RECYCLED PAPER MILL SLUDGE WITH SULPHUR OXIDIZING BACTERIA AS BIOFILTER TO TREAT MALODOUR FROM PALM OIL MILL EFFLUENT

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by

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NOMENCLATURE

H_2S	Hydrogen Sulphide
NH_3	Ammonia
CH_4	Methane gas
CO_2	Carbon Dioxide
S^0	Sulphur
SO_4^{2-}	Sulphate
N	Nitrogen
CH_3COOH	Acetic Acid
H_2O	Water
NH_3-N	Ammoniacal Nitrogen
Pa	Pascal

LIST OF ABBREVIATIONS

RPMS	Recycled Paper Mill Sludge
SOB	Sulphur Oxidizing Bacteria
POME	Palm Oil Mill Effluent
SEM	Scanning Electron Microscope
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
VSS	Volatile Suspended Solid
TS	Total Solid
SS	Suspended Solid
CER	Certified Emission Reduction
OUE	Odour Unit European
VOC	Volatile Organic Compound
EBRT	Empty Bed Residence Time
TDR	Time Domain Reflectometry

ENAPAN DARIPADA KERTAS KITAR SEMULA DENGAN BAKTERIA PENGOKSIDAAN SULFUR SEBAGAI PENAPIS BIOLOGI UNTUK RAWATAN BAU DARI SISA KILANG KELAPA SAWIT

ABSTRAK

Antara bahan cemar yang bermasalah dalam biogas adalah hidrogen sulfida (H_2S) dan amonia (NH_3), yang dipancarkan dari proses industri yang menyebabkan gangguan bau. Penyiasatan menggunakan enapcemar kertas kitar semula (RPMS) sebagai potensi media dalam proses biofiltrasi dilakukan untuk mengkaji ciri dan menentukan kesesuaiannya sebagai media baru dengan pengaruhnya terhadap kecekapan penyingkiran H_2S, NH_3 dan kekuatan bau dari efluen kilang kelapa sawit (POME). Banyak kajian membuktikan bahawa bakteria pengoksidaan sulfur (SOB) dapat membantu meningkatkan penyingkiran kepekatan H_2S. Oleh itu, dalam kajian ini bakteria *Paracoccus Solventivorans ATCC 700252* digunakan sebagai SOB melalui proses imobilisasi. Berdasarkan keputusan akhir, media RPMS mengandungi SOB menunjukkan penurunan H_2S dengan penyingkiran lebih tinggi sebanyak 64.02% dengan kandungan sulfat 21mg/l berbanding RPMS mentah (46.84%). Walau bagaimanapun, kecekapan penyingkiran NH_3 pada RPMS mentah lebih tinggi (49.64%) daripada media RPMS mengandungi SOB (32.75%). Untuk kekuatan bau, kecekapan penyingkiran lebih tinggi berlaku pada media RPMS mengandungi SOB (72.15%) daripada RPMS mentah (66.89%). SOB mempunyai kemampuan untuk menyerap bau ‘telur busuk’ dan berubah menjadi sulfur yang tidak lagi berbahaya. Dalam hal ini, penggunaan RPMS yang dicampur dengan *Paracoccus solventivorans ATCC 700252* (SOB) dapat mewujudkan industri baru untuk rawatan H_2S dan penghapusan bau, sehingga dapat melindungi persekitaran dari pencemaran bau.

RECYCLED PAPER MILL SLUDGE WITH SULPHUR OXIDIZING BACTERIA AS BIOFILTER TO TREAT MALODOUR FROM PALM OIL MILL EFFLUENT

ABSTRACT

One of the most problematic contaminants in biogas is the presence of hydrogen sulphide (H_2S) and ammonia (NH_3), which are emitted from industrial processes and cause odour nuisance to the surrounding community. An investigation using recycled paper mill sludge (RPMS) as a new potential media in biofiltration process was carried out to study the characteristics and determine its suitability as a new media with its effect on the removal efficiency of H_2S, NH_3 and odour strength from palm oil mill effluent (POME). Numerous studies have proved that sulphur oxidizing bacteria (SOB) can help to enhance the removal of H_2S concentration. Hence, in this study the bacteria of *Paracoccus Solventivorans ATCC 700252* were used as SOB based on RPMS media by immobilization process. Based on final result, RPMS with immobilized SOB demonstrated reduction of H_2S with higher removal efficiency of 64.02% with sulphate concentration is 21 mg/l compared to raw RPMS (46.84%). However, the removal efficiency of NH_3 on raw RPMS is higher (49.64%) than RPMS with immobilized SOB (32.75%). For odour strength, the removal efficiency is higher occurs at RPMS media contained immobilized SOB (72.15%) than raw RPMS (66.89%) during 28 days. SOB has the ability to absorb the odorous 'rotten egg' smell and changes into elemental sulphur that is no longer hazardous. In this regard, the utilization of RPMS mixed with *Paracoccus solventivorans ATCC 700252* (SOB) can create a new industry for application in H_2S and odour removal, thus can protect the environment from odour pollution.

CHAPTER 1

INTRODUCTION

1.1 Background

Recycled paper mill sludge (RPMS) is a solid organic residue that is recovered from the wastewater treatment process by activities of the pulping and papermaking process. Usually, Malaysia generates about 50 tons of RPMS every day from different mills. The sludge produced by all paper industries accumulates in large quantities each year, which can have an impact on the country's environmental problems. However, the use of paper is unavoidable because paper is at the centre of everyone's life, whether reading a newspaper to start the day, using notebooks to teach kids in school or at universities, paperwork in offices, and more recently, serving plates and packing bags as paper is much more recyclable than plastic bags. Nonetheless, further research should be done to explore the possible use of RPMS as a value-added product, a strategy that can partially solve the problem of paper sludge disposal (Rosazlin et al., 2011).

Recycled paper mill sludge contains high carbon and a proportion of cellulose fibres, which can make it an excellent additive for bio composites and adsorbent-absorbent materials. However, the potential of RPMS as an odour biofiltration medium has yet to be investigated. So, this study was conducted with the purpose of determining the characteristics of RPMS and determining its suitability as a medium for the biological treatment of malodour.

Biogases are usually created from anaerobic sewerage sludge digestion, bio-waste from the agro-industry such as palm oil mill effluent (POME), and manure from livestock. The components that are contained in biogas include methane (CH4),

carbon dioxide (CO_2), dinitrogen (N_2), water (H_2O), oxygen (O_2), hydrogen sulphide (H_2S), ammonia (NH_3), hydrocarbon contents and siloxanes (Muñoz et al., 2015). Aside from that, a high concentration of H_2S in biogas will cause concrete and steel corrosion, endanger the use of cogeneration systems, become toxic to humans, and cause odour pollution. In addition, sulphide content in the liquid stage will also induce corrosion in the water transport system and accumulation of metal sulphides (Promnuan and Sompong, 2017). As to the effect of NH_3, due to high exposure concentration in air can cause immediate burning of the eyes, nose, throat and respiratory tract that can result in blindness and lung damage (Loh et al., 2019).

Conventionally, different physical (adsorption, oxidation, and dilution), chemical (absorption, neutralization, and combustion) and biological (activated sludge and biofilter) methods were used to extract H_2S from waste gas (Lin et al., 2013). However, physical and chemical processes are further constrained, with large maintenance costs and minor pollutant production whenever the H_2S production is large (Panza and Belgiorno, 2010). The biological approaches, by comparison, are value-effective relative to the physical and chemical processes for extracting H_2S in biogases (Zhang et al., 2008). Furthermore, this technology is a promising alternative because it is energy-savings, eco-friendly and has low operating costs. However, biofiltration demonstrated the ability to remove H_2S and NH_3 from odorous emissions at wastewater treatment facilities (Kleinheinz and Langolf, 2016; and Rabbani et al., 2016), industry (Shareefdeen, 2015), swine farm (Kafle et al., 2015), and waste facility (Hou et al., 2016) via the natural microbial action of bacteria. Consequently, the biofiltration efficiency cycle using immobilized microorganism technology is one of the possible effective methods for enhancing biogas treatment performance (Lebrero et al., 2013).

Biological removal of sulphide in this case is based on the sulphur oxidizing bacteria (SOB) activities. The SOB is able to oxidize sulphur from H_2S to sulphate ion or elemental sulphur and use that as an energy source. In essence, the majority of known sulphur oxidizing bacteria (SOB) such as *Thiobacillus, Thiothrix, Thiomicrospira, Achromatium, Desulfuromonas* and *Paracoccus,* which occur in soil and marine isolated heterotrophic bacteria. *Paracoccus* strains can therefore oxidize and reduce compounds of sulphur such as thiosulfate, thiocyanate, carbon disulphide, carbonyl sulphide and elemental sulphur to generate energy for autotrophic growth. Thus, *Paracoccus solventivorans ATCC 700252* was chosen as the new SOB as it is one of the identified bacteria found in the palm oil itself (Tajarudin et al., 2020). These are also ideal for the high sulphide oxidation rate with moderate nutritional requirements and extremely high sulphide and oxygen affinities. These properties allow them to cope successfully with chemical sulphide oxidation in both the natural environment and bioreactors with a restricted oxygen supply.

Therefore, the objective of this study is to investigate the use of *Paracoccus solventivorans ATCC 700252* isolated from palm oil mill effluent pond, in terms of its growth requirement and immobilization behaviour onto a RPMS media. The odour removal mechanism between RPMS media as a biofilter medium and immobilized SOB is investigated by examining optimal parameters for the immobilization process and the corresponding odour reduction in terms of removal H_2S, NH_3 and odour strength. The findings from this study would form the fundamental understanding of the microbial behaviour of this locally resourced RPMS media and immobilized SOB. Such knowledge is important in designing a green technology for odour treatment that would be sustainable for operation in Malaysia.

1.2 Problem Statement

Palm Oil Mill Effluent (POME) discharge from the factory produces nuisance odour due to the presence of an odorous gas known as methane (CH_4), hydrogen sulphide (H_2S), ammonia (NH_3), and other elemental sulphur (Azmi and Yunos, 2014). H_2S gas, in particular, has a rotten egg odour, whereas NH_3 gas is an irritating gas with a pungent and suffocating odour. Furthermore, H_2S is a corrosive gas, a highly flammable explosive gas that may threaten life if it is handled poorly. In low concentration, continuous inhalation of H_2S would lead to nausea, headache and irritation of the skin, eyes and respiratory tract, while in high concentration, it is fatal. It also corrodes the surrounding structure and pipeline, as well as causing leakage or infiltration in the soil. Also, there are numerous complaints and reports issued to the authorities regarding the odour nuisance (Nicell, 2009; Brancher et al., 2017). Thus, concentrations of H_2S and NH_3 need to be reduced for abatement of odour and health control.

RPMS, a solid organic residue, contain high carbon and a proportion of cellulose fibers, which can make it an excellent additive for bio composites and adsorbent-absorbent materials. However, its potential as an odour biofiltration medium has not been tested. However, under natural media, compost, and wood chip mixture with a ratio of 30 to 70 by weight is recommended as one of the best choices. But, under synthesized support media, RPMS has not been evaluated as one of the potentials for odour biofiltration media. Because the use of RPMS as a medium bed in biofilter technology has yet to be investigated, we will have an advantage in determining its suitability as a possible medium for the biological treatment of malodour.

In addition, not much research has utilized the immobilization of specific microorganism in the RPMS media for their study to treat biogas in POME. As such, only a few species of microorganisms are considered capable of reducing the accumulation of H_2S and NH_3. However, the use of SOB was shown to be capable of reducing H_2S concentration by oxidizing H_2S to harmless products like elemental sulphur (S^0) and sulphate (SO_4^{2}) in the presence of O_2 or nitrate (NO_3) (Valdebenito-Rolack et al., 2011). But there are few SOB species in Malaysia in particular and not all are tested in the research on odour reduction. Even in the POME itself, there is SOB that can be found such as *Paracoccus Solventivorans ATCC 700252*. However, this species has received little attention in the field of odour abatement research, particularly when it comes to the use of RPMS media in the biofiltration process. Thus, its effectiveness is not well known.

Moreover, some work was carried out to refine the operating parameters or to check the performance of filter materials RPMS and functional bacterial strains, but there is limited information about the microbial community due to biofilter operations themselves. Furthermore, the optimal condition for the immobilization process via RPMS media as a carrier onto immobilized SOB is unknown. Unfortunately, the operating parameters including contact time, agitation speed and various concentrations of polyvinyl alcohol (PVA) used were identified as a key factor that influenced the performance of the immobilization process and stability of the immobilized bacteria.

1.3 Objective

The objectives of the study are to:

i. To determine the characteristics of recycled paper mill sludge (RPMS) as a new potential media for biofilter treatment of malodour.

ii. To determine the behavior of the new sulfur oxidizing bacteria from palm oil mill effluent and bacteria growth requirement.

iii. To investigate the correlation of biomass formation between recycled paper mill sludge as a potential media and new immobilized sulfur oxidizing bacteria against biofilter environmental condition.

iv. To determine removal efficiency for hydrogen sulphide (H_2S), ammonia (NH_3) and odour strength from biofilter based on RPMS media with new sulfur oxidizing bacteria from palm oil mill effluent.

1.4 Scope of Work

This study generally focused on the ability of RPMS as a biofilter media to reduce the effluent of odour from palm oil factories with the using of species bacteria *Paracoccus Solventivorans ATCC 700252 (Paracoccus sp.).* The RPMS were obtained from Nibong Tebal Paper Mill Sdn Bhd, Nibong Tebal, Pulau Pinang and will go through some physical characteristic tests which is water holding capacity, moisture content, bulk density, and porosity in order to defines its suitability as a new medium for biological treatment in terms of elimination of H_2S, NH_3 and odour strength.

The POME was purchased from United Palm Oil Industries Sdn Bhd, Sungai Kechil, Nibong Tebal, Pulau Pinang and stored in a 100L tank. It will be kept in an anaerobic condition for 36 to 48 hours to obtain the sufficient amount of the target

gas which is H_2S and NH_3. Furthermore, the total duration of this study is 30 days and palm oil mill effluent (POME) sample was collected two times per month. The sample was taken from the fourth pond, which is the anaerobic pond 2 at the palm oil processing factory. In addition, for the original cultured Paracoccus sp. used in this research was obtained from the Microbiology Lab at School of Industrial Technology, Main Campus, Universiti Sains Malaysia, Pulau Pinang. Then, a laboratory scale biofilter was developed into 2 operational condition of biofilter based on RPMS media- which is the pure medium bed material (as a control) using paper mill only and the other one is using RPMS immobilized with *Paracoccus sp.* While, for the dimension of column used is 480mm height with 10mm diameter. Then, odour sample were collected before and after it passes through the medium bed in the biofilter and run over a month. For this research, the depth of media is fixed with 150mm and Empty Bed Residence Time is 45s with the flowrate about 2.5 L/min.

The treatability studies were done on environmental laboratory of Civil Engineering in Engineering Campus, Universiti Sains Malaysia, Pulau Pinang and simulate the operational condition for immobilization process at particular time by finding the optimum parameter such as contact time, agitation speed and various concentration of PVA. Lastly, the removal efficiency for odour strength and concentration of H_2S and NH_3 were determined by using Scentroid Olfactometer SS400 and Scentroid TR8 Odortracker respectively. At the same time, the pressure drop and bacterial count includes SEM test were also tested for monitor the performance of biofilter during this period.

1.5 Outline of Dissertation

Such dissertations consist of five chapters which are arranged as follows: Chapter 1 (Introduction) briefly describes the context of the research, the description of the problem, the study purpose, and the scope of the works. Chapter 2 (Literature Review) discusses the information related to studies including the characteristics of recycled paper mill sludge, the palm oil mill effluent, the treatment for odour abatement, the criteria for immobilization process on new sulphur oxidizing bacteria and the mechanisms for biofilter. All that information is collected from reviews of literature. Chapter 3 (Methodology) carried out the techniques, the materials and the processes used. Chapter 4 (Results and Discussion) describes the results and discussions obtained from the laboratory tests including the graph, tables and chart. As regards Chapter 5, this article is concluded and recommendations for further studies are proposed.

CHAPTER 2

LITERATURE REVIEW

2.1 Recycled Paper Mill Sludge (RPMS)

Recycled paper mill sludge (RPMS) is a by-product composed from residues of pulp and ash formed from processes of pulping and paper making. The composition of PMS is determined by the processes of fabrication and effluent treatment applied at individual mills (Battaglia et al., 2003; Kang et al., 2010). Specifically, paper mill sludge contains water, small particles of cellulose, organic compounds, inorganic salts, and mineral fillers which can cause serious environmental pollution (Asquini et al., 2008).

The paper mill sludge produced by the Malaysian paper industry was wet, sticky and had a heavy odour. Nearly all mill sludge collected from the different mills has similar characteristics, except for the contents of nutrients and heavy metals which differed from one another (Goel and Kalamdhad, 2017). Table 2.1 shows the physical and chemical characteristics of PMS collected at the site of industry located at Wilayah Persekutuan. However, paper processing generates a large amount of waste all over the world. This is unavoidable because paper is at the centre of everyone's life, whether reading a newspaper to start the day, use notebooks to teach kids in school or at universities, paperwork in offices, and more recently, serving plates and packing bags as paper is much more recyclable than plastic bags. Therefore, there is growing environmental problem due to paper waste, more restrictive paper sludge disposal was implemented as the government faced serious problem with the large quantities of PMS (Bajpai, 2015). Also, other researchers

have been looking new approaches for managing into recycled paper mill sludge (RPMS).

Table 2.1 Physical and chemical properties at the industrial site of paper mill sludge (Abdullah et al., 2015)

Parameters	Compositions
Moisture content (%)	65.08
pH	7.09
Cellulose content (%)	29.13
Organic matter (%)	44.04
Carbon (%)	25.61
Nitrogen (%)	1.45
Phosphorous (%)	0.18
Magnesium (%)	0.61

2.1.1 Utilization of RPMS

Sludge from paper mills has already been found to be useful in the cement, brick, building, and road construction industries, as well as the processing of ethanol, lactic acid, animal feed, composting, vermicomposting, and the paper and board industries (fiberboard, soft board, and millboard) (Ince et al., 2011).

Other researchers have conducted several studies on the utilization of RPMS to become value-added product. According to Goel and Kalamdhad (2017), addition of RPMS with fired bricks leads towards sustainable and economical construction by enhance the mechanical and durability properties of bricks itself. Results obtained with 10% mix of PMS was found suitable for support to the brick industry at firing temperature 900ºC which leading to sustainable use of resources. For the first time, the behaviour of modulus of elasticity as a function of this organic waste content was investigated.

A study by Mari et al., (2009) found that paper mill sludge can serve as asphalt fiber additive at 0.3% to 0.5% additions which achieve the optimum asphalt content within 5% - 6%. To explain, RPMS can provide the highest stability value at any amount of addition of the sludge. Other than that, after extraction these fibers prove that they can endure the rough processing including the high asphalt mixing temperature. It showed that RPMS could be possible fiber additives for road applications and other high value materials.

Paper mill sludge also was studied to evaluate its use as a supplementary cement material in the manufacture of mortars and concrete (Fava et al., 2011). Based on data obtained, it was determined that using PMS to replace up to 10% of portland cement has a positive effect on mortar mechanical efficiency. Otherwise, it required higher amounts of water because of its high fineness and thus high-water absorption. It was concluded that the use of PMS should not be above 10%, unless the mortar mixtures are properly proportioned, by weight of the substituted cement. This shows potential of PMS for application in cement industry based on their characteristics.

Traditional treatment methods also have implemented for PMS include landfill, composting, and use this organic material for ceramics making (Charest and Beauchamp, 2002). These methods are still limited for applications of small scale. Given the high organic carbon content in PMS, some scholars such as Khalili et al. (2002) and Bagreev and Bandosz (2004) paid attention to the manufacture of PMS into carbon adsorbent.

Based on following reasons, organic material of recycled paper mill sludge may be chosen as a new possible carrier for biofilter treatment. Due to its