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Shear Enhanced Flotation Separation Technology for Winery Wastewater Processing

by

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A thesis submitted in fulfilment of the requirements for the degree of
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Thesis Abstract

The agricultural industry requires and uses a significant quantity of fresh water around the world. Copious amounts of fresh water are used to make commercial wine, and an extensive amount of wastewater is generated through different processes during the production of wine. Winery wastewaters often have high levels of chemical oxygen demand (COD), total suspended solids (TSS), and an acidic pH ranging from 2 to 5. Additionally, they may also have varied levels of salinity and nutrients. Winery wastewaters possess inherent chemical qualities that make it a possible threat to the environment if not handled and discarded in a suitable manner.

This research investigates the implementation of hydrodynamic shear with coagulation, flocculation and air flotation using a technology called shear enhanced flotation separation (SEFS) to destabilize and separate particulate matter in winery wastewater. The individual and synergistic effects of hydrodynamic shear, coagulation, flocculation and flotation in processing winery wastewater was evaluated. Previous studies have shown the effectiveness of coagulation, flocculation and flotation in treating winery wastewater, however, to date, limited research has been conducted to evaluate the effectiveness of a hybrid technology, which includes hydrodynamic shear to treat winery wastewater.

This study consisted of three phases. The first being the design and assembly of a laboratory scale shear (rotor/stator) enhanced induced air flotation (IAF) apparatus. Secondly, the treatment of winery wastewater at a wine farm on the West Coast of South Africa using an industry supplied (Abrimix Pty Ltd) mobile wastewater treatment plant, which consisted of a shear mixer and induced air flotation configuration. Lastly, a pilot plant was designed and fabricated with a shear (rotor/stator) mixer integrated into a conventional dissolved air flotation (DAF) unit to treat winery wastewater. Turbidity, zeta potential (**ζ),** TSS, total dissolved solids (TDS), electrical conductivity (EC), particle size distribution (PSD) and COD, were measured pre and post treatment, to determine the overall effect of shear enhanced IAF and DAF on the treatment efficiency of winery wastewater.

The laboratory scale SEFS study yielded impressive results where treatment efficiencies of turbidity, TSS and COD were 95%, 97% and 54%, respectively. The Abrimix mobile treatment plant displayed a notable reduction in turbidity (81%) and TSS (92%). The reduction in COD

using the Abrimix mobile treatment plant was however sub-optimal, with a COD treatment efficiency of 38%.

A comparative study was conducted where winery wastewater was treated with conventional DAF (without hydrodynamic shear) and DAF with hydrodynamic shear; referred to Shear Enhanced Flotation Separation (SEFS) throughout this study. The pilot scale SEFS technology once optimized, removed nearly 100% of both turbidity (99.6%) and TSS (99.4%). Whilst conventional DAF treated displayed turbidity and TSS removal rates of 95.9% and 97.1%, respectively. General authorizations to use treated winery wastewater for irrigation purposes states that the COD value must be below 5,000 mg/L, to irrigate up to 50 m^3 per day. Conventional DAF treatment displayed COD values of 5,490 mg/L, whereas SEFS treated wastewater had COD values of 3800 mg/L. Furthermore, it was observed that SEFS treatment required around 34% less chemicals than with conventional DAF treatment. The energy consumption associated with DAF treatment amounted to 0.6 kWh/m^3, while the SEFS treatment required 1.1 kWh/m^3. The roughly doubled energy use was, nevertheless, justified by the quality of the treated wastewater as well as overall operational expenses required to treat 1 m^3 of wastewater.

The solids (froth) generated during the treatment process was examined and showed the potential for it to be used as a source of fertilizer based on the nutrients contained therein. The effects of adding the dried froth to soil should be investigated in future, as this did not fall within the scope of the study.

The results of this study concluded that the incorporation of a stator/rotor high shear mixer enhances the treatment of winery wastewater, albeit at a R0.26 operational cost difference compared to a conventional DAF system. The SEFS treatment produces water that can be either used as grey water to wash winery floors during production processes or can be further biologically treated to obtain a quality where the treated wastewater may be used for beneficial vine crop growth throughout the wine and/or agricultural industry.

Keywords

Alkalisation
Coagulation
Conductivity
Colloid
Chemical Oxygen Demand
Flocculation
Flotation
Hydrodynamic Shear
Induced Air Flotation
Irrigation
Microbubble
Particle
Sedimentation
Shear
Separation
Total Dissolved Solids
Total Suspended Solids
Turbidity
Winery Wastewater
Zeta Potential

Declaration

I declare that **"Shear Enhanced Flotation Separation Technology for Winery Wastewater Processing "**, is solely my own work. It has not been previously submitted for any academic degree or examination at any other institution. Furthermore, I have provided comprehensive references to acknowledge and indicate all the resources that have been quoted and utilized in this research.

David Eswald Vlotman March 2024

Signed: ……… Vlotman. ……………………………

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List of Abbreviations

A	amperes
Alum	aluminium sulfate
ACH	Aluminium Chlorohydrate
ANOVA	analysis of variance
(aq)	aqueous phase
CC	chemical coagulation
cm	centimetre(s)
COD	chemical oxygen demand
DAF	dissolved air flotation
DGF	dissolved gas flotation
DLVO	Derjaguin, Landau, Verwey and Overbeek
DSD	Droplet size distribution
EC	Electrocoagulation
EDL	electrical double layer
g	gram(s)
GDP	gross domestic product
g/mol	grams per mole
h	hour(s)
Hz	hertz
SEFS	shear enhanced flotation separation
IBC	intermediate bulk container
IAF	induced air flotation
IEP	isoelectric point
IGF	induced gas flotation
L	liter(s)
(l)	liquid phase
L/h	liter(s) per hour
L/min	liters per minute
m	metre

m^3	cubic metre
max	Maximum
MR	Million Rand
mm	millimetres
mL	milliliter(s)
min	minute
mins	minutes
mg	milligram(s)
mg/L	milligram(s) per liter
mV	millivolts
mol	mole
M	Molarity
PAC	polyaluminium chloride
ppm	parts per million
P&ID	piping and instrumentation diagram
rpm	revolutions per minute
s	second(s)
SAIAMC	South African Institute for Advance Material Chemistry
SAWIS	South African Wine Industry Information & Systems
SEFS	Shear Enhanced Flotation Separation
SS	suspended solids
TDS	total dissolved solids
TSS	total suspended solids
NTU	nephelometric turbidity unit
TOC	total organic content
US	United States
UWC	University of the Western Cape
vdW	van der Waals

List of Symbols

µ	micro
η	nano
µm	micrometer
mS/cm	millisiemens per centimetre
µS/cm	microsiemens per centimetre
ηm	nano meter
ζ	zeta potential
%	percentage

Research Output

Publication 1:

- **Vlotman D.E.**, Key D., Bladergroen B.J.: Technological Advances in Winery Wastewater Treatment: A Comprehensive Review. *South African Journal of Enology and Viticulture*, 43(1), 58-80. https://doi.org/10.21548/43-1-4931

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CHAPTER 1 BACKGROUND AND INTRODUCTION

This chapter presents an overview of winery wastewater, focusing on the identification of typical pollutants present in the wastewater, the environmental consequences associated with these pollutants, appropriate methods for disposal, and the conventional wastewater treatment technologies commonly employed within the wine industry. This chapter additionally outlines the problem statement, research questions, goals and objectives, research methodology, thesis delimitation. An overview of this thesis is presented at the end of this chapter.

1.1. Introduction

Water is an essential component that is utilized at every stage during the production of wine, from the management of vineyards through to the bottling of the finished product. Water also serves as a medium for chilling, cleaning, sanitization, and sterilizing [1]. The production of wine for commercial purposes is inextricably tied to the consumption of substantial quantities of fresh water. During this production process, a sizeable portion of the fresh water used becomes wastewater (ranging from 50% for small wineries to 80% for medium to large wineries) [2]. On average, 3 to 5 m^3 of wastewater is generated per metric ton of grapes processed. The issue of water scarcity continues to be a significant concern for wineries of all sizes, as the increasing costs associated with water use and its availability can pose a serious threat to a winery's efforts to create or maintain economic and environmental sustainability [3].

Wineries produce a significant amount of wastewater that contains a diverse range of organic and inorganic compounds. The management of wastewater within the wine industry is imperative due to its impact on the recipient environment. Consequently, the wine industry has to adopt specific protocols to address this issue [4]. This is done to ensure compliance with wastewater discharge regulations established by national and local authorities [5]. Due to increasingly strict normative and legislative regulations pertaining to wastewater discharge, the treatment of winery wastewater is focused on eliminating the pollutants present in order to achieve a desired level of water purity for reuse in wine production processes. This overall approach helps contribute to sustainable wine making practices.

The wine industry in South Africa holds a prominent position within the country's agricultural sector, boasting a rich historical background and international recognition. Moreover, it serves as a substantial contributor to the nation's export earnings. Vink *et al.*, (2010) undertook a survey to examine the expansion of the South African wine sector. These authors noted that

South Africa's wine exports experienced a significant increase from 20 million liters in 1992 to 400 million liters in 2008 [6]. According to industry association SAWIS (South African Wine Industry Information & Systems), the wine business sector in South Africa employs around 270,000 people across the value chain, approximately 80,000 of whom work on farms and in cellars [7]. These employees are crucial for the preservation of the wine industry and plays a vital role during wine grape crop harvesting.

The wine grape crop harvest of 2021 was roughly 1.46 million tonnes, representing an increase of 8.9% compared to the previous year's harvest [7]. In a similar vein, the yield for South Africa's wine grape harvest in 2022 amounted to approximately 1.37 million tonnes [7]. This represents a decrease of 5.5% compared to the previous year's crop, yet it remains higher than the average yield of 1.34 million tonnes observed over the five-year period from 2018 to 2022 [8]. These figures highlight the significant role that cultivation and commercialization of wine has played in the agricultural industry of South Africa.

In the present context, the exported volume of South African wine in 2022, was 369 million liters, which represented a decline of 5% when compared to the export volume of 2021, which stood at 388 million liters [8]. As of 2022, South Africa ranks as the eighth largest global wine producer, contributing approximately 4% to the total global wine production [9].

The South African wine industry contributed 9% (equivalent to R55 billion, with an export component worth R10 billion) to the overall gross domestic product (GDP) of South Africa, as per the numbers published for the fiscal year 2021/2022 [10]. This includes the sale of various wine products, along with wine tourism and auxiliary activities associated with the wine industry. It is evident that the wine industry plays a significant role in the South African economy. However, notwithstanding its positive impact on the GDP and job creation, this industry consumes large volumes of fresh water, leading to the generation of extensive amounts of wastewater [11]. The management of agricultural, and more specifically, winery wastewater thus poses a considerable challenge for many wine farms [12]. It is vitally important that this wastewater is treated and disposed of in compliance with regulations to preserve the environment for future generations.

The typical water-to-wine ratio is 4:1, meaning that 1 L of wine is produced for every 4 L of water consumed [13]. Given the aforementioned ratio, an important question to pose would be: what is the fate of the remaining water that does not ultimately find its way into the wine bottle?

The resulting water primarily end up as wastewater, encompassing all the water used and produced within the winery throughout various activities, including tank cleansing, process equipment and floor washing (predominantly involving the application of chemical cleaning agents).

The presence of a diverse range of chemicals used throughout the process of wine production results in winery wastewater containing substantial quantities of both organic and inorganic substances [14]. If this wastewater is not properly treated, it can have harmful consequences on the environment [15]. The discharge of untreated winery wastewater has been found to result in the salinization and eutrophication of natural water bodies such as streams, rivers, dams, and groundwater [16]. Eutrophication refers to the process by which an excessive accumulation of nutrients in a water body leads to rapid growth of plant life, posing a threat to biodiversity. The discharge of untreated winery wastewater onto land also results in the soil becoming contaminated with various organic and inorganic substances, including sodium and potassium derived from cleaning agents containing these elements. This contamination has a detrimental effect on soil chemistry, making it challenging for plants to grow [17]. The inclusion of both organic and inorganic substances in wastewater has prompted wineries to explore more effective approaches to wastewater management. This is done with the aim of enhancing water recovery and reutilization, thereby encouraging sustainable wine production practises and mitigating the strain on already depleting water resources [18,19].

At present, there is a diverse array of treatment technologies that have been extensively studied and documented, with ongoing investigations into additional treatment methods. These studies aim to address the challenges encountered by conventional winery wastewater treatment plants or to improve existing technology through the implementation of hybrid winery wastewater treatment technologies that leverage a synergistic approach. There are, however, conflicting views concerning the optimal approach to wastewater management in wineries of varying scales [14,20–23].

The objective of this study is to apply a relatively unknown wastewater treatment technology known as Shear Enhanced Flotation Separation (SEFS) technology and optimise its process conditions specifically for the treatment of winery wastewater.

1.2. Problem statement

During the harvest season, wineries produce significant quantities of wastewater, which is of substandard quality and cannot be directly discharged into natural ecosystems like rivers without appropriate pre-treatment measures. Winery wastewater is produced as a result of different activities, including cleaning tanks, sanitizing floors and equipment, rinsing transfer lines, cleaning barrels, loss of wine and other products, operating bottling facilities, running filtration units and incorporating rainwater into the wastewater management system [14].

The pH range of winery wastewaters is usually between 3 and 5. This is because they contain organic acids like lactic, tartaric, citric and malic acid [24]. These wastewaters also possess a high organic content, mainly attributed to sugars and ethanol, as well as a substantial chemical oxygen demand (up to nearly 300,000 mg/L) and a considerable quantity of total suspended solids (up to 30,000 mg/L) [17,23,25]. Electrical conductivity (EC) of winery wastewater is reported to be in the range of 162 to 615 mS/m [26]. These factors are essential for determining if winery wastewater is suitable for irrigation. Among these parameters, the chemical oxygen demand (COD) holds particular significance. COD serves as a measure of the oxygen needed to fully oxidise all organic components in the wastewater and is widely employed as an indicator of wastewater quality [27]. In the context of small-scale wastewater irrigation (up to 50 m^3/day), the maximum allowable COD level in the wastewater is 5,000 mg/L. Additionally, the ideal pH range should fall between 6 and 9, whilst the electrical conductivity should not exceed 200 mS/m. These guidelines are established by the South African Department of Water Affairs [5]. In order to adhere to the prescribed irrigation regulations, wineries must incorporate a minimum of one wastewater treatment method [28].

Wastewater treatment technology usually consist of a primary, secondary and a tertiary phase. Primary wastewater treatment methods, such as alkalization followed by sedimentation (or clarification) is most often used in typical wastewater treatment plants. However, these techniques have certain limitations. Firstly, they require extended retention times due to the reliance on gravitational settling for sedimentation/clarification to occur. Additionally, these processes generate significant amounts of chemical sludge, which typically requires external processing [29]. Previous studies have demonstrated that conventional winery wastewater treatment techniques, such as activated sludge (secondary treatment), can effectively produce high-quality wastewater, with COD removal rates ranging from 78% to 98% [30,31].

Nevertheless, the operational expenses associated with this treatment approach often render it impractical, particularly for small to medium-sized wineries.

The costs associated with processing wastewater can frequently increase, especially as the volume and composition of wastewater increases. In addition, ensuring the appropriate pH levels and precise dosage of chemicals are crucial factors in optimising the efficiency of conventional wastewater treatment methods. Achieving this objective does however pose challenges due to the considerable variability in the chemical composition of winery wastewater. Continuous evaluation and targeting of alternative treatment methods are therefore necessary in order to mitigate the operational and cost implications associated with commonly utilised winery wastewater treatment technologies, as well as to comply with the stipulated municipal discharge standards [32–34].

This research project is focused on the primary treatment stage where the investigation of a technology called shear enhanced flotation separation (SEFS) technology will be conducted and evaluated for its potential to treat winery wastewater by transforming it into one or more valuable product streams.

1.3. Justification of the study

The persistent issue of water scarcity has generated significant apprehension within the wine industry due to its potential consequences on vineyard productivity and the overall quality of wine produced. The substantial volume of water used and wastewater generated during the course of wine production highlights the importance of prioritising water recycling within the wine making sector. The implementation of winery wastewater recycling would enable wineries of varying sizes to effectively repurpose the wastewater generated throughout the wine production process. The extent to which this can be achieved will be dependent upon the intended quality of the treated wastewater. If the desired quality of the treated wastewater is attained, it can be either for reused in wine production processes or for beneficial irrigation of vineyard crops.

Treating, followed by recycling winery wastewater can reduce expenses associated with fresh water use in operational processes of wine production, as well as providing the advantageous cultivation of crops without significant financial implications on a winery's annual operational budget. Given that wine grape production is a substantial and enduring investment that requires preservation for the benefit of future generations, it is advisable for wine producers to explore intelligent production trends in order to safeguard a stable position in the international wine market. One potential strategy for promoting the sustainability of the wine industry involves the identification and resolution of challenges pertaining to winery wastewater and its subsequent management [35,36].

On average, a volume of winery wastewater ranging from 3 to 5 m^3 is generated per metric tonne of grapes processed [37]. In order to provide a contextual background, the South African wine industry processed a cumulative quantity of 1.37 million metric tonnes of grapes during the 2021/2022 harvest season [8]. This figure serves as an indicator of the overall magnitude of wastewater produced throughout the aforementioned vintage, estimated to range between 3.9 and 6.5 million cubic metres in volume. This large quantity of winery wastewater poses serious environmental concerns specifically if disposed of in its untreated state.

The existing literature extensively documents conventional methods for treating winery wastewater. However, these techniques have various limitations. Firstly, certain treatment technologies, such as constructed wetland systems, require large land areas, making them space intensive [38]. Secondly, these techniques are not capable of effectively removing a wide range of contaminants [39]. Lastly, some of these treatment methods are energy-intensive [14].

Membrane bioreactors, among other advanced treatment alternatives, present a viable option for winery wastewater treatment. Nevertheless, it is important to acknowledge that these treatment processes are susceptible to fouling and require significant energy demands. Moreover, these processes generate excess sludge and encounter challenges related to biomass settling, which may impact the suitability and long-term viability in smaller wineries. Conversely, larger wineries might find membrane reactors to be a more suitable solution. Several studies have examined various primary treatment approaches involving coagulation/flocculation and sedimentation. These techniques have demonstrated the ability to effectively decrease turbidity, suspended solids, and, to a lesser extent, chemical oxygen demand [40–42].

The majority of suspended particles in wastewater exhibit a negative surface charge when present in an aqueous environment. The presence of this charge establishes repulsive forces that mitigate the tendency of particles to aggregate and settle, or to be transported towards the surface in the context of flotation mechanisms. The primary purpose of a coagulant is to counterbalance the electrostatic charge of negatively charged colloidal particles in wastewater by adding chemicals with counterions to the solution. After the neutralization/destabilization of these colloids, the interplay of van der Waals forces becomes evident, where these electrically neutral entities are subject to weak attractive forces, leading to aggregation into clusters. Once a sufficient number of these particles have aggregated, they form a conglomerate of flocs that can be either settled or removed from the water through flotation [43].

Traditionally, metal compound coagulants such as alum (aluminium sulfate), ferric chloride, and ferrous sulfate have been employed in wastewater treatment processes. Despite the affordability, accessibility, and ease of use, these chemicals have drawbacks in terms of pH compatibility (specifically outside the range of pH 6.5 – 7.5). Additionally, these coagulants tend to generate substantial quantities of sludge that consist of metal hydroxides [44]. Metal salts employed as coagulation aids have also been observed to decrease the alkalinity of the treated wastewater water, consequently leading to a reduction in its pH [45]. Chemical coagulation utilizing metal salts typically involves the use of large quantities of chemicals, rendering it a chemically intensive procedure. Consequently, these metal based coagulants are limited in the ability to achieve a maximum reduction of organic content in the treated wastewater, with a COD reduction of up to 40% [46]. Based on the previously mentioned shortfalls, there has been a growing interest to use polymeric coagulants as a viable alternative to traditional metal coagulants.

Pre-polymerized coagulants, including polyaluminium sulfate (PAS), polyaluminium chloride (PAC), and polyaluminium chloro-sulfate (PACS), have demonstrated effective performance across a broader pH range (pH 6 – 9.5), wider temperature ranges and colloid concentrations, in comparison to traditional metal-based coagulants used in the treatment of wastewater [40,47]. Polymeric coagulants offer several benefits in the context of wastewater treatment. These advantages include a reduction in the amount and concentration of coagulants required to destabilize colloids, as well as a decrease in the generation of sludge when compared to coagulants based on metal salts. There is a subsequent positive correlation with reduced sludge production which results in decreased costs associated with solid waste disposal for wineries that choose to utilize these particular coagulants in their primary treatment processes.

The implementation of hydrodynamic shear forces has the potential to enhance the efficiency of coagulation. The stability of colloids in suspension can be decreased by hydrodynamic shear forces, thereby facilitating particle aggregation. Hydrodynamic shear involves particles present in a liquid medium being brought together through the application of a shear force [48]. The phenomenon of hydrodynamic shear is brought about by bringing particles in a highly turbulent environment, overcoming hydrostatic forces and causing collisions. Upon collision, the particles will undergo aggregation provided that the net interparticle force is attractive and possesses sufficient strength to surpass the effects of thermal agitation and hydrodynamic drag. This enables the particles to adhere to one another [49].

Hydrodynamic shearing is a process that facilitates both the destabilization and formation of particles with a tendency to adhere to air bubbles, thereby potentially improving the efficiency of solid/liquid separation in flotation [50]. The efficacy of this process is not consistently optimal, as it can yield delicate aggregates that are prone to disintegration under the influence of external mechanical forces. Suspensions with a homogeneous representation of aggregates, where micro-aggregates predominate, are produced when a higher velocity gradient ($\bar{G} > 100$ s^{-1}) i.e., low shear is applied. The size distribution of aggregates in suspension is relatively broad when a lower gradient, i.e., low shear ($\bar{G} < 100$ s^{-1}) is employed. The system contains both large aggregates (macroaggregates) and smaller ones (primary aggregates and micro-aggregates), and the suspension is significantly more heterogeneous [51].

Polyelectrolyte flocculants are commonly employed in low shear environments to counteract the development of small and delicate flocs. This is done to ensure that the flocs remain agglomerated. The purpose of using these flocculants is to bring together and agglomerate the micro-flocs that settle slowly during the coagulation process. By doing so, larger and denser flocs are formed, which aids in the subsequent removal during sedimentation, flotation, and filtration stages [52]. The combination of hydrodynamic shear, coagulation and flocculation forms the first part of the technological aspects of the treatment used during SEFS treatment.

The second technological aspect employed in SEFS technology is: (i) induced and (ii) dissolved air flotation, renowned for its capacity to generate a highly distinct waste stream consisting of solid and liquid components, while also exhibiting exceptional rates of water recovery [53]. Flotation is a separation process that relies on the utilization of gas bubbles as the primary means of transportation. In this process, the suspended particulate matter becomes adhered to the bubbles, direct impaction of the bubble with a larger floc as well as incorporation into the floc, thereby, facilitating the upward movement towards the water's surface, resulting in aggregation as froth. The origin of flotation technology can be traced back to the domain of mineral processing, although its utilization has extended to diverse contexts [52].

The SEFS treatment process thus represents a distinctive combination of shear-induced colloid destabilization, aggregation and flotation. Ultrafine organic and inorganic suspended particles in aqueous solutions are envisaged to be successfully separated and removed by the bubble regime produced during SEFS treatment.

An objective of a winery is to employ the most optimal technological advancements that enable sustainable production practices while minimizing the ecological footprint on natural resources. The implementation of SEFS technology holds promise in mitigating the limitations associated with traditional treatment methods. This technology is envisioned to be capable of effectively treating winery wastewater, resulting in reclaimed water that can be utilized for irrigation purposes or even reused in the production of wine. Additionally, the solid waste (froth) that is produced during the flotation process presents an opportunity for additional cost savings, as the accumulated solids waste could potentially be repurposed as a viable fertiliser for grape vines. A comparative evaluation of the Shear Enhanced Separation and Flotation (SEFS) technology will be conducted in relation to established primary winery wastewater treatment methods, with a focus on the individual winery wastewater treatment efficiencies.

As a result of the treatment system's complexity (being a non-symmetrical system with a liquid component and gas bubbles in a multi-phase medium), it is difficult to estimate the shear rate/speed in the rotor stator mixer design. As a result, revolutions per minute (rpm) have been utilized to quantify and simplify the phrases shear rate and speed used throughout this thesis document.

1.4. Thesis statement

Given the current demand for cost-effective and user-friendly systems that can accommodate limited land availability, integrate well with existing methods, and ensure consistent treatment performance across seasonal fluctuations, it is plausible that the implementation of SEFS technology could effectively resolve primary stage wastewater treatment challenges experienced by wine farms. By reducing the bulk load of contaminants in the primary treatment stage, it creates a favourable environment for further (biological/tertiary) treatment processes to produce better quality wastewater.

Shear enhanced flotation separation technology may decrease retention times, operating footprint, and chemical consumption rates in comparison to conventional coagulation, flocculation, and flotation treatment systems. Therefore, it is envisaged that SEFS technology will comprise innovation, resilience, and a level of novelty that has not been seen before in winery wastewater treatment applications. Once the parameters have been fully understood and effectively optimized, it becomes feasible to develop and construct a pilot plant unit with the objective of treating winery wastewater at a suitable winery.

1.5. Research questions

In this project, the following research questions will be examined:

- Does hydrodynamic shear alone cause colloidal destabilization?
- What levels of shear are required to destabilize colloids in winery wastewater?
- Is it possible to use hydrodynamic shear in a hybrid method that combines coagulation, flocculation and flotation techniques?
- To what extent does shear enhanced flotation separation accomplish processing and separation efficiency?
- Is it possible to incorporate a shear unit with a traditional flotation system?
- Will there be a reduction in the amount of treatment chemicals required, when shear enhanced flotation separation technology is implemented?
- Is it viable to further develop a laboratory-sized system for shear enhanced flotation separation to a pilot-scale plant?
- Does the treated wastewater have a potential end-use?
- How does shear + DAF compare with standard flash mixer + DAF in terms of total costing (chemicals savings vs higher electricity/power use & capital cost difference between shear unit and standard flash mixer)
- Is there a potential use for the solid waste (froth) generated during SEFS treatment of winery wastewater?

1.6. Significance of the Study

Table 1.1 outlines the potential positive impacts of SEFS technology on the South African wine sector:

Table 1.1. Potential beneficial SEFS influence on the South African wine industry.

Classification	**Justification**
Agriculture	The implementation of SEFS technology has the potential to address the financial implications associated with the discharge of untreated wastewater, while also enhancing the suitability of treated wastewater for irrigation purposes. This, in turn, can alleviate the responsibility of municipalities to treat wastewater, resulting in a reduced burden on their resources.
Job Creation	The implementation of SEFS technology may contribute to cost reduction in winery operations, while also offering potential benefits to the supply chain. Consequently, this would result in the creation of additional employment opportunities as well as exercising knowledge transfer within underprivileged communities.
Transformation	SEFS technology is anticipated to enhance the competitiveness and sustainability of the wine industry, thus driving economic transformation and strengthening the country's capabilities.
Global change	Seasonal variations result in significant unpredictability of the wastewater quality and quantity, but the robustness of SEFS technology and its predicted acceptability in treating fluctuating industrial wastewaters may help to reduce the environmental impact of conventional technologies.
Sustainability	SEFS technology has the potential to enhance sustainability within the wine industry. This is primarily due to the potential generation of valuable product streams that result from the treatment of the wastewater. The water that has undergone treatment has the potential to be utilized again in the wine farms' production process and maintenance activities.
Innovation and Infrastructure	SEFS technology may potentially be utilized across various other industries (e.g., dairy, textile etc), resulting in accelerated economic growth, increased investment in the development of human capital, and enhanced employment opportunities. The SEFS technology is also designed to align with policies promoting zero liquid discharge.

1.7. Aims and Objectives.

The objective of this study is to develop and examine a novel hybrid technology, known as shear enhanced flotation separation (SEFS) to transform polluting winery wastewater to a valuable product stream, in a manner that is robust and efficient. The study's aims and objectives are outlined as follows:

AIMS:

1. Investigate the effectiveness of hydrodynamic shear as a parameter in treating winery wastewater.
2. Combine coagulation, flocculation, and flotation with hydrodynamic shear in a hybrid treatment method
3. Compare SEFS treatment efficiency using induced air and dissolved air flotation mechanisms.
4. Reduce turbidity, Total Suspended Solids (TSS), and chemical oxygen demand (COD) levels of winery wastewater.
5. Reduce the dependency on already stressed natural water resources.

OBJECTIVES:

1. Design and fabricate a bench scale SEFS unit.
2. Understand and define the chemical and physical changes taking place in the shear enhanced flotation separation (SEFS) reactor.
3. Design, fabricate and compare a system which uses either induced air flotation or dissolved air flotation.
4. Optimize reaction conditions and parameters to suit the specific wine farm needs.
5. Once optimized, design and fabricate a pilot plant SEFS system to treat larger amounts of wastewater.
6. Investigate the potential of re-using the treated wastewater and solid waste.

1.8. Limitation of the study

This study is envisaged to have certain limitations. These limitations are discussed below:

- **Seasonal dependence**
    - Wine making is a seasonal activity, harvesting/crushing/pressing etc., generally occurs within three months of a year and this is when the most contaminated wastewater can be collected. Thus, this study is limited by not having access to highly contaminated wastewater throughout the year.
- **The SEFS technology is limited to reducing the physicochemical properties of the winery wastewater**
    - The complete removal of highly soluble alcohols, acids, sugars, and compounds like tannins and polyphenols, which are responsible for the presence of organic matter in winery wastewater, cannot be achieved through the use of physicochemical techniques alone. These soluble fractions can be removed by biological treatment but this does not fall within the scope of this study.
- **Literature on hydrodynamic shear applications.**
    - Most hydrodynamic shear studies involve theoretical models, whilst its application is limited to mineral and emulsion processing. Based on the consulted literature, this is the first application of hydrodynamic shear in combination with coagulation, flocculation and flotation in winery wastewater treatment.

1.9. Thesis outline

The outline provides a concise overview of the topics that will be covered in each chapter.

Chapter 1: Background and Introduction

The present chapter provides an overview of the contextual information pertaining to the research project. This chapter presents the problem, proposed solution, as well as the aims and objectives of the project.

Chapter 2: Literature Review

A literature review is presented regarding the prevalent pollutants typically found in winery wastewater. Herein, a comprehensive analysis of the environmental consequences associated with these pollutants, as well as an examination of the various techniques employed for mitigation is discussed. This chapter provides an investigation of the application of shear enhanced separation in conjunction with advanced flotation techniques. There is a scarcity of research conducted on the topic of hydrodynamic shear induced coagulation, flocculation and flotation for winery wastewater treatment. Therefore, this chapter aims to examine the viability of employing shear enhanced separation methodologies. A large part of this chapter has been submitted by the author of this thesis and accepted for publication in the form of a review paper entitled: **Technological Advances in Winery Wastewater Treatment: A Comprehensive Review**, in the *South African Journal of Enology and Viticulture (Vol. 43., No. 1, 2022)* and is currently archived within the repository of Turnitin, a software system designed for detecting instances of plagiarism.

Chapter 3: Experimental Detail

A questionnaire that was distributed among four wine farms located in the Western Cape region of South Africa is presented. This section provides a detailed overview of the materials and methods employed in this study, highlighting the experimental intricacies of the techniques used for the construction of SEFS technology. The variables that were examined in order to determine the most optimal processing conditions are outlined. The experimental methodology employed for assessing the treatment efficiencies of SEFS technology is elucidated. This chapter additionally presents the design specifications of a laboratory-scale shear enhanced separation and flotation setup, along with the constructed pilot-scale winery wastewater treatment plant.

Chapter 4: Shear Enhanced Flotation Separation Technology in Winery Wastewater Treatment: Laboratory and Abrimix Mobile Treatment Plant Investigations

This chapter highlights the utilization of a laboratory-scale and a mobile unit (supplied by Abrimix Pty Ltd) SEFS unit in a winery located in South Africa. Certain sections of this chapter have been published as a research article entitled: **Shear Enhanced Flotation Separation Technology in Winery Wastewater Treatment**, in *MDPI Water (Vol. 15., No. 13, 2023),* explaining the scientific rationale and application behind the SEFS technology [54]. The study aimed to assess the effectiveness of real-time wastewater monitoring and treatment in determining the reliability of the SEFS system. This evaluation involved analyzing the system's performance under different influent conditions, including variations in organic and inorganic concentration loads and volumes.

Chapter 5: Wastewater Treatment Using Shear Enhanced Flotation Separation Technology: A Pilot Plant Study for Winery Wastewater Processing

In this chapter, the viability of constructing and modifying a pilot plant for the treatment of winery wastewater using shear enhanced flotation separation technology is examined. Various reactor conditions and treatment efficiencies are outlined. A substantial portion of this chapter has been published as a research article entitled: **Wastewater Treatment Using Shear Enhanced Flotation Separation Technology: A Pilot Plant Study for Winery Wastewater Processing** in *MDPI Processes, Special Issue: Separation Processes for Environmental Preservation (Vol. 12., No. 3, 2024).*

Chapter 6: Conclusions

A comparison between the laboratory -scale, mobile treatment plant and pilot scale treatment efficiencies is outlined. An overview of the whole research project (achievements, observations, limitations etc.) is briefly elucidated.

Chapter 7: Recommendations For Potential Future Studies

This chapter presents a summary of possible future research that can be conducted based on the general findings and results gathered in this study. The evaluation of the study findings is conducted by examining its implications in respect to current theory and practice.

Chapter 8:Appendix: Supplementary results discussed in different chapters are displayed in this section. Tables and figures of raw data are also presented in this section.

CHAPTER 2 LITERATURE REVIEW

2.1. Use of relevant databases

The literature review was undertaken by utilizing materials obtained from the library database of the University of the Western Cape (UWC), Google Scholar, and the Vinpro/Winetech (SA Wine) Research library. The objective of the review was to examine the available database of literature, elucidate key concepts, assess the research executed thus far, and highlight the present shortcomings in winery wastewater treatment technology.

The materials included in this study were confined to literature written in the English language, covering the period from about 1980 to 2023. These resources covered books, journal articles, and websites.

To efficiently manage the references acquired from the aforementioned sources, a freely available reference management tool was used. The reference management software used throughout this study was Mendeley Reference Manager.

During the preliminary assessment, an extensive database of research terminology related to winery wastewater treatment facilities was established, focusing on the elimination of organic and inorganic contaminants commonly present in such systems. The identified terms are as follows:

> *Pollution of winery wastewater, efficiency of separation, colloid stability, destabilization mechanism, solid/liquid separation in wastewater, coagulant aids, flotation, colloidal matter aggregation, DAF, contamination of agricultural wastewater, Brownian dynamics in water pollution, encapsulation, aggregate breakup, aggregate stability, shear stress, hydrodynamic shear, conventional, emerging, hybrid winery wastewater treatment techniques.*

To establish relevant keywords for the above-mentioned electronic databases, these terms were further explored. The following were among the research keywords:

> *Agriculture, winery wastewater, induced air flotation, dissolved air flotation, coagulation, effluent, flocculation, colloid phenomena, constructed wetland, aerobic, anaerobic, membrane, advanced oxidation, chemical oxygen demand, suspended*

solids, dissolved solids, turbidity, zeta potential, bubble size, particle size, organic, inorganic, potassium, sodium. vinasse.

Commentaries, editorials, and non-scientific publications were not included in the literature review. The aforementioned screening technique was employed for the material obtained through website searching. Excluded from the analysis were materials sourced from websites, which typically feature less formal and interpretive explanations of a research or investigation.

A large part of this chapter has been previously published as a review article in the South African Journal of Enology and Viticulture, 43(1), 58-80. entitled: Technological Advances in Winery Wastewater Treatment: A Comprehensive Review. https://doi.org/10.21548/43-1-4931.

The objective of this review is to provide a detailed investigation of the currently available body of literature, highlight key concepts, assess the research initiatives undertaken thus far, and identify the prevailing technological deficiencies with regards to winery wastewater treatment. This chapter evaluates the composition of winery wastewater, various treatment techniques employed, the environmental implications associated with winery wastewater, existing knowledge gaps, technological and operational challenges faced in the treatment process, as well as alternative options for disposal and recycling of treated winery wastewater.

2.2. Introduction

A significant proportion of global freshwater withdrawals, approximately 70%, can be attributed to the agricultural sector, while in developing countries, this figure can reach up to 95%. The wine industry encompasses three key sectors of the economy, namely agriculture, manufacturing, and trade [55,56]. In the year 2022, South Africa successfully exported a total of 369 million liters of wine, resulting in a substantial revenue of R10 billion [8]. The wine industry in South Africa is a significant contributor to the country's Gross Domestic Product (GDP), accounting for approximately 9% of the total GDP of the nation [57].

The wine production industry generates substantial quantities of wastewater that are contaminated with elevated levels of both organic and inorganic substances [58]. Typically, a quantity of winery wastewater ranging from 3 to 5 cubic meters is generated per metric tonne of grapes processed [37]. In order to provide a contextual background, it is worth noting that during the 2021/2022 season, the South African wine industry processed a combined quantity of 1.2 million metric tonnes of grapes [10]. Consequently, it can be inferred that the overall amount of wastewater produced during this particular vintage season ranged between approximately 3.6 and 6 million cubic meters. **Table 2.1** compares the quantity of grapes processed (in tonnes), to the estimated volume of wastewater generated (in cubic meters), in a South African, Australian and USA context.

Table 2.1. Quantity of grapes processed vs wastewater produced during 2022 harvest season.

Geographical Winery Location	Quantity of Grape s Processed (tonnes)	Estimated Wastewater produced (m^3)	Reference
South Africa	1.2 million	3.6 - 6	[10]
Australia	1.7 million	5 -10	[59]
United States of America	3.6 million	10.5 - 17.5	[60]

These volumes of wastewater generated is a matter of concern due to the combination of limited water resources and a continuously expanding population, which has resulted in the global challenge of insufficient access to high-quality water [61,62]. The volume of wastewater that wineries produce creates additional discharge-related sustainability challenges. This is made worse by the different amounts, characteristics, and consistency of wastewater from wineries, which varies according to the season and often contains compounds that are harmful to the environment. Consequently, ensuring appropriate disposal becomes an imperative undertaking [63].

Wineries function as distinct entities, characterized by variations in size and winemaking practices, which consequently contribute to the diversity in both the volume and quality of wastewater produced during the process of vinification. Total suspended solids (TSS), total dissolved solids (TDS), and chemical oxygen demand (COD) are all more elevated in the wastewater produced by wineries accompanied by inherent low pH, and variable salinity and nutrient concentrations. These characteristics collectively suggest that winery wastewaters have the potential to pose environmental risks [23]. The subsequent sections of this review will address the fluctuations observed in the levels of these parameters.

The environmental consequences associated with winery wastewater are significant and encompass various aspects. These include the contamination of water bodies, the deterioration of soil quality, harm to vegetation resulting from wastewater disposal methods, and the emission of unpleasant odors primarily caused by the substantial organic content found in these wastewaters [64]. The majority of wineries employ wastewater treatment methods, but ongoing research and proposals focus on enhancing the treatment process to optimize efficiency and adaptability in managing variations in impurity concentrations (both organic and inorganic species) and wastewater volumes. These alternative methods also aim to moderate capital costs, simplify operation and maintenance, reduce spatial requirements, and ensure compliance with specified discharge standards for winery wastewaters [65].

The following section presents a detailed overview of the contaminants typically encountered in winery wastewater, along with the associated parameters used for their detection. The determination of winery wastewater characteristics will provide valuable information regarding the nature and quantity of pollutants present, enabling wineries to select an appropriate treatment method based on the average concentration of contaminants detected in their specific wastewater samples.

2.3. Winery wastewater characteristics

The wastewater produced during the commercial winemaking process is composed of a wide range of elements that differ not only between wineries but also according to their respective sizes. The wine production process comprises five distinct stages, namely: (i) harvesting, (ii) crushing, (iii) fermentation, (iv) racking and clarification, as well as (v) aging and bottling. According to a study by Chapman *et al.*, (2001), it has been observed that during the harvest season, a significant proportion of winery wastewater, approximately 80%, is generated by small wineries. On the other hand, medium to large wineries generate around 50% of their wastewater during the same period [36].

The quantity of winery wastewater produced per unit volume of wine ranges from 0.2 to 4 liters [13]. The acidic pH levels (pH 3 - 5) commonly observed in winery wastewaters can be primarily attributed to the presence of organic acids, including lactic, tartaric, citric, malic, and succinic acid [66,67]. The electrical conductivity (EC) values of winery wastewater have been documented to fall within the range of 1.62 – 6.15 mS/cm [26]. The concentrations of total nitrogen (TN) and total phosphorous (TP) nutrients in winery wastewater vary from 100 to 640 mg/L and 240 to 657 mg/L, respectively, as reported in previous studies [68,69]. The quantification of organic pollution in wastewater is a crucial task, for which the chemical oxygen demand (COD) serves as a significant parameter. The chemical oxygen demand (COD) in winery wastewaters is primarily the result of soluble alcohols, sugars, recalcitrant compounds such as polyphenols, acids, tannins, and lignin [70]. The literature reports indicate that winery wastewater typically exhibits a minimum COD of 340 mg/L, a mean of 11,600 mg/L, and can reach maximum levels as high as nearly 300,000 mg/L [23,70,71]. Extensive investigations pertaining to the composition of winery wastewater have yielded findings indicating that a significant proportion, up to 90%, of the organic load is comprised of ethanol and sugars, namely glucose and fructose [72].

Untreated winery wastewaters that contain the above described organic and inorganic elements have the capacity to cause natural streams, rivers, and dams to become saline and eutrophic. Additionally, if untreated wastewater is discharged through irrigation, it can result in soil salinity and contamination with various chemicals [73]. The efficacy of the wastewater treatment plant and the chemical makeup of additives used in wine-making operations are the main factors influencing the quality of treated winery wastewater [19].

Winery waste can be classified into two distinct categories: (i) solid waste materials, such as seeds, pomace, and lees, which are generated during the processes of destemming, pressing, and settling; and (ii) wastewater, specifically referring to wash and rinse water [74]. Grape pomace, a type of solid waste, comprises various components such as skin, stem, residual pulp, seed, stalks, and yeast cells resulting from the fermentation process [75]. The pollutants present in winery wastewaters can further be categorized into two main groups: organic and inorganic compounds. In order to better understand the intricate nature of winery waste, **Table** 2.2 presents an overview of the diverse chemical constituents present in wine. These constituents play a significant role in contributing to both organic and inorganic pollution within wastewater.

In broad terms, wine is composed of various components such as water, alcohols, sugars, acids, phenolics, minerals, nitrogenous compounds, vitamins, and volatile compounds. Each of these constituents plays a role in shaping the distinct aromas, taste, and overall sensory experience of the wine, ultimately influencing its perceived quality. The presence of potassium (K^+) and sodium (Na^+) salts in winery wastewater is primarily attributed to the natural occurrence of K^+ in grapes and the byproducts generated during grape fermentation [76].

Table 2.2. Chemical composition of wine [77–80].

Chemical Component	Wine (mg/L)
Carbohydrates	10,000 – 20,000
Alcohol (Ethyl alcohol)	100,000 –140,000
Glycerol	5,000 – 15,000
Organic acids	
- Tartaric acid	2,000 – 5000
- Lactic acid	200 – 400
-Malic acid	1,000 – 8,000
- Succinic acid	200 – 1,500
- Citric acid	100 – 500
Minerals	2,000 – 4,000
Calcium as Ca^{2+}	34 – 140
Chlorine as chloride	<500
-Mg^{2+}	60 – 150
- K^+	660 – 1160
- $PO4^{3-}$	<500
- $SO4^{2-}$	<300
Tannin and colour pigments	100 – 2,000
Nitrogenous Matter	200 – 800
Amino acids	50 – 800
Protein and other nitrogenous matter (humin amide, ammonia and others)	100 – 350
Volatile acids (acetic)	<1200
Esters (Ethyl acetate)	44 – 257
Aldehydes (acetaldehyde)	15 – 200
Higher alcohols (isoamyl, methyl, butyl, isobutyl, propyl)	11 – 311
Vitamins (thiamine, riboflavin, pyridoxine, and ascorbic acid)	Traces

The assessment of K^+ and Na^+ levels in winery wastewater holds significance in the context of utilizing such wastewater for vineyard irrigation. These ions play a crucial role in soil fertility, with K^+ having a greater impact than Na^+. However, excessive concentrations of these ions can have detrimental effects on plant growth. The prevalence of these ions is additionally associated with the utilization of alkaline cleaning agents employed in the process of wine production. The conventional cleaning procedure during wine production commonly entails the use of caustic cleaning agents, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH). These chemicals are used for the purpose of eliminating solid accumulations of tartrate and other organic acids that are typically bound to the inner surfaces of vessels and equipment. Subsequently, solutions containing diluted citric and tartaric acids are employed as acidic agents for the purpose of removing caustic residues. As a clean-up step, clean water is then used for the purpose of eliminating residual cleaning substances [36].

Table 2.3 presents an overview of prevalent contaminants and associated detection parameters identified in winery wastewater. In addition to organic matter, nitrogen and phosphorous are significant areas of focus. The release of these substances into wastewater has the potential to cause eutrophication and result in the decline of aquatic organisms [13].

Table 2.3. Summary of common winery wastewater pollutant detection parameters as reported in literature.

Parameter	Unit	Min	Max	Average	Reference
Chemical oxygen demand (COD)*	mg/L	340	296,119	11,554	[20,46,68,73,76,80–88]
Biochemical oxygen demand (BOD)**	mg/L	125	130,000	8,024	[23,31,58,74,89–92]
Total Solids	mg/L	1,602	79,635	11,311	[26,74,76,93–95]
Total volatile solids	mg/L	130	54,952	4,174	[65,96–98]
Suspended Solids	mg/L	60	30,300	1,435	[14,23,46,58,68,99,100]
pH		3.0	12.9	5.3	[2,20,46,100,101]
Total Nitrogen	mg/L	10	415	110	[14,23,31,87,102–104]
Phosphorous	mg/L	3.3	188.3	39.5	[2,13,66,91,105–107]
Potassium	mg/L	7	1,000	400	[23,74,76,105,108]
Sodium	mg/L	29	460	241	[20,23,74,76,105,108,109]

*COD is a parameter measurement of the oxygen equivalent of organic materials in wastewater and extensively used as an indicator of wastewater quality [110].

**BOD is the measurement of the amount of oxygen consumed by microorganisms in decomposing organic matter in liquid streams.

A detailed account of the various classes of contaminants typically encountered in winery wastewater is provided in **Table 2.4**, along with the respective sources and the corresponding environmental impacts. Grape juice, wine, and lees are the sources of organic contaminants like phenols, ethanol, and sugars. These materials also add to the wastewater from wineries' excess of nutrients, including phosphate and nitrogen. The environmental impacts encompass the emission of unpleasant odors and an overabundance of nutrients in the wastewater.

Table 2.4. Contaminants commonly found in winery wastewater, sources and possible environmental effects [25].

Contaminant Class	Examples	Sources	Environmental Effects
Organics	Phenols, tannins, glucose, glycerol, ethanol, citric acid, tartaric acid	Juice, wine and lees losses, residues in cleaning waters and filters, solids reaching drains	Organism deaths, odors generated by anaerobic decomposition, solubilization of nutrients and heavy metals
Nutrients	Nitrogen, Phosphorus, Potassium	Juice, wine and lees losses, washings, and ion exchange	Surplus nitrate in water results in eutrophication
Salinity	NaCl, KCl	Juice and wine, cleaning agents	Impacts water taste, toxic to plants
Sodicity	Sodium	Wash water	Degradation of soil structure, toxic to plants
Heavy Metals	Al, Cd, Cr, Co, Cu, Ni, Pb,	Al, Cu, piping and tanks, brass fittings	Adversely affects toxicity in plants and animals
pH effects	Organic, sulfuric and phosphoric acids, sodium, magnesium and potassium hydroxides	Juice, wine and lees losses, cleaning agents, wine stabilization	Toxicity to macro and microorganisms, effect on solubility of heavy metals
Disinfectants	Sodium chloride, sodium hypochlorite	Sterilization of tanks, bottles, transfer lines	Formation of carcinogens (e.g., Trihalomethanes; THM)

The cleaning procedures employed in wineries make a substantial contribution to the overall volume of wastewater produced. **Table 2.5** provides a summary of the effects of the primary winemaking processes on the generation of wastewater in wineries and its subsequent impact on the quality of the wastewater. The potential environmental impacts that affect the established parameters for legal wastewater quality are also demonstrated [73]. The significance of these processes in generating winery wastewater necessitates the implementation of a treatment method to ensure compliance with environmental regulations, as elaborated in the subsequent section.

The majority of wineries have implemented wastewater treatment systems, but ongoing research is focused on identifying alternative methods that aim to optimize the treatment process. These techniques seek to accomplish multiple goals: The goals of the treatment process are to: (i) increase its flexibility and efficiency to handle variations in wastewater volumes and impurity concentrations; (ii) moderate capital costs; (iii) guarantee ease of operation and maintenance; (iv) minimize spatial requirements; and (v) meet the required discharge standards for winery wastewaters [65].

Table 2.5. Significant processes associated with winery wastewater generation, its role in wastewater quantity, quality and effects on legal wastewater quality parameters [73].

Winery operation	Contribution to total wastewater quantity	Contribution to wastewater quality*	Effect on legal wastewater quality parameters*
Cleaning water			
Alkali washing (removal of K bitartrate), neutralization)	Up to 33%	Increase in Na^+, K^+, COD and pH	Increase in EC, SAR, COD and pH
Rinse water (tanks, floors, transfer lines, bottles, barrels, etc.)	Up to 43%	Increase in Na^+, P, Cl^-, COD	Increase in EC, SAR, COD, Variation in pH
Process water			
Acidification and stabilization of wine	Up to 3%	H_2SO_4 or NaCl	Decrease in pH
Cooling tower waste	Up to 6%	Various salts	Increase COD and EC

*Chemical oxygen demand, Electrical conductivity, SAR: Sodium adsorption ratio

In South Africa, the Department of Water and Sanitation (DWS) encourages wineries to irrigate their wastewater. However, it is a requirement for wineries to register the intended end-use of the wastewater before commencing irrigation. In order to properly implement the intention of irrigating wastewater, it is important to strictly follow the rules outlined in the General Authorization as shown in **Table 2.6** [5]. The authorizations additionally stipulate that ground or surface water contamination is strictly prohibited, and measures must be taken at all times to prevent over-irrigation, waterlogging, and the degradation of soil qualities [2]

Table 2.6. General Authorizations for legislated limits for irrigation water quality in South Africa [5]

	Maximum irrigation volume allowed (m^3/day)		
Parameter*	<50	<500	<2 000
pH	6 - 9	6 - 9	5.5 – 9.5
Fecal coliforms (per 100 mL)	1,000,000	100,000	1,000
COD (mg/L)	5,000	400	75
EC (mS/m)	200	200	70 - 150
SS	-	-	<25
SAR	<5	<5	<5

*(COD) - Chemical oxygen demand; (EC) - Electrical conductivity, (SS) Suspended Solids; (SAR) - Sodium adsorption ratio.

Given that wineries differ greatly in terms of wastewater production and contamination levels, it appears nearly impossible to design ecologically acceptable and sustainable waste treatment solutions that are applicable to all of them. This is further supported by the fact that there is not a single treatment method that wineries can use to achieve the same results. Therefore, in order to take a reasonable approach to the identification and execution of suitable treatment procedures, it is important to have a basic understanding of the origins and final destination of winery wastewaters. The management of the winery's wastewater quality can be achieved through the implementation of control measures that regulate the entry of substances into the waste stream. To effectively address the management of winery wastes and mitigate the potential environmental consequences, it is imperative for wineries to identify the potential pollutants, their sources and locations of generation, and the available management strategies to minimize its impacts [36].

In the section that follows, the principles of treating wastewater from wineries are covered, along with new and established physicochemical, biological, advanced oxidation, and hybrid wastewater treatment technologies that are particularly relevant to the wine-producing sector. Here, knowledge gaps, operational technological difficulties, and alternative solutions for disposing of and reusing treated winery wastewater are assessed.

2.4. Winery Wastewater Treatment

Appropriate steps can be taken to enhance wastewater quality and reduce volume if an in-depth understanding of water usage and the presence of pollutants in waste streams is attained. The purpose of this section is to address the most appropriate treatment techniques for a given winery's unique wastewater treatment needs, especially with regard to the wastewater's intended final use. It is essential to consider the following elements while selecting the appropriate treatment technology to use:

I. Characteristics of winery wastewater,

II. Minimum requirements for the quality of wastewater (for example, irrigation, municipal discharge, etc.),

III. Availability of space, annual budget and capital, and technical proficiency necessary to operate the treatment system at the winery.

If wineries carefully assess the aforementioned factors, the subsequent discussion on treatment options may offer sufficient guidance for choosing a treatment technology that is suitable for the intended use of the treated wastewater.

2.5. Winery Wastewater Treatment Technologies

Several studies have been carried out to examine diverse methodologies for mitigating the difficulties involved in the disposal of effluent in wineries [23,111,112]. In general, wineries implement a sequence of treatment stages, which consist of preliminary, primary, secondary, and tertiary operations. The utilization of a final clean up step for disinfection of the treated wastewater is a common practice, with its effectiveness heavily dependent upon the intended purpose of the wastewater. This section of the review will primarily examine three fundamental treatment variations, along with a variety of derivative methods. These methods have the potential to effectively achieve wastewater treatment objectives when employed in an appropriate combination. The three main treatment variations are as follows: (i) physicochemical treatment, (ii) biological treatment, and (iii) advanced oxidation treatment. The diagram presented in **Figure 2.1** depicts common procedures employed in the collection and treatment of winery wastewater.

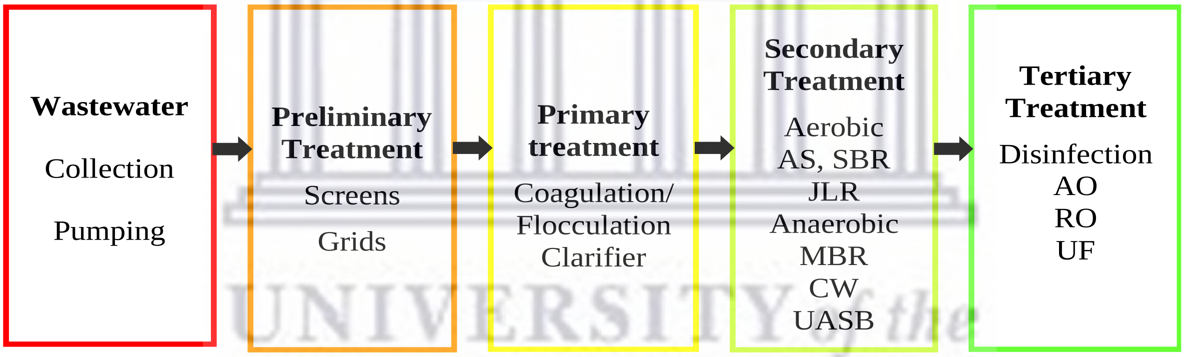


Figure 2.1. Winery wastewater collection and treatment steps. AS (Activated sludge), SBR (sequencing batch reactor), JLR (jet-loop reactor), MBR (membrane bioreactor), AO (Advanced oxidation), RO (Reverse osmosis), UF (ultrafiltration).

2.5.1. Preliminary Winery Wastewater Treatment

The majority of wastewater treatment processes typically incorporate a physical treatment phase, aimed at the separation and sedimentation of solid particles contained within the wastewater. The described step is characterized by its simplicity, effectiveness, and its ability to prevent the accumulation of solid materials such as seeds, stalks, and leaves in primary and secondary treatment equipment [23]. The process involves employing screens/grids to eliminate substantial components (such as skins, pips, stems, and lees) with particle sizes exceeding 500 µm, while filters are utilized for particles within the range of 100 – 500 µm [113].

2.5.2. Primary Physicochemical Treatment Methods

Physicochemical treatment methods involve a combination of both physical and chemical procedures to affect the physical characteristics of colloidal particles through the use of chemicals. This alteration in properties enhances the particles' stability and renders them more susceptible to coagulation for subsequent treatment [114]. The application of this treatment methodology has the potential to significantly impact the biodegradation capacity of organic matter in winery wastewater. The technique of chemically assisted settling, employing flocculation, is commonly employed for the treatment of fine particles having a particle size smaller than 10 µm [20]. Physicochemical treatment techniques, including coagulation and flocculation, sedimentation tanks, centrifugation, and microfiltration, are used to efficiently extract suspended solids/matter from wastewater [115]. Physicochemical treatment is commonly used as an initial measure to reduce the organic content and cloudiness of winery wastewater before it undergoes biological treatment [116]. These treatment methods offer several advantages. Firstly, they can reduce sludge buildup and minimize wear on treatment pumps. Secondly, these methods can decrease the concentration of biochemical oxygen demand (BOD) in wastewater, making it suitable for discharge or reuse. Thirdly, the addition of chemicals during physicochemical treatment can enhance its efficacy. For example, adjusting the pH can facilitate the rapid settling of solids. Additionally, these techniques may improve the appropriateness of wastewater for land disposal [20].

Winery wastewater has been treated using a variety of physicochemical treatment techniques. These techniques include sedimentation on land, coagulation and flocculation, electrocoagulation, and chemical precipitation using chelating agents [14]. For winery wastewater, coagulation and flocculation are frequently used as one of the main primary treatment methods.

2.5.2.1. Coagulation and Flocculation

The assessment of treatment efficiency in this specific technology entails evaluating key parameters like total dissolved solids (TDS), turbidity, and chemical oxygen demand (COD). The purpose of the coagulation/flocculation process is to destabilize the colloidal matter and promote the formation of bigger flocs by aggregating small particles. This makes it easier to eliminate them from wastewater. This treatment process aims to reduce the turbidity, natural organic matter, and inorganic substances present in the wastewater [117]. The process encompasses two main steps. Firstly, the dispersed coagulant is rapidly mixed into the liquid matrix through intense agitation. Secondly, small particles are agglomerated into distinct flocs through flocculation, which is facilitated by moderate agitation. Following that, the flocs undergo sedimentation and are eventually removed as sludge, while the treated water can be discharged or directed for further processing [118].

The process of coagulation takes place when coagulants, such as aluminum and iron salts (e.g., aluminum sulfate, aluminum chloride, ferric chloride, ferrous sulfate, etc.), are introduced and vigorously mixed with the wastewater generated by wineries [114]. The primary function of the coagulant is to counterbalance the typically negative charges present on the surface of colloidal particles. In the absence of these coagulants, colloids have the potential to create a stable suspension, characterized by particle sizes ranging from 0.01 to 1 μm [46]. After inducing the destabilization of colloid suspensions and introducing flocculants, sedimentation has traditionally been utilized as a pre-treatment method, which has been documented to effectively reduce TDS), turbidity, and, in certain instances, COD in winery wastewater [119].

Sedimentation is a process that involves the separation of suspended particles by means of gravitational force, which arises from the difference in density between the particles and the surrounding fluid. Sedimentation can be used either before coagulation to reduce the amount of coagulant chemicals needed, or after coagulation or flocculation to decrease the concentration of suspended solids. This decrease in solids concentration helps to reduce the concentration load before it reaches downstream processes like filtration [120]. **Figure 2.2** depicts a conventional coagulation, flocculation and sedimentation process, which is commonly employed in water treatment systems.

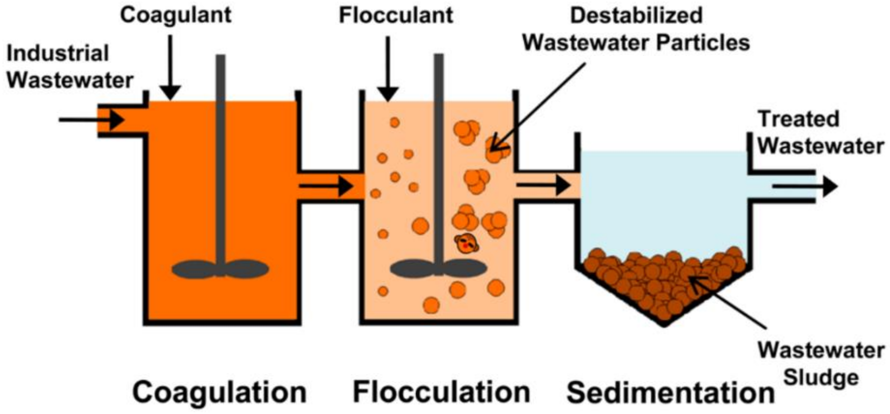


Figure 2.2. Coagulation, flocculation and sedimentation process employed during wastewater treatment [118].

The efficacy of a pre-treatment technique utilizing chemical precipitation with chelating agents, specifically 2,4,6-trimercaptotriazine (TMT), was evaluated in a study done by Andreoletta *et al*., (2007) [121]. The researchers examined the decrease in levels of suspended solids and heavy metals (copper and zinc) in raw/untreated winery wastewater, which had a chemical oxygen demand ranging from 3,090 to 7,438 mg/L [121]. The researchers conducted laboratory-scale experiments employing jar tests to identify the optimal doses of TMT and the efficiency of metal elimination. Subsequently, they conducted a pilot-scale investigation where chemical precipitation was accomplished through the sequential addition of various substances. Firstly, sodium hydroxide (NaOH) was introduced to correct the pH. Thereafter, TMT was added at a dosage of 0.84 mL of TMT (15%) per 1 mg of copper removed. Additionally, a cationic polymer and polyelectrolyte (flocculant) were employed, followed by the settling process. The researchers observed a substantial decrease in TSS from 281 to 28 mg/L, representing a reduction of 90%. Additionally, there was a noteworthy reduction in the concentration of heavy metals, with copper levels decreasing from an average of 1.09 to 0.041 mg/L, indicating a reduction of 96%. Similarly, zinc levels decreased from 0.68 to 0.154 mg/L, resulting in a reduction of 76%. This discovery held significant importance as it aligned with the discharge thresholds outlined in The Italian regulations for copper and zinc at that time were set at concentrations of 0.4 mg/L and 1.0 mg/L, respectively. The study further observed a reduction in COD values through the use of TMT, with a decrease of less than 9% (from 4,720 to 4,302 mg/L). The observed decrease in concentration by approximately 418 mg/L was ascribed to the reduction of particulate matter in the COD and the precipitation of suspended solids. As per the authors, the reason for the modest 9% decrease in COD could be the high concentration of around 92% of organic matter in the winery effluent, which is dissolved in solution. Additionally, the authors noted that the process of chemical precipitation is ineffective in removing dissolved compounds, further contributing to the observed reduction limitations [121]. A thorough economic analysis was undertaken to assess the expenses associated with treating winery wastewater. This analysis considered multiple elements, such as the expenses associated with chemical doses, plant administration, electricity usage, sludge disposal, wastewater quality regulation, and taxes linked to wastewater discharge to the municipality. Based on the aforementioned variables, an estimation was made regarding the mean expense associated with treating winery wastewater. The study concluded that high-quality wineries located in the Province of Trento, Italy, would have an average expense of €14.6 per cubic meter for treating wastewater.

Rytwo *et al.*, (2011) used a two-step approach to decrease the amount of dispersed solids in winery wastewaters. They achieved this by using raw sepiolite (0.1%) and crystal violet modified sepiolite (0.1%), which led to the formation of bigger particles. The researchers examined the impact of a two-step procedure on wastewater, comparing the results obtained from both untreated wastewater (pH 4.9, COD 4,940 mg/L) and pH-corrected wastewater (pH 7.0, COD 2,120 mg/L). The application of this technique resulted in a significant reduction in total suspended solids levels. The concentration of TSS dropped by 96% (from 1,600 mg/L to 70 mg/L) for wastewater that underwent pH correction, and by 98% (from 1,400 mg/L to 10 mg/L) for untreated wastewater. The turbidity of the treated wastewater was decreased to 55-65% of the starting values for both pH-adjusted (initial value of 163.3 NTU) and untreated wastewater (initial value of 130.3 NTU). The authors noticed a slight decrease in COD, with reductions ranging from 20% to 40% in both the treated and untreated samples. The presence of a significant amount of dissolved organic matter in the wastewater, which does not undergo coagulation, was linked to this occurrence [122].

Rizzo *et al.*, (2010) conducted a study to examine the utilization of chitosan, a natural organic coagulant, for the treatment of winery wastewater. The objective was to investigate the feasibility of chitosan as a substitute for conventional metal-based coagulants, while simultaneously evaluating its capacity to generate reusable organic sludge. The use of the coagulant led to a substantial reduction in turbidity (92%, from an initial turbidity of 180 NTU), COD (73%, from an initial COD of 1,550 mg/L), and TSS (80%, from an initial TSS of 750 mg/L). These reductions were observed at an optimal chitosan dosage of 20 mg/L and a pH of 6.8. The researchers also examined the effects of suboptimal chitosan dosage in their study, observing particle bridging and effective settling of aggregates. On the other hand, an excessive amount of chitosan dosage resulted in the reversal of particle charge in the suspension, which can be attributed to an increased rate of formation of positively charged chitosan-solid aggregates. Because of this, there was an electrostatic repulsion, which made the settling process less effective [93].

Braz *et al.*, (2010) examined the treatment of winery wastewater using four distinct coagulants: ferric sulfate, ferric chloride, alum, and calcium hydroxide [46]. The initial chemical oxygen demand concentration ranged from 31,369 to 38,391 mg/L. The sample volume used in their study was 500 mL. Aluminium sulfate, commonly known as alum used, exhibited an effective treatment efficiency pH range of 5 to 7. The recommended coagulant volume for alum was 20 mL, with a concentration of 2,000 mg/L. On the other hand, ferric chloride and ferrous sulfate had a pH range of 5 to 8. For these coagulants, the recommended volume was 10 mL, also at a concentration of 1,000 mg/L. Lastly, calcium hydroxide, which falls within the same pH range of 5 to 8, required a coagulant volume of 20 mL at a concentration of 2,000 mg/L. The researchers found that achieving an optimal pH of 5 and using an appropriate dosage of coagulant resulted in a highly effective reduction of turbidity, with a removal rate of 92.6% when using aluminium sulfate. Additionally, the use of calcium hydroxide led to a significant removal of total suspended solids, with a removal rate of 95.4%. With the exception of ferric chloride, the coagulants employed in this study exhibited a reduction in TSS and turbidity exceeding 60%. However, the average reduction in COD for all coagulants was found to be less than 30%. Subsequently, the researchers assessed the efficacy of prolonged aerated storage in conjunction with the coagulation/flocculation procedure. The findings of the study indicated that the addition of calcium hydroxide as a coagulant to the long-term (an aeration period of 4 h/day and a hydraulic retention time of 11 weeks.) aerated storage wastewater, under optimal operating conditions, resulted in significant reductions in various parameters. Specifically, a reduction of 84.5% in COD, 96.6% in turbidity, 98.7% in volatile suspended solids (VSS), and 99.1% in total TSS were achieved. These results suggest that calcium hydroxide is the most suitable coagulant for achieving effective treatment of the mentioned wastewater.

Table 2.7 presents a summary of the various coagulants used in the above studies, along with the respective impacts on the mitigation of total suspended solids (TSS), turbidity, volatile suspended solid (VSS), and chemical oxygen demand (COD).

Table 2.7. Coagulant type and effects on winery wastewater pollutant parameters.

Coagulant used	Achieved reduction (%)				Ref
	TSS	Turbidity	VSS	COD	
2,4,6-trimercaptotriazine (TMT)	90	-	-	9	[121]
Sepiolite	98	44	-	40	[122]
Chitosan	80	92	-	73	[93]
Calcium hydroxide	95	80	96	30	[46]
Aluminium sulfate	82	63	82	21	[46]
Ferric chloride	86	23	86	15	[46]
Ferrous sulfate	84	69	83	25	[46]
Calcium hydroxide + long-term aerated storage	99.1	96.6	98.7	84.5	[46]

In addition to chemical coagulation, electrocoagulation has garnered significant attention as a viable method for winery wastewater treatment. The subsequent section provides an overview of the electrocoagulation process and examines relevant literature pertaining to its application in the treatment of winery wastewater.

2.5.2.2. Electrocoagulation

Electrocoagulation is a process that involves the application of direct current electrolysis to wastewater, wherein metallic electrodes made of iron or aluminum (specifically, an anode and a cathode) are immersed in the wastewater. The treatment technology involves two main electrochemical reactions. At the anode, the positively charged ion (either Fe^{2+} or Al^{3+}) is discharged into the solution. At the cathode, water undergoes reduction, resulting in the production of hydrogen gas in the form of bubbles and hydroxyl ions [123]. Electrocoagulation involves the generation of highly charged cations by the anode, which leads to the destabilization of colloidal particles via the formation of mono- and polymeric hydroxo complex species [124]. The metal hydroxo complex species exhibit notable adsorption characteristics, leading to the formation of robust aggregates containing pollutants present in wastewater [124]. The utilization of this procedure has been widely employed in the context of industrial wastewater treatment and has garnered growing attention in the realm of agricultural wastewater treatment [125].

Kirzhner *et al.,* (2008) examined the utilization of electrocoagulation as a means of treating winery wastewater in preparation for subsequent processing. The findings of their research demonstrated that a maximum of 42% of chemical oxygen demand was eliminated, with an initial influent concentration ranging from 1,500 to 17,000 mg/L. In contrast, biological oxygen demand (BOD), with an initial influent values ranging from 1,500 to 2,500 mg/L, exhibited only a partial removal of 28%. The experimental configuration comprised of a pair of aluminium electrodes, positioned at a distance of 1.5 cm from each other. These electrodes were linked to a direct current (DC) power source, which was set to operate at a current of 2.5A and a voltage of 10V. The duration of the experiments varied between 10 and 40 minutes. Subsequently, the researchers introduced ozone gas at a flow rate of 1 L/min, resulting in a marginal improvement in COD reduction from 42% to 48%. The introduction of a 2.5% hydrogen peroxide (H_2O_2) resulted in a significant increase in the COD levels, escalating from 11,172 mg/L to 21,700 mg/L within a 40-minute period. The study examined a two-stage methodology aimed at improving the efficiency of COD removal. In the first stage, the wastewater underwent electrocoagulation treatment, while in the second stage, purification was achieved through the utilization of aquatic plants, specifically salt marshes containing rushes. After a treatment period of 23 days, the utilization of this particular configuration in conjunction with aeration resulted in a substantial reduction of 97.5% in BOD and 98.2% in COD [126]. The decrease in COD and BOD was ascribed to the superior sorption properties and rapid reproductive capacity of aquatic plants, in comparison to the utilization of electrocoagulation as a stand-alone technique.

Kara *et al.*, (2013) used electrocoagulation with aluminium and iron electrodes during their treatment of winery wastewater. After optimization, the working conditions for the iron electrode were as follows: The pH was 7, with a current density of 300 A/m^2, and an operating period of 90 minutes. For the aluminum electrode, the pH was 5.2, the current density was 300 A/m^2, and an operating period of 120 minutes. The removal efficiencies under these conditions of COD (initial influent 25,200–28,640 mg/L) and turbidity (initial influent 2490 NTU) were found to be 46.6% and 92.3%, respectively for the Fe electrode whereas that of Al was 48.5% and 98.6%, respectively. The COD values remained excessively high (Al: 13,180 mg/L and Fe: 15,200 mg/L) even after treatment with both electrodes, making it unsuitable for disposal. This suggests that electrocoagulation is ineffective in reducing COD values to meet the legal limits for discharge [127].

In a pre-treatment step, Orescanin *et al.*, (2013) used electrocoagulation to treat winery wastewater using electrode sets made of stainless steel, iron, and finally aluminum in conjunction with sonication and a sodium chloride support electrolyte. Their experiment had removal efficiencies of 55% COD reduction (10,240 mg/L initial influent vs. 4,580 mg/L final treated wastewater), 98% turbidity reduction (3,190 NTU initial influent vs. 61 NTU final treated wastewater), and 98% suspended solids reduction (2,680 mg/L initial influent vs 52 mg/L final treated wastewater). The authors proposed that the removal of suspended particles could be ascribed to the coagulation/flocculation process, which was aided by the release of Fe^{2+}, Fe^{3+}, and Al^{3+} ions into the treated solution through electrochemical corrosion of sacrificial Fe and Al steel electrodes. This procedure involved the formation of hydroxides and the subsequent simultaneous formation of Fe and Al hydroxides.

Electrocoagulation has several notable advantages, such as its compact spatial footprint, high level of automation capabilities, and the absence of chemical additives. Consequently, this technique produces lower levels of secondary contamination and reduces the amount of sludge compared to chemical coagulation procedures. On the other hand, the periodic replacement of sacrificial anodes and the energy demands pose additional challenges in the operation of this process [128]. Hence, unless renewable energy can be used to supply power to the electrodes, this treatment option may not be feasible in countries that frequently experience electricity shortages.

The aforementioned investigations on electrocoagulation treatment indicate that making use of common aluminum (Al) and iron (Fe) electrodes leads to significant efficacy in eliminating turbidity. However, these electrodes do not exhibit significant effectiveness in reducing COD, as evidenced by COD reduction levels consistently below 60% in all instances (as indicated **Table 2.8**). Therefore, this approach could potentially serve as a preliminary measure to partially decrease the organic content of the wastewater before implementing secondary treatment techniques, like biological treatment, to further remove soluble organic components in the wastewater. This will be elaborated on in subsequent sections.

Table 2.8. Electrochemical treatment comparison of winery wastewater

Electrode(s) used	Achieved reduction (%)		
	Turbidity	COD	Reference
Al	-	42	[126]
Al	44	40	[127]
Fe	99	49	[127]
Stainless steel, Al, sonication	98	55	[129]

2.5.3. Flotation

Flotation methods have been extensively and effectively employed in the treatment of minerals. In recent years, there has been a greater awareness of employing these methods as an alternate approach to treat various types of wastewaters [130–132]. In contrast to alternative methods, Flotation technologies have demonstrated success in systems characterized by small differences in density between the continuous phase and particulate phase [53,133,134]. Flotation is a separation method that relies on the use of gas bubbles as the means of transportation. In this process, the suspended particulate matter adheres to the bubbles and ascends towards the water's surface, eventually being collected as froth. The bulk of floc-bubble interaction is by the small, (<100 μm) bubble impacting somewhere along the bottom of the (much larger, 500 - 3000 μm) floc. Therefore, only the (mostly small mass fraction of) very small flocs are removed by adhering to the bubble, and only if coagulation achieves a close to an iso-electric point [135–137]. The process originated in the industry of mineral processing but has also been applied in other areas such as in the use upstream of sorbent materials [134].

Flotation devices are in most cases, compact equipment and require low operational energy. According to a study done by Yoon (1993), “the first order flotation rate is directly proportional to the superficial gas rate and varies approximately as the inverse cube of bubble size”. This effectively means that a smaller bubble size (microbubbles) is more effective in increasing the flotation rate as opposed to the gas rate [138].

The flotation technologies used for wastewater treatment includes induced air/gas flotation (IAF) and dissolved air flotation (DAF). The principles of operations and differences is discussed on the following subsections.

2.5.3.1. Induced Air/Gas Flotation

An induced air flotation (IAF) process uses only mechanical mechanisms, such as impellers, air jet nozzles, or venturi devices to extract air directly from the environment above the atmospheric liquid level and introduce it to the water. Large air bubbles (in range of 100 – 1,000 microns) are produced by the induced air flotation method [139]. Air bubbling or sparging, when implemented under suitable conditions, serves as a transport mechanism for induced air flotation.

A mechanical IAF is presented in **Figure 2.3**. In this setup, the reaction cell is fitted with an impeller to induce a state of high turbulence. This turbulence serves multiple purposes, including the suspension of particles, the generation and dispersion of bubbles, and the facilitation of collisions between bubbles and particles. This mechanical cell is similar to the one used in this project (as explained in a section 3.4).

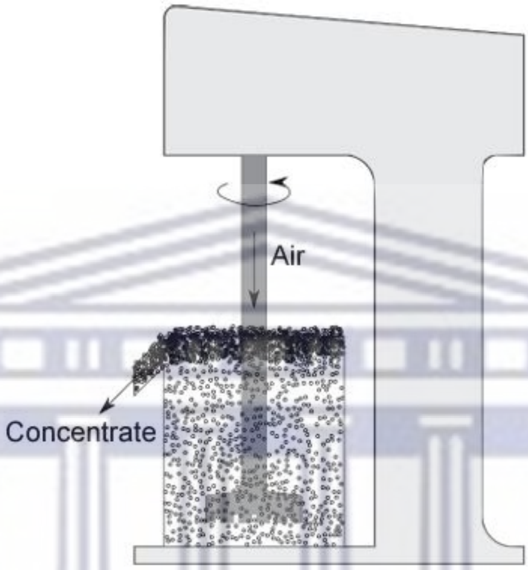


Figure 2.3. Mechanically agitated induced air flotation system [140].

2.5.3.2. Dissolved Air Flotation

The basic purpose of dissolved air flotation (DAF) is to achieve solid-liquid separation by means of flotation. This process involves introducing a highly pressured and supersaturated solution of gas-liquid mixture into the incoming flow. When a mixture is subjected to pressure and then released to normal atmospheric pressure, it will generate gas bubbles that cause the upward movement of suspended solids or colloidal solids towards the surface. Bubbles generate an agglomeration consisting of particulate materials and bubble particles. The phenomenon of bubbles experiencing buoyant force within a liquid medium leads to a reduction in the density of suspended solids, causing them to ascend and remain afloat at the liquid's surface [141].

Bubbles are generated from a reduction in pressure exerted on water saturated with air. The process involves the passage of supersaturated water through needle-valves or specialized orifices, resulting in the formation of cloud-like clusters of bubbles with diameters ranging from 30 to 100 µm immediately after the constriction [53]. A typical DAF configuration is depicted in **Figure 2.4**.

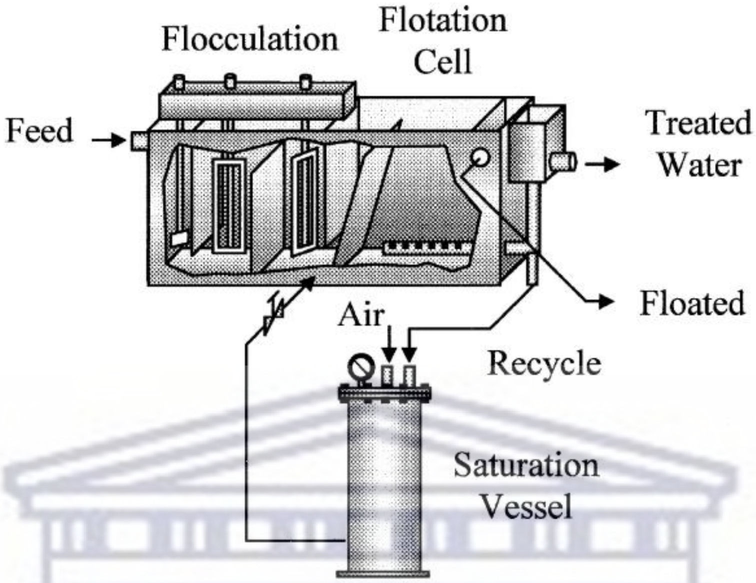


Figure 2.4. Dissolved Air Flotation unit [53].

The mechanisms for gas bubble generation in IAF and DAF exhibit fundamental differences, resulting in variations in bubble sizes, mixing conditions, hydraulic loading rates, and retention times. **Table 2.9** presents a comparison of the methodologies. The key differences between the two gas flotation approaches lie in the respective methods of gas bubble generation, leading to variations in processes and overall surface areas of bubbles.

Table 2.9. Induced and Dissolved Gas Flotation systems comparison [53,139].

Parameters	IAF	DAF
Bubble size	100–1,000 µm	10–100 µm
Method of bubble generation	Velocity based via entrainment and dispersion of gas bubbles	Pressure based bubble formation upon saturation and depressurization of gas liquid
Bubble generation volume	High	Low (limited by saturation)
Operating environment	Turbulent multi-cell configuration	Quiescent, single-cell environment
Retention time	<5 min	5 - 15 min
Capital investment	Low	High
Footprint	Compact	Large
Maintenance	Substantial; due to wear and tear in mechanical IAF systems	Relatively low, minimal moving parts

In practical terms, the induced air flotation method offers several advantages over the dissolved air flotation method. One such advantage is the presence of a small flotation system that may be conveniently established at a laboratory size. IAF typically produces bubbles with sizes larger than 100 µm which occurs within turbulent hydrodynamic conditions and characterized by relatively short retention periods of less than 5 minutes. On the contrary, DAF generates bubbles that are less than 100 µm in size and operates in quiescent environments. The use of smaller bubble sizes in the DAF process results in enhanced efficiency in the removal of suspended particles when compared to the IAF method.

2.5.4. Hydrodynamic Shear Mixing

Hydrodynamic shear mixing also referred to as stator rotor mixing, has emerged as a popular device in several applications within the process sector, including but not limited to mixing, dispersion of particles in solvents, and emulsification.

During the operation of hydrodynamic shear mixing in context of solid-liquid separation procedures, such as those employed in waste-water treatment, an intentional destabilization of a suspension is carried out. This destabilization is accomplished by subjecting the suspension to shear flow by mechanical agitation. The primary objective of this approach is to facilitate the aggregation of small solid particles, leading to the formation of larger flocs. The larger size of these flocs facilitate a more effective separation from the liquid phase [142].

The rate at which colloids aggregate in the presence of shear flows is dependent upon the frequency of collisions and the likelihood of two particles adhering to one another to establish a stable interaction. The aggregation of colloidal particles arises from two primary mechanisms. If colloidal suspensions are kinetically stabilized and have a high energy barrier that prevents aggregation, it is possible for the convective energy of the fluid (the transfer of thermal energy through the movement of matter) to help the particles overcome the repulsive barrier and aggregate. In the second instance, when dealing with entirely disrupted suspensions, the frequency of collisions is exclusively controlled by the intensity of the flow field. This results in a substantial increase in the rate of aggregation compared to a simply diffusive process. This phenomenon is commonly referred to as "perikinetic” aggregation [143].

Hydrodynamic shear mixing can be categorized into three distinct practical applications:

1. The process of liquid-liquid emulsification is used to create liquid-liquid dispersions with reduced viscosity [144].
2. Solid–liquid suspension, to create homogenous, stable, and rheologically desirable nanoparticle suspensions for use in the production of pharmaceutical, medical, and electronic products [145].
3. Chemical processes to create intermediates or fine compounds [146].

Hydrodynamic shear mixers find extensive application in many industries such as cosmetics, paint, food, pharmaceutical, and chemical industry. They are employed for the production of emulsions characterized by narrow droplet size distributions (DSDs), as well as for the generation of small droplets possessing large interfacial areas [147].

Table 2.10 provides a comparison of the energy dissipation range and size distribution range across high shear mixers, static mixers, agitated vessels, valve homogenizers, and ultrasonics. The comparison shows that increasing the local energy input results in the creation of smaller droplet sizes.

Table 2.10. Performance of different dispersion devices [137].

Type of devices	**Energy dissipation range (kg·m^2/s^3)**	**Typical size range (μm)**
Static mixers	10–1,000	50–1,000
Agitated vessels	0.1–100	20–500
Hydrodynamic shear mixers	1,000–100,000	0.5–100
Valve homogenizers	~10^8	0.5–1
Ultrasonics	~10^8	0.2–0.5

Hydrodynamic shear mixers are regarded as innovative and attractive process intensification equipment. These mixers have the potential to significantly improve the liquid-liquid extraction process within solid-liquid-liquid systems. Nevertheless, there is a lack of literature documenting this particular aspect.

Hydrodynamic shear mixers, much like flotation devices, have primarily been used in emulsion processing [148–151]. Yet, its efficacy as a viable alternative for treating winery wastewater is yet to be proven. Further investigation is warranted to explore the practical implications of this technology in terms of modifying both bubble size and surface charges of colloidal particles.

As such, one of the objectives of this thesis is to evaluate hydrodynamic shear mixing as a component to enhance the treatment efficiency of winery wastewater.

A variety of organic matters exists in winery wastewater that cannot usually be removed using only physicochemical methods due to the presence of highly soluble alcohols, acids, sugars, and chemicals like tannins and polyphenols [152]. Thus, biological treatment of the dissolved organic contaminants in winery wastewater is commonly used as a secondary treatment phase. Section 2.6 examines the application of biological treatment techniques in the particular context of winery wastewater. The preliminary and primary treatment phases are crucial prerequisites for optimizing the wastewater's suitability for further biological treatment operations.

2.6. Biological Treatment Methods

The most often employed biological treatment methods in wastewater treatment involve making use of aerobic, anaerobic, and combination anaerobic/aerobic systems, typically implemented during the secondary treatment phase. The classification of these processes as being environmentally friendly is attributed to the high biodegradability of the organic materials present in winery wastewater. The treatment of winery wastewater in biological systems involves the careful choice of a diverse consortium of microbial flocs, achieved by making use of recycled settled biomass. Additionally, the development of high-performance reactors is crucial, which involves improving the biomass concentration within these reactors [153].

2.6.1. Aerobic Treatment

One of the most popular technologies for treating wastewater is the aerobic system, which consists of lagoons with large pumps where air movement promotes the growth of naturally occurring aerobic bacteria in wastewater [20]. Although aerobic procedures are frequently sufficient to meet with legal discharge restrictions, unpleasant odors and ground water pollution have been reported [154]. Aerated ponds are the simplest, most widely used, and least expensive type of on-site wastewater treatment for most sizable wineries [155]. However, it has been noted that these systems experience decreased biological activity throughout the winter, which is problematic for wineries that operate all year long [156]. Additionally, the sludge generation and disposal issues may arise as a result of the high organic load of these wastewaters, which may promote excessive biomass growth and necessitate an increase in the air supply. Aerobic procedures are significantly hindered by the overproduction of sludge [157].

2.6.1.1. Activated Sludge Process

One of the first study groups to use traditional (long-term) activated sludge (LTAS) as a winery wastewater treatment technology was Fumi *et al.*, (1995) [34]. The authors stated that this technology enables quick and adaptable winery wastewater treatment. In order to facilitate cellular synthesis, it is required to add urea and phosphate salt to winery wastewater because of its low nutrient content [119]. Their reactor consisted of vertically oriented tanks, reinforced with polyester. The tanks consisted of three completely mixed aeration tanks, one equalization tank, and a conical, up-flow settling tank. Each tank was equipped with a rotating-drum filter and a diffused-aeration membrane plate located at the bottom of the tank. Through this configuration, the authors achieved a remarkable reduction in COD, averaging 98%, resulting in final COD levels ranging from 50 to 130 mg/L. The untreated influent water had initial COD values between 2,000 and 9,000 mg/L [34]. Additionally, total suspended solids in the treated wastewater ranged from below 60 mg/L in treated wastewater to 200–1,200 mg/L in untreated wastewater.

Petruccioli *et al.*, (2000) investigated the decrease of organic load in winery wastewater by employing activated sludge and three different types of bioreactors: an air bubble column bioreactor (ABB), a fluidized-bed reactor (FBB), and a packed-bed bioreactor (PBB) [158]. There was a pattern observed whereby increasing organic loads were associated with higher COD removal rates. ABB achieved the most favorable outcomes, with a 92.2% reduction in COD with a hydraulic retention time (HRT; the average duration that a soluble component remains in the bioreactor) of 0.8 days. In comparison, PBB achieved a COD reduction of 91.1% with a retention period of 1.2 days. The FBB, running under optimal conditions, produced an 88.7% reduction in COD with a retention time of 2.2 days. The ABB was subsequently given a lengthy treatment regimen (280 days; COD range, 2,700 - 6,600 mg/L) with a daily organic loading rate of 8,800 mg/L at its highest possible level. When operating over a critical loading rate of 8,240 mg/L per day during this time, the COD reduction dropped to a minimum of 80% from its typically higher than 90% level.

The viability of co-treating municipal and winery wastewaters with the traditional activated sludge process was assessed by Brucculeri *et al.*, (2005). Their treatment process consisted of a pre-denitrification/oxidation stage the rest of the year and an extended-oxidation procedure during vintage. They demonstrated that both cases resulted in COD and nitrogen reduction. A 90% decrease in COD was achieved, with initial influent COD levels ranging from 200-400 mg/L during the vintage period and 87% during the non-vintage period. Both vintage and non-vintage periods exhibited a nitrogen reduction of 65%, with initial values ranging from 20-25 mg/L whilst treated wastewater continuously maintained levels below 15 mg/L [159].

Petruccioli *et al.,* (2002) used a jet-loop reactor (JLR) to aerobically treat winery wastewater. In simple terms, a JLR consists of a jet and a loop reactor. The primary function of the jet loop reactor is to recycle a fraction of the reaction medium and reintroduce it into the feed at the entrance of the reactor [160]. This configuration is an advantageous implementation of mass transfer limited multi-phase reaction systems due to its straightforward assembly, user-friendly operation, and enhanced mixing efficiency with comparatively low energy consumption rates [161]. The treated wastewater continuously reached COD levels below 200 mg/L at organic concentrations ranging from 400 to 5,900 mg/L per day, indicating that the COD reduction was between 96% and 98%. The experiment was subsequently conducted for a further 12 months, with the loading rate periodically changing and hydraulic retention time fluctuating between 2.3 and 4.4 days. Within a year, the COD reduction averaged 90%. The researchers concluded that this system will be sufficiently adaptable and versatile to manage wastewater from wineries, which is notorious for having a wide range of seasonal variations because of variations in both volume and organic content. This conclusion was based on the system's outstanding reactivity to rapid variations in loading rates. Insufficient homogenization, however, resulted in a decrease in the selectivity of the reaction. Hence, achieving a proper equilibrium between mixing and mass transfer is a critical factor in the design of jet loop reactors [162].

Eusébio *et al.,* (2004) utilized a JLR system for over a year to extract different acclimatized microorganisms from various sources of activated sludge. These sources included winery wastewater, pulp and paper wastewater, biomass from a thermal natural spring, and freeze-dried commercial inoculum, preserving a high degree of productivity and conversion. The findings demonstrated the emergence of a particular consortium of microorganisms, which, under more demanding bioreactor conditions for a longer period of time (390 days), reduced COD by 80% (from an initial value of 3,100–27,200 mg/L. However, this system had certain issues, such as pump failures, periodic foaming incidents, and changes in wastewater composition, which led to some variances in COD reduction (40–95%) over the course of the system's 390-day operation period [153]. The main bacterial isolates that decreased the organic load were primarily from the genera *Bacillus* and *Pseudomonas*. The absence of *Spirillum* (a microaerophile) in their study supported the high aeration rate achieved in the JLR, as indicated by the dissolved oxygen levels that consistently remained between 75-90% saturation. A tabulated summary of the aerobically treated winery wastewater methods is shown in **Table 2.11**.

Table 2.11. Comparison of aerobic winery wastewater treatment techniques

Raw/Untreated Winery wastewater quality characteristics	Technology used	Analysis	Main findings/ removal efficiency	Ref
pH: 7 - 12.9 COD: 2,000 – 9,000 mg/L TSS: 200 – 1,200 mg/L Nitrogen: 25 -75 mg/L	Full scale Activated sludge	COD	pH: 8.3 – 8.6 98% COD reduction (50 – 130 mg/L) TSS: <60 mg/L TN: <10 mg/L	[34]
pH: 3.5 COD 800 – 1,100 mg/L	Activated sludge with: - Air bubble column bioreactor (ABB) - Fluidized bed bioreactor (FBB) - Packed-bed bioreactor (PBB)	COD	pH 7.5 - 92.2% COD reduction (450 mg/L) - 88.7% COD reduction (500 mg/L) - 91.1% COD reduction (400 mg/L)	[158]
COD 200 – 400 mg/L TN: 20-25 mg/L	Co-treated winery and municipal wastewater using conventional Activated sludge (CAS)	COD TN	90% COD reduction (<50 mg/L) 65% TN reduction: <15 mg/L	[159]
COD: 800 – 12,800 mg/L	Jet-loop activated sludge reactor	COD	96 - 98% COD reduction (<200 mg/L)	[163]
COD: 3,100 – 27,200 mg/L	Jet-loop activated sludge reactor	COD	>80% COD reduction	[153]
COD: 1,000 – 4,000mg/L	Membrane bioreactor	COD	97% COD reduction	[164]
COD: 100 – 8,000 mg/L	Membrane bioreactor	COD	97% COD reduction	[31]
COD: 2,000 mg/L	Membrane bioreactor	COD	95% COD reduction	[165]

2.6.1.2. Membrane bioreactors

In recent decades, the membrane bioreactor (MBR) has gained attention as a promising technology for wastewater treatment and reuse [166]. These systems provide an efficient secondary treatment option. In contrast to conventional activated sludge processes, a secondary clarifier is not employed in membrane filtration. High-quality treated water is produced by these portable wastewater treatment devices. In addition, an MBR provides superior control over solids concentration compared to systems with secondary settlers because the membranes retain the fraction of suspended particles that is often washed out [167]. Artiga *et al.*, (2005) conducted research on the treatment of wastewater from wineries and tanneries, employing a membrane biological reactor [164]. The trial lasted 120 days, with the first 50 days dedicated to treating winery wastewater and the remaining days to treating tannery wastewater. Soluble COD influent for winery wastewater varied from 1,000 to 4,000 mg/L, while for tannery wastewater, it was 350 to 4,000 mg/L. For wastewater from wineries, the authors achieved a COD reduction of 97%, and for wastewater from tanneries, 86%. Despite the fact that the nature and COD of the two wastewaters under study were different, the concentration of organic matter in the wastewater was often less than 100 mg/L and relatively comparable throughout the treatment procedure.

In a study conducted by Melamane *et al.*, (2007), the efficacy of a submerged membrane bioreactor (SMBR) combined with a secondary digester was evaluated for the treatment of wine distillery effluent in Worcester, South Africa. The configuration comprised of four individual reactors, and the duration of the testing phase spanned 30 days. The pH was regulated by adding 1,000 mg/L of $CaCO_3$ and K_2HPO_4 for the initial 10 days, and then the concentrations were increased to 8,000 mg/L of $CaCO_3$ and 4,000 mg/L of K_2HPO_4 for the rest of the study. Reactor A, serving as a balancing tank, provided wastewater to reactor B (the SMBR), which in turn supplied the permeate balancing tank (reactor C) and ultimately fed the secondary digestor reactor (reactor D). Using this setup, a 76% reduction in COD was achieved after 22 days, and 25% of the COD was removed within the first 10 days of operation, with an average influent of 4,840 mg/L. However, the treated wastewater still did not meet the standards for crop irrigation due to consistently high phosphate levels of 100 mg/L throughout the study [168].

Valderrama *et al.*, (2012) performed a case study in which they examined the treatment of winery wastewater using both conventional activated sludge (CAS) and a membrane bioreactor

(MBR) [31]. The MBR (97%) achieved a slightly greater reduction in COD (influent 100–8,000 mg/L) than the CAS (95%). According to Spanish legislation, the high-quality treated wastewater obtained in their study met the criteria for reuse in agricultural activities.

Vergine *et al.*, (2020) developed self-forming dynamic membrane bioreactors (SFD-MBR) for the treatment of canning and winery effluent [165]. The system effectively reduced the COD of the canning wastewater by 94%. The soluble COD fraction remained below 100 mg/L, starting from an initial COD concentration of 1,000 mg/L. In a comparable manner, winery wastewater saw a 95% reduction in COD (from an initial COD of around 2,000 mg/L). The SDF-MBR's filtering effectiveness was negatively impacted by the feed composition and operating conditions, necessitating regular cleaning (once every four days for 80 days).

The MBR technology offers advantages such as its adaptability to fluctuating influent loads, small environmental footprint, reduced sludge production, and a compact system that is exceptional in solid removal and disinfection capabilities [169,170]. However, like other membrane systems, it is important to consider membrane fouling, which leads to a decrease in flux, and ultimately the need for membrane replacement when implementing this technology. Membrane fouling is the result of the accumulation of particles, colloids, and solutes on or inside the membrane pores through processes like adsorption, pore-clogging, and pore-blocking. When membranes become contaminated, the permeability is greatly diminished. However, performing cleaning operations such as backwashing can restore permeability. Nevertheless, this significantly affects the amount of time that MBR systems are not functioning [171].

2.6.1.3. Fixed bed biofilm reactor

Winery wastewater was treated by Andreoletta *et al.*, (2005) using a full-scale, two-stage fixed bed biofilm reactor (FBBR) that was loaded with plastic carriers [101]. The FBBR consisted of a first stage divided in two parallel reactors that allowed for flow rate flexibility over the year's vintage and non-vintage seasons and removed 70% of COD (7,000 mg/L of influent COD on average annually). After that, a third FBBR was put in place to improve the wastewater's quality, resulting in an overall average COD reduction of 91% over the course of a year of operation. The first stage of the FBBR system primarily contributes to the oxidation of biodegradable COD, whereas the second stage essentially refined the effluent arising from the first stage having slowly biodegradable COD or flow rate peaks. The authors were unable to clearly identify the non-biodegradable soluble COD fraction, which accounted for around

10% of the total. Both FBBR and settling processes were ineffective in removing this fraction. Furthermore, the need for back-washing of the FBBR was eliminated during the seasonal period (September-March) as a result of the ample void area provided by the plastic carriers.

2.6.1.4. Rotating biological contactor

Coetzee *et al.*, (2004) conducted a study to examine the use of a pilot-scale rotating biological contactor (RBC) for the treatment of winery wastewater. Their findings suggest that this biological system has insufficient efficacy in eliminating organic materials, as it only achieved an average reduction of 23% and a maximum reduction of 43% in COD (influent: 4,000 – 8,000 mg/L) [95]. While acknowledging the potential efficiency of this pretreatment approach, the use of RBC for winery wastewater is limited. When compared to the other approaches discussed previously in this section (refer to **Table 2.12**) it may be a more appropriate choice in terms of its efficiency in removing the overall organic load.

2.6.1.4.1. Advantages and disadvantages of aerobic winery wastewater treatment technologies

A comparison of aerobic wastewater treatment options for winery wastewater is presented in **Table 2.12** and covers membrane bioreactors, fixed bed biofilm reactors, jet loop reactors, and activated sludge.

Table 2.12. Winery wastewater Aerobic treatment processes comparison: Advantages and disadvantages (modified from Andreottola *et al.*, 2009; and Lofrano *et al.*, 2015) [22,119].

Aerobic treatment systems	**Advantages**	**Disadvantages**
Activated Sludge	>80% COD and BOD reduction efficiency Less retention time required Easy management	High operational costs pH control Periodic bulking Phenolic compounds adversely affect biomass growth Energy intensive Nutrient supplementation required
Jet loop reactor	>80% COD reduction High oxidizing potential High mixing and turbulence High reduction of phenolic compounds	Moderate operational costs Decreased sludge settleability
Membrane bioreactor	High quality treated wastewater (>95%) Direct reuse on site possible Compact Rapid startup Small footprint Less sludge produced Simultaneous nitrification–denitrification	High operational costs Fouling (decreased filterability) pH control Limited data on membrane longevity (i.e., often module replacement might be required) Nutrient addition may be required
Fixed bed biofilm reactor	High organic reduction efficiency (>90%) in organic matter) Compact No return flow and back washing	High operation costs pH control Nutrient addition may be required

According to the comparative analysis, it can be concluded that membrane bioreactor (MBR) systems are the most suitable and adaptable for managing changes in influent flow and effectively treating wastewater with high levels of organic matter to meet quality standards for discharge or reuse. Nevertheless, membrane fouling must be considered when evaluating this particular treatment technology. The MBR method incurs higher capital and operational costs due to the expenses associated with membranes and antifouling measures, which may be a feasible reason for their limited use in wastewater treatment in South Africa [172].

2.6.2. Anaerobic Treatment

As mentioned previously, winery wastewater consists of a substantial amount of organic matter. Therefore, it is worth considering the potential for energy generation through the combination of anaerobic digestion processes and wastewater treatment. Anaerobic digestion is a process that takes place in the absence of oxygen and relies on alternative metabolic processes employed by a diverse array of bacteria [23]. This technique focuses on harnessing dissolved organic matter by using a group of anaerobic microbes present in winery wastewater. The primary advantage of this treatment approach is the generation of biogas [173]. One significant benefit of anaerobic treatment technologies is the ability to produce biogas, an energy source that may be utilized to meet operational process requirements.

Wolmarans *et al.*, (2002) investigated the use of an up flow anaerobic sludge blanket (UASB) as a pre-treatment method for treating wastewater from distilleries [174]. This system successfully achieved a significant reduction in COD (with an average influent concentration of 26,669 mg/L and treated wastewater concentration of 2,814 mg/L) of over 90%. The initiation process of this system was carefully observed for a duration of three weeks. During this phase of the process, the volumetric loading rates, which indicate the amount of COD introduced to the reactor per cubic meter of total reactor volume per day, had been set to 4,000 and 18,000 mg/L per day. The primary difficulty associated with UASB lies in the startup procedure, which typically spans from one week to two months, in order to form the granules required for fast settling in the UASB reactor. The authors achieved successful shutdown and startup processes, taking approximately one day to establish a stable reduction of COD of over 90% after acclimatization. The startup process also included incremental increases in feed concentration (ranging from 4,000 to 8,000 mg/L, then increased to 18,000 mg/L). However, it was noted that caution should be exercised when abruptly decreasing and subsequently increasing loading rates, as this may lead to a decline in granule stability and consequently a decrease in reactor performance.

Ganesh *et al.*, 2010 evaluated the use of three up-flow anaerobic fixed-bed reactors filled with the different polyethylene floating carriers for the treatment of winery wastewater [175]. Three polyethylene floating carriers (S9, S30, and S40) were utilized in this investigation as the media for immobilizing and retaining biomass. The organic loading rates were 42,000; 27,000; and 22,000 mg/l per day, respectively. Using this arrangement, 80% of COD (with an influent COD value of 18,000–21,000 mg/L) could be removed. The authors noted that for cellular growth during the biological phase, additional nutrients (nitrogen and phosphorus) were needed to maintain a C:N:P ratio of 400:7:1. The 80% reduction in COD highlights that this biological treatment process requires less land space, less energy, and a smaller reactor volume when compared to traditional activated sludge techniques. The disadvantage of this method (normally the case for all types of anaerobic reactors) is that in order to render the final wastewater suitable for disposal, aerobic treatment or additional tertiary post-treatment technology is necessary.

Laing undertook a study to determine if an anaerobic sequencing batch reactor (AnSBR) could effectively treat synthetic winery effluent in South Africa [176]. The treatment parameters for two types of synthetic wastewater (1,000–4,000 mg/L and 4,000–7,000 mg/L COD, respectively) were optimized through the utilization of laboratory-scale reactors (14.7 L capacity, with granular mesophilic biomass maintained at 35°C). An average COD reduction of 88% was attained during the initial phase (COD 1,000–4,000 mg/L), followed by a COD reduction of 80% during the subsequent phase (4,000–7,000 mg/L), both of which were conducted at a controlled pH of 7.2. The parameters that were investigated for optimization included the pH, feeding duration, and mixing frequency. Moreover, in the absence of nitrogen, this system generated biogas in which the methane fraction constituted over 80% of the total, in contrast to the conventional biogas production process that comprises 30% carbon dioxide and 70% methane. This was achieved by increasing the COD:N fraction in the reactor, ultimately producing (according to the authors) an “upgraded biogas”. During this step, when the mixing time in the reactor was optimized, less granule shearing occurred and better methanogen protection was observed. The authors subsequently suggested that, on the basis of these results, this reactor could be expanded to a pilot scale configuration, which could be utilized to assess the cost and viability of the AnSBR process at a larger scale [176].

An investigation into the viability of anaerobic membrane bioreactors (AnMBR) was conducted by Basset *et al.,* (2016) [173]. The specific organic loading rate in this investigation was maintained below the level of methanogenic activity, at 300 mg/L of mixed liquid suspended solids (MLSS) each day. The wastewater had a total COD of 6752 mg/L and a soluble COD of 4,040 mg/L. The AnMBR system attained a 96.7% COD reduction, resulting in the generation of biogas comprising 87.1% methane during the course of the process. However, an important element that reduced the membrane flux by 80% was membrane fouling, particularly inside the membrane pores. Membrane fouling is a significant problem because it degrades the effectiveness and quality of treatment while also increasing the energy required to run the systems.

Winery wastewater treated anaerobically typically shows COD reductions of 80–98% and biogas production of 500–600 L per kilogram of COD removed, of which 60–80% is methane [177]. The biogas produced by anaerobic treatment generally produces less sludge and is odor-free, but it is not consistent enough in reducing COD/BOD to be released into water bodies without first undergoing post-aerobic treatment [86]. **Table 2.13** compares aerobic and anaerobic treatment methods.

Table 2.13. Comparison between aerobic and anaerobic treatment system [111] .

Parameter	Aerobic	Anaerobic
COD reduction	65 – 90%	90 – 98%
Energy potential	Low: only CO_2 released	High: CH_4 is produced
Energy consumption	Low	High
Sludge production	Low	High
Nutrients (N/P) removal	Low	High
Space requirement	Low	High
Interrupted operation	Easy	Challenging

2.7. Constructed Wetlands

A constructed wetland is an engineered shallow basin containing substrate (such as soil or gravel) and planted with vegetation that is exceptionally tolerant to saturated conditions. Its purpose is to replicate the bioremediatory process that takes place in natural wetlands [38]. Constructed wetland vegetation metabolizes accessible nutrients, potentially leading to the accumulation of heavy metals and the degradation of certain organic contaminants [38]. With a sufficient land area, constructed wetlands can serve as an economically viable, environmentally sustainable, and visually pleasing alternative for the remediation of wastewater [178]. The wastewater treatment processes in constructed wetlands involve sedimentation of particulate matter, filtration, and chemical precipitation due to water-substrate interaction. Additionally, adsorption and ion-exchange take place on plant and substrate surfaces, while microbial degradation and transformation of pollutants occur through plant uptake [179]. In essence, constructed wetlands can be categorized as secondary or tertiary treatment methods, however they are generally regarded as an integration of primary, secondary, and tertiary treatment techniques.

The potential phytotoxicity of winery wastewaters towards wetland plant species has been demonstrated in the literature; this provides a fundamental justification for the design and development of constructed wetlands. A constructed wetland plant should possess the capability to withstand substantial masses of organic matter and effectively eliminate considerable quantities of contaminants, thus expediting the process of wastewater purification [87].

Shepherd *et al.,* (2001) conducted a study to illustrate the application of a horizontal subsurface flow (HF) constructed wetland at prototype scale (6.1 m long × 2.4 m wide × 1.2 m deep) in a medium-sized winery. The winery generated 18,200 m^3 of wine annually and experienced daily flows ranging from 80 to 170 m^3 and COD organic loads ranging from 500 to 45,000 mg/L. Their system had a surface area of 14.9 m^2 and was packed with pea gravel of hydraulic conductivity 2 mm/s. It was designed to receive effluent that had been pretreated using an up-flow coarse sand filter for a duration of 10 days. The CW was planted with *Typha dominicus, Scirpus acutus* and some *Sagittaria latifolia* and the wastewater was diluted and fed to the CW at 500 L/day with an initial COD concentration of 993 mg/L which was then increased to COD values of 5,000 mg/L. The experiment yielded a minimum COD removal efficiency of 97% when the influent concentration was below 5,000 mg/L, and a 97% removal of TSS when the influent values were 450 mg/L [180].

Grismer *et al.,* (2003) investigated the relationship between winery wastewater treatment performance and retention time in a full-scale constructed wetland process. Data was obtained from two full-scale subsurface wetlands located near Hopland (medium sized winery) and Glen Ellen (medium sized winery) both in California, USA, during the harvest crush and spring season. The wetland implemented at Hopland achieved a reduction in COD ranging from 49% to 79%, as well as a removal rate of tannins ranging from 46% to 76%. The authors achieved a substantial reduction in COD at the Glen Ellen winery, with influent COD concentrations of 8,000 mg/L and treated wastewater reaching as low as 5 mg/L [181].

Milani *et al.,* (2020), undertook a study to investigate the viability of a multistage constructed wetland for reusing winey wastewater for irrigation purposes. The multistage system at the Marabino winery in Sicily, Italy, comprises a vertical subsurface flow bed (VF), a horizontal subsurface flow bed (HF), and a free subsurface flow unit (FSF). This configuration was able to treat 3 m^3 of wastewater per day and achieved a decrease of 81% in COD and 69% in TSS. The wastewater utilized in this investigation was combined with sewage generated by the ablution facilities used throughout the winery. Following the horizontal surface flow wetland, 96% of the samples successfully complied to the legal Italian irrigation limit for COD. This compliance level was further improved to 100% following the final free subsurface flow unit, which treated influent with a concentration of 2020 mg/L and achieved a minimum effluent concentration of 3 mg/L through a multistage treatment process. In addition, the TSS limits (10 mg/L) had been exceeded in only 34% of the samples, while the BOD limit (20 mg/L) was exceeded in 18% of the samples after treatment. The rationale behind this observation was elucidated by the rapid growth of algae during the FSF stage, resulting in a subsequent elevation of both the TSS and BOD5 levels in the wastewater. As per the authors' findings, the implementation of this multistage constructed wetland is a viable option for treating winery wastewater. It demonstrates great effectiveness and adherence to irrigation standards outlined in the Italian legislation. Furthermore, the authors have observed that constructed wetlands are highly suitable for wineries of small to medium size. This is because the expenses associated with building, operating, and maintaining traditional wastewater treatment facilities may not be financially feasible for the owners of the winery. Based on the findings obtained in this subsection of the thesis, it can be inferred that constructed wetland systems are better suited for medium to large wineries, which typically have larger (unused) land area and can accommodate the space requirements of constructed wetlands.

Constructed wetlands are simply streamlined treatment systems that have low energy demands. Wineries can derive aesthetic advantages from it. The process of designing, constructing, and maintaining it is quite simple. Furthermore, its operational expenses are lower compared to other winery wastewater treatment methods such as activated sludge and membrane technology. Despite the aforementioned benefits, constructed wetlands require a substantial amount of land and are only suited to wineries where sufficient unused land area is available.

Furthermore, removing suspended matter is essential to the wetland system's functionality, and a pre-treatment stage is required to avoid the system being clogged.

In addition to the treatment technologies already described, tertiary treatment methods, such as advanced oxidation processes, have been the subject of much research in recent decades and will be discussed in the section that follows.

2.8. Advanced oxidation processes

There has been a growing interest in advanced oxidation techniques as a means of treating various agro-industrial wastewaters [182]. It has been shown that using biological approaches to fully clean wineries' wastewaters might be difficult [183]. Recent studies have demonstrated that implementing advanced oxidation methods for treating wastewaters that change seasonally and exhibit variations in flow can yield positive outcomes. These processes can subsequently be employed as a preliminary treatment step before exposing the wastewater to aerobic biological treatment [88]. The main goal of advanced oxidation processes (AOPs) in wastewater treatment is to partially or fully degrade organic contaminants [184]. Following partial breakdown, there may remain oxidizable substances that are less toxic. In instances where total oxidation occurs, mineralization, which involves the transformation of all organic components into carbon dioxide and mineral salts, also occurs [184]. In the field of AOPs, oxidation mostly happens through the generation of highly reactive hydroxyl free radicals. These radicals have the ability to react with organic substances that are susceptible to oxidation in a non-selective manner with fast reaction kinetics [184]. Typically, ozone (O_3), hydrogen peroxide (H_2O_2), and ultraviolet (UV) irradiation, or combinations of these, are employed to create hydroxyl radicals as the initial stage of oxidation. These radicals react with organic pollutants, resulting in the formation of precipitates [100]. The upcoming subsection will cover advanced oxidation techniques that are based on the Fenton process.

2.8.1. Fenton Process

The Fenton reagent, composed of Fe^{2+} ions and hydrogen peroxide (H_2O_2), is extensively employed in wastewater treatment owing to its capacity to readily oxidize organic molecules and generate hydroxyl radicals as shown in **Equation 2.1** and **Equation 2.2**.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH\cdot$$ **Equation 2.1**

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH \cdot + H^+$$ **Equation 2.2**

The effectiveness of this technique is attributed to the generation of highly reactive hydroxyl radicals (·OH) and the conversion of Fe^{2+} to Fe^{3+}. Since both of these ions act as coagulants, the Fenton process exhibits a synergistic effect, combining oxidation with coagulation [185].

Ippolito *et al.,* (2019) investigated the application of the Fenton process to treating winery wastewater. Their findings indicate that this technique has the potential to decrease COD values by up to 60%, with an influent COD concentration of around 20,000 mg/L. The pH of the untreated wastewater was adjusted from 4.6 to 8 using hydrated lime. The addition of bentonite was employed to enhance the precipitation of suspended particles prior to the pH correction. Simultaneously, there was a significant decrease of 75% in the total dissolved solids (TDS) concentration, from 4,680 mg/L to 1,170 mg/L. In addition, an analysis of variance (ANOVA) test was performed to determine the optimal concentrations of H_2O_2/Fe^{2+}. The results showed that a decrease of around 60% in COD values was achieved with a dosage of 60 L/m^3 of hydrogen peroxide and 30 kg/m^3 of ferrous sulfate heptahydrate. An investigation into the impact of pH was conducted, and the ideal concentrations, as stated before, were applied to untreated wastewater with a pH range of 3.5-4.5. The decrease in COD value observed throughout these experiments varied from 40% at pH 3 to around 50-52% at pH 4-4.5.5 [186].

In addition to stand-alone Fenton processes, the application of photo-Fenton processes has also been investigated for winery wastewater treatment. When UV/Vis light is applied, such as in photo-Fenton reactions, it generates extra radicals which aid in the restoration of the catalyst. (**Equation 2.3** and **Equation 2.4**) [88,187]. Due to iron precipitation, the photo-Fenton process is pH-dependent, requiring strict pH control (optimal pH = 2.8) [188].

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + H^+ + OH \cdot$$ **Equation 2.3**

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH \cdot$$ **Equation 2.4**

An overview of Fe-based advanced oxidation techniques used with winery wastewater is provided in **Table 2.14** below.

Table 2.14. Fe-based advanced oxidation processes used during winery wastewater treatment [39].

Raw winery wastewater quality characteristics	Technology used	Main findings/ removal efficiency	Ref
COD: 20,074 mg/L TDS: 4,680 mg/L	Fenton: Fe^{2+}/H_2O_2 pH 4.6 Fe^{2+} = 30,000 mg/L H_2O_2 (30% w/v) = 60 L/m^3	pH: 8 Treatment time: 1 h 54% COD reduction (10,020 mg/L) 75% TDS reduction (1,170 mg/L)	[186]
COD: 1,110 – 4,630 mg/L TPh: 130 – 290 mg/L	Fenton: Fe^{2+}/H_2O_2 Pretreatment: bio-oxidation (CSTR) pH 3.5, T = 25 ± 0.5°C Fe^{2+} = 2,800–27,800 mg/L H_2O_2 = 2,100–13,600 mg/L	pH: 8.3 – 8.6 Treatment time: 3 h 50-80% COD reduction (926 – 2,315 mg/L) >90%Total polyphenol	[189]
COD: 1,560 mg/L	Fenton: Fe^{2+}/H_2O_2 Pretreatment: bio-oxidation (CSTR) pH 3.5, T = 30°C, H_2O_2/Fe^{2+} = 15 H_2O_2/COD = 0.25–2.5 H_2O_2 = 400–3,900 mg/L Fe^{2+} = 30–260 mg/L	93.2% COD reduction (106 mg/L) Treatment: 30-720 min Max molar ratio H_2O_2/COD = 2.5 Max H_2O_2 concentration = 3,900 mg/L Max Fe^{2+}concentration = 260 mg/L	[190]
COD=970 mg/L TOC=370 mg/L BOD_5 =291 mg/L TPh=3,505mg/L	Fenton: Fe^{2+}/H_2O_2 pH 3 T = 30°C Fe^{2+} = 68–271 mg/L H_2O_2 = 4,148 – 16,592 mg/L	Treatment time: 6 h 83% COD reduction (164 mg/L) 67% TOC reduction: (122 mg/L 58% BOD_5 reduction (122mg/L) 100% TPh reduction	[191]
COD: 3,880 mg/L	Fenton-like: Fe^{3+}/H_2O_2 pretreatment: coagulation pH 2.75, Fe^{2+} = 920 mg/L H_2O_2 = 300 – 2,900 mg/L	Treatment time: 8 h 42.1% COD reduction (2246 mg/L)	[21]
COD: 3,880 mg/L TOC: 4,440 mg/L TPh: 93 mg/L	Photo Fenton: Fe^{2+}/H_2O_2/UV compound parabolic collector solar reactor pH 3 Fe^{2+} = 55–110 mg/L H_2O_2 = 252 mg/L	54% TOC reduction in t_{30W} = 500 min (55 mg/L Fe^{2+}) Air stripped ethanol-free synthetic reduction efficiencies: 98% COD reduction in t_{30W} = 82 min 96% TOC reduction (t_{30W} = 130 min) 92% TPh reduction	[192]
COD: 1,200 mg/L	Photo Fenton: Fe^{2+}/H_2O_2/UV Pretreatment: primary sedimentation DW glass batch reactor solar simulator (150 W, λ> 280 nm, incident photon flux = 58 × 10^{-8} E/(Ls), I = 7.5 W·m^{-2}); V = 0.3 L (a) pH 2.8, Fe^{2+}: 5–25 mg/L H_2O_2 = 100–900 mg/L (b) pH 2.8, Fe^{2+}: 5–25 mg/L H_2O_2 = 100–500 mg/L	38% COD reduction Treatment time: 3 h 80% COD reduction in t_{30W} = 340	[193]
COD: 120 mg/L	Photo Fenton: Fe^{2+}/H_2O_2/UV Pretreatment: biological oxidation (MBR) bench-scale solar simulator (1 kW, I = 272.3 W·m^{-2}), batch mode pH 3, T = 15 - 45°C Fe^{2+} = 1-10 mg/L H_2O_2 = 25 - 500 mg/L	Optimum conditions: Fe^{2+} = 3 mg/L, H_2O_2 = 250 mg/L T = 25ºC, Treatment: 2 h Reduction efficiencies: 70% COD reduction 53% DOC reduction 75% colour reduction	[194]
COD 1,060 mg/L	Photo Fenton: Fe^{2+}/H_2O_2/UV Pretreatment: grid removal, biological oxidation (SBR) stirred glass batch reactor; UVA black lamp (125 W, λ = 315– 400 nm, I = 13 W·m^{-2}) pH 2.5, T = <40°C, Fe^{2+} = 139-556 mg/L H_2O_2 = 700- 3,800 mg/L	Optimum conditions: Fe^{2+} = 278 mg/L H_2O_2 = 3,000 mg/L Removal efficiencies 78% COD reduction Treatment time: 4 h	[187]

* CSTR: continuous stirred-tank reactors, TPh: Total polyphenols

The utilization of iron salts in advanced oxidation processes demonstrates significant promise as pre- or post-treatment methods in the treatment of winery wastewater, resulting in a decrease of up to 90% in COD values in certain instances [190]. The advantages of photo Fenton processes include: (i) the catalyst is effective and safe even at low iron concentrations, (ii) dilute hydrogen peroxide can be used, and (iii) there are no mass transfer constraints because all chemicals are in the liquid phase [14]. Nevertheless, advanced oxidation techniques that use iron salts also have several constraints, which are outlined in **Table 2.15** below.

Table 2.15. Advantages and drawbacks of advanced oxidation processes and its application in wastewater treatment (Modified from Coha *et al.*, [184]).

Process	Advantages	Drawbacks
AOP Common characteristics	Suitable for treating wastewater with varying contents of organic components through the process of non-selective oxidation facilitated by OH· radicals Ability to eliminate inorganic substances such as cyanides, sulfides, sulfites, nitrites, and heavy metals Applied at atmospheric pressure and room temperature	Scavenging effects by Cl^- Possibility of incomplete degradation Pre-treatment steps are generally required to minimize the adverse effect of scavengers.
Fenton	Good removal efficiency achieved in a short time Reagents are easily available	Acidic pH requirement (pH 2.5-3.5) (i.e., acidification and final re-basification of the aqueous matrix)
Photo Fenton	The reduction efficiency is higher and the process duration is shorter compared to the standard Fenton procedure Higher concentration of OH· due to photolysis with the same amount of hydrogen peroxide	Demands additional and thorough pre-treatment to enhance the transmission of light within the reactor Higher costs due to energy consumption (light source always needed)

2.9. Conclusion

Wineries have difficulties choosing the best treatment options due to the varying amounts of wastewater and its composition fluctuations over the course of the wine-making process. Based on the literature mentioned for the treatment of winery wastewater, a consistent pattern was found, showing that the limitations of many treatments are related to the variations in the volume and organic content of the wastewater. Additionally, the several stages of wastewater management: primary, secondary, and tertiary are crucial to regulating the wastewater quality and heavily depend on the final use of the wastewater and applicable laws. It is important to note that winery wastewater treatment facilities are not obligated to turn their wastewater into drinkable water; rather, they aim to make the water clean enough to be reintroduced into the water cycle naturally (via land application) without harming the environment.

Primary-treatment technologies play a significant part in the overall treatment process. These technologies are employed to remove a significant portion of the particulate matter present in the wastewater that could damage equipment in the secondary wastewater treatment stage and prepare the water for additional filtration. Primary treatment techniques that have been found to be beneficial include coagulation, flocculation, electrocoagulation, and sedimentation. These technologies remove up to 95% of total suspended solids (TSS) reduce wastewater turbidity (up to 80%), and to a lesser extent, reduce organic content (typically 40% COD reduction). A serious drawback of these technologies is the production of excessive amounts of sludge, which is often processed externally. Costs associated with sludge processing can rise, especially as wastewater levels rise. Furthermore, coagulation (and all processes following downstream) can only be efficient if effluent flow and quality can be kept as constant as possible. Since winery effluent is highly variable, large, aerated (and with recycle) equalization volumes (tanks, ponds) may thus be required.

The activated sludge treatment process and its variations are the most studied and commonly used ways to treat wastewater produced from wineries. For high COD effluents, air requirements become too high to allow activated sludge to be used and anaerobic processes are employed. Thus, biological treatment is one of the most frequently employed techniques. Due to the high biodegradability of the wastewater (owing to the presence of ethanol and sugars in the wastewater), the use of biological treatment technologies in winery wastewater treatment is justified. These processes typically result in high-quality wastewater with COD reduction values of up to 98%, but the energy requirements, air supply, excess sludge production, and biomass settling challenges affect the suitability (and long-term viability) for wastewater treatment at smaller wineries. Larger wineries may be a better fit for these processes.

Due to the straightforward design and construction, low electrical energy requirements, and shown ability to use treated wastewater as irrigation, constructed wetlands have been employed extensively throughout the wine industry for a long time. This treatment system's main disadvantages include its large footprint and long retention times. Although this method's treatment effectiveness is high (60–100% COD reduction), the lengthy retention intervals may provide problems, especially during harvest when there is a significant influx of wastewater that needs to be treated.

In this chapter, advanced oxidation treatment processes (those based on iron salts) showed that they were effective at the removal of COD, with COD levels decreasing by 40–80% when used alone and by up to 95% when paired with biological pretreatment techniques like membrane bioreactors. Treatment times were also fairly short (on average, 4 hours). High reaction rates, a high oxidation potential, and a non-selective nature are typical characteristics of advanced oxidation processes. In comparison to methods like activated sludge and constructed wetlands, a substantially smaller footprint is maintained in this system because of the high oxidation potential of the generated hydroxyl radicals. However, these treatment methods might require additional pre-treatment procedures (particularly for the photo Fenton process) requiring energy to operate the light source and enhanced light transmission in the reactor. This can be avoided by implementing energy-efficient photo-assisted advanced oxidation processes using sunlight as an irradiation source. Since hydrogen peroxide may potentially have negative impacts on subsequent treatment processes, advanced oxidation systems containing this chemical should be properly monitored and managed (careful system design may mitigate such occurrences).

In summary, activated sludge, constructed wetlands, and anaerobic digestion would be suitable for medium to large-sized wineries since anaerobic systems produce methane gas which can be used by the wineries to meet the energy needs of biological plants. On the other hand, physicochemical treatment mixed with aerated lagoons may be an effective method to treat wastewater for small wineries. This results in treated wastewater that can be used on land (irrigation). Although the quality of treated wastewater from wineries can be improved by using advanced oxidation processes, this technique has scarcely been used in South Africa's wine industry. Thus, future research in this area should focus on implementing this technique there.

For the research covered in this work, crucial factors like system capital costs, running costs, and hydrodynamic circumstances (such as retention times) are not always known. The wine industry should find the matters listed and addressed in this study helpful in comparing what has been done, what is being done, and what the future holds for winery wastewater treatment.

CHAPTER 3 EXPERIMENTAL DETAIL

This chapter discusses the research methodology and experimental design which was developed to evaluate the use of hydrodynamic shear with flotation to process winery wastewater. Three different studies were conducted where winery wastewater was collected from Lutzville winery and treated a) On a lab-scale, b) onsite at Lutzville winery and c) on a pilot plant system located at the University of the Western Cape.

3.1. Winery wastewater questionnaire

A questionnaire was compiled and distributed to four wineries in the Western Cape in order to understand common practices and process during wine production. Three of these wineries preferred to remain anonymous. Winery X is situated in the Constantia region of the western Cape, Cape Town, South Africa. Winery Y and winery Z are both situated in the Stellenbosch region of the Western Cape, Cape Town, South Africa. The aim of the questionnaire was to gain industry information on current wastewater treatment capabilities within the legislative and regulatory framework, water consumption and associated wastewater treatment expenditure. Once completed, the questionnaire shed light on current industry standards as well the gaps in existing processes and how shear enhanced flotation separation (SEFS) technology may be beneficial for the current treatment process with potential future integration. The questionnaire includes a breakdown of annual running costs.

The preliminary outcome of the questionnaire showed that the wineries involved (winery X, winery Y and winery Z) handle their winery waste well without significant challenges to keep discharge pH, TSS, TDS, COD levels within current municipal discharge limits. The incurred cost from both wastewater treatment and municipal disposal cost are relatively low. A fourth winery, Lutzville, contacted our research team inquiring if we would be able to assist them with their wastewater management. **Table 3.1** illustrates the data obtained using the winery questionnaire. It should be noted that amongst the four listed wineries, winery Z, was the only winery that treated their wastewater to an irrigation friendly standard.

Table 3.1. Summary of cost to run and maintain winery waste treatment plant (2021)**.**

	Winery			
	X	Y	Z	Lutzville
Wine production capacity (m^3/a)	300	12,000	1,000	32,250
Winery wastewater production (m^3/a)	1,179	72,465	1,960	21,017
Wastewater generated (m^3/day)	3.2	198.5	5.4	57.6
Running cost of treatment plant in MR/a	0.18	0.44	0.32	1.39
Chemicals for cleaning winery (R/a)	R10,000	R245,987	R120,175	R791,776
Chemicals related to wastewater treatment (R/a)	R10,780	R64,500	*	R185,388

*Data not provided

The questionnaire results suggested that the SEFS technology would potentially be most beneficial at Lutzville Winery. Lutzville winery showed the largest expenses associated to water treatment and was expected to gain the most from the implementation of SEFS technology. Upon obtaining various data and access to Lutzville premises, a plan was accepted by the winery to conduct a trial winery wastewater treatment experiment during the vintage season between 2021 and 2022. Following trial experiments, a pilot plant was fabricated and modified and the wastewater during the 2023 vintage season was subsequently treated with the pilot plant treatment system (discussed in Chapter 5).

3.2. Raw/Untreated winery wastewater collection

Untreated wastewater was collected from Lutzville winery, situated on the West Coast of South Africa, during the vintage period spanning from February to April in the years 2021, 2022, and 2023. This wastewater was used as the source of raw/untreated wastewater for batch and continuous laboratory/pilot plant experiments. Briefly, the winery's wastewater operational structure involves the untreated wastewater being gravitationally transported from the cellar through a 2 mm screen grid, which separates solid constituents larger than 2 mm, such as grape pomace. After passing through the screen grid, the wastewater is fed to the settling dams. These solid materials comprise various components such as grape skin, stem, residual pulp, seed, small fragments of stalks, and yeast cells originating from the wine fermentation process [75]. The initial untreated wastewater for laboratory batch experiments was obtained directly after passing through the 2 mm screen grid, as depicted in **Figure 3.1**. It was then transferred into an intermediate bulk container (IBC) using a Pedrollo RX2/20 submersible pump.

The collected wastewater presented a dark colour and strong odour. After passing through the grid, the wastewater is directed to a lime alkalisation pit, where a pre-prepared lime slurry is introduced to maintain the pH level of the wastewater at a value higher than 9. Once the pH level in the lime pit falls below 9, the lime water dosing pump is triggered. The discharge from the lime pit is directed into three interconnected settling dams (referred to as Dam A, Dam B, and Dam C in **Figure 3.1**) where solid/liquid separation takes place gravitationally. Subsequently, around five weeks later, the wastewater is transferred to three biological treatment dams (referred to as Dam 1 – 3 in **Figure 3.1**). The wastewater eventually flows into nearby fields driven by irrigation pumps, either in its concentrated or diluted state, based on the properties of the treated wastewater. Given that the SEFS process serves as a primary treatment stage technology, the primary objective of this study was to address the treatment of the untreated wastewater prior to its arrival to the settling dams. It is important to note that the investigation excluded the wastewater present in the upstream secondary biological dams (i.e., Dam 1 – 3).

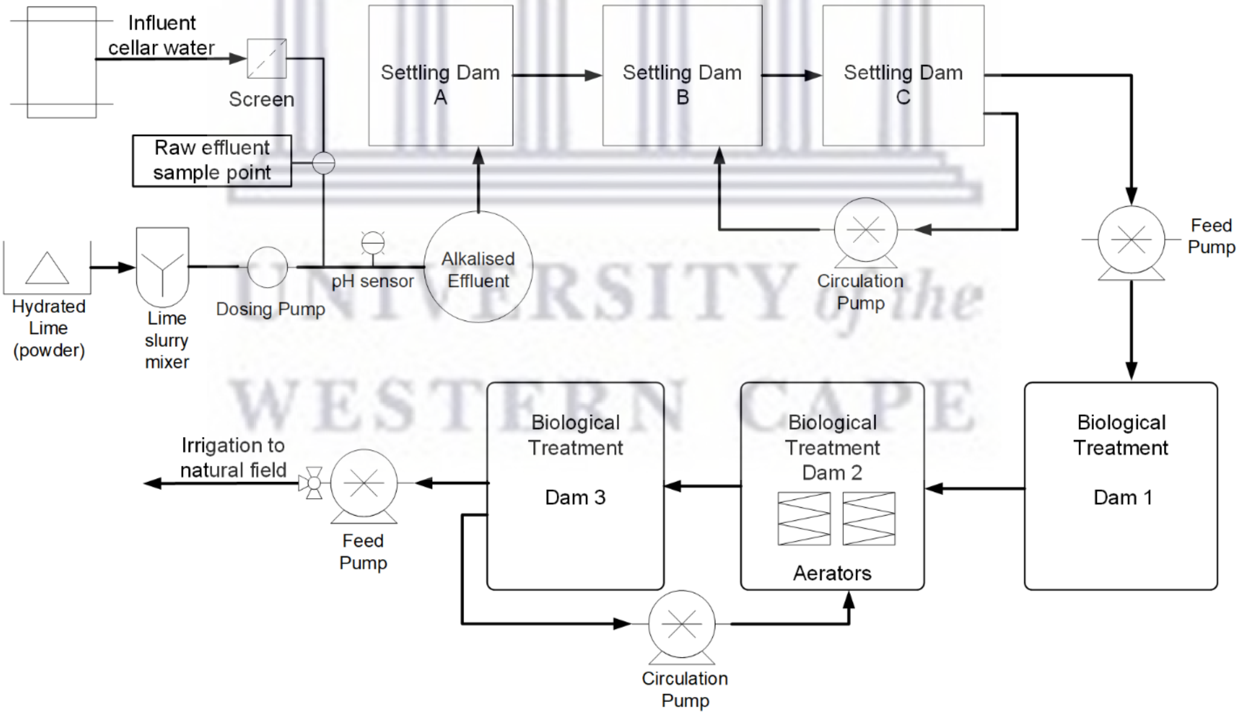


Figure 3.1. Wastewater treatment plant at Lutzville winery.

3.3. Laboratory Raw/Untreated Winery Wastewater Alkalization

The experimental investigations were carried out in laboratory batch studies using beakers with a capacity of 5 L, where the volume of the sample used was 4 L. These studies were conducted under standard atmospheric pressure and temperature conditions. A lime slurry solution was prepared through the mixing of 100 g of hydrated lime ($(CaOH)_2$), sourced from Cape Lime (Pty) Ltd, with 900 mL of distilled water in a volumetric flask. The water used in all the alkalisation experiments consisted of ultra-pure water, using Milli-Q water purification equipment provided by Millipore (South Africa). The resistivity of this water was measured to be 18.2 MΩ·cm, while the total organic carbon (TOC) concentration was 2 parts per billion (ppb). The pH of the untreated wastewater, initially at pH 4, was adjusted to pH levels of 7, 8, 9, and 10 using lime slurry concentrations of 725 mg/L, 788 mg/L, 825 mg/L, and 900 mg/L, respectively. After making pH adjustments in the 5 L beakers, a total of 8 samples, each with a volume of 500 mL, were utilized as a batch for each pH value.

3.4. Laboratory-scale Shear Mixing

The hydrodynamic shearing of the wastewater at the laboratory scale was performed using a PUXIL JRJ300-1 high speed shearing emulsifier. The high shear unit consisted of a drift shaft, stator rotor, and control box, as depicted **Figure 3.2**. This mixer has a processing capacity of 40 L, output power of 300 W and speed range 200–11,000 rpm.

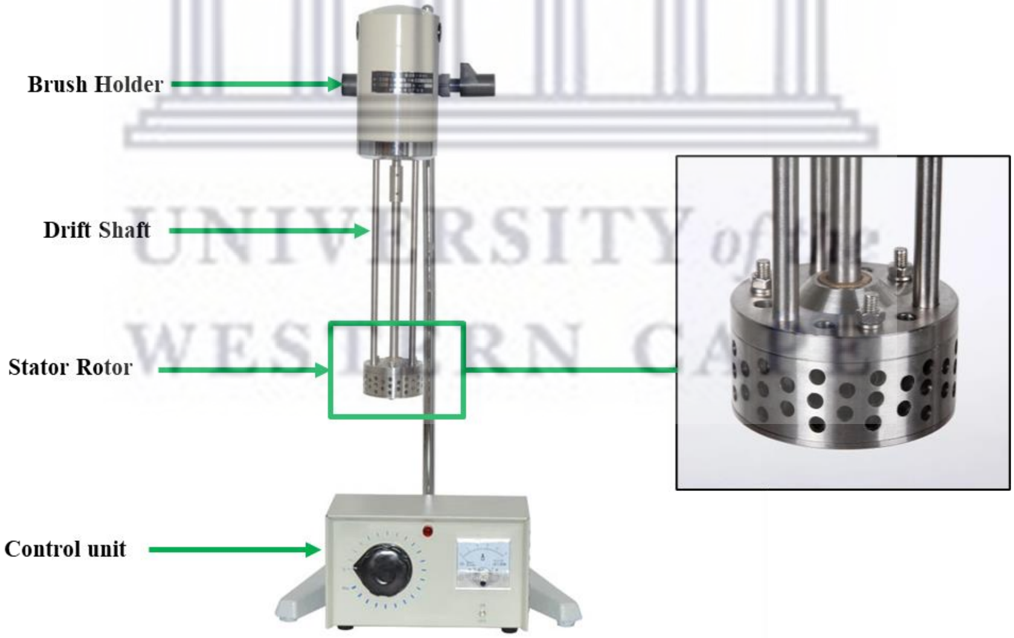


Figure 3.2. High-speed homogenizer mixer with 5 mm rotor stator head.

The principle of the shear mixing operation is depicted in **Figure 3.3** and explained as follows:

A. Within the shear mixing process, the rapid spinning of the rotor blades in the stator-rotor head generates a significant suction force, causing the upward movement of both liquid and solid substances from the lower portion of the container towards the central region of the head.

B. Materials are subsequently driven by centrifugal force toward the outer edge of the head, where they undergo a milling action in the space created between the inner wall of the stator and the ends of the rotor blades.

C. Hydrodynamic shear occurs as particles are forced to exit through the pores in the stator at a high velocity and disperse into the primary composition of the mixture.

D. The materials that are released from the head travel rapidly in a radial direction toward the sidewalls of the mixing vessel. The mixing cycle is maintained by continuously drawing new material into the head at the same time.

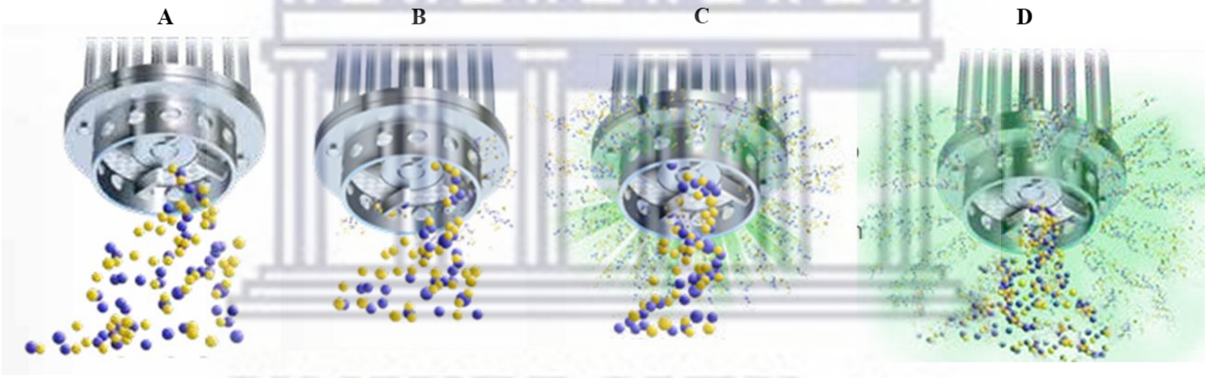


Figure 3.3. Hydrodynamic shear mixer: stator-rotor head operation [195].

During shear experiments, various shear speeds were investigated using the alkalised wastewater and thereafter, the effect of shear speed on coagulation efficiency was determined. This mixer was used throughout the laboratory scale shear-induced air flotation treatments of winery wastewater.

3.4.1. Shear-Induced Air Flotation

A laboratory-scale induced air flotation (IAF) system has been designed and constructed. The integration of a hydrodynamic shear mixer unit was incorporated into the IAF a component of the overall system.

The shear-induced air flotation unit incorporates several components, including a gas input, rotor, stator, air flow meter, speed control, and two pressured air nozzles (**Figure 3.4** shows the laboratory-scale hydrodynamic shear mixing setup of which the two pressurized air nozzles were adjusted to provide an airflow rate of 450 ln/h (normal liters per hour). A normal liter is defined as the volume of one liter of gas at a pressure of one atmosphere and a standard temperature of 20°C [196].

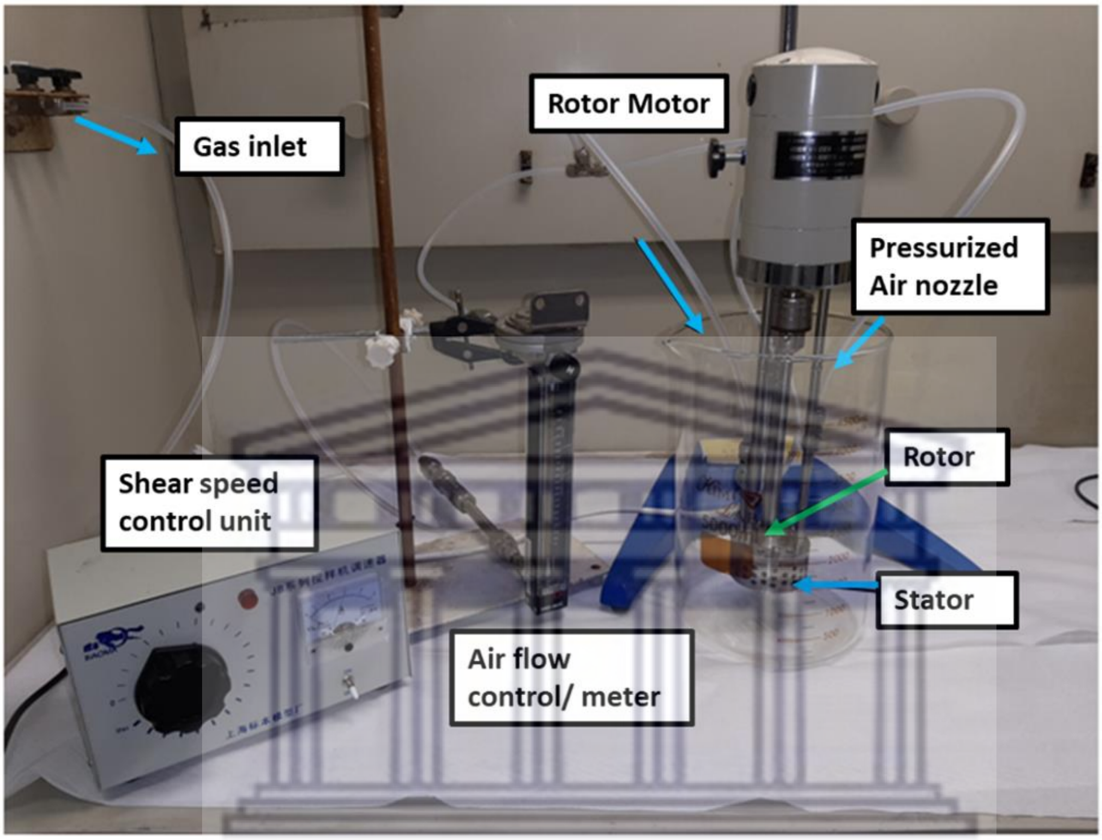


Figure 3.4. Shear separation and flotation laboratory scale unit.

3.4.2. Coagulation and flocculation

In this investigation, the selection of treatment chemicals was based on the efficacy of aluminum-based polymeric coagulants and polyacrylamide flocculants in treating different types of wastewater [49,115,136,197–199]. The coagulant used during this investigation was AB121, a composite of aluminium chlorohydrol (ACH) with a specific gravity of 1.3. It was obtained as a solution with a concentration of 1% (w/w). The flocculant employed in the experiment was AB796, a mixture of polyacrylamides (PAM) in granule form. It was prepared as a 1% (w/v) solution using ultrapure distilled-deionised water supplied from a Milli-Q system (Millipore Co.) system. The coagulant and flocculant chemicals used in this study were obtained from Abrimix (Pty) Ltd, a company based in South Africa. The coagulant was used in its original form, while a stock solution of flocculant with a concentration of 1% (w/w) was prepared weekly. The impact of coagulant dosage was examined via the optimal pH values determined through alkalization experiments. Zeta potential analysis was employed to assess the ideal dosage of coagulant as explained in Section 3.5.4.

3.4.2.1. Coagulation and flocculation Jar tests

A jar test was conducted for chemical experiments. This method facilitates adjusting of pH, variations in coagulant and flocculant dosage to predict the effectiveness of chemical treatment. In a typical coagulation experiment, aliquots of coagulant with various concentrations (1, 2, 3, 4, 5, or 10 mg/L) was added directly to the 500 mL sample while stirring with the high shear mixer for 2 min at 250; 2,000; 4,000 and 6,000 rpm, respectively. At the point where the coagulant dosage reached a zeta potential value close to 0 mV (i.e., iso-electric point), the addition of flocculant (2, 4, 6, 8, 10 and 12 mg/L) commenced where the sample was stirred using low shear at 250 rpm for 10 minutes [54].

3.4.2.1.1. Calculation of Coagulant/Flocculant dosage

The concentration of the coagulant required was calculated as per **Equation 3.1**.

$$Cc\left(\frac{mg}{L}\right) = \frac{Cv\ (mL) \times Sc\left(\frac{mg}{L}\right)}{Sv\ (mL)} \qquad \textbf{Equation 3.1}$$

Where *Cc*, is the coagulant concentration (mg/L), *Cv*, is the coagulant volume (mL), *Sc*, is the solution concentration (1%, i.e., 10,000 mg/L and *Sv*, is the sample volume (500 mL). Thus, to obtain a coagulant dosage of 10 mg/L, **Equation 3.1** was used to determine the volume of coagulant required:

$$Cv(mL) = \frac{500\ (mL) \times 10\ \left(\frac{mg}{L}\right)}{10\ 000\ \left(\frac{mg}{L}\right)} = \ 0.5\ (mL$$

Hence, the required coagulant volume needed to achieve a dosage of 10 mg/L in a 500 mL sample is 0.5 mL, with the total sample volume of the solution then equating to 500.5 mL (*Sv* + *n* mL coagulant). The same equation was used for the calculation of flocculant dosage.

3.5. Analytical methods

3.5.1. pH analysis

The pH measurements were conducted using a portable multi-meter (Hach, HQ40d). Calibration of the pH meter occurred using pH 4, 7 and 10 standards.

3.5.2. Conductivity and Total Dissolved Solids

The measurements of conductivity were performed using a Hach HQ40D portable multi meter provided by Agua Africa CC, South Africa and affiliated with Hach Pty Ltd. The probe has a measurement range covering from 0.01 µS/cm to 200,000 µS/cm.

The quantification of total dissolved solids (TDS) was determined by the meter through the multiplication of the electrical conductivity (EC) measurement with a conversion factor. The conversion factor from electrical conductivity (EC) in millisiemens per meter (mS/m) at 25 C to total dissolved solids (TDS) in milligrams per liter (mg/L) has been reported to have an average value of 6.5 [109].

3.5.3. Turbidity

The turbidity of the sample was assessed using a Hach TL2350 turbidimeter equipped with a tungsten filament lamp, which was obtained from Agua Africa CC (Johannesburg, South Africa). The measurement was conducted using the nephelometric method. The range of measurement allowed values ranging from 0 to 10,000 nephelometric turbidity units (NTU).

3.5.4. Zeta Potential Analysis

The difference in electrical potential between a particle's surface and the surrounding solution is measured by the zeta potential. The zeta potential is widely used as an indicator of the stability of colloidal systems and its ability to quantify charge neutralization makes it relevant in the context of wastewater applications. The zeta potential of a given system can be influenced by its chemical composition and concentration. Typically, dispersion systems characterized by a greater absolute zeta potential tend to induce particle repulsion, hence resulting in higher stability. Conversely, dispersion systems characterized by a lower absolute zeta potential will induce particle agglomeration [200].

The purpose of zeta potential analysis in this study was to assess the inherent surface charge of the wastewater, subsequently investigating colloidal stability and destabilization after successive treatment steps (which includes alkalisation, chemical addition, hydrodynamic shear and flotation)

The zeta potential study was performed using a Malvern Zetasizer NanoZS series instrument, which utilizes the electrophoretic light scattering measurement technique [201]. The investigation focused on analysing the zeta potential measurements with respect to changes in shear speed and coagulant dosage. The laser used in the Malvern Zetasizer Nano instrument was a helium-neon (He-Ne) laser with a power output of 4 milliwatts (mW) and a wavelength of 633 nanometers (nm) [201]. In this investigation, the determination of zeta potential was conducted using a dip cell equipped with palladium electrodes (ZEN1002). Zeta potential determination was conducted in triplicate and the reported values were taken as an average of three measurements.

During zeta potential experiments, the minimal volume of sample required is 0.7 ml. However, at least 1–20 ml of sample was on-hand in order to obtain good quality data. For the filling of the cuvette, it was tilted to a maximum angle of 45 during sample addition and filled down the inside wall to prevent bubbles forming. It is important to make sure that the sample volume is sufficient to allow full immersion of the palladium electrodes. Once the electrodes are immersed in the sample, the base of the dip cell cap and top of the cuvette are held simultaneously and placed in the cell holder in the NanoZS instrument [202].

3.5.5. Total Suspended Solids (TSS) Determination

The determination of total suspended solids was conducted in accordance with the ASTM D5907–18 standard. In this experiment [203]. Briefly, a 0.45 µm filter paper was initially weighed on a watch glass prior to the filtration process. The samples were subsequently filtered using a Buchner filter filtration set-up. The solid samples that had been filtered were subjected to a temperature of 105°C in an oven for a duration of 1 hour. Following this, the sample was removed from the oven and transferred to a desiccator for a duration of 30 minutes, enabling the sample to cool inside an atmosphere free of moisture. After the sample had been cooled, its weight was measured, and the total suspended solids were determined using **Equation 3.2**.

$$TSS\left(\frac{mg}{L}\right) = \frac{Wa\,(g) - Wb\,(g)}{Sv\,(L)} \times 1000\left(\frac{mg}{g}\right) \qquad \textbf{Equation 3.2}$$

Where *TSS* is the total suspended solids (mg/L), *Wa* (weight after) is the weight of the oven dried filter paper + dried residue (g), *Wb* (weight before) is the weight of the filter paper (g) and *Sv* is the sample volume (0.1 L). The total suspended solids determination was conducted in triplicate and the reported values were taken as an average of three measurements.

3.5.6. Bubble Size Analysis

For the examination of the bubbles produced during the treatment process, an RS PRO USB Digital Microscope was used. This microscope has a magnification ratio of 20X to 230X (optical zoom) and a capture resolution of 1920×1080. The examination of bubble size was performed using the ImageJ software designed for Windows operating system. ImageJ is an open-source Java-based image processing software that is similar to NIH Image, a component of the National Institutes of Health in the United States of America.

3.5.7. Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is the measurement of the amount of oxygen required to oxidize the organic substances in a sample, employing strong chemical oxidizers such potassium permanganate or potassium dichromate [204]. This test is commonly used as a measure of the quality of wastewater.

In a typical COD test, potassium dichromate ($K_2Cr_2O_7$), a strong oxidant, is used to completely oxidize organic molecules in a sample into carbon dioxide (CO_2) and water. Dichromate rapidly gives up oxygen (O_2) to bond with carbon atoms and produce carbon dioxide. During this process, the trivalent (Cr^{+3}) state of potassium dichromate is formed from its hexavalent (Cr^{+6}) state. The wavelengths at which the two chromium ions absorb light vary, and they are both coloured. The dichromate ion ($Cr_2O_7^{-2}$) absorbs light at 420 nm, whereas the chromic ion (Cr^{+3}) absorbs light in the 600 - 620 nm region. The number of oxidized organic molecules can be determined by measuring the colour change of the solution during the reaction. The low range COD test (<150 mg/L) determines the decrease in dichromate, whereas the high range COD test (>1,500 mg/L) measures the increase in chromium ions [205].

The measurement of COD in the samples was conducted using a Thermo Fisher Scientific Orion Aquafast 3140 colorimeter in conjunction with an Orion COD165 Thermo-reactor. The reagent vials employed in this study were the Aquafast COD HR (High Range) vials, which have a measurement range of 0 to 15,000 ppm (mg/L).

3.5.7.1. Determination of Chemical Oxygen Demand (COD)

500 ml of the sample was homogenized in a vortex mixer for 2 minutes. An Orion COD165 Thermo-reactor digestion block was pre-heated at 150°C. Then, a volume of 0.2 ml of the sample was carefully transferred into the vial using a micro-pipette. For samples with COD

concentrations ranging from 0 to 1,500 mg/L, 2 ml of sample should be used. For samples with COD concentrations ranging from 0 to 15,000 mg/L, a smaller volume of 0.2 ml should be used. The cap of the COD reagent vial was firmly tightened, and the vial was afterwards inverted multiple times in order to thoroughly homogenize the contents. The vial was placed into the preheated digester block, and a digestion period of 2 hours was administered. After 2 hours had elapsed, the digestion was turned off and the samples allowed to cool for a duration of 15 to 20 minutes. The digested samples and the reagent blanks were quantified using a Thermo Fisher Scientific Orion Aquafast 3140 colorimeter. The COD equipment is shown in **Figure 3.5**.

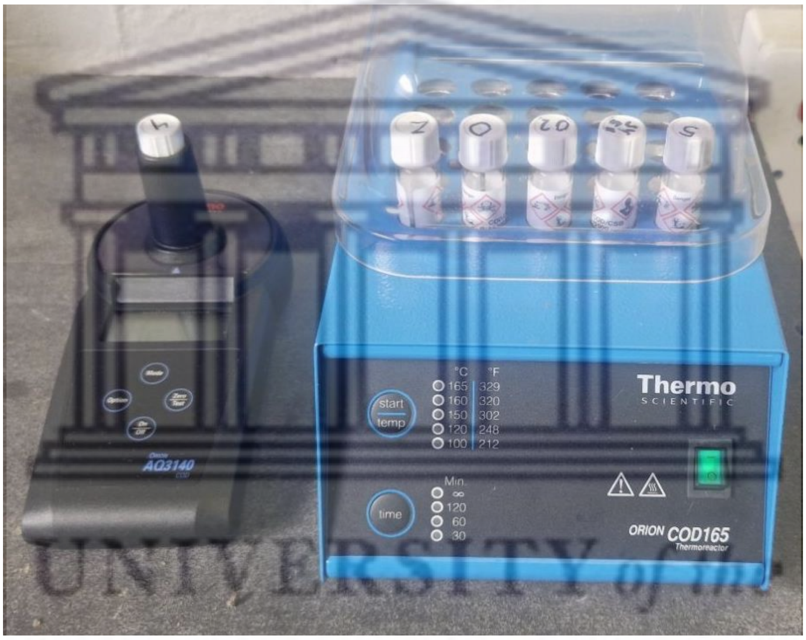


Figure 3.5. Orion COD165 Thermo-reactor digestion block and Thermo Fisher Scientific Orion Aquafast 3140 colorimeter utilised for COD measurements.

3.6. Lutzville/Abrimix Mobile Plant Wastewater Treatment Experiment.

Figure 3.6 illustrates the adopted site setup where the wastewater treatment plant at Lutzville winery was retrofitted with an Abrimix mobile treatment plant. The green and dotted section of the P&ID in **Figure 3.6** denotes the adopted Abrimix retrofitted setup., whereas the solid black lines illustrate the inherent wastewater treatment system at Lutzville winery.

In this site study, untreated winery wastewater samples were collected in the lime pit (denoted as alkalized effluent in **Figure 3.6**) via a submersible pump (PEDROLLO RXM 2/20). The variability of the influent was observed on a daily and often hourly basis where typically the pH of the influent was observed to be pH 1.5 at one stage, and 1 hr later the pH of the untreated wastewater increased to 5.2. The pH target range was pH 7 - pH 9, based on the requirement for the operational pH window of the coagulant to be used which was further confirmed with on-site jar tests. The jar testing procedure is employed to replicate a full-scale water treatment process, enabling operators to gain insights into the behaviour and performance of a treatment chemical when exposed to a certain untreated water composition.

Alkalised wastewater was pumped into three intermediate bulk container (IBC) tanks which were interconnected to the Abrimix mobile treatment plant (**Figure 3.7**), where the amount of coagulant, flocculant and air was varied (based on preliminary jar tests conducted before). Initially the coagulant and flocculant dosing pumps were set to operate at 100% capacity and upon the entry of the first 100 L of neutralized wastewater, the dosing pumps were adjusted according to the quantities obtained in the on-site jar tests. Following optimization tests on the Abrimix mobile treatment plant (the first 200 - 400 L), the exit pipe of the unit was extended to discharge this roughly 400 L wastewater back in to Settling Dam A. The collected treated wastewater was subsequently stored in an intermediate bulk container. Thereafter, 1 L aliquots of the treated wastewater were carefully preserved in a freezer and maintained at a temperature of 4°C. These preserved samples were then dispatched for laboratory analysis, specifically targeting parameters such as turbidity, electrical conductivity (EC), sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), suspended solids (SS), total dissolved solids (TDS), and chemical oxygen demand (COD).

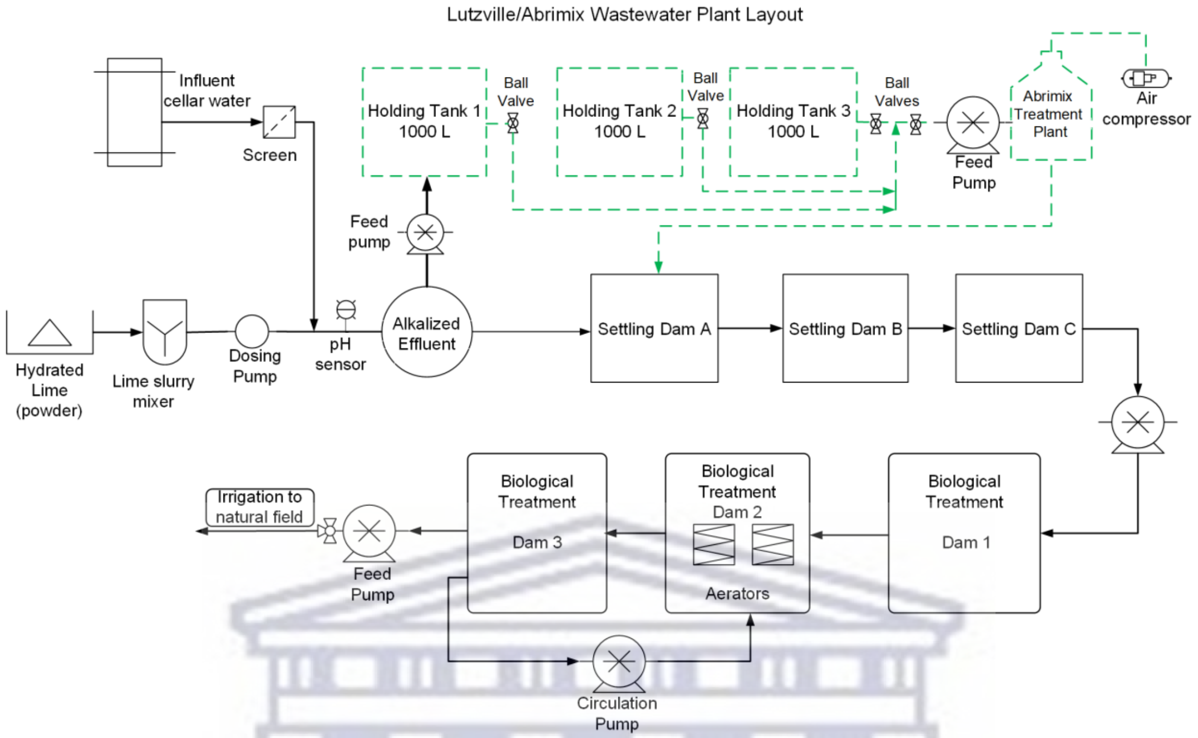


Figure 3.6. P&ID Lutzville/Abrimix treatment plant set up.

A visualization of the Abrimix site setup is shown in **Figure 3.7**. Abrimix technology employs shear forces to enhance the efficiency and completeness of chemical reactions in aqueous solutions. It has been reported that this unit employs a hydrodynamic flow route that has been meticulously constructed, drawing upon established principles of fluid engineering mechanics. The design of this treatment system results in increased variations in velocity gradients and distinct impact regions, which in turn produce repeated molecular collisions, elevated shear forces, and intensified mixing [206].

Under the scope of this thesis, the precise construction and inner workings of the Abrimix mobile treatment plant are restricted due to the accompanying patent associated with the treatment plant, however, the general operation of this system is shown in Chapter 4.

Figure 3.7. Image of Abrimix treatment plant used at Lutzville winery (2021-2022).

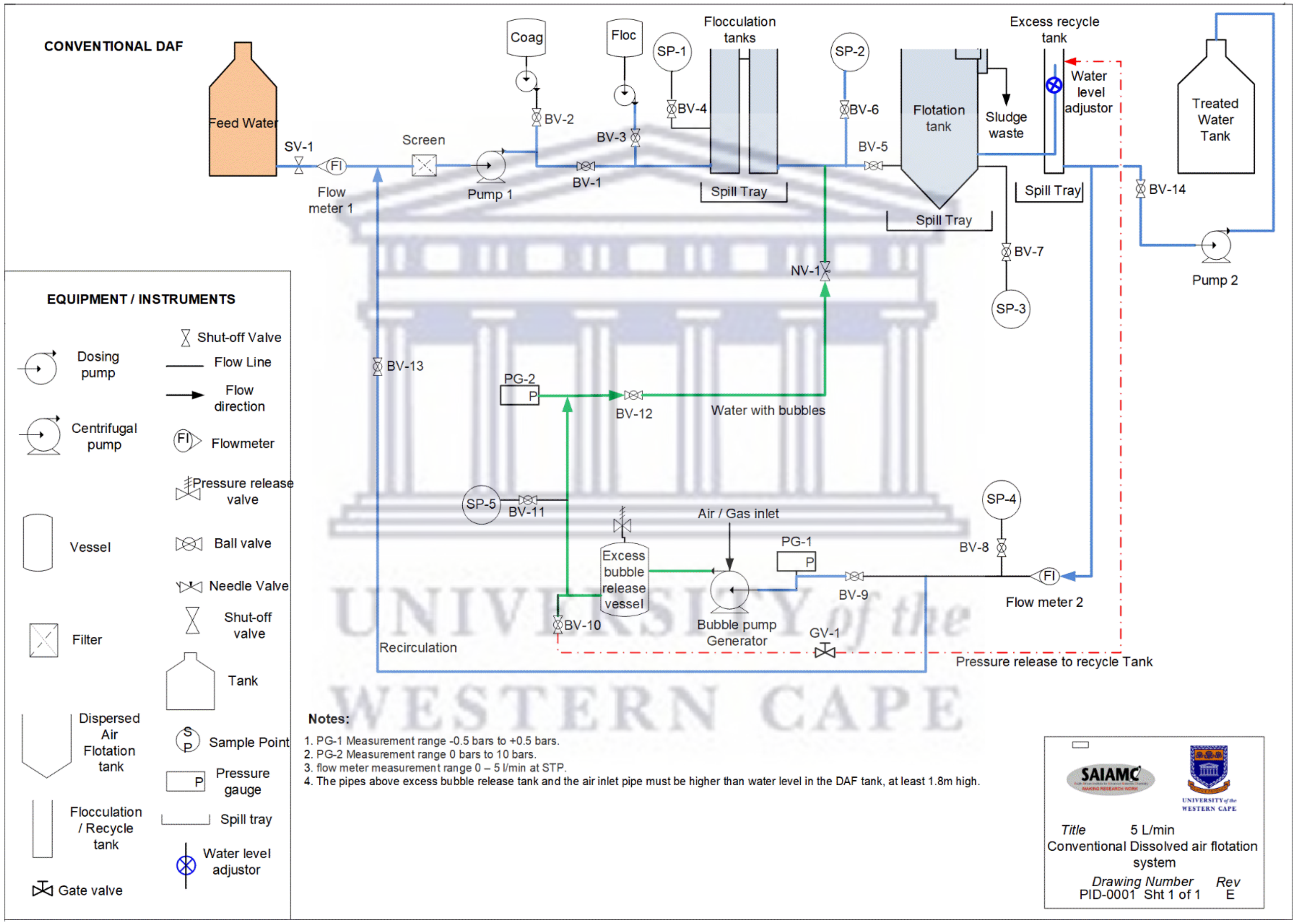
3.7. DAF Pilot Plant

A pilot plant treatment system which was fabricated to treat winery wastewater using conventional DAF. This system was subsequently modified to incorporate a shear mixer to treat winery wastewater. The modification and implementation of the pilot plant was based on the trial experiments conducted onsite as well as the optimized reaction conditions as established on the laboratory scale. The pilot plant system consisted of intermediate bulk containers (IBC) flocculation tanks, a stainless-steel flotation tank, a recycle tank, an excess bubble release vessel, a microbubble generation pump, chemical dosing vessels, chemical dosing pumps, a needle valve (NV), gate valve (GV), shut off valve (SV), water level adjustor, flow meters (Fl), and ball valves (BV).

Pilot plant chemicals were purchase from Aqua Aero Vitae, Paarden Eiland Cape Town, South Africa. The coagulant chemicals used during this part of the study was a blend of polydiallyldimethylammonium chloride (polydadmac) and aluminium chlorohydrate (ACH) with a specific gravity of 1.2 at 25°C. The flocculant used for pilot plant treatment was polyacrylamide.

Figure 3.8 illustrates the P&ID of a conventional dissolved air flotation system. Using this system, DAF can be applied with the addition of coagulant by opening ball valves (BV-1 and

BV-2), addition of flocculant (opening BV-3) and microbubbles (opening BV-12) with the needle valve (NV-1) being opened, facilitating the entry of the recycling stream containing micro-bubbles into the flotation tank. Samples to be analysed was collected using sampling points SP-1 to SP-5. Modification of the conventional DAF allows a hybrid option via addition of hydrodynamic shear as discussed in Section 3.8.



Notes:

1. PG-1 Measurement range -0.5 bars to +0.5 bars.
2. PG-2 Measurement range 0 bars to 10 bars.
3. flow meter measurement range 0 – 5 l/min at STP.
4. The pipes above excess bubble release tank and the air inlet pipe must be higher than water level in the DAF tank, at least 1.8m high.

Title 5 L/min
Conventional Dissolved air flotation system
Drawing Number PID-0001 Sht 1 of 1
Rev E

Figure 3.8. Conventional DAF Pilot Plant treatment system.

3.8. Hybrid hydrodynamic shear/DAF treatment system pilot plant description

A hybrid shear/DAF wastewater pilot plant with a flow rate of 5 L/min has been designed, built, and installed for use at the University of the Western Cape (UWC) to study the treatment of winery wastewater. The system incorporates a typical DAF treatment unit with a hydrodynamic shear mixer. The objective the pilot plant treatment system was to study the extent to which organic and inorganic pollutants in winery wastewater can be removed utilizing hydrodynamic shear, coagulation, flocculation, and dissolved air flotation.

The shear/DAF system is made up of two units: a DAF unit and a hydrodynamic shear unit. The P&ID, in **Figure 3.9** shows the conventional DAF treatment unit that has been modified. During experimental tests, the preconditioned winery wastewater (pH adjusted with lime slurry) was introduced and circulated through the unit until the pressure at PG-2 was stabilized at 2.5 bar. At this point only BV-1 and BV-12 were open. After reaching this steady state, various processes and parameters were investigated, which included conventional dissolved air flotation treatment where coagulation (BV-2), flocculation (BV-4) and microbubbles (BV-8 inlet, and BV-11 outlet as indicated by the green line) and needle valve (NV-1) is opened. A hydrodynamic shear mixing unit was added (pink line) where the wastewater can be exposed to excessive mechanical agitation by way of shear. This is achieved by opening BV-13 and BV-16. The system was designed so that each individual subsystem could be evaluated as well as to evaluate the synergistic effects of these subsystems. The treated wastewater consists of a treated product underflow, and concentrated solids collected as froth.

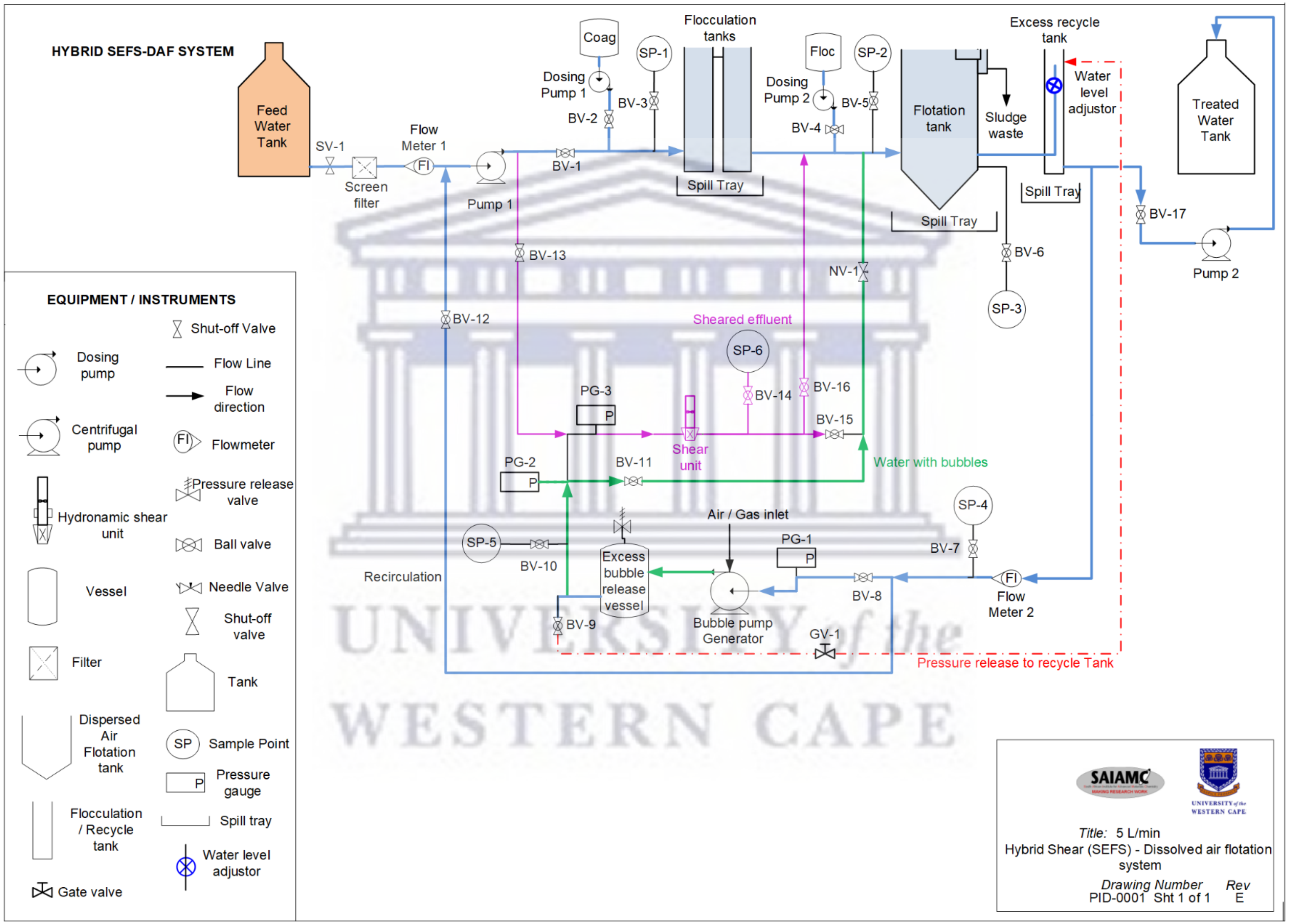


Figure 3.9. Hybrid hydrodynamic shear/DAF treatment system.

The key parts of the modified shear/DAF treatment unit are listed below and defined as the wastewater passes through the system:

- A feed water tank (1 m^3 IBC) for winery wastewater in the unit before processing (denoted feed water tank in **Figure 3.9**)
- A 2 mm filter screen, to remove big particles from wastewater (denoted screen filter in **Figure 3.9**)
- 40 L/min inlet and outlet pumps for effective wastewater transfer in the unit (pump 1 and pump 2 in **Figure 3.9**).
- Chemical dosing vessels (2 × 25 L), which are equipped with dosing pumps, to facilitate the precise administration of chemicals, such as coagulants and flocculants.
- The DAF unit was equipped with one 9 L interconnected to an 18 L flocculation tank. These tanks were however bypassed during this study since they did not serve a potential purpose for the winery wastewater treatment.
- A 142 L flotation tank, which facilitates the interaction between dissolved air, bubbles, and wastewater within the contact zone. The flotation tank serves as the location where the wastewater that has been treated and separated suspended matter will rise to the surface.
- A motorized scraper was installed on the rectangular DAF tank to scrape off floating froth from the water surface.
- An 88 L recycle tank equipped with a water level adjuster, which serves the purpose of containing treated water and regulating the overall water level within the system.
- A 1 m^3 treated water tank, which serves the purpose of extracting processed water from the system.
- Micro-bubble pump, designed to generate pressurized water with an elevated concentration of dissolved air, resulting in enhanced efficiency of air dissolution in water, reaching levels of up to 90% [207]. This pump increases the air content of wastewater. Bubbles are only generated by the process of pressure reduction across the needle valve.
- Excess bubble release vessel, to facilitate the discharge of excessive air that is drawn into the pump in the form of large bubbles. Additionally, it serves to provide for an appropriate period of time for the air to dissolve properly into the water.
- Additionally, the excess bubble release (i.e., pressure relief) vessel is designed to release the gas if the pressure exceeds 3 bar.
- Needle valve before the DAF flotation tank, to alleviate pressure and facilitate the escape of air from solution in the form of micro-bubbles. This step is crucial as it ensures that the bubbles are efficiently and consistently introduced into the flotation tank's contact zone.

- An electric control panel was utilized to effectively manage the system, which includes controls for the inlet/outlet pumps, dosing pumps, shear unit, micro-bubble pump and scrapper.
- Spillage trays were fabricated and placed in the unit to collect any excess wastewater overflowing during the treatment process.
- Pressure gauges, to quantify and verify safe/optimal system operational parameters.
- Flow meters to precisely gauge and keep the ideal flow rate at different parts of the system.
- Ball valves with low flow resistance

The hybrid shear/DAF treatment system, along with its various components, provides the flexibility to incorporate or exclude various components, hence enabling a range of treatment possibilities:

- Dissolved air flotation with coagulation and flocculation
- Dissolved air flotation with hydrodynamic shear, and
- Dissolved air flotation with shear, coagulation and flocculation

Post DAF unit, the system enables the following water processes to take place:

- Wastewater can be pumped back to the DAF unit via the micro-bubble pump so that flocs which were not floated can be retrieved.
- Wastewater may be pumped back to the DAF unit via the micro-bubble pump with the inclusion of the hydrodynamic shear mixer.
- Addition of winery wastewater (feed water) and removal of treated/processed water from the DAF unit into a product water tank.

A three-dimensional view of the pilot plant is illustrated in **Figure 3.10**.

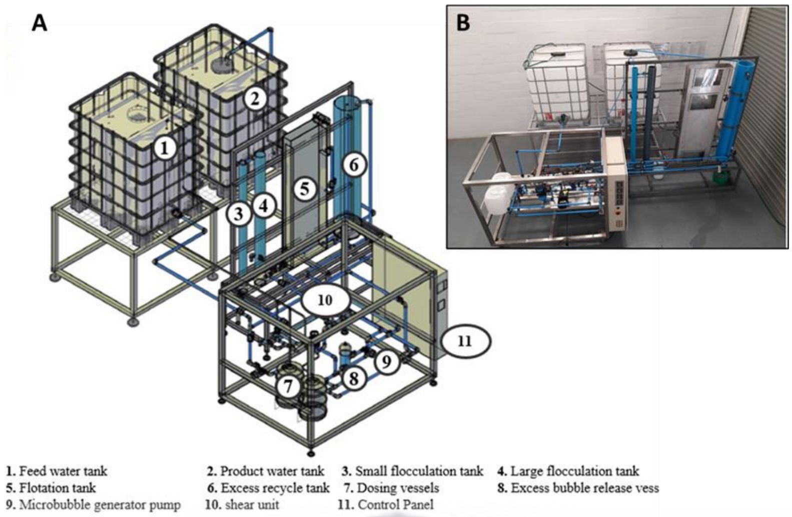


Figure 3.10. (A) 3D view of Shear/DAF hybrid treatment system and (B) image of built pilot plant [208].

The shear unit was constructed from steel sheets that were assembled to form a robust external framework and an internally rotating waterproof unit. The multi-layered steel structure enables the creation of an extended gap for shearing between the rotor and stator, which permits the flow of wastewater through an inlet and outlet as illustrated in **Figure 3.11** and **Figure 3.12**.

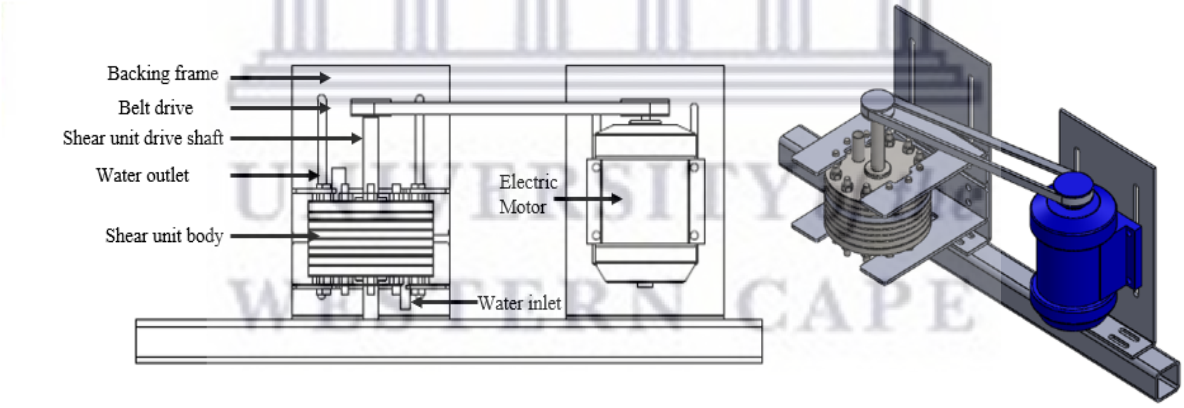


Figure 3.11. Driving belt connected to shear unit assembly via an electric motor [208].

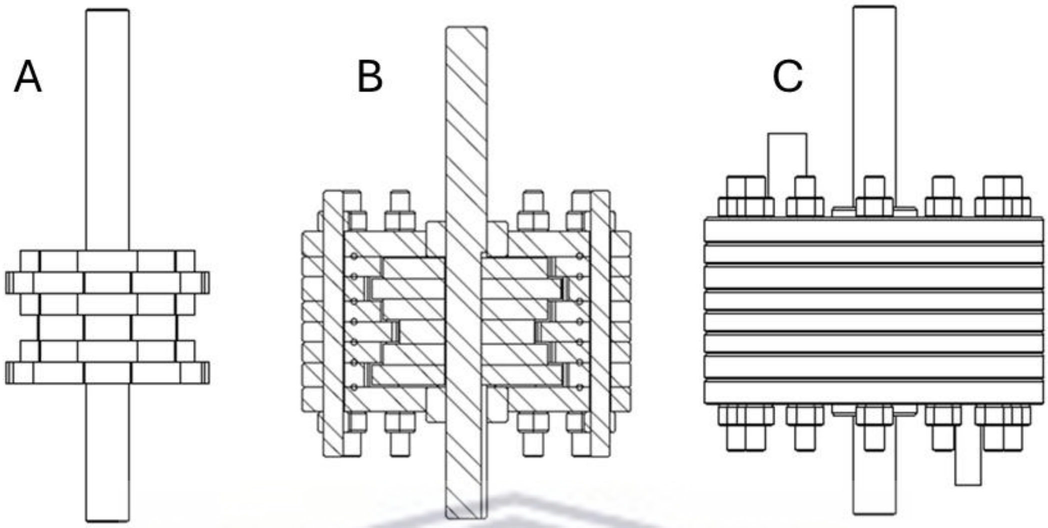


Figure 3.12. Arrangement of the shear unit assembly's internal components [208].

Figure 3.12A depicts the stator part of the shear unit, **Figure 3.12B**, shows a cross sectional view of the stator and rotor assembly in the shear unit and **Figure 3.12C,** illustrates the enclosed shear unit body.

CHAPTER 4 SHEAR ENHANCED FLOTATION SEPARATION TECHNOLOGY IN WINERY WASTEWATER TREATMENT: LABORATORY AND ABRIMIX MOBILE TREATMENT PLANT INVESTIGATIONS

4.1. Overview

This chapter investigates two separate winery wastewater treatment approaches. **Section 4.2 – 4.7** describes and discusses the treatment using shear enhanced flotation separation technology on a laboratory scale, whereas **Section 4.8** discusses the treatment of winery wastewater using the patented Abrimix mobile treatment plant. A significant portion of this chapter has been published as a research article in MDPI’s *Water* Journal (2023, *15*, 2409), entitled: Shear Enhanced Flotation Separation Technology in Winery Wastewater Treatment. https://doi.org/10.3390/w15132409.

4.2. Untreated winery wastewater composition

During the vintage period of March 2021 to April 2022, the Lutzville winery processed a combined total of 43,000 tons of grapes, consisting of 38,000 tons of white grapes and 5,500 tons of red grapes. The average composition of the winery's wastewater during this period is presented in **Table 4.1**. Samples were collected to serve as representative snapshots of the stream's quality at a specific point in time.

Table 4.1. Average untreated winery wastewater characterization.

	pH (25 C)	**Turbidity** (NTU)	**EC** (mS/m)	**Ca** (mg/L)	**TSS** (mg/L)	**TDS** (mg/L)	**COD** (mg/L)
Mar 23rd – 28th 2021	4.0±2.1	630±75	175±25	130±100	2,275±400	3,546±400	22,620±1,500
Apr 9th – 14th 2022	4.5±3.0	570±65	230±30	222±40	1,840±260	1,476±400	12,400±1,800

The chemical composition values of the wastewater collected from the winery and utilized in this study are consistent with findings from previous published research conducted on winery wastewater composition in South Africa [23,74,209]. The data presented in **Table 4.1**, indicates that the untreated wastewater exhibited acidic properties, as well as elevated levels of total suspended solids (TSS), total dissolved solids (TDS), and chemical oxygen demand (COD).

Previous investigations into the composition of winery wastewater have yielded findings indicating that ethanol and sugars (specifically glucose and fructose), collectively account for 90% of the overall soluble organic load [72].

To ensure the proper management of winery wastewater for reuse in irrigation applications, it is crucial to adhere to specific legislative constraints [5]. The aforementioned constraints are presented in **Table 4.2**. After conducting a comparative analysis of the data provided in **Table 4.1** and **Table 4.2**, it is evident that the untreated winery wastewater does not meet the prescribed limits specified in the general authorization for irrigation water quality in South Africa. Thus, the wastewater is required to undergo some form of treatment in order to decrease the pollutants found therein before irrigation can be considered. The first step for pre-treating winery wastewater usually consists of pH adjustments (i.e., alkalisation of the wastewater).

Table 4.2. General Authorizations for legislated limits for irrigation water quality in South Africa [5].

	Maximum irrigation volume allowed (m^3/day)		
Parameter	<50	<500	<2,000
pH	6 - 9	6 - 9	5.5 – 9.5
COD (mg/L)	5,000	400	75
EC (mS/m)	200	200	70 – 150
TSS (mg/L)	-	-	<25
TDS (mg/L)*	1,300	1300	488 – 975

Chemical Oxygen Demand (COD); Electrical Conductivity (EC); Suspended Solids (TSS), Total Dissolved Solids

*TDS based on EC using a conversion factor of 6.5.

4.3. pH adjustments

In accordance with wastewater discharge permits, it is typically mandated that acidic waste must undergo alkalization to achieve a pH level within the range of 6.0 to 9.0 [5]. It is widely recognized that winery wastewater exhibits a significant presence of negatively charged colloidal particles [46]. The colloidal particles in question tend to remain suspended in aqueous solutions as a result of the net repulsive forces acting on the surfaces [210]. The process of pH adjustment is employed in order to induce a partial disruption of these repulsive forces. In order to attain these objectives, the process of lime alkalization is frequently employed as the pH alkalization agent [2,211,212].

The presence of acidic conditions in winery wastewater promotes the generation of hydrogen sulphide, which is a malodorous gas [213]. Increasing the pH level of the stored wastewater significantly mitigates the generation of hydrogen sulphide, subsequently reducing the adverse effects of unpleasant odours on the wine farm as well as adjacent properties. This step holds significant importance, particularly within the framework of this case study, as the selected winery has been subject to frequent complaints from neighbouring residents regarding the emission of unpleasant odours originating from the wastewater plant.

Figure 4.1 illustrates the correlation between pH and both zeta potential and turbidity.

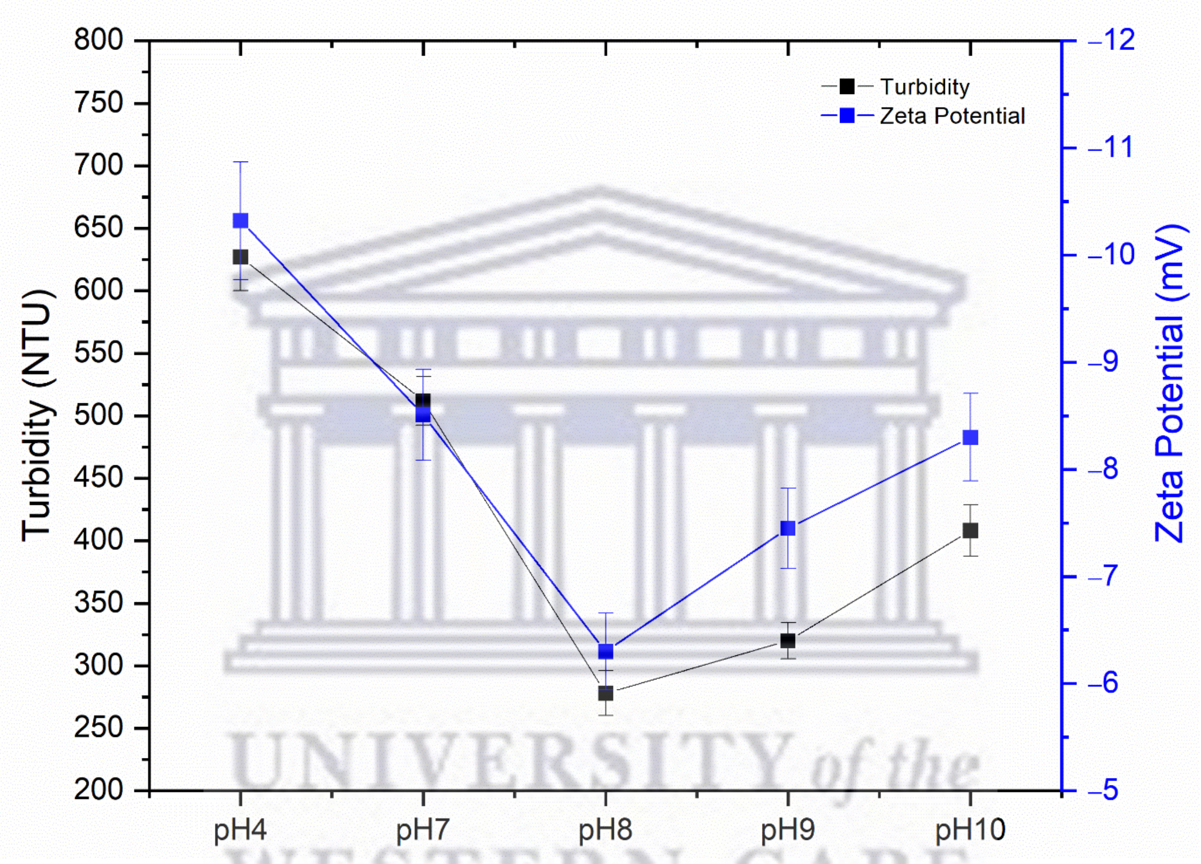


Figure 4.1. Zeta potential and turbidity as a function of pH.

It can be deduced from **Figure 4.1** that the zeta potential of untreated (pH 4) winery wastewater is high, compared to the alkalised wastewater (pH 7 – pH 10), suggesting a higher degree of colloid stability. The increased turbidity observed in the untreated wastewater is a result of the lower tendency of colloids to agglomerate and subsequently precipitate. This can be attributed to the higher electrostatic charges present, which create repulsive forces between colloidal particles.

The addition of lime is widely recognized for its dual role as an alkalizing agent as well as a coagulant [214]. Consequently, the introduction of lime leads to a noticeable reduction in zeta potential, as documented in previous studies [215]. A general decrease in turbidity was observed as the pH increased from 4 to 8. This observation was supported by a study conducted by Luz *et al.*, (2021) [212]. The results of the study demonstrated that the addition of lime for alkalization led to a significant reduction in the turbidity of the wastewater, decreasing it from an initial value of 159 NTU to a final value of 2 NTU [212]. The results of the pH adjustment experiment, highlighted that the pH value which resulted in the lowest zeta potential and turbidity readings was found to be pH 8, indicating the most favourable conditions for the aggregation via surface charge destabilization and sedimentation of the particulate matter. The zeta potential of the solution decreased at pH values exceeding 8 (particles became slightly more stable), attributable to an excessive dosage of lime resulting in oversaturation. Additionally, the resuspension of particles can be observed through the noticeable rise in turbidity measurements. Awodiji *et al.*, (2020), reported a comparable pattern [216].

The visual observation of the impact of alkalization on turbidity in the context of alkalization investigations is illustrated in **Figure 4.2**. In this context, the addition of hydrated lime serves the dual purpose of elevating the pH of the solution and facilitating the removal of suspended particles. The data presented in **Figure 4.1** and **Figure 4.2** enabled the identification of the optimal pH range (pH 8 – pH 9) for conducting subsequent coagulation experiments.

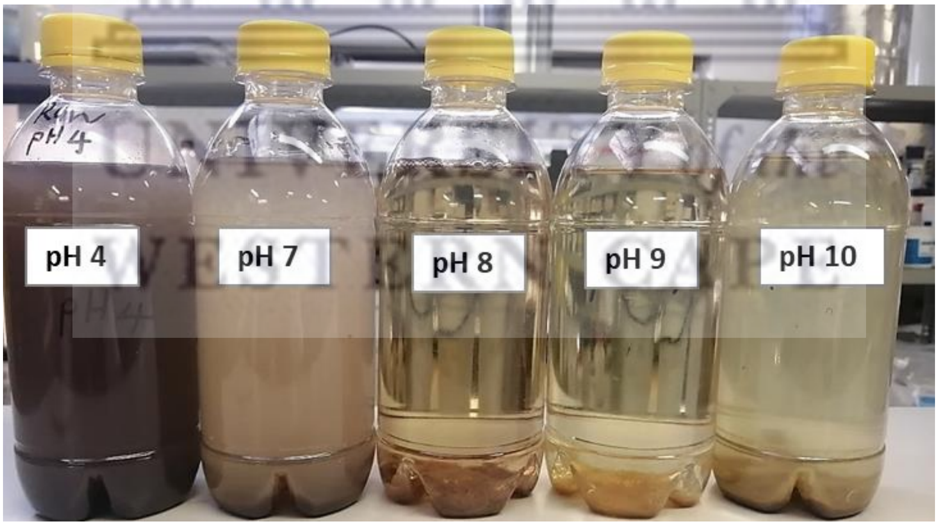


Figure 4.2. Lime alkalization studies as a function of pH.

4.4. Application of shear

After conducting pH adjustment experiments, the effect of subjecting the wastewater to shear forces was investigated, without the addition of coagulation or flocculation chemicals other than the lime previously added. The wastewater, which had been alkalised to a pH of 8, was exposed to varying shearing speeds for various time periods. One batch of this particular wastewater was subjected to intense shearing speeds (2,000, 4,000, and 6,000 rpm) using a rotor-stator mixer, while another batch was exposed to gentler shearing speeds (250 rpm) using a magnetic stirrer. The samples underwent shearing for various time intervals, specifically: 0 minutes, 1 minute, 5 minutes, 10 minutes, 20 minutes, and 30 minutes, in order to investigate the impact of increasing shear time. Following the completion of the designated shearing time, samples were extracted from the central region of the container used in the SEFS laboratory experiments, precisely 5 cm below the liquid surface, two minutes after agitation. These samples were then immediately taken for zeta potential analysis. An image of the experiment is shown in **Figure 4.3**.

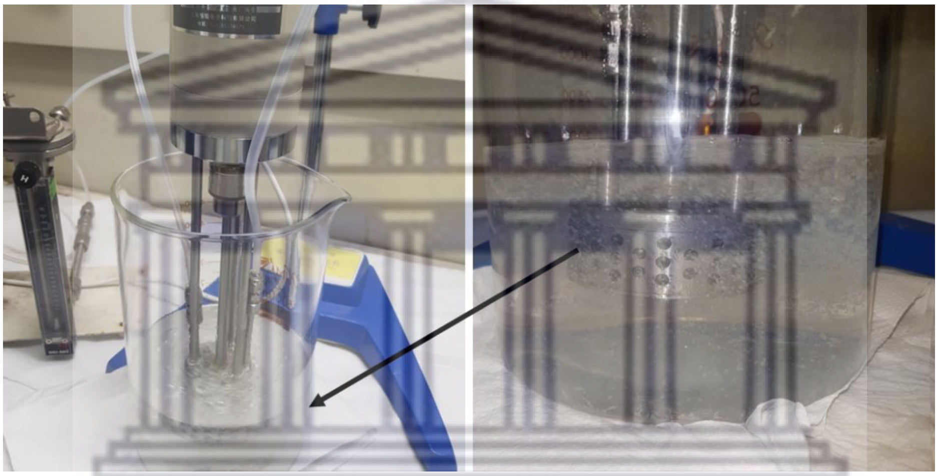


Figure 4.3. SEFS laboratory experiment.

Figure 4.4 illustrates the effect of various shear speeds over time on colloid stability. The experimental findings demonstrate that when aqueous samples are subjected to a specific shear environment, the resulting wastewater exhibits zeta potential values that tend towards 0 mV. This observation indicates a higher probability for the destabilization of colloidal particles to take place. The rapid stirring process employed in this step induces the destabilization of the suspended colloids, leading to the aggregation of colloidal particles through the influence of Van der Waal's forces. The analysis of zeta potential reveals that hydrodynamic shear exerts a significant influence on the destabilization of colloidal particles. The fundamental concept underlying shear flocculation in this investigation is predicated on the generation of colloid collisions with sufficient momentum. These collisions are characterized by kinetic energy levels that exceed the surface repulsive force, thereby facilitating the process of particle agglomeration [48].

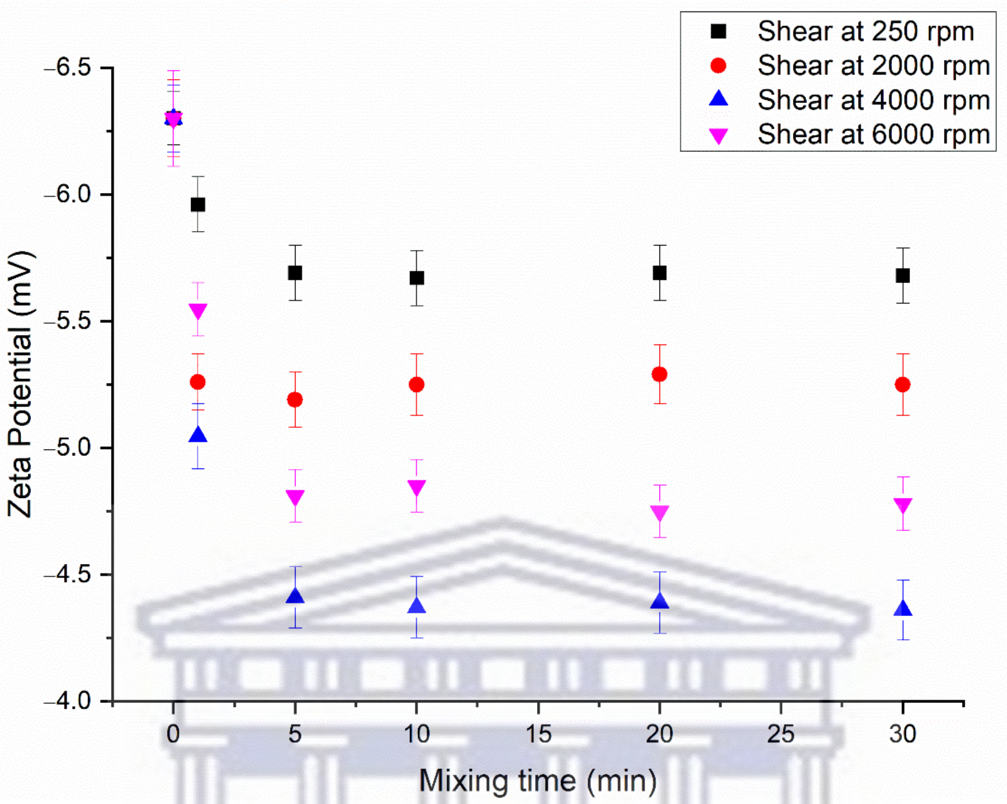


Figure 4.4. Effect of shear rate and time (pH 8) on colloidal stability based on zeta potential.

The optimal shear speed was found to occur at 4,000 rpm, resulting in the attainment of the lowest zeta potential. The findings obtained in **Figure 4.4** suggest that elevating the shear rate beyond 4,000 rpm resulted in a moderate re-stabilization of the suspended colloidal particles. When comparing the results, it was observed that batch tests conducted at low shearing speed (250 rpm) exhibited only a marginal reduction in zeta potential values. The zeta potential findings pertaining to various shear speeds and times demonstrate that a steady state is achieved after 5 minutes of agitation. Therefore, the optimal destabilization of particles through shear, at both low and high shear speeds, is achieved following a shearing time of 5 minutes.

The forces exerted on a suspended particle include van der Waals forces, electrostatic forces and hydrodynamic forces [217]. Based on the zeta potential analyses, it is possible to hypothesize that the particles' surface charge has undergone alteration as a result of the application of a hydrodynamic shear force. The incorporation of hydrodynamic shear into wastewater treatment processes enhances the likelihood of collisions between particles. The observed rise in collision frequencies suggests that the surface chemistry of the particles might undergo modifications, leading to the aggregation of suspended particles and the subsequent formation of larger clusters.

The cohesive forces that promote the aggregation of particles are commonly referred to as van der Waals forces, while the repulsion between particles is attributed to electrostatic forces arising from the electric double-layer surrounding the particles. The electrostatic forces present in the system oppose the process of aggregation, thereby providing stability to the suspended particles. By applying hydrodynamic shear and adding ions with opposite charges to the colloidal suspension, the electric double-layer can be altered and the particles in the solution can more easily become destabilized [142]. Shear forces induce interparticle collisions among the dispersed particles. The phenomenon of particle aggregation induced by shear is commonly referred to as orthokinetic agglomeration [49]. In the study conducted by Elizaveta Forbes (2011), it was found that hydrodynamic shear plays a crucial role in the recovery of small particles [48]. This process leads to the formation of particle aggregates that have the ability to adhere to air bubbles and subsequently be collected through flotation [48].

4.5. Zeta potential studies on coagulation

Real-time determination of appropriate coagulant dosage of varying raw wastewater quality in a treatment plant is a challenging task due to the nonlinear relationship between coagulant dosage and raw wastewater characteristics [218]. Zeta potential analysis is an important tool to determine optimal chemical dosages in wastewater treatment. Coagulation studies examined the impact of coagulant type and dosage on the wastewater. The optimal pH values were determined, and the most suitable coagulant type and dosage were assessed using zeta potential analysis.

The zeta potential results provided valuable information regarding the optimal dosage of chemicals necessary to attain the highest level of particle destabilization and agglomeration in a suspended state. The zeta potential was measured after each successive addition of coagulant. A decrease in the absolute zeta potential values towards zero, indicates that the introduced coagulant is causing destabilization of the colloidal particles in the wastewater, leading to particle aggregation.

An iso-electric point was observed for the AB121 (which is blend of aluminium chlorohydrol) coagulant (1% w/w solution) during the conducted coagulation experiments. This observation is represented by the presence of a dotted line at 0 mV in **Figure 4.5**. At the isoelectric point, which was obtained at a concentration of 5 mg/L (250 µL in a 500 mL sample), colloidal particles are situated within an optimal region of destabilization. In this state, the particles no longer exhibit repulsive forces in relation to each other, thereby creating favourable conditions for the processes of agglomeration and micro-flocculation to take place. The introduction of a flocculant at this point would enhance both the size and stability of the floc.

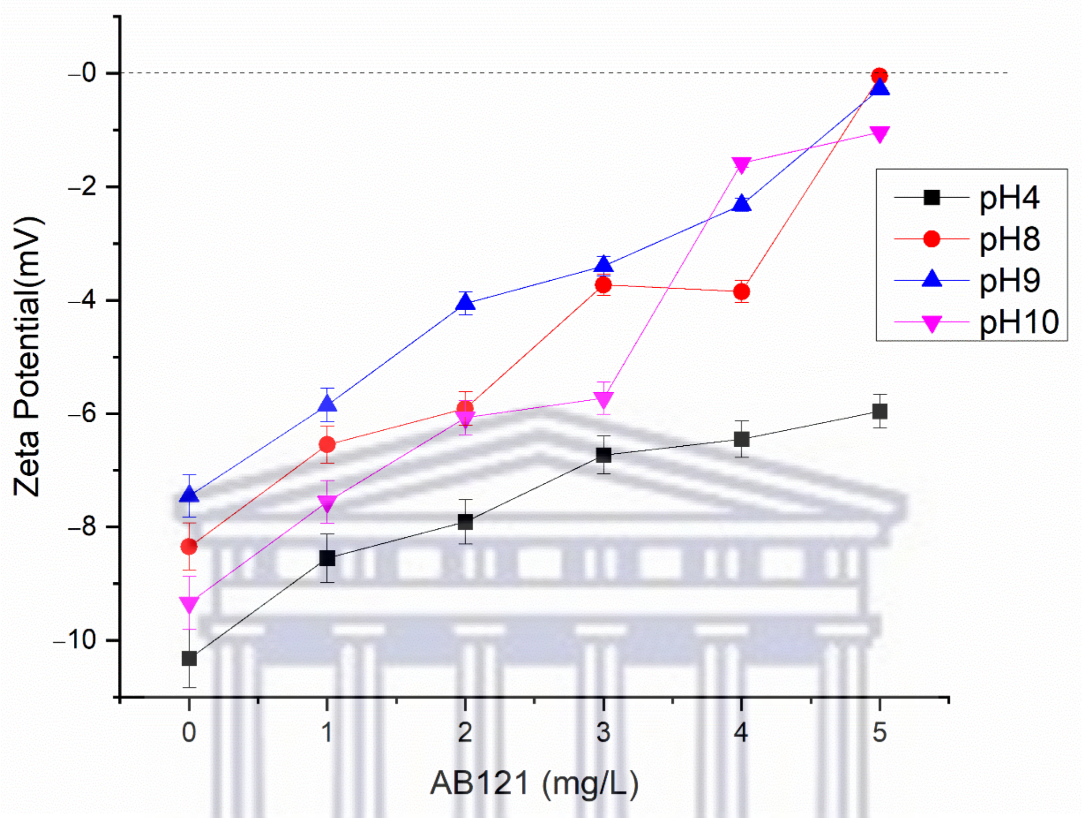


Figure 4.5. Effect of AB121 coagulant dosage on pH and zeta potential.

The effectiveness of coagulant AB121 in alkalizing the counterions in solution was demonstrated, through the adsorption mechanism proposed by Lee *et al.*, 2014 [219]. The possibility of adsorption arises from the presence of specific macromolecular structures in this coagulant, which consist of various functional groups such as carboxyl and hydroxyl. These functional groups have the ability to interact with the contaminants present in the wastewater [220].

As mentioned earlier, it is commonly observed that colloids present in wastewater exhibit a negative charge. However, upon the introduction of a coagulant, these negatively charged colloidal particles undergo destabilization due to the presence of a cationic coagulant. This process leads to an overall reduction in surface charge and the subsequent formation of micro-flocs. Nevertheless, the coagulation process frequently yields small and delicate aggregates that are prone to disintegration under the influence of mechanical stresses. In order to address this issue, the introduction of flocculant chemicals is commonly used to enhance the density and structural integrity of the flocs that are formed [219]. This following section will examine the impact of flocculant dosage on the efficacy of the coagulation process. The treatment efficiency was assessed based on the quality parameters of total suspended solids and turbidity.

4.6. Flocculation

Prior to the flocculation experiments, the wastewater was adjusted to a pH of 8 with the addition of lime. Subsequently, it was subjected to mechanical agitation at a speed of 4,000 rpm and treated with coagulant (AB121) at a concentration of 5 mg/L. The samples that had undergone pre-conditioning were treated with a polyacrylamide flocculant (AB796, Abrimix). It is important to note that in the flocculation process, gentle mixing had been used (250 rpm with the aid of a magnetic stirrer) to prevent the breakup of the generated flocs, as opposed to the high shear conditions used for coagulation. The stirring of the mixture of flocculant and preconditioned wastewater was stopped 5 minutes after initiation. After a duration of 2 minutes, the samples were extracted from the central region of the holding container by use of a micropipette.

Both turbidity and the value of total suspended solids (TSS) were measured and shown in **Figure 4.6**. The findings show that adding 10 mg/L flocculant (500 µL to a 500 mL sample) to the pre-conditioned solution reduced both turbidity and suspended solids by 85%. **Figure 4.6** demonstrates a strong link between turbidity and suspended solids. Further addition of the flocculant (>10 mg/L) proved to be ineffective as it did not cause any changes in both the turbidity and TSS [54].

The research conducted by Iakovides *et al.*, (2014) examined the effectiveness of using a combination of polydadmac and hydrated lime ($CaOH)_2$) for the treatment of olive mill wastewater [221]. The findings of the study demonstrated that with a lime dosage of 20,000 mg/L and a polydadmac flocculant concentration ranging from 750 to 200 mg/L, an overall reduction of 27% in TSS and 43% in total solids was seen [221].

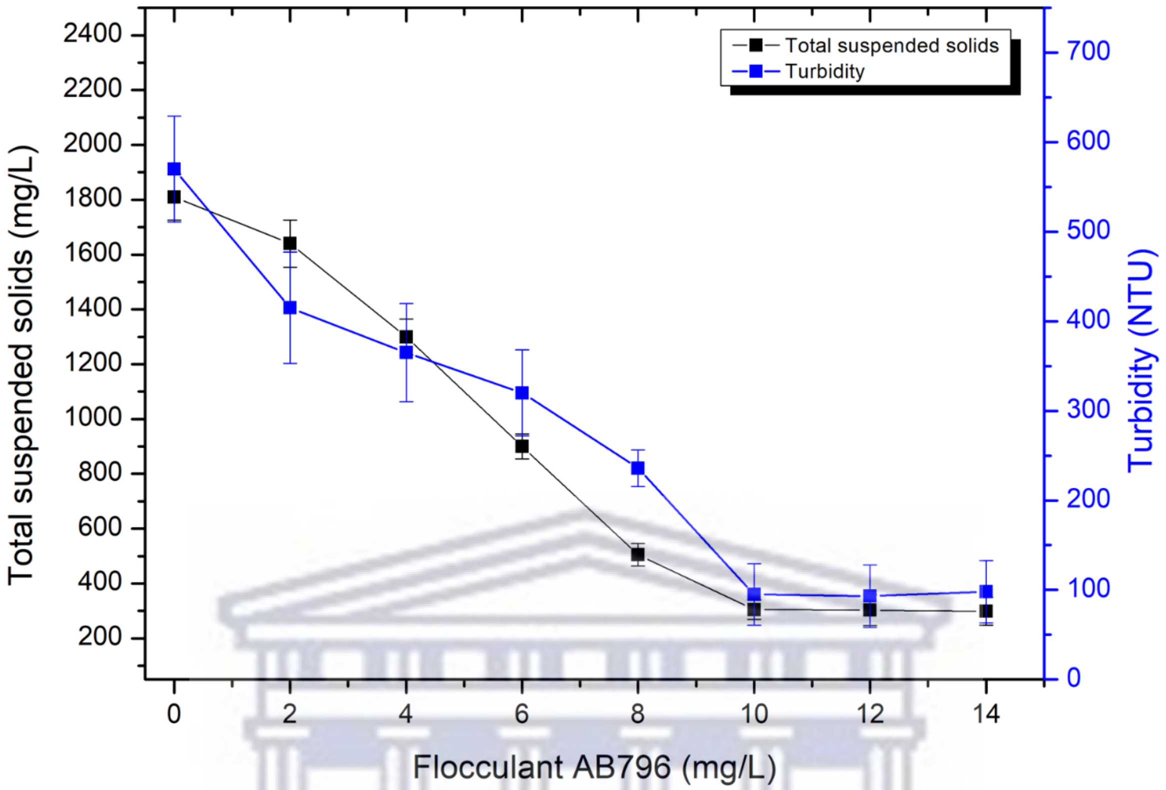


Figure 4.6. Turbidity and total suspended solids as a function of flocculant dosage

The particles that have been effectively destabilized tend to aggregate, forming agglomerates. These agglomerates are then captured by the polymer chains present in the flocculant, leading to the formation of larger settling flocs [222]. The flocculant functions by facilitating the aggregation of individual micro-flocs, thereby serving as a structural support for the developing floc and enhancing its mechanical strength. The majority of these flocs settle within a minute, resulting in a transparent solution with significantly decreased turbidity and TSS levels. The mechanism of shear coagulation and flocculation induces the aggregation of contaminant particles in the wastewater, enabling the separation through treatment with dispersed air bubbles. This process facilitates the flotation of the aggregates to the liquid's surface, where they can be extracted as froth, leaving a clear treated wastewater as the supernatant.

4.7. Introduction of Air

In the course of examining the final process parameter, which involved the introduction of air along with shear/coagulation and flocculation, the wastewater was alkalised using lime to achieve a pH of 8. Subsequently, it underwent high shear speed of 4,000 rpm, followed by the addition of 5 mg/L of coagulant (AB121) and 10 mg/L of flocculant (AB796). After the addition of coagulation/shear/air, the shear mixer was turned off and the solution was then stirred at a speed of 250 rpm using a magnetic stirrer, while air was supplied (into the stator unit) to the stirring solution for 10 minutes at 450 L/h. In **Figure 4.7** the TSS and turbidity measurements are presented for wastewater samples: untreated wastewater, alkalised wastewater (pH 8) and shear treated (SEFS) wastewater (subjected to shear, coagulation and flocculation processes). The wastewater samples have been processed using two methods: flotation (with the addition of air at a rate of 450 L/h) and sedimentation (without the introduction of air). The measurements and samples were taken near the rotor stator cavity.

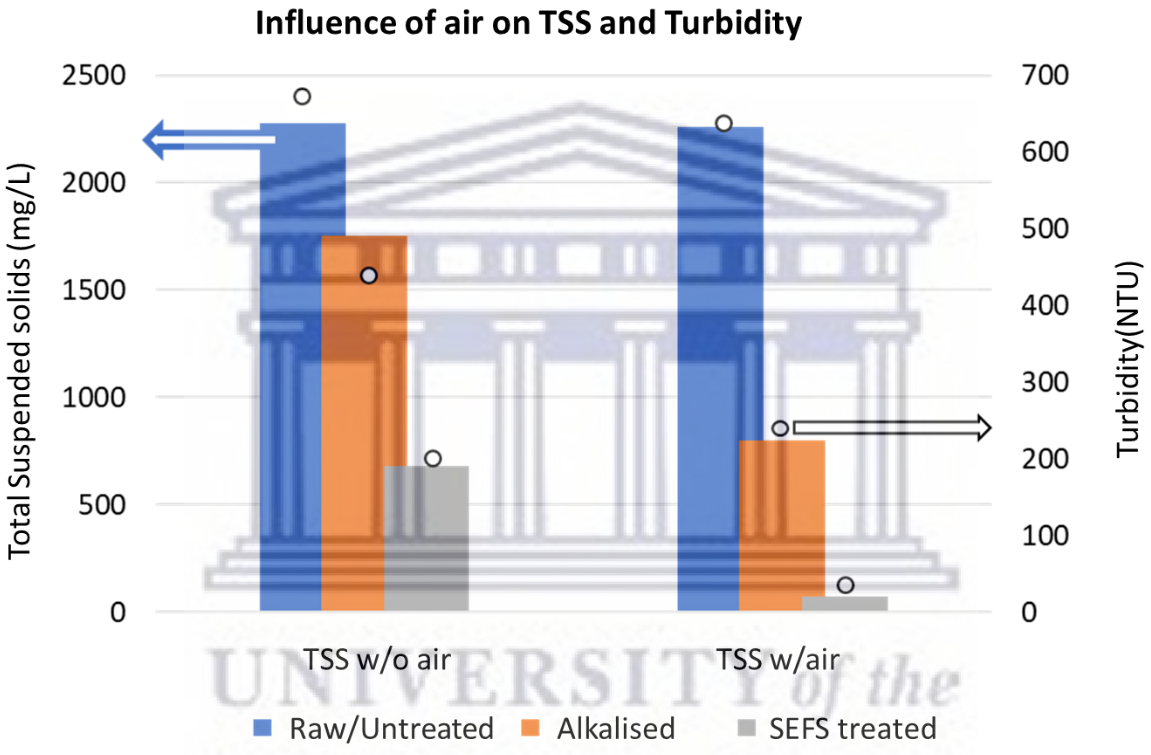


Figure 4.7. Influence of induced air on turbidity (o) and total suspended solids (blocks)

The favourable nature of the small bubbles generated by the SEFS rotor lies in its capacity to offer a larger surface area, hence facilitating enhanced bubble particle attachment and promoting the buoyancy of suspended solids more effectively. Published research indicates a strong association between the importance of reducing bubble size and the increased probability of collisions between bubbles and particles [132].

The results indicate that the introduction of air has a beneficial impact on the quality of treated wastewater, providing evidence that flotation is more efficient than sedimentation (the results without air depend on sedimentation rates) within the specified conditions. It is worth noting that the samples were collected 2 minutes after the respective procedures, allowing minimal opportunity for re-sedimentation but adequate time for flotation to take place. The presence of air bubbles without applying shear in an alkalised solution, interestingly also resulted in a substantial reduction in TSS and turbidity. This observation is supported by the comparison of the orange blocks in **Figure 4.7**.

Table 4.3 shows the values associated with the bar chart shown in **Figure 4.7**. The untreated sample refers to the wastewater that was collected from the winery before undergoing processes such as lime treatment, shear treatment, and the addition of coagulants and flocculants. The alkalised sample refers to the wastewater subsequent to the addition of lime in order to elevate the pH level to 8. The sample treated with SEFS corresponds to the alkalised sample that underwent shear (at 4,000 rpm). This sample was subjected to a coagulant dosage of 5 mg/L (AB121), a flocculant dosage of 10 mg/L (AB796) and induced air.

Table 4.3. Total suspended solids (TSS) and Turbidity values of wastewater at different stages of treatment.

Sample type	**TSS (mg/L)**		**Turbidity (NTU)**	
	Without air	With air	Without air	With air
Untreated	2,275	2,260	660	635
Alkalised	1,750	800	470	280
Alkalised + SEFS treated	680	70	220	30
% Reduction (SEFS vs Untreated)	70	97	67	95

The introduction of air into the SEFS reactor resulted in an enhanced treatment efficiency. The data demonstrates a significant reduction in TSS of 97% (from an initial concentration of 2,275 mg/L to a final concentration of 70 mg/L) when air was introduced. In contrast, the reduction in TSS without the introduction of air was only 70%. In a comparable manner, the introduction of air resulted in a noteworthy decrease of 95% in turbidity, whereas the absence of air led to a comparatively lower reduction of 67% in turbidity.

4.8. Bubble sizes analyses of induced air flotation (IAF) and shear SEFS experiments

Experiments were carried out to evaluate the size of the bubbles produced within the bubble swarm of the IAF experimental setup, using the experimental technique outlined in Section 3.4.1.

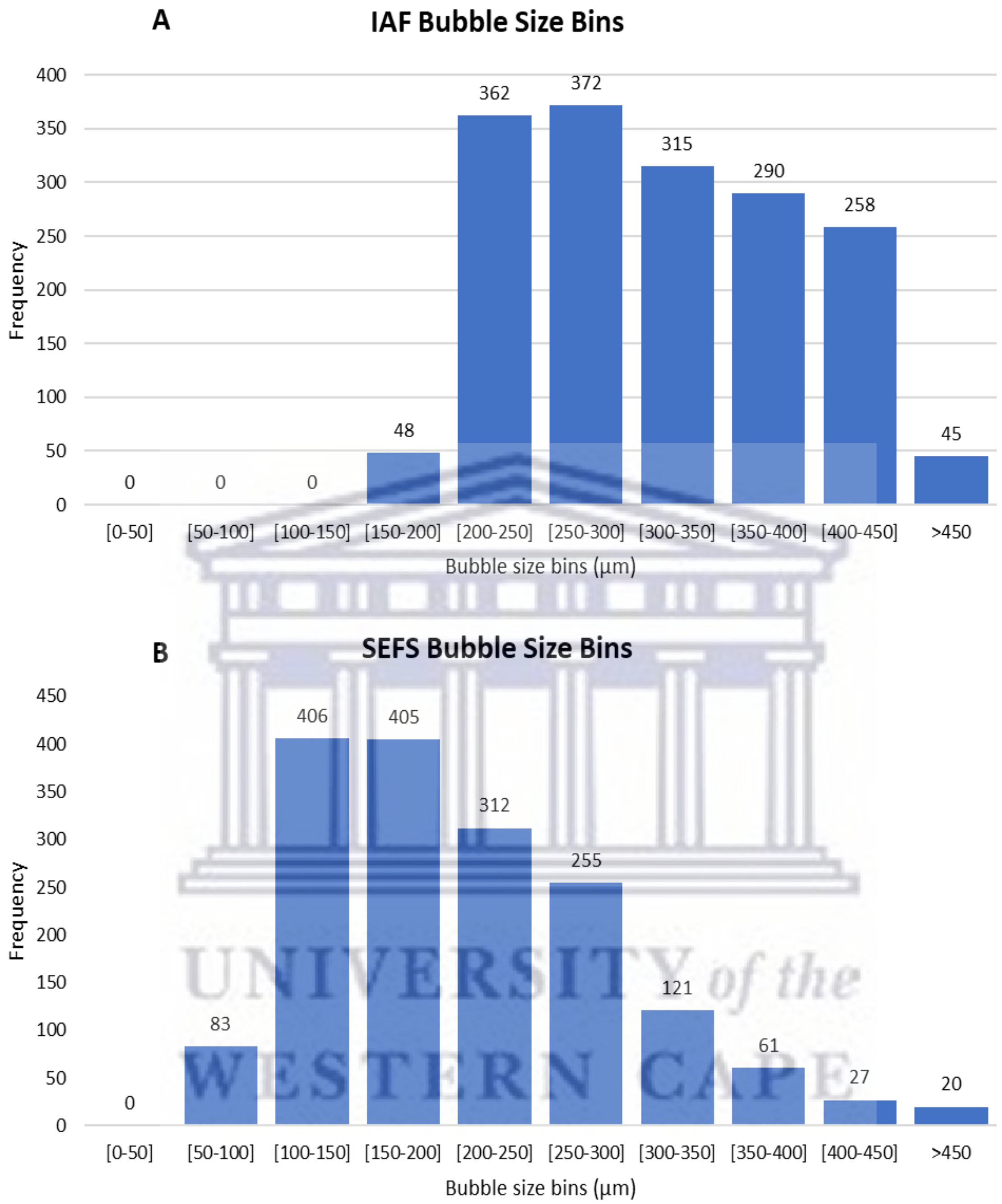


Figure 4.8. Histogram of bubble sizes for (A) IAF (without shear) and (B) SEFS-treated wastewater.

A total of 1,690 bubbles were quantified and the different bubble size bins are illustrated in **Figure 4.8**. The average size of the IAF bubbles, in the absence of shear (**Figure 4.8-A**) ranged from 200 to 450 µm, which incorporates approximately 94% of the bubble's sizes. Exposing the wastewater to hydrodynamic shear (**Figure 4.8-B),** resulted in an increase in the frequency of smaller microbubbles. The bubbles generated during shear treatment had average sizes in the range of 100–300 µm. Additionally, 5% of the bubbles generated during SEFS treatment ranged between 50–100 µm, unlike the wastewater without shear which did not produce bubbles <150 µm. The increase in treatment efficiency as denoted by the turbidity and TSS removal percentage may therefore be attributed to the higher frequency of small bubbles generated with SEFS treatment. Subsequently leading to the removal of suspended particles that fall within this same magnitude of particle size. The size of the bubbles generated during induced air flotation (both with and without shear) falls within the range reported in literature [223].

4.9. Influence of SEFS on COD

The efficacy of the SEFS treatment was evaluated based on its capacity to decrease the chemical oxygen demand, both with and without the addition of air, as depicted in **Figure 4.9**. The COD for the SEFS treated wastewater exhibited a reduction of 54%, decreasing from 11,250 to 5,220 mg/L.

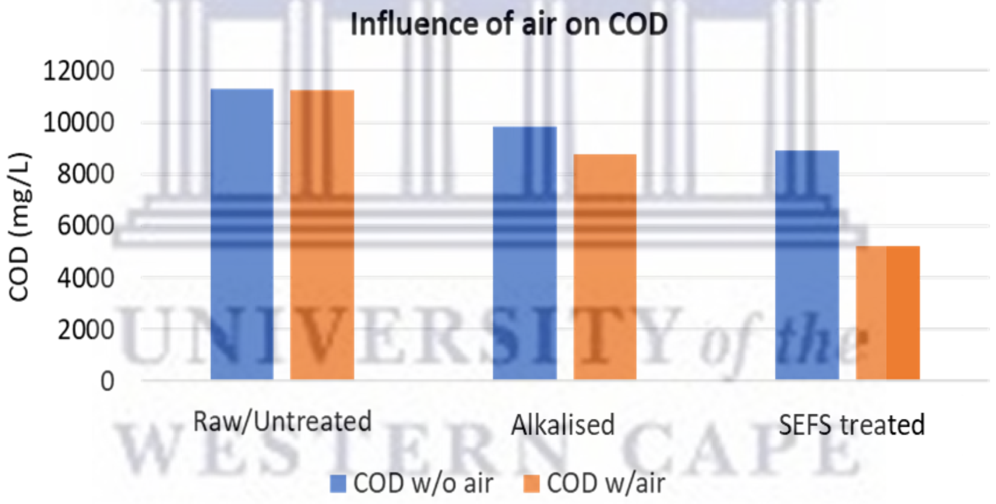


Figure 4.9. Influence of air on COD reduction.

These encouraging results, particularly in respect to suspended particles and turbidity but less so for COD, may be explained by the enhanced particulate destabilization process coupled with optimized flocculant dosing. Measurements of COD values include those coming from both soluble and insoluble organic compounds. As shown in **Table 4.4**, the synergistic effects of the SEFS method significantly reduce the amount of insoluble COD portion. Therefore, it is likely that SEFS caused a smaller COD decrease compared to the >95% TSS reduction in turbidity because dissolved organic species were not affected by SEFS treatment.

Table 4.4. COD values of wastewater at different stages of treatment

Sample type	**COD (mg/L)**	
	Without air	With air
Raw/Untreated	11,310	11,250
Alkalised	9,820	8,750
SEFS treated	8,920	5,220
% Reduction (SEFS vs Untreated)	21	54

A graphical representation of the overall SEFS laboratory treatment process is illustrated in **Figure 4.10**. This figure depicts a visual summary of the treatment process from start (with initial wastewater values) to finish (with final wastewater treated values).

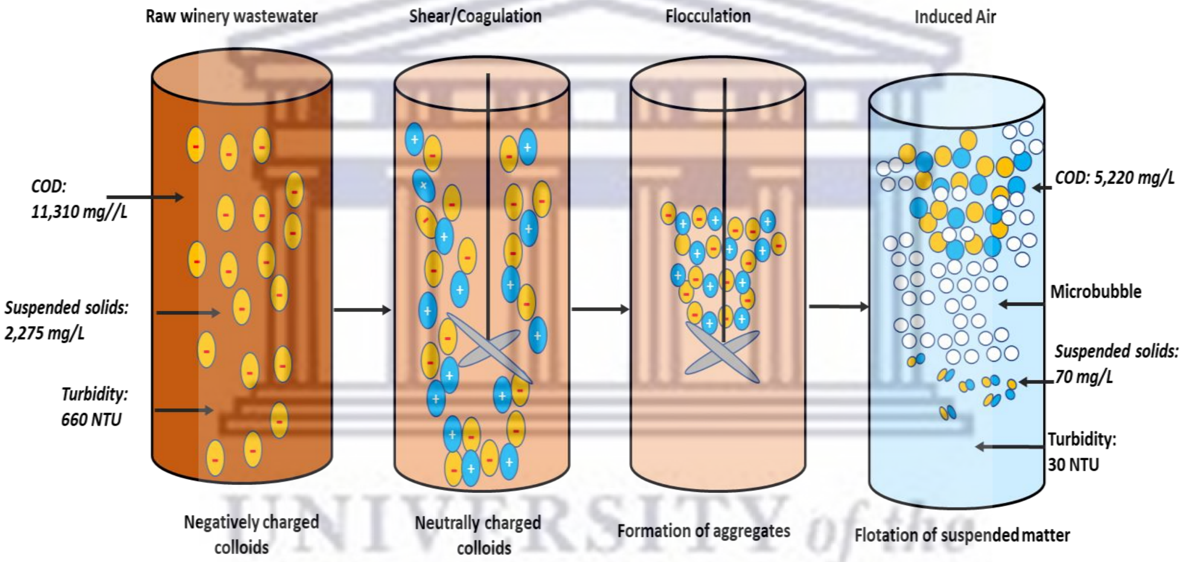


Figure 4.10. Laboratory -scale SEFS treatment process.

Individual ion analysis was carried out to quantify the concentration as shown in **Table 4.5** which contribute to the total dissolved solids (TDS).

Table 4.5. Ion concentration in untreated and SEFS treated wastewater.

Wastewater	**pH**	**Ca**	**K**	**Mg**	**Na**	**Cl**	**SO_4**	**PO_4**	**NH_4**
	-	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Untreated	4.20	392.1	413.8	22.3	36.3	49.6	267.5	59.7	9.1
SEFS Treated	8.4	880.0	283.4	20.0	29.8	34.5	184.8	19.4	2.9

The results displayed in **Table 4.5** show that besides an increase in calcium concentration (which is attributed to the addition of lime slurry during alkalisation), all of the ions have been marginally reduced in concentration. Igwegbe and Okechukwu obtained similar results during their coagulation and flocculation study, where the authors also attributed the decrease in individual ion concentrations to the alkalisation of the sample water [224].

Following the encouraging results of the laboratory-scale experiments, a mobile treatment plant was provided by Abrimix Pty Ltd and commissioned at Lutzville winery during the 2022 harvest season.

4.10. Abrimix Mobile Unit On-Site Treatment

This system was used to treat on site Lutzville winery wastewater and its treatment efficiency compared to that of the results obtained in the laboratory. The description of the mobile treatment plant has been discussed in Chapter 3**. (Figure 3.6 and Figure 3.7).**

The general winery wastewater treatment process taking place with the on-site mobile unit is shown in **Figure 4.11**. This patented Abrimix mobile treatment process consisted of chemical dosing, a shear mixer and induced air flotation.

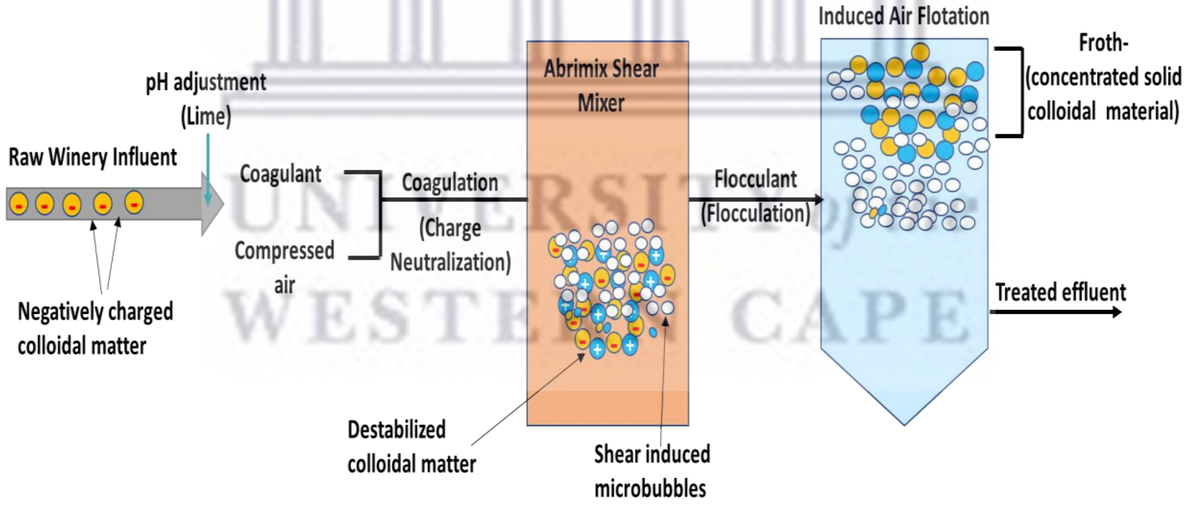


Figure 4.11. Abrimix mobile treatment process.

The process conditions are shown in **Table 4.6**. The flow rate of the pilot plant was maintained at 2m^3/h.

Table 4.6. Abrimix mobile treatment plant process conditions and treatment results.

Batch no.	Air flow rate	Coagulant	Flocculant	Turbidity	TDS	TSS	COD
-	L/min	mg/L	mg/L	NTU	mg/L	mg/L	mg/L
1	0	0	0	520	1,975	1,850	12,450
1	2	5	10	450	1,315	520	9,480
2	0	0	0	615	1,590	1,550	11,050
2	4	15	25	265	1,306	430	9,110
3	0	0	0	690	2,240	2,495	13,150
3	6	10	45	120	1,080	210	8,200

The results in **Table 4.6** shows that there was a moderate decrease in total dissolved solids (TDS) and COD. The untreated wastewater had TDS average values of 1,935 mg/L and upon optimum reactor conditions (batch 3), the value of TDS decreased to a minimum of 1080 mg/L (initial TDS of 2,240 mg/L), corresponding to a 52% reduction in the concentration of the dissolved solids. The average COD of the initial wastewater was 12,210 mg/L. Using a combination of coagulant/flocculant (AB2121/AB796) in a ratio of 10/45 mg/L and air flotation rate of 6 l/min as well as shear mixing, reduced the COD value to 8,200 mg/L (initial COD of 13,150 mg/L for batch 3). This corresponds to a reduction of 38%. The turbidity of the wastewater was decreased post treatment compared with the untreated wastewater having turbidity values of 610 NTU and the treated wastewater turbidity values of 120 NTU (81% reduction in turbidity for batch 3). Finally, a substantial decrease in suspended solids was observed where the initial values were 2,495 mg/L compared to 210 mg/L after treatment (reduced by 92%). These results are significant since they are comparable with the tests conducted on a laboratory scale (refer to **Table 4.3** and **Table 4.4**). The visual changes between raw/untreated and treated wastewater are shown in **Figure 4.12**.

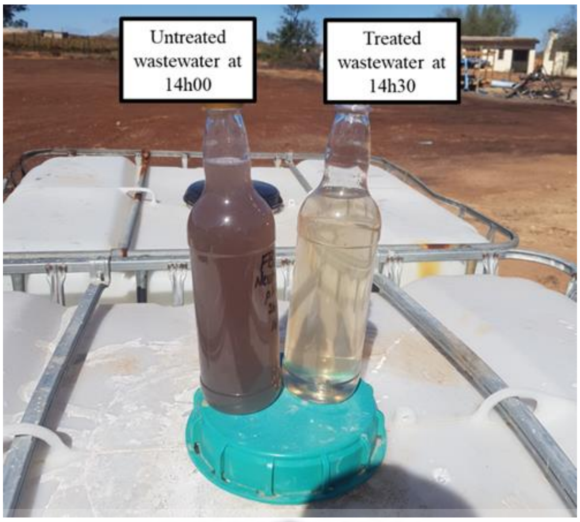


Figure 4.12. Untreated wastewater vs treated wastewater during on-site experiments.

4.11. Winery wastewater treatment efficiency comparison as case study

The average COD and TSS levels of winery wastewater at different stages in the treatment plant are provide in **Table 4.7**. The figures presented here are exclusively that of the inherent effluent treatment plant (i.e., these results have no relation to SEFS or Abrimix treatment). Over the years spanning from 2020 – 2022, the COD of the untreated wastewater showed a significant increase. The COD of wastewater analysis after aerobic treatment, had decreased in 2022 compared to samples analyse from 2020 and 2021. There are two potential reasons for this improvement; A) Lutzville winery makes use of a different supplier of aerobic bacteria used in the secondary treatment phase, B) The pH control has improved following the installation of the lime pit, since pH fluctuations have a negative effect on the biological activity of microbes.

Table 4.7. Lutzville winery water quality at different analysis points in the inherent wastewater treatment facility.

	Average COD (mg/L)			**Average TSS (mg/L)**			**EC (mS/m)**
	2020	**2021**	**2022**	**2020**	**2021**	**2022**	**2022**
Raw/untreated wastewater	7,350	8,400	13,150	1,950	2,100	2,550	330
Lime alkalised wastewater	6,050	6,200	10,400	920	1,800	1,060	360
Wastewater after aerobic treatment	4,900	5,400	3,800	690	850	460	270
% Reduction (Treated vs Untreated)	33	36	71	65	60	82	18

The value of the TSS in the wastewater after aerobic treatment was 460 mg/L and the COD was 3800 mg/L. The limits as imposed by the department of Water and Sanitation (shown in

Table 2.6) illustrate that the treated wastewater would be compliant if the volume would be only 50 m^3/day. Since the average daily volumes of wastewater at this winery are around 140 m^3/day, the COD of the treated water should be limited to 400 mg/L and the EC should be below 150 mS/m. In order words, the winery wastewater treatment facility does not currently achieve the required levels of water quality even after aerobic treatment.

4.12. Conclusions from the laboratory and Abrimix experiments

The main objective of this study was to investigate the application of shear enhanced flotation separation (SEFS) technology as a viable option for the treatment of winery wastewater. The implementation of the SEFS treatment process resulted in a significant decrease of 97% in the concentration of total suspended solids (TSS). This reduction was observed when treating raw wastewater samples with an initial TSS value of 2,275 mg/L, which decreased to 50 mg/L after SEFS treatment. The turbidity showed a significant decrease of 95% following the SEFS treatment, as seen by the reduction in initial turbidity readings from 630 NTU for the untreated wastewater to 25 NTU. The findings suggest that there is a close correlation between turbidity and TSS reductions as a result of the SEFS treatment.

During the Abrimix on-site treatment, three winery wastewater batches were treated and tested. The average untreated turbidity, TDS, TSS and COD values for these batches is shown in **Table 4.8**. These values were taken from the average of untreated and Abrimix treated wastewater over the three investigated batches presented in **Table 4.6**.

Table 4.8. Average untreated, and Abrimix treated winery wastewater characteristics.

	Turbidity (NTU)	TDS (mg/L)	TSS (mg/L)	COD (mg/L)
Untreated winery wastewater	610±30	1,935±110	1,965±350	12,210±1200
Treated winery wastewater	278±20	1,224±200	387100±	8,930±300

The study demonstrated that SEFS technology may be deemed a suitable technique for reducing the COD of real winery wastewater. Optimal operational conditions for winery waste were establish leading to 54% (initial COD: 11250 mg/L vs final COD: 5220 mg/L) reduction of COD during laboratory scale experiments and 38% (initial COD: 13150 mg/L vs final COD: 8200 mg/L) during Abrimix mobile unit on-site experiments.

The difference in treatment efficiency between the laboratory studies and Abrimix may be attributed to the process by which shear is introduced. In the laboratory set-up, the rotor stator provided a higher degree of mixing efficiency and particle destabilization as opposed to the patented mixer contained in the Abrimix mobile treatment plant.

This comparison of the treatment efficiencies achieved in the laboratory, mobile unit and compared with those in current winery wastewater processing plants supported the value in undertaking this research project to redesign and modify a DAF pilot plant to include shear for the treatment the winery wastewater. The results obtained seemed promising and due to the understanding of the reactions taking place during SEFS treatment, a level of confidence was established that the proposed pilot plant would be more efficient as a treatment process.

CHAPTER 5 WASTEWATER TREATMENT USING SHEAR ENHANCED FLOTATION SEPARATION TECHNOLOGY: A PILOT PLANT STUDY FOR WINERY WASTEWATER PROCESSING

5.1. Overview

Following the work carried out with winery wastewater treatment using SEFS on a laboratory scale and with the Abrimix mobile unit as described in the preceding chapter, an up scaled pilot plant was fabricated and modified with the aim of investigating its treatment efficiency towards potentially further reducing the commonly found pollutants in the wastewater. The wastewater used during this part of the study was collected during the 2023 harvest season.

The design of the pilot plant has been explained in **Section 3.8** and **Figure 3.8**. Unlike the SEFS laboratory scale system, the pilot plant was equipped with a microbubble pump generator which delivers dissolved air as opposed to induced air.

A significant portion of this chapter has been published as a research article entitled: Wastewater Treatment Using Shear Enhanced Flotation Separation Technology: A Pilot Plant Study for Winery Wastewater Processing in MDPI: *Processes*, Special Issue: Separation Processes for Environmental Preservation (Vol. 12., No. 3, 2024). https://doi.org/10.3390/pr12010003.

5.2. Experimental

The parameters of interest during the pilot plant study were the zeta potential, TSS, turbidity and COD. Apart from the analysis of the liquid, the solid waste (froth) was also analysed where the purpose of its analysis was to determine its suitability as a potential fertilizer for crops.

5.2.1. Coagulant comparison

Two commercially available coagulants were investigated, namely aluminium chlorohydrate (ACH) and a polydiallyldimethylammonium chloride (polydadmac)/ACH blend. ACH was previously used as described in the preceding chapter and obtained from Abrimix and subsequently branded as AB121. The alkalised wastewater was subjected to various coagulant dosages, where its effect on the stability (zeta potential) of the particles was measured. **Figure 5.1** displays the relationship between coagulant type and dosage on the zeta potential. Both coagulants used in this part of the study performed well, however an iso-electric point was reached at a lower concentration for the polydadmac/ACH blend than that for the ACH as a standalone coagulant.

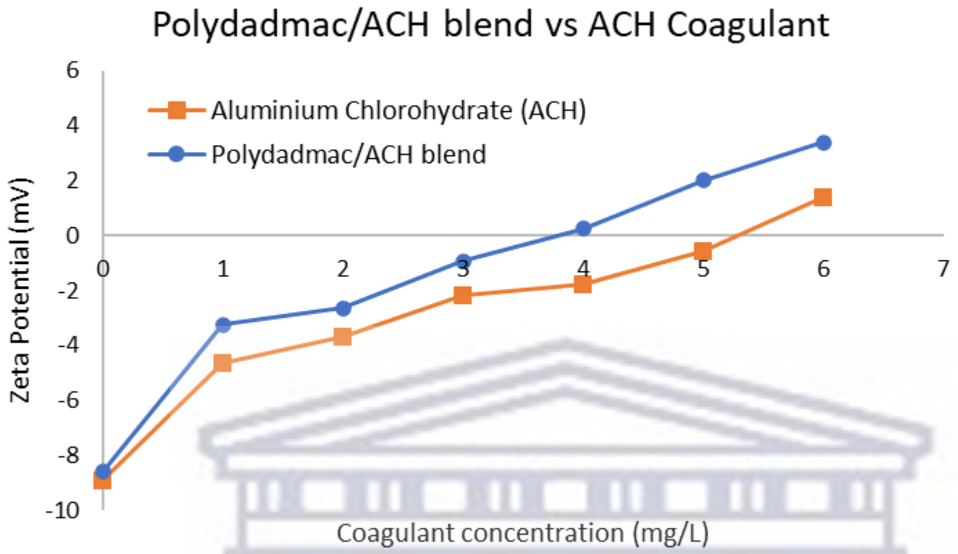


Figure 5.1. Zeta Potential of preconditioned effluent with coagulation.

5.2.2. Pilot Plant conditions

For coagulation experiments, a Puritech dosing pump was used. This pump has a flow rate of 6 L/h. For flocculation experiments, a SEKO APG603 dosing pump was used having a flow rate: from 4 to 8 L/h. The flow rates of these pumps are tabulated in the Appendix (**Chapter 8**). The design and dimensions of the DAF unit is illustrated in Appendix (**Figure 8.3**)

5.2.3. High Shear Mixing

The shear unit was constructed using steel sheets that were assembled to create a robust exterior structure, together with an internally rotating impermeable component. The multi-layered steel structure enables the formation of a wide gap between the rotor and stator, which permits the flow of wastewater through an inlet and outlet. The rotational speed of the mixer was measured using a High Precision Tachometer, model DT2236E, manufactured by Addendorff in South Africa.

5.3. Results and Discussion

5.3.1. Winery wastewater Composition

The average untreated winery wastewater composition during the 2023 harvest is illustrated in **Table 5.1**. The presented data aligns with the characteristics of untreated winery wastewater documented in literature on the subject [225–228].

Table 5.1. Average untreated winery wastewater characteristics

Sampling Date	**pH**	**Turbidity**	**EC**	**TSS**	**TDS**	**COD**
	(25°C)	**(NTU)**	**(mS/m)**	**(mg/L)**	**(mg/L)**	**(mg/L)**
3–7 April 2023	3.2±1.4	849±200	430±200	2620±180	1740±60	11,140±800

The pH, EC, TSS, and COD play a crucial role in determining the suitability of wastewater for irrigation, as specified by the water regulations in South Africa [5]. According to the regulations and restrictions, the pH, EC, TSS, and COD levels must be within the ranges of 6 to 9, <200 mS/m, <25 mg/L, and < 5000 mg/L, respectively, in order to be used for irrigation with treated wastewater of up to 50 m^3/day. Based on the wastewater characteristics presented in **Table 5.1** it is clear that action is necessary to mitigate the environmental consequences if this untreated wastewater is disposed in its current state.

5.3.2. Rotational Speed of Shear Mixer

The influence of rotational speed of the shear mixer was examined by analysing the zeta potential of the colloids, as depicted in **Figure 5.2**. The optimum shear speed for the pilot plant study was determined to be 3250 rpm. The speed was established by analysing the ideal variations in surface charge of the particles using zeta potential analysis. Increasing the rotational speed of the shear mixer above 3250 rpm

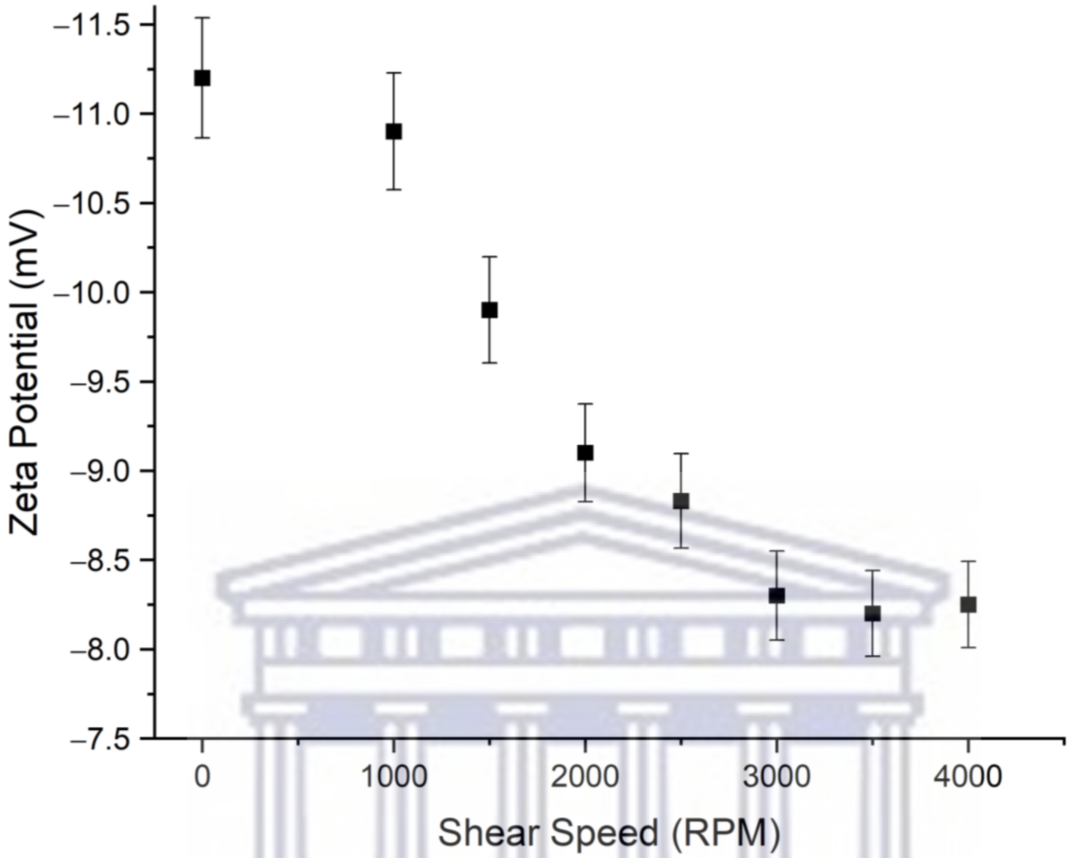


Figure 5.2. Shear speed as a function of zeta potential.

5.3.3. Particle Size Distribution

The particle size of untreated and treated wastewater is shown in **Table 5.2**.

Table 5.2. Particle size (in µm) of winery wastewater.

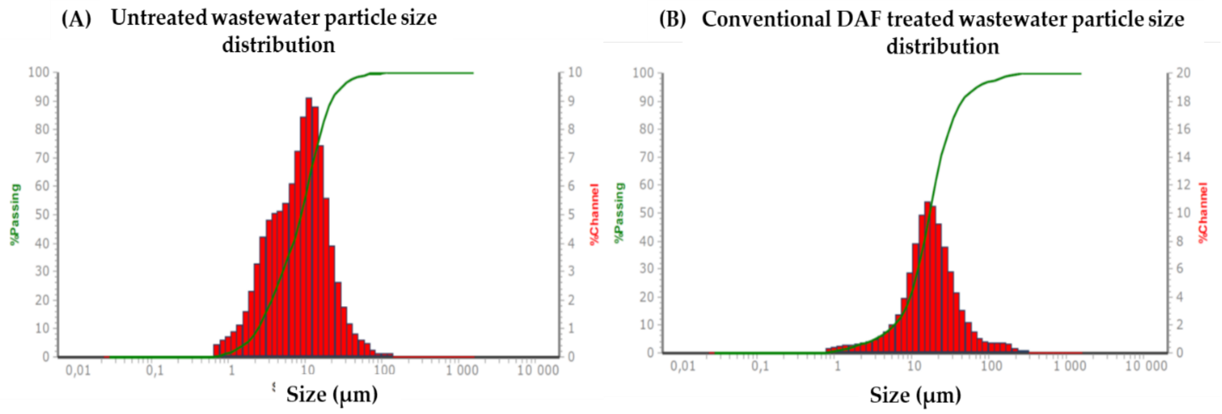
Sample	d10[1]	d50[2]	d90[3]
Untreated	2.205	7.99	34.45
DAF	5.49	15.36	40.79
SEFS	10.49	23.65	56.19

1) Size of particle in microns below which 10% of the sample lies [229].

2) Size of particle in microns at which 50% of the sample is smaller and 50% is larger [229].

3) Size of particle in microns below which 90% of the sample lies [229].

Figure 5.3 illustrates the particle size distribution of untreated wastewater, as well as wastewater treated using DAF and SEFS.



(A) Untreated wastewater particle size distribution

(B) Conventional DAF treated wastewater particle size distribution

(C) SEFS treated wastewater particle size distribution

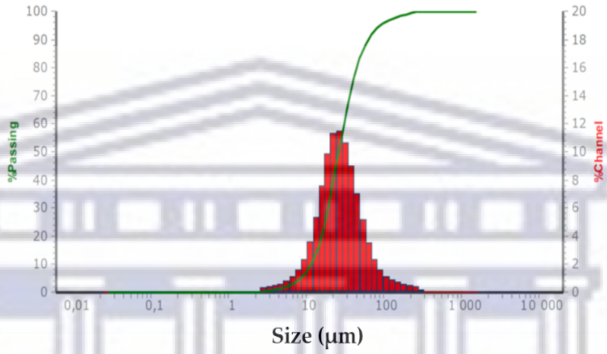


Figure 5.3. Particle size distribution of (A) untreated, (B) conventional DAF and (C) SEFS treated winery wastewater.

The particle size distribution (PSD) observed in **Table 5.2** and **Figure 5.3** demonstrates an overall increase when comparing untreated wastewater to wastewater treated with conventional DAF and SEFS. The untreated wastewater contains particles with an average diameter (D50) of 7.99 µm. The average D50 particle size of the wastewater, after undergoing DAF treatment without hydrodynamic shear, was measured to be 15.36 µm. The increase in particle size can be attributed to the coagulation and flocculation processes, which cause particle destabilization through charge neutralization. This leads to the formation of larger agglomerates, which are subsequently removed during flotation [115]. On the contrary, the wastewater treated by the SEFS exhibited an average D50 particle size of 23.65 µm.

The substantial increase in particle size is due to the hydrodynamic shear mixing, which leads to the formation of larger particle clusters and subsequently results in higher degree of destabilization of the particles in the solution, [146]. According to literature, particles tend to clump together more rapidly when they are subjected to shear forces, as this leads to an increase in the frequency of particle collisions [230].

5.3.4. Zeta Potential Analysis

Flotation, sedimentation, and filtration are widely recognized as fundamental processes within the scope of physical treatment techniques employed in the field of wastewater treatment. The efficiency of these procedures is dependent upon the size, density, and charge characteristics of the particles that are to be eliminated. The role of surface charge (zeta potential) is widely recognized as a crucial element in understanding the underlying physical mechanisms that take place throughout the processes of aggregation and settling.

Solid particles in aqueous systems can exhibit various surface charges. The presence of oppositely charged counterions in the solution often counterbalance these charges. The resulting structure is widely identified as the electric double layer (EDL) [231]. Electric double layers impose a substantial influence on the physical and chemical characteristics of heterogeneous systems. The EDL model is a fundamental framework for understanding the principles of electrostatic force and its impact on the stability of colloids. Hence, it is crucial to have techniques that can precisely evaluate the electrical charge status of solid surfaces in relation to key solution parameters, such as pH, ionic strength, or solute composition. Because of its relationship with surface charges, the zeta potential is commonly employed to derive key physical and chemical properties of interfacial systems, such as aqueous particle suspensions. This extends to the factors affecting the stability and aggregation of colloidal particles [232].

Figure 5.4 demonstrates the relationship between the zeta potential and each subsequent treatment phase.

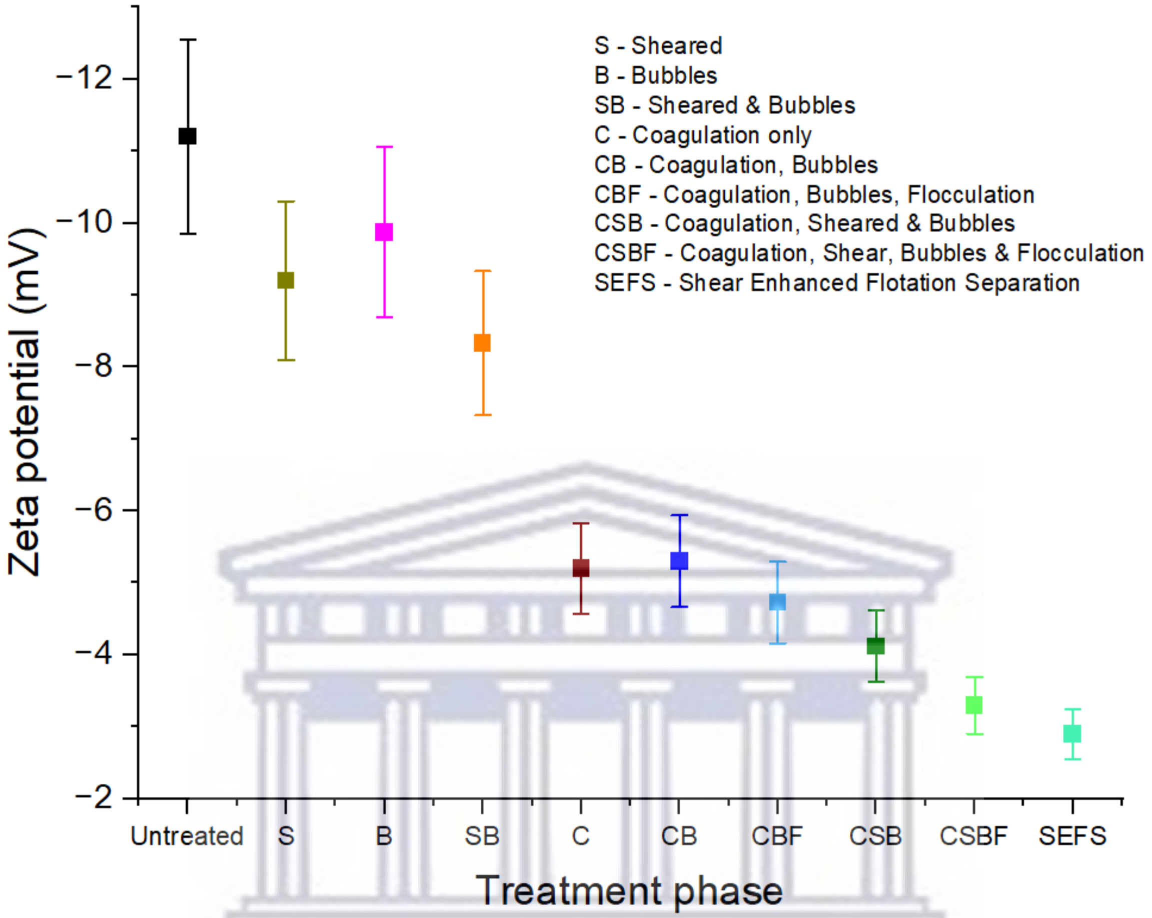


Figure 5.4. Zeta potential as a function of treatment phase

The general trend in the zeta potential as a function of treatment showed that the particles' surface charge changed with each subsequent treatment phase. Zeta potential measurements for the untreated wastewater were -11.4 mV. Under shear conditions, the solution displayed an average zeta potential of -9.1 mV, indicating a 19% change in zeta potential. Conversely, the introduction of bubbles resulted in an increase of the zeta potential to -9.8 mV, indicating a higher negative charge. The microbubbles in water exhibit a negative zeta potential due to the adsorption of OH^- ions at the bubble interface, which originate from the water molecules [233]. Due to the surface charge of microbubbles, experimental evidence suggests that the substantial negative charge limits the process of microbubble coalescence. As a result, the bubbles maintain their structural integrity at different depths and can remain intact for extended periods of time [234].

The addition of the coagulant resulted in a substantial shift of the zeta potential, changing it from -8.2 mV (in the presence of shearing and bubbles without the coagulant) to -5.4 mV following the coagulation process. The zeta potential shift is explained by the addition of positively charged counterions during the coagulation process, which causes ion adsorption and surface charge neutralization. Conventional DAF samples labelled in **Figure 5.4** as CBF (coagulation, bubbles and flocculation) caused surface charge reduction to -4.2 mV. These samples were taken from SP-3 (refer to **Figure 3.9**). The CSBF (coagulation, shear, bubbles and flocculation) as denoted in **Figure 5.4** relates to samples taken via the recycle sample line (SP-4). The SEFS samples, meanwhile, were collected directly from the exit point (SP-3) of the DAF tank. The results demonstrate that the combined effects of shear, coagulation, flocculation, and flotation (SEFS) significantly improved the overall destabilization of colloidal particles in the wastewater compared to conventional DAF treatment (CBF) - where the conventional DAF system did not have in-line mixing done.

5.3.5. Influence of Microbubbles

There has been considerable academic debate over the precise definition of microbubble sizes. Agarwal *et al.,* (2011) characterized these small bubbles of between 10 and 50 μm in size [235]. Interestingly, Takahashi *et al.,* (2007) classified these particular type of bubbles as having sizes smaller than 50 μm [236]. Terasaka *et al.,* (2011) conducted a separate analysis where they classified the microbubbles as small bubbles, with sizes ranging from 10 to 60 μm [237]. This categorization was based on the particular application of the bubbles within a study that examined physiological activity [237].

The size of the bubbles was measured to assess the effects of hydrodynamic shear, as explained in Section 3.5.6. By comparing the bubble size shown in **Figure 5.5** with the particle size in **Figure 5.3**, one can deduce that the separation process was more efficient when the bubble size and the particle size were of similar magnitude. For instance, the conventional DAF treated wastewater had an average bubble size of 126 μm. By comparison, the size of the wastewater treated with SEFS was 62 μm. The shear unit induces a significantly turbulent environment, hence increasing the likelihood of collisions between colloids and bubbles. This, in turn, improves the efficiency of the solid/liquid separation process in comparison to conventional DAF treatment without shearing. Improved separation efficiencies can be achieved by increasing the frequency of collisions between bubbles and particles and enhancing capture efficiencies [238].

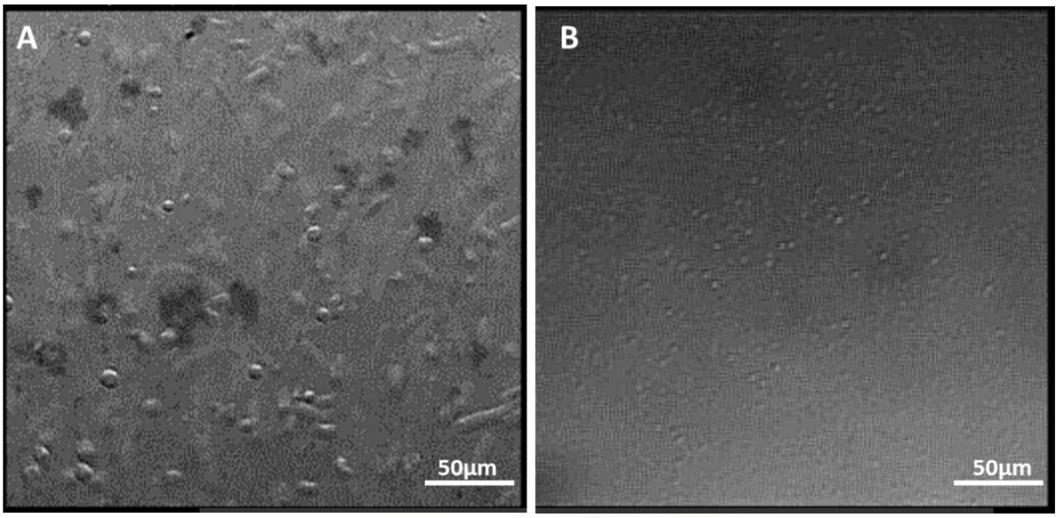


Figure 5.5. Snapshot of Bubble Size analysis of (A) Conventional DAF and (B) SEFS treatment.

A total of 1,456 bubbles were quantified and the different bubble size bins are illustrated in **Figure 5.6**. The average size of the conventional DAF bubbles (**Figure 5.6-A**) ranged from 50 to 150 µm, which incorporates approximately 60% of the bubble's sizes. The bubbles were captured at the point where the feed enters into the DAF contact zone. Based on literature research, the sizes of these bubbles fall within the indicated range when using DAF to treat wastewater [134,215,239]. Exposing the wastewater to hydrodynamic shear (**Figure 5.6-B),** resulted in an increase in the frequency of smaller microbubbles. The bubble size in the range of 50–100 µm exhibited a 30% increase when subjected to shear treatment compared to conventional DAF treatment. Furthermore, the SEFS treatment generated bubbles that were smaller than 50 µm, unlike the DAF treated wastewater. The increase in the frequency and number of smaller bubbles (typically less than 100 µm) may therefore explain the higher removal rates achieved through the use of a shear mixer. According to Wu *et al.*, (2015), a steady hydrodynamic disruptive shear force is created in an environment where smaller gas bubbles are present because of the capacity to spread out across the particle and increase the contact area [240]. In other words, hydrodynamic shear-induced microbubbles adhere to micron-sized particles selectively while still retaining its mechanical integrity and strength.

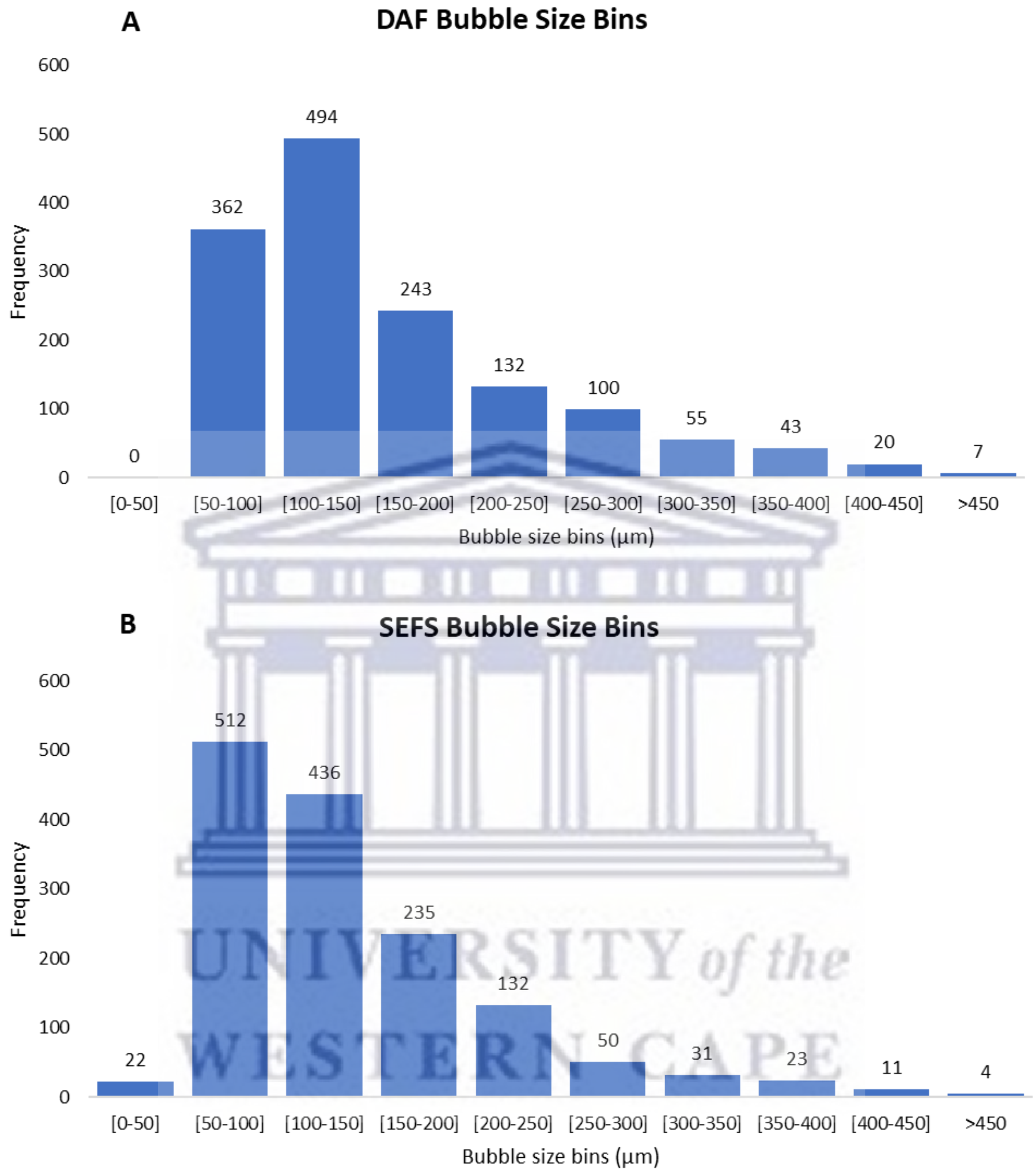


Figure 5.6. Histogram of bubble sizes for (A) conventional DAF and (B) SEFS treated wastewater.

Given that it has a greater surface area for particles, the shear mixer's smaller microbubbles are advantageous because they improve particle attachment to the bubbles and increase the suspended solids' buoyancy. Research findings demonstrate a strong relationship between the requirement to reduce bubble size and an increased probability of bubbles and particles colliding [132]. Turbidity and total suspended solids experiments, which are covered in the section that follows, clearly demonstrate the significance of particle and bubble sizes with respect to the efficiency of treatment.

5.3.6. Turbidity and Total Suspended Solids

Figure 5.7 illustrates turbidity values as a function of treatment phase. Turbidity is a term used to quantify the optical property of water and refers to the relative transparency of a liquid. More specifically, the quantification of light scattering caused by the presence of particulate matter within a water sample, when illuminated by a light source. Elevated turbidity values are a result of particulate matter with high concentrations affecting the penetration of light.

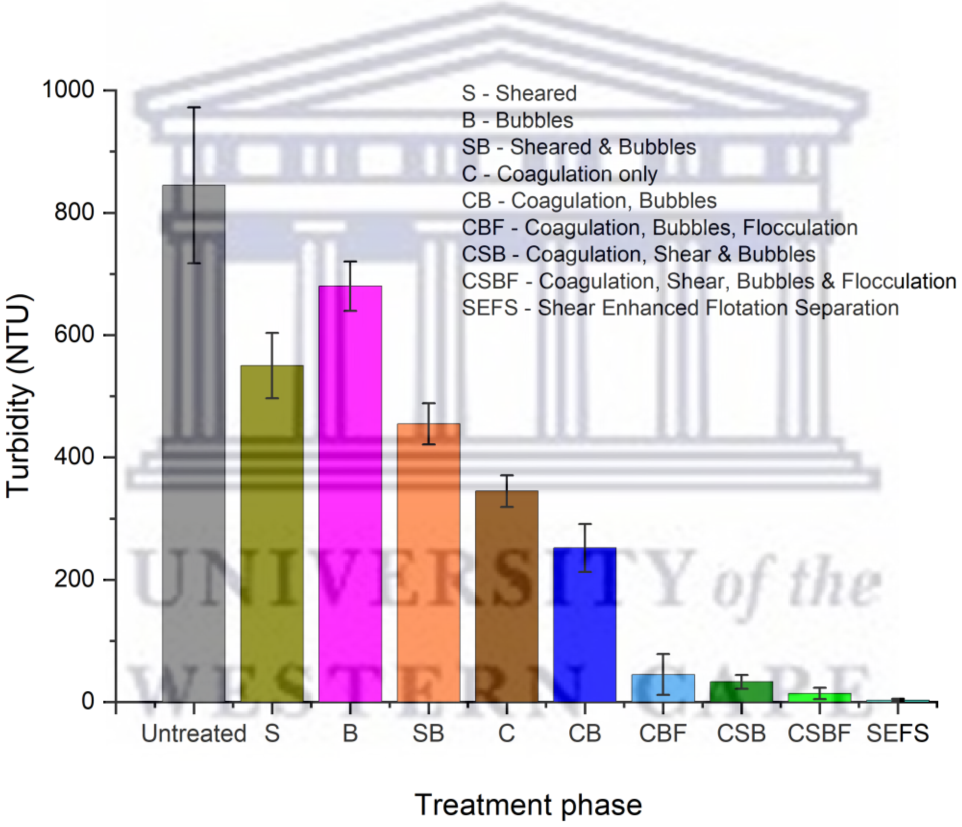


Figure 5.7. Turbidity studies as a function of treatment phase.

Turbidity values depicted in **Figure 5.7** demonstrate how the turbidity progressively decreased with each treatment phase. Untreated wastewater had turbidity values of 849 NTU, while the final (SEFS) treated wastewater had values that were comparable to drinking water (3 NTU). The marginal rise in turbidity observed in the samples subjected to bubbles only (labelled as B in **Figure 5.7**) can be attributed to the flotation mechanism operating without the presence of chemical additives. This mechanism disrupts the equilibrium of the solution, resulting in a greater concentration of suspended particles in the solution.

Table 5.3 presents the TSS and turbidity treatment values of the wastewater and compares the effects of adding shear during SEFS treatment compared to conventional DAF treatment.

Table 5.3. Total suspended solids (TSS) and Turbidity values of wastewater at different stages of treatment.

Sample Type	**TSS (mg/L)**		**Turbidity (NTU)**	
	Conventional DAF	**SEFS**	**Conventional DAF**	**SEFS**
Untreated	2,620	2,620	849	849
Treated	75	17	35	3
% Treatment Efficiency (Treated vs. Untreated)	97.1	99.4	95.9	99.6

The data provided in **Table 5.3** demonstrates that both treatment procedures resulted in a substantial decrease in both TSS and turbidity. However, the treatment efficiency for both TSS and turbidity quality parameters displayed an increase when subjected to shear. These values are further complemented with the visual differences in haziness as depicted in **Figure 5.8**.

Figure 5.8. Visual comparison between (A) Untreated, (B) Conventional DAF, and (C) SEFS treated wastewater.

5.3.7. Chemical Oxygen Demand

The efficiency of the SEFS treatment was assessed by measuring its ability to reduce the chemical oxygen demand, as shown in **Figure 5.9**, both before and after treatment. The conventional DAF treatment reduced the COD of the wastewater from an initial value of 11,140 mg/L to 5,490 mg/L (indicating a 51% decrease in COD). The application of the SEFS to the wastewater led to a substantial decrease of 66%, reducing the initial concentration from 11,140 mg/L to 3,800 mg/L.

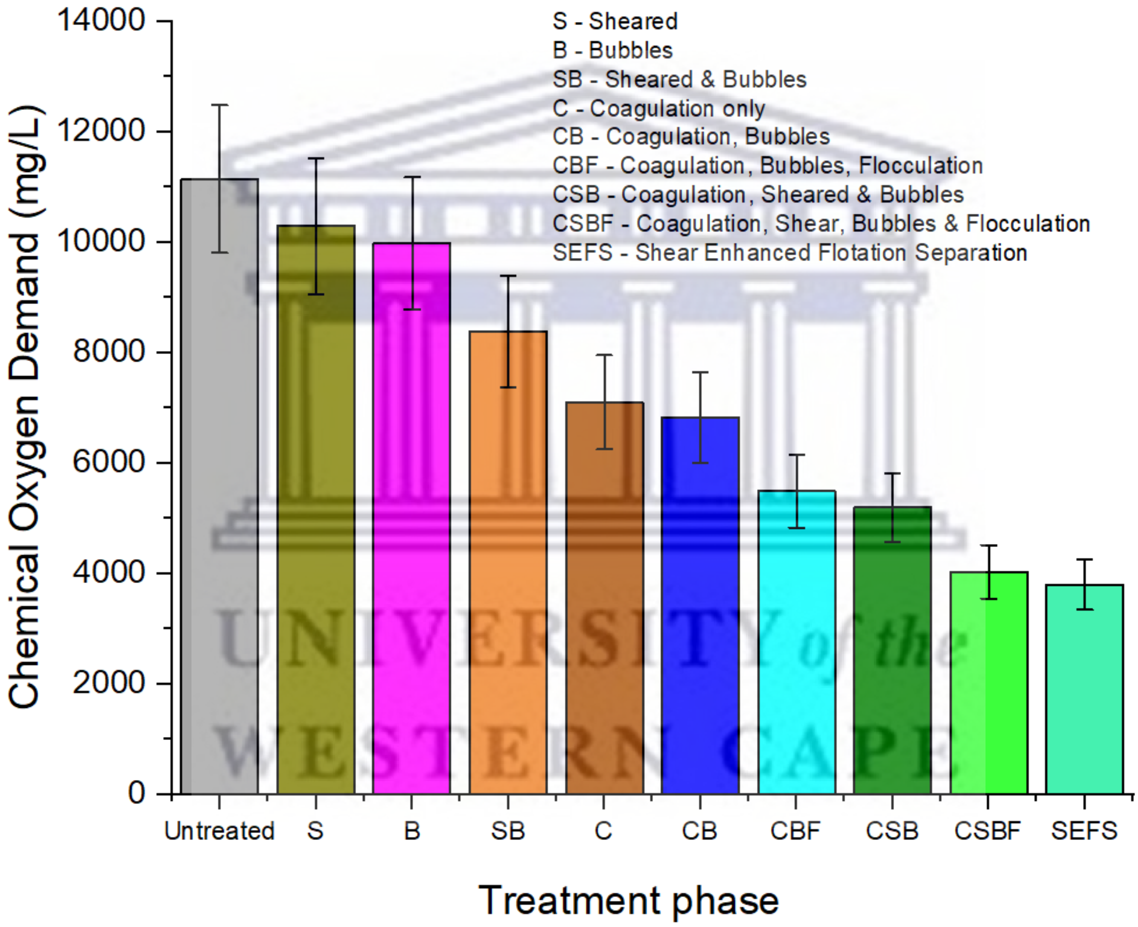


Figure 5.9. Chemical oxygen demand as a function of treatment stages.

The notable improvements, namely in relation to suspended solids and turbidity, can mainly be ascribed to the combined effects of the enhanced particle destabilization and the flotation process. However, it is important to mention that the influence on COD levels seems to be less significant compared to its effect on TSS and turbidity. The SEFS treatment process much like that observed during lab scale studies, efficiently removes a significant portion of the particulate (insoluble) COD component, as evidenced by the data provided in **Table 5.4**. The reason for the smaller decrease in chemical oxygen demand (COD) compared to the average reduction of 96% in total suspended solids (TSS) and turbidity for conventional DAF, and the average reduction of 99% in TSS and turbidity for SEFS treated wastewater, is likely due to the remaining dissolved organic compounds in the wastewater.

Table 5.4. COD values of wastewater at different stages of treatment.

Sample Type	**COD (mg/L)**	
	Conventional DAF	**SEFS**
Untreated	11,140	11,140
Treated	5490	3800
% Treatment Efficiency (Untreated vs. Treated)	51	66

Table 5.5 presents a comparison of chemical requirements for winery wastewater treatment with and without shear (SEFS vs DAF treatment). The variations that are seen can be explained by the different mechanisms of aggregation. Perikinetic aggregation, which occurs during traditional DAF treatment, is mostly influenced by the Brownian motion of the particles. On the other hand, when an external flow field like shear mixing is applied, the process of aggregation leads to the creation of orthokinetic aggregates. Studies have demonstrated that orthokinetic aggregation accelerates the rate at which colloids aggregate, exceeding the aggregation rate achieved through Brownian mechanisms [241]. Furthermore, hydrodynamic shearing has the benefit of enhancing chemical reaction processes characterized by fast intrinsic reaction rates but relatively slow mass transfer rates [242].

Table 5.5. Chemical requirements during wastewater treatment : conventional DAF versus SEFS.

Parameter	**Conventional DAF**	**SEFS**	**% Difference**
Shear Speed (RPM)	0	3250	-
Coagulant Concentration (ppm)	4.4	2.8	36.4
Flocculant Concentration (ppm)	10.3	7.1	31.1

Cagnetta *et al.*, (2019) assessed the effectiveness of combining DAF technology with a pilot-scale high-rate activated sludge system at the municipal water treatment plant in Aartselaar, Belgium [243]. After implementing their activated sludge and DAF treatment, the results showed a significant decrease of 78% in TSS and 68% in COD. Comparatively, the SEFS pilot plant treatment demonstrated that the use of shear technology resulted in a noteworthy decline in COD values by 66%, whereas conventional DAF treatment achieved a reduction of only

51%. It is important to note that no supplementary technologies, such as activated sludge as mentioned in the study by Cagnetta *et al.*, (2019), were employed in our approach.

5.3.8. Froth Analysis

The DAF treatment method generates various amounts of dense and concentrated froth, as depicted in **Figure 5.10**. The initial phase in the process of dissolved air flotation comprises using pressure to obtain air saturation. Following this, the water that has become saturated is released from pressure to the atmosphere, resulting in the formation of microbubbles [244]. The incorporation of microbubbles into the flotation tank enhances its ability to interact with the contaminants present in the water. Through the process, the bubbles adhere to the pollutants and rise to the surface of the water, creating a froth made up of compounds consisting of bubbles and contaminants. Theoretically, this froth should consist of the majority of the particulate matter that was separated during the processing of winery wastewater. A dense and concentrated form of froth was generated as shown in **Figure 5.10**.

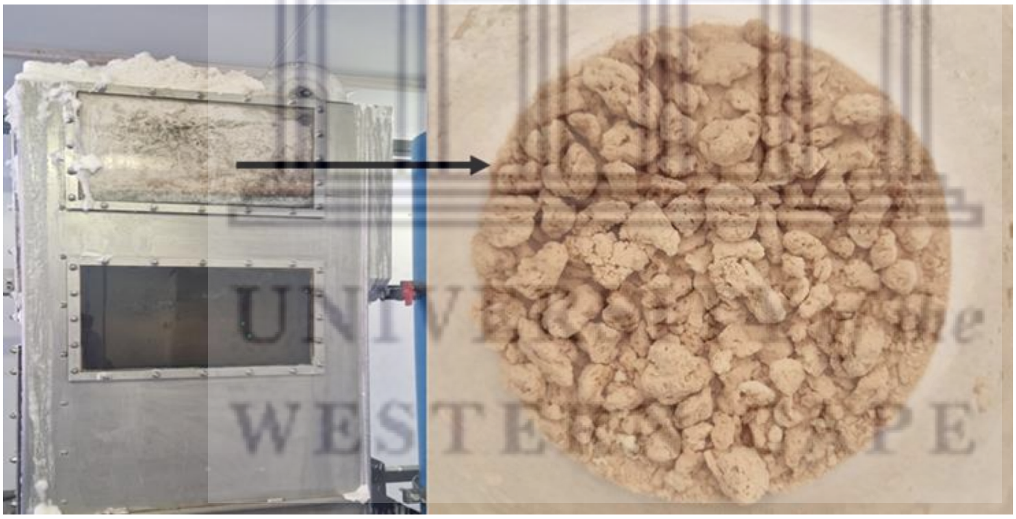


Figure 5.10. Froth produced during SEFS treatment process.

The soil used by the winery in this particular case study mainly consists of sand with a 1% composition of stone. The soil at a depth of 30 cm, has a pH of 6.1 and is saturated with sodium (5.6%), potassium (3.5%), calcium (45.9%), and magnesium (20%). The growth and productivity of grapevines, like any other crop, rely on adequate nutrition. Nitrogen is the main nutrient that affects the health and quality of grapevines. Research has shown that the addition of potassium can significantly improve grape productivity, specifically by the enhancing both grape cluster quantity and weight [245]. Magnesium and calcium are both essential nutrients required for optimal grapevine performance. In general, these nutrients are plentiful in soils with pH values within the ideal range (5.5-6.5), making the need for fertilization of these nutrients unnecessary [246]. Agriculture relies heavily on the application of fertilizers to regularly yield high-quality grapes. One of the aims of this research was to examine the composition of the froth in order to assess its possible viability as a fertilizer. Table 5.6 presents the properties of macronutrients and micronutrients found in the froth, as well as those of a commercially available fertilizer.

Table 5.6. Chemical composition of macro and micro-nutrients in froth and commercial fertilizer.

Element	Unit of measurement	Conventional DAF	SEFS	Commercial Fertilizer
Ca	(%)	1.7	1.9	8.2
Mg	(%)	3.1	3.4	5.7
S	(%)	7.9	7.8	8.1
N	(%)	6.1	5.8	17.1
P	(%)	4.2	3.9	14.2
K	(%)	2.6	2.8	18.5
Fe	mg/kg	79.1	87.6	950
Cu	mg/kg	6.7	6.5	13
Zn	mg/kg	13.3	13.1	117
Mn	mg/kg	30.8	36.1	220
B	mg/kg	5.8	8.9	242
Mo	mg/kg	3.5	4.2	6.5

The data presented in **Table 5.6** indicate that the macronutrient composition (typically quantified as a percentage) of the froth remained consistent, independent of the inclusion of shear in the treatment. In comparison, the water treated in the pilot plant does not currently meet the criteria for using the solid waste as fertilizer in its current state. A study was conducted by Conradie *et al*., (2020) which investigated the annual nutrient requirements to produce 30 tonnes of grapes per hectare in South Africa [246]. The results presented demonstrated that macronutrients (N, P, K, Ca and Mg) required to produce one tonne of grapes is (N) 3.93 kg/ha, 0.7 kg/ha (P), 3.2 kg/ha (K), 2.77 kg/ha (Ca) and 0.77 kg/ha (Mg). The study of the froth, as presented in **Table 5.6** showed the presence of important macronutrients necessary for crop development, but in relatively low proportions when compared to the commercial fertilizer. The decomposition of this organic matter in the soil releases nutrients that plants can absorb, including potassium, phosphate, and nitrogen, hence reducing the required amount of fertilizer for the vines. Considering the macronutrient composition of the froth, it is possible to combine the dried froth with commercial fertilizer as a means to reduce operational expenses in the vineyard. An additional benefit is that this is an environmentally friendly way to dispose of the sludge. On the other hand, micronutrients are mineral elements that plants need in trace amount, typically measured in milligrams per kilogram (mg/kg), in order to grow and develop healthily. The micronutrient contents in the froth were significantly lower than those in commercial fertilizer. Based on the nutrients presented here, it can be assumed that applying froth to soil is unlikely to cause severe damage. However, further research will need to be done to determine the consequences of adding dried froth to the soil.

Taking into account the positive results obtained associated with the effectiveness of the treatment, it is also important to assess the energy demands associated with applying DAF and SEFS to treat winery wastewater. The next section of this study focuses on the analysis of energy consumption, as well as the costs associated with materials and operations.

5.4. Pilot Plant Energy Requirements and Cost to Treat Winery Wastewater

The treatment efficiency of both conventional DAF as well as SEFS have been discussed in section 5.3. **Table 5.7** displays the power consumption values for each parameter during treatment.

Table 5.7. Energy consumption during wastewater treatment.

	Power Consumption(kWh/m^3)
Inlet Pump	0.032
Coagulant Dosing Pump	0.048
Flocculant Dosing Pump	0.076
Microbubble Generator	0.418
Shear Mixer	0.478
Outlet Pump	0.034

The energy consumed to treat 1 m^3 of winery wastewater using conventional DAF amounted to roughly 0.6 kWh/m^3 whereas the SEFS treatment energy was 1.1 kWh/m^3, as also illustrated in **Figure 5.11**. The quality of the treated wastewater may outweigh the total energy expenses even though SEFS treatment requires more energy than DAF treatment, as shown in **Table 5.8**.

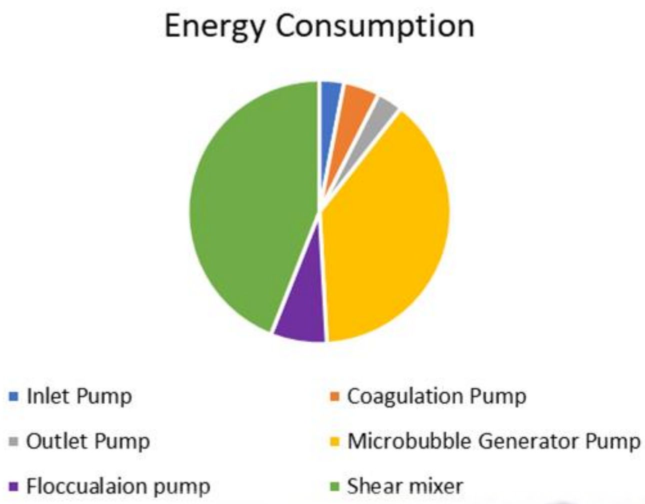


Figure 5.11. Energy consumption of individual treatment process

Table 5.8 illustrates the operational and materials costs during the treatment of 1 m^3 of winery wastewater. Considering the achieved outcomes, particularly the treatment efficiency, the added energy input expenses of the SEFS treatment system are thus considered reasonable. More specifically, the results highlight the cost saving during chemical treatment with SEFS. Wineries that opt for SEFS treatment have the potential to reduce both their overall energy expenditures (e.g., from secondary treatment processes) and their expenses related to wastewater disposal.

Table 5.8. Material and operational costs to treat 1 m^3 of winery wastewater.

Material and Operational Costs			
	Units	DAF	SEFS
Energy consumed	kWh/m^3	0.6	1.1
Coagulant	ZAR/ m^3	R0.86	R0.37
Flocculant	ZAR/ m^3	R0.34	R0.13
Energy cost in ZAR	ZAR */kWh	R1.09	R1.95
Total cost per/m^3	R	R2.29	R2.45
Treatment Efficiency			
TSS	%	97.1	99.4
Turbidity	%	95.8	99.6
COD	%	51	66

5.5. Conclusion of Pilot Plant Treatment

This chapter focused on the development and implementation of a hybrid shear enhanced flotation separation (SEFS) pilot plant for the treatment of winery wastewater. It comprised of the individual and synergistic effects of chemical additives and microbubbles, with and without shear. To the best of the author's knowledge, this study represents one of the first instances in which hydrodynamic shear has been incorporated as a treatment component in winery wastewater treatment. Hydrodynamic shear has been demonstrated to be a component that improves treatment efficiency overall. The energy consumption for DAF treatment was 0.6 kWh/m^3, whereas that of SEFS treatment was 1.1 kWh/m^3. Total material and operation costs are R2.29/m^3 for DAF and R2.45/m^3 for SEFS. Nevertheless, the small additional costs of SEFS are justified by the improved treatment efficiencies achieved by SEFS when compared to DAF.

The SEFS treatment resulted in a significant reduction of 99.6% in turbidity (from 849 NTU to 3 NTU) and 99.4% in TSS (from 2620 mg/L to 17 mg/L). In comparison, the conventional DAF achieved a reduction of 95.9% in turbidity (from 849 NTU to 35 NTU) and 97.1% in TSS (from 2620 mg/L to 75 mg/L). The SEFS treatment furthermore achieved a 66% reduction in chemical oxygen demand values, decreasing them from 11,140 mg/L to 3800 mg/L. The conventional DAF treatment system achieved a 51% decrease in COD, reducing it from 11,140 mg/L to 5490 mg/L. However, the remaining concentration of COD in the wastewater may be attributed to the soluble portion, which could not be eliminated through the use of SEFS or DAF treatment.

It was demonstrated that shear not only improves treatment effectiveness, but it also requires 33% less coagulant and 37% less flocculant compared to conventional DAF treatment. Another advantage of SEFS is that you do not need to go through floc tanks for flocculation to be successful. The differences in COD reduction between the two treatment methods can be ascribed to the increased agglomeration of particles and the generation of smaller bubbles during shear, resulting in an increased likelihood of collision between bubbles and particles. The higher frequency of microbubbles within the 0 – 100 µm range in SEFS treatment resulted in an enhancement in flotation and overall improvement in the separation of solids and liquids compared to DAF treatment.

The analysis of solid waste indicated that the froth produced during the treatment procedure may be a viable fertilizer component due to the presence of valuable nutrients such as sodium, nitrogen and phosphorus. Prior to utilizing this solid waste as a component for commercial fertilizers, it is important to conduct an in-depth study on the potentially detrimental or advantageous characteristics of the froth when applied to soil.

The value of SEFS technology in treating agricultural wastewater has been demonstrated, and it may also be useful for treating other types of wastewater, such as pharmaceutical and municipal wastewater.

CHAPTER 6 CONCLUSIONS

This chapter provides an overview of the research findings pertaining to the stated aims and objectives listed in Chapter 1. It furthermore clarifies the research's contribution to the existing body of knowledge.

6.1. Overview

The importance of winery wastewater treatment has been highlighted in Chapter 1 and Chapter 2. Several studies have noted the advantages and disadvantages of different treatment technologies, which include preliminary, primary, secondary and tertiary treatment stages.

As a result of more stringent rules on wastewater discharge, winery wastewater treatment aims to remove pollutants to attain a specific degree of water purity for reuse in wine processing. This overarching strategy aids in the promotion of sustainable methods in wine production.

An objective of a winery is to employ the most optimal technological advancements that enable sustainable production practices while minimizing the ecological footprint on natural resources. This research was targeted at evaluating hybrid flotation techniques to treat winery wastewater utilizing shear. This study encompasses the primary treatment stage during winery wastewater treatment, where nearly all particulate matter could be removed, producing treated wastewater of exceptional clarity and substantially reduced organic pollutant levels.

Based on the results obtained in Chapter 4 and Chapter 5, it was proven that hydrodynamic shear can be incorporated into both an induced air flotation (IAF) system as well as a dissolved air flotation (DAF) system, with the latter proving to be significantly more efficient in reducing TSS, turbidity and COD than the former treatment technique.

The findings demonstrate that both the IAF system used in the laboratory and the DAF system used on the pilot scale were capable of generating micro-sized bubbles, which are essential for achieving effective flotation.

6.2. Laboratory scale SEFS Winery Wastewater Treatment

Exposure of untreated winery effluent to shear yielded an important observation. Namely an alteration in the surface charge of colloidal matter. It was subsequently observed that with the application of shear, less chemicals were required to destabilize the colloids during treatment.

The implementation of SEFS treatment led to a substantial reduction of 97% in the concentration of total suspended solids (TSS). The decrease in TSS was observed after subjecting untreated wastewater samples, initially containing 2,275 mg/L of TSS, to SEFS treatment, resulting in a final TSS concentration of 50 mg/L. The turbidity exhibited a substantial decline of 95% after undergoing the SEFS treatment, as evidenced by the decrease in initial turbidity values from 630 NTU for the untreated wastewater to 25 NTU.

During laboratory scale experiments, shear-IAF treatment, a small portion of the bubbles fell below 100 µm (5% of the bubbles), whereas the bulk of the bubbles generated had average diameters of between 100 µm and 300 µm (82% of the bubbles). In contrast, IAF treatment without shear largely produced bubbles sizes in the range of 250 µm to 450 µm (73% of the bubbles). The higher frequency of small bubbles created with SEFS treatment can be linked to the improvement in treatment efficiency, as indicated by the turbidity and TSS removal rates. Consequently resulting in the elimination of suspended particles that are of a similar size.

The investigation subsequently proved that SEFS technology is an effective method for decreasing the COD of real winery effluent. Optimal operating conditions were established for winery wastewater, resulting in a 54% reduction in COD (initial: 11,250 mg/L vs. final: 5,220 mg/L).

6.3. Abrimix mobile treatment plant for Winery Wastewater Treatment

An Abrimix supplied, mobile treatment plant was tested at a wine farm on the West Coast, South Africa. During Abrimix on-site treatment, the average untreated turbidity, TSS, TDS and COD values for were 610 NTU, 1,935 mg/L, 1,965 mg/L and 12,220 mg/L, respectively. The turbidity, TSS, TDS and COD values for the Abrimix treated wastewater displayed average values of 278 NTU, 387 mg/L, 1,224 mg/L and 8,930 mg/L, respectively.

The difference in treatment efficiency between the laboratory study and Abrimix may be attributed to the process by which shear is introduced. In the laboratory set-up, the rotor stator provided more effective mixing and particle destabilization as opposed to the mixer contained in the Abrimix mobile treatment plant.

6.4. Pilot Plant Investigation for Winery Wastewater Treatment

During this part of the study, a pilot plant was designed and modified, which consisted of a hybrid shear mixer incorporated into a conventional dissolved air floatation treatment system to process winery wastewater.

The study examined the individual and synergistic effects of chemical additives and microbubbles, with and without shear. It has been demonstrated that the use of hydrodynamic shear significantly improves the overall effectiveness of the treatment process. The SEFS treatment resulted in a significant reduction in turbidity and TSS compared to the conventional DAF treatment (not fitted with flash mixers for chemicals mixing). Specifically, there was a 99.6% decrease in turbidity (from 849 NTU to 3 NTU) and a 99.4% decrease in TSS (from 2,620 mg/L to 17 mg/L) with SEFS. In contrast, the reduction in turbidity with conventional DAF was 95.9% (from 849 NTU to 35 NTU) and the reduction in TSS was 97.1% (from 2,620 mg/L to 75 mg/L).

With the SEFS treatment system, chemical oxygen demand values were reduced by 66%, from 11,140 mg/L to 3800 mg/L. In comparison, the conventional DAF treatment approach resulted in a 51% decrease in COD (from 11,140 mg/L to 5,490 mg/L). Following shear treatment, the COD values obtained indicate that this wastewater could possibly be a viable option for irrigation applications of vineyard crops for wineries discharging <50 m^3/day. The remaining concentration of COD in the wastewater is attributed to the soluble portion, which could not be eliminated through the use of SEFS or DAF treatment. The portion of soluble COD is generally regarded as highly biodegradable since it contains components such simple sugars and disaccharides. Hence, future investigations will need to encompass the further management and reduction of soluble COD by the utilization of biological treatment methods.

It has also been demonstrated that shear improves treatment efficiency, and in comparison, to conventional DAF treatment (not performing flash mixing after coagulation and flocculation), this method required 33% less coagulant and 37% less flocculant. The greater particle agglomeration and smaller bubbles produced during shear treatment, increases the likelihood of a collision between bubbles and particles, which is attributed to the COD reduction between the two treatment approaches. Compared to DAF treatment, there was an increase in solid/liquid separation due to the higher frequency of microbubbles in the 0–100 µm range. For treatment on the pilot scale, 61% of the bubble sizes fell within the range of 50 µm to 150 µm with shear (SEFS), whilst DAF treatment in the absence of shear, displayed mean bubble sizes of between 100 µm to 200 µm, corresponding to 51% of the total bubbles.

Based on the nutrients found, solid waste studies revealed that the froth produced during the treatment process might be regarded as a suitable source of fertilizer if mixed adequately with commercial fertilizer. Prior to considering this solid waste to be combined with commercial fertilizer, a full investigation into the foam's helpful and detrimental qualities is necessary. If the floated sludge could be utilized as fertilizer, the issue of sludge disposal to a landfill site will be averted.

During energy requirement evaluations, it was concluded that the treatment of 1 m^3 winery wastewater using conventional DAF requires around 0.6 kWh. In contrast, that of SEFS treatment requires roughly 1 kWh. The quality of treated wastewater outweighs the total energy utilised, even though SEFS treatment requires somewhat more energy than traditional DAF treatment. The roughly doubled energy use was, nevertheless, justified by clarity and substantially reduced organic pollutant levels. Therefore, wineries that consider SEFS treatment may be able to save money on both general wastewater discharge expenses and upstream energy-intensive treatments (such biological treatment).

The results of this research thus indicate that SEFS treatment shows potential as a practical and effective approach for treating wineries wastewater to meet the required discharge standards. The SEFS technology shows significant potential for expansion, as seen by its effective reduction of COD and significant decrease in turbidity and total suspended solids. Furthermore, there is potential for significant long- term economic benefits, such as reduced sludge disposal costs due to lower chemical usage, potential revenue from the sale of treated water for irrigation, and savings from decreased freshwater consumption.

To the authors knowledge, there are very few reported studies available in literature that have addressed winery wastewater treatment by means of hydrodynamic shear. The feasibility of SEFS technology to successfully treat agricultural wastewater has thus been proven and it could potentially be applied to treat other types of wastewater (e.g., pharmaceutical and municipal etc).

CHAPTER 7 RECOMMENDATIONS FOR POTENTIAL FUTURE STUDIES

This chapter presents suggestions for prospective research initiatives in the field of winery wastewater treatment, focusing particularly on the application of hydrodynamic shear and flotation technologies. The thesis statement, aims, and objectives articulated in Chapter 1 have been effectively addressed. However, it is crucial to recognize that there exist additional notable aspects that extend beyond the scope of the present study and merit exploration in future research efforts. Based on the findings and conclusions drawn from this study, it is advisable to do more research to explore the following domains in greater depth:

- The investigation of natural/green coagulant chemicals such as chitosan.
- The incorporation of combined chemical/biological treatment step following flotation e.g., ozone/microbial aeration to remove soluble organic compounds.
- Fitting an in-line pH and zeta potential monitoring system on the pilot plant unit.
- Investigation of electrocoagulation with hydrodynamic shear.
- Exploration of integrating SEFS with advanced oxidation processes (AOPs) to enhance the degradation of recalcitrant organic compounds.
- Comparative studies with other hybrid treatment systems, such as membrane bioreactors (MBRs) combined with SEFS, should also be conducted to evaluate their feasibility and efficiency.
- The substitution of air used during SEFS treatment with inert (N_2), oxidizing (O_2, O_3), acidic (CO_2), or basic (NH_3) gasses.

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CHAPTER 8 APPENDIX

8.1. Chemical dosage tests during pilot plant treatment

Table 8.1. Coagulation pump capacity.

Coagulation with Polydadmac/ACH blend	
Pump Setting	mL/min
180	125
150	99
120	81
90	62
60	44
30	20
15	12
5	4

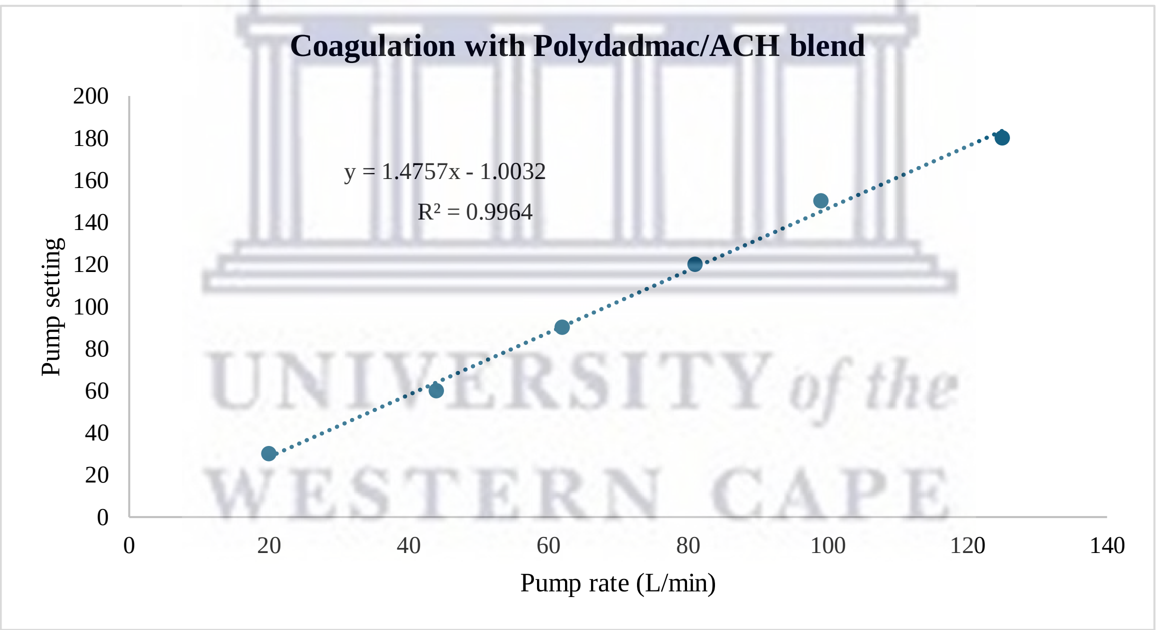

Figure 8.1. Coagulation Pump Rate

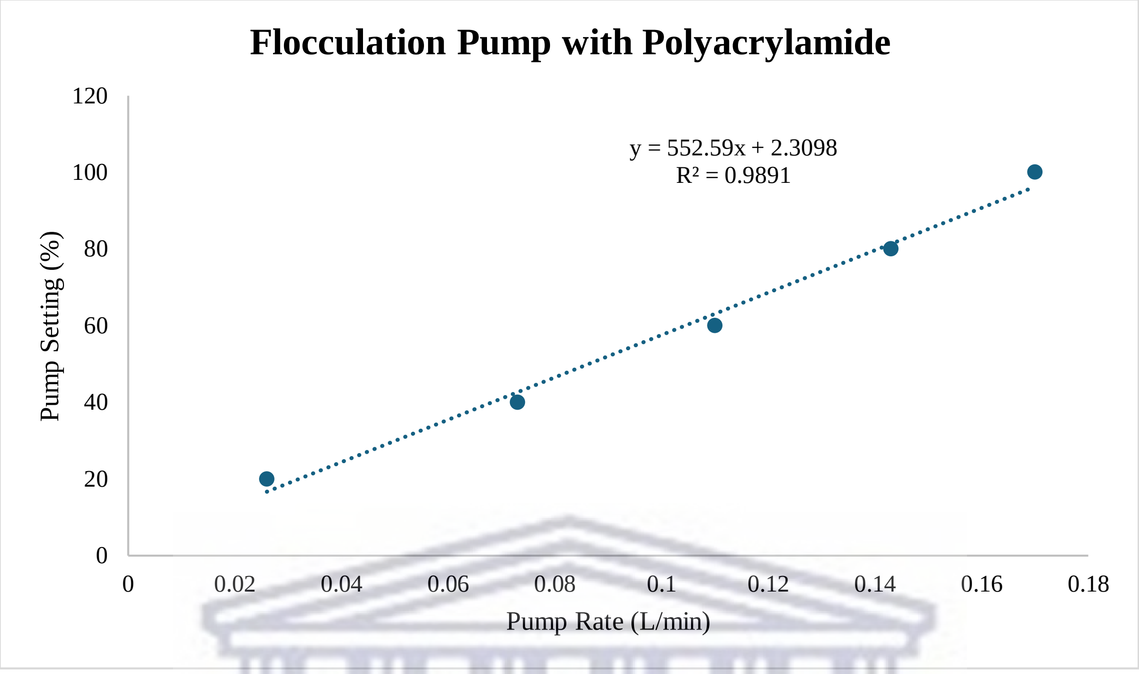

Figure 8.2. Flocculation Pump Rate

8.2. DAF shear system tank sizes and volumes

Dimensioned front view of a scale model of the flotation tank and the excess recycle tank used in the pilot plant winery wastewater treatment application.

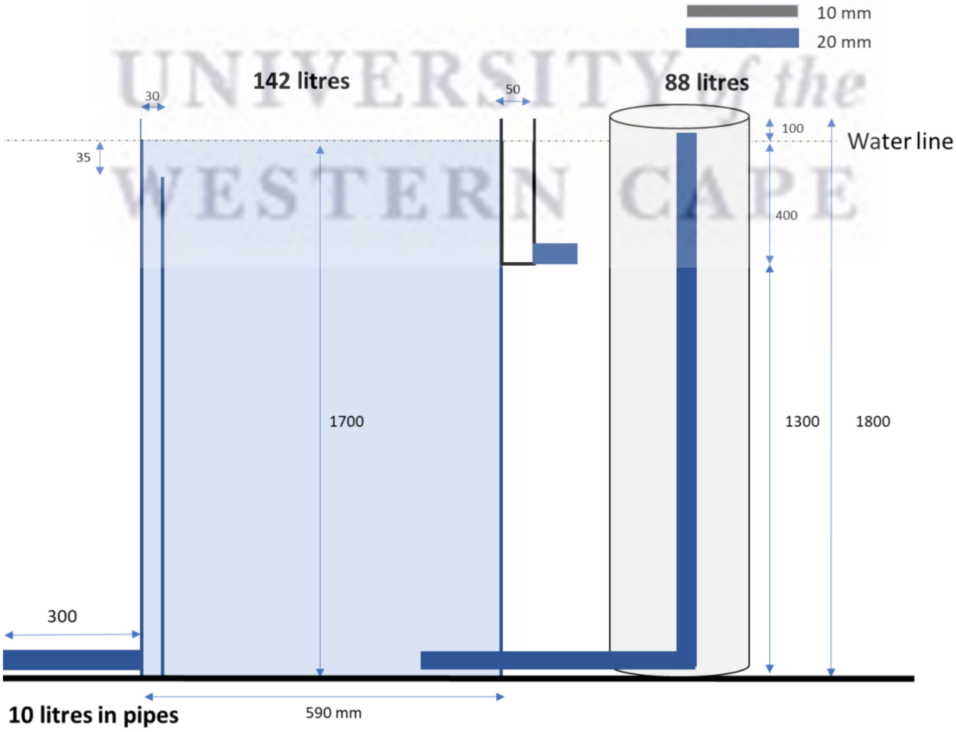

Figure 8.3. DAF unit design and dimensions.