justifies no need for an alteration to minimize personal error. The effects of the parameters for the percentage of fatty matter removal are to generate one-factor response and surface plots of the equation.

4.7.3. Optimization of the Response

To find the optimum value of each independent variable, four statistical metrics such as the larger regression coefficient (R^2), smaller lack of fit F-value, lower p-value, and higher sum squares have been used. The response optimization was used to identify the combination of independent variables particularly, time, initial concentration, and coagulant dose within the response of foam power removal efficiency using neem extract. The goal of the process was to obtain high foam power removal percentage. Therefore it has been set as a maximum while the process parameters such as initial detergent concentration and coagulant dose have been set as "within the range", while the time target to minimize the response surface method was used to optimize the process versus process parameters. According to the result obtained from optimizer Design-Expert version 13 software the maximum optimum removal efficiency of the foam removal was achieved 100 % % at time =12.3 hr, initial detergent concentration =1.46 g/l , and coagulant dose of 4.42 g/l.

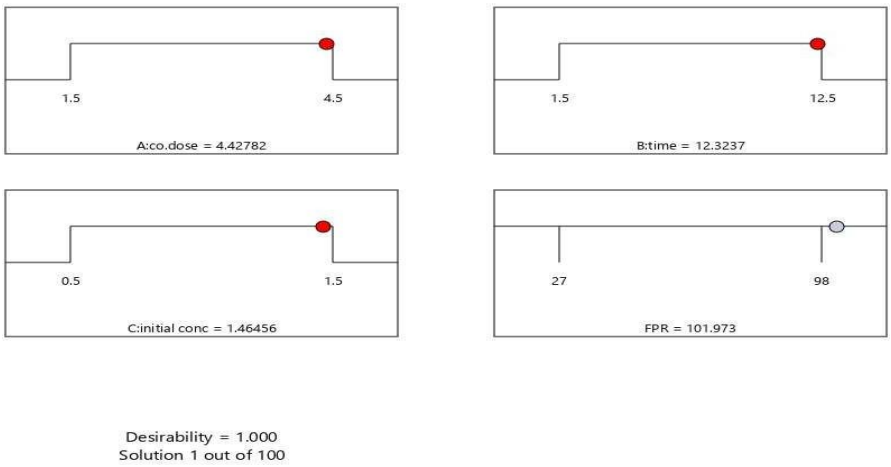

Fig 4.17 response optimization

4.7.4. Response Surface plots Interaction Effects

The effect of the interactions between the three independent input and output variables and their interactions on the dependent variables can be seen using three-dimensional (3D) response surface plots. As observed from Figure 4.22 - 4.24 indicates the Plots of three-dimensional response surfaces of the function of two variables with the response and the remaining variables at the central level of the other variables.

Figure 4.18 illustrates the 3D interaction effect of coagulant dose and time on foaming power removal efficiency at constant initial detergent concentration and mixing rate and time. As the coagulant dose increased, there was an increment in foaming power removal efficiency. However, the percentage of foam removal did not increase with increasing time at any coagulant dosage. The coagulant has reached the maximum removal capacity within or after 12 hours. In other word, the surface coverage of the coagulant was already saturated with the foam in greater than 12 hours. Therefore, it can be concluded that the percentage of foam removal was highly dependent on the coagulant dose and time but foam removal did not more depend on the contact initial concentration of detergent.

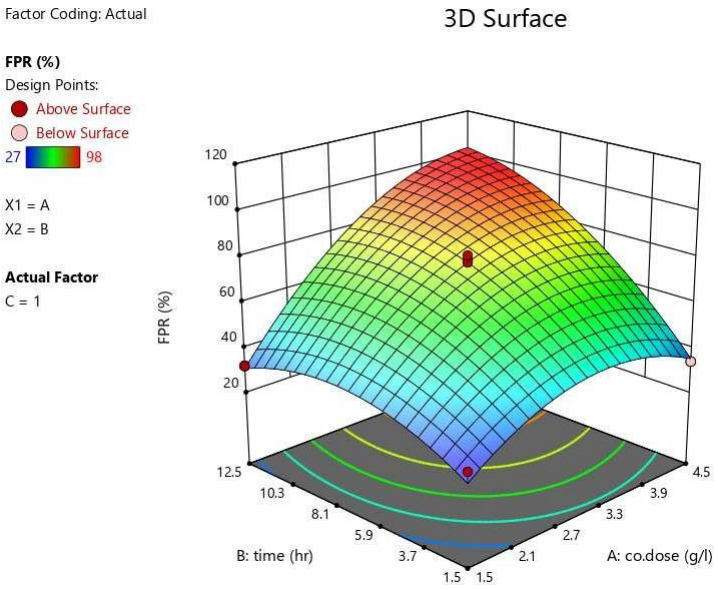

Figure 4. 18. 3D interaction effect of time and coagulant dose

Figure 4.19 indicates the interaction effects of time and initial detergent concentration on foam power removal at a fixed coagulant dose and mixing rate and time. Initially, as initial concentration

increases, the removal efficiency of foam also increases. The rise of initial soap concentration leads to increments in the removal of foam from the solution due to the occurrences of large vacant places in the neem extract coagulant. As the initial concentration beyond 1 g/l increases, the removal efficiency decreases because the vacant sites of the coagulant are occupied by the pollutant. In the other case as the time increases leads to an increase in the removal efficiency of foam and reached an optimum of 100 at 12.3 hr. The rise of time leads to increments in the removal of foam from the solution due to the high surface contact of the pollutant and the coagulant.

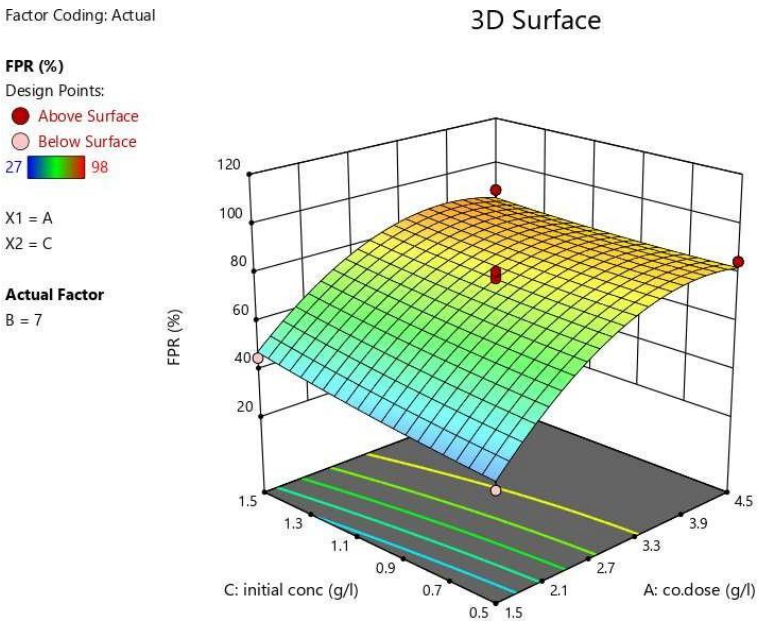

Figure 4. 19 3D interaction effect of time and initial detergent concentration

Figure 4.20 showed the interaction between initial detergent concentration and coagulant dose. As demonstrated by increasing the initial detergent concentration, the percentage removal of foam removal increased proportionally. The process happened due to a higher concentration gradient that was performed as a driving force to conquer the mass transfer between the bulk solution of active ion and coagulant surfaces of neem extract. The coagulant dose has no more effect on foam removal at a lower value of initial detergent concentration. As the initial detergent concentration increased, the percentage of foam removal also increased as a result of the coagulant dose

increased. Therefore, the coagulant dose was the main independent variable that affects the removal of foam from the solution.

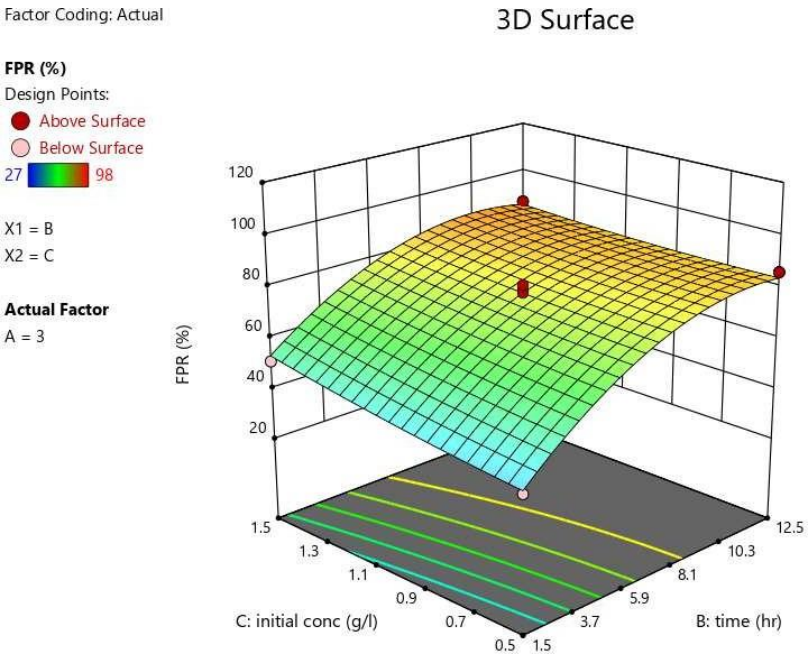

Figure 4.20 3D interaction effect of coagulant dose and initial detergent concentration

CHAPTER FIVE

5. Conclusion and Recommendations

5.1. Conclusion

This research work focuses on the extraction, purification, and characterization of Neem seed for coagulation-flocculation process and the modification of coagulant aluminum Nano particle for the application of detergent wastewater treatment. Both TLC and FTIR result analysis confirmed that the Neem seed extract was purified qualitatively and detergent wastewater pollutant was successfully trapped by bio-based coagulant and AlNPs. In addition, the peak at 1420; 1270 and1050 cm^{-1} after the coagulation process was responsible for detergent ion, which shows Al^{+3} (COONa). Detergent wastewater was used as a model pollutant. The sample of wastewater before and after treatment was characterized for its physicochemical properties. The chemical oxygen demand in the raw sample of wastewater was found to be 1500 mg/L. The pH, foaming power and active matter values of the effluent were on average, 9.7, 10g/L and 0.8g/m^{-3}, respectively. The treatment process was carried out at different settling time (1.30-12.30hr), coagulant dose (1-4.5g/l) and initial detergent concentration (1g/L) in the bio-based. The maximum foam removal efficiency was attained at settling time (10.30hr) and coagulant dose (3.5g/l) which was 90% and then coagulation-flocculation was performed using ferric chloride with the same parameter as neem extract and the maximum foam removal was 92% attained at time 12 hr and dose 3.2g/. Modification of the natural coagulant was done (aluminium nano particle) to improve the process performance of coagulation-flocculation as well. The maximum foam removal was 98% (time 11.30hr and dose 3g/l) .The result shows the interaction effect of those parameters had a significant effect on the removal process. The Response Surface Method (RSM) was adopted to explore the model equation for foaming power removal efficiency. The central composite design was selected to study the effect of variation in coagulant dose, time, and initial soap concentration of the coagulation process. The validation of the model using ANOVA analysis verified that the quadratic model selected is accurate, and statistically significant with a p-value less than 0.05. The optimum removal efficiency of neem seed extract was obtained 77.65% % at time= 10.77 hr, initial concentration =1.372 g/l, and coagulant dose 2.87 g/l, and the optimum removal efficiency of aluminium nano particle was obtained 98.5 % % at time= 12.3 hr, initial concentration =1.46 g/l,

and coagulant dose 4.42 g/l. The result shows the interaction effect of those parameters had a significant effect on the coagulation process.

The batch experimental studies for real wastewater from Bekas chemicals as a detergent wastewater source. The result investigated showed that 85 % of its foam was removed from wastewater by using aluminium nano particle. The reduction in removal efficiency from that synthetic wastewater was due to a large number of competing pollutants within the waste.

5.2. Recommendation

For future work, the following recommendations are suggested based on the result obtained.

- Concentration of azadiracthin must be analyzed using known concentration of azadiracthin (pure) by using calibration curve method using HPLC. The lack of pure azadiracthin in the market limits this study from determining the concentration.
- It is better to study the removal efficiency of this bio-based coagulant on detergent wastewater by varying the other operational variables like agitation speed, mixing time, and temperature in detail to improve the treatment efficiency of the system.
- It is better to study neem extract and aluminium nitrate by varying their ratio.
- It is recommended to optimize the other responses like, pH, COD and active matter.
- It is better to characterize AlNPs using XRD and SPA.
- Future research should be done using this technology in combination with other cost-effective treatment methods to further treatment to improve the removal efficiency of foaming.

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Aklilu Gebrehawaria, AAU, *AAiT – ETHIOPIA 20017*

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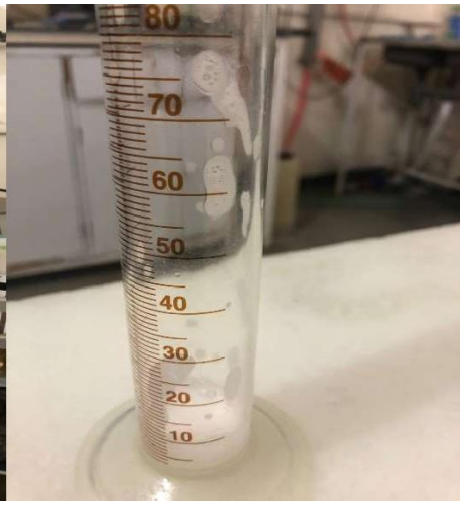
Appendix

Appendix A: Photographic Representation of laboratory work

Sieving

crushed Neem

COD reactor



foaming measuring cylinder