DEVELOPMENT OF FORMATION MITIGATION OF PALM OIL MILL EFFLUENT (POME) CRYSTALS

BY

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ABSTRACT

Scaling problems in palm oil mill effluent (POME) treatment facility, has a long history of causing adverse impact on the efficiency of the POME treatment process. The accumulation of scaling in POME treatment pipelines has led to consequential impacts of reduced pipe diameter thus affecting the effective flow rate, leading to clogging of pipes as well as reduction in the treatment plant hydraulic retention time (HRT). Its occurrence has become more frequent in recent years with the increase of tank usage in the treatment process of POME. This study was formulated with the objective to determine the physicochemical characteristics of the crystal found in the POME treatment facilities, examine the influence of pH and temperature on the solubility of the crystal grown in POME treatment system and explore reactive crystallization method in growing crystal from POME under a controlled manner and predicting its growth location using computational fluid dynamics (CFD). Scale deposit samples were collected from two palm oil mills in Selangor and Johor in which both were from different stage of POME treatment. The characterization of the crystal found magnesium, phosphorous and oxygen as the major elements in the sample with 21.33, 24.85 and 46.22 wt%, respectively. The scale deposit was found to be a struvite mineral constituted more than 90% of the sample. The POME crystal was found to be soluble in strong acid and alkaline condition. Maximum solubility was recorded at pH of 3 and temperature of 40 ºC yielding averaged maximum solubility of 275.6 mg L^{-1} while averaged minimum solubility of 123.6 mg L^{-1} was recorded at pH 7 and temperature of 25 ºC. 67% of phosphate was removed from POME after being subjected to reactive crystallization. This study concludes that POME crystal has the potential to be regarded as a future value-added product from palm oil milling sector of the oil palm industry. Further research needs to be done to explore the feasible and economical way of producing POME crystal in which with its success, natural grow of POME crystal in POME treatment facility can simultaneously be mitigated.

خلاصة البحث

مشاكل القشرة في منشأة معالجة النفايات السائلة لزيت النخيل (POME) لها تاريخ طويل في التسبب بتأثير سلبي على كفاءة عملية معالجة زيت النخيل. وأدى تراكم القشرة في خطوط أنابيب معالجة زيت النخيل إلى تأثيرات تبعية لخفض قطر دائرة الأنبوب وبالتالي تؤثر على معدل التدفق الفعال ، مما يؤدي إلى انسداد الأنابيب وكذلك إلى تقليل وقت الاحتفاظ الهيدروليكي (HRT) لمحطة المعالجة. وأصبح حدوثه متكررا كثيرا في السنوات الأخيرة مع زيادة استخدام الخزان في عملية معالجة زيت النخيل. فتمت صياغة هذه الدراسة بهدف تحديد الخصائص الفيزيائية والكيميائية للبلورة الموجودة في مرافق معالجة زيت النخيل ، وفحص تأثير درجة الحموضة ودرجة الحرارة على ذوبانية البلورة النامية في نظام معالجة زيت النخيل ، واستكشاف ردود فعل طريقة التبلور في نمو البلورة من زيت النخيل في ظل طريقة خاضعة للرقابة والتنبؤ بموقع نموها باستخدام ديناميكا الموائع الحسابية (CFD) . تم جمع عينات القشرة المتشكلة من مطاحن زيت النخيل في سيلانجور وجوهور ، وكلاهما من مرحلة مختلفة في معالجة زيت النخيل. وعند توصيف البلورة وُجد المغنيزيوم والفوسفور والأكسجين كعناصر رئيسية في العينة مع 21.33 و 24.85 و 46.22 الوزن في المئة على التوالي. وتم العثور على أن معدن ستروفيت شكل أكثر من 90 %من عينة الرواسب الحرشفية. ثم وجد أن بلورة زيت النخيل قابلة للذوبان في حالتي الحمض والقلوية القويتين. وتم تسجيل الذوبانية القصوى عند الرقم الهيدروجيني 3 ودرجة الحرارة 40 درجة مئوية مما أسفر عن متوسط الذوبانية القصوى $275.6\ mg\ L^{-1}$. بينما تم تسجيل متوسط الحد الذوبانية الأدنى $123.6\ mg\ L^{-1}$ عند درجة الحموضة 7 ودرجة حرارة 25 درجة مئوية. وتمت إزالة 67 ٪ من الفوسفات من زيت النخيل بعد تعرضه للتبلور التفاعلي. واستنتجت هذه الدراسة إلى أن بلورة زيت النخيل لديها القدرة على اعتبارها منتجة مستقبلية ذات قيمة مضافة من قطاع المطاحن في صناعة زيت النخيل. ويجب إجراء المزيد من البحث لاستكشاف الطريقة الممكنة والاقتصادية لإنتاج بلورة زيت النخيل التي يمكن من خلالها تقليل النمو الطبيعي لبلورتة في مرفق معالجتة في وقت واحد.

APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Biotechnology Engineering)

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DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at IIUM or other institutions.

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LIST OF ABBREVIATIONS

€	Euro
μA	micro ampere
2D	two dimensional
3D	three dimensional
AN	ammoniacal nitrogen
BOD	biological oxygen demand
CFD	computational fluid dynamic
CHNS	carbon, hydrogen, nitrogen and sulphur
cm	centimetre
CRIM	Centre for Research and Instrumentation Management
CSTR	Continuously Stirred Tank Reactor
DOE	Department of Environment
e.g.	for example
EAF	electronic anti-fouling technology
EDS	energy dispersive spectroscopy
FBR	fluidized bed reactor
g	gram
GAC	granular activated carbon
HDPE	high density polyethylene
ICDD	The International Centre for Diffraction Data
IUPAC	The International Union of Pure and Applied Chemistry
kg m^{-3}	kilogram per cubic meter
kV	kilovolt
L	litre
M	molarity
m	meter
m s^{-1}	meter per second
MBR	membrane bioreactor

MFC	microbial fuel cells
mg L-1	milligram per litre
mm	millimetre
mol L^{-1}	mol per litre
MT	metric ton
MYR	Malaysian Ringgit
nuclei L^{-1} s^{-1}	nuclei per litre per second
^{o}	degree
O&G	oil & grease
^{o}C	degree Celsius
Pa	pascal
pH	potential of hydrogen
PN	nominal pressure
POME	palm oil mill effluent
POMTEC	Palm Oil Milling Technology Centre
rpm	rotation per minute
SEM	scanning electron microscope
SS	suspended solids
TAN	total ammonia nitrogen
tonne hr^{-1}	tonne per hour
UKM	Universiti Kebangsaan Malaysia ,
USD	United States Dollar
XRD	X-Ray Diffraction

LIST OF SYMBOLS

α	Volume shape factor.
ρ	Density of the grown crystal
t	Time for complete growth in second.
a_i	A vector that lies in different direction to span the lattice.
M_i	Initial crystal mass.
Mf	Final crystal mass.
n_i	Any integer.
N	The number of individual crystals.
R	A vector to describe the crystal array.

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

The Malaysian oil palm industry has been growing at a rate of 3-5% based on yearly oil palm planted area making up to a total of 5.85 million hectares by end of 2018. To cater for the production of fresh fruit bunch (FFB) from this huge amount of planted area, the number of mills has also increased proportionately to 455 palm oil mills nationwide (MPOB, 2018). In line with the growth, there were also a growing concern on environmental footprint of the industry. Government policies, initiatives by the industry player, establishment of environmental certification programs and research and developments programs have been actively taken place in the efforts to lift the environmental image of the industry.

In palm oil milling sector, FFB was processed through multiple separation method with the objective to extract maximum amount of oil from the FFB. In the process of extracting the oil, palm oil mill requires significant amount of water. For every tonne of crude palm oil (CPO) produced, 7.5 m^3 of water was consumed (Vijaya et al., 2014). Hence it also produces huge amount of wastewater specifically known as palm oil mill effluent (POME). For every tonne of FFB processed, about 0.65 to 1.0 m^3 of POME was generated (Lim and Biswas, 2019). Although POME is considered as non-toxic wastewater, it is acidic and contains an extremely high organic loading. It was once considered as the most expensive and difficult waste to manage (Madaki & Seng, 2013).

Many challenges were recorded in the history of POME management. In the early times, POME was treated partially using retention ponds and was send to the nearby plantation in trenches and furrows. This practice was called land application and the POME was discharged when the biological oxygen demand (BOD) - an effluent quality parameter used for regulation of POME discharge - was still around 5,000 mg L^{-1} (Wood et al., 1979). Apart from the benefit of having high nutrient being recycled to the plantation, this practice however triggered the issue of river pollution. This is due to sedimentation of solids in POME which later reduced the soil porosity of the trenches/furrow. Porosity of the soil is important for land application in order to maximize the absorption of POME. As a result, these furrows/trenches failed to absorb incoming POME thus causing overflow to nearby creek that will then propagate to bigger rivers.

When land application method seemed to be challenging, the industry moved towards adaptation of advanced polishing treatment technologies for treatment of POME. The objective was to comply to Department of Environment (DOE) regulation on the limit of POME discharge (Loh et al., 2013). This approach led to heavy usage of tanks, piping, pumps, agitator, diffuser and mixer in handling the POME. This has created another concern which is the gradual scale deposit formation on the surface of everything that is in contact with POME most importantly the piping system.

Scale formation pose a threat in terms of reducing the piping diameter up to 50% of its original diameter. This has affected the conveyance capacity of the piping system thus reducing the efficiency of POME treatment process. In worst-case scenario, it could also result in overflow of POME from a treatment pond due to incapability of its outlet pipe to discharge POME from the pond at a desired rate. In another case where the affected pipe is an outlet pipe of a closed tank, it will create backpressure which will then induce a backflow phenomenon. This will entirely upset the whole treatment process.

In recent years, application of biogas technology becomes increasingly popular. In 2017, a total of 85 biogas plant have been installed in palm oil mills nationwide (Loh et al., 2017). Biogas plant in palm oil mills, in general, replaced the open anaerobic treatment pond with closed anaerobic digester tanks. It has increased the usage of piping system, tanks, pumps and other effluent handling components. Certainly, it has higher possibility of scale deposit growth. Palm oil millers and biogas plant operators have not only seen the piping scale deposit, there have also been a rock scale grown suspended in anaerobic digester tank. This has interrupted the mechanism of COD removal that is essential in biogas production.

As for now, the industry depends on its own experience in dealing with scale deposit issue. There is currently very less literature on the topic of scale deposit from POME. However, a lot can be learned from other industries' experience in facing with almost similar problem. Swine farming, dairy, petrochemical as well as municipal waste treatment has had their share in exploring into this area of research; formation of certain form of scale from its wastewater. It was often being referred to as scaling or fouling phenomenon in these industries (Blandin et al., 2015, Steinhauer et al., 2015).

This study, however, prioritizes the identification of POME scale deposit by conducting a characterization study. This provides the audience with basic understanding of the scale deposit generated from POME treatment facility. Secondly, the solubility of the scale deposit was studied by having it exposed to the variable of pH and temperature. Then this study also explored the potential of growing the scale deposit in a controlled manner by adapting a reactive crystallization method. Finally, favourable location or area inside the piping system for the scale deposit to grow was investigated using computational fluid dynamic (CFD).

1.2 STATEMENT OF THE PROBLEM

The increased usage of effluent handling components; piping system, anaerobic digester tanks for biogas, pumps, diffuser and etc. in recent years have exposed palm oil millers to greater scale deposit problems. Clogged pipes, overflow of the treatment tanks, reduced flow rates, breakdown of valve, flowmeter and pump has always been the impact of scale deposits and definitely affecting the efficiency of a wastewater treatment system (Le Corre et al., 2013)

There is a substantial gap in scientifical information and data to support the palm oil mill in managing the problem of scale deposit. Current approach has always been learning through experience. Firstly, palm oil millers have difficulty in identifying the location affected by the scale deposit as it is an in-pipe disturbance. Once identified the affected component was assessed for its reduction in performance. Then, the follow up action was either to add relevant mechanical devices (for example additional pump) based on the component's deterioration degree in assisting the affected component to continue working or to totally replace the component. In some cases, hacking tools were used to break the scale deposit. However certain areas that were not easily reachable for example diffuser, valve and pump will normally be replaced.

There was some technological approach to remove scale deposit from other industries for example by using acid cleaning and ultrasonic cleaning (Wang et al., 2016; Phakam et al., 2018). In the case of acid cleaning, some of the scales can be removed however the pipes were physically affected and their structural strength was jeopardized. Ultrasonic cleaning was experimented for the removal of fouling in landslide mitigation draining pipes (Mandrone, 2016). The technology was reported as working well in removing the fouling however it can be quite costly for POME treatment considering the deposition of scale in POME treatment system is much faster and more aggressive. This could possibly lead to the increase of maintenance cost and downtime of the treatment system. The operation of a particular palm oil mill might also be affected and ultimately makes management of the POME polishing plant more difficult and challenging.

Struvite precipitation was considered as a rare subject when it comes to POME wastewater. For many years, only few studies were found to be exploring struvite precipitation from POME (Tadza et al., 2015; Salsabili et al., 2015). On the other hand, this subject matter has already gained much popularity as one of the methods to recover nutrients from other wastewater treatment facility for example swine, sewerage as well as cattle manure (Jordaan et al., 2010; Zeng et al., 2018; Rico 2011). It was done especially for the extraction of phosphorous, a depleting natural resource (Bing Li et al., 2019). By taking the definition of mass balance, therefore, struvite precipitation could potentially mitigate the scale deposit formation in POME treatment system as it has the ability to reduce the concentration of phosphorous in the POME itself. This will be one of the areas to focus on in this study.

1.3 PURPOSE OF THE STUDY

This research was intended to investigate the formation of scale deposits generated daily from a POME treatment system; its physicochemical characteristics, mechanism of its formation and current developments for its mitigation. The study was carried out with the aim to help the industry especially the palm oil millers to understand clearly the scale deposit that has been a recurring issue in palm oil milling activity. The study also sought to identify and discuss potential methods based on existing technologies in order to solve the problem that in return is expected to reduce the current cost and time incurred in dealing with the aggressive formation of the scale deposit.

1.4 RESEARCH OBJECTIVES

Three objectives were outlined for this study which are:

i. To determine the physicochemical characteristics of the scale deposit formed in the POME treatment system pipelines.
ii. To examine the effect of pH and temperature towards the structural integrity of the scale deposit as well as establishing POME scale deposit solubility curve.
iii. To explore struvite precipitation method of reactive crystallization for mitigation of the scale deposit formation and CFD simulation in predicting growth location.

1.5 RESEARCH SCOPE

This study covers the characterization of the POME scale deposit; establishment of its solubility curve against pH and temperature; adaptation of struvite precipitation method in mitigation of scale deposit formation and prediction of scale deposit growth location. In conducting the solubility test, this study limits the temperature range between 25 to 40^{o}C and pH value between 3 to 11 as to the general condition in a conventional POME treatment facility. The researcher also limits the struvite precipitation method by adapting only to the reactive crystallization method taking into consideration of its high rate of adaptability in other wastewater industries. In predicting the location favorable for scale deposition in a POME piping system, computational fluid dynamic (CFD) tool was used. Assumptions such as constant temperature and pH value across the piping setup, as well as a steady POME flow covering the whole pipe diameter was made.

1.6 DISSERTATION ORGANIZATION

The thesis is organized into five chapters, where chapter one is an introduction/background of research work, while chapter two presents review of related literature. The material and methodology of the research are covered in chapter three, giving a detailed description of materials, and the experimental procedures used in the study. The findings of the research work are thoroughly discussed in chapter four. Finally, chapter five concludes the findings together with some recommendations on how to improve further research.

CHAPTER TWO

LITERATURE REVIEW

2.1 PALM OIL MILL EFFLUENT

Since the main subject of this study is the scale deposits generated from POME, it is of high importance to understand the said effluent that is generated from a typical palm oil mill in the first place. POME in its earliest form after discharged from milling activities is a brown thick colloidal liquid waste that is usually discharged at high temperature of around 80 - 90^{o}C and in an acidic condition (Kaman et. al., 2017). In 2016, an approximate 58 million m^3 of POME were generated from palm oil mills in Malaysia. If it is discharged in its original form untreated to the water streams, it will deprive the aquatic living organism from oxygen. This is due to the fact that it has a very high BOD and COD of around 20 000 to 30 000 mg L^{-1} and 80 000 to 90 000 mg L^{-1} (Hadi et al., 2019; Jalani et al., 2016). Apart from that discharging of POME can also cause accumulation of solids that actually originates from the milling process. Total solids in POME can be measured up to 4 to 5% of the POME volume (Zafisah et al., 2018). Therefore, treatment of POME is paramount to maintain environmental sustainability of the palm oil milling process.

Treatment of POME is done by using a ponding system. It is a series of retention ponds with stages of treatment process that mainly includes pre-treatment, anaerobic digestion and aerobic digestion (Hadi et al., 2019). Almost all of palm oil mills in Malaysia treat POME by using this system due to its low operation cost (Choong et al., 2018). In Malaysia, POME discharge is regulated by the Department of Environment (DOE) under the 1977 Environmental Quality (Prescribed Premises)(Crude Palm Oil)

Regulations where the main parameters being monitored is biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), ammoniacal nitrogen (AN), oil & grease (O&G), pH and temperature (DOE, 2014) (Table 1). Increasing trend in the attention given from global society towards environmental well-being of the planet has led to the demands for a cleaner production in many industries. Palm oil industry is one of them and the DOE has since begun to urge palm oil millers to be more sustainable and environmentally friendly followed with enforcement of stricter regulations (Zainal et al., 2017). This has in return creates opportunity for the treatment of POME to evolve. Many palm oil millers have chosen to further treat the POME post aerobic process by adapting a polishing plant technology used by some other industries. Apart from that, more and more palm oil millers have now also involved in the development of biogas capturing facility utilizing POME. This is to take advantage of the excessive energy produced through generation of methane from anaerobic digestion in a POME treatment system at the same time reducing the load in the POME treatment stream.

Table 2.1 Palm Oil Mill Effluent Final Discharge Standards Set by the Department of Environment (DOE) (last updated on January 2015)

Parameter	**Limit for discharge (1984 & thereafter)**	**Standard A**	**Standard B**
Temperature (°C)	45	40	40
pH	5.0–9.0	6.0-9.0	5.5-9.0
BOD (mg L^{-1})	100	20	50
COD (mg L^{-1})	-	50	100
Suspended solids (mg L^{-1})	400	50	100
Oil &grease (mg L^{-1})	50	1/ND	10