Optimisation of dissolved air flotation (DAF) for separating industrial mineral oil from water

A dissertation submitted in fulfilment of the academic requirements for the degree of

Master of Engineering

Department of Chemical Engineering,

Faculty of Engineering and the Built Environment,

Durban University of Technology

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Supervisors: Prof S. Rathilal & Ms K. Robinson

Preface

This project was carried out under the joint support from Durban University of Technology, Department of Chemical Engineering and FFS Refiners (Pty) Ltd, under the supervision of Prof. Sudesh Rathilal and Ms Kate Robinson as respectively affiliated. The batch DAF jar test experiments were conducted at Wiggins Umgeni Water, Process Evaluation Facility (PEF) centre. The yield analysis of the soap oil and grease (SOG) was carried out at the FFS Refiners production laboratory. This project was completed over a stipulated period of 21 months, from April 2016 to January 2018.

I, **Emmanuel Kweinor Tetteh**, hereby declare this research report titled "**Optimisation of dissolved air flotation (DAF) for the separating industrial mineral oil from water"** is my own investigation results under the guidance of my supervisors, and unless otherwise indicated or acknowledged. The results presented has not been submitted in part or in full to any other University or Institute for any award of degree. Furthermore, I have indicated in detail the part that is reproduced of which I am an author, and have fully listed such publications and others been acknowledged in the reference section.

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Declaration

I, **Emmanuel Kweinor Tetteh**, the undersigned candidate declare that

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As the candidate supervisors, we do agree to the submission of this dissertation that has orally been defended.

Prof. Sudesh Rathilal (Main supervisor) Ms Kate Robinson (Co-supervisor)

Signature of supervisor:…………….. Date:…………………….

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Dedication

This dissertation is dedicated to my lovely parents Mr Felix Tetteh and Mrs Mary Amoah Tetteh, my siblings and my good friend Light Josephine Amgbo for their support and guidance.

Abstract

Industrial mineral oil wastewater from oil refineries and petrochemical processing poses a major environmental concern. Effluents from these processes is usually poor as it is heavily polluted, thus have high chemical oxygen demand (COD), soap oil and grease (SOG), turbidity, total suspended solids (TSS) amongst others. This wastewater, if discharge without treatment, causes severe pollution, oxygen depletion, and imbalanced ecosystem and human health risks. The main aim of this research was to modify, optimise and evaluate the performance of a continuous process using dissolved air flotation (DAF) pilot to treat wastewater from a local South African oil refinery wastewater treatment plant (WWTP) with the benefit of recovery of the oil from the wastewater.

The study evaluated the feasibility of using different acids and coagulants. One factor at time (OFAT) approach was used on the DAF jar tester to identify the most important variables that affects the DAF treatability performance. The factors considered were; pH, flotation time, coagulant dosage, air to water ratio and air saturated pressure. The ranges considered for the factors were pH (4−6), flotation time (5−15 minutes), coagulant dosage (10−50 mg/L), air to water ratio (5–15%) and air saturated pressure (300–500 kPa). The key process operating parameters obtained from the OFAT were optimised using the Box Behnken design (BBD) adapted from response surface methodology (RSM). The BBD used had three levels, three factors and five centre points. This was employed to establish the relationship that existed between the water quality (contaminants) and the key interacting factors of the DAF jar tester, thus employing the most applicable combination of the factors on a continuous DAF pilot plant.

The study was configured into two; Acid – Coagulation-DAF (pre-treatment) and Acid –DAF – Coagulation (post treatment). Three acids were investigated for their efficiency in the pre-treatment step, while four cationic inorganic coagulants and three polymeric organic coagulants were used both for the pre and post treatments.

The OFAT experiments resulted in more than 75% removal efficiency of COD, SOG, TSS and turbidity. The removal efficiency was obtained at the following optimum values of pH 5, flotation time of 15 minutes at a coagulant dosage of 50 mg/L and an air to water ratio of 10% and finally, air saturated pressure was 350 kPa. On the other hand, BBD results showed 85% treatability performance at a lower coagulant dosage (30–45 mg/L), moderate air saturator pressure (300–425 kPa), and air-water ratio (8–12%) on the batch scale. While on the continuous process, the optimum coagulant dosage was around 100–180 mg/L. From the BBD results, the interacted factors for consideration were the air saturated pressure and coagulant dosage. These factors enhanced process control. The validation of all the response quadratic models were in good standing with the analysis of variance (ANOVA). The experimental results and the predicted models results agreed at 95% confidence level, finally, the models were significant and verified.

Comparative studies of the pre and post treatment showed that 1 M H_3PO_4 was the most effective, economical and environmentally friendly acid to be used for both processes. Two cationic inorganic (alum and ferric chloride) and two polymeric organic (Z553D-PAC and Zetag32-FS/A50) coagulants were found to be effective with remarkable performance to destabilise and neutralise the oil droplets to coalesce larger flocs to enhance the oil-water separation. Far and above, the cationic inorganic coagulants were more cost effective than the polymeric organic coagulants, even though, the inorganic coagulants were cheaper they had higher conductivity (salts), thus raising environmental concerns.

In conclusion, the pre-treatment of the DAF process yielded more recovery of water and oil, and hence this step was economically viable. The RSM demonstrated to be more effective and reliable in finding the optimal conditions of the DAF process than the OFAT method. Thus, the RSM offered a better option than the OFAT, because it included both the interactional and individual factors.

Author’s publications

The present author was the corresponding author in all the papers, while the co-authors assisted in writing by making valuable comments and corrections. The author was also the presenter at both the local (Paper -VIII) and international (Paper-IX) conferences.

I. **Tetteh, E.K**. and Rathilal, S., 2018. Decontamination of oil refinery wastewater evaluating acidification techniques, Pollution Research (PF-F-999 in press),37(3):75-81

II. **Tetteh, E.K**. and Rathilal, S., 2018. Effects of a polymeric organic coagulant for industrial mineral oil wastewater treatment using response surface methodology (RSM). Water SA, 44 (2), 155-161.

III. **Tetteh, E.K.** and Rathilal, S., 2018. Evaluation of the Coagulation Flotation process For Industrial Mineral Oil Wastewater Treatment Using Response Surface Methodology (RSM). *International Journal of Environmental Impacts*, 1 (4): 491-502. DOI:10.2495/EI-V1-N4-491-502

IV. **Tetteh, E. K.,** Rathilal, S. and Robinson, K., 2017. Treatment of industrial mineral oil wastewater – effects of coagulant type and dosage. *Water Practice and Technology*, 12 (1): 139-145. https://doi.org/10.2166/wpt.2017.021

V. **Tetteh, E. K.** and Rathilal, S., 2017. Application of Response Surface Methodology (RSM) -Reduction of Industrial Wastewater Chemical Oxygen Demand. In *CBU International Conference Proceedings*, 5:1226-1233. Central Bohemia University. http://dx.doi.org/10.12955/cbup.v5.1101

VI. **Tetteh, E. K**., Rathilal, S. and Chollom, M.N., 2017. Pre-Treatment of Industrial Mineral Oil Wastewater Using Response Surface Methodology. *WIT Transactions on Ecology and the Environment*, *216*:181-191 .DOI:10.2495/WS170171

VII. **Tetteh, E.K.,** Rathilal, S. and Chollom, M.N., 2017. Treatment of Industrial Mineral Oil Wastewater-Optimisation of Coagulation Flotation process using Response Surface Methodology (RSM). *International Journal of Applied Engineering Research*, *12*(23), 13084-13091.

VIII. **Kweinor Tetteh**, **E.**, Rathilal, S. and Chollom, M.N., 2017. Evaluation of dissolved air flotation-organic coagulants for the treatment of industrial mineral wastewater, Books of Abstracts 7th International Colloids Conference, Barcelona-Spain 18-21 June 2017 (COLL2017_0577)

IX. **Kweinor Tetteh, E.,** Rathilal, S., and Robinson, K., 2016. Effects of Polymeric Organic Coagulant for Industrial Mineral Oil Wastewater Treatment Using Response Surface Methodology (RSM). Books of Abstracts, International Conference on Environment, Materials and Green Technology 24-25th November 2016 – VUT Southern Gauteng Science and Technology Park, Sebokeng South Africa (ISBN 978-1-77012-141-6)

X. **Kweinor Tetteh, E.,** and Rathilal, S., 2018. Response surface optimization of oil refinery wastewater treatment process, Environmental Engineering Research (Under review- EER-D-18-00179)

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Nomenclature

AC	Aluminium Chloride
Alum	Aluminium Sulphate
API	America Petroleum Industry)
BBD	Box-Behnken design
BTEX	Ethylbenzene and xylene
COD	Chemical oxygen demand
DAF	Dissolved air flotation
df	Degree of freedom
DOE	Design of experiment
EC	Conductivity
FC	Ferric Chloride
FS	Ferric Sulphate
G	Velocity gradient
HLR	Hydraulic loading rate
LOF	Lack of fit
MOW	Mineral oil wastewater
NTU	Nephelometric turbidity units
OFAT	One factor at a time
PAS	Polyaluminium sulphate
RSM	Response surface methodology
SOG	Soap oil and grease
TDS	Total dissolved solids
TSS	Total suspended solids
WWTP	wastewater treatment plant
Z553D	Polyaluminium chloride
Zetag32-FS/A50	Polyferric sulphate

CHAPTER 1 -INTRODUCTION

1.1 Background

Water scarcity is a critical issue in most parts of the Globe because water is not equally distributed; some countries have a surplus supply while others have limited supply. South Africa is a semi-arid country, thus it is physically stressed about the supply of fresh water. Thus threatening the livelihood of many sectors such as agriculture, households, food supply and energy security which has a great impact on its economy (Metcalf and Eddy, 2003; Diya'uddeen et al., 2011; Santos et al., 2015; Pintor et al., 2016; Saththasivam et al., 2016; Zheng et al., 2016). This scarcity is driven by factors such as climate change, and high usage of fresh water over the years. Others includes an increase in population and industrial activities, which place a high demand on the water supply. The activities from the industries and household activities produces a high pollution load, which are in most instances not properly treated before they are discharged into the environment. Discharging such polluted waters into the receiving water bodies and environment reduces the quality of fresh water (Jamaly et al., 2015).

Most industries consume large volumes of water. The intake of fresh water in most industries is higher than the rate at which it is replenished (Sahu and Chaudhari, 2013). Industrial sectors such as the oil producing and textiles industries are amongst the highest consumers and as such, some of the greatest producers of pollution. For instance, the specific water intake (SWI) of local refineries vary between 0.51 and 0.67 m^3/t of crude (Saththasivam et al., 2016; Yu et al., 2017). Due to these existences, most regulating bodies are putting modalities in place to curb the generation of pollution. This is by introducing strict guidelines to reprocess wastewater for reuse and compelling them to pay more for fresh water intake and wastewater generation (Altaher and Alghamdi, 2011; Diya'uddeen et al., 2011; van Wilgen and Wannenburgh, 2016). This has become an important matter of concern to make available more water for appropriate usage (Tsagarakis et al., 2003; van Wilgen and Wannenburgh, 2016; Demirbas and Kobya, 2017).

1.2 Separation of Oil-water

The refining sector produces some of the most important products that have helped alleviate the standard of living in every modern society. Nevertheless, the production stages produce some of the most recalcitrant environmental pollutants, such as oil, which is constituted in the industrial mineral oil wastewater (MOW) (Jamaly et al., 2015). As such, the continuous growth of petrochemical industries and widespread utilization of oil-related products have increased the threat of oil pollutions. Pollutions from MOW degrades the quality of water sources hence the need to separate the oil from the water and treat this waste before discharging into receiving bodies (Al-Shamrani et al., 2002; Metcalf and Eddy, 2003; Sahu and Chaudhari, 2013; Pintor et al., 2015). MOW is characterized to have smaller size oil droplets (less than 10 µm), organic and non-organic matter with low charged density which does not settle out of suspension by gravity within a reasonable period (Daud et al., 2015; Yu et al., 2017). Hence, the application of sedimentation is not feasible since the oil droplets does not have an economical settling rate. In practice, the chemical treatment process coupled with DAF has gained much interest over sedimentation in the mining, potable water and wastewater treatment industries.

The effectiveness of most conventional methods to treat MOW is limited due to the variation in composition and properties of the MOW (Canizares et al., 2008; Saththasivam et al., 2016). For instance, the discrepancy in the concentration of oil emulsions ranging from 50–1000 mg/L, based on its originated source becomes quite challenging in phase separation by some of the conventional practices (Jamaly et al., 2015; Pintor et al., 2016; Yu et al., 2017). This is because the oil droplet size and the relative charge density will have a vast influence on the mechanism of oil-water emulsified phase separation. According to Santos et al. (2015), treatment of MOW should not be done with a single method alone but rather a combination of various unit operations to achieve acceptable treatment outcomes. This has led to a great demand for advanced, cost-effective as well as environmentally friendly treatment techniques for MOW to meet ever-stricter environmental regulations (Tsagarakis et al., 2003; Sahu and Chaudhari, 2013; Jamaly et al., 2015; Munirasu et al., 2016; Pintor et al., 2016). Furthermore, some of the well-known conventional methods such as gravity separation, coagulation, acidification, biochemical and air flotation treatment is limited in the treatment of stable oil-water emulsions that contain fine oil droplet sizes less than 20 µm alone, but can be combined with membrane technology to enhance separation efficiency

(Pintor et al., 2016; Yu et al., 2017). However, it has been assessed that about 15 to 20% of the cost of supplying water is usually incurred at the treatment phase due to chemical usage, energy and maintenance (Metcalf and Eddy, 2003; Adlan et al., 2011; Edzwald, 2011; Mousa and Hadi, 2016; Demirbas and Kobya, 2017). Remarkable optimisation strives to attain suitable water quality while minimising operational cost.

Meanwhile, the development of the America Petroleum Industry (API) separator and flotation over the decades have been used to separate fine oil droplets from water (Zouboulis and Avranas, 2000; Zheng et al., 2015; Pintor et al., 2016). However, it has been observed that the treatment of stable oil emulsions is not achievable when a gravity separation or sedimentation process is used (Edzwald, 2010; Pintor et al., 2016). On the other hand, researchers have reported that the use of dissolved air flotation process (DAF) is more effective for the reduction of low-density particles or oil droplets. In the same vein, removal of turbidity, colour, total suspended solids (TSS), chemical oxygen demand (COD), and soap oil and grease (SOG) of over 80% from MOW is achievable when coagulation is combined with the DAF process (Al-Shamrani et al., 2002; Behin and Bahrami, 2012; Karhu et al., 2014; Jamaly et al., 2015; Safari et al., 2015; Saththasivam et al., 2016; Tetteh et al., 2017).

It is anticipated that effective DAF removal of oil emulsions will rise by increasing the droplet size and decreasing the bubble size or the air saturator pressure (Al-Shamrani et al., 2002; Lakghomi et al., 2015). Edzwald (2010) then suggested that research is required especially on the ability of DAF to serve as a pre-treatment process with coagulation to remove dissolved organics and other contaminants before the downstream process. Thus, coagulation or chemical addition breaks the stable oil - water emulsion to be entrapped by the air bubbles to form larger oil droplets that enhances the performance of the DAF. Therefore, this research study was initiated to evaluate the hypothesis of optimising acidification and coagulation chemistry, and the key operational factors in the DAF process to improve the treatment performance of MOW.

1.3 Coagulation-DAF techniques

The main principle behind the DAF techniques is the formation of upward flow air bubbles, which can be operated in three modes; full-flow, split-flow and recycled-flow pressurisation. In wastewater treatment applications, the recycle - flow pressurisation mode is suitable as the other modes could be difficult to be operated with the coagulation process (Karhu et al., 2014). However, the performance of a DAF process is primarily dependent on efficient chemical pre-treatment for the generation of stable flocs (Al-Shamrani et al., 2002).

Conservatively, the most physicochemical treatment process frequently used includes acidification, coagulation, and flotation (Al-Shamrani et al., 2002; Atadashi et al., 2011; Tetteh et al., 2017). Flotation is a gravity separation process, which involves the transfer of the oil droplet flocs to the surface by means of bubble attachment. The driving force for the separation results from the buoyancy difference of the charged oil droplets attached to the surface of the air bubbles (Al-Shamrani et al., 2002; Abdelaal, 2004; Edzwald, 2010; Lakghomi et al., 2015).

The pH adjustment enables the breaking of the oil emulsion surface tension, neutralization and destabilization to liberate the charge oil droplet for precipitation. Although the addition of the coagulant increases the size of the oil, droplets and collision ability to entrap the air bubble. This then lowers the apparent density of the emulsion, allowing the agglomerated bubble - oil droplet to float to the surface (Edzwald, 1995; Al-Shamrani et al., 2002; Bensadok et al., 2007).

The latest development of flotation in wastewater treatment consists of three conventional techniques namely electro-flotation, induced or dispersed air flotation and DAF (Edzwald, 2010). The application of DAF is advantageous due to its ability to generate micro-bubbles as a carrier phase to enhance the separation of micro oil droplets from the water (Edzwald, 1995; Welz et al., 2007; El-Gohary et al., 2010; Rattanapan et al., 2011). In DAF techniques, the oil droplets are separated by adhering to the surface of rising air bubbles. In addition, it has proved to be effective in both practical and consistent separation approaches for the removal of soap, oil, and grease (SOG), as well as other contaminants from water (Saththasivam et al., 2016; Tetteh et al., 2017).

The chemical and physical techniques such as mechanism have been widely used in industrial wastewater systems for separating oil from water due to its effectiveness. In addition, the principal focus of the addition of coagulating chemicals for physical separation processes is to effectively reduce the workload to the downstream treatment (Al-Shamrani et al., 2002; Diya’uddeen et al., 2011; Jamaly et al., 2015). More so, aluminium and iron salts are widely used in most of the first and third world countries for the coagulation-DAF treatment for potable water and wastewater treatment (Hosny et al., 2016; Tetteh et al., 2017;

Yu et al., 2017). For instance, the coagulation-DAF mechanism was used in treating oil-water emulsions stabilized with a non-ionic surfactant. Ebrahimi et al. (2010) then reported an oil removal of up to 99.3% and 99.9% using aluminium sulphate and ferric sulphate respectively. In a similar study, more than 95% of the emulsified oil was removed when ferric chloride was used to optimise a DAF for the treatment of oil-water emulsions (Zheng et al., 2015). In view of this, the selection of the right type of coagulant depends on the sensitivity and its operating conditions. Thus application of coagulant dosage in the right proportion to initiate neutralization, stability and mobility of the colloidal oil droplets is necessary to enhance treatment effectiveness (Sarika et al., 2005; Bolto and Gregory, 2007; Hosny et al., 2016; Tetteh et al., 2017).

Schalkwyk et al. (2016) reported on a pilot plant in Wahnbach Reservoir, Germany on the evaluation of the effects of coagulation on the performance of DAF. The authors reported that coagulant dosage and pH had a stronger influence on DAF performance than physical conditions. However, some other factors like reaction time, air-water recycle ratio, energy input and the air saturator pressure had influence on the separation efficiency (Rodrigues and Rubio, 2007; Edzwald, 2010; Painmanakul et al., 2010; Dassey and Theegala, 2011; Rattanapan et al., 2011; Karhu et al., 2014; Lakghomi et al., 2015). Nevertheless, the destabilization of the oil emulsion is more important than the floc size. The chemical or coagulation process increases the DAF separation efficiency through either a charge or a sizing mechanism (Edzwald, 2010). Thus, the charge mechanism transforms the surface charge of the oil droplet while the sizing mechanism increases the size of the oil droplets resulting in a higher possibility of collision between the oil droplets and the air bubbles (Al-Shamrani et al., 2002; Abdelaal, 2004; Li et al., 2007; Edzwald, 2010; Karhu et al., 2014). According to Hempoonsert et al. (2010), coagulating agent and dosage, ionic strength, pH and the nature or chemistry of the MOW can be used as a general criteria to access the performance of the coagulation-DAF process (Al-Shamrani et al., 2002). There is also variation in the charge density and oil droplet size, which affects the coagulation-DAF mechanism. Hence, to increase the oil droplet charge size and the bubble generation, the coagulant type (organic or inorganic) and the flow pressure to the DAF must be selected appropriately (Tsagarakis et al., 2003; Li et al., 2008; Yang et al., 2010; Diya’uddeen et al., 2011; Daud et al., 2015; Pintor et al., 2016). However, this has its own limitation with high sludge production and the high cost of operational chemical procurement (Metcalf and Eddy, 2003; Bolto and Gregory, 2007; Hosny et al., 2016; Demirbas and Kobya, 2017).

The DAF process, being a solid-liquid or liquid-liquid phase separation unit, is widely utilized in both drinking and oily water treatment. Unlike sedimentation, DAF works with rising velocity by first dissolving air into water at high pressures and introducing it into the bottom of the DAF flotation zone. Dissolved microbubbles are formed due to the impulsive drop in pressure, which along the way attaches to flocs as they rise to the surface of the clarifier to be removed (Canizares et al., 2008; Rattanapan et al., 2011; Daud et al., 2015).

The pioneering research on application of DAF for clarification of water was industrialized for improving drinking and industrial water in the 1960s in Sweden and Finland, and also autonomously in Namibia, Australia, Canada, and South Africa. For the past 30 years, the full-scale application of DAF in South Africa is known to be economically viable alternative in improving water quality (Zabel, 1985; Welz et al., 2007; Schalkwyk et al., 2016; van Wilgen and Wannenburgh, 2016). For instance, Umgeni Water in the Kwazulu Natal Province of South Africa has three large treatment plants with capacities between 350 and 10000 mega liters per day coupled with DAF for clarification of 75% of the water supply to the community (Demirbas, 2007; Schalkwyk et al., 2016).

Moreover, to ensure the effectiveness of DAF, modification is required to align with other techniques. Because, the DAF process involves a number of physical phenomena occurring simultaneously, some of the operating parameters have a high influence on the process. These operating parameters have to be identified, and a relationship between the response (water quality) and the multiple operating parameters established (Edzwald, 1995; Hempoonsert et al., 2010; Dassey and Theegala, 2011; Behin and Bahrami, 2012).

1.4 Problem statement

Besides refining of oils, most refining industries are compelled to treat and reuse their wastewater to enable them to meet the policies on energy and water for vision 2030 (Schreiner and Hassan, 2010; McCafferty et al., 2012; Jamaly et al., 2015; Munirasu et al., 2016). In this view, the total overhauling of wastewater treatment plants (WWTPs) must meet the requirement of effluent discharged to the sewer, which should contain SOG below 50 mg/L (DWAF, 1996; SANS-SABS, 2007). In this case, an effluent treatment plant with a capacity of 20 kilolitres per hour with the combination of force-feed evaporation, gravity separation (API), DAF and post coagulation treatment methods are currently used by a local South Africa oil refinery industry located at Durban in the Kwa-Zulu Natal province to separate oil from water. Moreover, the plant capacity is not consistent with the actual design to match up with the charge-loading rate leading to the backlog and poor quality of water and oil recovered (FFS 2016). In addition, the DAF being the most important physicochemical separation unit is facing a great challenge in removing the oil to an expected requirement. Due to the variations in the MOW sources; which are obtained from stocks of ship slops; refinery off-specs and other waste streams resulting in a difference in droplet size and charge density. This increases the workload for further chemical treatment to remove the emulsified oil. This has some consequences, which includes: generation of huge amounts of sludge, increased operational cost and eventually posing a problem in the downstream to meet the strict environmental legislation and disposal by-laws (ISO 14001:2004)(SANS-SABS, 2007; Welz et al., 2007; Edzwald, 2010; Amaral Filho et al., 2016). Over the years, the research on DAF has regularly been on effects of pre-treatment coagulation (Edzwald, 2010), floc-bubble interactions and hydrodynamics (Edzwald, 2011), clarification flotation zone configuration and hydraulic loading rates (HLRs) (Zouboulis and Avranas, 2000; Edzwald, 2010; Painmanakul et al., 2010; Lakghomi et al., 2015). Furthermore, little research has been done on optimising multiple parameters on the coagulation-DAF process (Behin and Bahrami, 2012). Thus, there is limited information on simulating experimental data to establish a relationship of the input parameters as a function of the response water quality depending on the source of the water (Lakghomi et al., 2015). Hence, a strategy for optimisation in the wastewater treatment process to improve upon the performance with less cost for the end usage of the water is necessary.

Therefore, in this study, the effects of different coagulant types and the DAF performance was evaluated to maximise the separation of the oil from water, besides identifying the most influential operating parameters by characterizing the wastewater quality before and after the treatment process. To further buttress the effectiveness of the DAF process, process parameters were optimised using design of experiment based on response surface methodology (RSM). The RSM as an effective optimisation tool was used to identify and understand the relationship that existed between multivariables on the response (water qualities) using quantitative data obtained from the experimental design (Baş and Boyacı, 2007; Ferreira et al., 2007; Tir and Moulai-Mostefa, 2008; Tetteh and Rathilal, 2017).

1.5 Aim and objectives

The main aim of this research was to modify, optimise and evaluate the performance of a continuous treatment DAF pilot process to treat wastewater from a local South African oil refinery wastewater treatment plant (WWTP) with the benefit of recovering the oil from the wastewater. The study was configured into two; Acid – Coagulation-DAF (pre-treatment) and Acid –DAF – Coagulation (post treatment). The measure for the removal of COD, SOG, TSS and turbidity were used as the key performance indicators. One factor at a time (OFAT) approach and RSM were employed to evaluate the following specific objectives:

(i). To evaluate three different acidification treatment effects with an existing polymeric coagulant on the effluent in terms of pH adjustment (2 to 10).

(ii). To evaluate the effects of air saturator pressure (200 to 600 kPa), flotation time (15–30 minutes) and air to water ratio (5 to 20%) for bubble generation with an existing polymeric coagulant on the effluent.

(iii). To evaluate and compare the feasibility performance of four cationic inorganic and three polymeric organic coagulants on the effluent in terms of coagulant dosage based on simple economic analysis.

(iv). To use the superlative cationic inorganic and polymeric organic coagulants to determine the more significant configuration (pre or post treatment) with regards to the DAF effectiveness.

(v). To evaluate and optimise appropriate combination factors with RSM on the effluent using DAF jar tests.

(vi). To evaluate the relationship that exists between the effluent qualities and the key interacting factors from the DAF jar tests with RSM being employed on the DAF pilot plant.

1.6 Approach

A feasibility study was done on a DAF unit currently in the primary treatment stage of a local South African oil refinery industry located at Durban in the Kwa-Zulu Natal province. This was done to determine the most effective operating conditions to enhance the possible design and modification of the DAF pilot plant. The oil waste concentration has been the main pollutant, and the physiochemical treatment has been inefficient in reducing the oil droplet concentration to the expected discharge limit (50 mg/L). The MOW sample obtained from the local oil refinery plant before and after the DAF was characterised. This was carried out to determine the most effective parameters to define the range of which it operates such as the pH, coagulant dosage, and the air saturator pressure base on the water chemistry.

For the first stage, a DAF jar tester was used to evaluate the acidification treatment performance for the three different acids using the existing polymeric organic coagulants as a controlling coagulant and NaOH for pH adjustment with characterised feed entering the main effluent plant, to identify the most appropriate acid. This was followed by the bubble generation performance, which is the effects of air saturator pressure and air to water ratio. In addition, improving the water quality with the most economical coagulant, involved the simple cost comparative study based on the coagulant dosage for the four inorganic and three polymeric organic coagulants.

The second stage was carried out using the Box-Behnken design (BBD) matrix adapted from the RSM to design the experiment, and analyse the results statistically in order to develop an empirical model to establish the relationship between the input multi-variables and the response water qualities on the DAF jar tester. This was done to determine the sensitivity of the coagulation-DAF operating parameters using the DAF jar tester. Finally, the DAF pilot plant’s most sensitive operating parameters were optimised with most superlative cationic inorganic and polymeric coagulants, which were found to be economically viable. The experiments was conducted according to the generated BBD matrix.

The following effluent parameters: pH, COD, SOG, TSS, and turbidity were analysed as performance criteria using standard methods. Although high conductivity (EC) and total dissolved solids (TDS) were also analysed for the influent, it was found that the DAF performance had no significant effects on their removal, hence it was ignored. It is deduced that, optimisation of wastewater treatment is complicated; the performance of a single process affects the subsequent process due to interdependency. It is therefore advantageous to ascertain suitable designs or operating regimes by taken into account the interactional effects of the process conditions on the response (specified water quality).

1.7 Structure of dissertation

This dissertation consists of five chapters as follows:

The first chapter is the introduction; it presents a brief background related to the separation of oil from water and the problem statement that motivated this study to optimising the DAF unit for MOW treatment.

Chapter 2 gives a review of the literature related to the study where the available and emerging physiochemical treatment technologies for oil refinery wastewater are reviewed. It also introduces types of DAF and coagulants, their shortcomings and the need for improvement in relation to mineral oil wastewater characteristics as well as the key water quality that is regulated. It also provides the knowledge on design of experiment, a tool for process optimisation, as used by other experimenters.

Chapter 3 presents the research methodology thus the materials, methods, and description of equipment and procedures used for the characterization and treatment of the effluents. It also describes the analytical and data simulation procedure for the process optimisation.

Chapter 4 presents the results and discussion from the experiments. The results are presented and discussed as follows: the effects of acidification treatment on the water quality, the bubble generation, effects of air saturator pressure and air to water ratio for DAF performance regarding the water parameter of interest. Likewise, the economic viability of different inorganic and polymeric organic coagulants performance was produced. In addition, the sensitive operating parameters of the coagulation-DAF mechanism using DAF jar tester was evaluated and finally the pilot DAF plant operating parameters was optimised with RSM.

Finally, Chapter 5 provides the conclusion and recommendations. It summaries the significant findings from the study and gives a recommendation for further research and decision-making.

CHAPTER 2 -LITERATURE REVIEW

2.1 Introduction

The DAF is an effective separation process, which uses micro-bubbles as a carrier phase for separating oil from water. In general, coagulation and flocculation requirements for oil-water separation by DAF are similar to solid-liquid separation for sedimentation. This chapter presents the literature review of separation mechanisms related to coagulation and flotation for inorganic and polymeric organic coagulant floc formation for effective DAF of a local oil refinery effluent plant. A literature survey on issues related to oil in water, characteristics of the MOW, contaminants of concern, and its global environmental impact is studied. An extensive review was conducted to investigate some conventional techniques, most influential factors of coagulation-DAF; mechanism types and limitations of using those processes as a focus. Finally, the knowledge of response surface methodology; the design of experiments of multiple factors interactions on response degree of water quality is provided. At the end of the chapter, a summary of the literature review is presented and the gap in knowledge of this study that forms the basis of optimisation of the DAF is identified.

2.2 Industrial MOW treatment and its environment impacts

The world’s population growth and demand on mineral oil which is a source of energy, makes global demand on conversion of fossil fuels and domestic oil production to be associated with water pollution. Thus, the industrial demand on freshwater supply and production of mineral oil are co-dependent, because the amount of mineral oil pursued determines the amount of MOW produced resulting in fresh water depletions. Reclamation of water from MOW reuse becomes a good option to eradicate water scarcity worldwide, and conserve and present opportunity for pollution reduction (Patterson 1985; Clément et al. 2002; Demirbas 2007; Jiang 2009; McCafferty et al. 2012).

The rational for wastewater treatment, water protection, conservation and reclamation for water usage are vital elements for water management. Since water management is a universal problem, effective ways of recovering is very essential for both developed and underdeveloped countries (Mišković et al. 1986; Demirbas 2007). However, decisions for wastewater treatment are very important and are related to the location, operation and maintenance of the treatment facility. In this case, the potential worth to recover oil and water for reuse, and reducing the stress on already existing resources is vital (Demirbas 2007; Jiang 2009).

In sub-Sahara Africa alone, 21 billion barrels of oil wastewater was generated through onshore and offshore activities, of which 80% was by oil production in 2007 (Clark and Veil 2009). Furthermore, Zheng et al. (2016) also reported that in 2012 the global amount of oil wastewater generated was 9 to 14 billion cubic meter. This refinery effluent is a dark yellowish, cream-coloured, highly turbid and pungent smelling, and has a high content of aliphatic and aromatic petroleum hydrocarbon (Demirbas 2007; Jiang 2009).

The MOW is normally rich in heavy metals, organic and inorganic matter, TSS, COD, biological oxygen demand (BOD) and SOG, which usually has effects on WWTPs by corroding the pipeline systems and depleting the water quality of water bodies (Moursy and El-Ela 1982). Therefore, cost effective treatment facilities are usually required to reduce the oil droplets and other contaminants in the MOW to an allowable value for degradation prior to discharge to the environment (Patterson 1985; Jiang 2009; Elias Tibane 2015).

The current demand for wastewater treatment is advancing along with technologies such as membranes (Munirasu et al. 2016), and flotation (Yu et al. 2017), however, the selection of the treatment type is dependent on the water chemistry. As a result, a typical treatment plant might consist of many treatment units, of which each plays different roles in potable and wastewater treatment (Santo et al. 2012). Likewise, in an oil refinery plant, about 80% of the waste stream contributes to MOW from some units like distillation, hydro-treating, desalting, cooling systems, surface water runoff, product lines, sanitary and refinery off specs (Diya'uddeen et al. 2011; Santo et al. 2012; Hosny et al. 2016).

Ecologically, most substances found in the MOW have low biodegradability and when discharged via wastewater, might affect the biosphere (Demirbas 2007). In addition, oil droplets forms a froth thin layer on the surface of water bodies, this affect aquatic life by decreasing both penetration of oxygen and light exchange between the air and the water (Jamaly et al. 2015). The variations in the diverse quantities of compounds has called for continuous review on regulatory limits impose by individual countries as a strict environmental law for the discharge limits of SOG (Ngamlerdpokin et al., 2011; Li et al., 2014). For instance, about 70% of China's freshwater is polluted due to population growth and demand on energy. Therefore, the allowable discharge limits by the Chinese Petroleum Corporation (CNPC), is 2 mg/L oil and a TSS of 10 mg/L (Jiang 2009; Li et al. 2014).

Above all, South Africa is faced with severe scarcity of fresh water supply, which is expected to escalate by the year 2030 by 25% (Elias Tibane 2015), due to the stress of low rainfall, which is between 40-60% (averagely 500 mm per annum). This has resulted in the country's economy and population growth to outpace the supply of freshwater (Chollom et al. 2015). The National Development plan has established in the vision 2020, the need to reuse the reclaimed water of about 35% (Schreiner and Hassan 2010; Elias Tibane 2015).

Therefore, treatment of MOW for reuse with well-optimised DAF unit will help conserve fresh water supply and be environmentally friendly and economically viable (Zouboulis and Avranas 2000; Karhu et al. 2014).

2.3 Oil refineries in South Africa and their challenges

The production of petrochemical and oil refinery products are at the verge of an increase due to global demands on their useful products. For instance, oil, which is a global energy source, has improved the living standard of people in modern day society. However, with the rapid urbanisation and industrialisation, the demand on the production of oil generates a large amount of oil wastewater, which is carcinogenic and endangers aquatic and human health when released into the environment without treatment (Zheng et al. 2016). There is therefore, the need for effective treatment processes to ensure downstream clarification.

However, to meet the demand of petroleum products in South Africa, about 60% of South African crude oil is being imported from Saudi Arabia, Nigeria and Angola. But, South Africa, having the second-largest oil refinery capacity in Africa after Algeria, has six refineries such as Cape town refinery (Chevron), Engen refinery (Petronas), Sapref refinery (Shell and BP), Sasol refinery, National petroleum refinery of South Africa (Natref) and Mossel Bay Gas to liquid (GTL Petro SA) (Uzoekwe and Oghosanine 2011; Elias Tibane 2015).

These refineries and petrochemical plants generate large quantities of wastewater during the crude oil exploration. When left untreated before discharge into the sewer, they cause environmental degradation, health hazards and threaten the ecosystem (Uzoekwe and Oghosanine 2011; Yu et al. 2017). Although treatment of wastewater has been made mandatory to all industries, not all the industries have the treatment facilities to adequately treat these effluents to conform to the environmental protection legislations by laws (Diya'uddeen et al. 2011; Jamaly et al. 2015). This is because most of the conventional wastewater treatments used have some limitations in terms of capital investment and maintenance on a large scale (Tsagarakis et al. 2003; Stewart and Arnold 2008). In addition, the lack of trained personnel and the required skills to operate the system affects the efficiency of the treatment plant.

More so, the ecological influence of SOG affects the wastewater treatment plants, hindering biological activity in activated sludge reactors and instigating clogging and fouling of pumps and piping (Patterson 1985; Saththasivam et al. 2016; Demirbas and Kobya 2017). As stated earlier, the presence of oil droplets in wastewater contributes to toxic pollutants, especially those which are hydrophobic in nature such as BTEX, COD and SOG (Diya'uddeen et al. 2011). To protect the refinery treatment plants, emissions of oil and grease to the local wastewater drainage system are also subject to the municipality limit sanctions with surcharge bills for offenders (SANS-SABS 2007; Santos et al. 2015).

Although WWTPs plays a vital role in reclamation of wastewater for reuse with a friendly environment, there is a broader nexus between water usage and energy utilisation required (Saththasivam et al. 2016). This requires a large amount of energy mostly electricity, which is likely to increase in the future with stricter discharge regulations and population demand (Rojas and Zhelev 2012). Hence, the higher energy footprint of the WWTPs will have a negative impact on global water industries in terms of the climate (Hirasaki et al. 2011; Ngamlerdpokin et al. 2011). Therefore, there is always the need to address the concern of WWTPs with eco-friendly sustainability and economic viability simultaneously (Patterson 1985; Chollom et al. 2015).

Furthermore, sludge generations and the cost of disposing, poses a major problem in WWTPs to acquire landfills (Patterson 1985; Metcalf and Eddy 2003). This has resulted in competition for land acquisition for landfills and human settlement (Munirasu et al. 2016). This has increased pressure on process engineers to design a wastewater treatment system and operation to be economically viable and sustainable.

2.4 Conventional treatment technology

The selection of a particular treatment technology is steered by the expected reclaimed water quality, oil droplet size and chemistry of the wastewater, and the set of discharge regulations (Zabel 1985). Conventional wastewater treatment methods are categorised as physical, chemical and biological. However, the performance of physical treatment processes such as screening; sedimentation and flotation are predominantly influenced by physical properties such as the size and density of suspended solids to be removed and the viscosity of the oil droplets. Chemical processes such as acidification, coagulation and flocculation are dependent on the interaction between the chemical properties of the contaminants and the type of chemical used (Ebrahimi et al. 2010; Coca et al. 2011; Saththasivam et al. 2016).

2.4.1 Acidification

Acids such as hydrochloric acid, sulphuric acid, sodium hydroxide and phosphoric acid, are used to neutralise and breakdown the oil molecules from water to enhance the separation (Hempoonsert et al. 2010). This involves neutralisation to removal excess alkalinity or acidity at low or high pH (Yang et al. 2010). The adjustment of pH is necessary due to the variation in the MOW source. However, because of the labour-intense nature of acid treatment, many of the recent treatment development methods combine acidification with other processes to make the treatment of oily wastewater stress-free and more efficient (Oliveira et al. 2014). In addition, the application of a suitable chemical or acids will depend on dominant economics and convenience to use (Coca et al. 2011). Lime, which is cheaper, is the most widely used chemical for pH adjustment but is slower in reaction rate (Bolto and Gregory 2007). Most importantly, chemical neutralisation or pH adjustment also enhances the chemical precipitation reaction (Canizares et al. 2008). This result causes solubility of different elements in the wastewater to precipitate out the necessary pollutants, especially heavy metals (Saththasivam et al. 2016).

2.4.2 Coagulation and flocculation

Coagulation is the process of adding chemicals or coagulants with the goal to destabilise colloidal particles or oil droplets to ignite the initiation point to coalesce together. Flocculation is then instigated after the destabilised colloidal particles are induced to come together and form agglomerates. The performance of DAF can be improved radically by coagulant addition with good chemical treatment systems (Bensadok et al. 2007; Ngamlerdpokin et al. 2011). Studies have shown that this process can remove about 90% of suspended solids (Ebeling et al. 2004). Effects of aluminium and ferric salts has been widely used with DAF for oil separation (Bensadok et al. 2007). A study by Al-Shamrani et al. (2002) reported 99% of oil efficiency for both alum and ferric salts. According to Daud et al. (2015), about 85% of COD, oil and grease can be removed by using coagulation coupled with DAF.

2.4.3 Biological treatment

The biological treatment with membrane bioreactors is encouraged to enhance the effective removal of the oil emulsions to meet the stringent limits (Munirasu et al. 2016). This involves biodegradability of the MOW, whereby the microbial metabolism will transform the COD into more environmentally safe compounds (Saththasivam et al. 2016), to create a suitable condition for the microbial organisms to have a beneficial influence on the water quality. Although some water sources could achieve the required improvement in terms of water quality, the application of a single biological treatment process is usually used as a polishing process; it is more common when several corresponding processes are applied (Cheryan and Rajagopalan 1998; Ebrahimi et al. 2010; Munirasu et al. 2016).

2.4.4 Other treatment technologies

Some of the techniques of separating oil from water include:

(a) Gravity separators (API), which is based on the specific gravity of the immiscible fluids (Altaher and Alghamdi 2011),

(b) Hydro cyclone, whereby the influent is accelerated into a cyclonic chamber using a tangential feed (Atadashi et al. 2011),

(c) Media filtration, which involves the use of sand filtration and anthracite for the separation (Jamaly et al. 2015).

All the above-mentioned technologies have drawbacks, which limits its implementation on large scales. Some of the advantages and disadvantages of the methods of removing oil from water are shown in Table 2-1, while coagulation (chemical treatment) and flotation treatments techniques, which is the area for this study, are discussed (section 2.5 and 2.6) in detail.

Table 2-1 Comparing of oil removal methods (adapted from Saththasivam et al., 2016)

Technology	Advantage	Disadvantage
Chemical treatment	(i). Easy to remove, coalesce and aggregated oil droplets (larger oil droplet flocs). (ii). Contributes to the removal of solids and organic matter. (iii). Effective as first treatment step in removing oil from water.	(i). Inorganic coagulants (alum and ferric salts) might pose problems downstream. (ii). High volume of sludge generation. (iii). Chemical usage contributes to cost.
Flotation (DAF)	(i). Suitable for removal of oil droplets of smaller size (20 µm). (ii). It easily removes lighter and smaller oil droplets that are difficult to settle. (iii). Have a smaller footprint as compared with sedimentation. (iv). Cheap maintenance and easy to operate. (v). Better sludge handling and float thickening.	(i). Addition of chemicals to enhance efficiency. (ii). Generation of microbubbles contributes to high-energy costs.
Membrane separation	(i). Variation in feed water have a low impact on permeate quality. (ii). Compact with small footprint for finishing treatment. (iii). Moderate and easy to operate.	(i). Subjected to fouling from oil and biological content in the influent. (ii). Polymeric membrane degrades easily at high temperatures (>50 °C)

2.4.5 The need to separate oil-water using DAF

Studies has shown that the DAF process is easy to operate with high capacity to handle high surface loading rate, hence its footprint is usually acceptable and smaller than that of alternative treatment techniques. In addition, it has a short response time (Saththasivam et al. 2016). The degree of water quality determines the suitable treatment process to be selected. However, most industrial wastewater treatment companies face the challenge to acquire effective treatment techniques to comply with the environmental regulations and balance with sustainability and economic viability (Edzwald 1995; Schreiner and Hassan 2010).

In this scenario, optimising the DAF will boost its efficiency for the removal of mineral oil (MO) from water before downstream treatment is desirable as the oil recovered can be reprocessed for sale as low-grade oil (Misković et al. 1986). The oil concentrate can be sold to oil recycling companies, thereby generating income revenue and employment opportunity (Tetteh et al. 2017). In addition, recovering some salt metals like aluminium from the MOW, especially from petrochemical industries, present a viable economic opportunity but the implementation seems complicated (Rabah 2004).

Therefore, reclamation of the wastewater contributes to conservation of freshwater supplies, which echoes the MOW to be environmentally friendly and more economical. This is because the reclaimed water is available near urban areas where water supply reliability is most crucial. Thus reducing the stress on farmers and industries where freshwater been supplied is priced very high. In addition, reuse of the treated water can be used for the oil refinery steam boilers, which will cut down the cost on freshwater supply (Schreiner and Hassan 2010).

2.5 Characterisation of MOW quality

Wastewater characterisation is the most important outcome usually considered in water treatment processes, due to its impact on the water quality for reuse, environmental and economic complaints, and the strategic aim of the operator and engineering decision-making on existing WWTPs (Binnie et al. 2002). Moreover, water quality affects the effectiveness of the treatment technology applied to each individual source of water. This is because independent treatment technology is dependent on its unique water quality, such that different contaminants demand different treatment conditions (Patterson 1985; Misković et al. 1986; Metcalf and Eddy 2003).

Consequently, MOW originates from both crude oil extraction and oil refineries, which is blackish in colour with some degree of salts and needs to be treated before discharge (Pintor et al. 2016). As a criterion for evaluating water treatment systems, characterisation of water and wastewater is usually determined under three categories namely physical, chemical and biological properties. Physical properties include temperature, pH, colour, turbidity, TSS, viscosity, taste and odour. Chemical properties of MOW comprises of organic materials, inorganic materials and hydrocarbons, which mostly depend on the geological location of exploration. Some of the chemical compositions include sulphides, BTEX, SOG, BOD and COD (Zheng et al. 2015; Zheng et al. 2016). Meanwhile, biological properties relate to microorganisms (algae) present in the water. In this study, to monitor the success of the DAF coupled with coagulation for its application, the water parameters considered are COD, SOG, TSS and turbidity (Tetteh et al. 2017).

The TSS represents the dissolved inorganic and organic salts and residual trace of chemical additives like scale and corrosion inhibitors (Sarika et al. 2005). The COD refers to the amount of dissolved oxygen that is altered into carbon dioxide, water and ammonia in the presence of an oxidant or depreciated by organic matter such as the oil droplet foam formed on the water surface (Safari et al. 2015). The turbidity is the measure of the clearness of the water, thus the degree of light scattering by suspended particles (Daud et al. 2015). In addition, turbidity of the MOW is associated with the amount, colour and size of the oil droplet suspended in the MOW sources (Ebeling et al. 2004; Coca et al. 2011). The SOG is the measurement of total emulsified oil and dissolved hydrocarbons present in the water. To evaluate the treatment system, a regulatory standard is always required (Jiang 2009; Edzwald 2011).

In this study, the measurement of SOG is the key parameter been used to evaluate the DAF performance obliged for the system control and compliance monitoring. However, to comply with environmental regulations, disposing of SOG differs from one country to another ranging from 15 to 50 mg/L such that, for USA, the limit is 29 mg/L (Stewart and Arnold 2008), and for Canada, the limit is 30 mg/L (Clément et al. 2002).

The regulatory limit of SOG in South Africa is 50 mg/L (Schreiner and Hassan 2010) and other regulatory limits of the South African Department of Water Affairs (DWA) (DWAF 1996; SANS-SABS 2007) and their associated problems is depicted in Table 2-2.

Table 2-2 Discharge limits of oil refinery effluent (DWAF, 1996; SANS-SABS, 2007)

Parameters	Discharge limits
BTEX (mg/L)	5
Sulphides (mg/L)	1
SOG (mg/L)	50
COD (mg/L)	1000
TSS (mg/L)	1000
Turbidity (NTU)	1000
pH	6-10
Marine Toxicity (MATD)	200

2.5.1 Types of industrial mineral oil

The separation of oil from concentrated oil emulsions and water is a global concern, which occurs in a number of industries. Concerning this, the MOW forms the major by-products in the oil and gas industries, accounting for 80% of the waste stream (Diya'uddeen et al. 2011).

Produced water contains various organic and inorganic impurities in emulsions, and are not thermodynamically stable, which tend to break during a physicochemical mechanism such as, coagulation, flocculation, and acidification and phase inversion (flotation). The destabilisation of stable emulsions with smaller oil droplet sizes makes them complex for separation (Hosny et al. 2016).

According to Patterson (1985), mineral oil droplets in water, exceeding 150 μm can be classified as free oil, dispersed oil with droplets between 20 and 150 μm, emulsified, and dissolved oil with droplet size less than 20 μm. In addition, the geographical condition and the field conditions might contribute to the complex composition of the MOW including the organic and inorganic matter like salts, metals, dispersed oils, phenols, organic acid and dissolved hydrocarbons as benzene, toluene, ethylbenzene and xylene (BTEX) (Patterson 1985; Sarika et al. 2005; Sahu and Chaudhari 2013; Pintor et al. 2016).

In general, mineral oil sources are from the petroleum industries and its derivatives with different chemical structures, while biological oil originates from animal and vegetables. The difference between biological and mineral oil depends on the ability to biodegrade by natural occurring organisms. Thus, the biological oil is easy to biodegrade as compared with mineral oil that is complex (Atadashi et al. 2011). In addition, there are several units in the petrochemical and oil refinery process configuration, which have consequences on the water quality and quantity been discharged. This includes distillation, hydro treating, desalting, cooling systems, surface water runoff, product lines and refinery off specs (Patterson 1985; Maksimov et al. 2015).

It is essential that the oil droplet and size distribution be characterised prior to designing a water treatment facility for a specific application. Without the accurate value of the characterised oil droplet size, the designed facility may not be able to treat the effluent to meet the controlling compliance specifications (Zabel 1985; Younker and Walsh 2014). It has also been reported that characterization of the wastewater is an important aspect of the treatment procedure. Therefore, the results of this characterization and analysis are critical factors for selection of the applicable treatment method (Al-Shamrani et al. 2002; Saththasivam et al. 2016). Studies have shown different types of oil-water separation process works with different oil droplet sizes as depicted in Table 2-3.

Table 2-3 Summary of de-oiling methods and corresponding oil droplet sizes (adapted Al-Shamrani et al., 2002; Saththasivam et al., 2016)

Oil-water separation process	**Oil droplet minimum size removed (microns)**
API gravity separator	150
Corrugated plate separator	40
Flotation (no coagulation)	25
Flotation (with coagulation)	3-5
Hydrocyclone	10-15
Mesh coalesce	5
Media filter	5
Centrifuge	2
Membrane filter	0.01

2.5.1.1 Free or Dispersed oil –water

The dissolved oil is also termed soluble oil and contains hydrocarbons and other organic compounds in the form of oil droplets that are soluble in the MOW. The dispersed oil droplets are stabilised by electric charges and other interparticle forces. However, there are various variations in the MOW, which is associated with many factors such as the upstream process and pipelines, oil density and the turbulence created by the equipment resulting in different oil droplet sizes. The size distribution of the dispersed oil droplets range from 20 to 150 μm (Welz et al. 2007).

However, addition of chemicals will cause the free oil droplets to rise quickly to the surface, due to the imbalanced force caused by the differential density between the oil and water. The relative distribution of oil droplet sizes, which is above 150 µm, is a key design factor, which is usually influenced by temperature and the trace chemical additions (Painmanakul et al. 2010). Hence, the difference in densities between the oil and water molecules serve as a driving force to move the oil droplet to the surface for coalescence aggregate formation for separation (Sahu and Chaudhari 2013; Pintor et al. 2016).

2.5.1.2 Oil in water emulsions

Most emulsions found in the oil refinery have complex molecules (hydrophilic and lyophilic groups) with water droplets in an oil continuous phase. This is due to the friction that exists between them, caused by chemical addition and hydrodynamic mechanism or physical agitation (Yu et al. 2017). This action causes the stabilised electric charge developed to be dispersed at the oil-water interface in a form of tiny droplets less than 20 µm in size. At this instance of instability of the oil emulsions, the oil droplets coalesce with each other when in contact to form larger droplets (Stewart and Arnold 2008).

However, chemicals, heat, settling time and electrostatics are used to alter and cause emulsion breakdown (Sarika et al. 2005). Some of these emulsion breakers or destabilisers are lyophilic which are normally injected into the water streams after the first oil-water separation vessel. Thus, the chemical has additional time to react in the subsequent separators to enhance the oil to form dispersed droplets after the emulsion film is broken down (Vedoy and Soares 2015). However, small droplets require excessive acceleration and gravity settling time to enhance the separation; hence, equipment selection depends on the oil droplet size and the concentration (Stewart and Arnold 2008).

2.5.1.3 Dissolved oil-water emulsions

The dissolved oil represents all the hydrocarbons and other organic compounds soluble in the MOW. Thus, the source of the MOW defines the quantity and quality of the dissolved oil present. For instance, MOW from gas or condensate production will exhibit higher levels of dissolved oil than glycol regeneration vapour recovery systems containing BTEX. The chemical characteristics of the soluble oil compounds includes aliphatic hydrocarbons, phenols, acids, and aromatic compounds (Jamaly et al. 2015). MOW chemistry that is associated with high salinity and hydrocarbon solubility will eventually lead to toxicity. In relation, the issue of clogging and corrosion in the pipelines are of major concern as the oil droplets flows in the pipes. (Younker and Walsh 2014; Yu et al. 2017).

2.6 Chemical treatment (coagulation) process

Chemical treatment is an essential requirement as a pre-treatment process for DAF for effective flotation. Thus, before the DAF, relatively high surface area, destabilised charged oil droplets flocs and hydrophobic nature are required to attain good attachment with the air bubbles. The addition of the coagulant destroys the protective action of the emulsifying agents of the oil-water and overcomes the repulsive double layers. This then allows the oil droplets to conglomerate to form larger droplet flocs (Moursy and El-Ela 1982; Coca et al. 2011).

Moreover, in the DAF tanks, there exists turbulent flow that causes high shear forces that makes the smaller flocs capable to withstand, while the larger flocs are easily detached. In view of this, to achieve high relative surface area, the bubbles generated has to be smaller than 10-100 µm. This reduces the detachment caused by the shear forces (Lakghomi et al. 2015). In addition, the footprint of the DAF is usually smaller with high surface loading rates. This makes it more advantageous to couple chemical treatment than other alternative treatments (Moursy and El-Ela 1982; Zabel 1985).

The selection of the type of coagulant as a chemical requirement for a treatment process is important. A wide range of some of these coagulants exist as inorganic and polymeric organic coagulants (Abdelaal 2004). There is therefore the need for investigation to select the suitable coagulants (a) for long-term performance of the treatment plant (b) to reduce cost of chemical usage and (c) to ensure consistent water quality (Vijayaraghavan et al. 2011).

With the suitable coagulant selected, it is necessary to ensure routine jar testing for the following reasons: (a) the nature and the quality of the MOW are paramount to change which may affect the coagulant dosage (b) to ensure quality check and strength of the coagulant for effective coagulation process (Moursy and El-Ela 1982; Santo et al. 2012; Schalkwyk et al. 2016).

2.6.1 Types of coagulants

Coagulation is an essential mechanism via the addition of coagulants responsible for neutralisation and formation of smaller flocs to agglomerate into larger flocs. With respect to this, coagulants, which are categorised as mineral compounds, or inorganic and organic polymeric coagulants, are discussed in detail in Sections 2.6.2 and 2.6.3 respectively. However, Table 2-4, shows some factors to consider in selection of the coagulants.

Table 2-4 Factors to consider in selecting coagulants (Abdelaal 2004; Altaher and Alghamdi 2011)

Coagulant characteristics	MOW characteristics	Physical characteristics
Coagulant type	Water quality	Flotation/settling time
Coagulant dosage	Suspended solids	Mixing intensity
Coagulant quality	Temperature	Coagulant dosage end point
Coagulant life span	pH	Chemical stability during storage
Proper solution makeup and dilution	Alkalinity or Ionic constituents	

2.6.2 Mineral compounds or inorganic coagulants

The inorganic coagulants contain divalent or trivalent metal ions used to neutralise the surface charges of the oil droplet and coagulate them into larger flocs. Metal salts of iron and aluminium are two most widely used inorganic coagulants. Both the aluminium and iron metal salts undergo a series of reactions with the hydroxyl ions (OH^-) forming both monomeric and polynuclear species that in turn react with the oil droplet charge. This results in dissociation of the salts to give their trivalent ions, which hydrates to give complex water molecules and strongly adsorbs onto the surface of the negatively charged oil droplet (Ryan et al. 2008; Schalkwyk et al. 2016).

The primary functions of the hydrolysis products are the destabilisation and strengthening of the oil droplet flocs to reduce the breakup. Therefore, the observable reasons for the use of metal salts or inorganic coagulants is to satisfy the practical constraints, thus, it is relatively inexpensive, easy to handle, available and effective. However, there are some drawbacks in their application such as sludge management, high dependence on pH, and weakness of temperature and high coagulant dosage requirements (Hosny et al. 2016; Tetteh et al. 2017; Yu et al. 2017). In recent studies, the innovation by some researchers is to use pre-hydrolysed inorganic coagulants, whose effectiveness as primary coagulants does not depend on pH and temperature, for example polyaluminium chloride (PAC) or polyalumium sulphate (PAS) (Bolto and Gregory 2007).

2.6.2.1 Aluminium chloride

Manufacturers refer to aluminium chlorohydrate, a typical trivalent metal salt coagulant, as aluminium chloride ($AlCl_3$) with a basicity of 83%. It is white in colour but sometimes contaminated with iron trichloride, which makes it yellowish in colour. This can be prepared through the reaction of hydrochloric acid gas with aluminium substrate. The $AlCl_3$ is covalently bonded with sheet like layered cubic structures. The presence of the high charged aluminium species (Al^{3+}) increases the hydrolysis product in the coagulants with its basicity (Ryan et al. 2008; Edzwald 2011). The $AlCl_3$ is used in chemical industries as a catalyst for isomerisation, polymerisation reactions and antiperspirant. However, its application as a primary coagulant in the wastewater industries is to improve upon water quality with its excellent operational performance (Canizares et al. 2008).

Ideally, the application of $AlCl_3$ in the MOW treatment destabilises the oil droplets and promotes the growth and coming together to form larger flocs. This eliminates the oil droplets from the emulsified effluent using the adsorption properties of the growing metal hydroxide (aluminium hydroxide). However, $AlCl_3$ is considerably effective at higher pH of minimum solubility than that of alum (Khuntia et al. 2012).

There is a concern of meeting aluminium standards in the discharge effluent due to carry over of the aluminium metals. This has led to the development of the active species of pre-hydrolysed coagulants, such as those made from aluminium chloride (PAC) , which has been understood to be more effective with lower volumes of sludge produced (Yang et al. 2010; Butler et al. 2011; Daud et al. 2015).

2.6.2.2 Aluminium sulphate

The predominant wastewater treatment coagulant mostly used is aluminium sulphate, popularly known as alum. The advantages associated with alum includes its availability, low cost, easy to handle and effective high predictable performance (Amirtharajah and Mills 1982; Al-Shamrani et al. 2002).

Reacting bauxite or certain amounts of clay with sulphuric acid can produced alum often rich in acidic nature. Its storage therefore requires corrosion–proof tanks, pumps and pipework. However, pure alum is white which sometimes can be prepared from low-grade clays and waste acid with the presence of iron as an impurity making it yellow or orange in colour (Schalkwyk et al. 2016). Though Iron metal is a coagulant on its own, it does assist the coagulation process, but in some cases leads to undesirable concentrations of toxic metals.

A hydrolysis reaction forms a number of dissolved monomeric aluminium species and hydroxide precipitates when added to the MOW. During the reaction, the metal salts releases hydrogen ions, which lowers the pH and consumes the alkalinity in an equivalent basis (Saritha et al. 2015). Thus, the pH determines the charge of the chemical reaction and the solubility of the aluminium. Theoretically, alum is effective in the broader hydrolysing pH range of 5.5 to 7.7 and forms positively charged aluminium species that adsorb onto the negatively charged organic matter resulting in charge neutralisation (Painmanakul et al. 2010; Yang et al. 2010).

Therefore, higher pH will correspond to higher solubility resulting in higher amounts of aluminium present in the discharge water. The trivalent species of the alum is of great concern because of the impacts it has on the adsorption of the oil droplets, of which about 70% removal of oil droplets can be attained at an acidic medium or low pH (Abdelaal 2004; Ryan et al. 2008).

Alum toxicity has the potential of leading to neurological conditions and consequently requires constant monitoring before carrying over in the sewer (Rabah 2004). The water regulations has stipulated that the total aluminium should be less than 50 to 200 µmg/L (Li et al. 2008). Therefore, the use of alum is questionable due to its tenacity to crystallise at lower temperature and the risk not to exceed the regulatory limits (30 mg/L) (Binnie et al. 2002; Yang et al. 2010).

This can be controlled by a routine monitoring of the quantity of coagulant been added to the MOW, which can be quite challenging given that the coagulation process depends on the oil droplet concentration, nature of the organics and the pH of the MOW (Sahu and Chaudhari 2013). It is therefore important to assess more efficient and environmentally friendly coagulants to enhance the economic profile of the wastewater treatment processes (Patterson 1985; Schalkwyk et al. 2016).

2.6.2.3 Ferric chloride

Ferric chloride is also a primary hydrolysis ionic coagulant used in the wastewater treatment industries. It is commercially available both in liquid and in powdered form, readily prepared from reacting iron and hydrochloric acid. Ferric chloride solution is highly acidic, colourless to light brown and has a pale hydrochloric acid odour. In addition, it is highly corrosive to nearly every metal including grades of stainless steel and needs to be stored, pumped and carried in synthetic corrosion-resistant materials (Binnie et al. 2002).

The coagulation mechanism using ferric chloride depends on the interaction between its divalent or trivalent metal salts and the contaminants presence. Because of that, it has been extensively used to destabilise and coagulate the oil droplet into bigger flocs to be clarified by using DAF or separators, which offers effective removal of dissolved organic matter and turbidity (El-Gohary et al. 2010; Schalkwyk et al. 2016).

2.6.2.4 Ferric sulphate

Ferric sulphate is also a high-performance wastewater treatment primary inorganic coagulant based on its trivalent metal salt. The charge of the elemental iron content determines the strength of the coagulant, which may range from about 8% to 14% depending on the type of chemical. It is brownish in colour, produced in commercial quantity by reacting sulphuric acid and ferrous sulphate using an oxidising agent such as nitric acid or hydrogen peroxide. In addition, it has a lower pH and is more corrosive compared with that of alum (Binnie et al. 2002).

Ferric sulphate is a readily available coagulant and cost effective for wastewater treatment over a wider pH range. In South Africa, it is more applicable in the wastewater treatment system where low pH is required, for example, the removal of SOG, high colour and turbidity (Canizares et al. 2008). Ferric sulphate can also be used as an effective odour-controlling agent in forming hydrogen sulphide that will constrain corrosion (El-Gohary et al. 2010).

2.6.2.5 Ferrous sulphate

Ferrous sulphate is a bivalent iron salt coagulant applied in wastewater treatment to enhance and clarifies the effluent for effective downstream treatment. Although, its usage has no drawbacks except that the chemical cost is based on the charge of the iron and does not contain any heavy metals in substantial quantities. The ferrous sulphate is used together with lime or chlorine to enhance precipitates of the iron hydroxides in the ferric form. However, it forms complex compounds with phosphorus and is effective in odour control by preventing the formation of hydrogen sulphide in the wastewater treatment (El-Gohary et al. 2010).

2.6.2.6 Lime

Lime, which is economical, is the most widely used chemical for pH adjustment but is slower in reaction rate. In wastewater treatment, it is usually used to balance the pH to enhance effective floc formation. However, the use of lime has some exemptions to the use of both aluminium and ferric salts for coagulation. Thus, it depends on the type of wastewater, lime type and the pH requirement (Binnie et al. 2002).

For instance, if hydrated, slaked or dolomitic lime is added to water to raise the pH to above 10.5 to 11.5 will cause the initial flocs to form magnesium hydroxide. However, re-carbonation of the wastewater using quicklime to a pH of 8 will also precipitate the calcium presence to form flocs (including the calcium bicarbonate originally present in the water) (Amirtharajah and Mills 1982; Binnie et al. 2002). The use of lime in wastewater treatment systems enhances the elimination of the heavy metals (manganese) and softens the water. In addition, application of lime is very active depending on the pH and temperature. Therefore, high temperature reduces the solubility, while raised pH provides excess hydroxyl (OH-) ions to enhance the reaction of the oil droplets to form sludge at the clarifiers (Schalkwyk et al. 2016).

2.6.3 Polymeric organic coagulants

Hydrophobically modified polymers have recently become the subject of extensive research due to their unique characteristics and applications. It is able to improve the efficiency in solid-liquid separation, making it important in water and wastewater applications (Bolto and Gregory 2007). The use of polyelectrolytes in wastewater treatment are of high molecular weight, synthesised form polymeric units called monomers. During the manufacturing of the polyelectrolytes, many polymers are produced with polymer chains of linear, branched or cross-linked forms adding to their complexity structure (Guan et al. 2014).

Organic polymeric coagulants are natural or synthetic hydrophilic compounds with long chain molecules consisting of repeating chemical units held together by covalent bonds (Abdelaal 2004; Altaher and Alghamdi 2011). Some naturally occurring polymers are virtually non-toxic to humans, rather, environmentally biodegradable and are readily available in rural communities. The use of some of these natural organic polymers may be limited because they are not effective in all cases and their properties cannot be modified (eg. Chitosan, starch, Moringa Oleifera) (Bolto and Gregory 2007). The synthetic organic polymers on the other hand, although can be toxic to humans can easily be modified during the manufacturing process for wider applications (Abdelaal 2004).

Synthesised organic polymers are able to produce organic coagulants with variation in molecular weight, charge density and chemical structure (linear or branched) (Vijayaraghavan et al. 2011). However, the charge density, molecular weight and the ionisation functional group of organic polymer aids separates solid-liquids (emulsified oil) whose molecules does not settle easily. The presence of the hydrolysed metal salts makes them have distinct characteristic attributes. In addition, they are sensitive to pH, and produces larger and stronger flocs which results in reduction of voluminous sludge when applied in wastewater (Vijayaraghavan et al. 2011; Yu et al. 2017).

Currently many researchers are blending inorganic coagulants with organic polymers to assess the effectiveness in removing oil from synthetic wastewater. Such innovation serves as a means of partially replacing of inorganic coagulants at a reduced cost (Yang et al. 2010). The author’s training experience at Umgeni Water with a process engineer found that some blends of organic-inorganic compounds produce good water quality such as Polyaluminium chloride (Z553D), Polyacrylamides (Zetag32- FS/A50) and Polyaluminium sulphate (PAS) (Abdelaal 2004; Guan et al. 2014; Schalkwyk et al. 2016; Tetteh et al. 2017).

Although, the use of organic polymers as coagulants have many advantages, nevertheless, its application can be quite challenging. Thus, the selection of the right polymer to use depends on the type of wastewater under discussion. To overcome some of this these drawbacks involves looking into their molecular weight, charge density, structure, dose, mixing conditions, amount and type of filths found in the water and pH reliance (Bolto and Gregory 2007).

Polymeric coagulants are used as primary coagulants, in contrast to aluminium or ferric ions, which do not form voluminous floc volumes. In view of this, they are widely used in pre-treatment of wastewater from various industries, such as dyes, paper and pulp and the treatment of waste sludge (Wang et al. 2007).

2.6.3.1 Cationic polymers

Cationic polymers are natural or synthetic based coagulants, which are positively charged and are commonly used as primary coagulants in water and wastewater treatment.

The dimethylamine (DMA), Polyacrylamides and PDADMAC are examples of cationic synthetic polymers while Chitosan is an example of cationic natural polymer. The PDADMAC and DMA (polyamines) are water-soluble containing about 10 to 50% active polymers, which are widely used in the water industry (Bolto and Gregory 2007; Vijayaraghavan et al. 2011).

The main distinct of polymers is their charge density, and that higher charge density gives an indication that the polymer has greater loops which will enhance the intermolecular bridging and more effective destabilization of the oil droplets (Vedoy and Soares 2015). The use of cationic polymers in lieu of inorganic coagulant performance is not dependent on pH, and requires low coagulant dosage. However, costs are competitive in taking into account disposal of the sludge formed.

2.6.3.2 Anionic polymers

Anionic polymers are amphoteric polymers, which have both the positive and the negative charges in the same molecular chain with different properties. Thus, they require a negative charge to enable the ionisable group to dissociate in the solution. The polymerisation of the anionic polymers are instigated by active anionic species (nitrile, hydroxide), whiles the cationic polymers are also instigated by the cationic species (hydrochloric acid, sulphuric acid, phosphoric acid) (Abdelaal 2004). This differentiates them and makes their polymerisation very sensitive to the solvent used.

However, there are series of reactions that occur in the polymerisation reactions by nucleophiles to the bond of the monomer such as initiation, chain propagation and chain termination. For instance, hydrolysis of the polyacrylamide under basic pH conditions produces a polymer with anionic charges. Some examples of anionic polymers include polyacrylamide, sulphate polysaccharides and starch with carboxylic substitutions (Abdelaal 2004; Vedoy and Soares 2015). Alternatively, non-toxic extract from brown seaweeds, called sodium alginate is usually used as a coagulant in the United Kingdom and in Japan as a natural polymer that produces a negative charge electrolyte (Bolto and Gregory 2007).

2.6.3.3 Non-ionic polymers

Polymeric coagulants that carry no charge are termed non-ionic polymers. However, they vary in structure, charge density, molecular weight and degradability. Some of the non-ionic polymers include gelatines, polyacrylamides, cellulose derivative, starches, and glues.

However, there have been some modification techniques by changing the structures of the various derivatives of polyacrylamides to aid flocculation performance in solid-liquid separation over the years (Guan et al. 2014). Some of the organic polymers are prepared based on their hydrophilic structure by introducing a relatively small amount of hydrophobic monomer into the hydrophilic macromolecular chain. In general, they are widely acceptable due to their toxic free nature and are environmentally friendly (Bolto and Gregory 2007; Edzwald 2011).

2.6.3.4 Organoclay

The Organoclay are by-products from natural or synthetic materials, which can be used as absorbents for minor treatments. They are generally known as low-cost adsorbents, which are readily available, which include ball clay, bentonite (smectile) and kaolin. However, the sorption capacities of clays can be improved further with inorganic or organic cations to give Organoclay (Bolto and Gregory 2007; Ebrahimi et al. 2010). Organoclay is also as a result of merging sodium montmorillonite clay with a cationic quaternary amine salt, which interchanges the adsorbed sodium through ion exchange (Ebeling et al. 2004).

The Montmorillonite is a three-layer clay mineral, which is made up of two silica tetrahedral and central alumina octahedral pieces. According to Bolto and Gregory (2007), the use of Organoclay together with a polishing stage of granular activated carbon (GAC) can be used to remove free and dissolved hydrocarbons from the MOW to achieve a desirable discharge.

2.6.4 Coagulation and flocculation mechanism

Treatment of the MOW is mainly a solid-liquid separation process, which involves the process of coagulation and flocculation as practised in the wastewater treatment. The process steps are considered in a three sequential order such as coagulation, destabilisation and inter-particle collisions (flocculation).

Coagulation as an electrochemical process, and involves the addition of a coagulant to stabilise or destabilise the oil droplet and reduce the inter-particle repulsion forces. This is frequently considered as a first step in separating the oil from water. The chemical reaction between the hydrolysing metal coagulants and the oil droplet, results in forming larger oil droplet flocs (Edzwald 2010). Whereas, the physical process that facilitates the presence of electrical layers to encapsulate the oil droplet for counter ion adsorption is termed flocculation (Zouboulis and Avranas 2000; Younker and Walsh 2014). Most emulsified oils or oil droplets in water are very complex in separation within a given time. This is due to negative surface charge and the balance between the attraction and repulsive electrostatic force (Edzwald et al. 1987; Sarika et al. 2005).

Figure 2.1 shows a negatively charged colloidal oil droplet, with a mist of ions (diffuse layer) around the oil droplet. In addition, the oil droplet is negatively charged, hence the excess ions of opposite charge accumulates in the interfacial region together with the primary charge to form the double layer (Schalkwyk et al. 2016). However, the charges cause the oil droplet to repel each other near the surface of the oil droplet, and the greater the repulsion, the greater the stability. The repulsion force is an exponential function of the distance between the oil droplets. The zeta potential, which is the measure of the electrophoresis, approaches zero. The negative charge becomes less effective for flocculation and consequent aggregation (Bolto and Gregory 2007; Painmanakul et al. 2010).

The surface charge of the colloid is dependent on the ionization of their functional units, the pH of the solution as well as the disparity to adsorption (Sarika et al. 2005; Safari et al. 2015; Saritha et al. 2015). An understanding of the reactions that occur upon coagulant addition is necessary to comprehend organic-metal salt interactions.

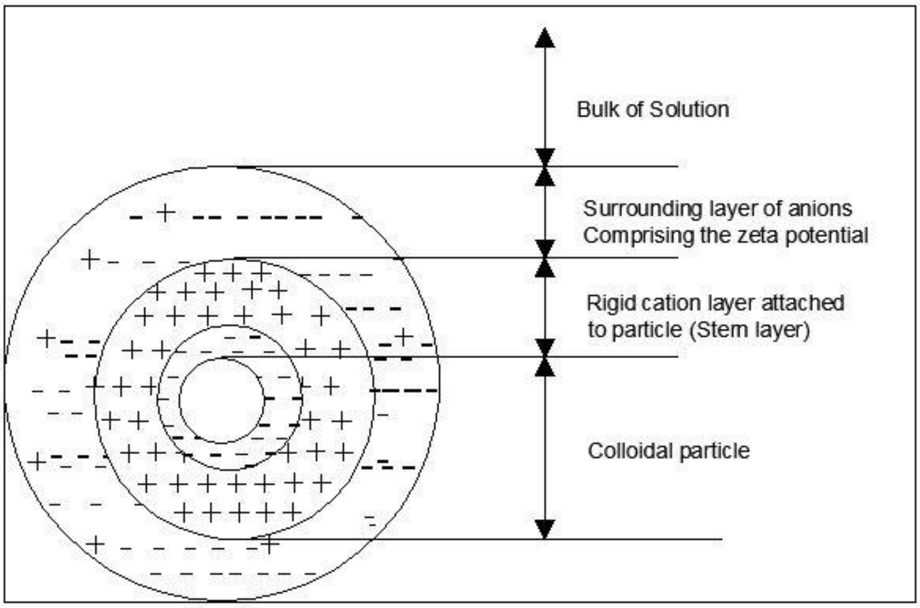


Figure 2.1 Illustration of a colloidal suspension in a solution (adapted from Schalkwyk et al., 2016)

2.6.4.1 Double layer compression

The double layer theory is associated with the electrostatic repulsion and the van der Waals force of attraction. This mechanism involves the addition of electrolyte into the MOW to increase the concentration of the ions. This makes the ions having net opposite charges to move closer to each other and decrease the thickness of the electrical double layer or the surface area that surrounds them. The double layer also referred to as the diffused layer, contains both negative and positive charges, being attracted by the stern layer causing the diffuse layer to be compressed (El-Gohary et al. 2010; Painmanakul et al. 2010).

A colloid with a demanding or stern layer is depicted in Figure 2.2, and shows that the electric outline around the colloidal surface. The double layer compression is an important destabilisation mechanism rarely employed in the wastewater treatment. Since it requires electrolytic solution, addition of the coagulant neutralises the electrostatic field of the charge that surrounds the oil droplet and keep separated. During coagulation, the double layer is compressed, which allows the oil droplet to come coalesce and form larger oil droplets flocs (Binnie et al. 2002; Painmanakul et al. 2010).

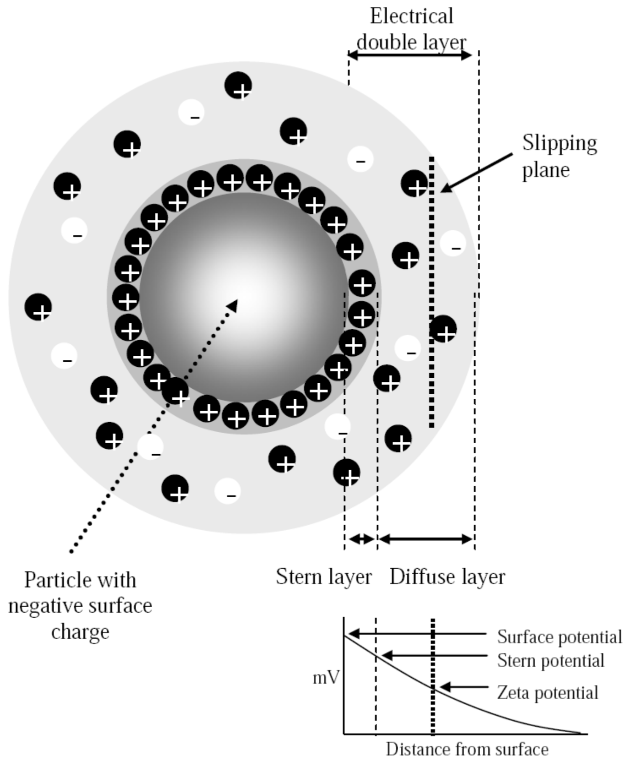


Figure 2.2 Representation of the distribution of ions around a charged particle in solution, showing the electric double layer (adapted El-Gohary et al., 2010; Painmanakul et al., 2010)

2.6.4.2 Zeta potential

The zeta potential (z-potential) of the MOW is an index used to quantify and determine the possibility of the charged oil droplet to flocculate. Thus, it signifies the surface charge of the oil droplets and therefore provides the stability of the emulsions and the optimal dosage required for the charge neutralisation. Breaking of the stable emulsion by addition of coagulants also affects the z-potential (Wang et al. 2011; Hunter 2013).

As shown in Figure 2.2, the distance between the charge surfaces can affect the z-potential to either increase or decrease, and hence making the emulsion to be unstable. The low potentials are associated with easy coagulation of unstable emulsions while high potentials relate to strong forces of separating stable emulsions (Binnie et al., 2002). However, a z-potential closer to zero signifies that there is a smaller repulsive force between the droplets (Wang et al. 2011). The charge of the oil droplet and the bubbles are phenomena in the flotation process, to maximise the flotation rate by the oil droplets to merge to each other, resulting in heavier agglomerated oil droplet flocs. It has been proposed that a reduction in electrostatic forces, such as the z-potential, is responsible for destabilization. The z-potential, therefore, serves as a guidance to avoid coagulant overdose and reduce coagulant and sludge disposal costs (Zouboulis and Avranas 2000; Al-Shamrani et al. 2002).

2.6.4.3 Surface charge neutralisation

As part of the double layer compression, the surface charge neutralisation involves a duo principal process (Figure 2.2). This involves the use of a coagulating agent with a net charge opposite to the net surface charge of the suspended oil droplets. This decreases the electrical forces holding the oil droplet together and tolerates easier agglomeration. In some cases where the addition of the coagulant is overdosed, this can lead to the net surface charge of the oil droplet being reversed or restabilised leading to poor oil-water separation and water quality (Zouboulis and Avranas, 2000; Binnie et al., 2002). This is because the reduced surface charge lowers the energy necessary for the coagulant and oil droplet to come together.

2.6.4.4 Entrapment in precipitate

This mechanism, also termed sweep floc coagulation, occurs when the aluminium and iron metal salts are being added to the MOW at a realistic pH value to enhance precipitation as hydroxide flocs. At the point where there is colloidal oil droplet appearance, the hydroxide tends to precipitate using the oil droplet as cores and forms flocs around it. In sweep coagulation, physical interaction occurs between the voluminous (Iron or aluminium) precipitates and the collided oil droplet (Zouboulis and Avranas 2000). Under these circumstances, the chemical conditions for the precipitation of the hydrolysis and subsequent flocculation are more important than the transport interactions between the colloidal oil droplet and the hydrolysis metals during destabilisation. This will then entrap other colloidal oil droplets more especially during flocculation (Binnie et al. 2002).

2.6.4.5 Inter-particle bridging

In most conventional surface wastewater treatment, during the interparticle bridging process, the particles together form a mesh like matrix consisting of the destabilised colloids and polymer branches. This mechanism occurs when high molecular weight polymers branch out and form bonds between the oil droplets (Phalakornkule et al. 2010). This polymerised organic coagulant adsorbs onto the multiple electrical charged ions. In some cases, the polymers chemically react with other polymers or share their charged ions to form ionic bridges. This sometimes leads to destabilisation and may cause restabilisation when excess coagulant is being added as well. This is because of the reactive polymer branches being extended to completely cover the aqueous surface where no further bridging can occur (Amirtharajah and Mills 1982; Al-Shamrani et al. 2002; Binnie et al. 2002).

2.6.4.6 Flocculation

Flocculation occurs after coagulation, which is a second phase solid-liquid separation process, to transform the smaller oil droplets into larger flocs. At this stage, there is physical conditioning of the emulsions to attach to each other into larger aggregates or flocs. However, the rate of aggregation is determined by the rate at which the oil droplet collisions occur. The inter-particle or oil droplet collisions can occur via three-physical transport processes, which leads to the formation of the oil droplet floc aggregates or floc (Binnie et al. 2002; Canizares et al. 2008; Edzwald 2011). These are

i. **Brownian diffusion:** This is due to the random motion of the particles caused by the continuous agglomeration of the surrounding charge oil droplet. This affects the movement of the colloidal oil droplet with minor influence on larger flocs greater than 1µm. Brownian flocculation is relatively a slow process as compared to most chemical reactions (Amirtharajah and Mills 1982; Canizares et al. 2008).

ii. **Fluid shear:** This occurs when there is a need to influence the oil droplets greater than 1µm and speed up the flocculation process. Mixing from an external source is then required. This causes a velocity difference or gradients in laminar or turbulent flow situations resulting in inter-particle interactions. The rising velocity gradient is directly related to the energy dissipated per unit mass of the liquid (Amirtharajah and Mills 1982; Canizares et al. 2008).

iii. **Rising or settling velocity**: The differential rising or settling of the flocs produces a vertical transport of the oil droplet flocs resulting in collisions. In some cases larger flocs, which may continue to aggregate individuals, are broken into smaller fragments and left in suspension. Where the driving force for either settling or rising velocity is the parameter controlling the mechanism. Studies have shown that with an increase in floc size, the absorbency increases resulting in a decrease in floc density and the settling velocity. The oil droplet flocs may grow until they reach a certain limiting size depending on the shear rate applied (Amirtharajah and Mills 1982; Bolto and Gregory 2007; Canizares et al. 2008).

2.6.5 Influential factors of coagulation and flocculation

Coagulation and flocculation include the overall chemical process to promote the inter-particle or oil droplet interaction and floc formation within the treated MOW. So, the effectiveness of coagulation for separation of oil from water can be determined by the amount of oil captured on the flocs as earlier discussed on the particle agglomeration of the oil droplets in emulsions (Section 2.6.4.5). This is because of the several oil droplet transportation mechanisms such as Brownian diffusion, fluid motion, and settling or rising velocity (Binnie et al. 2002; Khannous et al. 2011).

However, there are parallel and sequential reactions that occur when a metal salt is added to the MOW. The rate of this reaction depends on several factors that influence the efficiency and effectiveness of the coagulation process. Moreover, some of these factors seem to indicate an inter-dependency between the coagulant dose, coagulant type and the water characteristics (Binnie et al. 2002; Chen 2015). In addition, pH, alkalinity, temperature, ionic species presence in the MOW and the mixing conditions at the point of the coagulant addition may have an effect (Hempoonsert et al. 2010; Guan et al. 2014). These are some of the influential factors and are explained in more detail in the next sections.

2.6.5.1 pH adjustment

The pH plays a dominant role in coagulant-oil droplet interaction, which affects the oil–water density to cause the separation, as the oil-water emulsion usually consist of complex molecules, having both hydrophilic and lyophilic groups at both ends (Hirasaki et al. 2011). This is because oil emulsions have a strong affinity which overcomes the coalescing behaviour resulting in dispersed oil droplets in the water phase (Zhang et al. 2012) .

To demulsify and destabilise the oil droplets involves the reduction of the electric force or the double layers, which can be achievable by pH adjustment (Hempoonsert et al. 2010). The pH prior to and after coagulation is essential in finding the effectiveness of destabilisation. The initial pH defines the characteristic of the MOW as well as the tendency for the MOW to react with the coagulants. In addition, solubility of metal hydroxide species is also affected by pH (4 to 8), therefore pH adjustment prior to coagulant addition is very important to power the chain reactions that will occur (Binnie et al. 2002; Hempoonsert et al. 2010; Yang et al. 2010). Some of the effects of pH includes:

i. **Ionic effects**: The activities of the ions can affect the hydrolysis of the metal coagulants. For instance, it is difficult to obtain aluminium species when there is the presence of sulphates. Thus, sulphates may form precipitates in acidic medium where soluble polymeric aluminium species exist. The sulphate enhances precipitation based on the characteristics of the aluminium monomer units (Sahu and Chaudhari 2013).

ii. **Alkalinity effects:** The alkalinity of the MOW has some influence on the pH after the addition of the coagulant. In contrast, MOW with high alkalinity often prevent water utilities from operating at optimum pH by the initiators or coagulants for removal of the contaminants (eg. pH 4-5 for Iron, pH 5-6 for alum) (Binnie et al. 2002; Yang et al. 2010; Zhang et al. 2012). MOW with high alkalinity will require more acids to adjust the pH; whiles those with low alkalinity will require high basic salt or high coagulant dosage to balance the pH. In situations like this, the process becomes difficult to operate with influent variation in both coagulant dose and alkalinity. In addition, there will be the need to buffer the pH before and after the treatment, which will increase chemical usability cost (Binnie et al. 2002; Sahu and Chaudhari 2013).

However, the alkalinity demands of the most widely used ferric and aluminium salts such as ferric chloride and aluminium sulphate, can be determined by using the stoichiometric reactions in equations (2-1) and (2-1) respectively.

$$\mathrm{FeCl_3 . 6H_2O + 3(HCO_3^-) \rightarrow Fe(OH)_3 + 3Cl^- + 6H_2O + 3CO_2} \tag{2.1}$$

$$\mathrm{Al_2(SO_4)_3 . 14H_2O + 6(HCO_3^-) \rightarrow 2Al(OH)_3 + 3SO_4^{2-} + 14H_2O + 6CO_2} \tag{2.2}$$

2.6.5.2 Temperature

Temperature serves as the driving force for the chemical reaction rate to enhance the oil-water separation. In addition, temperature affects the oil droplets viscosity, mobility, collision, solubility, density, rising and settling velocity, coalescence and the physical characteristics of the oil droplets flocs formed. According to Hempoonsert et al. (2010), floc-settling velocity will decrease at lower temperature due to an increase in the water velocity. In addition, the difference in densities between the oil and water will also ensure effective separation. However, metal salts of aluminium are found to be less sensitive to temperature compared to that of ferric salts (Binnie et al. 2002; Zhang et al. 2012).

2.6.5.3 Mixing requirement

A procedure of floc formation, breakage, and re-formation can approximately show the floc strength. Several chemical reactions occur immediately after the addition of coagulants resulting in active coagulant species. In general, destabilisation and propagation of flocs by coagulation occurs predominantly by two mixing regimes, namely rapid mixing and slow mixing (Painmanakul et al. 2010).

The primary function of the rapid mixing is for transportation or collision interaction between the colloid and the hydrolysis product formed during the destabilisation. From a process engineer experience (Umgeni Water, Wiggins, South Africa), about 50% of plants use stirred flocculation tanks where the flocculation time varies between 6 and 120 minutes, and the others use in-line blenders and weirs (Schalkwyk et al. 2016). This requires high intensity (G values of 3000 to 4000 s^{-1}) and short duration (< 0.1s). Nevertheless, at times, flocculation intensities of 130 to 150 s^{-1} are applied. The tenacity of the slow mixing is to accelerate the formation of the aggregates by holding the particles in suspension for the collision to occur. Slow mixing provides a velocity gradient even for particles with similar size that are larger than 1µm. In practice, this is achieved by a suspension being stirred at high rate to cause floc breakage, and after the breakages, the slow mixing is initiated to increase the floc size (Binnie et al. 2002; Painmanakul et al. 2010).

2.6.5.4 Coagulant dosage

Coagulant additions is a vital factor in finding the final metal-hydroxide species formed. Therefore, the effectiveness of oil droplet destabilisation is directly proportional to the amount of coagulant added. There exist an optimal dosage for every coagulant, which depends on the specific water chemistry and the composition at which the coagulation is optimised (Painmanakul et al. 2010).

Theoretically, coagulation is optimised to find the amount of coagulant at the highest peak for the removal possibility. Nevertheless, under dose or too little coagulant may offer insufficient destabilisation to promote aggregation, whiles overdose or too much coagulant may lead to destabilisation as the concentration increases (Daud et al. 2015). For instance, oil droplets have negative charges and emulsified stable, sufficient dosage neutralises the charge whiles higher dosage will restabilised the emulsions. In addition, when the coagulant added is more than the expected charge neutralisation, the metal hydroxide precipitation occurs which might be carry over to the discharge sewer. Therefore, to safeguard the operation requirement and discharge regulations, it is essential to maintain coagulation dosage to avoid cost (Patterson 1985; Binnie et al. 2002; Vedoy and Soares 2015; Schalkwyk et al. 2016).

2.6.6 Comparative study on aluminium and iron based coagulants

The coagulation characteristics of the trivalent metal coagulants as said earlier depends on acidity, solubility and the extent of hydrolysis. It is important to know the behaviour of both the iron and aluminium based coagulants to maximise the treatment of the MOW. In addition, there has been a concerned raised about some metals such as aluminium being carried over into the finished treated water, which must be within the regulatory limit of 50 to 200 µg/L (Amirtharajah and Mills 1982; Binnie et al. 2002; Li et al. 2008; Yang et al. 2010). The chemistry associated with the reactions of metal salts in water is complex, in the form of many species which can be affected by both pH and temperature (Amirtharajah and Mills 1982; Schalkwyk et al. 2016).

Figure 2.3 shows the aluminium metal coagulation mechanism; while a similar coagulation diagram for ferric metal is presented in Figure 2.4. Some of the characteristic difference between the aluminium and iron based coagulants include the following;

a. On the bases of dry weight of coagulants, ferric metals have two times the metal species than aluminium metals.

b. In terms of specific surface charge; both ferric and aluminium hydroxide flocs are similar. However, the low active metal species in aluminium metals might produce less metal hydroxide when compared to a similar dose of iron, resulting in the surface area available for adsorption of aluminium to be lower than that of the iron (Amirtharajah and Mills 1982; Schalkwyk et al. 2016).

c. Ferric species show much lower solubility over a broad pH range of (5.5-8). But aluminium species show a much higher solubility at the normal coagulation pH values ($5 < pH < 7$), which enables the formation of hydroxide at a lower coagulant dose.

d. Polyelectrolytes that are synthesised from monomers of ferric and aluminium metals are said to be more expensive than the traditional species, but are effective over a wide working pH with lower dosage required and relatively low sludge volume produced (Amirtharajah and Mills 1982; Schalkwyk et al. 2016).

Some coagulants used as surface additives must satisfy some practical constrains, including low cost, availability and sludge disposal being environmentally friendly. However, there has not been any research indicating the most effective coagulant for wastewater treatment. This is because in most instances a coagulant can perform well with one water source and might perform differently with another water source as depicted in Table 2-5.

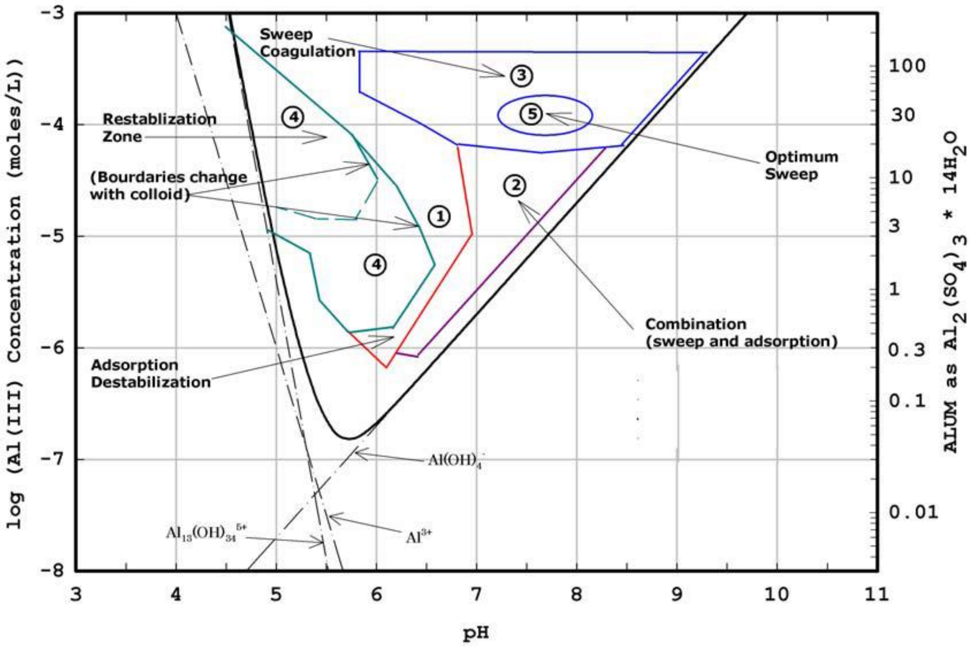


Figure 2.3 Representation of aluminium coagulation mechanism (Amirtharajah and Mills 1982; Schalkwyk et al. 2016); Zone 1-adsorption destabilisation, zone 2-flocculation and adsorption, zone 3 –coagulation, zone 4-restabilisation, and zone 5-optimum floc

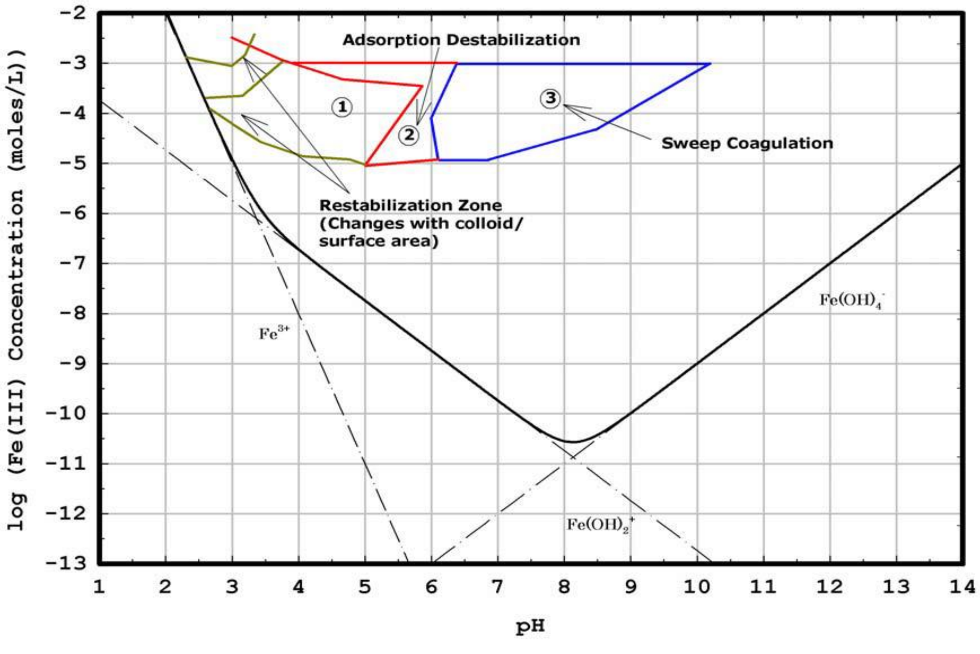


Figure 2.4 Representation of iron coagulation mechanism (Amirtharajah and Mills, 1982; Schalkwyk et al., 2016); Zone 1-restabilisation, zone 2-adsorption destabilisation, and zone 3 –coagulation

Table 2-5 Summary of coagulant performance with respect to different water chemistry

Coagulant type	Optimal dosage (mg/L)	pH	Influent (SOG mg/L)	Removal efficiency (%)	Reference
Aluminium sulpahte	100	8	1630	99.3	(Al-Shamrani et al., 2002)
	50	4	500	93	(Hosny et al., 2016)
	800-1400	8	-	99% COD	(Painmanakul et al., 2010)
	50	5	1218	94	*(Tetteh et al., 2017)
Ferric sulphate	120	7	1630	99.9	(Al-Shamrani et al., 2002)
	700-1000	8	170	73	(El-Gohary et al., 2010)
	50	5	1218	91	*(Tetteh et al., 2017)
Ferric chloride	500-700	8	170	73	(El-Gohary et al., 2010)
	100	6	500	95	(Zouboulis and Avranas, 2000)
	50	5	1218	92	*(Tetteh et al., 2017)
Aluminium Chloride	50	5	1218	93	*(Tetteh et al., 2017)
poly-aluminium chloride	30	6	100.9	90	(Li et al. 2007)
polyacrylamide	15	6	100.9	90	(Li et al. 2007)

*(present author)

2.6.7 Application of some coagulants for MOW treatment

One of the objectives of this work was to investigate the application of coagulants for the DAF treatment of the MOW on a pilot plant and furthermore on a large-scale. The comparative performance of polymeric organic and inorganic coagulants with respect to water quality or contaminant removal, coagulant dosage and cost is essential to select a coagulant for a particular water source (Table 2 5). The primary function of these chemicals in coagulation are to destabilise the oil droplet and strengthen the oil droplet flocs formed to not break up the external force easily. This occurs predominantly through the mechanism of (a) adsorption of hydrolysis species on the colloid causing the charge neutralisation, and (b) interparticle bridging where interactions occur between the metal hydroxides and the colloidal particle resulting in physical pulling of the flocs together (Zouboulis and Avranas 2000; Santo et al. 2012).

Therefore, it is necessary to identify the characteristics of the metal coagulant depending on the operational conditions, the particulates and the water quality. This knowledge will assist the water industries to select the most appropriate coagulant based on scientific knowledge. A standard jar test apparatus is usually used for the bench-scale testing while the pilot plant or finally full scale testing is used to improve the limitations of the jar test based on the hydrodynamic conditions (Younker and Walsh 2014). The apparatus and its application will be discussed in more detail in chapter 3.

2.7 Physical treatment (Flotation) process

Physico-chemical treatment systems, generally implemented for effective wastewater treatment plant design, encompasses DAF, which is operated based on the concept of flotation. Conventionally, flotation is a concentration process in which selective hydrophobic materials are separated from hydrophilic materials by a gravity separation process. Flotation, as an alternative to sedimentation in water clarification, has great potentials in the treatment of wastewater for high quality output (Zabel, 1985; Edzwald, 1995; Atadashi et al., 2011).

Flotation has gained prominence in the water and wastewater industries due to excellent effluent quality, high throughput, and flexibility in design and lower cost in construction compared to other separation processes (e.g. API separators, media filtration, hydrocyclones, membranes) (Cheryan and Rajagopalan, 1998; Atadashi et al., 2011; Diya'uddeen et al., 2011; Chollom et al., 2015; Munirasu et al., 2016).

The DAF unit comprises of an air saturator and pumps, which are high energy driven as compared with sedimentation. This serves as drawbacks for the flotation process (Zabel, 1985; Feris et al., 2000). In contrast, the flotation process is chosen over sedimentation in terms of treatment cost with respect to effluent quality. The advantages of DAF include, but are not limited to;

(i). A suitable hydrodynamic design of the entire flotation system, more especially the flotation chamber. The release of entrained air causes turbulence for the continuous removal of the oil droplets or the floated surface scum using a mechanical skimmer.

(ii). The design of the entire system can be operated automatically under certain conditions, which requires less attention of trained personnel.

(iii). As a pre-treatment process before secondary treatment units such as biological treatment in the wastewater and sludge thickening (Zouboulis and Avranas, 2000; Adlan et al., 2011; Amaral Filho et al., 2016).

(iv). The DAF mechanism involves the transfer of the suspended phase (oil droplets flocs) from bulk the dispersion medium (coagulated MOW) to the liquid phase by means of bubble attachment (Feris et al., 2000).

In a typical flotation process, the coagulated oil droplets adhere onto the air bubbles to lower the apparent density below that of the water. This then allows the conglomerate to float to the surface. The separation is by introducing compressed air into the liquid phase. The buoyant force of the combined oil droplets-air bubble then cause the rise to the surface. However, this process is somehow complicated because it requires the hydrodynamics and surface chemistry come in contact through the means of bubble attachment (Moursy and El-Ela, 1982; Zabel, 1985). Therefore, to obtain tremendous performance, studies have shown that coagulation chemistry has a stronger influence on DAF performance than physical flocculation parameters (Edzwald, 1995; Feris et al., 2000).

To enhance the flotation performance through bubble attachment involves mechanisms, such as (a) air bubble generation, (b) contact between air bubble and oil droplets, (c) attachment of gas bubbles to oil droplets, and (d) rising up of air-oil combination (Santo et al., 2012; Saththasivam et al., 2016). For a successful flotation system, oil droplets-air bubbles coalesce strongly until the bubbles reaches the surface of the flotation cell to allow them to form larger flocs. Most of the flotation process generates microbubbles (30-100 µm) for the oil droplet-air bubble capture phenomenon (Zabel, 1985).

2.7.1 Types of flotation techniques

There are different ways of producing air bubbles, which give rise to different types of flotation processes, including electrolytic flotation, dispersed-air flotation and dissolved-air flotation (Edzwald, 1995; Edzwald, 2010).

2.7.1.1 Electro-flotation

The bases of electrolytic flotation is the generation of micro bubbles of hydrogen and oxygen by the passage of direct current (DC) between two electrodes immersed in weak aqueous solution. Aluminium or steel electrodes normally used serve as drawbacks, such as high replacement costs and maintenance costs due to fouling (Al-Shamrani et al., 2002; Bensadok et al., 2007; Edzwald, 2010; Adlan et al., 2011; Amaral Filho et al., 2016; Yu et al., 2017).

In the electrolytic flotation system, reversible polarity occurs between the electrodes, where the aluminium ions are released from the anodes and hydrogen bubbles are generated from the cathode to enhance the flotation of the flocs. Although electrolytic flotation has limitations, it is effective under suitable conditions for the removal of light colloids such as emulsified oil from water. This is because the microbubbles generated does not create turbulence in the system, hence is suitable for fragile flocs (Edzwald, 1995; Edzwald, 2010). The bubble size generated in electrolytic flotation restricts the surface loading to less than 4 m/h as compared with up to 12 m/h for DAF (Zabel, 1985).

2.7.1.2 Dispersed air flotation

The dispersed air flotation system is made up of air injected with a high-speed mechanical agitator or spinning impeller to produce bubbles essential for the flotation process. However, there are two different types of this technology for industrial applications namely (a) foam and (b) froth flotation (Edzwald, 1995).

In foam flotation, air bubbles are generated by forcing the air through porous media made from metal, ceramic or plastic. Likewise, in froth flotation, the air bubbles are generated by introducing the air in the proximity of an impeller or turbine, and then breaking the air into micro bubbles by the shear movement of the impeller or turbine blades. Generally, dispersed air flotation is mainly used in the mineral industry and municipal wastewater treatment to remove solids from high volume of process water or waste. This is because it has the ability to produce relatively large air bubbles of size ranging from 700-1500 µm as compared with bubbles of 20 to 100 µm for DAF or electro-flotation (Moursy and El-Ela, 1982; Al-Shamrani et al., 2002).

This is unsuitable for fragile flocs because they are likely to break at high turbulence. The compact size makes it advantageous in the removal of relatively free oil and suspended solids. However, major drawbacks include high power requirements and dependence on strict hydraulic control. It is therefore highly recommended for thickening than clarification in potable water treatment (Zabel, 1985).

2.7.1.3 Dissolved air flotation

In the DAF, an air-water saturator system is the source of air bubbles, a flotation vessel facilitates the intimate contact between pre-formed flocs, and the air bubbles. This provides the required environment for the separation process to take place.

Ideally, the water is saturated under pressure with air saturator pressure ranging from 300 to 700 kPa. The pressure reduction in the DAF tank results in the formation of micro bubbles ranging in size between 20 and 100 µm. The difference between the operating pressure of the saturator and the outlet pressure in the flotation vessel is proportional to the volume of air injected into the system. The supersaturated water is forced through needle valves of distinct orifices and cloudy micro bubbles are produced at the constriction downstream (Zabel, 1985; Edzwald, 1995; Al-Shamrani et al., 2002).

As, the air bubbles move upwards through the water, they are then entrapped by the oil droplets and the organic matter. Nevertheless, to enhance the effectiveness of DAF, the MOW is usually acidified and coagulated effectively before introducing the micro-bubbles to form bubble-floc aggregates. The floating of the bubble-floc is due to the three distinct mechanisms as discussed previously viz (a) entrapment of the bubbles within the network of the oil droplet flocs (b) growth of bubbles-oil droplet floc and (c) attachment of bubbles during the floc collisions (Zabel, 1985; Al-Shamrani et al., 2002; Meyer et al., 2005).

2.8 Types of Dissolved Air flotation (DAF) system

Over the past years, there has been dramatic improvement on the design and specification of DAF, with the view of improving potable water treatment (Moursy and El-Ela, 1982). Besides potable water, the concept of DAF has wide application in wastewater treatment such as mineral industry, sludge thickening, separation of biological algae, the petrochemical and oil refinery industries (Edzwald, 2010). In addition, for the treatment of ultra-fine material with fragile flocs, the most appropriate system has been DAF since it require a less dense floc (Amaral Filho et al., 2016).

The DAF process has been reported to be more advantageous when treating high volumes of effluent (100-20,000 m^3/h) to yield recommended footprint (Schalkwyk et al., 2016). However, there are three leading designs of DAF, which depends on the mode of generating the air pressure namely vacuum flotation, micro flotation and pressure flotation (Zabel, 1985; Edzwald, 1995; Al-Shamrani et al., 2002; Younker and Walsh, 2014).

2.8.1 Vacuum flotation

All the flotation techniques require a source of air bubbles to enhance the liquid-solid separation. In vacuum flotation, the water to be treated is saturated with air at atmospheric pressure (1 atm). A vacuum is then applied to the flotation vessel to create a relatively supersaturated suspension resulting in releasing the air as small bubbles. The applicability of this process is limited with the feasibility of the vacuum on the amount of air available for the flotation. The application of vacuum flotation is mostly done in a batch process and a refined equipment is required to maintain the vacuum (Zabel, 1985; Edzwald, 1995; Al-Shamrani et al., 2002).

2.8.2 Micro-flotation

To increase the bubbles in micro-flotation, the volume of the water in the saturator vessel is firstly pressurised. Thus, in the down flow section, the water is aerated and the amount of air dissolved in the water increases with an increase in the hydrostatic pressure. As the water rises in the up-flow section, the hydrostatic pressure decreases, resulting in the release of the air bubbles. Acquiring effective floatability or bubbles generation is done by passing the water down and up a shaft approximately 10 m deep, where the amount of air provided determines the amount of air available (Zabel, 1985; Edzwald, 1995; Al-Shamrani et al., 2002).

2.8.3 Pressure flotation

Currently the most widely used DAF process is pressure flotation. In pressure flotation, the air is dissolved in water under pressure. The pressure of water pre-saturated with air at high pressure above the atmospheric pressure (1atm) is reduced. Thus, air is released resulting in the formation of micro air bubbles (Zheng et al., 2016; Yu et al., 2017). The advancement in DAF for the past 20 years has led to the increased efficiency and usage for industrial pre-treatment application. This advancement has contributed to a wide number of many designs and configurations. The three different flow schemes of pressure flotation includes full flow pressure flotation, split-flow pressure flotation, and recycled-flow pressure flotation (Zabel, 1985; Edzwald, 1995; Karhu et al., 2014).

2.8.3.1 Full flow pressure flotation

In this process, the entire influent is pressurised and aerated in the flotation tank to form bubbles. This flotation is often designated for influents that require a large volume of air bubbles. It is commonly used in industries with influent streams suspended with solids of above 800 mg/L. Addition of chemicals for pre-treatment of the influent flowing into a DAF tank is not always necessary (Zabel, 1985; Edzwald, 2010; Yu et al., 2017). Figure 2.5 shows the type of full flow pressure DAF.

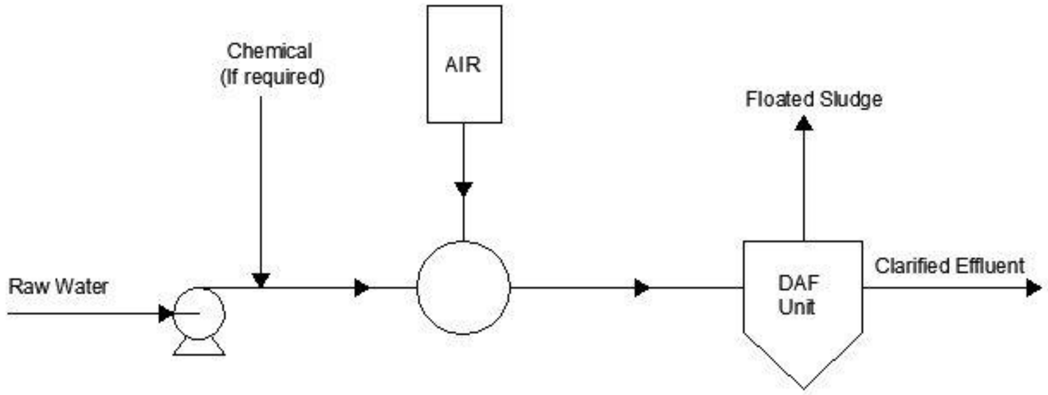


Figure 2.5 Schematic full flow pressure flotation (adapted from Edzwald, 2010)

2.8.3.2 Split or partial flow pressure flotation

In this process, a partial flow of the influent stream of about 30-50% is subjected to pressurisation, while the remaining flows directly to the flotation chamber as shown in Figure 2.6. This is commonly applied where suspended solids are of low concentration and hence requires micro bubbles to enhance the separation.

According to Edzwald (2010), both the full and split flow pressure system are not effective when coagulation and flocculation is required , because any floc formed before the air release facility will be destroyed due to high collision exerted during the pressure release. However, the major concern of the partial flotation arrangement is its energy and maintenance cost. The split flow pressure configuration system are more expensive than the full flow pressure, as the saturator and feed pump only handle a fraction of the full flow influent. In addition, split flow offers less air but still requires high pressure to provide the same amount of air (Zabel, 1985; Edzwald, 2010; Yu et al., 2017).

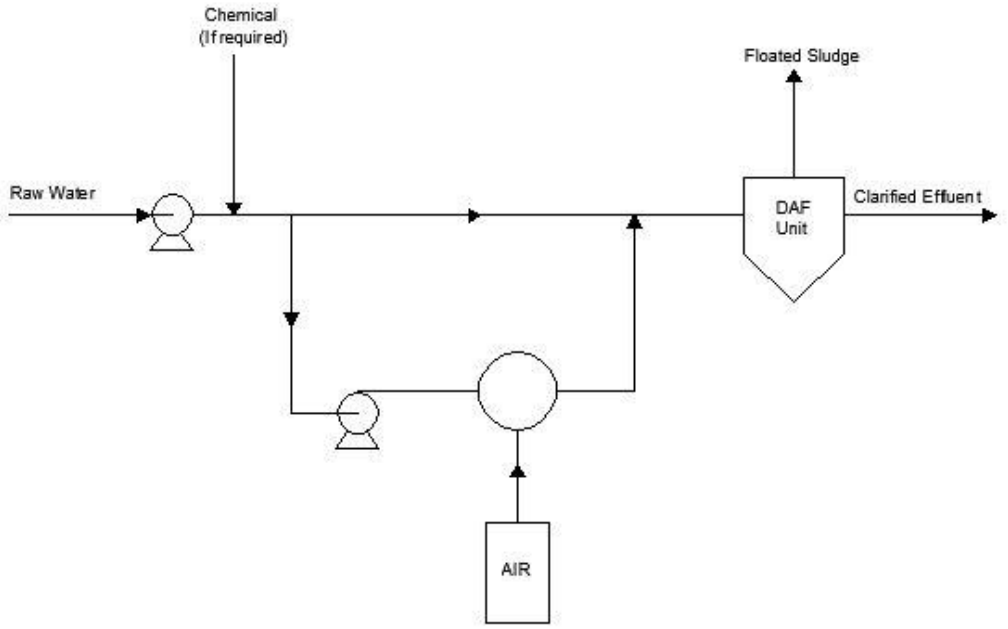


Figure 2.6 Schematic split or partial flow pressure flotation (adapted from Edzwald, 2010)

2.8.3.3 Recycle flow pressure flotation

The recycled flow flotation is the most widely used alternative system. Many manufactures have made transition from full-flow pressurisation to recycle-flow pressurisation for the creation of the dissolved air to induce the flotation. In this system, part of the clarified effluent of about 15 to 50% is pressurised and recycled to the flotation chamber as shown in Figure 2.7. The saturated and pressurised recycled effluent is introduced into the system by the pressure release device with air bubble size of 20 to 100 µm. This process is usually employed where coagulation is part of the treatment configuration system. The influent flows into the flocculation or flotation tank if not required. The air bubbles attach themselves to the floc and the bubble-floc conglomerate floats to the surface (Zabel, 1985; Edzwald, 2010; Yu et al., 2017).

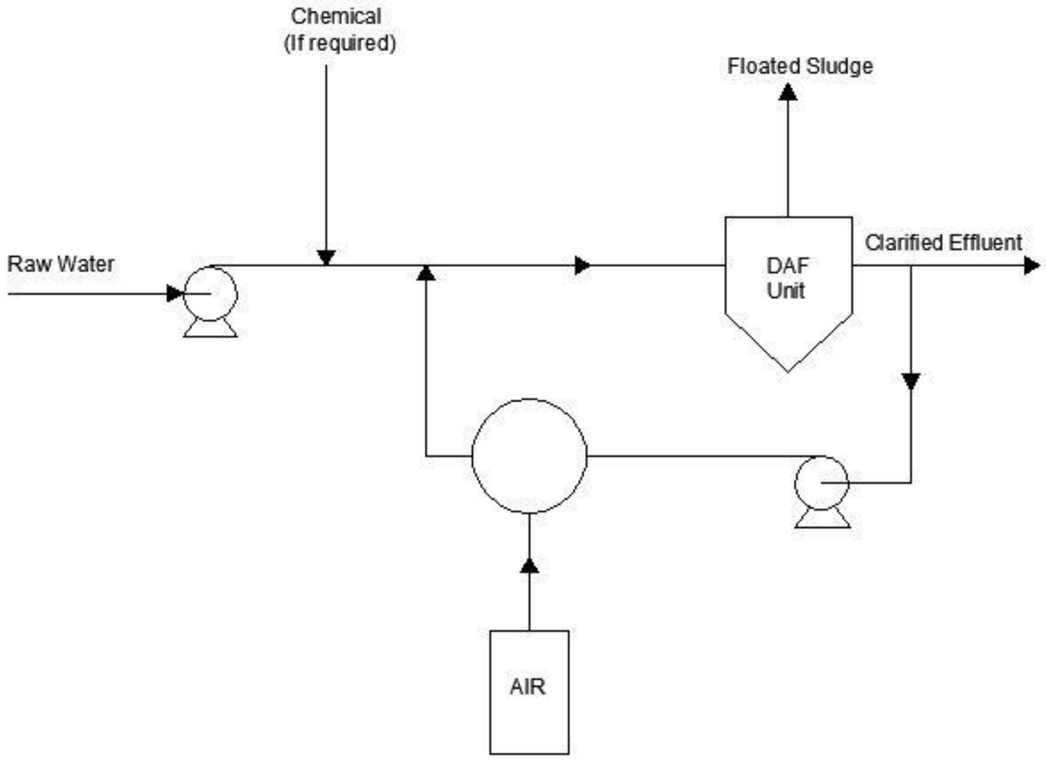


Figure 2.7 Schematic recycled flow pressure flotation (adapted from Edzwald, 2010)

2.9 The bubbles generation-DAF mechanism

The DAF plant for water and wastewater treatment consists of three independent unit processes: coagulation zone, air saturator and flotation zone. To ensure effective collision, which is followed by oil droplet-bubble adhesion, it is necessary to add surface-active agents in the DAF. Therefore, in the treatment chain, the inflow is firstly pre-conditioned for the formation of stable flocs. The air-water saturator system is the basis of the air bubbles and the flotation zone facilitates the intimate contact between the pre-formed flocs and the air bubbles thereby providing the required environment to enhance the separation to take place (Zabel, 1985; Edzwald, 1995).

In general, the favourable conditions to ensure the effectiveness of the DAF involves charge neutralisation and hydrophobic particle bubble adhesion (Khuntia et al., 2012). Most often, the affinity that exists between the water and oil droplet causes the collision between the air-bubble adhesion and the oil droplet to occur concurrently, which rise up to the surface to be skimmed off (Zabel, 1985; Edzwald, 2010; Yu et al., 2017).

The coagulant added entraps the air bubbles and enhances the formation of a very robust floc or sludge that resist fracture in the flotation zone. Ideally, the floc-air bubble conglomerate, and due to its acquired buoyancy and suitable hydraulics then moves to the surface of the flotation vessel (Khuntia et al., 2012). This accumulates as a floated sludge layer, while the clarified water moves to the bottom of the vessel where it is collected for further downstream treatment (Zabel, 1985).

2.9.1 DAF contact zone mechanism

In DAF, the flotation chamber has two zones namely the contact and separation zone. The purpose of the contact zone is to create an avenue for air bubble-floc aggregates while the separation zone provides the quiescent conditions for the aggregates to rise up to the flotation vessel surface. The contact zone serves as the meeting point for the pre-formed flocs and the stream of water saturated with air. The air bubbles precipitate out of the solution due to the pressure drop experienced by the incoming saturated air-water stream. Studies have proposed four models for air bubble-particle attachment to occur to form a stable air bubble agglomerate (Zabel, 1985; Edzwald, 1995; Al-Shamrani et al., 2002). These includes:

i. **Adhesion of bubbles to preformed flocs:** The pre-formed flocs are attached to the surface of the air bubbles. This occurs when oil droplets enter the surface of the air bubble. The probability of collision and adhesion to occur is proportional to the oil droplet size such that the oil droplet surface must be hydrophobic for the droplet to stick to the air bubble. The success of this depends mostly on the droplet size whereby a size less than 20 µm will be floated by bubbles as compared with bubbles greater than 40 µm (Zabel, 1985; Edzwald, 1995; Younker and Walsh, 2014; Schalkwyk et al., 2016).

ii. **Entrapment of the air bubbles into the floc:** This occurs when the bubbles become trapped in the structure of the oil droplet floc. When the flocs are larger than individual, there may be no adhesion, whereby the bubbles can be detached from the oil droplet. Hence, the collision effectiveness becomes lower than that for the adhesion (Al-Shamrani et al. 2002; Khuntia et al. 2012).

iii. **Incorporation of the air bubbles into a floc particle:** This is because of breakup of flocs and consequence of re-flocculation occurring in the contact zone. Thus as flocs are still in the process of being formed while air bubbles are introduced into the contact zone, air bubbles may be incorporated into the growing flocs (Zabel 1985; Edzwald 1995; Al-Shamrani et al. 2002).

iv. **Growth within flocs**: It is based on the principle that supersaturated air will specially precipitate out on existing floc nuclei when the pressure is slowly reduced. However, when saturated air is introduced over a layer of coagulated oil droplets, after a few minutes, small air bubbles begin to grow within the floc. However, under typical operating conditions, stable flocs are introduced into the contact zone. The bubble-droplet agglomeration by adhesion and entrapment for floc growth are usually considered as the superior contact mechanism (Zabel 1985; Edzwald 1995; Al-Shamrani et al. 2002).

2.9.1.1 Bubble size

There is a concern about small air bubbles (between 40 and 170 µm) requirement for effective separation in the DAF. This is because most large bubbles create hydraulic turbulence while rising to the surface and decrease the surface area of the oil droplet flocs (Edzwald, 1995; Al-Shamrani et al., 2002). Studies have shown that to decrease the bubble size depends on saturation pressure; recycle flow rate and nozzle geometry (Khuntia et al., 2012). Besides, the bubble size decrease as the saturation pressure and the recycle flow rate through the nozzle is increased. This is because smaller air bubbles move gently to the top, increase particle-bubble contact time, and creates a conducive environment for attachment between the droplet and the bubble (Zabel, 1985; Edzwald, 1995).

2.9.1.2 Particle size

In every treatment process there is variation in particle size for effective particle-bubble attachment and subsequent flotation. Thus, certain minimum particle size is not affected by the upward mobility of the water and bubbles in the contact zone resulting in poor flotation efficiency. In addition, if the particle size is at a maximum, it may be too heavy to be floated. In this case, the particle density becomes the determination factor for the floatability. According to Edzwald (2010), theoretically the particle diameters between 10 and 50 µm were ideal for the application of DAF in wastewater treatment. In practice, also particles with much higher diameters than 50 µm can be effectively treated by DAF (Zabel, 1985).

2.9.1.3 Attachment and detachment of oil droplets

In the contact zone, the turbulence and gravitational forces causes some of the flocs to detach from the bubbles as they move in the flotation zone. Thus, large agglomerated flocs are likely to be detached due to their higher inertia and greater strain on the oil droplet-bubble bond (Khuntia et al., 2012; Lakghomi et al., 2015).

Thus, force exerted by surface tension sometimes exceeds the shear force and gravitational force, which are very complicated and varies, depending on the flotation zone. Therefore, the contact zone design should allow for sufficient time for the oil droplet-bubble attachment. In addition, excessive turbulence should be avoided due to floc break up. Thus, moderate turbulence should be encouraged to facilitate collisions between the oil droplet and the air bubbles (Lakghomi et al., 2015).

More so, induction time and flotation time required to enhance the attachment to occur between the oil droplets and bubbles is vital. The oil droplet can only adhere to the air bubbles when the required holdup or flotation time for them to be bind together is greater than the induction time. This is usually affected by the fluid viscosity, particle and bubble size, and existing force between the oil droplet-bubble (Zabel, 1985; Edzwald, 1995; Zouboulis and Avranas, 2000; Al-Shamrani et al., 2002).

2.9.2 Air-water saturator system

In practise, air requirements for clarification by DAF are met by recycling a small fraction of the DAF treated water into the saturator operated at high pressure. The vertical packed saturators are normally used for the DAF clarification applications (Diya'uddeen et al., 2011; Chen, 2015; Amaral Filho et al., 2016).

However, according to Edzwald (1995) practically, air saturator pressure from 350 and 550 kPa and hydraulic loadings varying between 60 and 100 m/h will show no further decease in bubble size. It is very important to optimise the air saturator system to reduce cost of operations, because it contributes to about 50% of the power cost of the flotation process. Although there are various ways employed for dissolving air under pressure in the recycled streams, sparging air into the water in a pressure vessel via recycled airflow has been known to be the cheapest operating configuration system of the air saturator (Zabel, 1985). Air bubbles are injected into the contact zone of the flotation vessel in the form of a stream of water saturated with air via suitable chosen nozzles (30-100 mm) (Karhu et al., 2014).

The increase of solubility of air in water with pressure results in mass transfer from the gas phase into the liquid phase and this takes place at the point of supersaturated air-water. The saturated water experiences an equilibrium shift when it is released under atmospheric pressure into the flotation vessel. However, air solubility is dependent on temperature such that solubility of air in water decreases as temperature increases and then increases with the pressure (Khuntia et al., 2012).

Air is a composition of nitrogen and oxygen in the proportion of 79% and 21% respectively. Therefore, theoretically, air saturator efficiency can only reach 91% based on atmospheric air. Saturation air will therefore be about 9% less soluble than atmospheric air. Air requirement is generally expressed as the mass of air per volume of raw water being treated. According to Edzwald (1995), the quantity of air required for clarification generally varies between 5 and 10 mg/L.

2.9.3 Important DAF operating parameters

Several factors in the DAF treatment process affect the quality of the treated water. These include the coagulation variables as discussed in section 2.6.5 and the flotation parameters such as percent air-water recycle, contact zone upflow rate and residence time, crossflow velocity and hydraulic loading rate (Wang et al., 2007; Adlan et al., 2011; Khannous et al., 2011; Oliveira et al., 2014).

For smooth operation and effective DAF performance, all the parameters need to be set or optimised in such a manner that the desirable MOW quality produced is cost effective. The study on some operating parameters provides an insight for systematic optimisation of the DAF meant for MOW treatment processes and as an alternative for the economic consideration approach (Zabel, 1985).

2.9.3.1 Flotation or residence time

In DAF, the optimum retention time for the air-water mixture is determined after the release of the pressurised saturator air-water into the flotation zone. At this point, the flotation mechanism is observed as the air bubbles are either adhered to or entrapped in the floc. This action stimulate the increase in buoyancy of the floc and allows them to rise to the sludge layer, hence sufficient time is required. The time required for the flocculation is usually 10 to 15 minutes and in general practise the time is said to be 10 to 40 minutes (Younker and Walsh, 2014).

2.9.3.2 Bubble generation

The bubble is produced as a result of introducing compressed air into the flotation tank by dissolving air under pressure. The air supplied for the flotation is expressed as the ratio of air-water flowrate from 5 to 12% (Khuntia et al., 2012). This causes a rise up of the air bubbles attached with oil droplet to form foam, which is collected by a skimmer. However, micro bubbles moves slowly to the top with an increase in particle-bubble contact time, while larger bubbles will cause disruption or turbulence of the float layer (Zabel, 1985; Edzwald, 1995; Zouboulis and Avranas, 2000).

2.9.3.3 Rising velocity

The upward velocity is a function of the rise rate of the water in the flotation zone. This is a major concern in determining the efficiency of the DAF. It is mostly known as surface loading rate or overflow rate. It is defined as the flow per unit surface area of the clarifier. The shorter the flotation time, the better, since the floc will start to break at a longer time. Therefore, in this process the allocated time is said to be between 10 and 30 minutes (Edzwald, 1995; Karhu et al., 2014).

2.9.3.4 Air to water recycle ratio

Water saturated with air is produced in a pressurised vessel. The water occupies 80% of the total volume, which is then sealed closed. At the desirable saturator operating pressure, the compressed air is then released via the nozzle into the contact zone. The air to water ratio is the amount of air applied to the DAF to enhance float the suspended solids.

Unfortunately, there is no fixed theoretical values of air to solid ratio because it depends on the type of solids as well as the DAF system (Dassey and Theegala, 2011; Chen, 2015). According to Edzwald (2010) when water is recycled at 6 to 22% and saturated with air at 400 to 600 kPa, by injecting at the bottom of the DAF, the corresponding pressure drop injects the dissolved air to form smaller bubbles with size of 10 to 100 µm (Zabel, 1985).

2.9.3.5 Hydraulic loading rate

In practice, hydraulic loading rate (HLR) is an important factor for the clarification in the DAF unit with a high rate of 5-40 m/h as compared with sedimentation loading rates of 0.5 to 5 m/h, but both depend on the water quality, temperature and the flotation tank configuration (Zabel 1985). It has been reported by Edzwald (2010) that, a pilot plant DAF treatment facility may be designed and operated with a HLR of 30 to 40 m/h depending on the water quality.

The HLR is expressed as the amount of inflow that can be applied per the DAF surface area with time. However, the inflow is the flowrate of the influent plus that of the recycled air-water for the effective separation area. However, when HLR is controlled, it will not cause turbulence or re-entrainment of solids into the moving water (Dassey and Theegala 2011).

$$\mathrm{HLR} = \frac{\text{Effleunt flowarte}}{\text{Total clarifier footprint}} \tag{2.3}$$

Where HLR= hydraulic loading rate (m/h)

Effluent flowrate = clarified effluent (m^3/h)

Total clarifier footprint = footmark zone including contact and separation zones of the clarifier (m^2).

2.10 Design of experiment

Design of experiment (DOE) is a systematic way of generating a relationship between input factors that affect a process system and response as the output, to establish the cause-and-effect relationship of a robust system from an experimental outcome. It is also a method obtaining a suitable data, which can be analysed statistically to identify the optimum factors and level for the applicable purpose of interest (Iqbal et al., 2016).

In general, the DOE is associated with developing mathematical models with the experimental data designed for the process. However, the choice of DOE can have an impact on the accurate estimation and the cost of running experiments for the response or output (Ferreira et al., 2007; Bezerra et al., 2008). The response can be evaluated from the selected optimal points from the experimental design. This includes screening the variables and optimisation to identify the impactful factors for further analysis. However, there are three fundamental techniques to obtain experimental design outcomes, which includes:

i. **Randomisation**: This involves running experimental trials at an irregular order. This involves assigning different levels of the investigated factors to the experimental matrix in a random manner. This is done to avoid biased conclusion and prevent the influence of unknown variables.

ii. **Replication**: This is a repetition of the basic experimental runs. This concept allows approximation of the experimental error and the use of the sample mean to estimate the effect of a factor in a set of experimental runs.

iii. **Blocking**: This refers to a set of experimental design matrix arranged in groups based on their likenesses. This technique is used to improve the precision with which evaluations among factors of interests are completed.

2.10.1 Application of Response surface methodology

Over the past years, the driving force to improve and sustain WWTPs has been process control and optimisation. Optimisation is a means to obtain operating conditions applied to a process system to maximise and produce the best response. However, unsatisfactory strategy may lead to serious environmental problems, high-energy usage, high cost of maintenance and chemical usage (Dutta et al. 2015; Iqbal et al. 2016) .

Moreover, a high number of experimental runs are required before obtaining enough information for process optimisation. The application of DOE to generate the experiment matrix with less number of runs has become the alternative option to the use of the OFAT approach (Pambi and Musonge 2016). In this scenario, there is the need for systematic optimisation techniques based on simulation to quantify the effects of the operating parameters on the yield of contaminant removal (inlet minus outlet contaminant) (Baş and Boyacı 2007; Bezerra et al. 2008).

Recently, as optimisation is of great concern in production, many researchers are looking for the most important tool for process optimisation to maximise the efficiency of the process system understudy. RSM has been used for different effluent system optimisation including the present author’s on oil refinery wastewater (Tetteh and Rathilal 2017), sugar refinery wastewater (Pambi and Musonge 2016), biodiesel wastewater (Chavalparit and Ongwandee 2009), paper industry wastewater (Wang et al. 2007) and textile effluent (Dutta et al. 2015).

The number of experiment is determined by using RSM adapted from the Design Expert. However, after data collection, statistical analysis and modelling is done to identify the reasons for the most influential factor on the output variable or response (Baş and Boyacı 2007). Unfortunately, inaccuracy that occurs in physical experiments is associated with measured errors, while in computer simulations, numerical noise and round-off errors occur where an iteration does not converge completely. Hence, a strategy is adapted to select the point where the response evaluated is optimal. Nevertheless, using RSM at the optimal design, the input variables that have a large impact is identified and a response model is generated which corrects the errors (Li et al., 2016).

RSM can also be used in designing of experiments, modelling the experimental responses and explaining the effect of the main operating parameters and their interactions on the response. Moreover, the RSM initial step is to develop an empirical model to define the correlation between input factors and responses with least number of experimental runs, which provides enough information for process optimisation. RSM has been used to find a suitable evaluation for the accurate functional relationship between responses and a set of input variables (Bezerra et al. 2008; Iqbal et al. 2016).

Sometimes a first –order model is obtained when the response is well modelled by a linear function of the independent variables as expressed in equation (2.4) and (2.5).

$$Y = \rho_0 + \rho_1 X_1 + \rho_2 X_2 + \cdots + \rho_n X_n + \tau \tag{2.4}$$

Generally, higher order polynomials such as a second-order model are used when a functional design has centre points resulting in curvature of the response graphical presentation. Nevertheless, either the response surface can be represented in a three-dimensional space or contour plots to show the most critical points viz. maximum, minimum or saddle curvatures that are obtained from the quadratic polynomials.

$$Y = \rho_0 + \sum_{i=1}^{n} \rho_i X_i + \sum_{i=1}^{n} \rho_{ii} X_{ii}^2 + \sum_{i<j}^{n} \rho_{ij} X_i X_j + \tau \tag{2.5}$$

Where the linear parameters Y, ρ_0 , ρ_i , X_i and τ represents the response, constant term, coefficient, factor and the residual from the treatment respectively. In addition, the quadratic terms X_i and X_j represents the factors, ρ_{ii} and ρ_{ij} represents the coefficients of the quadratic and the interaction parameters respectively.

However, to design the experiment, there are some factors to consider which depend on the availability of resources, the number of factors considered and their level (low and high range) and the type of the RSM design. There are several experimental designs with centre points for multidisciplinary design optimisation. These include full factorial design, central composite design (CCD), the Doehlert design (DD) and the Box–Behnken design (BBD) (Ferreira et al. 2007; Li et al. 2016). Conversely, BBD experimental designs usually have fewer numbers of runs than the others, which makes it less expensive to run the same number of factors. Also unlike CCD, BBD designs never include runs where all factors are at their extreme setting, such as all of the low settings. Advantage of the BBD is that it does not contain combinations for which all factors are simultaneously at their highest or lowest levels. Therefore, these designs are useful in avoiding experiments performed under extreme conditions, for which unsatisfactory results might occur.

In the present authors papers, the relationship between the percentage removal of SOG, TSS, COD and turbidity with different sets of operating parameters such as pH, coagulant dosage and flotation time (Tetteh and Rathilal 2018) and pH, coagulant dosage and air saturator pressure (Tetteh and Rathilal 2017) were evaluated and optimised. The results showed over 80% removal of the contaminants, where the trend of RSM predicted values were in consistent with that of the experimental results.

2.10.2 The Box-Beknhen designs (BBD)

The Box-Behnken designs (BBD) are one class of the experimental designs for response surface methodology. They are rotatable or nearly rotatable second-order designs based on three-level incomplete factorial designs (Ferreira et al. 2007; Tetteh and Rathilal 2017). These designs require fewer treatment combinations than a CCD in cases involving three or four factors, with 3 levels per factor, unlike CCD designs which can have up to 5. Thus, the matrix has +1, 0, -1, representing the highest, middle and the lowest points.

However, the number of experiments accompanied with BBD is much lesser than with CCD. This makes it more advantageous when avoiding the input variable combinations impact partially at the extremes, thus focusing on the optimal region within the experimental boundaries to have a smooth function that expands the optimisation process to converge. The effects of noise or errors in optimisation process can be reduced through derivative-based algorithms (Ferreira et al. 2007). The graphical representation of the BBD can be seen as cube that consist of central point and the middle points of the edges. Figure 2.8 shows proposed three factor, 3 level BBD fitting a response surface. It is observed that all the points are within a sphere radius without any point on the vertices of the cubic region bounded by upper and lower limits for each input variable (A, B, C).

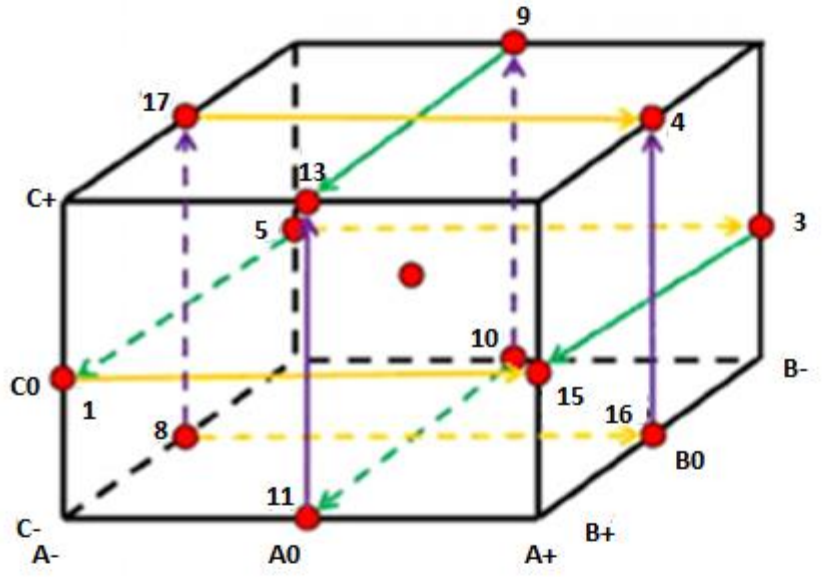


Figure 2.8 Response surface plot of 3-factors, 3 levels, and 5 centre points from Box-Behnken design for 17 experimental runs (Design Expert 10.01).

2.10.3 Merit of RSM over OFAT approach

The general strategy for optimisation in wastewater treatment processes is to improve upon the performance with less cost for the end usage of the water. However, the emerging paradigm in the analytical evaluation and graphical perceptions of a mathematical model has led to the use of RSM to help visualise the shape of the response surface. The conventional way of optimisation involves investigating one-factor-at-a-time (OFAT), thus by varying one-factor whiles keeping the rest constant overlooks the complex relationship among them.

However, OFAT is associated with some limitations like (a) lack of interactive effects among the input variables on the response; (b) demands much time and resources to complete an investigation of effects of parameters on the response; and (c) requires a high number of experimental runs which increases experimental expenses in terms of chemical usage and analyses (Bezerra et al., 2008). Therefore, the RSM stands more advantageous to simultaneously optimise a process with several operating variables to enhance the performance. More so, it has the ability to understand complex interactions between variables and responses, and assess the relative significance impact of that factor (Dutta et al. 2015; Iqbal et al. 2016).

From the present author's knowledge, the statistical tool can integrate both the input variables and the experimental data, and then finally generate a predictive model as the response or output. In addition, RSM predictive models provides results, which are consistent and closer with the response experimental data towards a desirable contaminant removal (Tetteh and Rathilal 2017).

2.11 Summary

The major concern in wastewater treatment is to make water consistently safe for reuse with efficient and cost effective treatment processes. However, water scarcity is escalating globally due to population growth, industrial activities, and with strict environmental regulations. Therefore, there is the need to treat wastewater with an optimised process to meet the strict regulations for water quality standards for reuse.

Wastewater generated from petrochemical and oil refinery industries are characterised as a complex emulsion with high content, COD, TSS, SOG, and organic and inorganic hydrocarbons. The integrated physicochemical technique, which is emerging as a coagulation-DAF mechanism, has gain much interest in the industrial wastewater treatment application as an alternative to the struggle of settling or sedimentation process. A typical integrated coagulation (chemical aspect) and DAF (physical aspect) treatment process involves acidification, coagulation and DAF, and is applied for MOW treatment to separate the waste oil from the water, thus to further favour the downstream treatment. Chemical coagulation involves the use of aluminium and ferric salts (inorganic coagulants) and some polymeric organic coagulants that are documented in the literature.

The DAF treatment process has a number of variables that could affect the treated water quality. These include the characteristics of the oil droplets (concentration, density, and size), chemical properties and physical parameters (coagulant type, pH, detention time, flowrate, and mixing speed), DAF operating parameters (volume of DAF geometry, air to water ratio, air saturator pressure), and the influence of the flocculation mechanisms in oil-water emulsions.

In this study, a DAF unit, which does not follow directly any of the DAF schemes (Section 2.8.3), in order to prevent the air saturator from being damaged by the oil, was used. However, the scheme used in these experiments is almost similar to recycle-flow pressure DAF with external raw water being pressurised by the air saturator to generate the dissolved air bubbles.

Therefore, it is very prudent to investigate the coagulation-DAF performance using a typical oil refinery wastewater in both batch and continuous processes, due to the differences between the jar test and the pilot plant with respect to size and geometry, and mode of operation (batch versus continuous). The data obtained from the experiments is then transformed into response models for effective decision-making. This approach offers a significant reduction in time and cost of experiments during scaling up and a better option for optimising, prediction, identifying the most influential factors and their interactive effect on the response water quality.

CHAPTER 3 -METHODOLOGY

3.1 Introduction

This chapter presents the feasibility study of effluent plant, water sample source, the chemicals used, water quality parameters measured and the respective standard analytical methods used. Two configuration processes, namely Acid─Coagulation─DAF (pre-treatment) and Acid─DAF─Coagulation (post treatment) were used in treating MOW from a local South Africa oil refinery. Firstly, an OFAT approach was used to evaluate the key factors that affect the DAF treatability performance on a bench scale (DAF Jar tester), followed up with optimisation of the DAF pilot plant. The experimental setup of the DAF pilot plant included installation, troubleshooting and commissioning. The BBD adapted from the RSM was employed to design the experiment runs, analyse the results and optimise the key interactive factors.

3.2 Feasibility study on a typical effluent treatment DAF

In South Africa, with high water scarce sources, there has been keen interest in the development and application of DAF over the last 40 years (Edzwald, 1995; Schalkwyk et al., 2016). In view of this, a local South Africa oil refinery has developed a technology to process highly emulsified waste oils and contaminated effluent. This plant is located at Durban in the Kwazulu-Natal province to facilitate conformance with more strict environmental legislation and disposal bylaws (ISO 14001:2004) of the EThekwini municipality.

Since the treatment of oily wastewater is one of the major concerns faced in the refinery industry. Feasibility study was done on a 20 kilolitres per hour effluent plant with the focus on the DAF process. This was done to give the present author the idea on how to design, modify and configure a DAF pilot plant for this study.

The effluent water delivered on site for the effluent plant are feedstock from ship slops, refinery off specs and other waste oil streams. The water content of these waste streams varies from 10% to 50% of the waste oil. The water is removed from the oil through various processes on sites, including force-feed evaporation and centrifugal processes. This water contains about 2000 mg/L of oil and requires treatment prior to discharge to the sewer. This will reduce the workload of the municipality WWTP.

As depicted in Figure 3.1, the discharge waste oil is pumped into a holding tank where there is a gravity flow separation based on the difference of relative densities between the water and the oil. From the holding tank (T-57), the effluent is automatically dosed with an acid to achieve a pH of 5. The MOW then enters a static separator in which the oil and water separates naturally by relative specific gravity. This oil is skimmed off from the effluent surface to the oil tank, which is then pumped back to the waste oil refinery plant for further processing. At this stage, the oil content after the separator reduces to about 2 to 5% and then flows to the DAF unit, which is the area of interest.

The air saturator is operated at a pressure of 300 to 500 kPa to compress the air-water. Afterwards the compressed mixture and the effluent from the separator is released into the DAF through a nozzle valve. Micro bubbles are then formed which attract the dispersed oil droplets and cause them to float to the surface. After the static separator, the oil droplets from the DAF are skimmed off into the oil tank. This is then pumped back to the waste oil refinery plant for further processing. At this point, the oil concentration in the effluent is recorded to be between 300 to 400 mg/L after the DAF unit.

At the coagulation section, the effluent is coagulated and flocculated with preferable dosage of lime and polymeric coagulant. The dosage of the lime is to balance the pH of the effluent prior to discharge into the clarifier. In addition, some of the effluent water is by-passed through a filter press after the clarifier. The dry oil sludge is derived and disposed off to a landfill with a certified safe disposal permit. The clean water obtained is reintroduced into the coagulation tank to prepare the solution. Final effluent with an oil content less than 50 mg/L is expected after flowing into the sewer.

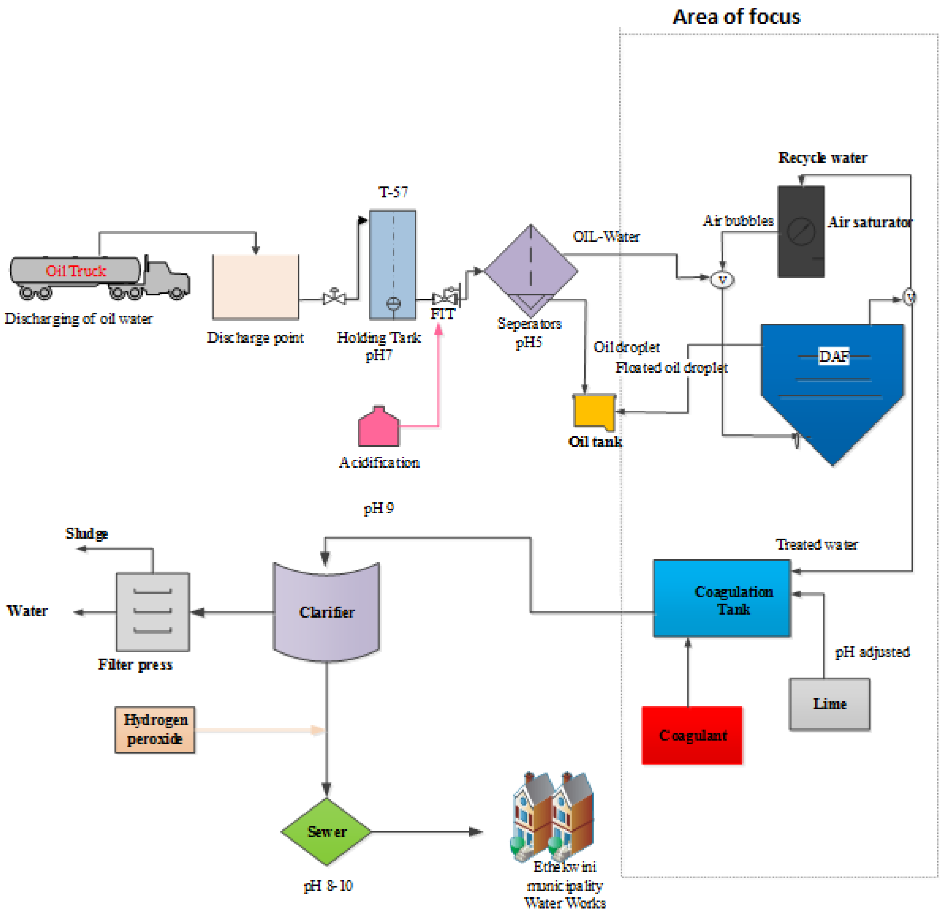


Figure 3.1 Representation of a local oil refinery effluent plant with the focus on the DAF unit.

3.3 Materials and analytical equipment

3.3.1 Sample

Effluent samples were obtained from a local South African oil refinery WWTP located in Durban, in the KwaZulu-Natal province. The samples were taken from before and after the DAF process unit as indicated in 3.1. The effluent plant constitutes about 65% water, and 35% oil droplets, which constitutes a variation of oily waste from ships slop, refinery off specs and industrial processes. The samples were collected from the effluent plant using 25 L drums and were thoroughly mixed before each trial to have a homogeneous feed mixture. Due to the wide variation in the physicochemical composition of the effluent and the oil droplet sizes, makes optimisation of DAF to be complex (Santo et al., 2012).

Characterisation of the samples were done at the time of collection accordingly, to suit each objective at hand and the performance criteria were well defined. This was carried out in three cases: firstly, during the evaluation of acids, air saturator pressure and air-water ratio. Secondly, the coagulant performance monitoring and evaluating the sensitivity of the coagulation parameters using the DAF jar tester, and then finally during the optimisation of the DAF pilot plant, which was done at the plant site as defined in Table 3-1. The results for each case study are also tabulated separately in Appendices C and D. The critical performance criteria were evaluated based on the removal efficiency of the residual oil concerning the water qualities such as COD, SOG, TSS and turbidity. However, the conductivity (EC) and the total dissolved solids (TDS) had no significant impact hence were ignored in this study.

Table 3-1 Raw sample composition of a local oil refinery effluent

Water parameter	Case 1	Case 2	Case 3
pH	7	7	5
Turbidity (NTU)	2753	2768	1770
TSS (mg/L)	1035	1051	867
COD (mg/L)	12365	12172	1810
SOG (mg/L)	1320	1268	1100
*EC us/m		62055	3466
*TDS mg/L		4330.5	2887

**Not considered as criterial for the DAF performance check*

3.3.2 Chemicals and Reagents

The chemicals and reagents used in this study are listed in Table 3-2. Four inorganic coagulants and three polymeric organic coagulants that are of aluminium and iron-based coagulants were used for the investigation. The Polyaluminium sulphate (PAS) was used as a control coagulant, due to its usability in the local oil refinery effluent and the goal of replacing it with a new coagulant, whiles the other two, Polyaluminium chloride (Z553D) and Polyferric sulphate (Zetag32-FS/A50) were recommendations for their effectiveness in potable water treatment by a process engineer (Umgeni Water).

Table 3-2 List of chemicals and reagents used for the study

Chemical	Purity	Supplied locally
Inorganic coagulant		
Aluminium Sulphate (alum)	SG=1.34, Dry weight = 48.5%	United scientific SA cc
Aluminium Chloride (AC)	SG = 1.35, Dry Weight =45.6% Basicity = 80%	United scientific SA cc
Ferric Chloride (FC)	SG = 1.41, Dry Weight = 40%	United scientific SA cc
Ferric Sulphate (FS)	SG = 1.59, Dry Weight = 60%	United scientific SA cc
Polymeric organic		
*Polyaluminium chloride (Z553D)	SG = 1.18, Dry Weight = 20-23% PACl, Basicity = 50%	Shalom Lab Supplies cc (ZetagChem)
**Polyaluminium sulphate (PAS)	SG = 1.34, Dry Weight = 40-45%, Basicity = 54%	Shalom Lab Supplies cc (ZetagChem)
*Polyferric sulphate (Zetag32-FS/A50)	SG = 1.54, Dry Weight = 43.7% , Basicity = 10%	Shalom Lab Supplies (ZetagChem)
pH adjustment		
Sodium hydroxide (NaOH)	ACS Grade-solid , 97.8% used for pH adjustment	Sigma Aldrich
Sulphuric Acid (H_2SO_4)	ACS Grade - 36% Normal used for acidification	Sigma Aldrich
Phosphoric Acid (H_3PO_4)	ACS Grade – 85% Vol/Vol used for acidification	Sigma Aldrich
Hydrochloric Acid (HCl)	ACS Grade – 36.5 % used for acidification	Sigma Aldrich
SOG analysis		
Dichloromethane (25 L)	ACS Grade -99.9% used for extraction of the oil	Laboratory analytical supplies
Sodium sulphate (500 g)	ACS Grade -99.9% used for extracting moisture	Laboratory analytical supplies
COD analysis	COD vials high range (0-1500 mg/L) Hanna	Laboratory analytical supplies

*Polymeric organic coagulants were already in a modified form

** Control polymeric organic coagulant for the study

3.3.2.1 Stock solution preparation

The acids and coagulants found in Table 3-2 were used to prepare individual stock solutions, to determine the correct dosages to facilitate the coagulation and flocculation of the MOW. In preparation of the concentrations, quantities suitable for use in the jar tests were measured precisely. The preparation was up-front; for instance, 1 g/L stock solution prepare with dry chemicals, constituted 0.8 g of the chemical and 800 ml deionised water. However, a real dilution step was required when the liquid solution was concentrated. During the preparation of each stock solution, the following steps were followed:

(i). Polymeric organic coagulant stock solution: Weigh 0.8 g polymeric organic coagulant into a beaker, then transfer into the 1L volumetric flask and dilute with distilled water to the marked level. This was stored to last for only 1-week. Hence, by injecting 1 ml of the stock solution into 800 ml of the effluent sample is equal to 1 mg/L.

(ii). Inorganic coagulant stock solution: by weighing out 0.8 g (1 ml = 1 mg/L) or 4.0 g (1 ml = 5 mg/L) or 8.0 g (1 ml = 10 mg/L). But when measuring the weight of aluminium or ferric salts, the supplied concentration was taken into account, for instance, to obtain 4.0 g active alum of 48.5% solution will require 8.25 g/L (active mass required per total mass). However, when the specific gravity was measured, the total volume was taken instead of the mass.

(iii). While preparing the feedstock solutions, 0.8 g (1 ml = 1 mg/L) of acid or NaOH was measured and added to a solution. This was done based on the acid or NaOH water chemistry.

(iv). Finally, the stock solutions was transferred and stored in an empty 1 L bottle. For safety consideration, each stock solution was labelled indicating the type of acid, NaOH or coagulant used and the preparation date.

3.3.3 Analytical equipment

The essential contaminants in the oil refinery effluent were used in determining the performance of the DAF for the treatment of the MOW including COD, SOG, TSS and turbidity. These parameters were analysed by their specific standards using the equipment listed in Table 3-3, and the procedure vividly explained in Appendix B. However, the SOG analysis involves liquid-liquid extraction coupled with gravity separation. Each procedure conforms to the standard methods for the examination of water and wastewater in an oil refinery (SANS-SABS, 2007; Apha, 2012).

Table 3-3 List of instruments and methods utilised to test the water quality

Water quality test	Instrument used	Method
pH	pH paper strip	Standard method
COD (mg/L)	Hanna HI 83099 COD and multi-parameter photometer	Standard method EPA 410.4 and USEPA reactor gestion digestion method 8000
TSS (mg/L)	Hach DR890 potable colorimeter	Standard method
Turbidity (NTU)	Hach 2100N turbidimeter	Standard method
SOG (mg/L)	Extraction (Dichloromethane), dry out moisture (Sodium sulphate)	South African Bureau of Standards Method 1051
*Conductivity	HJM C8 uS/TDS Meter (Using 1413 mS/cm and 2 mS/cm solution for calibration	Standard method
*TDS		Standard method

*Not used as performance criteria; DAF performance had no significant effects

3.3.4 Soap oil and grease analytical procedure

The liquid-liquid extraction and gravity separation method was the analytical method adapted to determine the SOG in the MOW (SANS-SABS, 2007). Since some compounds like SOG, fatty acids and hydrocarbons contribute to the interference, it is, essential to consider the extracting solvent used and the origin of the MOW.

In this case, SOG was the critical operating performance parameter. Hence, the results depend on the solvent extraction. To increase the surface tension of the oil droplet to enhance the separation, there was an addition of sodium sulphate salt to increase the density of the aqueous layer. The Dichloromethane was the solvent used for the extraction by adding 50 to

500 ml MOW sample collected in the volumetric ratio of 1:10 respectively. The precise, description of the procedure is found in Appendix B.

3.4 Experimental setup

Two experimental setups were identified to carry out the investigation of optimising the full-scale DAF process after the feasibility study and to determine the effectiveness of the coagulants. First (Section 3.3.1) was the DAF jar tester, which was considered an acceptable and economical method to simulate and investigate the operating parameters of full-scaled DAF and identify the sensitivity of the coagulants (Edzwald, 1995, 2011; Tetteh et al., 2017).

Secondly (Section 3.4), due to the difference in geometry and hydrodynamics between the full scale DAF and the jar tester, the DAF pilot plant was considered because of the full scale operating parameters, which can be simulated continuously.

3.4.1 Description of the DAF jar tester

The primary objective of the use of the DAF jar tester was to identify the coagulation and flocculation parameters to which the DAF treatment process of the MOW is sensitive concerning the water quality. Umgeni Water Process Evaluation Facility (PEF), Wiggins, supported this project by providing the DAF jar tester (Model DBT6, EC Engineering, Edmonton, Alberta, Canada) to be used. The DAF jar tester is a standard apparatus, which mimics a DAF system assist Umgeni Water PEF wastewater scientists and engineers to determine different chemical dosage rate to improve the water quality.

The DAF jar tester is equipped with an air compressor, 8 L recycle air saturator, two different compartments to which six impeller blades are attached to one, and another six bubble nozzles are attached. Also, it consisted of six identical Perspex square 1 L jars. The component housing the bubble nozzles possess a knob for each nozzle that is used to regulate the reflux (air-water ratio) via the nozzle. There is a rotor for regulating the mixing speed of the impellers mounted on the frame of impeller blades module.

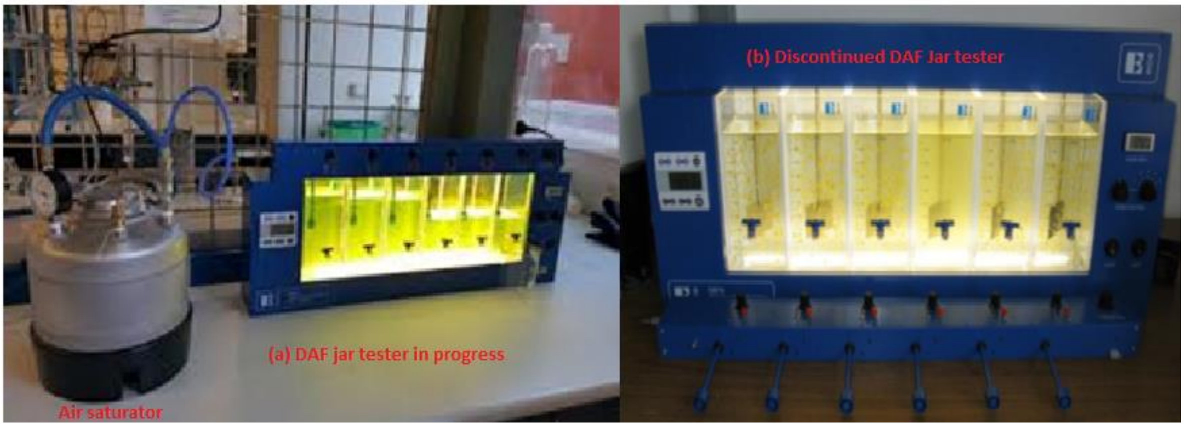


Figure 3.2 Demonstration of DAF jar tester at (a) coagulation (b) flotation process

The pictorial view of the apparatus in Figure 3.2 (a) shows coagulation in progress and (b) showing flotation process with a disconnected DAF unit and resting on the table is air injection component. The air-water ratio are introduced into the jars, after the insertion of one injector into each jar via the air release nozzles. To ensure proper visual comparison of the water quality and flocs formation depends on the white backdrop behind and the lights beneath the jars. There is also a fan in the base of the unit, to minimise the amount of heat transferred from the lights to the jars. The six 1 L square jars allow for evaluating different chemical dosage simultaneously. Each square jar has 20 % flotation headspace, with a capacity of 1200 ml and 90 mm diameter size as shown in Figure 3.3.

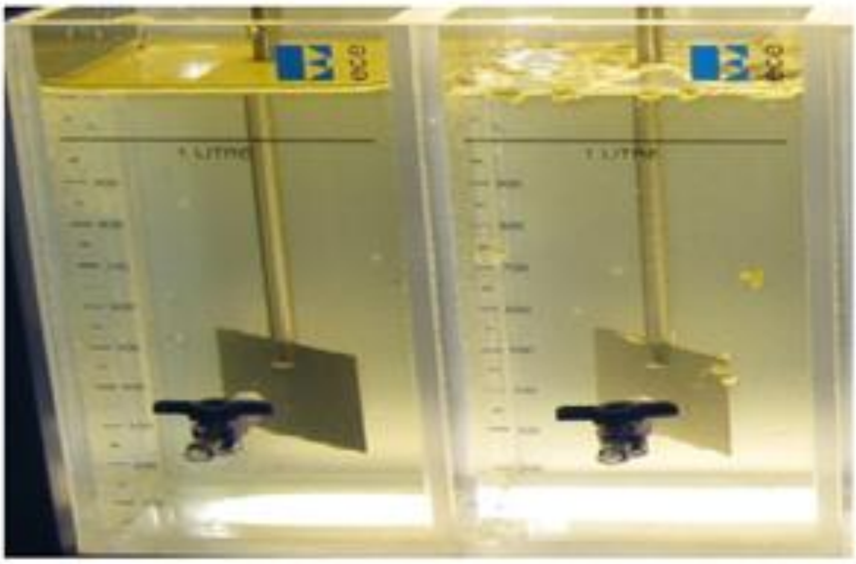


Figure 3.3 Schematic diagram of DAF jars demonstrating oil droplet flocs formation

3.4.2 DAF jar tester operational procedure

A sedimentation jar test protocol (Umgeni Water, Wiggins PEF) modified by the author to suit the operation of the DAF Jar tester, was followed as explained in Appendix A.

Figure 3.4, the air saturator vessel was filled with deionized water to about 80% of its total volume, sealed closed and appropriately connected to the compressor. To pressurise the water, the valve connecting the air compressor and the air saturator vessel was opened, and the compressor was switched on. The compressed air was injected until the pressure reached the desired saturator operating pressure (300 to 600 kPa). Afterwards, the compressor was deactivated and the valve then disconnected. There was an intermittent shaking of the vessel for 30 seconds; this assisted for a thorough mixing and dissolution of the air into the water. The six beakers on the DAF jar tester were each filled with a measured 800 mL aliquots of the raw MOW.

Afterwards, both the bubble and the impeller component were then mounted on the frame housing the six jars. According to the experimental plan, the needed acid and 1.0 M NaOH were used to adjust the pH of the MOW as preferred. To ensure fairness in the coagulant dosage, 6 syringes were filled to the desired dosage of each jar.

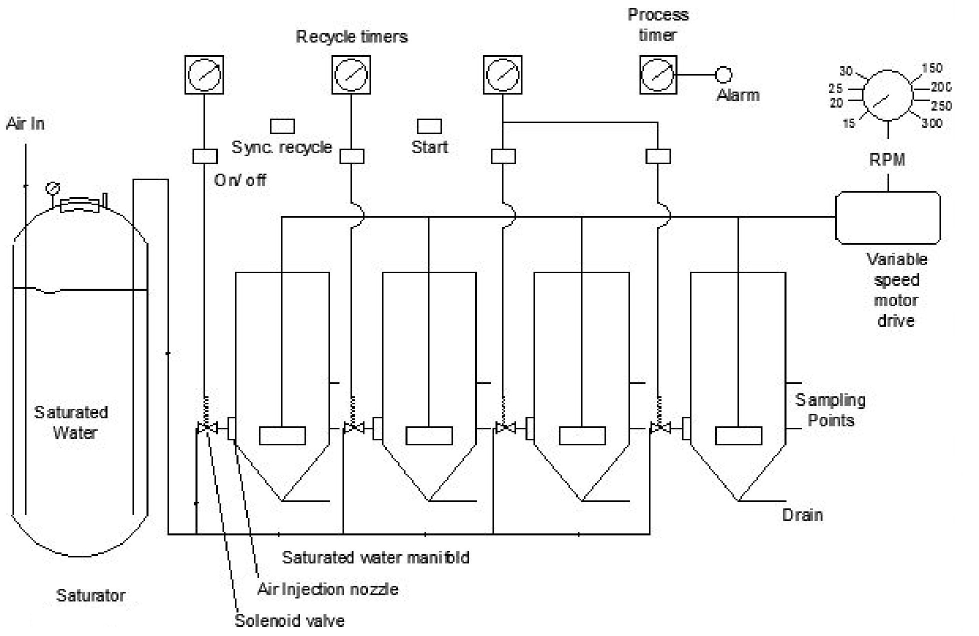


Figure 3.4 DAF Jar tester process and instrumentation diagram

Taking into account the safety and standard mode of operation of the DAF jar tester, each test trial was done at constant operating conditions of a rapid mixing rate at 250 rpm for 2 minutes, followed by a slow mixing rate of 30 rpm for 15 minutes. The mixing speed of the impellers were regulated by turning of the knob provided and observing the corresponding rate on the digital screen. There are timers linked to the jars that control the recycle air-water ratio injection.

After the mixing was completed, the knobs for all the nozzles were set to the standard start position at the same time. Unless opted by the trial operating conditions, all the six injectors inject air at a recycling ratio of 10%, retention time of 3 seconds, and air saturator pressure of 350 kPa, which were used as baseline conditions.

Once the injectors finished, the air injection module was immediately pulled out and the jar test unit was allowed to stand undisturbed for 15 minutes while the bubble-oil droplets rose to the surface As soon as the flotation time elapsed, a labelled sample bottle was placed under each sampling port to collect 500 ml samples for the analysis.

3.4.2.1 DAF Jar tester investigation conditions

This experimental procedure was followed to complete the investigation to determine the most sensitive operating parameters on the water quality using the DAF jar tester for the following;

(i). Using a polymeric organic coagulant at dosage at 5 mg/L, to evaluate the effect of each of the three acids (Hydrochloric acid, phosphoric acid, and sulphuric acid) at a pH range of 2, 4, 6, 8 and 10.

(ii). To study the effects of the air saturator pressure of 200, 300, 400, 500 and 600 kPa. Using polymeric organic coagulant dosage at 5 mg/L with the preferable acids and pH from the previous study.

(iii). To determine the performance and sensitivity of each of the seven coagulants at a dose of 0, 10, 20, 30, 40 and 50 mg/L, using the desirable conditions from the previous studies.

(iv). To investigate the interactional effects and the relationship between the most sensitive input variables for the coagulation (pH, coagulant dosage and flotation time) and coagulation-DAF (pH, coagulant dosage and air saturator pressure) using the experimental matrix of the BBD adapted from RSM as shown in Table 3-5.

3.5 DAF Pilot plant

The DAF pilot plant described in this section comprises of the initial commissioning of the pilot plant including calibration of the flocculator stirrers and certification of the air saturator to determine the air-water efficiency of the saturator as well. The DAF pilot plant, which is a continuous process system with a designed capacity of 1 m^3/h used for this study is shown in Figure 3.5. The plant comprises of a coagulation (flash) mixing vessel, three-stage mechanical flocculation, and flotation vessel and an air-water saturator. The pilot plant was designed with two views; one was based on the size to be small for easy transportation to sites and yet capable of generating reliable data which was meant for full-scale plants.

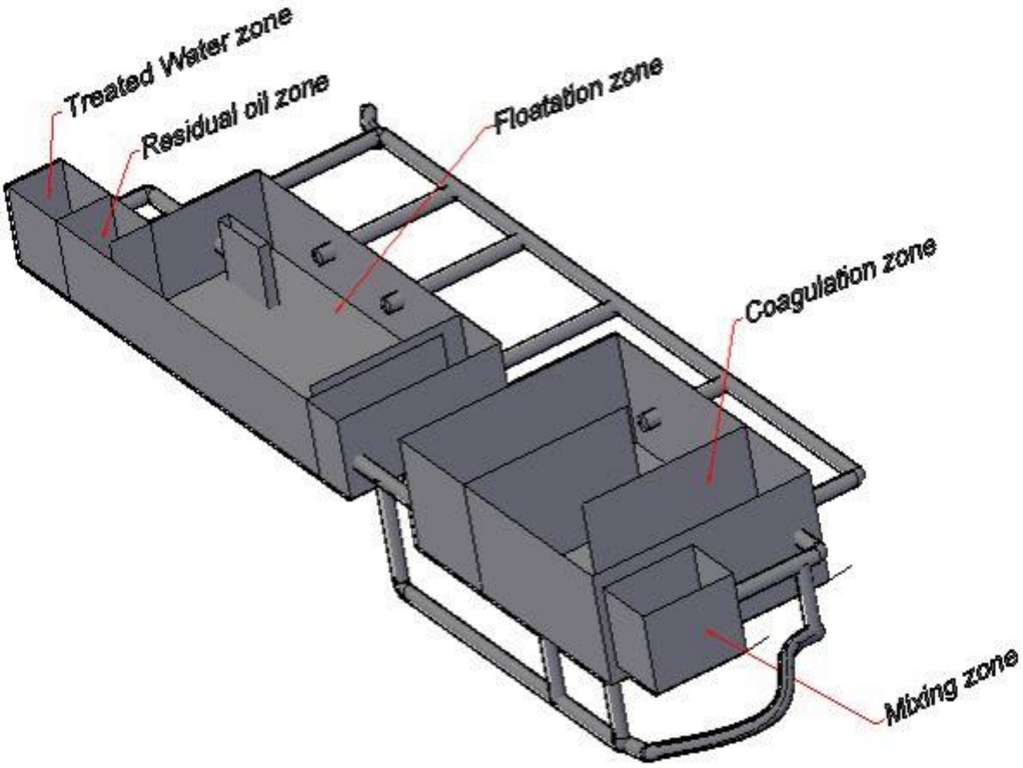


Figure 3.5 Isometric representation of the DAF pilot plant compartments

3.5.1 Overview of DAF pilot plant description

Figure 3.6 shows a cross-section view of the DAF pilot plant in operation. The process and instrumentation diagram (P& ID) is shown in

Figure 3.7.

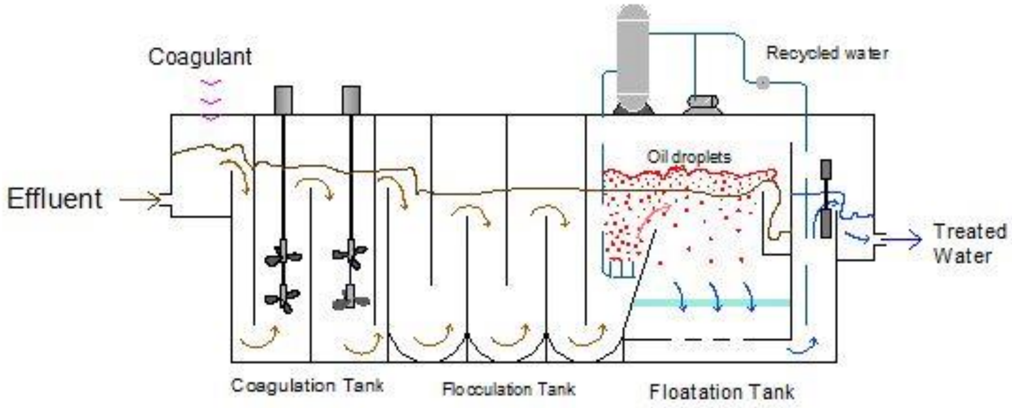


Figure 3.6 Process flow diagram of DAF pilot plant

3.5.1.1 Mixing and Coagulation vessels

The fixed baffle coagulation/flocculation vessel consists of a flashing or rapid mixing (coagulation) compartment, and three stage mechanically stirred flocculation compartment. The unit has been fitted with two dosing pumps for the addition of pre-treatment chemicals and coagulant directly into the rapid mixing compartment. The variable speed mono pump pumped the influent into the rapid mixing vessel. The influent flow rate was monitored using a mag-flow meter positioned on the delivery side of the mono pump.

- Coagulation zone

The coagulation (rapid mixing) vessel provides a residence time of 60 seconds. Mixing is achieved with a variable speed mixer with a built-in rev counter. The shaft is fitted with an axial impeller with a factory rated power number of 0.3 and is used in the turbulent Reynolds number range (Re >10000). The mixer is capable of generating speeds between 20 and 500 rpm.

- Flocculation zone

Each flocculation stage had an average residence time of 5 minutes at the design flow rate of 1 m^3/h. The water distribution pipework from the rapid mixing vessel to the flocculator makes it possible to vary the flocculation time from 5 to 15 minutes without changing the inlet flow rate.

Variable speed motors drive the mechanical stirrers with high torque output and are equipped with an electronic speed display. Rotational speeds between 10 and 130 rpm are possible. Two axial impellers were mounted on each stirrer shaft. Mixing speed in rpm is correlated to velocity gradient, (G), by incorporating energy dissipated to the stirred water and the geometry of the stirrer blades.

3.5.1.2 Flotation vessel

The flotation vessel was equipped with variable baffles and external supports for flexibility in hydraulic loading in both the contact and flotation zones. The baffles were adjustable for flexibility of varying the flocculated water velocity into the flotation vessel, upflow velocity in contact zone and final down flow velocity into the flotation zone. The residence time in the flotation vessel was 8 minutes. A relatively large diameter pipe (100 mm) connected the flocculator to the flotation vessel as shown in Figure 3.7 with valves HV-05 and HV-06. The arrangement helped to reduce turbulence that may cause shearing of the preformed floc.

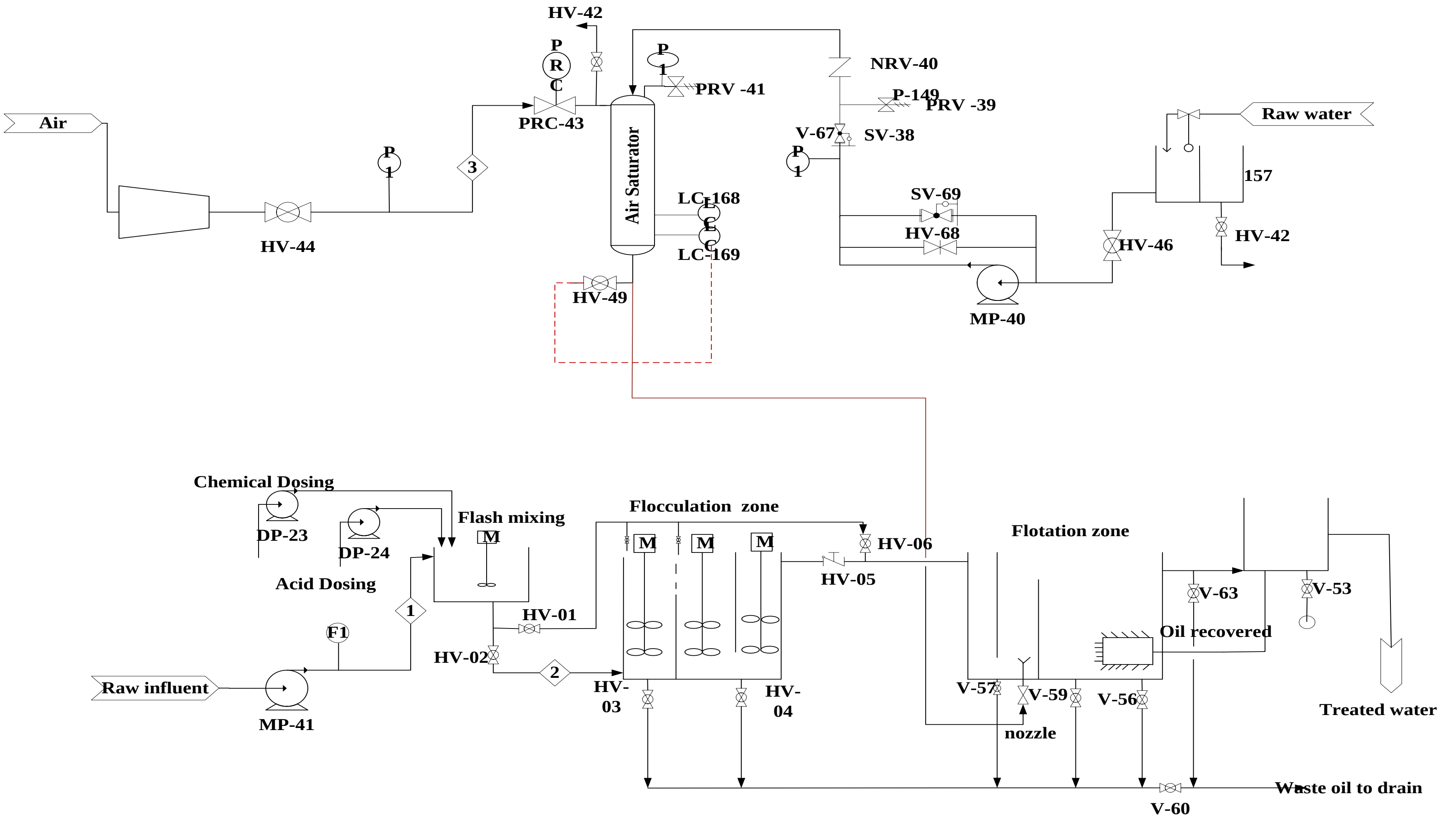


Figure 3.7 Process and instrumentation diagram of one cubic per hour DAF pilot plant

3.5.1.3 Air–water saturator system

The saturator system consisted of a pressure vessel, with a 0.25 m internal diameter and a total height of 1.3 m. The vessel was packed with plastic packing saddles (rings) to a height of 0.7 m. In Figure 3.7, raw water was pumped from a header tank (T57) by a mono pump (MP-40) to the top of the pressure vessel through the non-return valves (NRV-40). Compressed air was introduced co-currently to the water feed as shown in

Figure 3.7. An air pressure regulator (PRC-43) controlled the saturator pressure. The water was maintained by level controllers (LC-168 and LC-169) that activated the water feed bypass solenoid valve (SV-69).

The dissolved air stream (recycle) was introduced into the flotation vessel through a needle valve (V-59) connected to one of the air injection ports located on the side, near the bottom of the flotation vessel. The pressurised air saturated water injection point (at the bottom of the flotation vessel) was at right angles to the flocculated water feed.

3.5.2 Installation, troubleshooting and commission

The DAF pilot plant was first commissioned with raw water to check and rectify for leaks on the pipelines and the tanks, where necessary. Three mechanical static mixers were installed, and the rotational speeds were adjusted. Agitation and floc formation was then observed when the coagulant was added to the rapid mixing tank. A good flocculation performance was observed (sample was taken from the flotation zone and many flocs observed and settled quickly), when the rapid mixer was set to 250 rpm and the other two for slow mixing at 30 rpm. A two dosing pump was also installed to inject the acid and coagulant at the needed flow rate.

To ensure the safety of the air saturator vessel, pressure safety valves and pressure gauges were installed. East Coast Instruments CC SA, Durban, KwaZulu-Natal, did a pressure testing on the air saturator to certify its efficiency for operation with a regulatory limit of 750 kPa. The drive for bubble formation due to the air-water ratio was then observed when the air saturator was switched on from the control panel, after being connected to the air compressor. By adjusting the needle valve (V-59) of the nozzle. There were some checklist, which were done to ensure safe and successful troubleshooting of the pilot plant is shown in Appendix A.

3.5.2.1 DAF pilot plant operating conditions

In optimisation of the DAF pilot plant, the most influential operating parameters which were found during the DAF Jar test trials were the coagulant dosage, air saturator pressure and air-water ratio which were then investigated. This was done using the pilot plant designed operating conditions as shown in Table 3-4 and the BBD experimental matrix that was generated using the conditions in Table 3-5. Also, evaluation for each of the two superlative coagulants that emerged from both the inorganic and polymeric organic coagulants during the jar test trials was also used.

Table 3-4 Design parameters of DAF pilot plant (Al-Shamrani et al. 2002; Edzwald 2010; Behin and Bahrami 2012)

Operating parameter	DAF pilot plant Design guidelines	Set point
Influent flowrate	1 m^3/h	16.6 L/min
Coagulation and flocculation		
Rapid mixing intensity (rpm)	20 to 500	250
Slow mixing intensity (rpm)	10 to 130	40
Contact zone		
Residence time (s)	60 to 240	51
Hydraulic loading (m/h)	40 to 100	66
Flotation		
Crossflow velocity (m/h)	20 to 100	75
Hydraulic loading (m/h)	5 to 11	5
Side depth (m)	1.5 to 3.0	1.2
Residence time (min)	*	8
Air saturator		
Air -water recycle (%)	5 to 20	**
Saturation pressure (kPa)	300 to 600	**

*Unspecified in the DAF **According to optimisation design

❖ DAF pilot plant start-up

To start-up the DAF pilot plant in Figure 3.7, the following procedure was followed;

i. The coagulant was prepared, and the dosing pump (DP-23 and 24) selector switch was set to Auto mode.

ii. The feed pump (MP-41) was switched on, and the influent was used to buffer the tanks, including the flotation tank. The water level in the flotation was adjusted by the opening of the discharge collection valve (V-53) for the overflow.

iii. The air-water recirculation pump (MP-40) was set to Auto mode and the vessel filled with air, by opening valve (PRC-43).

iv. The air saturator pressure was evaluated, by adjusting the pressure with (PRC-43) to the required set point of 300, 400, or 500 kPa, according to the experimental design.

v. The flotation manual valve (HV-68) and the recirculation suction pump (MP-40) were adjusted to the preferred flow rate approximately 30-50% of the principal influent flow rate of pump (MP-41).

vi. The pressure-reducing valve (PRC-43) and the manual gate valve (V-59) of the nozzle were adjusted to control the air-water ratio (5, 10, or 15%) until a desirable micro bubble was obtained.

vii. The coagulant dosage pumps (DP-23 and 24) rates were adjusted according to the experimental design (100, 150 or 200 mg/L).

viii. The air saturator pressure was not motivated to exceed the regulatory pressure (750 kPa). However, when a high pressure was observed, the pressure release valve (PRV-41) was opened to reduce the pressure. Also, the incoming pressure was well regulated, and in case of abnormalities, the manual valve (HV-44) was used to shut off the air supply.

ix. Samples were taken from the influent and the treated water. The water quality was then analysed and the efficiency was calculated using equation (3-1).

$$\mathrm{Y_n}(\%) = \frac{\mathrm{y_o} - \mathrm{y_n}}{\mathrm{y_o}} \times 100 \qquad (3\text{-}1)$$

where Y_n , y_0 and y_n represents the demanded response (water parameter), initial and final water parameters values respectively.

❖ DAF pilot plant shut-down

These procedures were followed to shut down the DAF pilot plant.

i. The dosing (DP-23 and 24) and influent pumps (MP-41) were switched off to stop the inflow of the feed.

ii. The both the rapid and slow mixers were switched off.

iii. The inlet compressed air line was shut off (HV-44).

iv. The recirculation pump (MP-40) for the air to water ratio was shut off.

v. The inlet valves (HV-01 and HV-02) to the DAF was shut off, and the main drain valve (V-60) was opened.

vi. The pressure in the air saturator was released by opening valve (PRV-41), until the gauge, pressure reached zero, and the liquid in the vessel was drained through valve (HV-49).

3.6 Design of experiments (DOE)

In this study, a systematic design of experiment was done using Design Expert (10.0.3) software to obtain sufficient information to optimise the process with the least number of experiments. The goal was to identify the optimum range of the operating parameters and the most significant factors to control to enhance and maximise the efficiency of the DAF process for the treatment of the MOW. Also, to obtain data that could fit and be used to develop empirical models for each of the responses (COD, SOG, TSS and turbidity), so that a clear understanding of the interactional effects and relationships that exist between the input variables and the response (water quality) can be established.

Some of the functionalities of the Design Expert includes the following;

(i). **The design matrix construction**: This involves the use of the input factors to generate the experimental runs in order to follow to obtain the response (output) data.

(ii). **Data analysis and response modelling**: This requires the entering of the response data. Afterwards, modelling and statistical analysis are provided with model-graphs which shows the interactional effects of the input variables in actual vs predicted, contours and 3D surfaces. The analysis of variance (ANOVA) and the regression coefficient (R^2) are also provided which expresses the polynomial relationship between the factors and the response regarding actual or coded factors (-1, 0, 1).

(iii). **Process optimisation:** Design Expert combines the levels of each of the input factors that will simultaneously generate a satisfying condition for the response desired. However, optimisation of multiple factors can be done simultaneously using numerical and graphical representation.

3.6.1 The Box–Behnken design (BBD) procedure

Table 3-5 depicts the input variables. The BBD was adapted from the RSM, which was employed to obtain 17 trials with three input factors (for each case), three levels and 5 centre points. The following procedure was followed;

(i). The problem was identified as optimisation with experimental data.

(ii). The type of input factor levels and ranges were defined with the number of centre points.

(iii). The number of response variables were defined as the water quality (COD, SOG, TSS and turbidity).

(iv). The Box–Behnken design was selected as the suitable response surface experimental design to generate the matrix.

(v). The experimental matrix was followed, and the response data was generated.

(vi). The response data was entered, and the data was statically analysed.

(vii). The response models generated were verified by comparing its predicted values with that of the experimental results where necessary with the optimum conditions or the most influential factors.

(viii). Conclusion and recommendation were then deduced.

Table 3-5 Experimental design conditions and factor levels using BBD-adapted from RSM

Cases	**Process investigated**	**Input variables**	**Coded levels (X)**		
			-1	**0**	**1**
1	DAF Jar test (coagulation)	X_1 : pH	4	5	6
		X_2 : Coagulant dosage (mg/L)	30	40	50
		X_3 : Flotation time (min)	10	15	20
2	DAF Jar test (coagulation-DAF)	X_1 : pH	4	5	6
		X_2 : Coagulant dosage (mg/L)	30	40	50
		X_3 : Air saturator pressure (kPa)	300	400	500
3	DAF pilot plant (coagulation-DAF)	X_1 : Coagulant dosage (mg/L)	100	150	200
		X_2 : Air saturator pressure (kPa)	300	400	500
		X_3 : Air-water ratio (%)	5	10	15

CHAPTER 4 - RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter discusses the experimental results obtained from the treatment of the MOW using the DAF to establish the treatability performance, and likewise, the economic viability of different inorganic and polymeric organic coagulant performance. It further details the optimisation of the DAF pilot plant with RSM to establish the relationship that exists between the most important parameters and the water quality, using the emerged superlative coagulants.

Section 4.2 discusses the use of OFAT approach to identify the experimental design and operating parameters set points while section 4.3 is based on the evaluation of the coagulant performance in terms of dosage and cost. Section 4.4 is about the comparison of the pre and post coagulation configuration for the treatment of MOW using the DAF unit. In section 4.5, the use of RSM to evaluate the appropriate factor combinations on the jar DAF test was enumerated. Finally, section 4.6 establishes the relationship between the key factors and the contaminant removal to enhance optimisation of the DAF pilot plant using RSM.

4.2 Experimental design and operating parameter settings

This section discusses the batch bench scale (DAF jar tester) investigation performed to identify the effect of the major operational parameters and their respective ranges such as pH and acid type (see section 4.2.1), air saturator pressure (see section 4.2.2), air-water ratio (see section 4.2.3), coagulant dosage (see section 4.2.4) and flotation time (see section 4.2.5), using PAS as the coagulant and the characterised MOW in Table 3-1.

The primary purpose of optimizing the DAF was to obtain the optimum operating conditions that will be used for the treatment of the MOW. However, in practice, the effluent quality was not read online. Hence, the alternative way to obtain information about the water quality was driven by experimental analysis using the OFAT approach. The use of the OFAT approach provided the ranges with regards to the operating parameters. Values obtained were compared to what was available in literature for the process optimisation.

4.2.1 Evaluation of pH and acid type performance

The pH adjustment was done to enhance the deteriorating of the oil droplet surface tension and precipitation reaction between the oil droplet and the added coagulant charged surface as represented in Figure 2.1 and 2.2. From the reported literature data, pH adjustment affects the solubility of different elements in the MOW, which turns out to form unnecessary pollutants as precipitates especially SOG during the coagulation process (Canizares et al. 2008; Saththasivam et al. 2016). Therefore, the manipulation of the pH elevated the acidity or alkalinity of the oil emulsions to neutralise the oil droplet charge and help to stabilise the flocs in suspension to reach the expected floatability stage. However, a very high or low pH might lead to downstream complexity reaction and increased process costs (Coca et al. 2011). In this study, the significance of pH in the treatment of the MOW was indicated by determining the optimum pH range of the preferred acid type.

Baseline operating conditions were used in investigating the three different acids such as coagulant dosage (PAS) of 5 mg/L, rapid mixing speed of 250 rpm for 2 minutes, slow mixing of 30 rpm for 15 minutes, flotation time of 15 minutes, air-water ratio of 10% and air saturator pressure of 350 kPa. The pH of the MOW samples was adjusted by adding NaOH or selected acids. As depicted in Table 3-2, NaOH was used to increase the pH (7 to 10) whereas acids were used to decrease the pH (7 to 2) in the acid medium.

It was observed that each investigated acid affected the neutrality of the MOW (pH 7) by destabilising and breaking up of the emulsion to enhance the chemical treatment of the MOW. Thus charging the oil droplet for ionic exchange (cationic and anionic) between the oil emulsion and the coagulant added to promote coalescing of the oil droplet flocs for aqueous phase separation (Hempoonsert et al. 2010; Yang et al. 2010). Also, this appeared to have a significant impact on the contaminants removal (COD, SOG, TSS and turbidity) for all the acid treatments evaluated at pH of 2 to 10.

4.2.1.1 Effects of Hydrochloric acid (HCl)

The effects of the HCl addition on the aqueous phase separation of the oil emulsion stability is depicted in Figure 4.1.To ascertain the acids performance, the contaminants removal was defined as the average percentage value of all the contaminants at a specified pH. In addition, the maximum removal of SOG was taken into account, since it is the main contaminant in the MOW

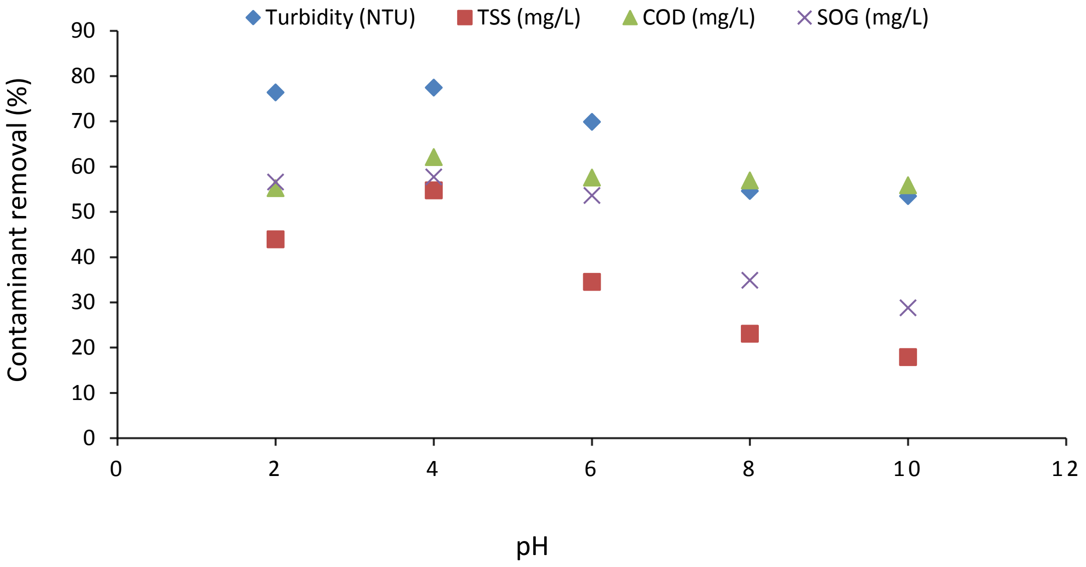


Figure 4.1 Effects of pH on contaminant removal (%) using 1 M HCl

The trend of the graph shows that the adjustment of the pH increased with decreasing contaminant removal. Thus at a pH of 2, there was about 65% removal of the contaminants as compared to the pH of 6 (60%) and 10 (40%). Consequently, sufficient removal of contaminants was obtained at an acidic medium for the pH in the range of 2 to 6. In addition, HCl, being a strong acid dissociated in the water at a moderate concentration. However, its chemistry reaction with PAS decomposed into hydrogen and chlorine species under an exothermic reaction, since most of the constituents in the MOW had either cations or anions which attracted the opposite charge of the HCl to form monomeric chain reactions to increase the coalescence of the oil droplets (Yang et al. 2010).

4.2.1.2 Effects of Sulphuric acid (H_2SO_4)

In the acidification treatment of the MOW using H_2SO_4, the response for the oil-water separation with the pH phase value being increased is shown in Figure 4.2.

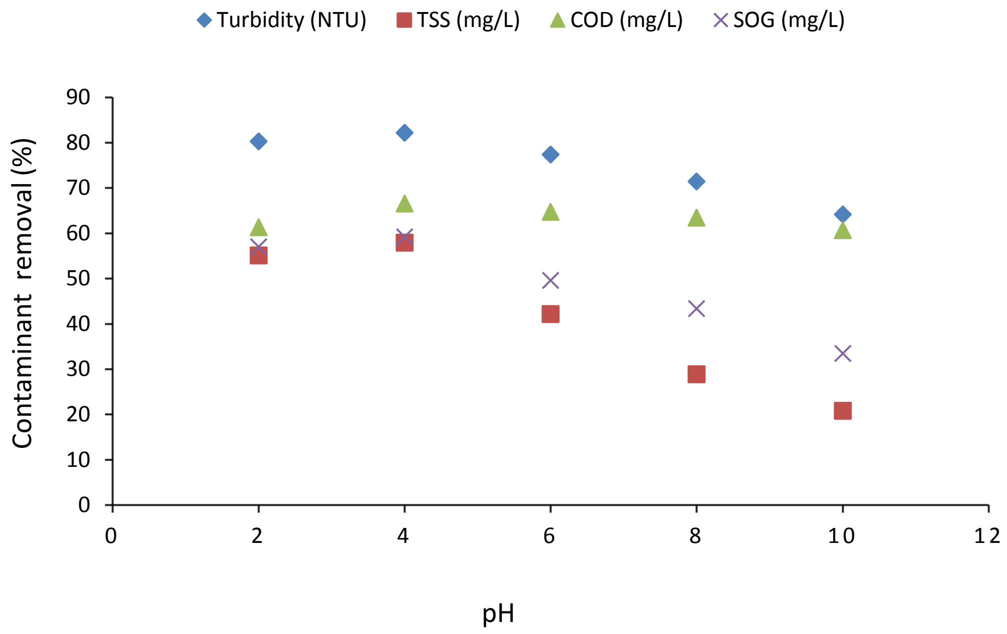


Figure 4.2 Effects of pH on contaminant removal (%) using 1M H_2SO_4

The graph presented shows the same trend as compared to that of the HCl (Figure 4.1), with respect to increased pH with decreasing contaminant removal. However, in this context, there was about 5% increase in the contaminants removal percentages. Thus at pH of 2, there was about 70% removal of the contaminants as compared to pH of 6 (65%) and 10 (45%). This demonstrated that for a strong acid like H_2SO_4 at lower pH affected the surface charge of ionization and the stability of the oil emulsion (Hempoonsert et al. 2010). On the other hand by increasing the pH, this altered the emulsion interfacial stability to gain enough strength to be repulsive towards the other charges (Al-Shamrani et al. 2002). Also, due to the lack of active surface interaction between the oil droplet and the coagulant charges resulted in a smaller amount of oil droplets flocs formed, with inability to cause oil-water separation.

4.2.1.3 Effects of Phosphoric acid (H_3PO_4)

The effect of the weak acid such as H_3PO_4, for the treatment of MOW, is presented in Figure 4.3, which shows the percentage of contaminant removal with pH adjustment.

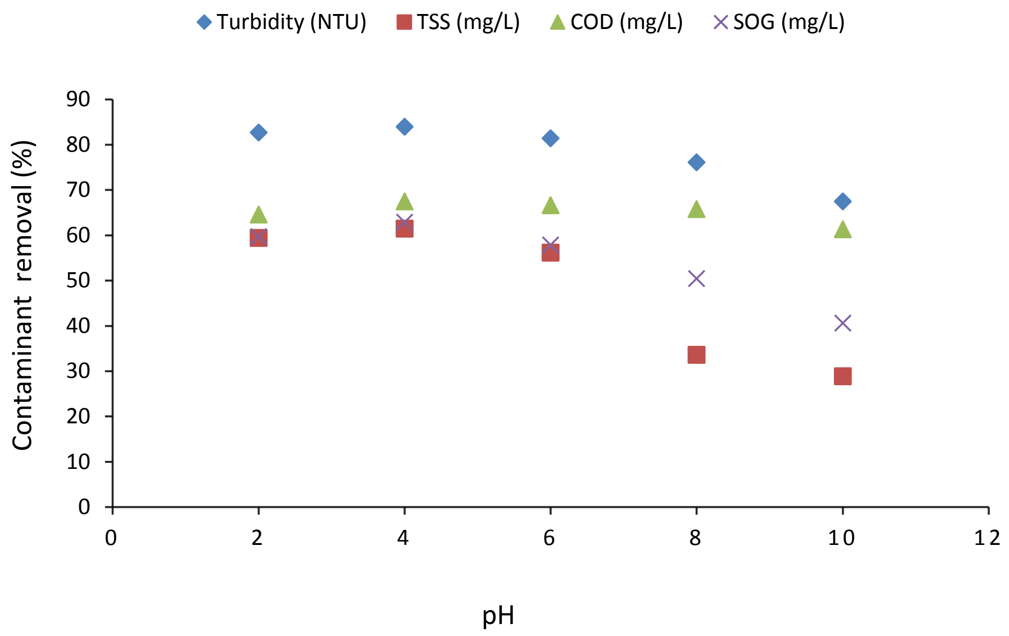


Figure 4.3 Effects of pH on contaminant removal (%) using 1M H_3PO_4

The results show that there was an increase in contaminant removal of 10% and 5% by using H_3PO_4, as compared to HCl (Figure 4.1) and H_2SO_4 (Figure 4.2) respectively. Thus at a pH of 2, there was about 75% removal of the contaminants as compared to pH of 6 (70%) and 10 (50%). It was found that the addition of the H_3PO_4 neutralised more of the oil charges by decomposing into positive charge H^+ species and negative charge PO_4^- species. This induced the oil emulsion and increased the surface stability of the oil droplet to coalesce to form larger flocs (Al-Shamrani et al. 2002). This, therefore led to the high removal of the contaminants both in the acidic and basic medium, due to the ability of the H_3PO_4, to break the oil emulsion surface and reduce its density to cause phase separation (Hempoonsert et al. 2010; Hirasaki et al. 2011).

4.2.1.4 Comparison of acid types with sensitive pH range

The acid treatment affected the contaminant removal in all the cases. Thus, it destroyed the protective action of the emulsified oil electrostatic repulsive force by breaking down the interfacial cohesion, and subsequently coalescing to form larger flocs to enhance floatability of the separated oil droplet floc phase (Zouboulis and Avranas 2000; Hirasaki et al. 2011). Also, the acids destabilised and reduced the electrostatic force of the doubled layer to power the polymerization reaction to enable the phase separation.

Comparing the effectiveness of the acids investigated, two pH levels (4 and 6) were considered as shown in Figure 4.4. This was because the performance seemed to be better in the acidic medium than in the basic medium. Moreover, the addition of the acids decomposed more H^+ species to neutralise the negative oil droplet charges during the polymerization reaction, hence contributing to a high precipitation of the oil droplets and other constituents in the MOW. Even though the lower pH of 2 eliminated a higher amount of the contaminants, it was more economical to reduce the initial pH from 7 to the range of 4 to 6, than to 2, due to chemical costs.

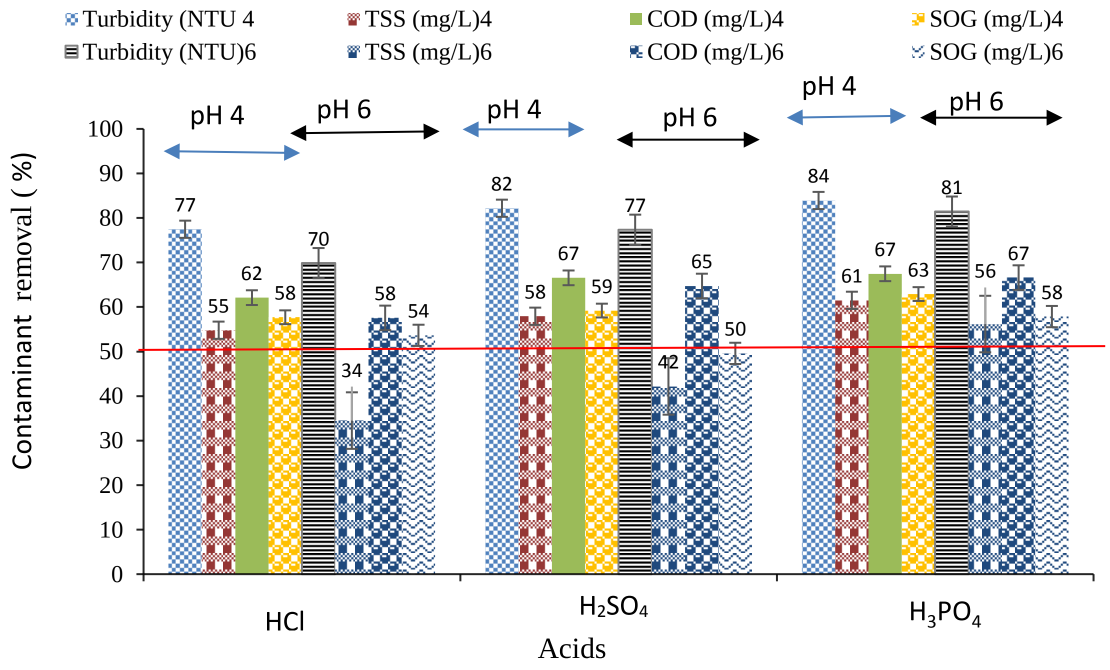


Figure 4.4 Comparing the effects of acids on contaminant removal (%) at pH 4 and 6

In Figure 4.4, the pH of 4 was found to have a greater effect than the pH of 6. Although all the acids were investigated at the same concentration (1 M), at 50% removal of the contaminant to enhance the process meet the discharge limit of SOG < 50 mg/L, it was found that H_3PO_4 being the weakest acid had the highest removal effect followed by H_2SO_4, and thereafter HCl.

Therefore, the weaker the acid, the higher the efficiency for the separation of the oil and water. Hence, the H_3PO_4 and pH range of 4 to 6 was recommended. H_3PO_4 was also the preferred acid since it was more environmentally friendly than the strong acids (H_2SO_4, HCl) which were more corrosive and could cause wear and tear.

4.2.2 Evaluation of air saturator pressure

The effects of the air saturator pressure were investigated by using the baseline conditions as discussed previously (see section 4.2.1) and H_3PO_4 and PAS as the acid and coagulant respectively for the destabilisation of the oil droplet. However, the treatment process was kept constant at a pH of 5. The quantity of air to be injected into the system was varied from 200 to 600 kPa, with a sequence interval of 100 kPa. It was observed that the amount of air dissolved and released was directly proportional to the gauge pressure, which contributed to the air bubble-oil droplet size being formed for the separation.

The result is presented in Figure 4.5, and shows a sharp increase in the of the contaminants removal from 200 to 400 kPa, followed by a gradual increase through to 500 kPa. However, the increase in the pressure from 500 to 600 kPa brought no significant change to the system performance regarding the contaminant removal. This was because the air saturator pressure at some point showed no further change in the bubble size to cause the attachment and precipitation of the oil droplets for the for oil-water phase separation (Karhu et al. 2014).

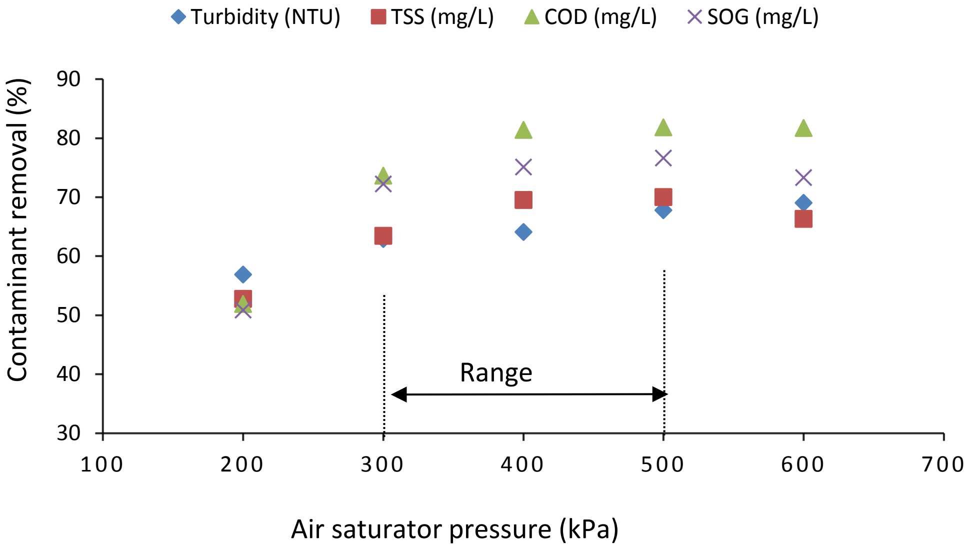


Figure 4.5 Effects of air saturator pressure (kPa) on contaminant removal (%); using H_3PO_4 at a pH of 5.

Therefore, the chosen sensitivity pressure for the investigation was from 300 to 500 kPa. This was because more than 65% of COD, SOG, TSS and turbidity were removed within that saturated pressure range, which is in agreement with the pressure range of 350 to 550 kPa as reported by Edzwald (1995). Moreover, increasing the pressure to 600 kPa might only contribute to more energy utilisation by the system since there was no significant change in removal percentage from 500 to 600 kPa. Furthermore, increasing of the saturator pressure caused an increase in the air to water ratio, which resulted in the bulk mass transfer of the oil droplet floc formation at the point of supersaturated air bubble-oil droplet attachment (Dassey and Theegala 2011).

4.2.3 Evaluation of air-water ratio

Having established the air saturator pressure range, the effect of variation in the air-water ratio flow into the system contact zone was investigated from 5 to 20% at a constant pressure of 350 kPa. The effect of increasing the air-water ratio on the contaminant removal is shown in Figure 4.6. It was found that about 70% of COD, SOG, TSS and turbidity removal was achieved with an increase of the air-water ratio from 5 to 15%. However, there was no significant improvement in the treatment of the MOW with an excess recycled rate of 20%.

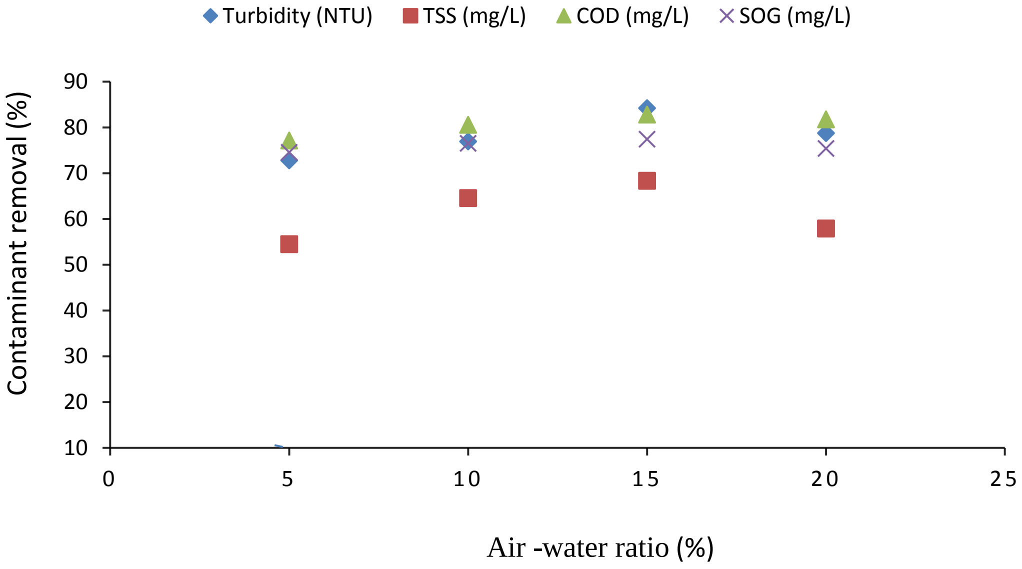


Figure 4.6 Effects of air-water ratio (%) on contaminant removal; using H_3PO_4 at a pH of 5.

Therefore, the air-water ratio range set for further investigation was 5 to 15%. This was because, the dissolved air supplied at that rate generated microbubbles at a lower rate, which increased the contact time between the air bubble-oil droplets to enhance the floc formation. Moreover, this was in agreement with 5 to 12% air-water rate which caused a substantial rise up of air bubble-oil droplet attachment as reported by Khuntia et al. (2012). Whilst at the rate of 20% generated larger bubbles, which cause disruption of the oil droplet flocs formation. On the other hand, lesser bubbles were generated due to their larger size, which resulted in decreasing the surface area to enhance the strong bond between the bubbles and oil droplets. This implies that the smaller the bubble size the better, because of the large surface area it generates for air bubble and oil droplet attachment.

4.2.4 Evaluation of coagulant dosage

The coagulant dosage was varied while the other parameters were kept constant as referred to as the baseline conditions. The coagulant (PAS) dosage was investigated at a lower range from 5 to 10 mg/L, with a sequence increase of 1 mg/L, to determine the PAS chemistry with the effluent. This gave a fair idea to the author on the grounds to select the appropriate coagulant dosage to work with on a bench scale according to literature (Table 2-5).

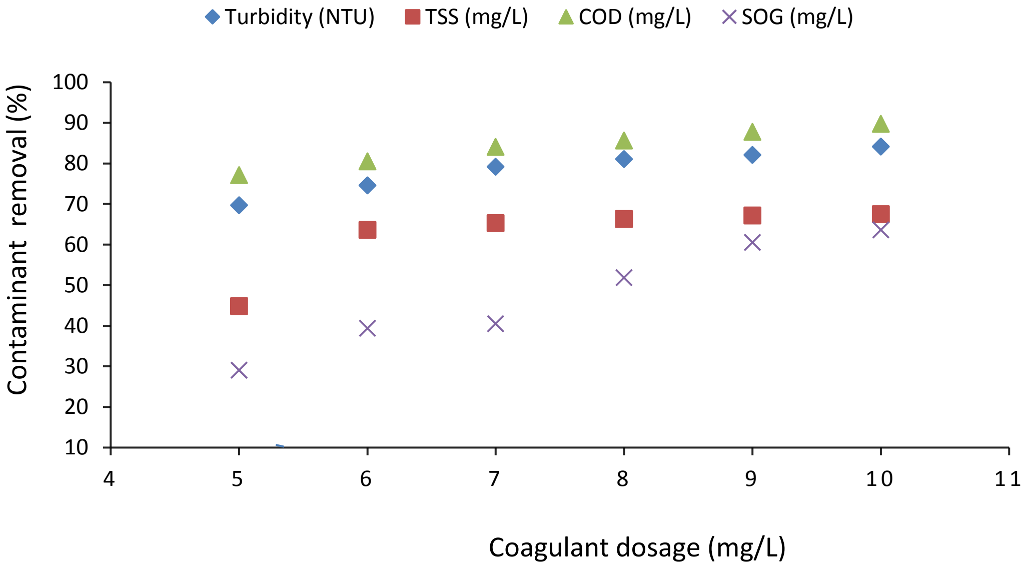


Figure 4.7 Effects of coagulant dosage (mg/L) on contaminants removal (%); using H_3PO_4 at pH of 5.

As shown in Figure 4.7, it was found that increasing the coagulant dosage had a significant change in the removal of COD and turbidity from 70 to 85%, and that of SOG and TSS from 35 to 70% from the lowest to the highest coagulant dosage (5 to 10 mg/L). Also, increasing of the coagulant dosage increased the air bubble-oil droplet attachment mechanism. This was due to a high charge layer around the oil droplet floc, which led to good agglomeration and floatability of the oil droplets, and clarification of the treated water (Mousa and Hadi 2016; Tetteh et al. 2017). However, coagulant dosage range of 10 to 50 mg/L was recommended for further investigation. This was because coagulant dosage performed differently regarding contaminants removal, which depends on the water chemistry and the type of coagulant being used (Tetteh et al. 2017). Therefore, increasing the coagulant dosage increased the surface area of the contact region between the air bubble and the oil droplets and hence strengthened the bond of the oil droplet flocs.

4.2.5 Evaluation of flotation time

The DAF performance in terms of flotation time is defined as a function of the contact time that exist between the air bubble and the oil droplet attachment. This phenomenon was expected for the air bubble to encapsulate the oil droplets and coalesce to form strong larger oil droplet flocs for easier removal without breakage by increasing the flotation time.

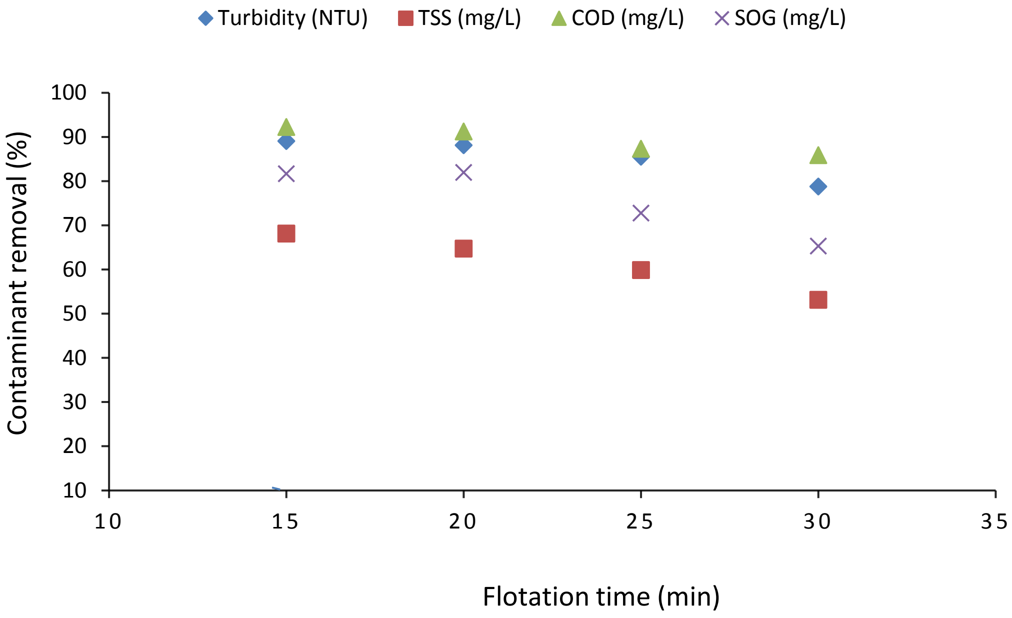


Figure 4.8 Effects of flotation time (minutes) on contaminants removal (%); using H_3PO_4 at a pH of 5.

However, the results presented in Figure 4.8 shows that increasing the flotation time decreased the contaminant removal. Thus the shorter the flotation time, the better the treatability performance. Such that, the shorter flotation time (15 minutes) was found more essential for the DAF to generate a lot of micro bubbles to remove more of the pollutants viz: COD (92%), SOG (82%), TSS (68%) and turbidity (89%). The longer flotation time affected the oil droplet flocs, hence reducing the removal of the pollutant rate viz: COD (78%), SOG (53%), TSS (86%) and turbidity (65%) for the 30 minutes time. This was because the oil droplet flocs formed within that specific contact time might be exposed to disruption (floc shear stress) in the contact zone of the vessel. Hence, this phenomenon regarding the more extended flotation time led to the breakage of the flocs for lower contaminant removal recorded. Also, the flotation mechanism which was stimulated by air bubbles to adhere to the oil droplet flocs required a shorter time to rise to the surface (Younker and Walsh 2014).

4.2.6 Summary

Among the three acids investigated at the same concentration, the H_3PO_4 was found to be more effective and environmentally friendly than the two strong acids (H_2SO_4 and HCl). Also, the treatment of the MOW was found to be more efficient under the acidic medium, and more economically within the pH range of 4–6, than using a lower pH of 2, which will increase the cost of chemical usage to balance the pH. The results of this section has been submitted for publication in Journal of Pollution Research (PF-F-999 in press).

The air saturator pressure between 300 to 500 kPa increased the buoyancy force, which was driven to generate more microbubbles. This increased the active surface area and encapsulated the oil droplets, and eliminated a high amount of the pollutants. The saturator pressure increased the air to water ratio from 5 to 15%. Also, the dissolved air supplied at that rate generated smaller sized bubbles, which increased the air bubble–oil droplet attachment for the floc formation.

It was deduced that to reduce the electrostatic repulsion force of the oil emulsion a binding force to coalesce and agglomerate the oil droplet flocs is required. Also, this could be achieved by increasing the coagulant dosage to improve the treatability performance. Although coagulant dosage was found to be the most sensitive factor, coagulant type performance depended on its characteristics and the chemistry of the MOW. Since insufficient coagulant dose or overdose might result in poor performance and cost, it was necessary to investigate coagulant type and identify its optimum dosage range to enhance the treatment performance. Coagulant dosage range of 10 to 50 mg/L was then recommended for further investigation. However, the flotation mechanism was found to be effective at a shorter flotation time (15 minutes) hence investigating the flotation time below 15 minutes was then recommended.

4.3 Evaluation of coagulant types and dosage

It was observed that several mechanisms via the effect of different operational parameters attributed to the efficiency of the DAF in the treatment of the MOW as discussed under section 4.2. However, the amount of coagulant required was critical to break up and stabilise the dispersed oil emulsion, which was attributed to several factors such as the coagulant type and dosage (Abdelaal 2004).

Therefore in an attempt to improve and establish favorable conditioning (pre or post) of the DAF efficiency, a comparative study was carried out to meet the objective of identifying the most effective and economically viable coagulant. The effects of the four inorganic coagulants as presented by Tetteh et al. (2017) and three polymeric coagulants have been investigated and are discussed in sections 4.3.1 and 4.3.2 respectively. Likewise, the efficiency of the DAF by pre or post-conditioning with two of each effective inorganic and polymeric coagulants is discussed in section 4.4. The results of the effects of the coagulant types on the MOW treatability, and a basic economic analysis and summary are discussed and presented under this section. .

4.3.1 Effects of inorganic coagulants on MOW treatment

It was observed that increasing both the aluminium and iron-based coagulant dosage (10 to 50 mg/L) increased the oil droplet stability by continually activating and replacing the emulsion surface charges by dissociating the Al^{3+} and Fe^{3+} ions. This mechanism enhanced the coalesced oil droplets to form larger flocs to float to the surface, thereby proportionally decreasing the presence of the pollutants in the MOW (COD, SOG, TSS and turbidity). Hence, the rate of removing the contaminants from the MOW was improved by increasing each coagulant dosage as presented in Figure 4.9 to Figue 4.12. However, at the point of optimum dosage, a further increase in the dosage brought no significant change in the water quality, instead just increasing the chemical costs (Tetteh et al. 2017).

4.3.1.1 Removal of COD and SOG

The result for the effects of the inorganic coagulant for the removal of COD and SOG are presented in Figure 4.9 and Figure 4.10 respectively. The graph presented in both scenarios indicated that alum and AC were more effective in removing the COD and SOG than the FS and FC coagulants. However, alum was seen as superior due to a lower chemical consumption rate, with lower economic costs.

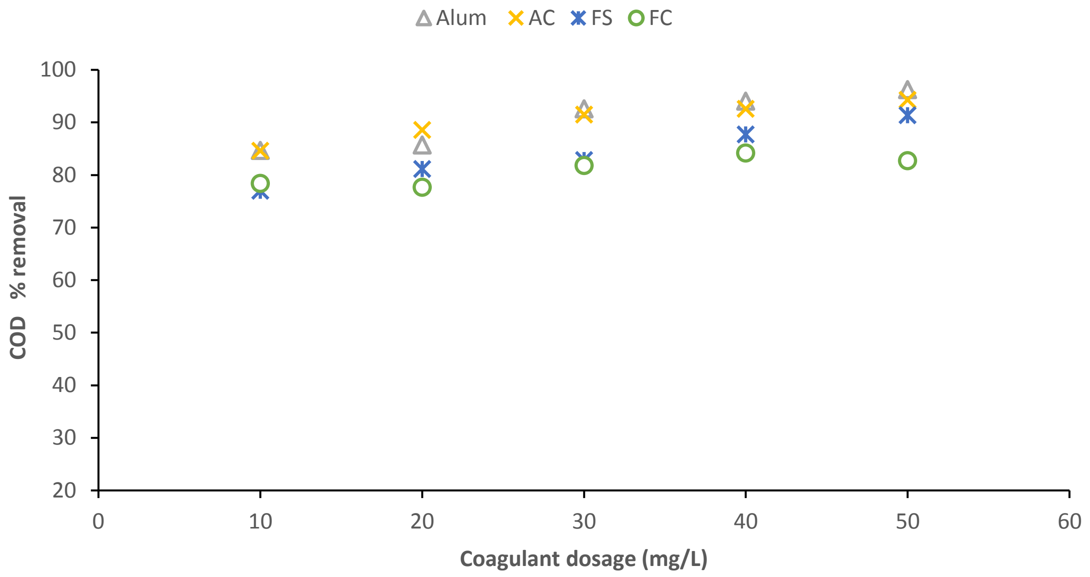


Figure 4.9 Effects of coagulant dosage (mg/L) on %COD removal; coagulating with alum at 50 mg/L dose rate removed 96% of the initial COD concentration.

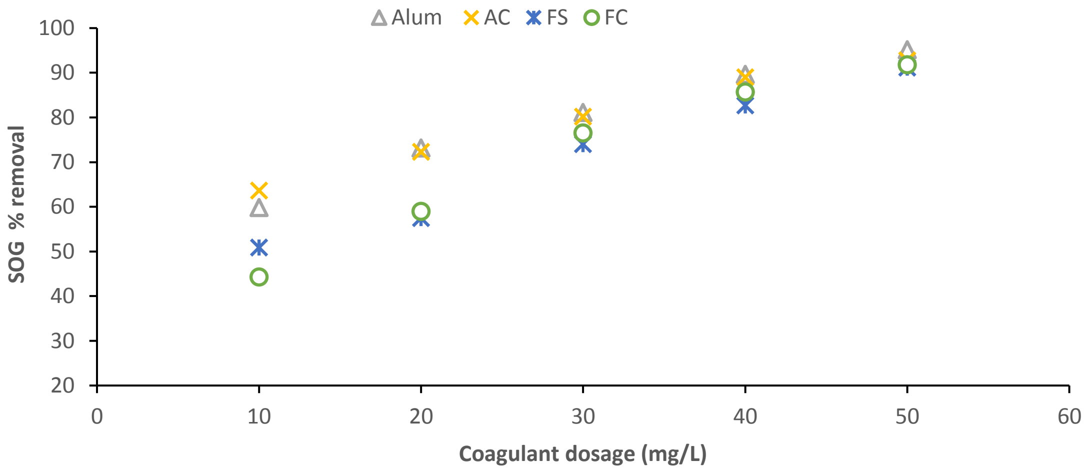


Figure 4.10 Effects of coagulant dosage (mg/L) on %SOG removal; coagulating with alum at 50 mg/L dose rate removed 95% of the initial SOG.

From the graphs presented above, it was deduced that the alum, AC, FS and FC at the highest dosage of 50 mg/L removed an average percentage of 96, 94, 83 and 91% of the initial COD concentration. Likewise, concerning the initial SOG, about 95, 93, 91 and 92% removal were recorded for the alum, AC, FS and FC coagulants respectively. However, regarding the dosage rate with FC from 40 to 50 mg/L, there was a slight retarding performance for the

COD removal, from 84 to 83%. This indicated that there was an overdose on the side of the FC, hence reducing its efficiency while increasing the chemical costs (Tetteh et al. 2017).

In that context, there was no connotation of increasing the FC dosage, which will eventually restabilised the oil droplet with the excess FC ions. This mechanism made the author appreciate the understanding of overdose and underdose and the consequences that follow. The inefficiency of the iron-based coagulant (FS and FC) was attributed to the instability of the ferric oil droplet flocs formed being unstable not to withstand the floatability period. This then affected the iron-based coagulant performance in the removal of both the COD and SOG and because of their excess trivalent ions restabilised with the oil emulsion, which resulted in inefficient treatability of the COD and SOG (Daud et al. 2015).

4.3.2 Removal of TSS and turbidity

The performance of the DAF was also monitored for the oil-water separation based on the removal of TSS and turbidity, which accounted for the dissolved organic and inorganic compounds that were constituted in the MOW. The relative removal of TSS and turbidity are shown in Figure 4.11 and Figure 4.12 respectively. The graphs presented below indicates clearly that a high percentage of the TSS (96%) and turbidity (91%) were removed when coagulated with the FC coagulant. Likewise, the neutralisation of the oil emulsion increased with the coagulant dosage (alum, AC, FS and FC) for the removal of the TSS and turbidity. However, the maximum TSS removal was achieved at a coagulant dosage of 50 mg/L corresponding to the other coagulants at 90, 94, and 88%, and likewise, the turbidity removal was 80, 84 and 78% for the alum, AC, and FS respectively. Because of the contaminant removal requirements and environmental restrictions, FC was preferable as it gave better results at a lower dosing rate than the others did.

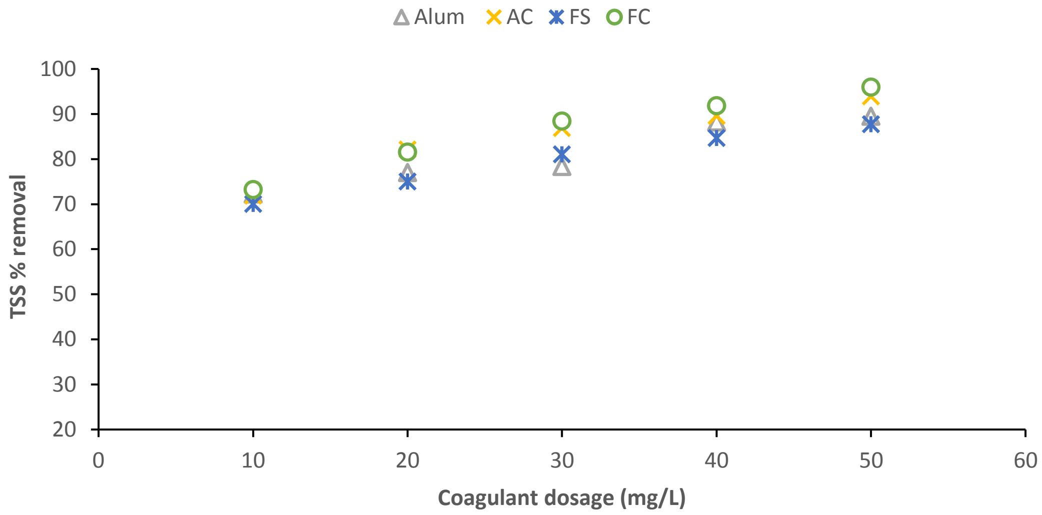


Figure 4.11 Effects of coagulant dosage (mg/L) on %TSS removal; coagulating with alum at 50 mg/L dose rate removed about 90% of the initial TSS as compared with FC at 96%

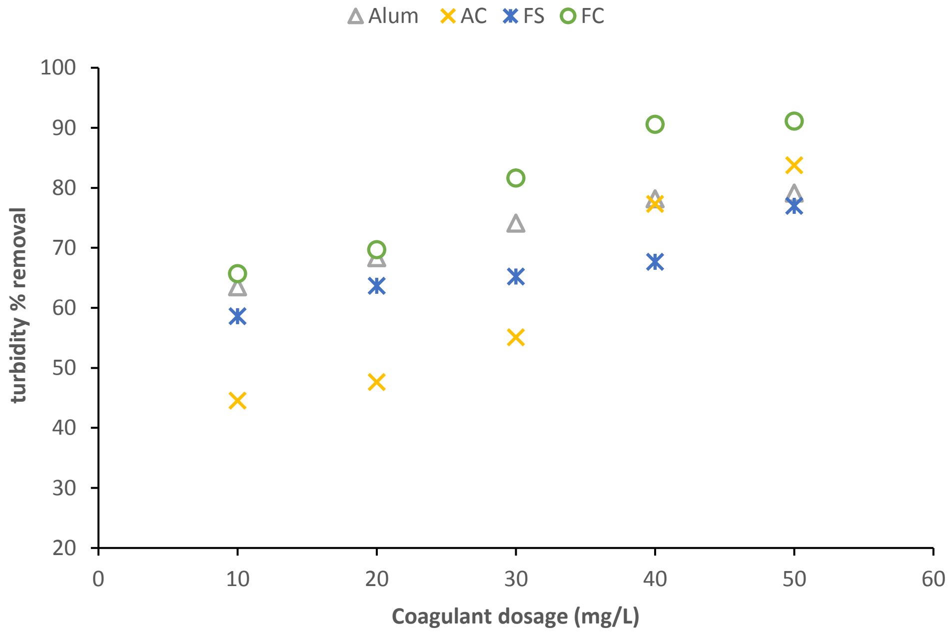


Figure 4.12 Effects of coagulant dosage (mg/L) on %turbidity removal; coagulating with alum at 50 mg/L dose rate removed about 80% of the initial turbidity as compared with FC at 91%.

4.3.2.1 Conductivity (EC) and Total dissolved solids (TDS) removal

Figure 4.13 and Figure 4.14 shows the correlation that exists between EC-SOG and TDS-SOG respectively. The correlations were determined for the control purpose of the coagulant types and dosage for treating the MOW. Moreover, the limitations associated with the use of inorganic coagulants such as high salt content in the effluent were in support with the findings studied by Abdelaal (2004) and Demirbas and Kobya (2017). It was insignificant that the use of the aluminium and iron-based coagulants increased the salts content and the inorganic dissolved solids such as the chloride, sulphate, aluminium and iron salts, which contributed to the poor TDS and EC removal from the effluent.

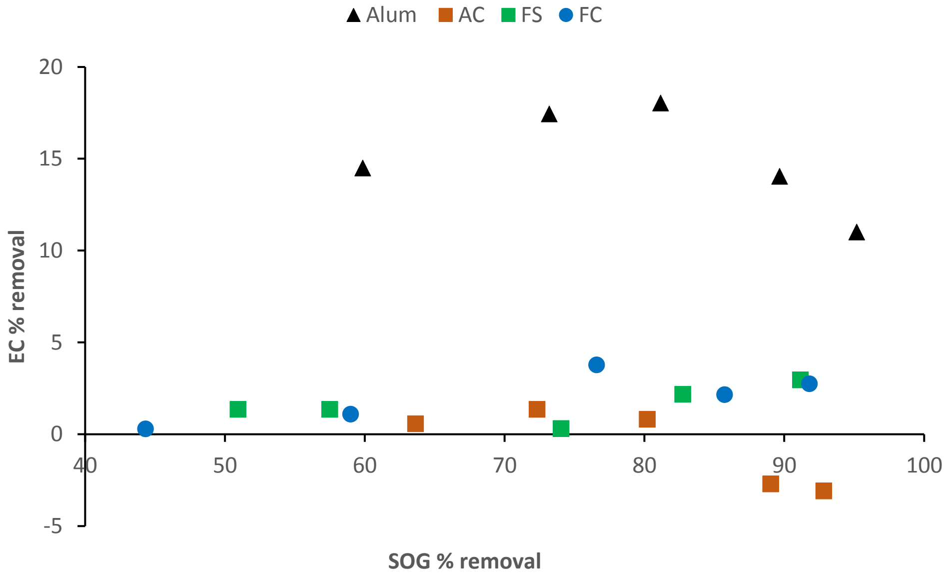


Figure 4.13 Percentage EC removal vs SOG

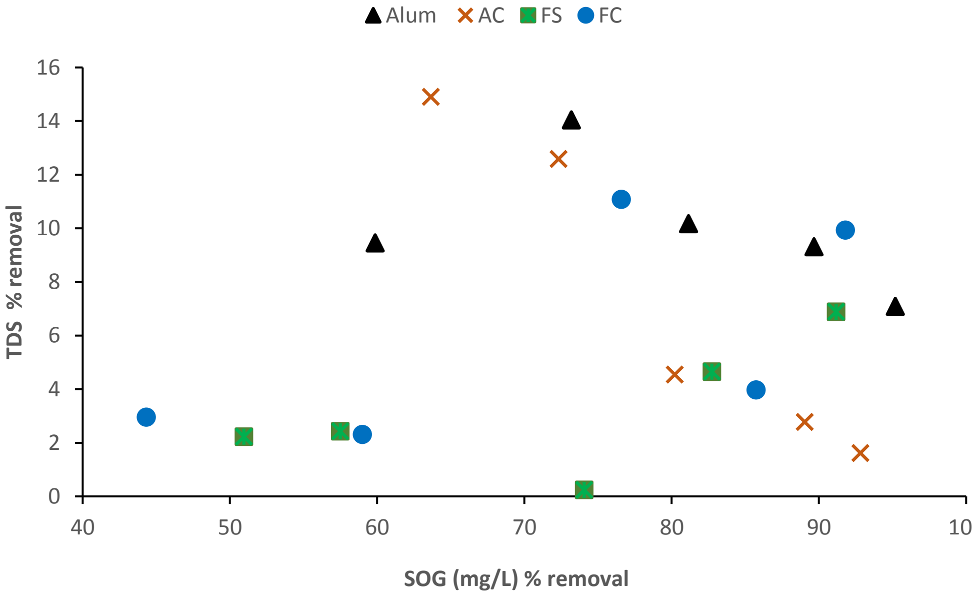


Figure 4.14 Percentage TDS removal vs SOG removal

In both cases, the use of the AC showed the poorest performance, such that an increase in AC dosage for the removal of EC (Figure 4.13) resulted in negative removal. The results of the TDS removal indicated similar performance trends by each individual coagulants like that of the EC removal. This confirms to a suggestion made by Metcalf and Eddy (2003) that the measure of EC concentration can be estimated by the TDS concentration of the MOW. Also the removal of the high salts content in the effluent will require downstream treatment with advanced membrane technology such as Donnan membrane process (Prakash et al. 2004; Chollom et al. 2015).

4.3.2.2 Cost comparison of Inorganic coagulants

The first priority in water and wastewater treatment is to produce good contaminant removal at the lower cost. A cost comparison of the four inorganic coagulants was undertaken based on the price of coagulants during the evaluation period.

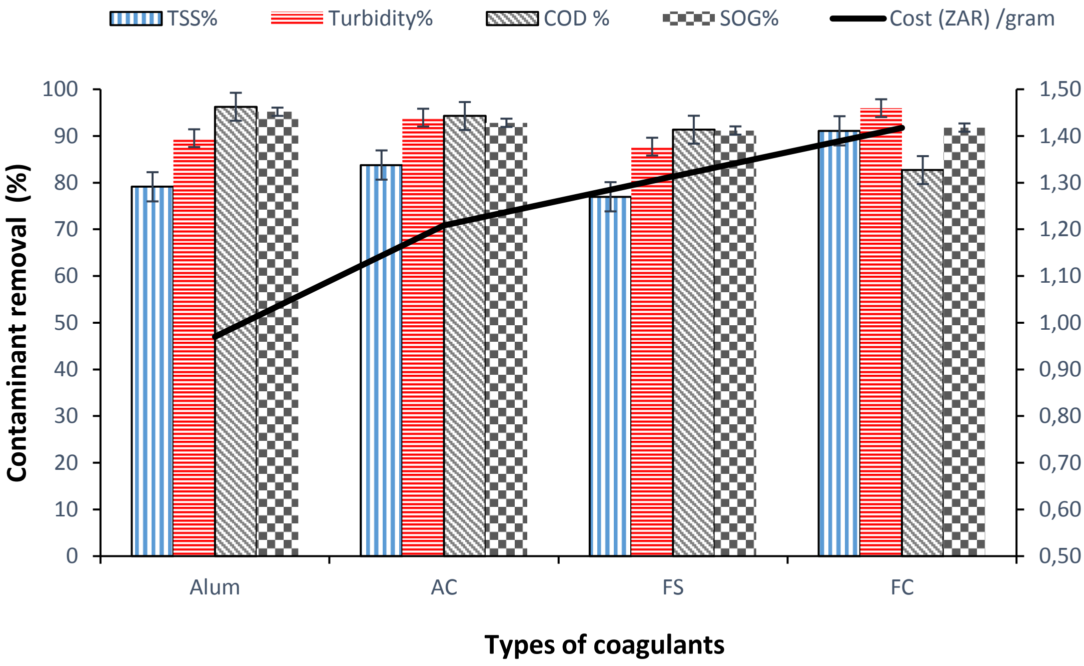


Figure 4.15 Economic comparison of coagulant efficiency at 50 mg/L dose rate. The costs of alum, AC, FS and FC per gram in South Africans Rand (ZAR) are 1, 1.2, 1.3 and 1.4, respectively (Tetteh et al. 2017)

A basic economic study comparing the cost of coagulants of 1 g/L is shown in Figure 4.15, with water contaminant removal at the optimum dose of 50 mg/L. The results also show the percentage removal of TSS, turbidity, COD and SOG were 79, 89, 96 and 94% for Alum;

84, 94, 94 and 93 % for AC; 77, 88, 91 and 91% for FS; 91, 96, 83 and 92% for FC, respectively (Tetteh et al. 2017).

The optimum coagulant dosing rate was taken as 50 mg/L where the coagulants were effective to reduce the oil in water by 90% and more. A further downstream treatment would result in limiting the soap oil and grease below the restriction limit. Also, all the coagulants have the potential capacity to reduce the oil droplets in water but in terms of chemical consumption costs, alum was the most effective and economically viable as compared to other coagulants.

4.3.2.3 Summary

This objective as published by Tetteh et al. (2017) aimed to investigate four different coagulants, and select the most economic and effective inorganic coagulant for pre-treatment of the MOW. The study indicated that the selection of coagulants based on their performance depends on the key contaminant removal parameters of interest and the treatment process. The ionic nature of the Fe^{3+} and Al^{3+} at a critical concentration brings about discontinuity of the oil droplets due to counter ionic exchange. Thus, the coagulant dosage increased the neutralisation of the negative charged oil droplet; hence, SOG and other pollutants were precipitated and removed. However, coagulant overdose could contribute to restabilisation of the oil droplets and increases operating costs. Therefore, the lower the dosage the better the cost of production. At an optimum dose of 50 mg/L, ferric chloride was seen to be better for the removal of turbidity and TDS. Likewise, alum was better for the removal of COD and SOG.

Above all, the best inorganic coagulant for the treatment of MOW was alum, due to its effectiveness and economic viability in removing SOG from water. Alum and FC were therefore recommended for further investigation. Adjustment of pH also destabilized the oil droplets for effective separation. Evaluating coagulants with the DAF jar test gave a preview of how effective the coagulant will be, when used on a pilot plant or large scale. In addition, due to the high salt content associated with the inorganic coagulants, a downstream treatment will be required with advanced membrane technology such as Donnan membrane process.

4.3.3 Effects of polymeric organic coagulants on MOW treatment

The nature of the coagulants depends on its polymeric species such as the concentration of the Al^{3+} or Fe^{3+} ions and the hydrolysis duration of the solution. During the treatment process, the three different coagulants (PAS, Z553D, and Zetag32-FS/A50) were evaluated to determine the rate of the hydroxide precipitation of the coagulant species. Thus, there was the potential ability to adsorb onto the oil droplet surfaces to neutralise the charge or chemically interact with dissolved organic and inorganic compounds in the MOW to reduce the contaminants. This destabilisation mechanism via coagulation with polymeric coagulants involves inter-particle bridging between the oil droplets and the organic monomers (Bolto and Gregory 2007; Guan et al. 2014).

This section presents and discusses the results on the effects of each polymeric organic coagulants together with economic analysis and summary. The author at the 7th International Colloids Conference, Barcelona-Spain (June, 2017), presented the results obtained from the three-different polymeric organic coagulants studied.

There a was variation to which the hydrogen ions reacted with the alkalinity of the MOW to form rapid and dense flocs to float on top of the water surface by the organic coagulants and the inorganic coagulants (see section 4.3.2).

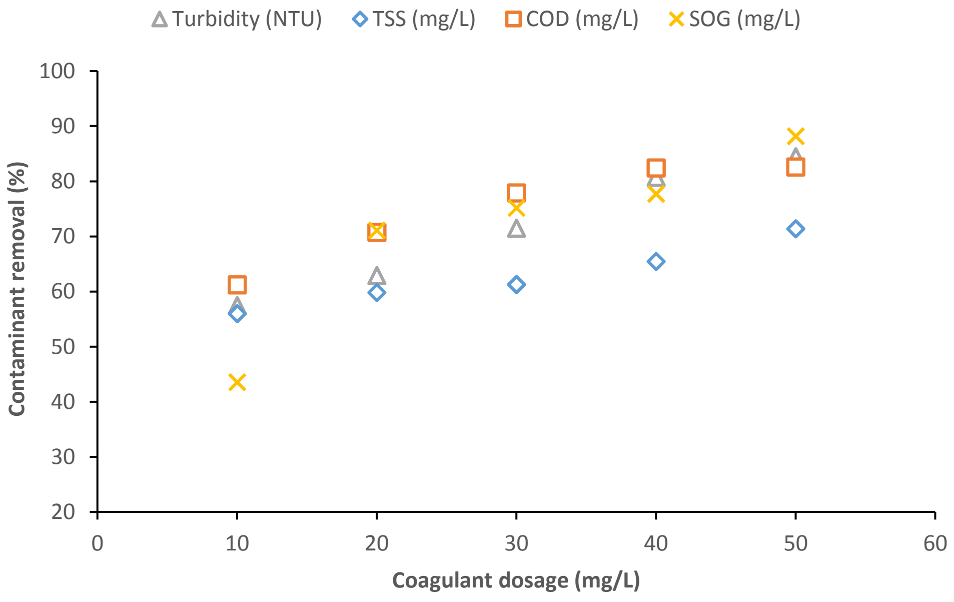


Figure 4.16 Performance of PAS on removal of contaminants from the MOW

Figure 4.16 depicts a linear progression for the removal of SOG, hence showing a continuous improvement. Similarly, COD, TSS and turbidity showed removal improvements. The trend observed in this stage suggested that the SOG (88%) contributed largely to the COD (82%) which also caused the TSS (72%) and turbidity (85%). However, the removal of SOG at the start of the coagulation process was slower as compared to the other coagulants.

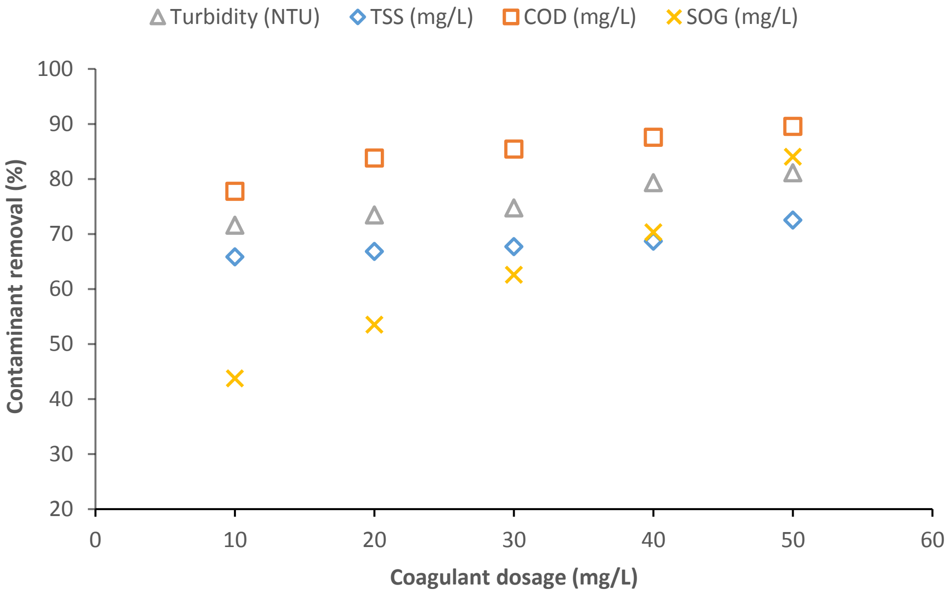


Figure 4.17 Performance of Z553D-PAC on removal of contaminants from the MOW

Figure 4.17 shows that increasing the dosage increased the contaminant removal. However, the removal of SOG started on a lower level until it reached a peak of 84% at a dosage of 50 mg/L. This eventually affected the removal of COD (90%), TSS (73%) and turbidity (82%).

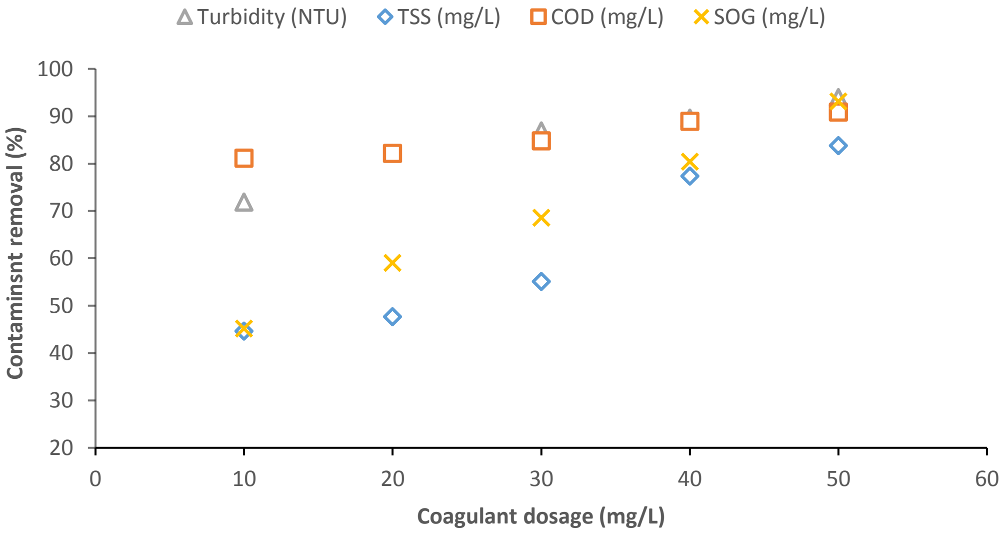


Figure 4.18 Performance of Zetag32-FS/A50 on removal of contaminants from the MOW

The graph presented in Figure 4.18 shows that increasing the Zetag32-FS/A50 dosage increased the contaminant removal. This trend is seen for all the contaminants. The removal of COD, SOG, TSS and turbidity were found to be 91, 93, 84 and 93%. This entails that the oxidation of the ferrous state iron solution was more effective for rapid precipitation and removal of a large quantity of the contaminants from the MOW.

4.3.3.1 Conductivity and TDS removal

The results presented in Figure 4.19 and Figure 4.20 shows significant removal of TDS and EC respectively with an increase in SOG removal than the use of inorganic coagulant as discussed previously (see section 4.3.1.3).

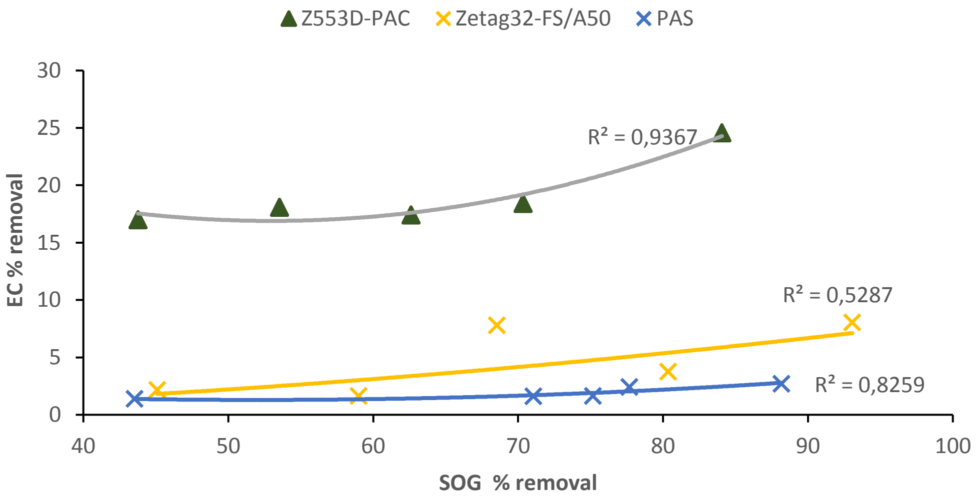


Figure 4.19 Percentage EC removal vs SOG; coagulating with Z553D-PAC at 10-50 mg/L dose rate

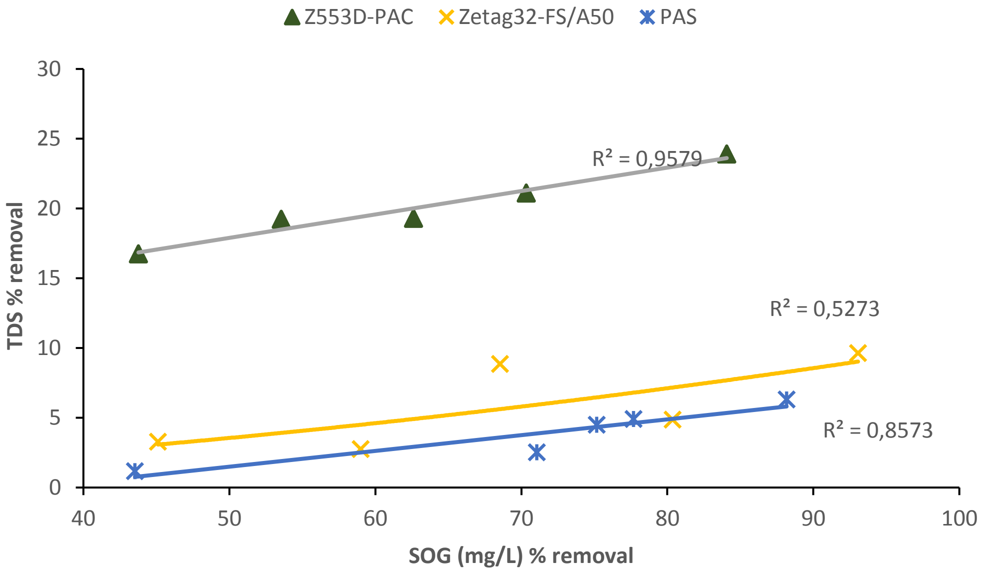


Figure 4.20 Percentage EC removal vs SOG; coagulating with Z553D at 10-50 mg/L dose rate removed 17-24% of the initial EC as compared with PAS (1- 6%).

Although, similar trends were observed in both graphs (Figure 4.19 and 4.20) for the TDS and EC removal, a polynomial function regression coefficient of R^2 values were determined, such as 0.9367, 0.5287 and 0.8259 for EC removal with Z553D, Zetag32-FS/A50 and PAS, and likewise TDS of 0.9579, 0.5273 and 0.8573 respectively. Therefore, the mechanism of the polymeric organic coagulation indicated a high entrapment of the dissolved solids and salts, which caused an increase in the flocs floatability for separation.

4.3.3.2 Cost comparison of polymeric organic coagulants

The polymeric organic cost comparison was estimated based on the average dosage and the purchased price. The cost comparison indicates that treatment with Zetag32-FS/A50 was the cheapest, followed by Z553D, and then PAS with the highest cost as presented in Figure 4.21 below. The optimum dosage for the three coagulants was found to be 50 mg/L, which resulted in the removal of 82 to 90% COD, SOG removal of 84 to 92%, and then TSS and turbidity removal of 72 to 83% and 81 to 92% respectively. Moreover, the average performance for contaminant removal indicated by Z553D, Zetag32-FS/A50 and PAS were 85, 87 and 83% respectively. Amongst the coagulants, Zetag32-FS/A50 was found superior because it outperformed the other coagulants; this could have been due to the trivalent ions and long monomeric chain that enhanced more oil droplets to coalesce. This enhances the buoyancy of the oil droplets to float and to be removed by the DAF.

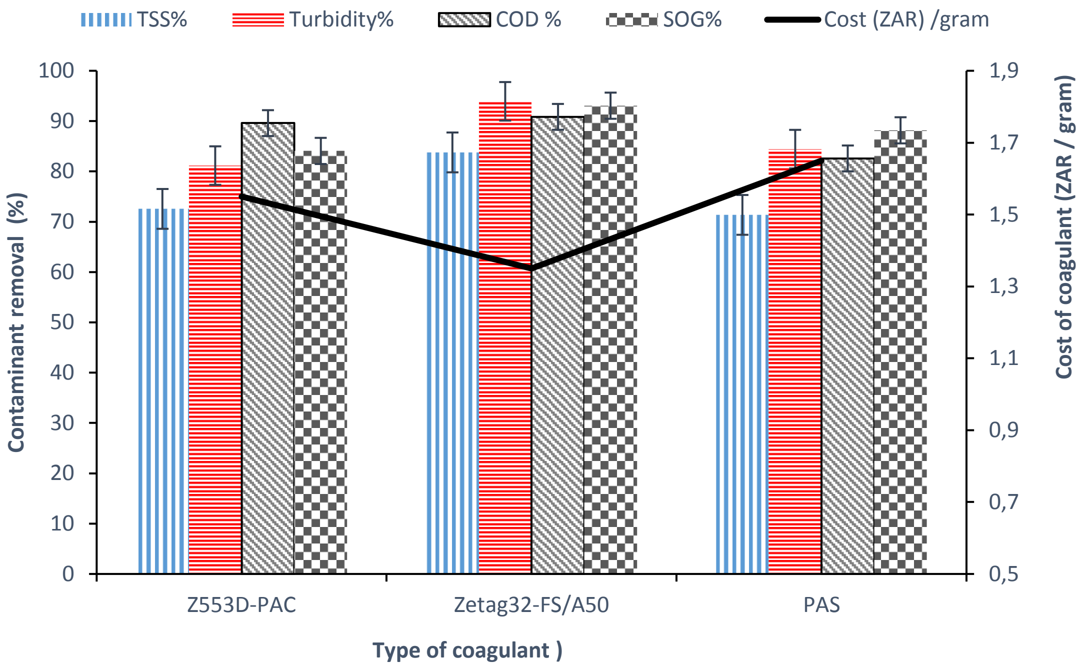


Figure 4.21 Economic study and comparison of coagulant efficiency at the optimum dose of 50 mg/L. The cost of Z553D, Zetag32-FS/A50 and PAS per gram in South Africans Rand (ZAR) are 1.55, 1.35 and 1.65 respectively (sigmaaldrich.com/south-africa.html, 2016).

4.3.3.3 Summary

It was found that the oil-water separation increased with a decrease in the electrostatic repulsion force via the addition of the coagulants, which increased the DAF efficiency. The coagulant dosage was considered very important since overdose or underdose will lead to poor performance. This was found to be crucial in obtaining an efficient treatment performance at the lower dosing cost. Also, the acidic medium of the MOW caused rapid hydrolysis leading to the precipitation of the oil droplets. Hence, without control the nature and chemistry of the coagulants would have resulted in poor performance.

Therefore, this investigation was aimed to treat the MOW and evaluate polymeric organic efficiency in the removal of the contaminants. It was deduced that the optimum dosage of the three optimised coagulants was 50 mg/L, with the Zetag32-FS/A50 being the most effective polymeric coagulants. Also, lower salts were attributed to the usage of the polymeric coagulants as a high salt content is related to the use of the inorganic coagulant. The organic coagulants constituted preformed polymeric species with a high cationic charge, which was able to persist long enough to enhance the rate of colloid charge neutralisation substantially. Hence, Z553D and Zetag32-FS/A50 were recommended for further studies.

Above all, coagulation of MOW were mainly dependant on the composition and the species of the coagulant used. Thus, these factors should always be considered first before application.

4.4 Pre and post–coagulation treatment configuration of DAF

For the efficiency of coagulation, the DAF mechanism depends on the process configuration, the coagulant type, the chemistry of the water and the effluent quality demanded (de Sena et al. 2009). Given that, coagulation before and after the DAF was investigated as one of the primary objectives to establish the best configuration.

It was deduced that increasing each coagulant dosage increased the MOW clarity in both scenarios; hence, at a coagulant dosage of 50 mg/L, the selected coagulants (alum, FC, Z553D and Zetag32-FS/A50) were evaluated and the performance compared. Also, it was evident that the treatment of the MOW using the DAF was effective, due to its ability to introduce the saturated air to generate the dissolved air bubbles, which increased the buoyancy of the oil droplet to coalesce and enhance the oil-water separation.

The results presented in Figure 4.22 to Figure 4.25 show the addition of the coagulants before DAF was more effective than the postcondition of the DAF with a difference of about 10% for each individual coagulant. It was also observed that the flocs formed during the post-treatment were larger with high density hence settled easily by gravity, as compared with those formed by preconditioning of the DAF, which resulted in light flocs that were easily floated for separation. Thus, the settling flocs (after coagulation) decreased the clarity of the water of interest at the bottom than the mechanism that raised the flocs to the top.

Therefore, pre-treatment (coagulation-flotation mechanism) was more effective with a significant advantage over the post-treatment (sedimentation-coagulation mechanism), which will require low investment costs in the downstream treatment with less sludge formed (Bensadok et al. 2007; Jamaly et al. 2015). Even though all the coagulants applied before the DAF were seen to be effective, it was found that alum and Zetag32-FS/A50 were the two most superior coagulants with 90–95% performance, but with regards to cost, alum was cheaper than the Zetag32-FS/A50.

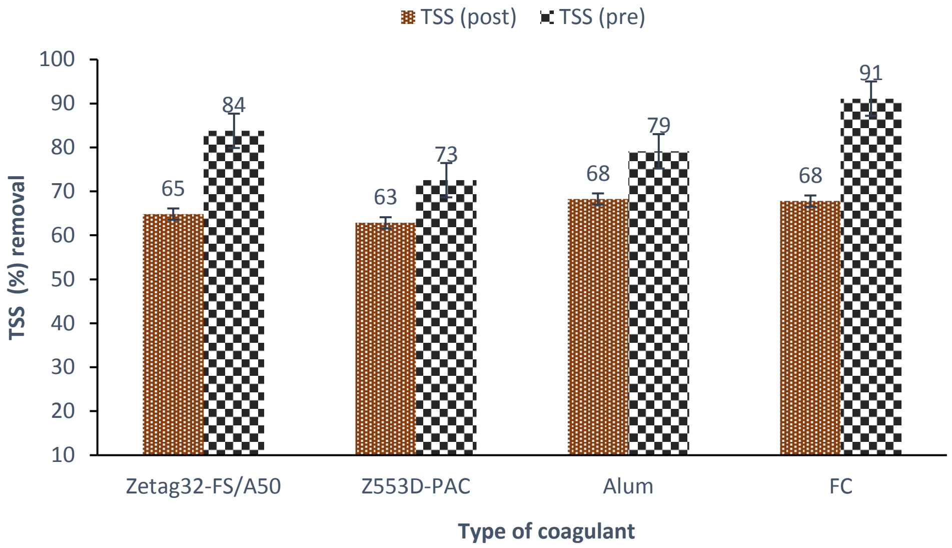


Figure 4.22 Removal of TSS with Zetag32-FS/A50, Z553D, alum and FC at 50 mg/L

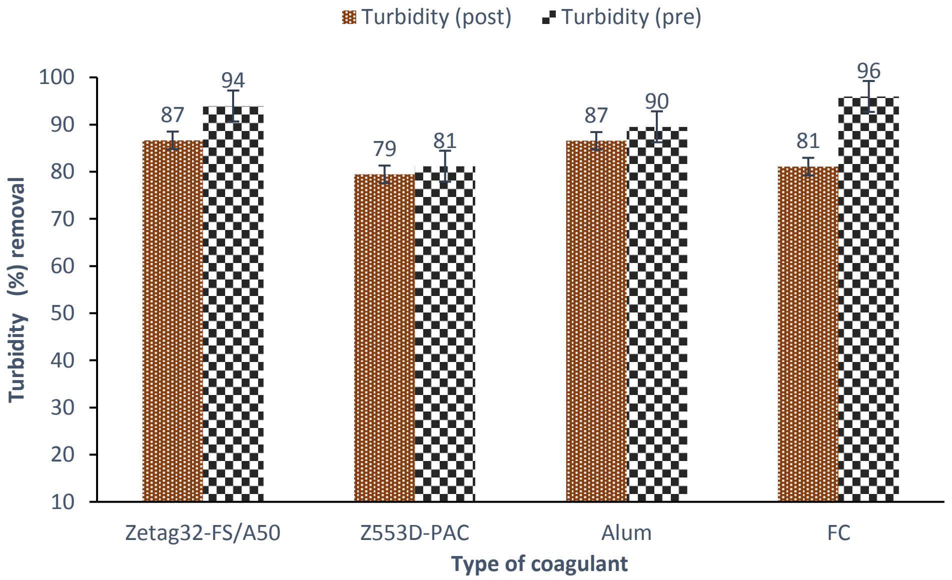


Figure 4.23 Removal of turbidity with Zetag32-FS/A50, Z553D, alum and FC at 50 mg/L

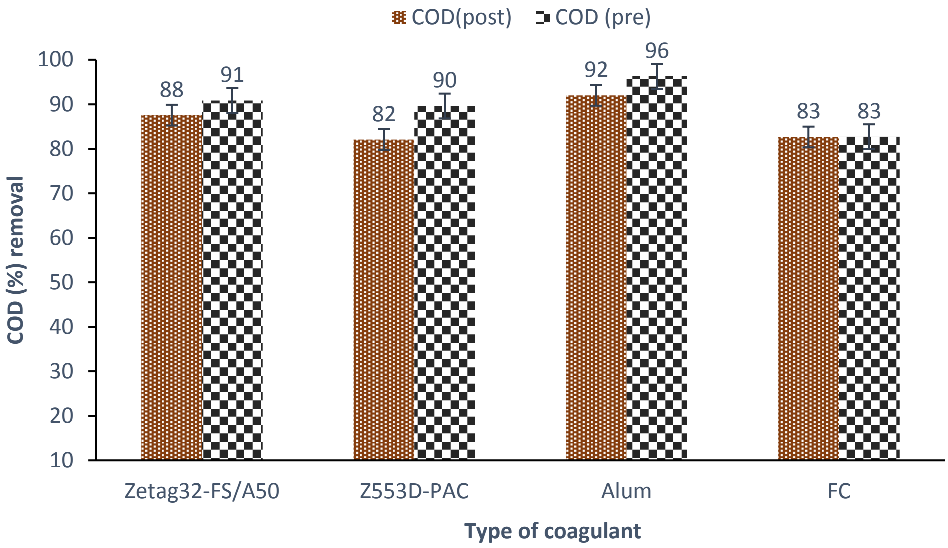


Figure 4.24 Removal of COD with Zetag32-FS/A50, Z553D, alum and FC at 50 mg/L

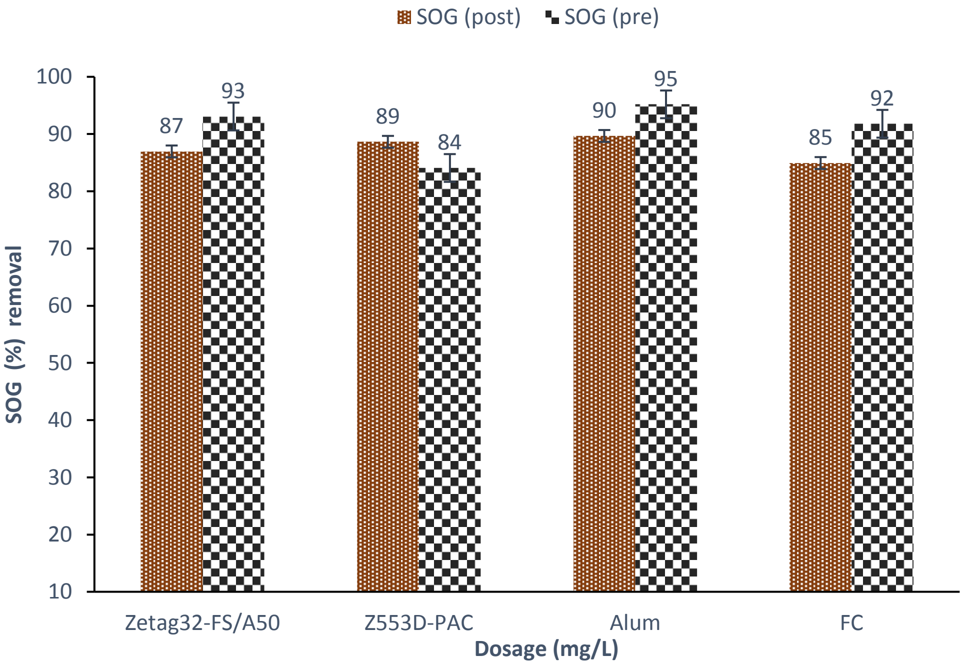


Figure 4.25 Removal of SOG with Zetag32-FS/A50, Z553D, alum and FC at 50 mg/L

4.5 Evaluation of the appropriate combination factors for the DAF Jar test using RSM

Process optimisation is a means to obtain optimum operating conditions applied to a process and maximise the response. The key combination factors and ranges were identified during the parametric evaluation using the OFAT approach (Section 4.2), and are therefore employed in this section. The experiments were designed with the BBD adapted from the RSM using three factors of interest, three levels (-1, 0, +1) and five centre points (replicated runs) for each interactive factor as depicted in Table 3-5.

The Design Expert (10.0.3) software and the design matrix generated 17 experimental runs for each case study. On this basis, the data obtained from the experiment was analysed to establish the effects and interaction on the responses. The analysis of variance (ANOVA) was used for the justification of the correlation that exists between the input, response variables, and the statistical significance for the response models. Effects of the factors on the response were also presented graphically in terms of 3D and 2D contour plots for each response. In addition, each response model generated was expressed in second-order polynomial functions, according to equation (4.1).

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_{ii}^2 + \sum_{i<j}^{n} \beta_{ij} X_i X_j + \varepsilon \qquad (4.1)$$

Where the terms Y, β_0 , β_i , X_i and ε represents the response, constant, coefficient of the input variable, predictors and the residual error from the treatment process respectively. Also, $X_i X_j$ represent the interaction terms, while β_{ii} and β_{ij} represent the coefficients of the interaction factors.

The study on the key interactive factors by using RSM on the DAF jar test are presented in section 4.5.1 and section 4.5.2. However, they are not discussed in details as the author has published most of his work on that study with regards to the different types of coagulants and their respective key combination factors. Section 4.6 explains the application of the key interactive factors on the DAF pilot plant. The section has two subsections, which accounts for the use of the alum (section 4.6.1) and Zetag32-FS/A50 (section 4.6.2).

4.5.1 Effects of pH-coagulant dosage-flotation time using RSM on the DAF jar test

The performance of polyaluminium chloride (Z553D) was investigated with three independent factors (pH, coagulant dosage and flotation time) on the water quality as a response as presented by Tetteh, et al. (2017a) in the pre-treatment of industrial MOW using RSM.

The optimum conditions obtained for the pH, coagulant dosage and flotation time were 5, 49 mg/L and 15 minutes respectively. The effects obtained on the response were 91%, 92%, 86% and 73% for COD, SOG, TSS and turbidity removal respectively. Such that, the mechanism between the pH and coagulant dosage before the DAF agglomerated more of the contaminants in the MOW for their removal. In addition, a comparative study was done on the OFAT approach and the RSM predictions where it was found that the RSM predicted results were in agreement with the OFAT results at 95% confidence level. The author further studied on the treatment of industrial mineral oil wastewater-optimisation of coagulation flotation process using RSM as presented by Tetteh el al. (2017b).

Aside this study, Tetteh and Rathilal (2018) presented the interactional effects between the input variables on the response using the DAF jar tester for the evaluation of the coagulation flotation process for industrial MOW treatment using RSM.

4.5.2 Effects of pH-coagulant dosage-air saturator pressure using RSM on DAF jar test

Evaluation of pH, coagulant dosage and air saturator to identify the most important factor and their state of interest were considered vital from the OFAT approach. This was to reduce cost of chemicals and energy usage. The, oil-water separation as discussed previously was effective under the acidic medium; while over dose or under dose of coagulant could lead to restabilisation of the oil emulsions rendering the coagulant ineffective. Likewise, high air saturator pressure had the tendency to cause turbulence resulting in oil droplet floc breakage. Therefore, the interactional effect of the pH, coagulant dosage and air saturator pressure were investigated with the polyaluminium chloride (PAC) using the percentage COD removal as the measure of performance. It was found that the change in response was directly proportional to the effect caused by the alteration in the level of the factors. The most interactive effects identified was found to be between the coagulant dosage and air saturator pressure.

Tetteh and Rathilal (2017) also applied RSM in the reduction of industrial wastewater COD, the experimental data obtained were fitted on the response (COD) predictive model to evaluate the effects of that input variable in enhancing the process efficiency. The optimisation goal was set to maximum, and the desirable outcome was achieved at 95% confidence level with over 80% COD removal. The combination of the input factors was found to be effective, within a pH range of 4.4–5.6, coagulant dosage of 34–48 mg/L and pressure of 320–400 kPa for COD removal of 80 to 98%. However, the optimum conditions obtained for the pH, coagulant dosage and air saturator pressure were 5, 48 mg/L and 350 kPa respectively for the removal of 98 % COD from the MOW.

The effect of the air saturator pressure affected the air bubble–oil droplet attachment via the mechanism of collision, adhesion and stabilisation. This mechanism depended solely on the collision that occurred between the air bubbles and the oil droplets. Meanwhile, the pH destabilised the oil droplet to release the ions to enhance the coagulation of the oil droplets. Likewise, the coagulant dosage contributed to the oil droplet surface charge neutralisation and by increasing the agglomerative force of the oil droplets to form a larger floc size for easy separation (Gregory and Zabel, 1990).

4.6 Evaluating key interactive factors of the DAF pilot plant using RSM

The continuous 1 m^3/h DAF pilot plant was optimised with the motivation from the batch DAF jar tester together with the RSM, where it was deduced that the most critical interaction factors are the coagulant dosage, air saturator pressure and the air-water ratio. It was important to scale up the coagulant dose from the batch mode to a continuous operation on the pilot plant. In addition, the DAF mechanism uses micro bubbles as the carrier for the liquid (oil-water) phase separation. It was found that the amount and size of the micro bubbles generated was directly proportional to the air-water ratio released by the saturator vessel at the elevated air pressure, which was in agreement with studies done by Zabel (1985) and Edzwald (1995). Thus, the micro bubbles depended on the air-water ratio, which determined the amount of the contaminants to be removed at the waste stream by the DAF.

To ensure consistency in optimising the DAF pilot plant with the aforementioned operating conditions on the responses (COD, SOG, TSS and turbidity removal), the samples were taken for analysis after the change in the process condition had elapsed after 30 minutes in accordance with the experimental design matrix.

The 17 experimental design matrix generated consisted of 12 factorial runs and 5 centre points runs. The runs were carried out randomly to minimise the effect of the uncontrolled variables on the responses. The optimisation was conducted for each of the two superlative coagulants (alum and Zetag32-FS/A50) under the same conditions using the RSM. The study on the effects and interactions of the factors were done on the four responses viz %COD removal, %SOG removal, %TSS removal and %turbidity removal. The results are presented and discussed in sections 4.6.1 (alum) and section 4.6.2 (Zetag32-FS/A50) respectively.

4.6.1 Effects of coagulant dosage-air saturator pressure –air to water ratio using alum on MOW treatment

In this section, the RSM was used together with alum to investigate the interaction and relationship that exists between the input factors and the responses. The data obtained from the experiments, which were inputted and simulated together with their corresponding predicted values are depicted in Table 4-1. The designed matrix by the BBD also shows different combination of the input variables at different levels, which covers the entire ranges of the factors.

Table 4-1 BBD matrix and respective response (actual and predicted) results using alum

Runs	**A-Coagulant dosage (mg/L)**	**B-Pressure (kPa)**	**C-Air/Water ratio (%)**	**Y_1- COD (%) removal**		**Y_2- SOG (%) removal**		**Y_3-TSS (%) removal**		**Y_4-turbidity (%) removal**	
				Exp	**Pred**	**Exp**	**Pred**	**Exp**	**Pred**	**Exp**	**Pred**
1	150	400	10	95	95	95	92	93	94	99	98
2	150	400	10	93	92	93	91	94	93	95	96
3	150	300	15	92	93	87	89	93	93	99	99
4	100	500	10	96	95	91	92	96	94	99	98
5	200	400	5	92	94	96	98	92	93	97	96
6	150	400	10	91	92	80	82	92	92	98	98
7	150	500	15	96	98	87	91	97	98	99	99
8	200	500	10	97	95	91	92	95	94	98	98
9	100	400	15	94	95	95	92	94	94	98	98
10	150	400	10	97	95	95	91	97	97	99	99
11	200	400	15	93	93	95	97	93	93	96	97
12	100	300	10	95	95	91	92	95	94	98	98
13	100	400	5	97	96	89	88	95	94	98	99
14	200	300	10	92	93	91	90	92	93	99	99
15	150	500	5	93	93	96	97	94	93	98	98
16	150	300	5	95	95	96	94	93	94	98	98
17	150	400	10	96	95	95	93	94	94	98	98

*Exp-experimental values *Pred-model predicted values

The results obtained from the experiments were fitted on a second-order polynomial equation for all the responses (Y_1- COD; Y_2-SOG; Y_3-TSS; Y_4-turbidity). The Design Expert software suggested quadratic model for each of the response and these were expressed as a function of the coagulant dosage (A), air saturator pressure (B) and air-water ratio (C), together with the sum of the constants, three linear effects (A, B, C), three quadratic effects (A^2, B^2, C^2) , and three interaction effect (AB, AC, BC). The order of the interactive factors to increase the %COD removal is found as AB > AC > BC. In terms of %SOG removal is AC > BC > AB, %TSS removal the order is AB> AC > BC, and %turbidity removal is AC > AB > BC. These model equations are expressed in terms of coded values for %COD, %SOG, %TSS and %turbidity removal as given in equations (4.2) to (4.5) respectively.

$$Y_1 = 95.41 - 0.622A - 0.959B - 0.242\mathrm{C} + 1.88\mathrm{AB} + 1.05AC + 0.318BC - A^2 + 0.366B^2 - 1.37C^2 \tag{4.2}$$

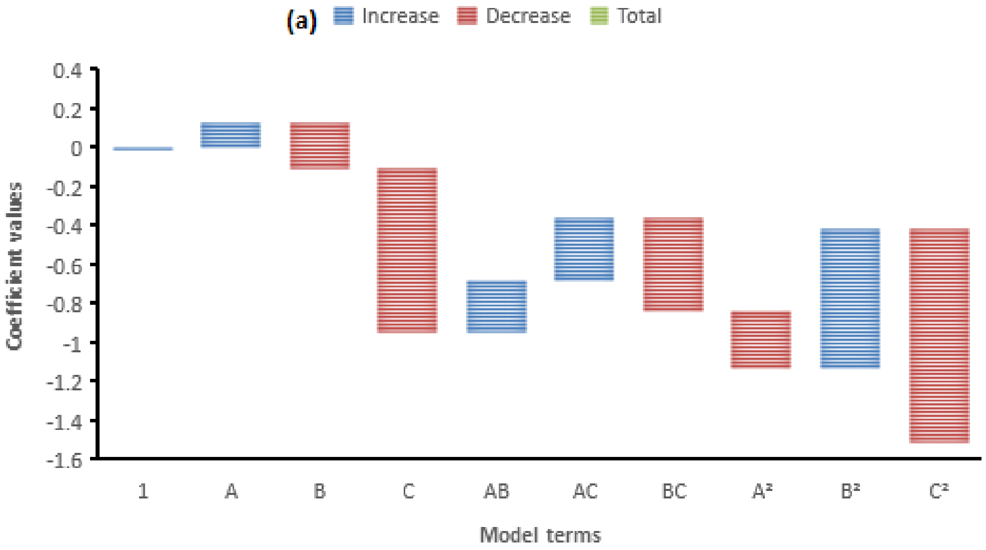
$$Y_2 = 92.36 - 1.59A + 1.58B + 3.18\mathrm{C} - 1.36\mathrm{AB} + 4.55AC + 0.91BC - 0.5A^2 + 0.409B^2 - 0.955C^2 \tag{4.3}$$

$$Y_3 = 94.44 - 0.447A - 0.288B - 0.043\mathrm{C} + 2.16\mathrm{AB} + 0.173AC - 0.028BC - 0.012A^2 + 0.015B^2 - 1.6C^2 \tag{4.4}$$

$$Y_4 = 98.41 + 0.127A - 0.233B - 0.841\mathrm{C} + 0.268\mathrm{AB} + 0.325AC - 0.48BC - 0.291A^2 + 0.712B^2 - 1.1C^2 \tag{4.5}$$

The main effect of the factors on the response are indicated by the coefficient of the first order terms, while the second and the third order terms show the relations among the concerned predictor factors.

The SOG and COD removal were used as the main indicators to explain the interactional effects that are deduced from equations (4.2) to (4.5) as shown in Figure 4.26. It is observed from this Figure 4.26, that the air saturator pressure and air-water ratio had the greatest effect on %SOG removal while coagulant dosage had the highest effects on %COD removal. Similarly, the air saturator pressure and the coagulant dosage showed a negative effect on the %COD removal. In addition, it is observed that the removal of all the contaminants were affected with the interactional effects of the coagulant dosage and the air saturator pressures. Significantly, the combination of the coagulant dosage and the air-water ratio showed an increase in the %SOG removal.



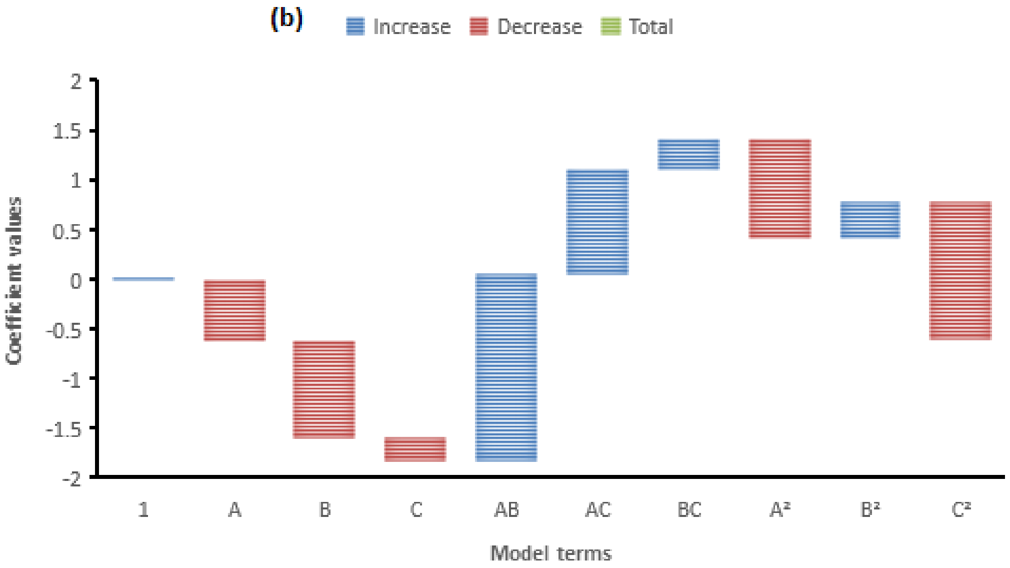


Figure 4.26 Parreto chart, effects of input parameters; alum dosage (A), air saturator pressure (B) and air-water ratio (C) and their interaction on the response; (a)%SOG and (b) %COD removal

4.6.1.1 Analysis of variance (ANOVA) for models validation

The response models were evaluated with the ANOVA to identify the significant factors that were well fitted on the models as presented in Table 4-2 to Table 4-5. The ANOVA assisted to ignore the factors that had no significant impact on the models, hence heightened the relationship between the linear, quadratic and interactional effects of the factors on the responses. All the models were found to be at 95% confidence level, thus with 5% significance level and a degree of freedom of 9. The sum of the regression (Sum of squares), Fisher variation ratio (F-values), probability (P-values), adequate precision (adeq precision) and the lack of fit (LOF) values were all found within the limits used to define the significance of the models. The P-values of less than 0.05 shows that the model terms are strongly significant, while between 0.05 and 0.1 indicates the models are slightly significant (Design Expert, 2017). In this case the P-values <0.0001 signifies that all the regression model equations were well fitted with the experimental data. The LOF values greater than 0.05 (5%) also implies that the models contain one or more terms that have no significant effects on the models due to pure error or noise, although the quadratic terms of the models were found to be partially significant, because of the P-values being greater than 0.1. Nonetheless, those terms were kept in the model to satisfy the parent terms of interaction (Design Expert, 217).

The models overall performance was assessed based on the regression coefficient of determination (R^2), the adjusted R^2 and predicted R^2. The R^2 established how closely the experimental data fitted the models, and thus ranged from 0 to 1, where 0 signifies no correlation between the data. All the R^2 values were found to be closer to 1, which represents a good fit for the data with the straight-line as presented in Figure 4.27.

The difference between the actual R^2 and the adjusted R^2 were found to be greater than 0.2, which validates the significance of the models. The high R^2 values were found to be 0.9966, 0.9858, 0.9972 and 0.9873 for %COD, %SOG, %TSS and %turbidity removal respectively. The adep precision, which is the measure of the signal to noise ratio, were acceptable for being greater than 4. These ratios were 4.898 for COD, 6.502 for SOG, 5.51 for TSS and 8.412 for turbidity.

Table 4-2 ANOVA for %COD removal using alum

Source	**Sum of squares**	**df**	**Mean square**	**F-value**	**P-value Prob>F**	**Comments**
COD-Model	42.91	9	4.77	1.53	< 0.0001	significant
A-C-dosage	3.09	1	3.09	0.9923	0.0024	
B-Pressure	7.37	1	7.37	2.37	0.0678	
C-Air-water ratio	0.4674	1	0.4674	0.1501	0.01	
AB	14.11	1	14.11	4.53	0.0708	
AC	4.41	1	4.41	1.42	0.0273	
BC	0.4037	1	0.4037	0.1296	0.0295	
A^2	4.22	1	4.22	1.36	0.824	
B^2	0.5641	1	0.5641	0.1811	0.832	
C^2	7.95	1	7.95	2.55	0.154	
Residual	21.8	7	3.11			
Lack of Fit	15.68	3	5.23	3.41	0.1332	not significant
Pure Error	6.12	4	1.53			
Cor Total	64.71	16				
Std. Dev. 1.76	**R^2 0.9966**	**Adjusted R^2 0.9866**	**Predicted R^2 0.947**	**Adeq Precision 4.898**	**Mean 94.47**	**C.V. % 1.87**

Table 4-3 ANOVA for %SOG removal using alum

Source	**Sum of squares**	**df**	**Mean square**	**F-value**	**P-value Prob>F**	**Comments**
SOG-Model	220.45	9	24.49	2.41	< 0.0001	significant
A-C-dosage	20.25	1	20.25	1.99	0.0012	
B-Pressure	20.25	1	20.25	1.99	0.0201	
C-Air-water ratio	80.99	1	80.99	7.96	0.0257	
AB	7.44	1	7.44	0.7309	0.042	
AC	82.64	1	82.64	8.12	0.0247	
BC	3.31	1	3.31	0.3248	0.0586	
A^2	1.05	1	1.05	0.1034	0.757	
B^2	0.7047	1	0.7047	0.0692	0.8	
C^2	3.84	1	3.84	0.377	0.0558	
Residual	71.24	7	10.18			
Lack of Fit	55.37	3	18.46	4.65	0.0858	not significant
Pure Error	15.87	4	3.97			
Cor Total	291.69	16				
Std. Dev. 3.19	**R^2 0.9975**	**Adjusted R^2 0.9858**	**Predicted R^2 0.9735**	**Adeq Precision 6.502**	**Mean 91.87**	**C.V. % 3.47**

Table 4-4 ANOVA for %TSS removal using alum

Source	Sum of squares	df	Mean square	F-value	P-value Prob>F	Comments
TSS-Model	33.14	9	3.68	2.03	< 0.0001	significant
A-C-dosage	1.6	1	1.6	0.8818	0.0379	
B-Pressure	0.6652	1	0.6652	0.367	0.0563	
C-Air-water ratio	0.015	1	0.015	0.0083	0.093	
AB	18.71	1	18.71	10.32	0.0148	
AC	0.1197	1	0.1197	0.0661	0.0804	
BC	0.0033	1	0.0033	0.0018	0.0967	
A^2	0.0006	1	0.0006	0.0003	0.986	
B^2	1.6	1	1.6	0.8847	0.378	
C^2	10.82	1	10.82	5.97	0.445	
Residual	12.69	7	1.81			
Lack of Fit	6.24	3	2.08	1.29	0.3925	not significant
Pure Error	6.45	4	1.61			
Cor Total	45.82	16				
Std. Dev. 1.35	**R^2 0.9972**	**Adjusted R^2 0.9866**	**Predicted R^2 0.9672**	**Adeq Precision 5.51**	**Mean 93.98**	**C.V. % 1.43**

Table 4-5 ANOVA for %turbidity removal using alum

Source	Sum of squares	df	Mean square	F-value	P-value Prob>F	Comments
Turbidity-Model	15.13	9	1.68	5.79	<0.0001	significant
A-C-dosage	0.1293	1	0.1293	0.4457	0.0525	
B-Pressure	0.4347	1	0.4347	1.5	0.026	
C-Air-water ratio	5.65	1	5.65	19.48	0.0031	
AB	0.2882	1	0.2882	0.9932	0.0352	
AC	0.4224	1	0.4224	1.46	0.0266	
BC	0.923	1	0.923	3.18	0.0117	
A^2	0.3567	1	0.3567	1.23	0.304	
B^2	2.13	1	2.13	7.36	0.301	
C^2	5.06	1	5.06	17.44	0.0142	
Residual	2.03	7	0.2902			
Lack of Fit	1.7	3	0.5677	6.92	0.463	not significant
Pure Error	0.3283	4	0.0821			
Cor Total	17.16	16				
Std. Dev. 0.5387	**R^2 0.9988**	**Adjusted R^2 0.9873**	**Predicted R^2 0.9746**	**Adeq Precision 8.412**	**Mean 98.09**	**C.V. % 0.5492**

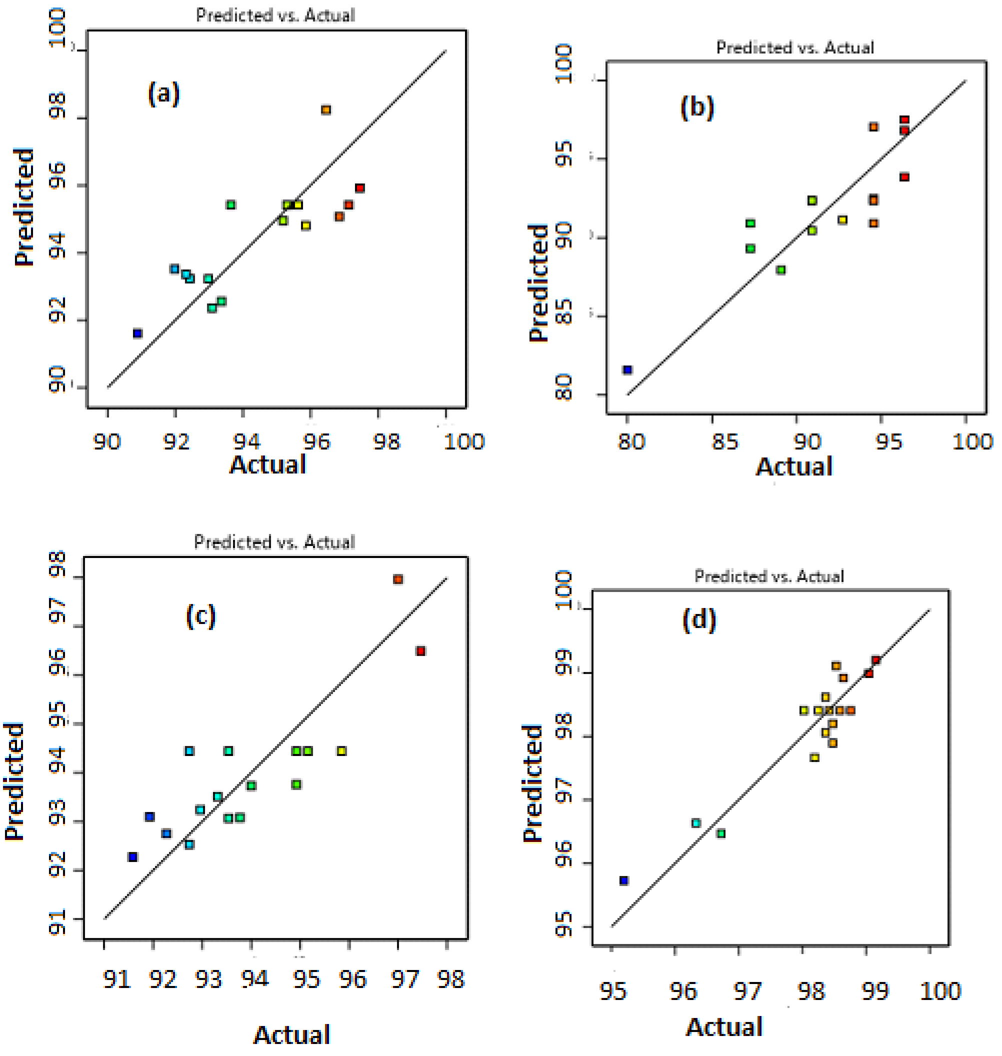


Figure 4.27 Predicted verses actual plots (a) COD, (b) SOG, (c) TSS and (d) turbidity removal using alum

4.6.1.2 Residual plot analysis

The residual plots is the difference between the inputted data values and the model’s predicted values. The normal probability plot was used to check the distribution of the residuals. It was found that the distribution was normal, such that all the points followed a straight line (Design Expert 2017). In addition, the plot of residual verses the predicted values also shows that all the data points were within the design space of the models, hence no data was excluded. These are presented in Figure 4.28 to Figure 4.31.

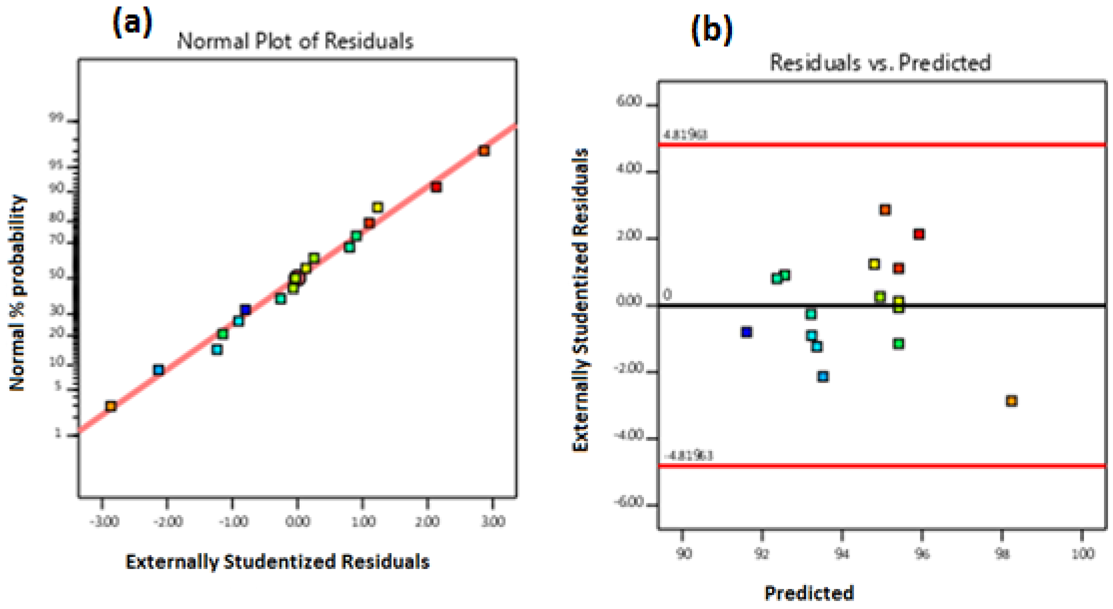


Figure 4.28 (a) Normality plot (b) residual verses predicted plot for %COD removal using alum

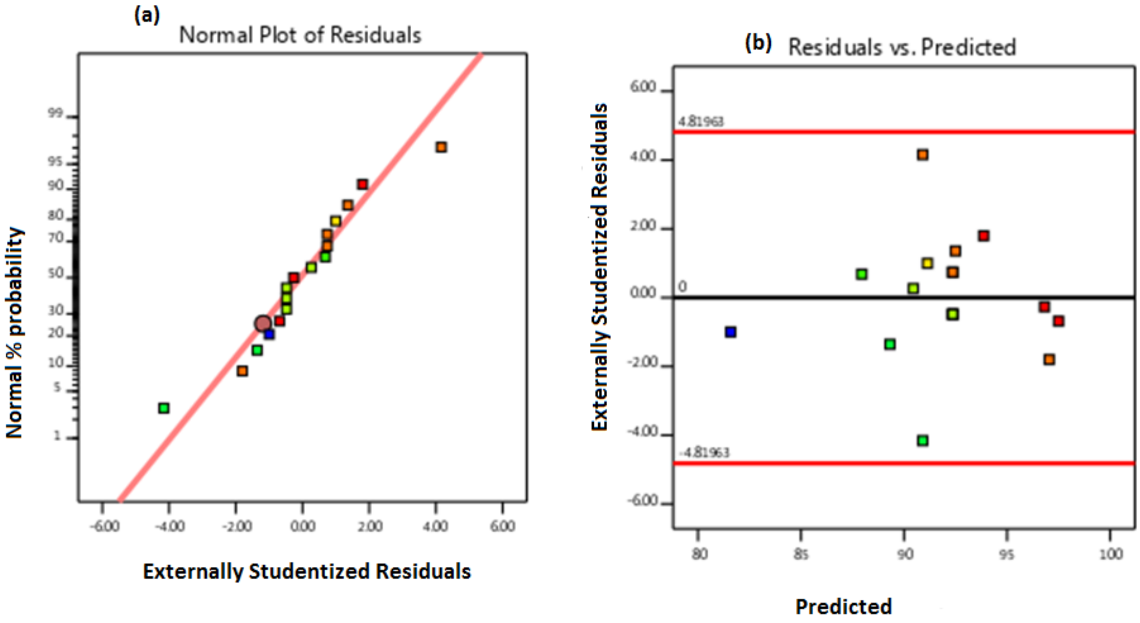


Figure 4.29:(a) Normality plot (b) residual verses predicted plot for %SOG removal using alum

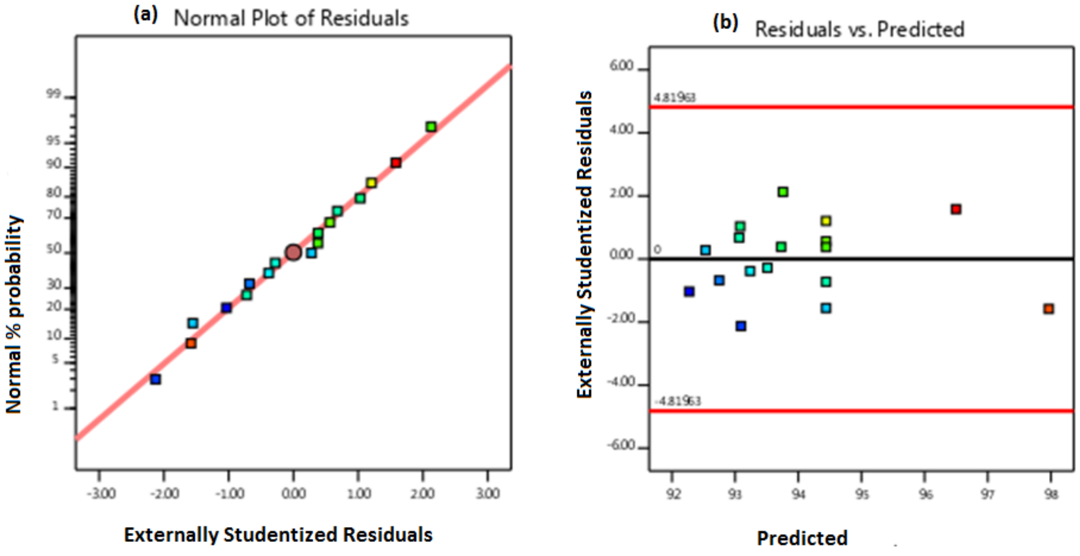


Figure 4.30 (a) Normality plot (b) residual verses predicted plot for %TSS removal using alum

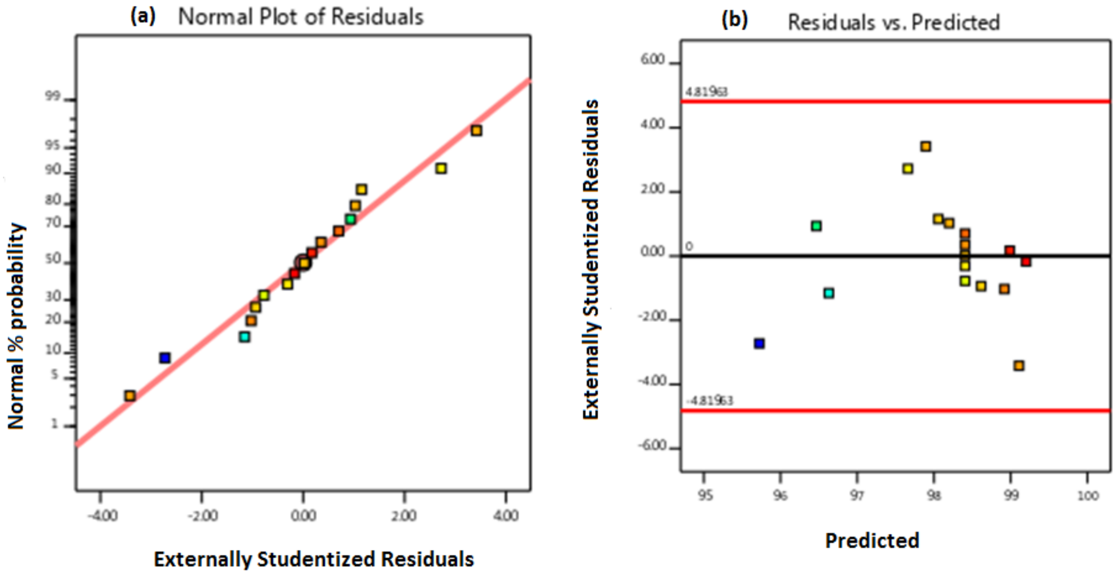


Figure 4.31 (a) Normality plot (b) residual verses predicted plot for %turbidity removal using alum

4.6.1.3 Optimisation

The numerical and graphical optimisation of the software was used to identify the specific points that maximise the response desirability function. The factors and responses desired goals were selected from five options; none, target, maximum, minimum, and within the range that might cause a change in the response goal. The process was then optimised within the ranges of the factors to maximise the responses. Among the solutions provided, the best five options were selected as depicted in Table 4-6. It was found that at desirability performance of 92% , at coagulant dosage of 100 mg/L , air saturator pressure of 350 kPa and air –water ratio of 10% ; the %COD and %SOG removal efficiency were 99% and 99% respectively. Likewise, the %TSS and %turbidity were 98% and 99% respectively. Therefore, the conditions for the option 1 was taken for experimental verification as shown in Figure 4.32. The experimental results were in good agreement with the models prediction, which affirms the application of the model within the designed space of the factors. The deviation between the predicted results and the experimental results was estimated to less than 2%.

Table 4-6 Optimisation solution results for the DAF process using alum

Number	C-dosage (mg/L)	Pressure (kPa)	Air-water ratio (%)	COD (%)	SOG (%)	Turbidity (%)	TSS (%)	Desirability (%)
1	100	350	10	99	92	99	98	92%
2	100	375	9	99	91	99	98	92%
3	190	450	11	95	93	99	96	91%
4	186	500	11	95	93	99	96	91%
5	176	500	10	95	93	99	96	91%

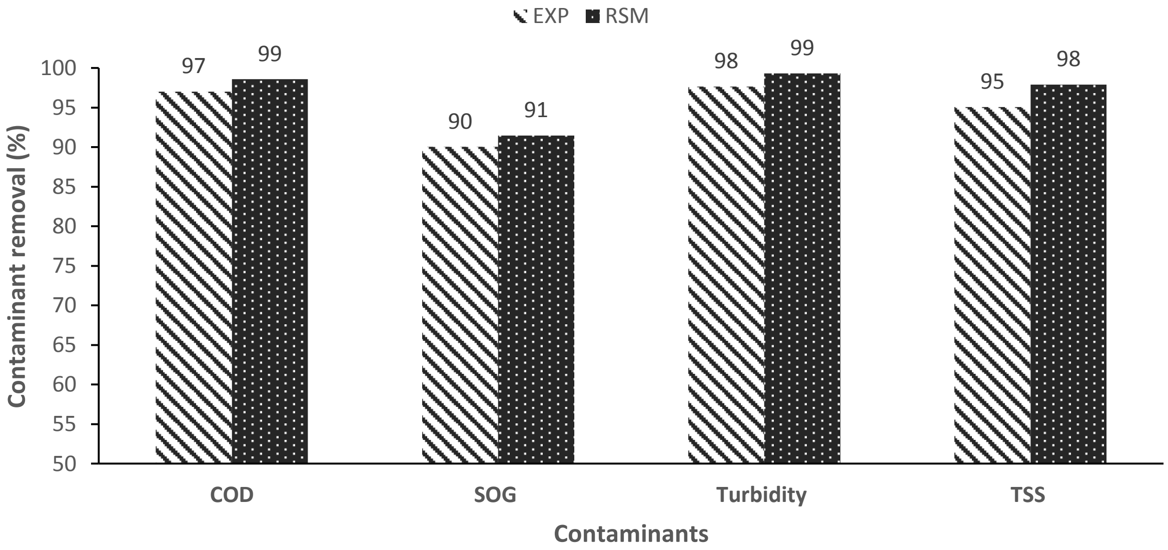


Figure 4.32 Comparation of the response predicted values verses the experimental results at pH 5, alum dosage of 100 mg/L, air saturator pressure of 350 kPa and constant air-water ratio of 10%.

4.6.1.4 3D representation of the effects on response

The graphical representation of the effects of the factors on individual responses are illustrated in 3D and contour plots in Figure 4.33 to Figure 4.36 with respect to each response regression models. The most sensitive factors identified were the coagulant dosage and air saturator pressure. This phenomenon increases the oil droplet density by attaching to the micro bubbles, which increases the floatability of the contaminants, such that the amount of coagulant dosage increased the charge neutralisation and the oil droplet flocs for the removal of the contaminants. While the air saturator pressure enhanced the rate of bubble generation for the floatability. Beside, a higher air saturator pressure has the tendency of breaking of the oil droplets flocs, which might result in the reduction of the contaminant removal (Al-Shamrani et al. 2002; Khuntia et al. 2012).

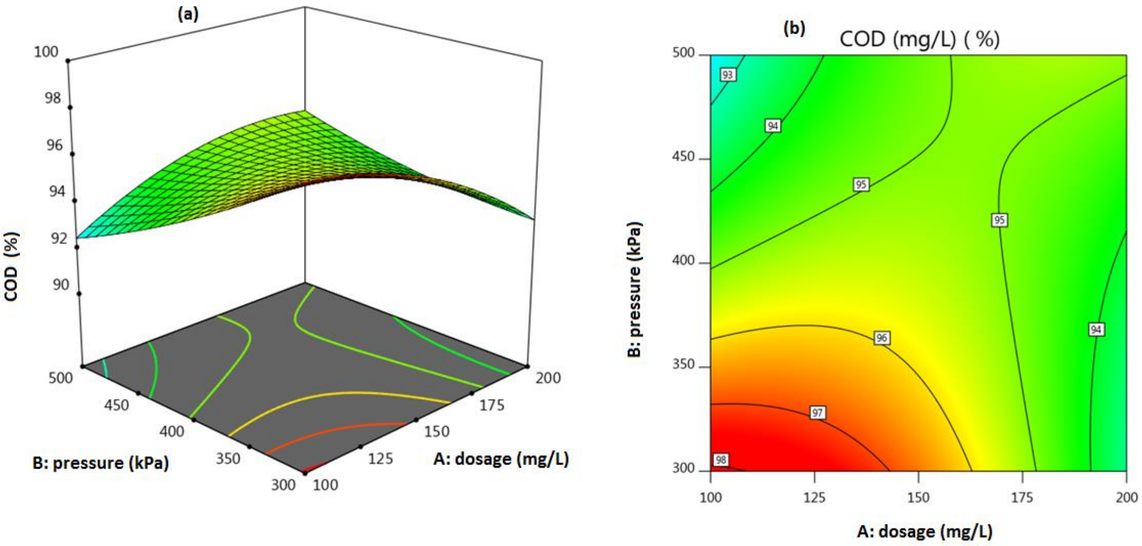


Figure 4.33 Effects of input factors on %COD removal; (a) 3D plot (b) contour plot using alum

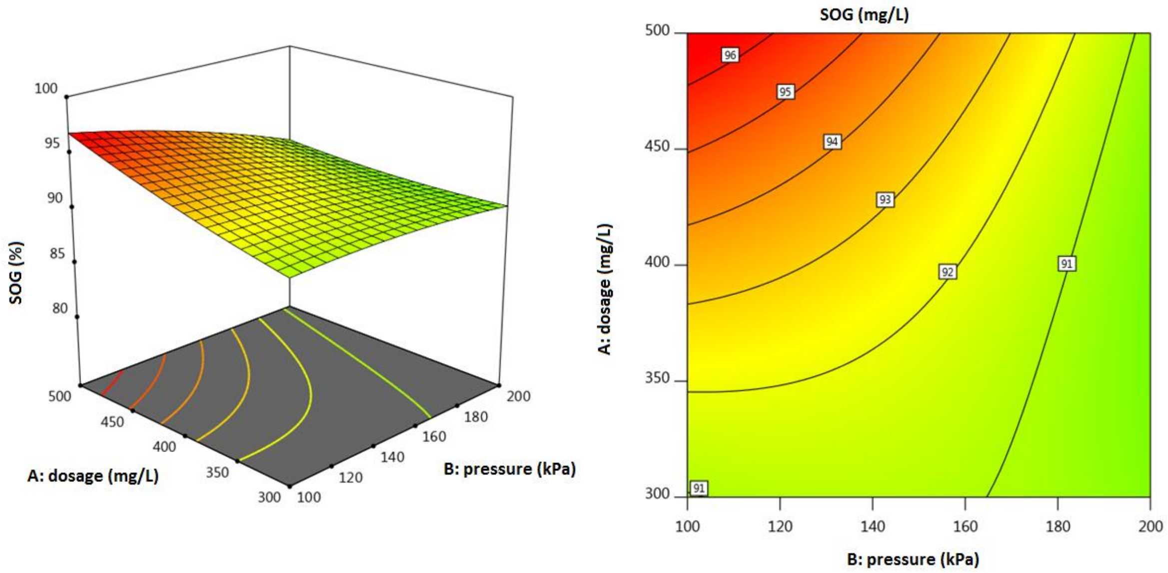


Figure 4.34 Effects of input factors on %SOG removal; (a) 3D plot (b) contour plot using alum

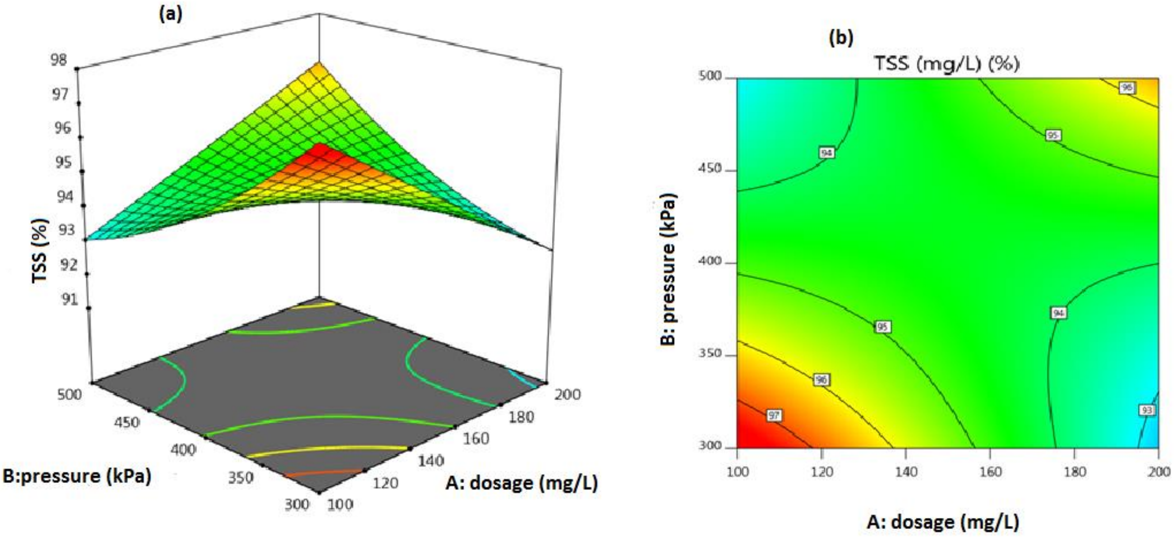


Figure 4.35 Effects of input factors on %TSS removal; (a) 3D plot (b) contour plot using alum

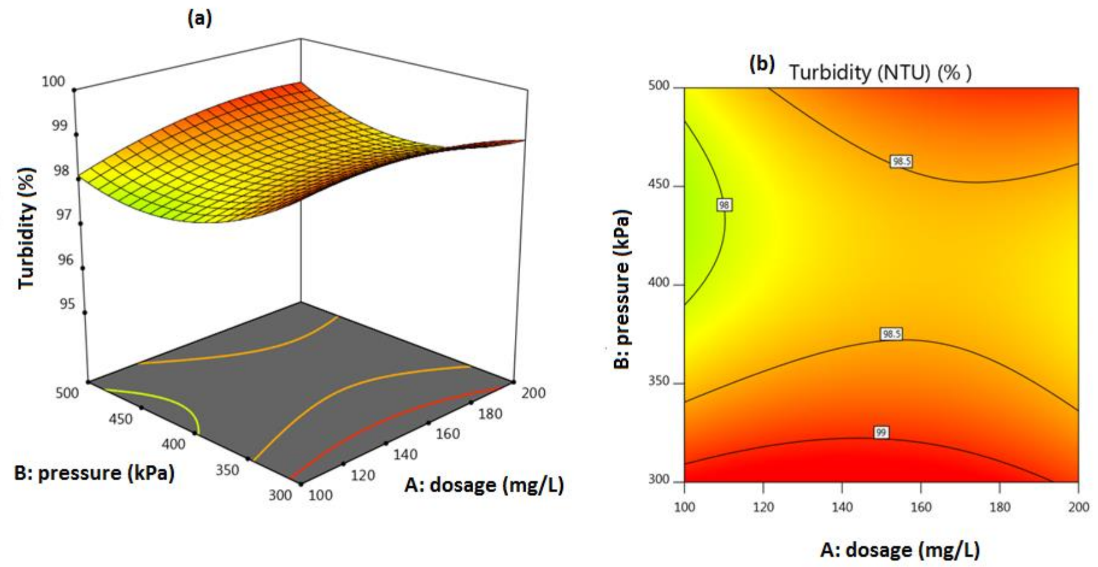


Figure 4.36 Effects of input factors on %turbidity removal; (a) 3D plot (b) contour plot using alum

Based on the 3D and the contour plots, the order of the key factors were identified. Such that for %COD removal was coagulant dosage > interaction between coagulant dosage and air saturator pressure > interaction between coagulant dosage and air-water ratio. This was similar for %TSS and %turbidity removal. In terms of %SOG removal, the order of the most significant factors was the interaction between coagulant dosage and air-water ratio > interaction between coagulant dosage and air saturator pressure > coagulant dosage.

Although, high saturator pressure with moderate coagulant dosage increased the %SOG removal, this might increase the cost of production, due to high consumption rate of power and the compressed air to generate the bubbles by the air saturator. Therefore, to enhance the DAF mechanism; the air-water ratio must be kept constant at 10%, at moderate air saturator pressure of 300-375 kPa and alum dosage of 100-160 mg/L.

4.6.2 Effects of coagulant dosage-air saturator pressure –air to water ratio using Zetag32-FS/A50 on MOW treatment

With the design matrix being used to investigate the performance of alum, the same was also used for the investigation of Zetag32-FS/A50. The results obtained were then fitted on a second –order polynomial function to represent each response. Table 4-7 shows the responses from the input factors with the models predicted results.

Table 4-7 BBD matrix and respective response actual and predicted results using Zetag32-FS/A50

Runs	**A- Coagulant dosage (mg/L)**	**B- Pressure (kPa)**	**C- Air/Water ratio (%)**	**Y_1- COD (%) removal**		**Y_2- SOG (%) removal**		**Y_3-TSS (%) removal**		**Y_4- turbidity (%) removal**	
				Exp	**Pred**	**Exp**	**Pred**	**Exp**	**Pred**	**Exp**	**Pred**
1	150	400	10	93	94	93	88	93	94	99	98
2	150	400	10	91	94	91	88	94	94	98	98
3	150	300	15	89	92	85	84	93	95	98	99
4	100	500	10	95	96	82	86	96	95	99	98
5	200	400	5	91	91	93	93	92	92	98	98
6	150	400	10	92	94	80	83	91	93	98	98
7	150	500	15	96	94	84	85	97	95	99	99
8	200	500	10	97	94	85	88	95	94	98	98
9	100	400	15	92	92	89	93	93	93	98	98
10	150	400	10	97	95	87	88	97	95	99	99
11	200	400	15	93	93	95	90	93	93	98	98
12	100	300	10	95	95	93	88	95	95	98	98
13	100	400	5	97	94	82	88	95	94	98	98
14	200	300	10	89	89	85	85	92	92	98	98
15	150	500	5	91	94	89	88	93	94	98	98
16	150	300	5	95	98	91	90	94	95	98	98
17	150	400	10	96	94	87	84	94	93	98	98

*Exp-experimental values *Pred-model predicted values

The results of the fitted models for the four responses (Y_1- COD; Y_2-SOG; Y_3-TSS; Y_4-turbidity), comprises of the sum of the constants, three linear effects (A, B, C), three quadratic effects (A^2, B^2, C^2), and three interaction effect (AB, AC, BC) terms. These terms are the coded form of the factors within the designed spaced, which are expressed in equations (4.6) to (4.9).

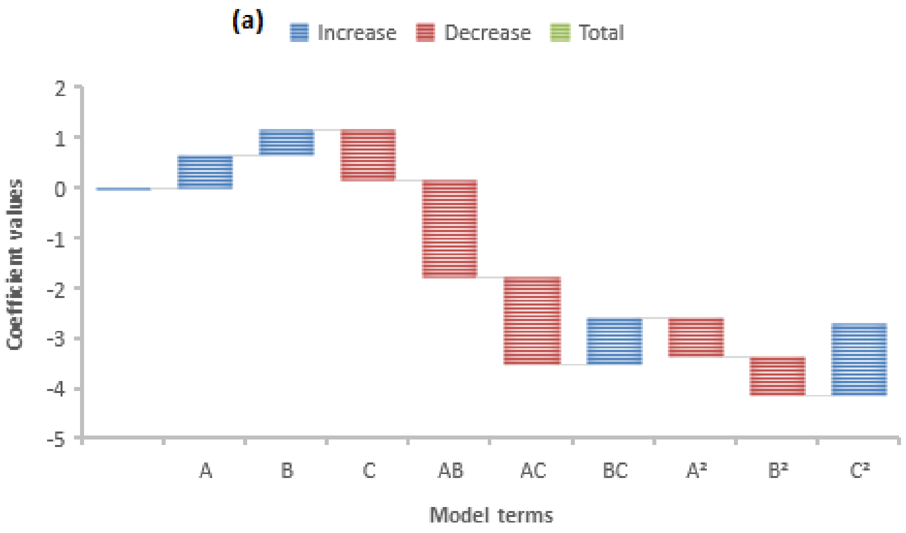
$$Y_1 = 93.56 + 0.649A + 0.51B - 0.98\mathrm{C} - 1.95\mathrm{AB} - 1.75AC + 0.924BC - 0.776A^2 - 0.75B^2 + 1.4C^2 \tag{4.6}$$

$$Y_2 = 88 + 2.05A + 159B - 0.455\mathrm{C} + 2.77\mathrm{AB} + 2.23AC + 0.455BC + 0.595A^2 - 0.218B^2 + C^2 \tag{4.7}$$

$$Y_3 = 93.77 - 0.014A + 0.043B - 0.144\mathrm{C} - 0.379\mathrm{AB} - 1.1AC + 0.115BC - 1.23A^2 - 0.129B^2 + 1.51C^2 \tag{4.8}$$

$$Y_4 = 98.23 - 0.1A - 0.049B + 0.042\mathrm{C} - 0.028\mathrm{AB} - 0.268AC - 0.127BC - 0.158A^2 + 0.096B^2 + 0.252C^2 \tag{4.9}$$

The effects of the individual terms on the response were defined based on the coefficients of the terms in the individual equations. It was found that the positive coefficient terms might increase the rate of contaminant removal, while the negative terms might decrease the contaminant removal. The most significant interactional effects was found between the coagulant dosage and air saturator pressure, and was explained based on COD and SOG removal as depicted in Figure 4.37. The order of the factors to increase the %COD removal was found to be the interaction between BC > AC > AB. In terms of %SOG removal, there is a reverse of the interaction factor order found in %COD removal which was observed such that AB > AC > BC. For %TSS removal the order is the C^2 > AB > AC. While the %turbidity removal is the C^2 > B^2 > BC > AB.



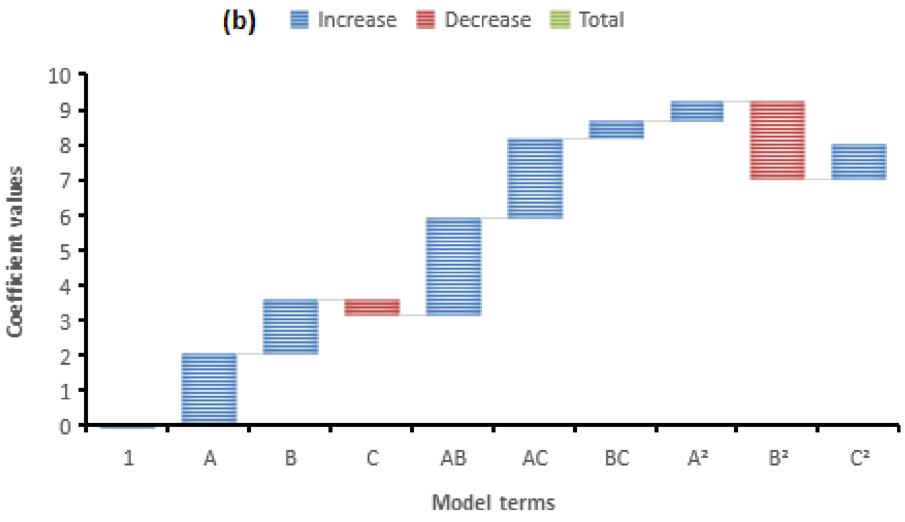


Figure 4.37 Parreto chart, effects of input parameters; Zetag32-FS/A50 dosage (A), air saturator pressure (B) and air-water ratio (C) and their interaction on the response; (a) %COD and (b) %SOG removal

4.6.2.1 Analysis of variance (ANOVA) for models validation

The ANOVA was used to evaluate the quality of the response models. The probability values (P-values) of the models were found to be less than 0.05, while some of the individual terms were strongly (p-values < 0.05) and partially (0.05 < P-values < 0.1) significant.

Tables 4-8 to 4-11, shows the regression coefficient of determination R^2, adjusted R^2, and predicted R^2. However, the values of R^2 were higher than the adjusted R^2, such that the closer the R^2 values to 1, the better the model correlated with the experimental data. The adep precision, which is the measure of the signal to noise ratio, was acceptable for being less than 4. These ratios were 3.64 for COD, 2.65 for SOG, 2.44 for TSS and 3.378 for turbidity.

Table 4-8 ANOVA for %COD removal using Zetag32-FS/A50

Source	**Sum of squares**	**df**	**Mean square**	**F-value**	**P-value Prob>F**	**Comments**
COD-Model	56.62	9	6.29	0.656	< 0.0001	significant
A-C-dosage	3.37	1	3.37	0.3515	0.057	
B-Pressure	2.09	1	2.09	0.2179	0.0654	
C-Air-water ratio	7.69	1	7.69	0.8022	0.04	
AB	15.17	1	15.17	1.58	0.0488	
AC	12.31	1	12.31	1.28	0.0946	
BC	3.43	1	3.43	0.3572	0.0689	
A^2	2.55	1	2.55	0.2655	0.6222	
B^2	2.37	1	2.37	0.247	0.6342	
C^2	8.31	1	8.31	0.8663	0.3832	
Residual	67.13	7	9.59			
Lack of Fit	30.95	3	10.32	1.14	0.434	not significant
Pure Error	36.19	4	9.05			
Cor Total	123.76	16				
Std. Dev. 3.1	**R^2 0.9945**	**Adjusted R^2 0.9823**	**Predicted R^2 0.9772**	**Adeq Precision 3.64**	**Mean 93.5**	**C.V. % 3.31**

Table 4-9 ANOVA for %SOG removal using Zetag32-FS/A50

Source	**Sum of squares**	**df**	**Mean square**	**F-value**	**P-value Prob>F**	**Comments**
SOG-Model	130.94	9	14.55	0.5764	< 0.0001	significant
A-C-dosage	33.47	1	33.47	1.33	0.0873	
B-Pressure	20.25	1	20.25	0.8022	0.002	
C-Air-water ratio	1.65	1	1.65	0.0655	0.0154	
AB	29.75	1	29.75	1.18	0.0136	
AC	20.66	1	20.66	0.8185	0.0957	
BC	0.8264	1	0.8264	0.0327	0.0861	
A^2	1.25	1	1.25	0.0496	0.483	
B^2	20.04	1	20.04	0.7941	0.125	
C^2	4.21	1	4.21	0.1668	0.695	
Residual	176.69	7	25.24			
Lack of Fit	100	3	33.33	1.74	0.297	not significant
Pure Error	76.69	4	19.17			
Cor Total	307.63	16				
Std. Dev. 5.02	**R^2 0.9956**	**Adjusted R^2 0.9831**	**Predicted R^2 0.959**	**Adeq Precision 2.65**	**Mean 87.7**	**C.V. % 5.73**

Table 4-10 ANOVA for %TSS removal using Zetag32-FS/A50

Source	**Sum of squares**	**df**	**Mean square**	**F-value**	**P-value Prob>F**	**Comments**
TSS-Model	20.85	9	2.32	0.7235	< 0.0001	significant
A-C-dosage	0.0017	1	0.0017	0.0005	0.0982	
B-Pressure	0.015	1	0.015	0.0047	0.0947	
C-Air-water ratio	0.1663	1	0.1663	0.0519	0.0826	
AB	0.5621	1	0.5621	0.1755	0.0687	
AC	4.8	1	4.8	1.5	0.026	
BC	0.0532	1	0.0532	0.0166	0.0901	
A^2	6.32	1	6.32	1.97	0.2027	
B^2	0.0709	1	0.0709	0.0221	0.885	
C^2	9.65	1	9.65	3.01	0.1261	
Residual	22.41	7	3.2			
Lack of Fit	19.11	3	6.37	7.72	0.386	not significant
Pure Error	3.3	4	0.8248			
Cor Total	43.26	16				
Std. Dev. 1.79	**R^2 0.9819**	**Adjusted R^2 0.9486**	**Predicted R^2 0.9188**	**Adeq Precision 2.4478**	**Mean 93.85**	**C.V. % 1.91**

Table 4-11 ANOVA for %turbidity removal using Zetag32-FS/A50

Source	**Sum of squares**	**df**	**Mean square**	**F-value**	**P-value Prob>F**	**Comments**
Turbidity-Model	0.8783	9	0.0976	0.9928	< 0.0001	significant
A-C-dosage	0.0898	1	0.0898	0.9138	0.0371	
B-Pressure	0.0196	1	0.0196	0.199	0.0669	
C-Air-water ratio	0.0144	1	0.0144	0.1462	0.0713	
AB	0.0032	1	0.0032	0.0325	0.0862	
AC	0.2882	1	0.2882	2.93	0.0306	
BC	0.0647	1	0.0647	0.6579	0.0444	
A^2	0.1054	1	0.1054	1.07	0.3341	
B^2	0.0389	1	0.0389	0.395	0.5492	
C^2	0.2663	1	0.2663	2.71	0.143	
Residual	0.6881	7	0.0983			
Lack of Fit	0.4288	3	0.1429	2.2	0.2301	not significant
Pure Error	0.2593	4	0.0648			
Cor Total	1.57	16				
Std. Dev. 3.13	**R^2 0.9345**	**Adjusted R^2 0.8823**	**Predicted R^2 0.8683**	**Adeq Precision 3.378**	**Mean 98.31**	**C.V. % 3.89**

Figure 4.38 shows good correlation plot of the predicted and experimental values, whereby the data points are evenly distributed around the straight line. Hence, the response models were a good reflection of the experimental within the design space.

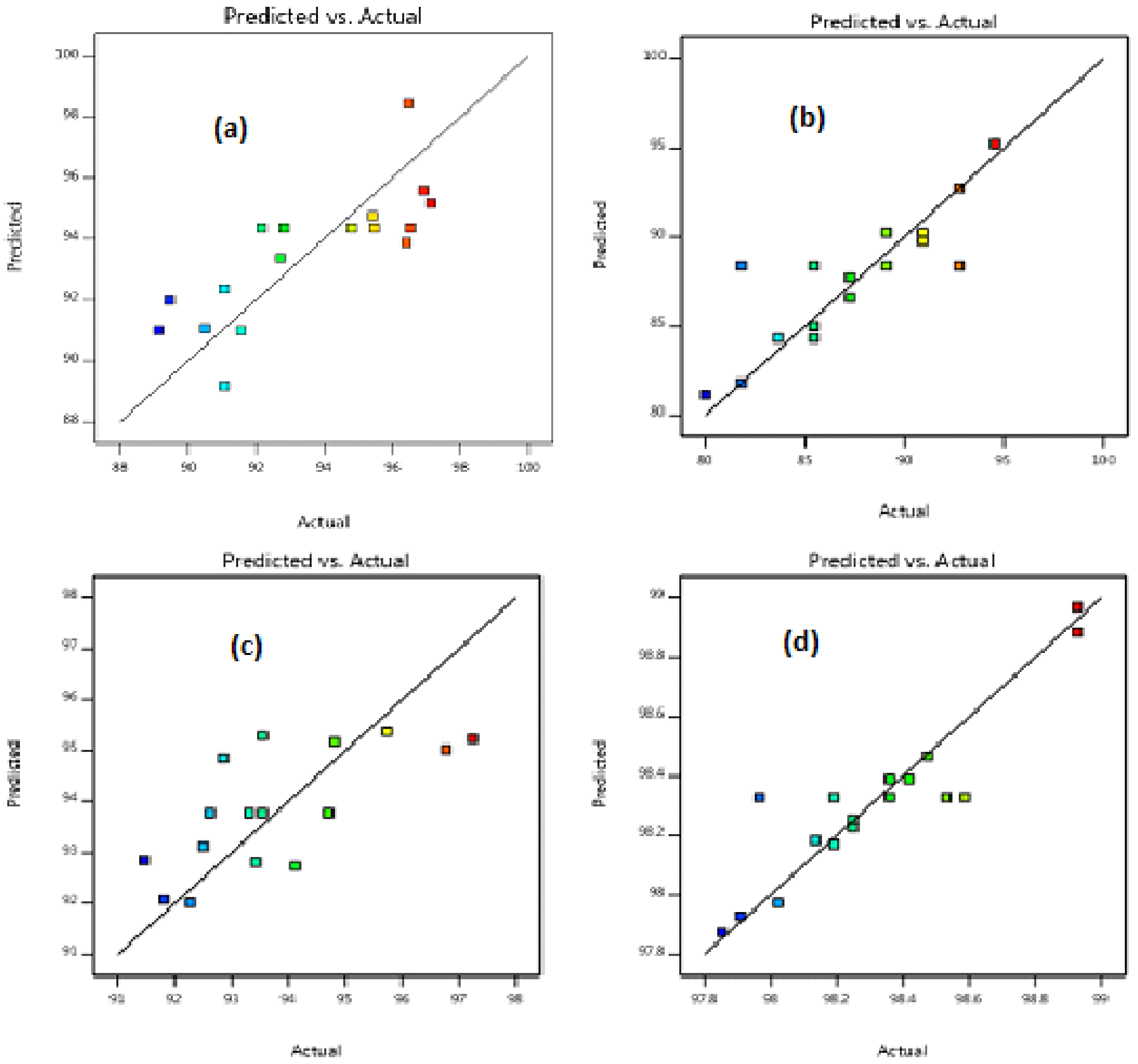


Figure 4.38 Predicted versus actual plots (a)%COD ,(b) %SOG ,(c)%TSS and (d)%turbidity removal using Zetag32-FS/A50

4.6.2.2 Residuals plots on response

The residual plots were also analysed to determine the quality of the models by assessing the difference between the predicted values and the fitted results. Figures 4.39 to 4.42, shows the normality plots and the residual versus the predicted plots. All the patterns in the normality plots were correlated to a straight line, the residual verses the predicted graphs shows that the data points were within the confined zone, which validates the adequacy of the models.

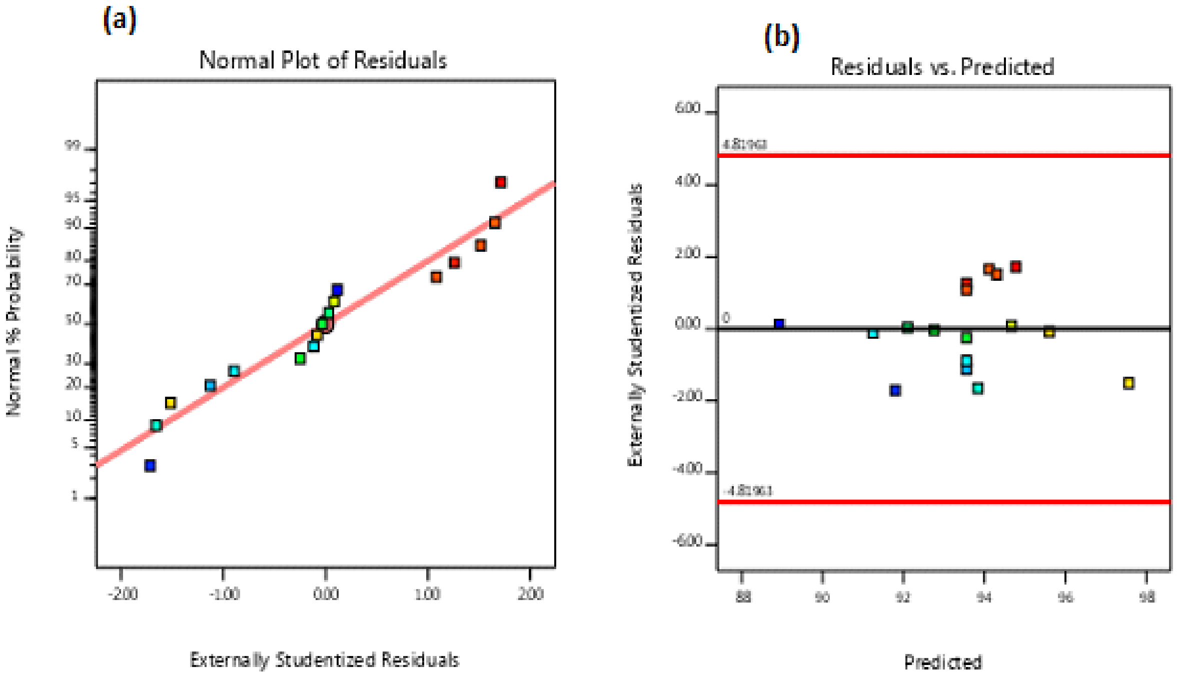


Figure 4.39 (a) Normality plot (b) residual versus the predicted plot for %COD removal using Zetag32-FS/A50

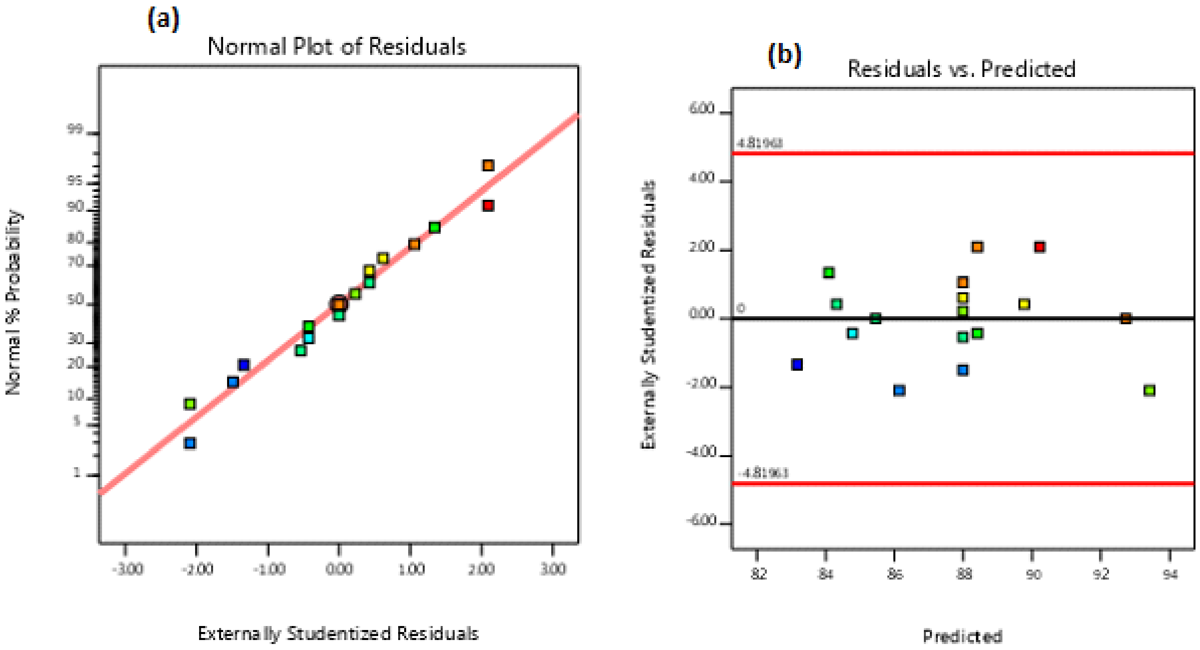


Figure 4.40 (a) Normality plot (b) residual versus the predicted plot for %SOG removal using Zetag32-FS/A50

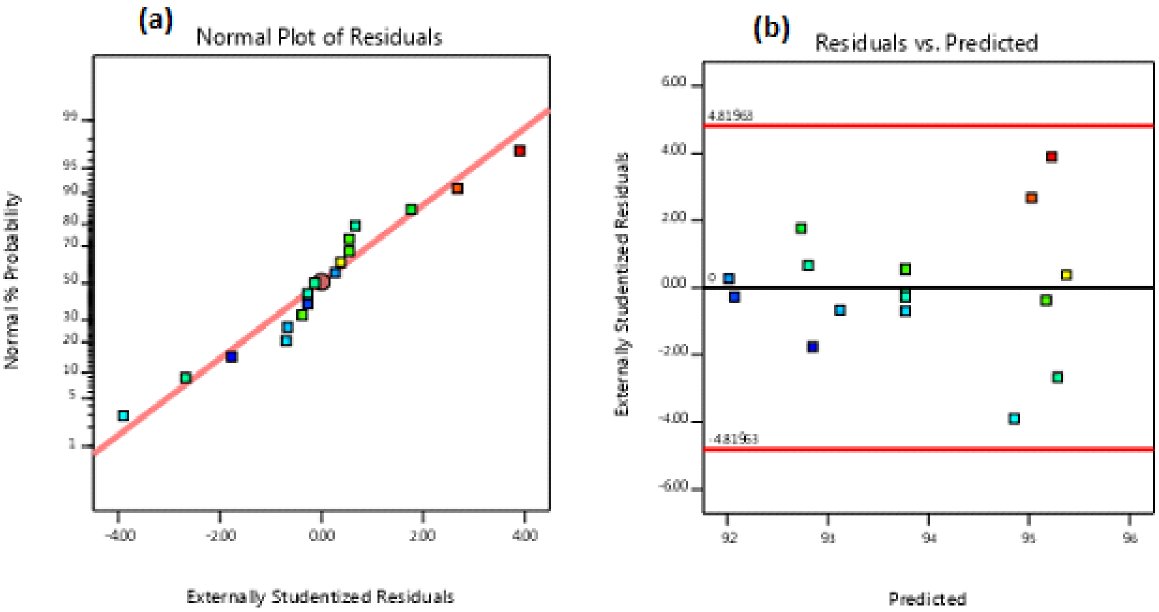


Figure 4.41 (a) Normality plot (b) residual versus the predicted plot for %TSS removal using Zetag32-FS/A5

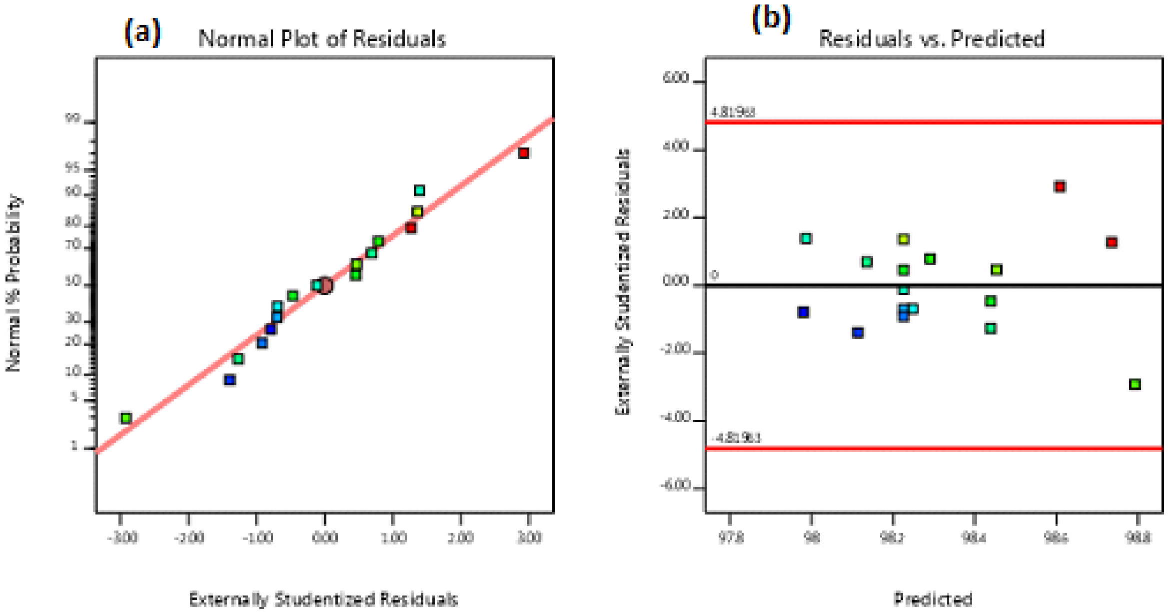


Figure 4.42 (a) Normality plot (b) residual versus the predicted plot for %turbidity removal using Zetag32-FS/A50

4.6.2.3 Optimisation

The numerical and graphical optimisation of the software was used to identify the specific points that maximise the response desirability function. Table 4-12 shows the solutions of the predicted model at different operating conditions within the design space. The first option was recommended as the optimum condition, because it shows high efficiency for the removal of 95% COD, 93% SOG, 99% TSS and 95% turbidity at a coagulant dosage of 100 mg/L, air saturator pressure of 350 kPa and constant air-water ratio of 10%. Experiment were then conducted using those conditions, which were in agreement with the predicted results with a deviation of less than 2% as shown in Figure 4.43.

Table 4-12 Optimised solution results for the DAF treatment option using Zetag32-FS/A50

Number	Coagulant dosage (mg/L)	Pressure (kPa)	Air-water ratio (%)	COD (%)	SOG (%)	Turbidity (%)	TSS (%)	Desirability (%)
1	100	350	10	95	93	99	95	93%
2	130	380	5	97	90	98	96	92%
3	135	440	12	95	87	99	95	91%
4	140	390	12	94	88	99	95	91%
5	145	450	5	96	90	99	96	91%

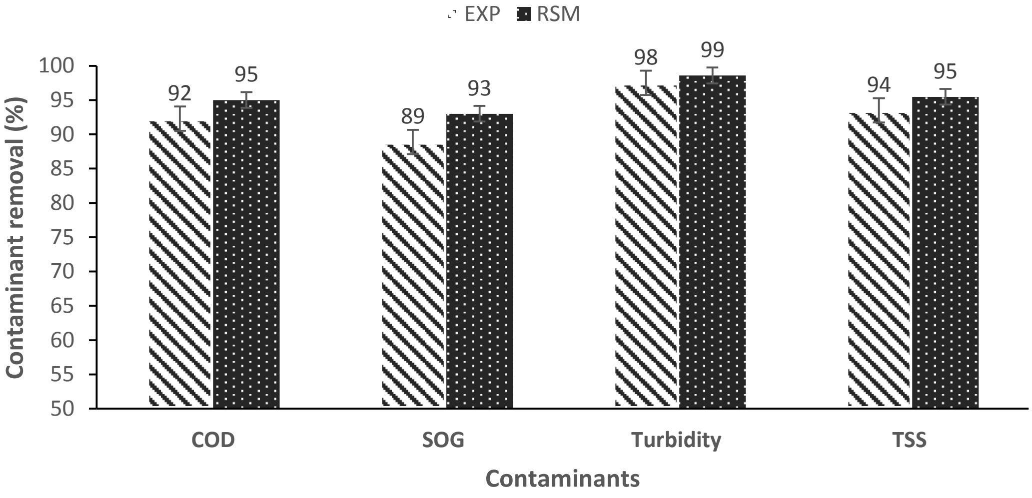


Figure 4.43 Comparison of the response predicted values verses the experimental results at pH of 5, Zetag32-FS/A50 dosage of 130 mg/L, air saturator pressure of 350 kPa and a constant air-water ratio of 10%.

4.6.2.4 3D representation of effects on response

The counter interaction effects of the coagulant dosage and the air saturator pressure were found to be the most significant factors. These input factors are presented as a response surface to visualise the relationship that exists between the input factors and the responses in both 3D and contour plots as shown in Figures 4.44 to 4.47. It was found that increasing the coagulant dosage (100 –180 mg/L) increased the oil droplet surface charge area, which required a moderate air saturator pressure (300–400 kPa) to enhance the bubble flux at a constant air-water ratio (10%). Besides, the probability of the air bubble-oil droplet flocs attachment depends on the amount of the microbubbles generated by the air-water ratio. This increased the contaminant removal (80–98%).

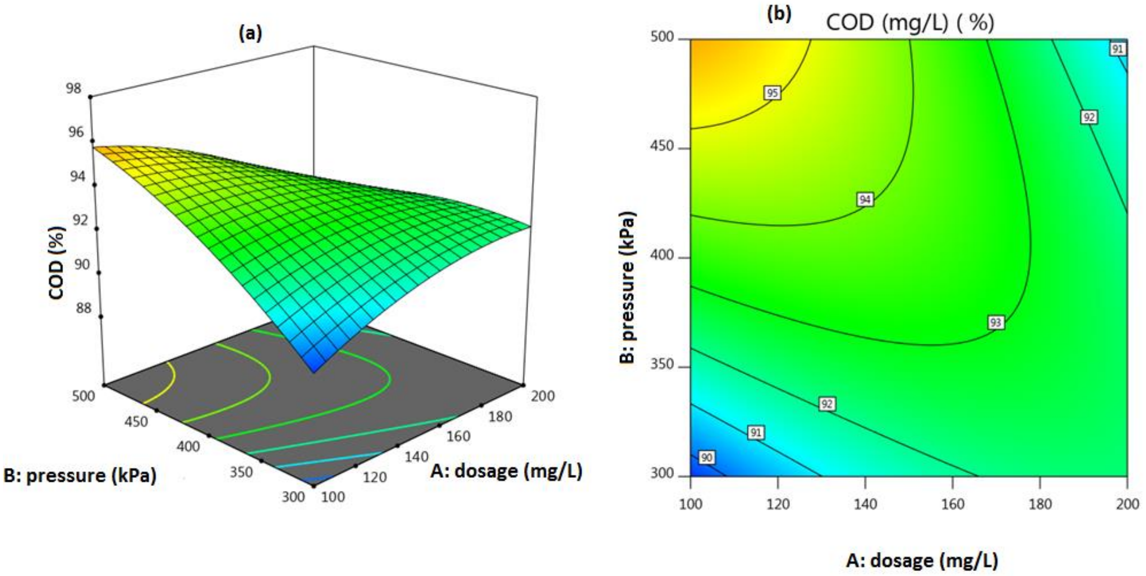


Figure 4.44 Effects of input factors on %COD removal; (a) 3D plot (b) contour plot using Zetag32-FS/A50

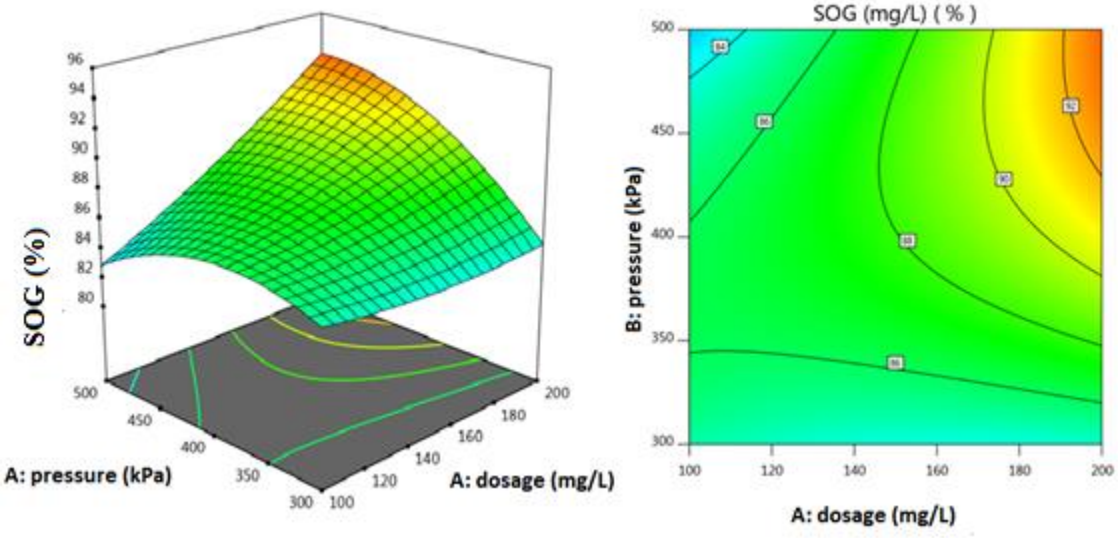


Figure 4.45 Effects of input factors on %SOG removal; (a) 3D plot (b) contour plot using Zetag32-FS/A50

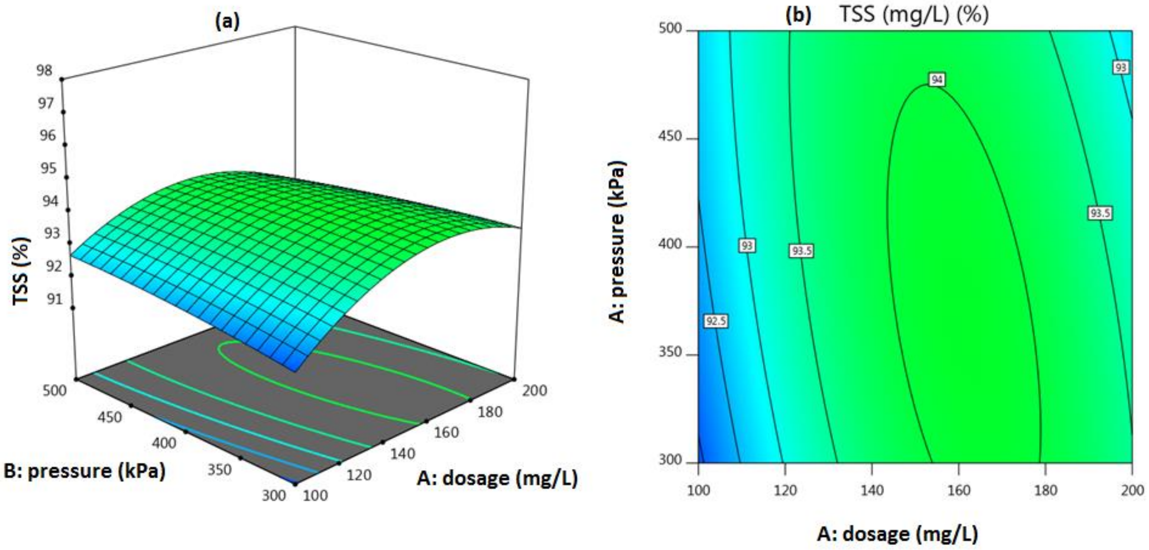


Figure 4.46 Effects of input factors on %TSS removal; (a) 3D plot (b) contour plot using a Zetag32-FS/A50

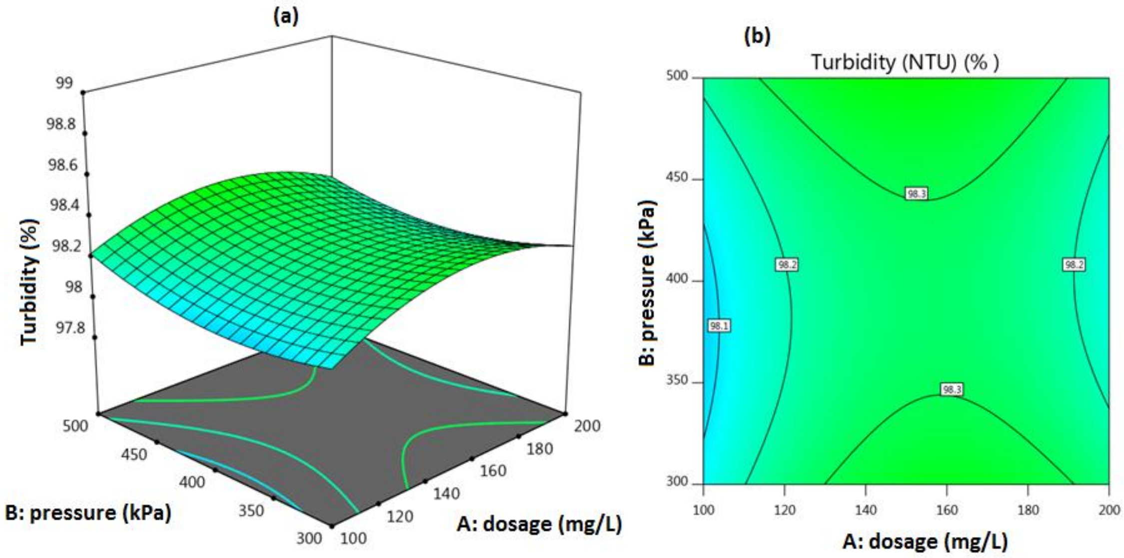


Figure 4.47 Effects of input factors on %turbidity removal; (a) 3D plot (b) contour plot using Zetag32-FS/A50

4.6.3 Summary

The optimisation of the DAF pilot plant using RSM was found to be economically feasible, with lesser number of experimental runs (in terms of chemical usage). To enhance the oil-water separation under the acidic medium by the use of the DAF showed that increasing the coagulant dosage increased the oil droplet charge surface area, while the moderate air saturator pressure enhanced the air bubbles flux. Thus, the mechanism of the coagulant dosage-air saturator pressure at constant air-water ratio increases the probability of the large oil droplet flocs, bubble–oil droplet floc attachment and floatability of the flocs to enhance the DAF carrier phase separation.

For the use of alum, the optimum condition was found to be 100 mg/L for the coagulant dosage, 350 kPa for air saturator pressure within an air-water ratio of 10%, and this was obtained at 92% desirability performance. While when using the Zetag32-FS/A5, a 93% desirability performance was obtained at that same conditions. The response performance for the alum were 99% removal for COD, SOG, and turbidity, while 98% removal for TSS. In terms of the Zetag32-FS/A50, 95% removal was obtained for COD and turbidity, while 93% was achieved for SOG and TSS. Although the Zetag32-FS/A50 is cost effective, it might be considered along with the alum, since both are effective in the treatment of the MOW by taking into account the optimised conditions, where both were able to achieve treatability performance of above 90% for the treatment of the MOW.

CHAPTER 5 - CONCLUSION AND RECOMMENDATION

This chapter summaries the significant findings from the research and gives a recommendation for further research and decision-making. The optimisation of the DAF operating parameters were done by OFAT and RSM data-driven approach on a batch and continuous DAF process, using industrial wastewater from a local South African oil refinery wastewater treatment plant (WWTP).

5.1 Conclusion

The following findings were drawn from the study, based on the observation from the experimental results, modelling and optimisation techniques.

- With the characterised MOW quality, Acid ─ Coagulation ─ DAF configuration under optimised conditions, represented the most suitable application of cost effective pre-treatment knowledge of DAF for the separation of the oil from water.

- Among the three acids investigated at the same concentration (1M), the phosphoric acid was identified as the most effective, economical and environmentally friendly. The decrease in the order of effectiveness is phosphoric acid < sulphuric acid < hydrochloric acid within a pH of 4 to 6.

- The chemical comparison based on the coagulant budget cost and dosage indicated that the superlative cationic inorganic coagulants (alum and ferric chloride) were more cost effective than the polymeric organic coagulants (Z553D-PAC and Zetag32-FS/A50), where alum emerged as the most effective and economic coagulant. However, overdose or under dose of the coagulant can lead to oil droplet surface charge being reversed, which then can decrease the coagulant potency resulting in low contaminant removal.

- An increase in air saturator pressure, pH and flotation time in both the OFAT and RSM approach had no significant effects on the DAF efficiency. However, the coagulant dosage and air-water ratio at a moderate pressure increased the DAF performance. Thus, the micro bubbles depends on the air-water ratio generated, which is directly proportional to the air saturator vessel pressure released. The increase in the coagulant dosage increased the agglomeration of the contaminant to be removed at the waste stream by the DAF.

- Both the OFAT and RSM approaches identified the most sensitive interactive factors as the chemical changes (pH, coagulant type and dosage) and the micro bubble generation (air saturator pressure). Having identified the key interactive factors with the same operating conditions viz coagulant dosage of 100 mg/L, air saturator pressure of 350 kPa and air-water ratio of 10%, the RSM then suggested that alum (92%) and Zetag32-FS/A50 (93%), have almost the same desirability performance for the treatment of MOW.

- Finally, the BBD adapted from the RSM was successfully employed in optimising the DAF, due to its ability to incorporate multiple interaction factors in the experimental design, modelling and optimisation, and analysis of the results. It has been established that there exists a good correlation between the input variables and the responses. Thus, the optimum condition experimental results were in good agreement with the response model predicted results.

Therefore, in concluding remarks, employing RSM in an integrated Acid ─ Coagulation ─ DAF configuration process optimisation in the oil refinery wastewater treatment is economically viable, even if there is variation in the influent composition. Thus, accurate predicted models might result in saving the cost of production.

5.2 Recommendation

The following recommendations were made based on the research findings and the feasibility study of the WWTP;

- Future research must focus on the proposed DAF configuration being implemented in the WWTP framework. That is, in a way transferring the knowledge obtained from the research to the large-scale treatment plant. This requires a platform to collect the operating conditions together with the influent and effluent data information, and reprocess with a modelling background. Then, in real time, give the response in both graphical and texted values to assist the process engineer and plant operator in decision making to optimally manage the plant.

- Future studies must also focus on generating virtual sensors with the data-driven approach, since installation of online sensors are costly and requires frequent maintenance. This can save production cost and provide inputs for high accurate predicting models database.

- The application of the superlative cationic inorganic coagulants are associated with environmental concern. Hence, in the future, attention must be given to the recovery of alum using Donnan membrane technology. Besides, further studies can be done using a blended form of the cationic inorganic coagulants and polymeric inorganic coagulants to replace the use of alum, apart from the Zetag32-FS/A50 for the treatment of the MOW.

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Appendix A: DAF jar test and DAF pilot plant checklist

A1: Modified Jar tester protocols for DAF

Introduction

The central concept of velocity gradient, for the simulation of coagulation and flocculation processes in a bench scale (beaker), is a widely accepted technique. In the waterworks, Jar tests are usually done to predict clarification performance. A properly designed and performed set of jar tests can give an operator a fair idea about the correct coagulant type and dose for developing the optimum floc size. The size and strength of the floc-developed help determines the efficiency of the coagulant for the removal of the coagulant. The sensitivity of the coagulants to physical and chemical conditions of the MOW quality, mixing conditions, coagulant chemistry and dosage rate, concerning the floc size, can easily be observed.

Scope

The main objective of the DAF jar test trials was to identify two sets of operating conditions, such as coagulation and flocculation conditions, and coagulation-DAF operating conditions to optimise the DAF pilot plant. To enhance efficiency of the DAF pilot plant, a checklist (Table A-2) and onsite installation process flow diagram (Figure A-1) were respectively observed. In addition to determining the optimum dosage range of different inorganic and polymeric organic coagulants for their primary use by comparing their performance in terms of the water qualities (TSS, COD, SOG and turbidity).

Interferences

Interferences are caused by the changes in the MOW conditions, such as temperature, pH, and the plant design and the mixing intensities.

Hazards

The air saturator must have a pressure test certificate for a working pressure of 600 kPa, which is valid within 26 months. There was an awareness of the dangers and treatment associated with the coagulants and the air saturator pressures.

Samples collection

Samples collected from the effluent plant using 25 L drums, were mixed thoroughly before each trial to have a homogeneous sample. Also, samples for analysis were collected with 0.5 L sample bottles.

Apparatus

- The DAF jar tester (Model DBT6, EC Engineering, Edmonton, Alberta, Canada) (Figure 3.2)
- Syringes (100 ml)
- Pipettes
- 500 ml beakers
- 500 mL conical flasks
- 1 L sample bottle of stock solutions

Reagents

Available inorganic and polymeric organic coagulants, 1.0 M NaOH, acids (1.0 M H_3PO_4, 1.0 M HCl, and 1.0 M H_2SO_4

Analytical procedure

The sample obtained must be characterised to know the amount of water quality, before any addition of chemicals using the appropriate analytical method.

The DAF Jar tests trials

i. Fill the air saturator with raw and cleared water until is two-thirds full. Connect the air supply –compressor to the IN position by pushing down and then releasing the ring. Then connect the full water feed for the Jar tester to the OUT position on the saturator.

ii. Measure out 800 mL aliquots of the raw MOW into the 6 beakers on the DAF jar tester and number them accordingly.

iii. Switch on the air supply, as the pressure rises the valve of the compressor must be set to the desired operating pressure. Shake the saturator vigorously for 30 seconds Allow to stand for 5-10 minutes, and re-shaking intermittently until the pressure does not fall. Thus, the water is saturated. Then purge the feed line from the saturator by activating the units start button.After completion of the purging, the compressor can be switched off.

iv. The mixers speed are set at the speed, which best simulates the conditions on the plant (this general between 100-300 rpm) and start the stirrer.

v. Introduce a chemical to adjust the pH of the MOW as desired. The chemical coagulant can be added simultaneously to all the beakers and the rapid mixing time can then be set. To ensure fairness in the dosage, a syringe is firstly filled to the desired dosage of each beaker dosage, before dosing at a short possible time.

vi. Depending on the chemistry of the water and unfamiliar, begin with a dosage range of 1 to 6 mg/L for polymeric organic coagulant or 5 to 60 mg/L for inorganic coagulants.

vii. After the introduction of the chemical coagulants, rapidly stir for 2 minutes.

viii. After the 2 minutes reduce the speed to 30 rpm for further 15 minutes, turn off the stirrer immediately to determine the optimum type of floc formed by using Table A-1

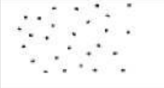
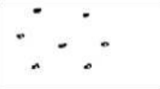
ix. The recycled water and the microbubbles of air are introduced to the base of the jars on activating the START bottom. Each beaker paddle is switched off, before and after the introduction of the recycle.

x. The air injection component was immediately pulled out, and the jar test was allowed to rest for the specific flotation time (10, 15, 20 minutes).

xi. Once the time has elapsed, 1L sample bottles were placed under the sampling port on each jar to collect a 500 ml sample.

xii. Allow flotation to occur within a specific period, before taking taken samples for further water quality quantification.

Table A-1: Types of flocs formed during flocculation (Umgeni, PEF)

A	B	C	D	E	F
					

A2: On-site installation and operational procedure

Beforehand the DAF pilot plant was moved from the Durban University of Technology, Steve Biko Campus to the local oil refinery effluent site by LovemoreBros Machinery SA, Durban, due to the availability of the effluent. From the feasibility study in Figure 2 9, the outlet of the API separator was identified to be the feed point for the pilot plant for the pre-coagulation before the DAF studies.

At this point, the air saturator line was connected to an airline instead of a compressor. Also, looking at Figure A1 , the equal capacity of influent (produced water feed) flowrate was pumped to the mixing zone, where the coagulant was added as required, and then to the flocculation zone. From the flocculation zone, the MOW is overflowed to the flotation zone. The purified effluent is discharged into the bottom of the flotation tank and delivered onto an outlet collection basin attached to the DAF. Microscopic air bubbles are formed when dissolved air was injected into the flotation tank to carry the flocs to the surface.

The oil droplet forms a sludge layer on the surface, which is then scrapped intermittently to the residual oil zone. The drain valves are opened to empty the flotation tank and other compartment zones. The setting of the operating parameters was guided by the feasibility study and the DAF jar tester experience, and theoretical values (Edzwald, 1995; Al-Shamrani et al., 2002) as shown in Table 3 5.

Table A2 : Checklist for troubleshooting the DAF pilot plant

Category	**Parameter**	**Remarks**
Air saturator and DAF	Is there enough clean water in the header water tank?	
	What is the pressure, and is it high?	
	Also, is there enough air entering the system?	
	The air-water recycle rate it enough.	
	Is there proper flotation occurring with saturated air?	
	Has there been desludging and cleaning of the system?	
	Is there leakage on the pipelines?	
	Are the right valves opened and the rest closed as required?	
	Drain off the liquid in the air saturator after shutting it off.	
Chemical addition	Is the coagulant concentration well prepared?	
	Is the coagulant dosing pump working correctly with consistency?	
	Is there proper mixing and flocculation?	
Others	Report as seen	

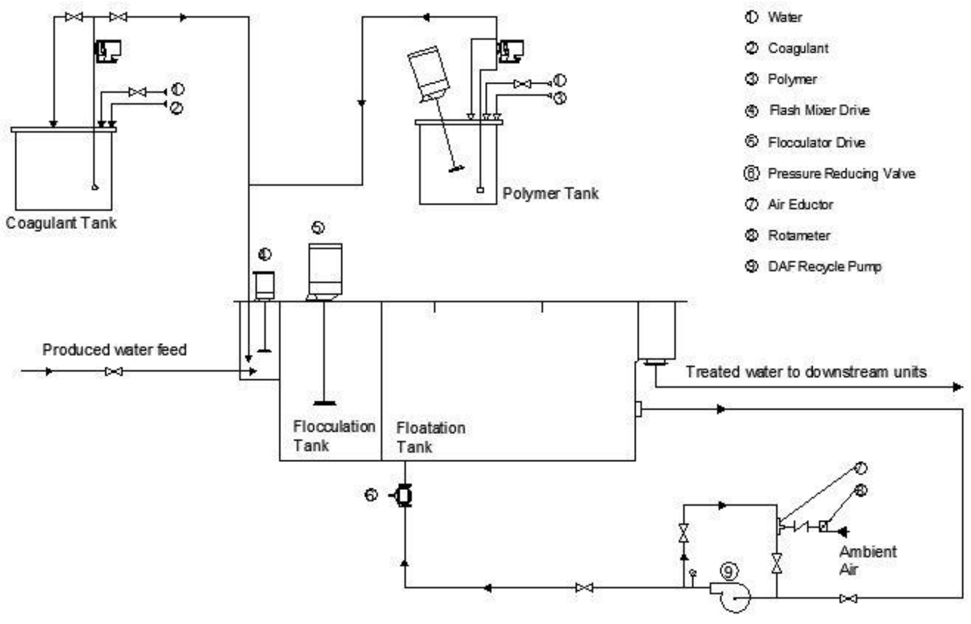


Figure A -1: Process and Instrumentation diagram of DAF pilot plant installed onsite

Appendix B: Analytical protocols

B1: Modified SOG analytical method

Scope

With the priority of protecting the environment in monitoring the discharge of petrochemical hydrocarbons into the environment. This method is by the South African Bureau of Standards (SABS) method 1051(SANS-SABS, 2007) to determine SOG in industrial and sewer effluent. This method is not applicable to measuring compounds that volatilise at temperatures below 85^0C.

Interference

The method is entirely empirical; hence, to obtain a high degree of precision requires strict observance of details. Such as time for extraction, heating and cooling must be consistent. However, the yield to extract the oil might be affected by the type of solvent and glassware. Thus, oil droplets are hydrophobic, hence will prefer to associate with the glassware rather than a simple water bottle. Therefore, plastics wares should be avoided and must be washed and clean with hot tap water.

Safety

Always have personal protection equipment's (PPE) on, by treating each chemical as a potential health hazard. Samples might contain high volatile toxic compounds; hence, containers should be opened in a hood and handled with gloves to prevent exposure. The laboratory is answerable to maintain a safe work environment and address the safe handling of chemicals.

Apparatus

- 1L Separating funnel
- 250 ml round bottom flask
- 1000 ml measuring cylinder
- Glass funnel 100 mm short stem
- Steam bath with 6 ports
- Erlen conical flask 250 ml
- Cotton wool rolls 500 g
- Spatula s/steel spoon end 150 mm

- Stopwatch
- Analytical balance-capable of weighing with 0.1 mg precision
- Tongs-for handling the boiling flasks
- Desiccator
- Oven
- Retort stand

Reagents

- Dichloromethane AR 2.5 L
- Sodium sulphate anhydrous 500 g

Procedure

A typical gravimetric-based method was used in measuring the SOG, depending on the amount of the SOG been extracted by the solvent used. The following was the procedure followed.

i. Clean, label and weigh the round bottom flask.

ii. Depending on the chemistry of the MOW, blend 50 ml of Dichloromethane with 500 ml of the MOW sample (1:10 ratio) in the separating funnel.

iii. Seal the funnel, shake vigorously and release the pressure intermittently for 2 minutes.

iv. Put the separating funnel on the retort stand, and was allowed for 15 minutes, to let the organic and aqueous phase settle.

v. Afterwards, drain the aqueous layer (lower part) into the Erlen conical flask placed under the separating funnel.

vi. After three times of extraction, a two-spatula spoonful of the sodium sulphate was added to the aqueous phase extracted to dry up the emulsions and allowed to stand for 2 -5 minutes.

vii. The extract is then filtered, using the glass funnel, cotton wool, and then collected in a flask, which has been weighed beforehand.

viii. The flask is placed in a steam bath to evaporate the solvent a temperature above 85 ℃ for 30-60 minutes. Ensure this is done in a closed fumed chamber.

ix. When the evaporation is complete, remove the flask using the tong, and wipe the outside to remove excess moisture content.

x. Then dry the flask in an oven at a temperature of 100 to120 ℃ for 2-3 hours.

xi. The flask is taken from the oven and quickly transferred to a desiccator to cool at room temperature for about 30 minutes.

xii. When cooled, the flask with the oil residual is weighed on a calibrated balance.

xiii. Knowing the weight of the empty flask, the gain weight is obtained by subtracting the initial weight from the final weight. Thus the SOG concentration (mg/L) is calculated using the below equations.

$$SOG\left(\frac{mg}{L}\right) = \frac{mass_{(sample+flask)} - mass_{(flask)} \times 1000}{Volume\ of\ sample} \qquad \text{B-1}$$

$$SOG\ \%\ removal\ = \frac{SOG_{(feed)} - SOG_{(sample)} \times 100}{SOG_{(feed)}} \qquad \text{B-2}$$

B2 :COD measurement

The COD’s were measured with Hanna HI 83099 COD and multi-parameter photometer at wavelength of 430 nm for high range (up to 1500 mg/L)

The following procedure was followed:

i. Preheat the COD reactor to 150°C block.

ii. Remove the cap of the COD digestion reagent vial selected for the test-based range on expected results.

iii. The first vial was marked with the effluent sample ID and the other as blank.

iv. Hold the vial marked blank at a 45- degree angle. Pipette 2 ml in the case of low range and 0.2 ml for a high range of deionized water into the vial and swirl. However, dilution factor can be used where necessary.

v. Prepare the effluent sample by repeating step 4, by substituting the deionized water with the effluent sample.

vi. The vial caps were capped tightly, rinsed with water and wiped with a clean paper towel to remove stains from the vails.

vii. The caps then held the vials, and inverted gently over two to three times to enhance proper mixing of the contents.

viii. The vials were placed in the preheated DRB 200 reactor, adequately closed and allowed to heat for 2 hours.

ix. After the heating, the reactor was turned off and allowed to cool down to a temperature of 120℃.

x. Each vial were inverted while still warm, eventually placed in a rack was allowed until the vials cooled to a room temperature.

xi. The COD programme was selected on the Hanna HI 83099 COD and multi-parameter photometer depending on the range. The vials were wiped again with clean paper.

xii. The empty vial was first inserted into the cell, and the instrument was zeroed. After that the effluent sample vial was inserted, and the reading was taken.

$$COD\ \left(\frac{mg}{L}\right) = \frac{COD_{(initial\,)} - COD_{(final)} \times 100\%}{COD_{(initial\,)}} \qquad \text{B-3}$$

B3: Turbidity measurement

The Hach 2100N turbidimeter was used to measure the turbidity. This equipment had a sample test cell of volume 10 cm. The cell was rinsed adequately with deionized water to get rid of any contaminants. One of the cells was filled deionised and the other with the effluent sample to the mark. The cell was placed into the meter and zeroed, then after the sample was also inserted and reading was taken and recorded (NTU). These techniques were carried out for all the samples tested.

$$Turbidity\ (\mathrm{NTU}) = \frac{T_{(initial\,)} - T_{(final)} \times 100\%}{T_{(initial\,)}} \qquad \text{B-4}$$

B4 :TSS measurement

The TSS was measured with Hach DR890 potable colourimeter, with 25 ml sample test cell.The following were the procedure used; this was calculated with the equation below .

$$TSS\left(\frac{mg}{L}\right)=\frac{TD_{(initial\,)}-TD_{(final)}\times 100\%}{TD_{(initial\,)}} \quad \text{B-5}$$

i. Enter the stored program number for suspended solids

ii. Press 94 and then Enter

iii. Fill the sample to the mark with 25 ml deionized water and label it as blank and the other with the effluent sample.

iv. Place the blank in the cell holder. Tightly cover the cell with the instrument cap. Then press to Zero.

v. Swirl the effluent sample cell to remove any bubbles to enhance uniform suspension of any residual.

vi. Repeat IV, but now used the effluent sample cell, then press the Read cursor and recorded the value (mg/L).

Figure B-1: Photo of Hach DR890 potable colourimeter

B4: Conductivity and Total suspended solids (TDS)

The conductivity and TDS were measured with the HJM C8 μS/TDS Meter. The conductivity measures the ability of the water's electrical current, whiles the TDS is the measure of the inorganic dissolved solids such as sulphate, chloride, aluminium, and sodium. Although both were not used as criteria to evaluate the process performance. These were calculate with the equations below;

$$EC\left(\frac{\mathrm{uS}}{m}\right) = \frac{EC_{(initial\,)} - EC_{(final)} \times 100\%}{EC_{(initial\,)}} \qquad \text{B-6}$$

$$TDS\ \left(\frac{mg}{L}\right) = \frac{TDS_{(initial\,)} - TDS_{(final)} \times 100\%}{TDS_{(initial\,)}} \qquad \text{B-7}$$

The following procedure was used in calibration;

i. The rear cover was removed.

ii. The cup was filled with the known conductivity solution and allowed for 5 minutes.

iii. The cup was emptied and refilled with new solution

iv. The 'Push to read' ottom button was pressed for 2 seconds

v. 'Up' or 'Down' button was pressed to enhance calibrate the meter.

vi. Press the 'Set' ottom button to save the setting

vii. Discard the used test solution

The following procedure was to measure the TDS and Conductivity

i. Press, 'Push to read' until the display switches on.

ii. The meter will auto-range and display 'μS = 0.0' and 'TDS = 0.0'

iii. Pour liquid into the cup. The Meter will display 'Ranging wait'.

iv. After a few second, the conductivity reading in μS /cm, as well as TDS, will be displayed.

v. Alternatively, pour the liquid into the cup and -press, 'Push to read'.

vi. The Meter will display 'Ranging wait'.

vii. After a few second, the conductivity reading in μS /cm, as well as TDS, will be displayed.

viii. The meter will switch off after 40 Seconds, or if the 'Push to read' button is pressed for 3 seconds.

ix. To switch off, press ‘Push to read’ until the display switches off.

Figure B-2: Photo HJM C8 µS/TDS meter

Appendix C: Data on evaluating operating parameters

Table C-1: Effects of acids

Acid type	HCl			**Dosage/Jar**	6mg/L	
Base type	1.0 M NaOH			**Dosage/Jar**	2mg/L	
Coagulant type	PAS			**Dosage/Jar**	5mg/L	
Rapid mixing	250 rpm			**Time**	2 min	
Slow mixing	30 rpm			**Time**	15 min	
Air pressure	350 kpa			**Flotation time**	15 min	
Air to water ratio	10 %			Res time	3 sec	
Sample ID	**Feed (F)**	**A**	**B**	**C**	**D**	**E**
pH	7	2	4	6	8	10
Observation	Brownish	Brownish	Brownish	Brownish	Brownish	Brownish
Water quality						
Turbidity (NTU)	2753	650	620.5	830	1250	1280
TSS (mg/L)	1035	580	468	678	796.5	850
COD (mg/L)	12365	5530	4686	5249	5324	5456.5
SOG (mg/L)	1320	573.5	558.4	612	860	940
Performance (% removal)						
Turbidity (NTU)		76.4	77.5	69.9	54.6	53.5
TSS (mg/L)		44.0	54.8	34.5	23.0	17.9
COD (mg/L)		55.3	62.1	57.5	56.9	55.9
SOG (mg/L)		56.6	57.7	53.6	34.8	28.8

Acid type	H_2SO_4 1.0 M			**Dosage/Jar**	6mg/L	
Base type	NaOH			**Dosage/Jar**	2mg/L	
Coagulant type	PAS			**Dosage/Jar**	5mg/L	
Rapid mixing	250 rpm			**Time**	2 min	
Slow mixing	30 rpm			**Time**	15 min	
Air pressure	350kpa			**Flotation time**	15 min	
Air to water ratio	10%			Res time	3 sec	
Sample ID	**Feed (F)**	**A**	**B**	**C**	**D**	**E**
pH	7	2	4	6	8	10
Observation	Brownish	Brownish	Brownish	Brownish	Brownish	Brownish
Water quality						
Turbidity (NTU)	2753	543	490.65	623.5	786	986
TSS (mg/L)	1035	465	435.53	598.6	736	820
COD (mg/L)	12365	4782	4136	4362.5	4523.2	4862
SOG (mg/L)	1320	567.2	538.6	665.5	748	878
Performance (% removal)						
Turbidity (NTU)		80.3	82.2	77.4	71.4	64.2
TSS (mg/L)		55.1	57.9	42.2	28.9	20.8
COD (mg/L)		61.3	66.6	64.7	63.4	60.7
SOG (mg/L)		57.0	59.2	49.6	43.3	33.5

Continued Table C-1 :Effects of acids

Acid type	H_3PO_4			Dosage/Jar	6mg/L	
Base type	1.0 M NaOH			Dosage/Jar	2mg/L	
Coagulant type	PAS			Dosage/Jar	5mg/L	
Rapid mixing	250 rpm			Time	2 min	
Slow mixing	30 rpm			Time	15 min	
Air pressure	350 kpa			Flotation time	15 min	
Air to water ratio	10%			Res time	3 sec	
Sample ID	**Feed (F)**	**A**	**B**	**C**	**D**	**E**
pH	7	2	4	6	8	10
Observation	Brownish	Brownish	Brownish	Brownish	Brownish	Brownish
Water quality						
Turbidity (NTU)	2753	477.5	442.6	511.4	658	896
TSS (mg/L)	1035	420.2	398.5	453.6	687	736
COD (mg/L)	12365	4382	4023.1	4129	4234	4784
SOG (mg/L)	1320	532.4	489.6	556.4	654.5	784
Performance (% removal)						
Turbidity (NTU)		82.7	83.9	81.4	76.1	67.5
TSS (mg/L)		59.4	61.5	56.2	33.6	28.9
COD (mg/L)		64.6	67.5	66.6	65.8	61.3
SOG (mg/L)		59.7	62.9	57.8	50.4	40.6

Table C-2: Effects of air-saturator pressure

Acid type	H_3PO_4			**Dosage/Jar**	6mg/L	pH 5
Coagulant type	PAS			**Dosage/Jar**	5mg/L	
Rapid mixing	250 rpm			**Time**	2 min	
Slow mixing	30 rpm			**Time**	15 min	
Air pressure	(200-600kpa)			**Flotation time**	15 min	
Air to water ratio	10 %			Res time	3 sec	
Sample ID	**Feed (F)**	**A**	**B**	**C**	**D**	
Air pressure (kPa)	0	200	300	400	500	600
Observation	Brownish	Brownish	Brownish	Brownish	Brownish	Brownish
Water quality						
Turbidity (NTU)	2753	1188	1022	989	1006	1052
TSS (mg/L)	1035	489	378.5	315.5	402	448.6
COD (mg/L)	12365	5951	3258	2304	3564	4125
SOG (mg/L)	1320	648.6	367	302	348	552.6
Performance (% removal)						
Turbidity (NTU)		56.8	62.9	64.1	63.5	61.8
TSS (mg/L)		52.8	63.4	69.5	61.2	56.7
COD (mg/L)		51.9	73.7	81.4	71.2	66.6
SOG (mg/L)		50.9	72.2	77.1	73.6	58.1

Table C-3 : Effects of coagulant dosage

Acid type	H_3PO_4			**Dosage/Jar**	6mg/L		
Coagulant type	PAS			**Dosage/Jar**	add 1mg/L		
Rapid mixing	250 rpm	pH 5		**Time**	2 min		
Slow mixing	30 rpm			**Time**	15 min		
Air pressure	350 kpa			**Flotation time**	15 min		
Air to water ratio	10 %			Res time	3 sec		
Sample ID	**Feed (F)**	**A**	**B**	**C**	**D**	**E**	**F**
Coagulant dosage	0	5	6	7	8	9	10
Observation	Brownish	Brownish	Brownish	Brownish	Brownish	Brownish	Brownish
Water quality							
Turbidity (NTU)	2753	834	699	572	520	492	435
TSS (mg/L)	1035	571	376	359	348.5	339.5	336
COD (mg/L)	12365	2830	2405	1969	1772	1511.5	1266
SOG (mg/L)	1320	936	800	785	635	520	480
Performance (% removal)							
Turbidity (NTU)		70	75	79	81	82	84
TSS (mg/L)		45	64	65	66	67	68
COD (mg/L)		77	81	84	86	88	90
SOG (mg/L)		29	39	41	52	61	64

Table C-4: Effects of flotation time

Acid type	H_3PO_4			**Dosage/Jar**	6mg/L
Coagulant type	PAS			**Dosage/Jar**	10mg/L
Rapid mixing	250 rpm	pH 5		**Time**	2 min
Slow mixing	30 rpm			**Time**	15 min
Air pressure	350 kpa			**Flotation time**	5 min intervals
Air to water ratio	10 %			Res time	3 sec
Sample ID	**Feed (F)**	**A**	**B**	**C**	**D**
Flotation time	0	15	20	25	30
Observation	Brownish	Brownish	Brownish	Brownish	Brownish
Water quality					
Turbidity (NTU)	2753	302	328	398	585
TSS (mg/L)	1035	330	365	415	485
COD (mg/L)	12365	958	1085	1565	1743.5
SOG (mg/L)	1320	242	238	360	458
Performance (% removal)					
Turbidity (NTU)		89	88	86	79
TSS (mg/L)		68	65	60	53
COD (mg/L)		92	91	87	86
SOG (mg/L)		82	82	73	65

Table C-5: Effects of air –water ratio

Acid type	H_3PO_4			**Dosage/Jar**	6mg/L
Coagulant type	PAS			**Dosage/Jar**	5mg/L
Rapid mixing	250 rpm	pH 5		**Time**	2 min
Slow mixing	30 rpm			**Time**	15 min
Air pressure	350kpa			**Flotation time**	15 min
Air to water ratio	(5 to 20%)			Res time	3 sec
Sample ID	**Feed (F)**	**A**	**B**	**C**	**D**
Air-water ratio	0	5	10	15	20
Observation	Brownish	Brownish	Brownish	Brownish	Brownish
Water quality					
Turbidity (NTU)	2753	985	925	822	758
TSS (mg/L)	1035	578	467	436	471
COD (mg/L)	12365	3951	2405	2138	2830
SOG (mg/L)	1320	523	364	325	356
Performance (% removal)					
Turbidity (NTU)		64.2	66.4	70.1	72.5
TSS (mg/L)		44.2	54.9	57.9	54.5
COD (mg/L)		68.0	80.5	82.7	77.1
SOG (mg/L)		60.4	72.4	75.4	73.0

Appendix D: Data on evaluation of coagulant types and dosage

Table D-1: Effects of cationic inorganic coagulants

Coagulant type	Aluminium Sulphate (alum)					Coagulant type	Aluminum Chloride (AC)				
Coagulant dosage (mg/L)	10	20	30	40	50		10	20	30	40	50
Turbidity (NTU)	72	77	78	88	90		72	82	87	90	94
TSS (mg/L)	64	68	74	78	79		45	48	55	77	84
COD (mg/L)	85	86	93	94	96		85	89	92	93	94
SOG (mg/L)	60	73	81	90	95		64	72	80	89	93
*TDS (mg/L)	9	14	10	9	7		15	13	5	3	2
*EC (us/m)	14	17	18	14	11		1	1	1	-3	-3
Coagulant type	Ferric Sulphate (FS)					Ferric Chloride (FC)					
Coagulant dosage (mg/L)	10	20	30	40	50		10	20	30	40	50
Turbidity (NTU)	70	75	81	85	88		73	82	88	92	96
TSS (mg/L)	59	64	65	68	77		66	70	82	91	91
COD (mg/L)	77	81	83	88	91		78	78	82	84	83
SOG (mg/L)	51	57	74	83	91		44	59	77	86	92
*TDS (mg/L)	2	2	0	5	7		3	2	11	4	10
*EC (us/m)	1	1	0	2	3		0	1	4	2	3

Table D-2 : Effects of polymeric organic coagulants

Coagulant type	Polyaluminium chloride (Z553D)					Polyferric sulphate (Zetag32-FS/A50)					Polyaluminium sulphate(PAS)				
Coagulant dosage (mg/L)	10	20	30	40	50	10	20	30	40	50	10	20	30	40	50
Turbidity (NTU)	72	73	75	79	81	72	82	87	90	94	57	63	71	81	84
TSS (mg/L)	66	67	68	69	73	45	48	55	77	84	56	60	61	65	71
COD (mg/L)	78	84	85	88	90	81	82	85	89	91	61	71	78	82	83
SOG (mg/L)	44	54	63	70	84	45	59	69	80	93	44	71	75	78	88
*TDS (mg/L)	17	19	19	21	24	3	3	9	5	10	1	3	5	5	6
*EC (us/m)	17	18	17	18	25	2	2	8	4	8	1	2	2	2	3

Table D-3 :Economic analysis of the coagulants

Coagulant type	**Price Zar /500gram**	**Cost (ZAR) /gram R/g**	**TSS%**	**Water quality % removal Turbidity%**	**COD %**	**SOG%**
		Inorganic coagulant				
Alum	485	0.97	79	90	96	95
AC	604.4	1.21	84	94	94	93
FS	656.56	1.31	77	88	91	91
FC	708.7	1.42	91	96	83	92
		Polymeric organic coagulant				
Z553D-PAC	775	1.55	73	81	90	84
Zetag32-FS/A50	675	1.35	84	94	91	93
PAS	825	1.65	71	84	83	88

Table D-4:Pre and Post coagulation treatment

Coagulant type	**TSS%**	**Turbidity%**	**COD %**	**SOG%**
		Pre-coagulation		
Zetag32-FS/A50	84	94	91	93
Z553D-PAC	73	81	90	84
Alum	79	90	96	95
FC	91	96	83	92
		Post -coagulation		
Zetag32-FS/A50	65	87	88	87
Z553D-PAC	63	79	82	89
Alum	68	87	92	90
FC	68	81	83	85