REMOVAL OF SULFATE FROM BIODIESEL PRODUCTION WASTEWATER THROUGH HYBRID OIL-WATER FILTRATION AND GYPSUM PRECIPITATION-NANOFILTRATION

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by

TEO YAO AIK

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LIST OF SYMBOLS

Symbol	Description	Unit
A	Effective Filtration Area	m^2
C_o	Initial Sulfate Concentration of Non-Precipitated Solution	mg/L or ppm
C_t	Final Sulfate Concentration of Chemically Precipitated Solution	mg/L or ppm
C_i^{feed}	Sulfate Concentration of NF Feed Solution	mg/L or ppm
$C_i^{permeate}$	Sulfate Concentration of NF Permeate Solution	mg/L or ppm
J	NF Permeate Flux	L/hr. m^2
n	Sulfate Removal Efficiency	%
V	Collected NF Permeate Volume	L
t	Time	hr

Subscripts

o	Non Precipitated Wastewater Sample
t	Precipitated Wastewater Sample
i	NF Solution Sample

LIST OF ABBREVIATION

Abbreviation	**Description**
APS, $(NH_4)_2S_2O_8$	Ammonium Persulphate or Ammonium Peroxydisulfate
ATR-FTIR	Attenuated Total Reflectance Fourier-Transform Infrared
$BaCO_3$	Barium Carbonate
BGL	Brown Grease Liquid
$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$	Ettringite
$Ca(OH)_2$	Calcium Hydroxide
C-O	Carbonyl
$-COO^-$	Carboxylate
$Cu(OH)_2$	Copper (II) Hydroxide
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscopy
HCl	Hydrochloric Acid
KF	Karl-Fischer
NaOH	Sodium Hydroxide
NF	Nanofiltration
O-H	Hydroxyl
RO	Reverse Osmosis
SDGs	Sustainable Development Goals
SO_4^{2-}	Sulfate
US	United States
USEPA	US Environmental Protection Agency
WCA	Water Contact Angle

WHO	World Health Organization

PENYINGKIRAN SULFAT DARIPADA AIR SISA BUANGAN KILANG PENGELUARAN BIODIESEL MELALUI GABUNGAN TEKNOLOGI PENAPISAN AIR MINYAK DAN PEMENDAKAN GIPSUM-NANOFILTRASI

ABSTRAK

Sejak beberapa dekad yang lalu, tahap penelitian dan perhatian yang lebih intensif telah diberikan kepada pengeluaran efluen industri khususnya yang mengandungi kepekatan sulfat yang terlampau tinggi kebanyakannya disebabkan oleh kesan kesihatan dan alam sekitar. Dalam laporan ini, satu kaedah rawatan air sisa hibrid telahpun diperkenalkan untuk mengendalikan dan merawat air sisa buangan kilang pengeluaran biodiesel yang mempunyai kandungan sulfat yang tinggi. Fokus utama kajian tersebut pada peringkat awal adalah pelucutan fasa asid lemak daripada air sisa tersebut melalui penggunaan penapis mesh kuprum superhidrofobik yang disediakan. Membran superhidrofobik yang mempunyai tenaga permukaan yang rendah telah disediakan melalui proses pengoksidaan kimia yang ringkas dengan morfologi dan kebolehbasahan permukaannya dicirikan dan dinilai melalui kaedah mikroskop elektron pengimbasan pelepasan medan, sinar-x penyebaran tenaga, spektroskopi inframerah transformasi Fourier dan goniometri sudut sentuhan masing-masing. Walaupun berjaya menyelesaikan fabrikasi penapis mesh superhidrofobik ini untuk tujuan rawatan air sisa mentah, kegagalan penapisan telah diperolehi dengan penyingkiran asid lemak yang mudarat dan sia-sia akibat kehilangan sifat permukaan superhidrofobik secara sepenuhnya semasa proses pemisahaan. Kejadian sedemikian menjurus kepada pembangunan keperluan pra-rawatan air sisa yang boleh dipenuhi oleh pelaksanaan pemendakan kimia pada air sisa buangan kilang pengeluaran biodiesel yang mentah sebelum melalui proses rawatan nanofiltrasi utama. Kecekapan penyingkiran sulfat

melalui pemendakan gypsum yang lebih tinggi dicatatkan pada konsentrasi tertinggi pemendakan kimia kapur dan suhu larutan terendah masing-masing. Dengan penggunaan keadaan eksperimen yang dioptimumkan ini untuk merawat sebahagian air sisa industri mentah dari segi kepekatan sulfatnya, kualiti larutan air kumbahan yang termendak kemudiannya dipertingkatkan lagi melalui penggunaan operasi NF di bawah tekanan transmembran yang lebih tinggi ke tahap yang memenuhi julat piawaian efluen perindustrian yang ditetapkan untuk ion sulfat (500 – 1500 ppm). Oleh itu, hasil kajian tersebut telah jelas membuktikan kebolehpraktisan sistem rawatan air sisa bersepadu yang serba upaya dalam mengendalikan air sisa buangan kilang pengeluaran biodiesel industri dengan kandungan sulfatnya yang lebih tinggi, seterusnya mempamerkan potensinya untuk dipakai dalam aplikasi komersial dalam masa terdekat dengan ciri-ciri kemampanan yang bagus ditunjukkan.

REMOVAL OF SULFATE FROM BIODIESEL PRODUCTION WASTEWATER THROUGH HYBRID OIL-WATER FILTRATION AND GYPSUM PRECIPITATION-NANOFILTRATION

ABSTRACT

Over the past few decades, an increased degree of scrutiny and attention had been developed over the production of industrial effluents with elevated sulfate concentration owing largely to its health and environmental impacts. In this particular report, a hybrid wastewater treatment method had been introduced for the treatment of highly sulfate-containing biodiesel production wastewater. The initial main focus of this study was performed on stripping off the fatty acid phase from the wastewater through the utilization of as-prepared superhydrophobic copper mesh filter. Such superhydrophobic and low-surface energy membrane was prepared through simple chemical oxidation process with its surface morphology and wettability being characterized and evaluated through the methods of field emission scanning electron microscopy, energy dispersive x-ray, Fourier-transform infrared spectroscopy and contact angle goniometry respectively. Despite the success on this superhydrophobic mesh filter fabrication for the treatment purpose of non-treated wastewater, a filtration failure was attained with in-vain fatty acid elimination due to the complete loss of surface superhydrophobicity during the separation process. Such happening fervently contributed into the necessary development of wastewater pre-treatment requirement which was fulfilled by the application of chemical precipitation upon the raw biodiesel wastewater, prior to the main NF treatment process. Higher sulfate removal efficiency through gypsum precipitation was recorded at the highest lime precipitant concentration and the lowest solution temperature respectively. With the utilization of these optimized experimental conditions to partially

treat the raw industrial wastewater in terms of its sulfate concentration, the quality of precipitated wastewater solution was then further polished through the use of NF operation under higher transmembrane pressure to a level that acceptably fulfilled the industrial effluent standard range specified for sulfate ions (500 – 1500 ppm). Thus, results of this work had distinctly proven the practicability of such integrated wastewater treatment system for effectively handling the industrial biodiesel production wastewater with higher sulfate contamination, subsequently promoting its potential to be introduced into commercial based applications in the near future with better sustainability characteristics being demonstrated.

CHAPTER ONE

INTRODUCTION

In this chapter, the detailed overview of this research and significance of removing sulfate compounds from biodiesel production wastewater is reported. This chapter clearly summarizes the research background of sulfate removal from industrial effluents with some important aspects like sulfate treatment techniques and separation concerns being addressed as well. In the end, the problem statement and the objectives of this final year research project are also briefly illustrated.

1.1 RESEARCH BACKGROUND

Sulfate is an ordinary constituent of a number of water bodies mainly like natural waters and industrial wastewaters where it appears as a dissolved compound or as insoluble salt-like gypsum (Silva et al., 2002). Industrial effluents which contain high sulfate concentration always account for a major contributor of anthropogenic emissions of sulfate into the environment. Biodiesel production, for example, produces wastewater that consists of higher sulfate content, as depicted by He et al. (2009). This is attributed to the conventional reaction pathway of biodiesel production which incorporates sulphuric acid as catalyst (Alptekin et al., 2014; He et al., 2009; Hughes et al., 2018). This issue is further intensified by the improper biodiesel processing step, making the final sulfate level in the effluent far above the recommended maximum sulfate discharge limits of 500 – 1500 mg/L (Alam et al., 2021; Bowell et al., 2004; He et al., 2009).

High levels of sulfate in the water medium can provoke a series of negative environmental outcomes like giving rise to water mineralization or salinization, toxic hydrogen sulfide release, scaling and corrosion issue on pipes or equipment, and interference in the balance of the natural sulfur cycle (Baldwin and Mitchell, 2012; Cao et al., 2011; Pikaar et al., 2014; Sun et al., 2017). With a significant exposure towards such sulfate levels, it may even cause severe disruptions to the ecosystems where the aquatic living plants and animals are highly exposed to these hazardous compounds (Cañedo-Argüelles et al., 2013; Ghigliazza et al., 2000; Kaushal et al., 2005; Soucek and Kennedy, 2005). Furthermore, the presence of an abnormal content of sulfate in the water can incur detrimental and laxative consequences upon mammals. For instances, higher sulfate levels can lead to health illnesses like diarrhea and thus it is considered very hazardous to mammals like moose and cattle as sulfates are actively converted to toxic hydrogen sulfide within their digestive system (Darbi et al., 2003; Silva et al., 2012). In light of this, the promulgation of new sulfate discharge regulations is developed to control the global sulfate discharge limits for different end-use parties. Currently, the discharge limits varies amongst the countries, for example, 2,000 mg/L for surface water discharge in Chile to 10 mg/L in the US state of Minnesota (Liang, 2014; Myrbo, 2017; Runtti et al., 2018).

There are a number of treatment techniques being used to remove sulfate from wastewater. In general, the methods include the physical method (e.g., reverse osmosis or nanofiltration), chemical method (e.g., gypsum precipitation) and biological method (e.g., sulfate reducing bacteria based method) (Fang et al., 2018; Fernando et al., 2018; Runtti et al., 2018; Sharma and Kurma, 2020). Each sulfate treatment method has their own pros and cons, for instance, the biggest challenge or issue of biological method encompasses on how to maintain the optimum and stabilized conditions for bacterial viability due to the strict operating conditions (Banerjee et al., 2015; Lens et al., 1998; Lorax, 2003; Runtti et al., 2018). Most importantly, such treatment approach is always associated with the production of metal sulfides and also metabolic waste which subsequently contributes to enhanced environmental concerns followed by higher operating costs because of additional sulfide management (Banerjee et al., 2015; Lens et al., 1998; Lorax, 2003; Runtti et al., 2018).

Chemical precipitation, on the other hand, is among the most widely adopted and proven technology for sulfate-rich wastewater treatment due to its simplicity (EPA, 2000; Fernando et al., 2018; Yu et al., 2018). The introduction of lime/limestone can raise the pH of wastewater samples and subsequently promote an effective sulfate precipitation in the solution, thus leading to a promising removal of dissolved sulfate compounds from the medium (Benatti et al., 2009; Dou et al., 2017; Fernando et al., 2018). As the result of sulfate precipitation by calcium based precipitants, gypsum is produced with no associated toxic risk, thus making lime/limestone precipitation an environmentally and economically viable treatment choice as compared to barite precipitation (Benatti et al., 2009; Lens et al., 1998).

Membrane separation is definitely a promising technology to be adopted for sulfate treatment in the wastewater due to its efficient sulfate removal capacity which can allow the production of treated effluents with higher quality that meets the environmental regulatory limits (Pino et al., 2018). At this point, nanofiltration is much more recommended to be applied as compared to RO membrane application because of its lower energy consumptions and operating costs in the comparison to reverse osmosis implementation which is highly energy intensive (D'Costa, 2015; Runtti et al., 2018). Better membrane fouling performance can also be addressed through the use of nanofiltration membrane during wastewater treatment for sulfate rejection (D'Costa, 2015; Fernando et al., 2018; Pino et al., 2018).

Although the above mentioned methods are known to be effective in removing the sulfate from the wastewater, however, the presence of higher fatty acid compositions in the biodiesel production waste makes the sulfate removal a challenging and troublesome task (Ashnani et al., 2014; Atadashi et al., 2011a; Atadashi et al., 2011b; Balan, 2014). This is because that fatty acids are known as highly reactive dissolved organic components in which reaction with alkali elements can further form undesired saponified products like calcium soap and then imposes additional hurdles in recovering sulfate from the wastewater (Bouaid et al., 2015; Fukuda et al., 2001; Goembira and Saka, 2013; Handojo et al., 2018). While for the course of membrane based technology application, the existence of such considerable amount of soluble fatty acid inside the wastewater shows higher affinity to be absorbed onto the pore walls, subsequently forming multiple cake layers upon the membrane surface (Amin et al., 2010; Ke et al., 2013). As its aftermath, a higher membrane resistance with significant flux decline is definitely expected, further aggravating the performance of sulfate removal from biodiesel wastewater. Therefore, an appropriate yet effective pre-removal of fatty acid content from biodiesel wastewater is required to guarantee a promising sulfate removal efficiency or performance. At this point, the adoption of a superhydrophobic filter to separate the sulfate-rich aqueous phase from the fatty acid phase is considered as a vital pre-treatment step that ensures that a better sulfate removal can be achieved. Copper mesh with excellent superhydrophobic properties not only can effectively separate oil/water mixture with desired efficiency and selectivity being attained, but also an excellent material with good recyclability (Liu et al., 2013; Ren et al., 2018). The application of effective sulfate treatment system which is accompanied by the utilization of above-mentioned treated filter for optimizing the quality of biodiesel wastewater with sulfate content being effectively reduced undeniably acts as a driving potential to enable the further utilization or application of such water medium as a sustainable resource for various applications, which is then highly favorable of accessing better socio-economic developments**.** However, based on the current researches' study, little attention has been paid or given to the sulfate removal from the biodiesel wastewaters (Atadashi et al., 2011a; Atadashi et al., 2011b; Yu et al., 2021). Therefore, the performance of the system to remove sulfate from the wastewater with superhydrophobic pre-filtration is yet to be fully understood. As regards to this concern, in this particular study, the feasibility study of sulfate rejection from biodiesel production wastewater through the application of integrated gypsum precipitation-nanofiltration method with preceding mesh filtration is performed and implemented.

1.2 PROBLEM STATEMENT

The generation of high volume of sulfate contaminated biodiesel production wastewater is alarming due to its adverse environmental impacts. The technological limitation of removing sulfate from the biodiesel wastewater is not only detrimental to the aquatic ecosystem but also poses much significant hurdles towards the downstream processing due to its corrosive nature.

Such sulfate-rich wastewater is causing stress towards the existing biological treatment method because of its production of poisonous hydrogen sulfide compounds under anaerobic condition. Thus, to comply with the stringent regulatory limits by minimizing the sulfate impacts, developing effective technologies on curing such biodiesel production wastewater with higher sulfate concentration has become a prominent subject to be focused in this study. On the other hand, the presence of a considerable fatty acid composition inside the biodiesel wastewater develops arduous challenges towards the separation of sulfate via precipitation and nanofiltration due to its inherent hydrophobicity and unstable reactivity that may give rise to the development of fatty acid fouling of the membrane with possible unwanted soap formation, which further complicate the sulfate recovery process.

In light of this, the application of superhydrophobic copper mesh filter as a pre-treatment step is shown to be an essential move for optimizing the efficiency of subsequent sulfate treatments due to its potential for oil-water separation. The success of subsequent sulfate removal through precipitation and nanofiltration lies on the efficiency of fatty acid removal using the mesh because the oil-water separation efficiency serves as an impactful factor on the fouling resistance of the membrane and also the precipitation efficiency.

1.3 RESEARCH OBJECTIVES

The objectives of this research study:

i. To develop and employ the superhydrophobic copper mesh as oil-water separator to filter out the sulfate-rich water from the fatty acid phase in biodiesel production wastewater

ii. To assess the feasibility of fatty acid removal from biodiesel production wastewater by using the fabricated superhydrophobic mesh filter

iii. To evaluate the respective separation efficiency of sulfate from biodiesel wastewater through gypsum precipitation and nanofiltration methods

1.4 SCOPE OF RESEARCH

The primary scope of this research study was to develop and evaluate the feasibility of a holistic and efficient integrated treatment approach for minimizing and eliminating the abundance of sulfate composition inside the raw biodiesel production wastewater. As regards to the co-presence of undesired fatty acid components was required to be essentially eliminated prior to further sulfate treatment upon the wastewater, the development of a superhydrophobic copper mesh filter was performed through the identification and utilization of appropriate yet consistent chemical oxidation formulations. At this point, the as-prepared mesh filters were subjected to the characterization analysis of its surface morphologies and wettability by various evaluation tools like field emission scanning electron microscopy (FESEM), energy dispersive x-ray (EDX), Fourier-transform infrared (FTIR) spectroscopy and contact angle measurement as well. Following that, the resulting fabricated superhydrophobic copper mesh filter was incorporated for the removal of oily fatty acid phase from the wastewater mixture.

Somehow, with the complete failure of fatty acid phase separation, the implementation of sulfate precipitation by calcium hydroxide (lime) was performed as pre-treatment phase in order to optimize the overall sulfate removal efficiency upon non-treated biodiesel wastewater. In this case, different process parameters like reaction temperature and lime precipitant dosage were briefly investigated with regards to their potential effects upon the sulfate precipitation mechanism as the utilization of the optimal operating conditions was declared as a stepping stone to account for an enhanced sulfate removal performance development for this proposed hybrid treatment system.

After the application of optimal gypsum precipitation for pre-treating the biodiesel production effluents, the main NF process was sequentially implemented whereby the possible influence of its transmembrane pressure being imposed across the membrane was significantly studied to identify how far the sulfate separation dynamics and efficiency could be affected by the magnitude of osmotic pressure developed inside the NF system through the indication of several performance parameters and also the FESEM-EDX analysis outcome. Lastly, the statistical error bar analysis was done upon all the important analytical parameters obtained throughout these experimental sections to access their respective data uniformity and reliability.

CHAPTER TWO

LITERATURE REVIEW

In this particular section, previous findings from a number of credible scientific reports are strongly related to this research topic. It covers an extensive yet critical review on biodiesel wastewater treatment, sulfate removal issue, possible sulfate removal alternatives including superhydrophobic based separation technologies available for sulfate enriched oil-in-water wastewater in pertaining to biodiesel wastewater production.

2.1 BIODIESEL WASTEWATER TREATMENT

Due to its environmental friendly and renewable characteristic with lower pollutant emissions, currently, the uses of biodiesel have been claimed as a promising energy source alternative to conventional fossil fuels. However, current biodiesel production is reported to be strongly associated with the generation of a large number of wastewater (around three times the volume of biodiesel), subsequently elevating its environmental concern (Atadashi et al., 2011a; Atadashi et al., 2011b; Kumjadpai et al., 2011; Low et al., 2011). In this case, biodiesel wastewater is characterized by higher content of residual oil, soluble salts (chloride and sulfate), remained catalysts, soaps and dissolved impurities, and therefore considered as a highly toxic and hazardous effluent to be vitally treated (Veljković et al., 2014). There are plenty reports on biodiesel wastewater treatment being published which include coagulation, electrocoagulation, biological, adsorption, microbial fuel cell and, additionally, their associated treatment processes, which consist of a combination of two or more processes (Daud et al., 2015; Veljković et al., 2014).

Biodiesel production activities are considered a vital sources of such anthropogenic aqueous sulfur because it is reported that the sulfate content in biodiesels being produced especially through the uses of brown grease lipid (BGL) can be explicitly higher than the conventional fossil diesel process (He et al., 2009; Hughes et al., 2018). In this case, the presence of such high sulfate content inside biodiesels can be due to high sulfur content of feedstock accompanied by sulfuric acid catalyst used during its production (Alam et al., 2021; Alptekin et al., 2014; He et al., 2009). Consequently, it renders the final sulfate level to be out of the recommended concentration fixed by US Environmental Protection Agency (USEPA) and World Health Organization (WHO) respectively (Edition, 2011; EPA, 2006; He et al., 2009). However, Bowell et al. (2004) stated that as compared to other metal impurity removal from industrial wastewater, little attention has been directed on the mitigation or removal of dissolved sulfate in the biodiesel production. There is only a handful of literatures on the sulfate treatment of biodiesel wastewater especially with respect to sulfate removal (Atadashi et al., 2011a; Atadashi et al., 2011b; Yu et al., 2021). As illustrated in the case study by the latter author, the application of catalytic combustion was performed where all the sulfur containing compounds inside the evaluated sample were burnt off and their content were significantly reduced from 30 mg/L to less than 1 mg/L (Yu et al., 2021).

2.2 SULFATE REMOVAL: INDUSTRIAL OVERVIEW AND ITS CONCERN

Sulfate or sulphate is a ubiquitous compound being found in natural sources where their sulfate content typically ranges from 2 - 250 mg L^{-1} in lakes, 0 - 630 mg L^{-1} in rivers, and 0 - 230 mg L^{-1} in ground water (Lens et al., 1998; UNEP, 1990). While other water bodies like seawater has much higher sulfate composition of 2700 mg L^{-1} or more (Hitchcock, 1975; Ul-Hamid et al., 2017). Other than these natural emissions, such chemical impurity is also usually found in the wastewaters particularly in discharge of many industrial processes like fertilizer and pesticide production, chemical manufacturing, food processing, petroleum refining, textile industry, paper milling and other possible industrial lines which involve the application of sulphuric acid or sulfur-containing materials (Lens et al., 1998; Nehb and Vydra, 2006; Pol et al., 1998; Tait et al., 2009).

There is a significant amount of literatures stating that sulfate in any fluid bodies can incur much considerable problems towards humans and environment due to its corrosive and purgative nature, and thus have been placed under increasing scrutiny from regulatory authorities over the past few decades (Bowell et al., 2004; Edition, 2011; EPA, 2006). In this case, it is reported that upon being exposed to high sulfate levels, it is much vulnerable to the development of health risks such as diarrhea, dehydration, catharsis, methaemoglobin and also sulfhaemoglobin level changes in mankinds and animals (Cocchetto and Levy, 1981; Darbi et al., 2003; Digesti and Weeth, 1976; Gomez et al., 1995; Paterson et al., 1979). With regards to this concern, in the state of Saskatchewan, three medical cases were reported where some infants had gone through gastroenteritis along with diarrhea and dehydration, upon ingesting the water that was equipped with high levels of sulfate of about 650 - 1150 mg/L (Chien et al., 1968). A relevant study conducted by Linn and Raeth-Knight (2010) also pointed out that sulfate concentration of greater than above 500 mg/L had developed laxative effects upon young animals, with increased resistance being observed for the cattle in a short period of time. In the case of freshwater medium, an elevated sulfate concentration has been treated as a problematic environmental threat where the aquatic species is subjected to significant lethal influence due to the osmotic stress or shock which is the result of increasing sulfate level that contributes much to the salinization of that particular water body (Cañedo-Argüelles et al., 2013; Kaushal et al., 2005; Soucek and Kennedy, 2005). As a result, a decline in the aquatic biodiversity is anticipated, thus potentially altering ecosystem structure.

In addition to these health and environmental concerns, during wastewater discharge, sulfate in high concentration which can lead to high levels of salinity can significantly expedite the corrosion and deterioration rate of the sewers which are usually made up of those concrete materials (Glasser et al., 2008; Monteiro, 2006; Tait et al., 2009). While having sulfate attack, it can then facilitate the metal release from the corrosion scales on the piping system and then may indirectly raise up another environmental issue (Sun et al., 2017). Somehow, the major complication confronting the presence of such high composition of sulfate inside any water bodies is significantly linked to pretty high potential of hydrogen sulfide production through sulfate reduction under anaerobic condition, which have been found out as an upset occupational health and safety, and also maintenance problem due to the poisonous behavior of hydrogen sulfide components being developed (Lens et al., 1998; Rubright et al., 2021; Tait et al., 2009). As a consequence, it tends to bring about the development of microbiologically influenced corrosion with a much high-odor wastewater effluent being resulted, as per stated by several authors accordingly (Enning and Garrelfs, 2014; Hamilton and Lee, 1995; Lens et al., 1998; Tait et al., 2009).

2.3 SULFATE TREATMENT/REMOVAL TECHNOLOGIES

The possibility of high sulfate removal or recovery from biodiesel production waste can be potentially done through the implementation of various well-established technologies such as chemical precipitation and membrane separation, as briefly discussed in the following sections. The recovery of sulfate compounds usually can happen from concentrates or solids formed in various treatment processes.

2.3.1 CHEMICAL PRECIPITATION

Sulfate removal is typically counted for its separation difficulty because of the high solubility and stability of sulfate salts present in the aqueous solution just like industrial wastewater (Yu et al., 2018). In this respect, chemical precipitation methods have been proposed as the most widely-applied technologies. Upon precipitation, the solid and insoluble "filter cake" residue can be disposed via landfilling (Fernando et al., 2018). Extensive reports on a number of different precipitation technologies for sulfate removal in virtue of formation of gypsum, barite or ettringite precipitations ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$) were revealed.

The application of ettringite precipitations which was initially developed as SAVMIN process had been reported to be much capable of dealing with highly sulfate-contaminated wastewater where a sulfate concentration of less than 200 mg/L could be attained via the addition of aluminium hydroxide to form the highly insoluble ettringite precipitate (Madzivire et al., 2010; Naidoo et al., 2018). Smit and Pretorius (2000) reported that the feed water samples which contained 3000 mg/L of sulfate was significantly reduced by the SAVMIN process to 75 mg/L which corresponded to an overall sulfate removal efficiency of 98 %. Sulfate removal efficiency and viability were further tested in a mini plant to treat the polluted mining wastewater. Results showed that recovery of 95% sulfate from the designated medium containing initial sulfate content of 2226 mg/L could be achieved (Smit and Pretorius, 2000).

Other similar precipitation alternatives like barite precipitation also offers an excellent candidate or solution as a removal phase for sulfate treatment. Maree et al.

(2004) found that a highly acidic industrial wastewater was able to be treated effectively through the implementation of barite precipitation which reduced or cut down the sulfate content to a lower concentration of around 50 mg/L (Bologo et al., 2010; Bowell et al., 2004; Fernando et al., 2018; Runtti et al., 2018). In this case, the pair ions for barium salts such as sulfides, carbonates and hydroxides are among the most common compounds removed during sulfate treatment methodologies (Bosman et al., 1990; Bowell et al., 2004; Kefeni et al., 2015; Maree et al., 2004). Both barium sulfide and hydroxide are highly effective in removing dissolved sulfate over the entire pH range, thus being much applicable in highly acidic wastewater treatment (Bowell et al., 2004; Runtti et al., 2018). However, the efficacy of barium carbonate is limited under certain extreme conditions (Bowell et al., 2004; Runtti et al., 2018). To cite an example, Hlabela et al. (2007) claimed that the uses of barium carbonate is only confined to sulfate removal associated with calcium. Besides, such precipitation alternative is usually accompanied by a lime pretreatment step in order to perform an efficient sulfate removal. At this point, with the initial addition of lime to partially remove the dissolved sulfate compounds, lesser dosage of barium is only required to perform sulfate removal by precipitation, thus eliminating the requirement of longer retention time for the particular treatment system with minimum barium residual concentration being formed in the treated solution. With such implementation, the major hurdles related to $BaCO_3$ usage as mentioned above including high financial costs involved can be overcome or addressed accordingly, as per stated in the study by Lens et al. (1998) and Kun (1972). From overall perspective, sulfate removal via barium precipitation is neither economically attractive nor environmental friendly. Nonetheless, the sludges can be further recycled to offset the exorbitant removal costs (Benatti et al., 2009; Bowell et al., 2004; Lens et al., 1998). However, there are potential risks associated with barium salts which require a close monitoring of barium traces in the effluent (Benatti et al., 2009).

As compared to the technologies above, gypsum precipitation which is considered as the forefront of all the precipitation methods in which adding lime and limestone precipitants is found to be rather under performing as far as sulfate removal is concerned (Yu et al., 2018). Lime addition can enhance the alkalinity of the media to promote the metal precipitation. The rate of sulfate precipitation depends on the solubility of gypsum which is controlled by the ionic strength and composition of the aqueous solution (Bader, 2007; Tait et al., 2009; Yu et al., 2018). As a result, the industrial application of gypsum precipitation as a single treatment process is often reported to be not able to fulfill the environmental regulatory limits where its final sulfate concentration being reduced always ranges from 1500 to 2000 mg/L which is right above the regulatory specifications (Liang, 2004; Lorax, 2003). Yet, such gypsum precipitation approach for sulfate treatment is still widely preferred and performed due to several competitive advantages against those aforementioned methods (Brown et al., 2002; Fernando et al., 2018; Yu et al., 2018). For instance, gypsum precipitation usually equips itself with enhanced process simplicity that the salts involved are much easier to be precipitated out and also better tolerance towards temperature fluctuation (Brown et al., 2002; Fernando et al., 2018; Lens et al., 1998; Yu et al., 2018). Contrarily, sulfate removal by ettringite precipitation is observed to be not that promising in terms of its process development where complex chemical operating conditions are needed for stable salt precipitation (Janneck et al., 2013). At this point, the ability of such gypsum precipitation to remove dissolved sulfate compounds have been further demonstrated by a number of their industrial application schemes being proposed and published, as obviously depicted and summarized in Table 2.1.

Table 2.1: Summarized overview on different gypsum precipitation applications for sulfate removal

Type of Gypsum Precipitation	Type of Wastewater	pH of Wasterwater Sample	Initial Sulfate Concentration in Wastewater Sample (mg/L)	Final Sulfate Concentration in Wastewater Sample (mg/L)	Sulfate Removal Percentage (%)	References
Lime/ Limestone Treatment	Highly acidic mine water from coalmine	2.1	3000	1219	59.4	Lorax (2003)
Lime Treatment	Tailing pond solution from gold mine	7.8 - 8.0	8900	1400	84.3	Kinnunen et al. (2018)
Lime Treatment	Acid mine drainage from copper mine	3 - 4	2000 - 3000	800 - 900	60 - 70	Khorasanipour et al. (2011)
Calcite Limestone Treatment (53.7% calcium and 0.28% magnesium)	Neutral mine water	6.5	588	87.4	85.1	Silva et al. (2012)
			800	222.4	72.2	
			1100	596.7	45.8	
Lime Treatment with the addition of calcium hydroxide and sodium aluminate mixture	Wet flue gas desulfurization (FGD) wastewater	4.5	5229	1935	63.0	Yu et al. (2018)
Limestone Treatment including sodium hydroxide	Acidic leachate from waste coal dump (mine water)	2.2	15000	2000	86.7	Maree et al. (1998)

Based on Table 2.1, a gypsum precipitation process was developed by Khorasanipour et al. (2011) for the sulfate removal from contaminated mining water through lime precipitation. It was found that under optimum condition, an initial sulfate concentration of about 2000 - 3000 mg/L was reduced to a lower value of 800 - 900 mg/L (Khorasanipour et al., 2011). While in the case of limestone application by Maree et al. (1998), an effective sulfate reduction from 15,000 to 2000 mg/L was achieved with about a removal effectiveness of about 87 % using lime precipitation method. As observed from these cases, it is expected that the precipitation process is not complete and leaving out a relatively gypsum-saturated (residual sulfate) solution to be further processed and polished for the environmental concerns (Fernando et al., 2018). As in the view of such phenomenon, it is of greater concern that being alert with the gypsum saturation level is necessary because the dissolution of more precipitants is no longer in the favor of sulfate precipitation upon gypsum saturation limit is attained (Geldenhuys et al., 2003). On the contrary, some consequences are induced when more unreacted lime or limestone are created, subsequently jeopardizing overall sulfate removal efficiency (Fernando et al., 2018).

Based on the above literature study, gypsum precipitation is mainly and preferably adopted as pre-treatment process for sulfate removal where its effluents can be further integrated with another well-developed treatment technology to perform favorable sulfate recovery (Bowell et al., 2004; Fernando et al., 2018; Gazea et al., 1996). As regards to this, Geldenhuys et al. (2003) demonstrated the enhanced sulfate removal ability of a well-established sulfate treatment system with the application of gypsum precipitation as pretreatment step whereby sulfate level could be further brought down to 300 mg/L, lower than the anticipated level of 1200 mg/L.

2.3.2 MEMBRANE SEPARATION

Alternatively, membrane separation process is regarded as another well-established yet advanced treatment technology that can be implemented for performing an effective sulfate removal. Membrane separation is a pressure-driven process that can be varied based on their pore size and separation capacity (El-Ghaffar and Tieama, 2017; Runtti et al., 2018). Among the membrane based technologies, nanofiltration (NF) is known to be the best approach to be used for sulfate rejection or treatment (Agboola et al., 2017; Ambiado et al., 2017; Banerjee et al., 2015; Bódalo et al., 2004; Eriksson, 1988; Kinnunen et al., 2018; Laskowska et al., 2014; Runtti et al., 2018; Sharma and Kurma, 2020). At this point, its separation mechanism not only involve steric hindrance but also charge repulsion. In the treatment of mine waters, the removal percentage of sulfate are found to be ranging from 93 % to 99 % and achieving a much lower sulfate concentration of 10 mg/L in the permeate either by single or two stage filtration (Agboola et al., 2017; Banerjee et al., 2015; Eriksson, 1988; Kinnunen et al., 2018; Laskowska et al., 2014; Runtti et al., 2018; Sharma and Kurma, 2020). As a result, the application of such NF based treatment alternatives allows the production of high quality effluents that comply with the discharge limits as mentioned above.

NF can reject both dissolved ions and salts effectively as compared to the conventional treatment methods (Fernando et al., 2018; Kinnunen et al., 2018; Runtti et al., 2018). It exhibits an enhanced capability to remove multivalent ions like sulfate and carbonate but has lower rejection for monovalent ion (Barr, 2001; D'Costa, 2015; Eriksson, 1988; Kinnunen et al., 2018; Tanninen et al., 2006). Other than having better sulfate recovery performance, NF based separation triumphs over RO membranes in several factor especially their energy consumption in which RO membranes requires higher operating pressure thus leading to a substantial energy consumption with lower overall cost effectiveness (Agboola et al., 2017; Runtti et al., 2018). D'Costa (2015) investigated the application of nanofiltration towards seawater sulfate removal. The research revealed that as compared to conventional RO membrane, the application of NF membrane had increased the sulfate removal efficiency by 20 - 30% along with lower fouling tendency and enhanced operating control towards harsh conditions (D'Costa, 2015). Table 2.2 holistically compiles the performance of NF membrane used for various applications of sulfate removal.

Table 2.2: Recent studies on the application of nanofiltration membrane technologies for sulfate removal

Type of Nanofiltration (NF) Membrane	Membrane Material	Type of Wastewater Sample	Initial Sulfate Concentration in Feed Wastewater Sample (mg/L or ppm)	Final Sulfate Concentration in NF Permeate (mg/L or ppm)	Sulfate Rejection Ratio (%)	References
Non-specified NF	N/A	Seawater	2708	181.4	93.3	Quist-Jensen et al. (2016)
NF 90	Polyamide composite	Seawater	2944	97.2	96.7	Llenas et al. (2013)
NF 200	Polyamide composite	Seawater	2944	26.5	99.1	
NF 270	Polyamide composite	Seawater	2944	73.6	97.5	
NF 90	Polyamide composite	Seawater	N/A	N/A	99.4	Song et al. (2011)
NF 270	Polyamide composite	Seawater	N/A	N/A	98.9	
NF 90	Polyamide composite	Seawater	2710	8.4	99.7 – 100.0	Vuong (2006)
Ultra-Low Pressure NF (ESNA3, Hydranautics)	Polyamide composite	Seawater	2310	24	93.3	Song et al. (2012)
			2304	37	98.4	
			2275	30	98.7	
NF 270	Polypiperazide amide composite	Acid mine drainage from gold mine	2000 - 2800	260 - 364	87.0	Aguiar et al. (2018)
NF 270	Polypiperazide amide composite	Acid mine drainage	790	7.9	99.0	Wadekar et al. (2017)
NFHL	Polypiperazide amide composite			150.1	81.0	