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FOCUS AND SCOPE

Jurnal Riset Teknologi Pencegahan Pencemaran Industri (Research Journal of Industrial Pollution Prevention Technology) seeks to promote and disseminate original research as well as review, related to following area:

Environmental Technology : within the area of air pollution technology, wastewater treatment technology, and management of solid waste and harzardous toxic substance.

Process Technology and Simulation : technology and/or simulation in industrial production process aims to minimize waste and environmental degradation.

Design Engineering : device engineering to improve process efficiency, measurement accuracy and to detect pollutant.

Material Fabrication : environmental friendly material fabrication as subtitution material for industry.

Energy Conservation : process engineering/ technology/ conservation of resources for energy generation.

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Center of Industrial Pollution Prevention Technology.
Jl. Ki Mangunsarkoro No. 6 Semarang, Jawa Tengah, 50136 Indonesia.
Telp. +62 24 8316315
Fax. +62 24 8414811
e-mail: jurnalrisettppi@kemenperin.go.id
Jam kerja : Senin – Jum'at
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PREFACE

Alhamdulillah Robbie 'Alamin, Journal of Industrial Pollution Prevention Technology (JRTPPI) again will publish scientific articles, especially in the field of environmental technology for volume 11 no 1. Our high appreciation is directed to the authors, editorial board, structural officials of BBTPPI who have actively participated so as to maintain consistency of quality and punctuality of our periodic publications.

This edition of the issue is fouth series published that in full-text English. This continous policy is an attempt of the editorial board to improve the author's performance in delivering the results of their researches. Articles in full-text English are more likely to be read by broader audience so that it will increase the number of citations. This policy is also applied in order to actualize our hope of being a globally indexed international journal.

The articles contained in this edition consist of air monitoring, wastewater treatment and a review, namely: DOAS sensor, biological and advance wastewater treatment technology. The review article that has been explored an ozonation method as advance technology in wastewater treatment. The five manuscripts accepted and published in this edition are from researcher in Ministry of Industry. The duration of submission, review, and editing of the manuscripts ranged from 3-5 months.

Hopefully, these scientific articles may be new source of knowledge and experience for readers from academic, researcher, industry, and society at large. We realize that nothing is perfect until the improvement of all parties involved is continuously done.

Semarang, May 2020

Chief Editor

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Potential of Catalytic Ozonation in Treatment of Industrial Textile Wastewater in Indonesia

Jurnal Riset Teknologi Pencegahan Pencemaran Industri, May 2020, Vol. 11, No. 1, p. 1-11, 2 tab, 41 ref

Industrial textile wastewater is one of the most heavily polluting in Indonesia. Wastewater from industrial textile contains organic contamination that is very difficult to remove. The pollutants are remaining even though it has been treated by the conventional wastewater treatment and bio refractory in nature. Toxic organic compounds discharged from the textile industry, such as colored dyes, heavy metals, and various chemicals, will hurt the environment. These contaminants have been proven toxic to the biotic environment, such as mutagenic, which can increase the incidence of cancer and endocrine disruptor effects. Removal of contaminants from industrial textile wastewater is currently one of the most critical subjects in water pollution prevention. Applications of catalytic ozonation treatment initially, powder catalysts have been employed, and later, the use of activated carbon materials in more advanced catalyst structures reported, and more sophisticated types of catalyst equipment namely carbon nanotube, and nanoparticles. In-depth research on the combination of ozonation and catalytic research of industrial textile wastewater treatment has the potential to become a well-developed approach to treatment industrial textile wastewater. This review provides process principles and characteristics, including the use of various catalysts, variations in reactor design, and application catalytic ozonation in synthetic textile wastewater and real industrial textile wastewater outlined and discussed. Include future research directions of the treatment of industrial textile wastewater in to clean water with drink quality. This first time published review of the potential catalytic ozonation for the textile industry's wastewater treatment in Indonesia.

(Author)

Keywords: Textile wastewater, Catalytic treatment, Ozonation, Solid catalyst

Hanny Vistanty[1*], Rizal Awaludin Malik[1], and Aris Mukimin[1] ([1]Center of Industrial Pollution Prevention Technology, Jl. Kimangunsarkoro no. 6, Semarang, Indonesia)

Performance of a Full-Scale Anaerobic Digestion on Bakery Wastewater Treatment : Effect of Modified Distribution System

Jurnal Riset Teknologi Pencegahan Pencemaran Industri, May 2020, Vol. 11, No. 1, p. 12-18, 4 ill, 3 tab, 16 ref

The effectiveness of a full-scale anaerobic digestion pretreatment was evaluated and the effect of wastewater distribution system was determined on the performance of bakery wastewater (BW) treatment. The BW was fed to 3 series of anaerobic compartments as the main degradation process. The distribution system of first compartment was modified and circulated to enhance contact and efficiency. While the effluent of last compartment was partly returned to the first compartment as an external circulation and the other part was further processed in activated sludge under aerobic conditions. The overall system was able to remove chemical oxygen demand (COD), total suspended solids (TSS), and biochemical oxygen demand (BOD) up to 97.7%, 99.7%, and 99.6%, respectively, at maximum organic loading rate of 6.3 kg COD/m^{3}day and internal and external circulation rate of 10 L/min and 15 L/min, respectively. High removal of pollutants indicated that modified distribution of circulation is advantageous to the BW treatment.

(Author)

Keywords: Internal Circulated, Anaerobic Digestion, Bakery Wastewater

Rustiana Yuliasni[1], Nur Zen[1], Nanik Indah Setianingsih[1] ([1]The Centre of Indutrial Pollution Prevention Technology, Semarang, Central Java)

Evaluating the Performance of Three Chambers Microbial Salinity Cell (MSC) Subjected to Different Substrate Concentrations to Accomplish Simultaneous Organic and Salt Removal in The Wastewater

Jurnal Riset Teknologi Pencegahan Pencemaran Industri, May 2020, Vol. 11, No. 1, p. 19-26 7 tab, 17 ref

This study aimed to identify the effect of substrate concentration on the performance of a three chambers Microbial Salinity Cell (a three chambers MSC). In this study, a three chambers MSC were made from plexiglass with total volume of 200 ml. An aluminium wrapped with platinum on vulcan carbon cloth was used as electrodes, with each working area of 63 cm^2. The result showed that a three chambers MSC was able to generate electricity and at the same time removed the salinity. The degree of electricity generation and salinity removal was influenced by initial substrate concentration in the anode chamber. The higher substrate concentration, the better performance of the MSC. The best performance of the MSC was achieved when the initial substrate was 2034 mg/L as COD, lead to a maximum voltage of 0.44 V, and maximum current density of 0.29 mA/m^2. With %CE was 5.4%. The maximum conductivity upsurge in salinity chamber was from 11.2 µS/cm to 1027 µS/cm (corresponding to salinity of 0.57% ppt).

(Author)

Keywords: Microbial Salinity Cell, three chambers MSC, Microbial Fuel Cell, electricity generation, salinity removal

Novarina Irnaning Handayani[1], Rustiana Yuliasni[1], Nanik Indah Setianingsih[1], Agung Budiarto[1]
([1]The Centre of Indutrial Pollution Prevention Technology, Semarang, Central Java)

Full Scale Application of Integrated Upflow Anaerobic Filter (UAF) - Constructed Wetland (CWs) in Small Scale Batik Industry Wastewater Treatment

Jurnal Riset Teknologi Pencegahan Pencemaran Industri, May 2020, Vol. 11, No. 1, p. 27-35, 7 ill, 1tab, 23 ref

This research was aimed to evaluate the implementation of integrated Upflow Anaerobic Filter (UAF)-Constructed Wetlands (CWs) in real condition of wastewater treatment plant in batik small scale industry. The full-scale reactor consisted of equalization chamber with Hydraulic Retention Time (HRT) of 2 days; Upflow Anaerobic Filter (UAF) with HRT of 6 days, and Horizontal Subsurface Constructed Wetlands (HSSCWs) with HRT of 1.5 days. The UAF - CWs integrated technology was used to treat batik wastewater with Chemical Oxygen Demand (COD) inlet of 1339 – 2034 mg/L and pH of 9.0 – 9.4. This study showed that single UAF technology alone was able to reduced COD 56 – 78%, while the integration UAF–CWs technology improved the performance to 85% and reduced the pH into 7.5 – 7.8

(Author)

Keywords: Batik wastewater, Upflow anaerobic filter, Constructed wetlands, Integrated technology UAF- CWs, Azo dyes

Januar Arif Fatkhurrahman[1,2], Ikha Rasti Julia Sari[2], Yose Andriani[2], Moh Syarif Romadhon[2,3], Nur Zen[2], Adi Prasetio[2], Ali Murtopo Simbolon[2] ([1]Environmental Engineering, Institut Teknologi Bandung, [2]The Centre of Indutrial Pollution Prevention Technology, Semarang, [3] Atmospheric, Oceanic and Planetary Physics Department, University of Oxford, [4]Departement of Environmental Engineering, Diponegoro University)

DOAS Calibration Technique for SO_2 Emission Measurement Based on H_2SO_4 and Na_2SO_3 Reaction

Jurnal Riset Teknologi Pencegahan Pencemaran Industri, May 2020, Vol. 11, No. 1, p. 36-45, 5 ill, 1 tab, 28 ref

The coal used as a primary fuel in an Indonesian power plant produces sulfur dioxide emission from its burning process. Several testing and monitoring methods developed, from laboratory analysis, CEMs based instrument, and absorption spectroscopy method developed for this purpose. Differential Optical Absorption Spectroscopy (DOAS) method based on Lambert-Beer law used as emission quantification. DOAS instrumentation developed in this research to measure sulfur dioxide as one of the emission parameters. Sulfur dioxide generated from the reaction between the sulfuric acid and dilute sodium sulfite. CCD spectrometer used to measure sulfur dioxide spectrum intensity at 260 to 350 nm absorption cross-section. There is a high correlation between sulfur dioxide gas produced by that reaction to spectrum intensity, with coefficient determination (r^2) 0.9783, 0.9822, 0.9866, 0.9928 or coefficient correlation (r) 0.989, 0.991, 0.993, and 0.996 from lowest range concentration to highest range concentration. Precision analysis from gas calibration standard using Horwitz ratio indicates instrument setup precise enough with 0.504 Horwitz ratio, according to its acceptable range. The suspended particulate matter may interfere with UV penetration into CCD detector in emission simulation test using gasoline generator exhaust that causes 2.5 times deviation error between typical 800 ppm concentrated sulfur dioxide from chemical reaction and gasoline generator exhaust

(Author)

Keywords: DOAS, Sulfur dioxide, Spectroscopy, Optical measurement, Horwitz ratio

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Potential of Catalytic Ozonation in Treatment of Industrial Textile Wastewater in Indonesia

Rame Rame [1,2,*], Purwanto Purwanto [1,3], and Sudarno Sudarno [1,4]

[1] Doctorate Program in Environmental Science, School of Postgraduate Studies, Universitas Diponegoro, Semarang 50241, Indonesia
[2] Center of Industrial Pollution Prevention Technology, Jl. Ki Mangunsarkoro No. 6, Semarang 50241, Indonesia
[3] Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro, Semarang 50275, Indonesia
[4] Department of Environmental Engineering, Faculty of Engineering, Universitas Diponegoro, Semarang 50275, Indonesia

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ABSTRACT

Industrial textile wastewater is one of the most heavily polluting in Indonesia. Wastewater from industrial textile contains organic contamination that is very difficult to remove. The pollutants are remaining even though it has been treated by the conventional wastewater treatment and bio refractory in nature. Toxic organic compounds discharged from the textile industry, such as colored dyes, heavy metals, and various chemicals, will hurt the environment. These contaminants have been proven toxic to the biotic environment, such as mutagenic, which can increase the incidence of cancer and endocrine disruptor effects. Removal of contaminants from industrial textile wastewater is currently one of the most critical subjects in water pollution prevention. Applications of catalytic ozonation treatment initially, powder catalysts have been employed, and later, the use of activated carbon materials in more advanced catalyst structures reported, and more sophisticated types of catalyst equipment namely carbon nanotube, and nanoparticles. In-depth research on the combination of ozonation and catalytic research of industrial textile wastewater treatment has the potential to become a well-developed approach to treatment industrial textile wastewater. This review provides process principles and characteristics, including the use of various catalysts, variations in reactor design, and application catalytic ozonation in synthetic textile wastewater and real industrial textile wastewater outlined and discussed. Include future research directions of the treatment of industrial textile wastewater in to clean water with drink quality. This first time published review of the potential catalytic ozonation for the textile industry's wastewater treatment in Indonesia.

1. INTRODUCTION

The textile industry is a manufacturing sector that receives development priorities accordingly, "Making Indonesia 4.0" action plan. Some radical changes need to be adopted in the textile industry by optimizing the use of automation technology that can boost productivity and quality efficiently. The textile industry became a significant foreign exchange earner with export value reaching the highest compared to the previous year. Also, a million jobs have been contributed to by the textile industry. These make the textile industry requires relatively more labor and export-oriented sector. In a textile industry process, besides producing textile industry products, the impact of the process is to produce waste. The types of waste can be in the form of wastewater, exhaust emissions, and solid waste. From the industrial process to get 1 ton of product, it produces wastewater up to 100 m^3. So that in one year, the industry with as many as 1 tons of textile industry products will donate wastewater up to 36,500 m^3 / year. The estimated production capacity of textiles in Indonesia is 13 million tons in 2018. These are the main problem; namely,

*Correspondence author.
E-mail : rame@students.undip.ac.id (Rame)

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the textile production process requires a very high quantity of water and massive discharge of wastewater at various stages of the coloring and finishing process.

The Indonesian textile industry's wastewater treatment technology in the early 1980s was conventional biological treatment. The basis for determining a wastewater treatment technology in the textile industry has not yet considered the factors of the availability of energy resources, sustainable water resources, and color parameters. It is because, at that time, there were no color quality standard requirements, Government still subsidized energy prices, and water resources were still abundant.

The determination of industrial wastewater treatment technology is entirely the policy of industry players or an awareness-based policy that meets the quality standard requirements. The first regulation was carried out by the Government by issuing Law Number 4 of 1982 concerning provisions of Principal Environmental Management. Law Number 5 of 1984 concerning Industry was continued. The Government does not have the authority to determine the type of wastewater treatment technology. However, the Government has regulatory authority in the requirements for achieving quality standards for industrial wastewater. The latest quality standards of industrial textile wastewater according to Indonesian Government regulations through ministerial regulations No. 16 of 2019 (Ministry of Environment and Forestry, 2019). The regulation contains the obligations of the textile industry to meet quality standards for wastewater, especially for color parameters. Because the textile industry is only concerned with profit alone without regard to the availability of natural resources, both water and air, and energy, is an inappropriate approach. Improvement of the environment through the prevention of water and air pollution will improve the welfare of the industry and society.

Precipitation and filtering is a physics-based wastewater treatment technology that is easily applied. The rough filtering using media such as sand, coral, and coconut shell charcoal, as well as palm fiber. However, precipitation and filtering are limited to coarse contamination and water-insoluble contamination. While dissolved contaminants in the water, there is still a lot in treated water. Furthermore, biological basis wastewater treatment technology was developed to overcome dissolved contamination. Conventional biological treatment processes applied to textile industry wastewater in Indonesia. The technology is useful for removing dyes that are not soluble in water (dye disperse). However, the price factor of the dye and ease of use cause the industry prefers to use dyes that are soluble in water (reactive dyes) so that biological wastewater treatment fail to meet the color quality standards according to regulations. Anaerobic bacteria cannot completely isolate the dye, causing unexpected reactions and toxic amine by-products formed in wastewater (Robinson et al., 2002). Coloring metabolites can cause anaerobic reactor function instability. A probably similar phenomenon applies to water-insoluble dye. Most likely Anaerobic bacteria will find it difficult to break down water-insoluble dye.

Furthermore, the aromatic amine from the anaerobic degradation process dye is not fully converted to CO_2 and H_2O in an open reactor with a degradation process is assisted by air circulation. Often wastewater from the textile industry, which still contains color, is channeled directly into the environment without adequate handling, which leads to the emergence of water pollution that is very difficult to handle because it has entered the river or other water bodies. Colored wastes will increase the need for chemical oxygen (COD) from the aquatic environment and reduce the re-oxygenation process, thus affecting the development of photoautotrophic organisms. Dyestuff contamination will have an impact on the stunted development and growth of aquatic organisms and damage the natural ecosystem in aquatic life due to the difficulty of photosynthetic activity due to the low quantity of sunlight energy that can be absorbed by the aquatic environment and thus significantly disrupting aquatic ecosystems (Venkatamohan et al., 2002). Most of the dyes with the main components of azo can cause poisoning at particular concentrations, can encourage the risk of cancer, and cause undesirable changes at the genetic level (Pinheiro and Touraud, 2004).

2. CURRENT INDUSTRIAL TEXTILE WASTEWATER TREATMENT

Textile industry wastewater in Indonesia is generally only treated by conventional methods. As a result, the water discharged into water bodies still contains relatively high levels of contamination. The conventional method is limited to the removal of coarse contamination and water-insoluble contamination. While many contaminants dissolved in the water remain. It also has the potential to produce intermediate toxic compounds. The contamination has the potential to pollute watersheds and coastal coasts. Even though residents still used river water as a source of water, irrigation, agriculture, and livestock.

Table 1. Comparison of different wastewater treatment technologies in the textile industry

Technologies	Result	Limitation	Ref.
Conventional physical method	removal of coarse contamination and water-insoluble contamination.	many contaminants dissolved in the water remain	(Buscio et al., 2015)
- Coagulation, flocculation,	adequate in removing dyes contaminants	produces potentially toxic sludge. Costly and not been able to remove some color	(Dotto et al., 2019)
Conventional biological method	Removal of biodegradable contaminants.	Only suitable for biodegradable contaminants. produce high deposition of sludge and not enough in removing ammonia	(Handayani et al., 2018)
Advanced method			
- Fenton	sufficient for soluble and insoluble colors, and there is no change in volume	problems in sludge disposal and is very expensive	(Su et al., 2011; Sarajar et al., 2019; Marlina et al., 2019)
- Ozonation process	removing azo dyes and no change in volume.	not suitable for dispersion / insoluble water dyes, aromatic dye releases, and short ozone half-lives	(Robinson et al., 2001)
- Photocatalytic	removing azo dyes and no change in volume.	the length of reaction time	(Syahroni and Djarwanti, 2015)
- A combination of ozonation and catalytic processes	reduce synthetic compounds, organic compounds, and colors in wastewater. environmentally friendly	short ozone half-lives	(Hassaan and Nemr, 2017)

Colored, smelly, and polluted rivers that look white foamy pollutants covering the surface of the river are the current conditions in some Indonesian rivers. The condition of the river is very concerning. The high level of river pollution is also due to the small flow of river water and the still tremendous burden of wastewater from industry and domestic activities. Several textile companies related to river pollution get administrative sanctions. However, this incident did not only occur in the Citarum River. The same pollution problems also occur in several other rivers such as the Cileungsi River, Cikeas River, and Bekasi River. With this condition, joint improvement needs to overcome controlling water pollution from its source. Correctly, the technology modification applied in wastewater treatment plants in textile companies. The conventional biological method less suitable applied to wastewater treatment from the textile dyeing process due to the low quantity of biologically biodegradable contaminants (Jain et al., 2014). Chemical oxidation has preferred a method to treat textiles (Hu et al., 2016b).

The other most commonly used methods are the Fenton and the ozonation process. The Fenton process is sufficient for soluble and insoluble colors, and there is no change in volume, but sludge formed, which causes problems in sludge disposal and is very expensive. Ozonation is useful for removing azo dyes that are applied in gas conditions so that there is no change in volume. However, ozonation is not suitable for dispersion / insoluble water dyes, aromatic dye releases, and short ozone half-lives (Robinson et al., 2001). Other studies using selected microorganisms that immobilized not enough in removing ammonia (Handayani et al., 2018). While the use of photocatalytic still has not shown satisfactory results because of the length of reaction time (Syahroni and Djarwanti, 2015).

Table 2. Comparison of removal contamination performances using the different catalyst

Catalyst	Input textiles	Result	Ref.
Fe^{2+} and zero valent iron nanoparticles	complex textile effluent	higher biodegradability index (BOD 5 /COD = BI) enhancement up to 0.61 (134.6%) along with COD, color and toxicity removal up to 73.5%, 87%, and 92% respectively.	(Malik et al., 2018)
alumina catalyst	real industrial textile WW	Removal 34.8% of TOC, 40.2% of COD and 75.1% blue dye	(Polat, Balci, and Özbelge, 2015)
copper-doped zinc oxide	real textile wastewater	removes 89% of COD within 30 min of reaction	(Nakhate et al., 2019)
mesoporous carbon aerogel supported cobalt oxide nanoparticles	the first spent dyeing bath	99% decolorization and COD reduction efficiency 70%.	(Hu et al., 2016a)
ceria-activated carbon composite	Synthetic textile dyes	mineralization degrees of 100%, 98%, and 97% after two hours, respectively for CI Reactive Blue 5, CI Acid Blue 113, and CI Reactive Yellow 3.	(Faria et al., 2009)
carbon aerogel supported copper oxide	Textile dyeing WW	COD removal could reach 46% in catalytic ozonation system after 60-min reaction	(Hu et al., 2016)
C-MgO doped on an eggshell membrane powder	real textile wastewater	the degradation and mineralization were calculated to be 93% and 78%, respectively.	(Asgari et al., 2019)
Perfluoro octyl alumina	Textile wastewaters (WWs)	98.37% removal for Basic Yellow 28 and 97.38% removals for Basic Red 18.1	(Polat et al., 2015)

Thus, the treatment of colored wastewater in the textile industry is a significant need at this time, so the development of new, innovative, and efficient and economical processing technologies are needed. Separation and reuse of treated water from the textile industry wastewater can be an additional advantage given the economic value of process water. The combination of ozonation and catalytic processes is one approach to environmentally friendly Advanced Oxidation Processes technologies (Duprez and Fabrizio, 2018; Gil et al., 2018). Catalytic ozonation can reduce synthetic compounds, organic compounds, and colors in wastewater (Wang et al., 2019). During catalytic ozonation, O_3 molecules oxidize organic molecules through selective or non-selective radical reactions. O_3 molecules also selectively attack unsaturated chromophore bonds through electrophilic or non-selective substitution through the formation of intermediate compounds in the form of hydroxyl radicals, generated in color loss continued by the degradation of other organic contaminants that are not biologically decomposed (Hassaan and Nemr, 2017). Several recent studies have shown that catalytic ozonation can increase the concentration of hydroxyl radicals to increase the mineralization of organic contamination (Ma et al., 2018).

3. CATALYTIC OZONATION FOR INDUSTRIAL TEXTILE WASTEWATER

Advanced oxidation processes (AOP) use different oxidations to turn most of the chemical contaminants in wastewater back into CO_2 gas and water. The performance of the technology depends on the quantity of formation of a compound between hydroxyl radicals that will break down contaminants in wastewater into smaller compounds. The various AOP because of differences in energy, sources, and stages of formation: photochemical, photocatalysis, and chemical oxidation use of solid catalysts homogeneous or heterogeneous. The AOP approach is more useful for the removal of color contamination contained in wastewater from the textile industry because of a high rate of TOC removal and decolorization (Duprez and Fabrizio, 2018).

Increasing the number of intermediate compounds in the form of hydroxyl radicals and increasing the speed of decomposition are positive impacts of catalyst used (Ikhlaq et al. 2012). However, these methods should be adopted when other kinds of other simple technologies have not been able to provide the required degree of pollution removal. Some textile industry wastewater treatment uses Fenton but requiring pH conditioning and iron hydroxide sludge (Asghar et al., 2015).

Catalytic ozonation can reduce COD, color, and toxicity, and increase the biodegradability index (BOD_5 / COD = BI) in wastewater (Malik et al., 2018). Catalytic ozonation has proven to become the best potential choice for reuse of wastewater that is still in the textile industry for reuse. Catalytic ozonation has been proven to be able to process dyeing/dyeing wastewater into successive dyeing/coloring process water without reducing the color quality of the dyed fabric. The quality of treated water is better compared to the photocatalysis method, Fenton reaction, or ozonation alone. The reuse process will support environmental protection and the development of sustainability in the textile industry (Hu et al., 2016a). Several research articles show an increase in the effectiveness and efficiency of the application of catalytic ozonation as an industrial wastewater treatment technology such as textiles (Asgari et al., 2019), pharmaceuticals (Chen and Wang, 2019), colors (Hu et al., 2016a), petrochemicals (Huang et al., 2019). Recent research shows catalytic ozonation with carbon nanotube (CNT) catalysts can increase the concentration of hydroxyl radicals 1000 times higher than in the water phase (Zhang et al., 2017) to increase the mineralization of organic contamination.

Several research articles show the efficiency of various types of material as a catalyst to improve catalytic processes. A comparison of removal contamination performances using different catalyst published in the literature is shown in Table 2. Various metal oxides such as magnesium oxide (C-MgO) carbon doped with carbon in powder (C-MgO-EMP) (Asgari et al., 2019)(Fe_3O_4 / Co_3O_4 (Chen and Wang, 2019), Fe_2O_3 / Al_2O_3 (Rame et al., 2017), cobalt oxide nanoparticles (Hu et al., 2016b), carbon aerogel supported copper oxide (Hu et al., 2016a), iron-nickel (Huang et al., 2019) can be useful as a single component or combination of catalysts for the catalytic ozonation process in wastewater. Other research investigates the catalytic activity of graphical structures of carbon nanotubes (Zhang et al., 2017) and catalysts based on Fe shavings of industrial wastes (Li et al., 2019) for catalytic ozonation in increasing hydroxyl radicals. However, the catalyst character has limited its application.

3.1 Synthetic Textile Wastewater

In this section, various catalysts, variations in reactor design for the ozonation catalytic in synthetic textile wastewater will be discussed. Single-bed reactors, reactors with continuous stirring, and fluidized have been applied in research studies for the removal of contaminants in the form of dyes and pigments that are still present in textile wastewater since they used as coloring agents. The increased oxidation rate results in the use of a catalyst in the form of copper sulfide powder in a single color removal in solutions such as Reactive Black, Remazol Brilliant Blue, or Red Acid (Pirgalioğlu and Özbelge, 2009).

Study of decomposition of oxamate, oxalate, and Reactive Blue (textile dyes) using catalytic ozonation with activated carbon, carbon xerogel, and cerium oxide catalysts and single ozonation control has developed demonstrate high-performance catalytic ozonation. The catalytic activity of the catalyst accrues with linear correlation with the quantity of activated carbon contained in activated carbon that is in contact with textile wastewater during the mineralization process (Orge et al., 2011). Approach to improving catalytic ozonation performance has been carried out with a more straightforward and more effective method of using polyacrylonitrile textile fibers (Gonçalves et al., 2015).

The optimum condition catalytic ozonation using mesoporous type bimetal catalyst with Ru-Cu / SBA-15 component obtained dose 5000 mg/m^3 and pH value 9 in artificial wastewater with reactive orange azo dye contamination, which results in the percentage of efficiency of color removal of 70.4% after the catalytic reaction for 1 hour. However, ideal catalytic ozonation will not be obtained if bicarbonate ions are present in textile wastewater because these ions act as inhibitors of hydroxyl radical formation, which decrease the COD removal efficiency significantly from 90% to 30.2% after four hours of catalytic ozonation (Ghuge and Saroha, 2018). Catalytic ozonation process obtained Reactive Black 5 removal efficiency of 54.03% using a bone-char (BC) ash decorated with MgO-FeNO$_3$. The optimal values for pH, dyes concentration, reaction time, and catalyst quantity, and were determined 10, 10 mg/L, 15 min, and 100 mg/L, respectively (Asgari et al., 2017).

3.2 Real Industrial Textile Wastewater

In this section, application catalytic ozonation in real industrial textile wastewater will be discussed, including their advantages and disadvantages, and include the use of various catalysts, variations in reactor design, and scale application. Pilot-scale catalytic ozonation of wastewater obtained from processes in the textile industry that was tested on a pilot scale use of copper-doped zinc oxide as catalysts already implemented. The 1000 mg/L Cu-doped ZnO by regulating ozone flow of 4000 mg/m^3 and pH 7.2 for 30 minutes the catalytic reaction was able to eliminate 89% COD. Reduction of COD by catalytic ozonation increased performance in sixfold compared with single ozonation. The catalytic ozonation is resulting in savings in energy consumption during the process of three folds more energy-efficient than that of single ozonation. Wastewater treatment uses an approach catalytic ozonation is a promising wastewater treatment solutions that are more efficient and effective compared to treatment technologies that have been widely installed in the textile industry (Nakhate et al., 2019).

However, much research on catalytic ozonation has a goal in removing single contaminants or specific azo dyes, but several studies have carried out treatment of wastewater taken directly from the textile industry. Research of catalytic ozonation of wastewater obtained from finishing and dyeing to follow by biological activated carbon has been done. The cost of applying catalytic ozonation with O_3/rGAC-BAC is USD 6 for 100 m^3 of textile industry wastewater for removal COD 71% and 43% of those for O_3/rGAC alone and BAC alone, respectively (Wang et al., 2019). While the efficiency of catalytic ozonation with C-MgO-EMP catalyst for textile industry liquid waste based on color and TOC parameters is to be 93% and 78%, respectively (Asgari et al., 2019). The results of other studies indicate there are still around 214 species of organic pollutants that are still detected from treated water in the biological treatment unit of the wastewater finishing process of the textile industry. However, after the biologically treated water is treated with ozonation catalytic, it is obtained a decrease into 34 harmless species (Wu et al., 2016).

Based on the COD parameters, one of the studies has successfully used catalytic ozonation in the treatment of real industrial textile wastewater. Research using a reactor that is divided into three containers is different from the alumina catalyst. The reactor is a fluidized cylindrical column with a height dimension of 100 cm and a radius of 4 cm. COD and dye degradation showed that alkaline pH degradation is more optimal when using alumina catalysts. The efficiency of catalytic ozonation depended much on the surface catalyst, characteristics of dyes, and pH of the solution (Polat et al., 2015).

4. FUTURE RESEARCH DIRECTIONS

From several results of catalytic ozonation research in textile wastewater, it turns out that the method is still not able to destroy the entire contamination. So that further processing is still needed to maximize the removal of the remaining contaminants. The treatment of industrial textile wastewater always faces limitations when using the current processing stage. An alternative breakthrough for these problems includes the approach to the right combination of advanced oxidation processes includes filtration. However, much current research has focused on the various catalyst, reactor catalytic process, and various input textiles. While the future tendency to optimize automatic analysis, with the sensor for controlling the whole treatment process. Also, process optimization, low energy consumption, and simple operational mechanism are commonly carried out in automatic catalytic reactors, which will be the best solution for industrial textile wastewater treatment.

Very little research conducted concentrating catalytic ozonation performance tests to find out whether it is included in the category of efficient and effective technology for treating textile wastewater for modem wastewater reuse. Future research needs to find the right and optimum technology for sustainable development of the textile industry and cleaner production of textile dyeing (Hu et al., 2016a). Also the analysis of ecological trails needs to be done to determine the capacity and durability of pollution loads (Budihardjo et al., 2013). In addition to the operator WWT has competence in knowing the characteristics of waste water including color, smell, and taste, fish can be utilized for biocentration as well as biomonitoring of wastewater treatment processes (Hidayah et al., 2014).

The application of WWT catalytic ozonation bases is still tricky in Indonesia. Research on catalytic ozonation prototypes with a combination of Aluminum and Iron base catalysts has succeeded in treating the textile industry wastewater (Rame et al., 2017). Nevertheless, the industry is still reluctant to implement catalytic ozonation technology. Some industries are still hesitant to build WWT catalytic ozonation because there are no concrete examples of WWT in the Indonesian industry. At present, the application of the industry is limited to ozonation combined with anaerobes and aerobes. The industry might be interested if WWT catalytic ozonation output can be reused as production process water, clean water, and drinking water.

Besides, the industry is still worried about WWT catalytic ozonation operational costs, which are considered very expensive in its investment. Research on the development of new renewable energy utilization in WWT catalytic ozonation operations will undoubtedly provide more significant benefits. Like solar cell energy and biomass. Instrumentation and automation based wireless sensors can be used as a quality monitoring system for waste water to lower the operational costs of treatment and electrical energy (Purwanto et al., 2019). The operational costs of WWT will not burden the industry. The operational cost has been a common obstacle for the construction of WWT industries.

The capacity and quality of the textile industry wastewater are very diverse. Because of the many types of textile production stages, there is almost no textile wastewater that has the same characteristics. Therefore, future research will focus on wastewater treatment technology that can automatically identify the quality and quantity of contaminants in wastewater as well as full control of the wastewater treatment system. So that later wastewater treatment plants with this technology can be applied to all types of textile industries.

The installation of monitoring units in realtime and online in treated water will become an industry requirement in the future. These are to ensure that the textile industry commits treating wastewater into clean water that will not pollute the surrounding environment. A more accessible, cheaper, and faster process approach while still considering the impact and benefits on the environment will also be the focus of future research in the textile industry wastewater management. So far, research is still limited to treating the textile industry wastewater into quality water for irrigation, washing water, and meeting plant needs. Research with output in the form of clean water with quality as drinking water, raw material water, and industrial production process water will be an exciting challenge for future research.

5. CONCLUSION

The practical and efficient application of wastewater treatment technology in the textile industry needs to be realized immediately to prevent the potential for environmental pollution due to installing technology that is still not optimal in destroying pollution. Awareness about conventional wastewater treatment that still passes pollution into the environment needs to socialized to the textile industry and the community. These are to prevent dangerous risks to public health and the environment due to exposure to pollution. Research on catalytic ozonation in synthetic textile wastewater and real industrial textile wastewater shows the potential for catalytic ozonation. This likely an alternative in removing contaminants from the textile industry wastewater. Research on the utilization of renewable energy in WWT catalytic ozonation for reuse textile wastewater today is one of the most critical subjects in preventing water pollution. The treatment of textile industry wastewater into clean water and drinking water using catalytic ozonation has the opportunity to improve processing performance so that it is faster, cheaper, and more sustainable.

6. ACKNOWLEDGMENT

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7. REFERENCE

Asgari, G., Somaye A., Abdol M.S.M., Ali P., and Bahman R. 2017. "Preparation and Catalytic Activity of Bone-Char Ash Decorated with MgO - FeNO3 for Ozonation of Reactive Black 5 Dye from Aqueous Solution: Taguchi Optimization Data." *Data in Brief* 13: 132–36. https://doi.org/10.1016/j.dib.2017. 05.025.

Asgari, G., Javad F., Hassan Z.N., and Hamied E. 2019. "Catalytic Ozonation of Industrial Textile Wastewater Using Modified C-Doped MgO Eggshell Membrane Powder." *Advanced Powder Technology* 30 (7): 1297–1311. https://doi.org/10.1016/j.apt.2019.04.003.

Asghar, ., Abdul A. A. R., and Wan M.A.W.D. 2015. "Advanced Oxidation Processes for In-Situ Production of Hydrogen Peroxide/Hydroxyl Radical for Textile Wastewater Treatment: A Review." *Journal of Cleaner Production* 87 (1): 826–38. https://doi.org/10.1016/j.jclepro.2014.09.010.

Budihardjo, S.,Hadi S.P., Sutikno, S., Purwanto, P. 2013. "The ecological footprint analysis for assessing carrying capacity of industrial zone in Semarang." Scientific Research Publishing.

Buscio, V., Marín, M. J., Crespi, M, and Gutiérrez-Bouzán, C. 2015. "Reuse of Textile Wastewater after Homogenization-Decantation Treatment Coupled to PVDF Ultrafiltration Membranes." *Chemical Engineering Journal* 265 (1): 122–28. https://doi.org/10.1016/j.cej.2014.12.057.

Chen, H., and Jianlong W. 2019. "Catalytic Ozonation of Sulfamethoxazole over Fe3O4/ Co3O4 Composites." *Chemosphere* 234: 14–24. https://doi.org/10.1016/j.chemosphere.2019.06.014.

Dotto, J., Márcia R.F.K, Márcia T.V., Soraya M.P., and Rosangela B. 2019. "Performance of Different Coagulants in the Coagulation/Flocculation Process of Textile Wastewater." *Journal of Cleaner Production* 208:656–65. https://doi.org/10.1016/j.jclepro.2018.10.112.

Duprez, D., and Fabrizio, C. 2018. *Handbook of Advanced Methods and Processes in Oxidation Catalysis.*

Faria, P. C.C., Órfão, J. J.M. and Pereira, M. F.R. 2009. "Activated Carbon and Ceria Catalysts Applied to the Catalytic Ozonation of Dyes and Textile Effluents." *Applied Catalysis B: Environmental* 88 (3–4): 341–50. https://doi.org/10.1016/j.apcatb.2008.11.002.

Ghuge, S.P., and Anil K.S. 2018. "Catalytic Ozonation of

Dye Industry Effluent Using Mesoporous Bimetallic Ru-Cu/SBA-15 Catalyst." *Process Safety and Environmental Protection* 118: 125–32. https://doi.org/10.1016/j.psep.2018.06.033.

Gil, A., Galeano, L. A. and Vincente, M. A. 2018. *Applications of Advanced Oxidation Processes (AOPs) in Drinking Water Treatment.*

Gonçalves, A.G., Jéssica M., Juliana P.S.S., José L. F., Manuel F.R.P., and José J.M.Ó. 2015. "Carbonized Polyacrylonitrile Fibers for the Catalytic Ozonation of Oxalic Acid." *Catalysis Today* 249: 59–62. https://doi.org/10.1016/ j.cattod.2014.12.045.

Handayani, Setianingsih, N.I. and M. Moenir. 2018. "Performance Of Immobilized-Selected Microorganisms In The Biodegradation Of Textile Industry Waste Wate." *Jurnal Riset Teknologi Pencegahan Pencemaran Industri* 9 (1): 29–37. https://doi.org/https://doi.org/ 10.21771/jrtppi.2018.v9.no1.p29-37.

Hassaan, M.A., and Ahmed E. 2017. "Advanced Oxidation Processes for Textile Wastewater Treatment." *International Journal of Photochemistry and Photobiology* 2 (3): 85–93.

Hidayah, A.M., Purwanto, P., Soeprobowati, T.R. 2014. "Biokonsentrasi faktor logam berat Pb, Cd, Cr dan Cu pada ikan nila (*Oreochromis niloticus Linn.*) di karamba Danau Rawa Pening." *Bioma: Berkala Ilmiah Biologi* 16 (1), 1-9

Hu, E., Xinbo W., Songmin S., Xiao M.T., Shou X.J., and Lu G. 2016a. "Catalytic Ozonation of Simulated Textile Dyeing Wastewater Using Mesoporous Carbon Aerogel Supported Copper Oxide Catalyst." *Journal of Cleaner Production* 112: 4710–18. https://doi.org/10.1016/j.jclepro.2015. 06.127.

Hu, S. S., Ming T. X., S. J., and Chiu, K. 2016b. "Regeneration and Reuse of Highly Polluting Textile Dyeing Effluents through Catalytic Ozonation with Carbon Aerogel Catalysts." *Journal of Cleaner Production* 137: 1055–1065. https://doi.org/https://doi.org/10.1016/j.jclepro.2 016.07.194.

Huang, Y., Mengyu L., Zhihua X., Daofang Z., and Liang L. 2019. "Catalytic Ozonation of Organic Contaminants in Petrochemical Wastewater with Iron-Nickel Foam as Catalyst." *Separation and Purification Technology* 211 (May 2018): 269–78. https://doi.org/10.1016/j.seppur.2018.09.080.

Ikhlaq, A., David R. B., and Barbara K. 2012. "Mechanisms of Catalytic Ozonation on Alumina and Zeolites in Water: Formation of Hydroxyl Radicals." *Applied Catalysis B: Environmental* 123–124: 94–106. https://doi.org/10.1016/ j.apcatb.2012.04.015.

Jain, R.M., Kalpana H.M., Jitendra K., and Bhavanath J. 2014. "Biological Neutralization and Biosorption of Dyes of Alkaline Textile Industry Wastewater." *Marine Pollution Bulletin* 84 (1–2): 83–89. https://doi.org/10.1016/j.marpolbul.2014. 05.033.

Li, X., Weiyu C., Luming M., Yuanxing H., and Hongwu W. 2019. "Characteristics and Mechanisms of Catalytic Ozonation with Fe-Shaving-Based Catalyst in Industrial Wastewater Advanced Treatment." *Journal of Cleaner Production* 222: 174–81. https://doi.org/10.1016/j.jclepro.2019. 03.084.

Ma, J., Yunlu, C., Jianxin, N., Luming, M. , Yuanxing, H., Liang, L. and Yan, L. 2018. "Pilot-Scale Study on Catalytic Ozonation of Bio-Treated Dyeing and Finishing Wastewater Using Recycled Waste Iron Shavings as a Catalyst." *Scientific Reports*, 1–11.

Malik, S.N., Prakash C.G., Atul N.V., and Sandeep N.M. 2018. "Catalytic Ozone Pretreatment of Complex Textile Effluent Using Fe^{2+} and Zero Valent Iron Nanoparticles." *Journal of Hazardous Materials* 357 (May): 363–75. https://doi.org/10.1016/ j.jhazmat.2018.05.070.

Marlina, E., Purwanto, 2019. "Electro-Fenton for Industrial Wastewater Treatment: A Review." *E3S Web Conf.* 125, 1–5. https://doi.org/10.1051/ e3sconf/201912503003

Ministry of Environment and Forestry. 2019. “Regulation of the Minister of Environment and Forestry of the Republic of Indonesia Number p.16/ Menlhk/Setjen/Kum.1/4/2019 Concerning the Second Amendment to the Regulation of the Minister of Environment Number 5 the Year 2014 About Wastewater Quality Sta.”

Nakhate, P.H., Chandrakanth R.G., Nandkumar T.J., and Kumudini V.M. 2019. “Engineering Aspects of Catalytic Ozonation for Purification of Real Textile Industry Wastewater at the Pilot Scale.” *Journal of Industrial and Engineering Chemistry* 69: 77–89. https://doi.org/10.1016/j.jiec.2018. 09.010.

Orge, C. A., Órfão, J.J.M. and Pereira, M. F.R. 2011. “Catalytic Ozonation of Organic Pollutants in the Presence of Cerium Oxide-Carbon Composites.” *Applied Catalysis B: Environmental* 102 (3–4): 539–46. https://doi.org/10.1016/j.apcatb.2010. 12.036.

Pinheiro, H. M, and Touraud, E. T. O. 2004. “Aromatic Amines from Azo Dye Reduction: Status Review with Emphasis on Direct UV Spectrophotometric Detection in Textile Industry Wastewaters.” *Dyes Pigm* 61: 121–139.

Pirgalioğlu, S., and Tülay A.O. 2009. “Comparison of Non-Catalytic and Catalytic Ozonation Processes

Robinson, T, Chandran, B. Naidu, S. and Nigam, P 2002. “Studies on the Removal of Dyes from Synthetic Textile Effluent Using Barley Husk in Static-Batch Mode and a Continuous Flow, Packed-Bed Reactor.” *Biores Technol* 85: 43–49.

Sarajar, A.E.E., Ramadhania, R.P., Purwanto, P., 2018. "Organic pollutant degradation of tapioca flour industrial waste with photo-fenton reaction." *MATEC Web Conf.* 156, 1–4. https:// doi.org/10.1051/matecconf/201815603048.

Su, C., Massakul P., Chavalit R., and Ming Chun L. 2011. “Effect of Operating Parameters on the Decolorization and Oxidation of Textile Wastewater by the Fluidized-Bed Fenton Process.” *Separation and Purification Technology* 83 (1):

of Three Different Aqueous Single Dye Solutions with Respect to Powder Copper Sulfide Catalyst.” *Applied Catalysis A: General* 363 (1–2): 157–63. https://doi.org/10.1016/j.apcata. 2009.05.011.

Polat, D., Irem B., and Tülay A.O. 2015. “Catalytic Ozonation of an Industrial Textile Wastewater in a Heterogeneous Continuous Reactor.” *Journal of Environmental Chemical Engineering* 3 (3): 1860–71. https://doi.org/10.1016/j.jece.2015.04. 020.

Purwanto, P., Suryono, S., Sunarno, S., 2019. "Design of Air Quality Monitoring System Based on Web Using Wireless Sensor Network." *J. Phys. Conf. Ser.* 1295. https://doi.org/10.1088/1742-6596/ 1295/1/012043

Rame, Agus P., and Agung B. 2017. “Treatment of Textile Waste Water Based Catalytic Ozonation With Iron (III) Oxide (Fe_2O_3) and Aluminum Oxide (Al_2O_3) Catalysts Using Micro Diffuser.” *Research Journal of Industrial Pollution Prevention Technology*. https://doi.org/http:// dx.doi.org/10.21771/jrtppi.2017.v8.no2.p67-75.

Robinson, M.G., Marchant R., and Nigam P. 2001. “Remediation of Dyes in Textile Effluent: A Critical Review on Current Treatment Technologies with a Proposed Alternative.” *Biores Technol* 77: 247–255.

100–105. https://doi.org/ 10.1016/j.seppur.2011.09.021.

Syahroni, C., and Djarwanti D. 2015. “Pengembangan Reaktor Fotokatalitik Rotating Drum Untuk Pengolahan Air Limbah Industri Tekstil.” *Jurnal Riset Teknologi Pencegahan Pencemaran Industri* 6 (2): 35. https://doi.org/10.21771/ vol6no2tahun2015artikel1238.

Venkatamohan, S, Rao, N. and Karthikeyan, J. 2002. “Adsorptive Removal of Direct Azo Dye from Aqueous Phase onto Coal-Based Sorbents: A Kinetic and Mechanistic Study.” *J Hazard Mater* B90: 189–204.

Wang, Z. H., Feifei, X.W., Xingaoyuan, T., Kun, Yubo, S. and Tingting, Y. 2019. “Application of

Heterogeneous Catalytic Ozonation for Refractory Organics in Wastewater." *Catalysts* 9, (241).

Wang, W.L., Hong Y.H., Xin L., Hui X.S., Tian H.Z., Chun W., Zheng Y.H., and Qian Y.W. 2019. "Combination of Catalytic Ozonation by Regenerated Granular Activated Carbon (RGAC) and Biological Activated Carbon in the Advanced Treatment of Textile Wastewater for Reclamation." *Chemosphere* 231: 369–77. https://doi.org/10.1016/j.chemosphere.2019.05.175.

Zhang, S., Xie Q., Jian F.Z., and Dong W. 2017. "Probing the Interphase 'HO[Rad] Zone' Originated by Carbon Nanotube during Catalytic Ozonation." *Water Research* 122: 86–95. https://doi.org/10.1016/j.watres.2017.05.063.

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Performance of a Full-Scale Anaerobic Digestion on Bakery Wastewater Treatment : Effect of Modified Distribution System

Hanny Vistanty[1*], Rizal Awaludin Malik[1], and Aris Mukimin[1]

[1]Center of Industrial Pollution Prevention Technology, Jl. Kimangunsarkoro no. 6, Semarang, Indonesia

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ABSTRACT

The effectiveness of a full-scale anaerobic digestion pretreatment was evaluated and the effect of wastewater distribution system was determined on the performance of bakery wastewater (BW) treatment. The BW was fed to 3 series of anaerobic compartments as the main degradation process. The distribution system of first compartment was modified and circulated to enhance contact and efficiency. While the effluent of last compartment was partly returned to the first compartment as an external circulation and the other part was further processed in activated sludge under aerobic conditions. The overall system was able to remove chemical oxygen demand (COD), total suspended solids (TSS), and biochemical oxygen demand (BOD) up to 97.7%, 99.7%, and 99.6%, respectively, at maximum organic loading rate of 6.3 kg COD/m^{3}day and internal and external circulation rate of 10 L/min and 15 L/min, respectively. High removal of pollutants indicated that modified distribution of circulation is advantageous to the BW treatment.

1. INTRODUCTION

Food industry shows a promising trend in order to meet the rising demand of food products, including biscuit, bakery, and dairy products. The market of food products in Indonesia has grown in a range of 5 – 10% annually and contributes up to 700 trillion rupiah of gross domestic income. Aside from the positive effect, it also may inflict negative consequences towards the environment, especially due to wastewater generated. Food industries, especially biscuit and bakery, consume large volume of water in their washing process that is discharged as wastewater. Bakery wastewater (BW) generated mainly contains flour, sugar, and high concentration of fat, oil, and grease (FOG) (de Santana, Zanoelo, Benincá, & Freire, 2018). It is generally high strength and contains high concentration of suspended and soluble organics with high chemical oxygen demand (COD) and biochemical oxygen demand (BOD) and low biodegradability ratio. Thus a proper wastewater manage ment is urgently needed to avoid high environmental risk.

Implementation of electrocoagulation method as bakery wastewater treatment was studied and the results showed that it efficiently separated insoluble FOG (de Santana et al., 2018). The author mentioned that it showed high performance in removing turbidity, color and grease. However, it was ineffective in removing soluble organic contained, therefore, the effluent still showed a high concentration of COD and BOD and it was applied only as a pretreatment prior to anaerobic digestion. Some conventional processes were also used, namely aerobic process, however the presence of oil layer in wastewater may wrap microorganisms and reduced the performance and efficiency (Pereira, Sousa, Mota, & Alves, 2004).

Previous studies applied anaerobic digestion FOG-containing wastewater treatment (Cammarota & Freire, 2006; Masse, Massé, & Kennedy, 2003; Wan, Zhou, Fu, & Li,

*Correspondence author. Tel. : *+6287832782426*
E-mail : hannyvistantybbtppi@gmail.com (H. Vistanty)

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2011). The author combined anaerobic digestion with hydrolysis pretreatment using Pancreatic Lipase as a way to enhance fat digestion (Masse et al., 2003). However, it only had a small effect on fat digestion (5%) compared to control substrates. In addition to that, pretreatment needs additional space and cost.

Lipids, as the main component of BW, are generally categorized into five types of form, namely, floating, dispersed, emulsion, soluble, and solid substances (Ren, Nie, Liu, & Jin, 2006). Floating, dispersed, and solid forms, are highly possible to be removed physically, while the emulsion and soluble forms are mostly difficult to separate. Soluble lipids are prone to form layer on the surface of microorganisms and particles, thus preventing further contact between pollutant and microorganism. In some cases, lipid-coated microorganisms are floated to the surface and washed out of the anaerobic reactor, thus will reduce the system performance.

In addition to fat particles, anaerobic digestion of FOG-containing wastewater is also constrained by the high possibility of pH drop as a result of accumulation of volatile fatty acids (VFA) produced by lipid hydrolysis. VFA overload may cause disturbance to anaerobic system as it will create an imbalance of acid and methane production. Process modification, such as, leachate recirculation to hydrolysis process was applied to prevent system failure on anaerobic system due to VFA overload (Veeken & Hamelers, 1999). Another report mentioned increased contact intensity between biomass and wastewater resulting into a higher performance of degradation (Wang, Xu, Yan, & Yu, 2014). Internal circulation has been intensevely applied on various wastewater treatment, such as tofu, brewery, and citric acid (Cui, Zhou, & Zhang, 2011; Deng, Zheng, & Chen, 2006; Vistanty & Malik, 2019). Anaerobic system with recirculation was improved in respect of system and pH stability and showed improved COD removal. Considering the challenge of wastewater treated and the advantages of wastewater flow modification, this study aims to modify the distribution system of wastewater fed to anaerobic unit to improve the performance and minimize the effect of fat insoluble particles, and to evaluate the effect in a full-scale FOG wastewater treatment process.

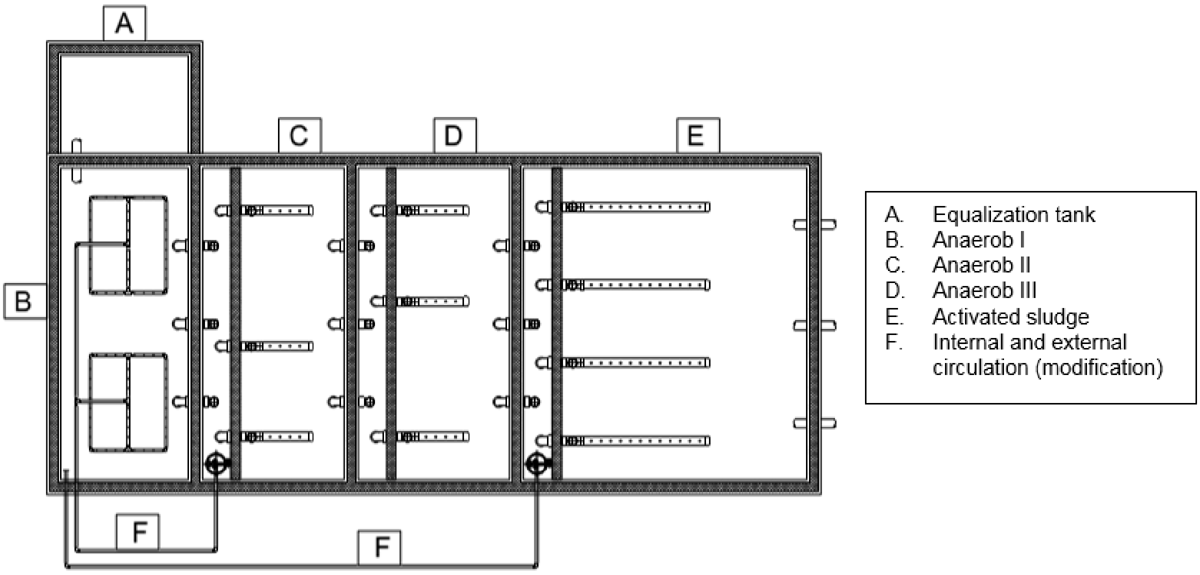

Fig. 1. Layout of wastewater flow modification and recirculation

Table 1. Wastewater characteristics as influent

Characteristic	Measurement	
Total suspended solids (mg/L)	1124	881
Biochemical Oxygen Demand (mg/L)	1603	3389
Chemical Oxygen Demand (mg/L)	3984	9672
pH	3.5	3.8

Samples were analyzed in BBTPPI laboratory

Table 2. Summary of wastewater treatment plant

Unit	HRT (h)	pH	COD
Anaerobic I	38.8	4.1	5824
Anaerobic II	39.2	5.5	3957
Anaerobic III	41.8	5.6	3531
Activated sludge	52.2	6	2800

HRT obtained from the industry, pH was measured in situ and COD was measured in BBTPPI laboratory

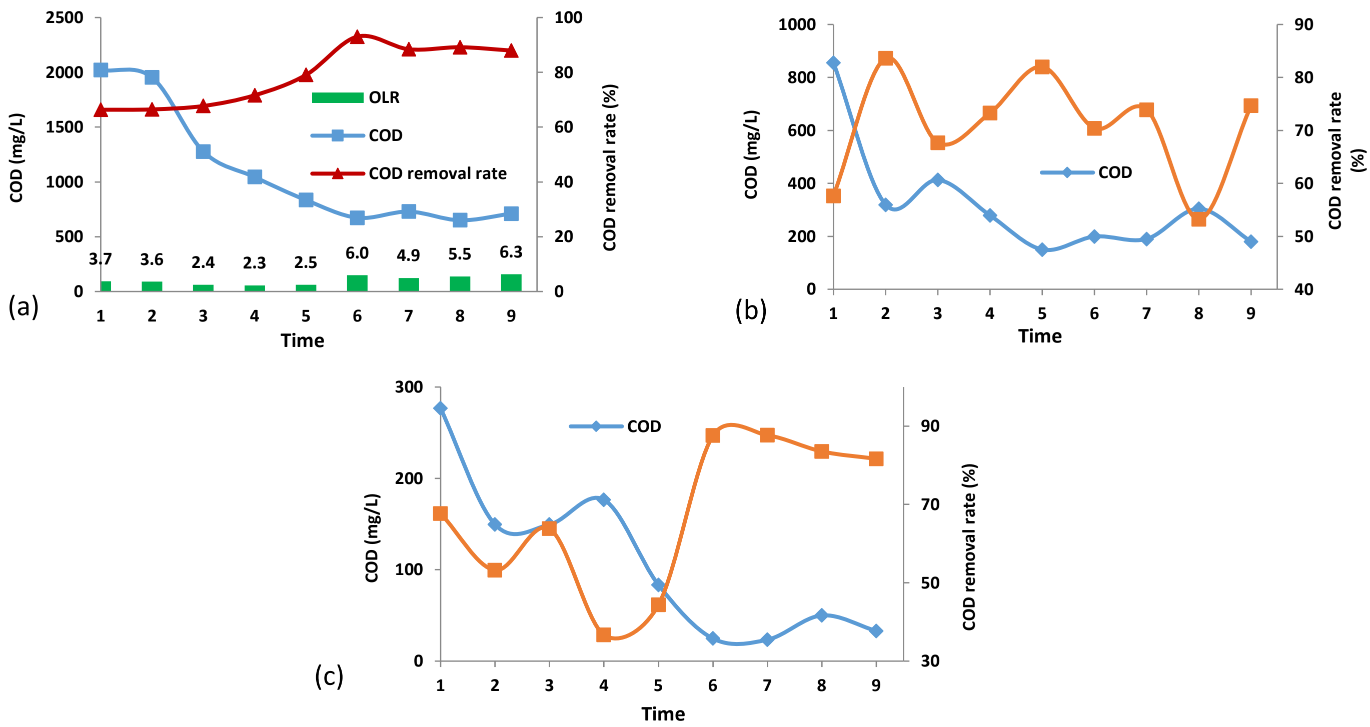

Fig. 2. COD profile and removal rate of (a) anaerobic I, (b) anaerobic II, and (c) anaerobic II

2. METHODS

2.1 Experimental setup

The schematic diagram of modified distribution and recirculation applied in an existing full-scale wastewater treatment (WWT) plant of a bakery industry is shown in Fig. 1. The WWT plant has three-staged anaerobic system and an activated sludge unit connected in series. Anaerobic unit was targeted because it is considered as the main engine in the degradation process in the WWT plant. Wastewater flow was modified by establishing a new internal circulation in the first compartment of anaerobic reactor and external circulation by feeding the outlet of third compartment into the first compartment of anaerobic reactor. Internal and external circulation was distributed in a separated pipeline and different setting of distribution. Internal circulation was taken from the outlet of the first stage and pumped back as feed, while external circulation was taken from the outlet of the third stage and partly fed to the first stage. Recirculation system used pipes of 0.5 inch diameter and wastewater was distributed via 3 mm diameter holes on the side of pipes.

COD removal rate was investigated under constant internal of 10 L/min and external circulation rate of 15 L/min. HRT was maintained constant (Table 2) at inlet flowrate of 890 L/h, while OLR was fluctuated dependent on the inlet COD concentration. Raw wastewater was fed to WWT plant for 8 h, while internal and external circulations were applied for 24 h.

2.2 Wastewater characteristics

Wastewater treatment plant received wastewater from production line, generated from utility washing process. The influent is characterized as fat-rich high organic, high suspended solids, and turbid wastewater. Wastewater characteristics and plant operation variables were directly obtained from the industry (Table 1 and 2). Samples were taken from the equalization tank and analyzed in our laboratory.

2.3 Analysis methods

Effect of modification was monitored regularly by collecting samples from each anaerobic compartment every 2 days. Monitoring was carried out by measuring Chemical Oxygen Demands (COD), volatile fatty acids (VFA), and alkalinity. COD removal rate was measured to evaluate the performance of each unit, while VFA and alkalinity was measured to observe the stability of anaerobic system. BOD, COD and alkalinity were measured in accordance to Standard Methods (5210 B, 5220 C and 2320 B) (E.W. Rice, R.B. Baird, A.D. Eaton, 2017). VFA was determined using modified spectrophotometric method (Siedlecka & Kumirska, 2008) while handheld pH meter was used to record pH fluctuation during modification and experiment.

3. RESULT AND DISCUSSION

3.1 COD removal rate

COD is evaluated as a main parameter in assessing the WWT performance, because the characteristics of wastewater treated is dominated by varied compounds, such as, fat or grease and sugar. Thus, COD removal rate was monitored and plotted to assess the stability of anaerobic unit (Fig. 2).

Due to the application of internal and external circulation at 5 L/min and 7 L/min, respectively, the upflow velocity was increased twofold from 0.235 m/h into 0.588 m/h. It leads into an enhanced mass transfer and contact between wastewater and biomass, which then directly improves degradation process.

As can be seen in Fig. 2, anaerobic I shows a more stable system compared to anaerobic II and III. A significant drop of COD was observed on the third day and gradually decreased to 673 mg/L. COD removal rate was also increased and reached 93%, even when the OLR was significantly increased to 6 kg COD/m^{3}d. It is in accordance to the TVFA/alkalinity ratio (Fig. 3), which indicates anaerobic stability. It is more stable than result reported in other studies which mentioned an early stage of overloading due to TVFA in two-stage anaerobic system (Zuo, Wu, Qi, & Dong, 2015). In contrast with anaerobic I, anaerobic II and III show a relatively fluctuated trend in regards of COD removal rate. It is possibly due to the absence of circulation system in anaerobic II and III, which resulted in slower response of anaerobic system to the organic load. However it shows an increase of COD removal rate in the latter stage of observation. It can be concluded that the anaerobic I is the first shield and do the main portion in degradation process, while anaerobic II and III are indirectly affected.

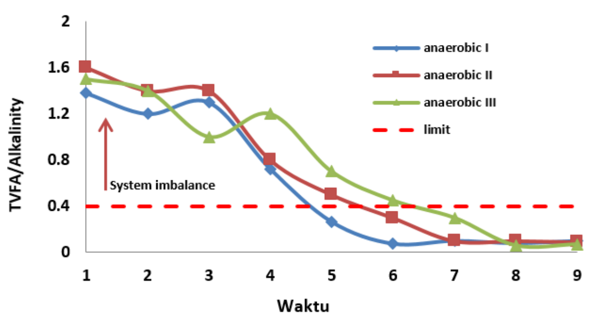

Fig. 3. TVFA/alkalinity ratio of anaerobic unit after modification

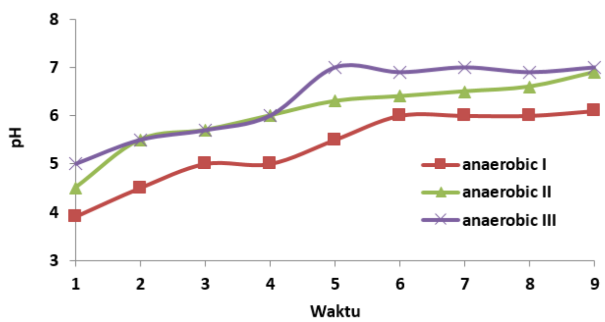

Fig. 4. pH trend of anaerobic unit after modification

Table 3. Effluent of wastewater treatment plant after modification

Parameters	1	2	3	Standard
TSS	25	63	42	85
BOD	25.15	11.29	32.7	85
COD	38.28	62.15	45.56	175
pH	8.6	8.6	8.0	6 - 9

3.2 Total VFA/alkalinity ratio and pH trend

Previous study mentioned that anaerobic digestion without recirculation was more susceptible to VFA overload and may lead to shock and inflict disturbance to anaerobic digestion (Zuo et al., 2015). VFA overload generally happens because the acidification stage of anaerobic system occurs faster than methanation. Thus, recirculation will transfer excessed VFA to be processed in the first stage of anaerobic digestion. Active methanogenic effluent will also be circulated and transferred to acidification stage and facilitate the methanation process. Alkalinity also holds a great role in maintaining the system stability and acts as pH buffer. In low pH environment, alkalinity will be used to maintain system pH and provide the optimal condition for methanation.

To monitor and identify any disturbance to the anaerobic system, we monitored total volatile fatty acid (TVFA) and alkalinity ratio (TVFA/alkalinity) as a key indicator. As shown in Fig. 3., in the early stage of experiment TVFA/alkalinity ratio of the anaerobic digestion was approximately 1.38, much higher than 0.3-0.4, which is known as the maximum limit to process stability. When TVFA/alkalinity ratio is more than 0.4, then the anaerobic digestion can be concluded as instable and is in risk of excessive acidification (Sánchez, Borja, Travieso, Martín, & Colmenarejo, 2005). As recirculation applied, TVFA/alkalinity ratio was significantly decreased less than 0.4, indicating that system has recovered its stability.

Other than VFA, effluent recirculation will increase pH in the early stages of anaerobic system, which will establish an optimal condition for methanation step (Fig. 4). It is evident in the result of our experiment, in which before modification, pH value in each unit was relatively low (around 4-5), while after recirculation, pH in anaerobic I was significantly increased to 6 and subsequently improved pH value in anaerobic II and III. It was possible because continuous circulation system will return a part of anaerobic III to anaerobic I which then directly increase pH on the system. It can be concluded that both pH and VFA reduction is linking and any change in one variable will affect the other.

3.3 Effects of recirculation modification on the performance of WWT plant

In addition to specific parameters, such as, COD, VFA, alkalinity, and pH of anaerobic system, this study also evaluates the performance of whole system of wastewater treatment plant. It aims to ensure that the final effluent can meet the discharge standard of local regulation. As shown in Table 3, the effluent of last stage of WWT plant, i.e., activated sludge was able to meet the water quality standard for discharge to receiving water body in Central Java. The overall wastewater treatment plant was able to remove TSS, BOD, and COD up to 97.7%, 99.7%, and 99.6%, respectively. A similar COD removal rate was also reported (96.2 – 97.5%) by another study treating soybean wastewater with square internal circulation anaerobic tank (Zeng, Hou, & Cui, 2011).

4. CONCLUSION

Modification in distribution system was applied in wastewater treatment plant (WWTP) of a biscuit industry in Central Java. Application of internal and external circulation exhibited great influence in improving system stability, indicated by decreasing trend of TVFA/alkalinity ratio to less than 0.4. COD removal rate was up to 93%, 82%, and 87% on anaerobic I, II, and III, respectively. pH value at anaerobic unit was also improved by recirculation system, and increased to more than 6. Based on these results, it is concluded that recirculation system positively affected wastewater treatment and can be a solution to overcome instability and shock to anaerobic digestion.

REFERENCES

Cammarota, M. C., & Freire, D. M. G. (2006). A review on hydrolytic enzymes in the treatment of wastewater with high oil and grease content. *Bioresource Technology*, *97*(17), 2195–2210. https://doi.org/10.1016/j.biortech.2006.02.030

Cui, P., Zhou, X., & Zhang, Y. (2011). The Feasibility Study of Cotton Pulp Wastewater Treatment with IC Anaerobic Reactor. *Procedia Environmental Sciences*, *11*, 686–692. https://doi.org/10.1016/J.PROENV.2011.12.107

de Santana, M. M., Zanoelo, E. F., Benincá, C., & Freire, F. B. (2018). Electrochemical treatment of wastewater from a bakery industry: Experimental and modeling study. *Process Safety and Environmental Protection*, *116*, 685–692. https://doi.org/10.1016/j.psep.2018.04.001

Deng, L.-W., Zheng, P., & Chen, Z.-A. (2006). Anaerobic digestion and post-treatment of swine wastewater using IC–SBR process with bypass of raw wastewater. *Process Biochemistry*, *41*(4), 965–969. https://doi.org/10.1016/J.PROCBIO.2005.10.022

and performance of a secondary upflow anaerobic sludge bed reactor treating piggery waste. *Bioresource Technology*, *96*(3), 335–344. https://doi.org/10.1016/j.biortech.2004.04.003

Siedlecka, E., & Kumirska, J. (2008). Determination of volatile fatty acids in environmental aqueous samples. *Polish Journal of Environmental Studies*, *17*(3), 351–356. Retrieved from http://www.6csnfn.pjoes.com/pdf/17.3/351-356.pdf

Veeken, A., & Hamelers, B. (1999). Effect of temperature on hydrolysis rates of selected biowaste components. *Bioresource Technology*. https://doi.org/10.1016/S0960-8524(98)00188-6

Vistanty, H., & Malik, R. A. (2019). Enhanced Performance of Multi-Stage Anaerobic Digestion of Tofu Wastewater : Role of Recirculation. *Jurnal Riset Teknologi Pencegahan Pencemaran Industri*, *10*(1),

E.W. Rice, R.B. Baird, A.D. Eaton, editors. (2017). *Standard Methods for the Examination of Water and Wastewater. 23rd ed. American Public Health Association, Washingto, DC, USA*. https://doi.org/ISBN 9780875532356

Masse, L., Massé, D. I., & Kennedy, K. J. (2003). Effect of hydrolysis pretreatment on fat degradation during anaerobic digestion of slaughterhouse wastewater. *Process Biochemistry*, *38*(9), 1365–1372. https://doi.org/10.1016/S0032-9592(03)00020-7

Pereira, M. A., Sousa, D. Z., Mota, M., & Alves, M. M. (2004). Mineralization of LCFA associated with anaerobic sludge: Kinetics, enhancement of methanogenic activity, and effect of VFA. *Biotechnology and Bioengineering*, *88*(4), 502–511. https://doi.org/10.1002/bit.20278

Ren, L., Nie, Y., Liu, J., & Jin, Y. (2006). [Impact of hydrothermal process on the dewaterability and degrease performance of restaurant garbage]. *Huan Jing Ke Xue= Huanjing Kexue*, *27*(9), 1906–11. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/17117654

Sánchez, E., Borja, R., Travieso, L., Martín, A., & Colmenarejo, M. F. (2005). Effect of organic loading rate on the stability, operational parameters

29–37.

Wan, C., Zhou, Q., Fu, G., & Li, Y. (2011). Semi-continuous anaerobic co-digestion of thickened waste activated sludge and fat, oil and grease. *Waste Management*, *31*(8), 1752–1758. https://doi.org/10.1016/j.wasman.2011.03.025

Wang, J., Xu, W., Yan, J., & Yu, J. (2014). Study on the flow characteristics and the wastewater treatment performance in modified internal circulation reactor. *Chemosphere*, *117*(1), 631–637. https://doi.org/10.1016/j.chemosphere.2014.09.088

Zeng, K., Hou, Y. J., & Cui, Y. P. (2011). The research of square internal circulation anaerobic reactor to treatmenting soybean protein wastewater. In *2011 International Conference on Multimedia Technology, ICMT 2011* (pp. 1329–1332). https://doi.org/10.1109/ICMT.2011.6001735

Zuo, Z., Wu, S., Qi, X., & Dong, R. (2015). Performance enhancement of leaf vegetable waste in two-stage anaerobic systems under high organic loading rate: Role of recirculation and hydraulic retention time. *Applied Energy*, *147*(17), 279–286. https://doi.org/10.1016/j.apenergy.2015.03.001

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Evaluating the Performance of Three Chambers Microbial Salinity Cell (MSC) Subjected to Different Substrate Concentrations to Accomplish Simultaneous Organic and Salt Removal in The Wastewater

Rustiana Yuliasni[1*], Nur Zen[1], Nanik Indah Setianingsih[1]

[1]The Centre of Industrial Pollution Prevention Technology, Jalan Ki Mangunsarkoro No. 6, Semarang, Central Java

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ABSTRACT

This study aimed to identify the effect of substrate concentration on the performance of a three chambers Microbial Salinity Cell (a three chambers MSC). In this study, a three chambers MSC were made from plexiglass with total volume of 200 ml. An aluminium wrapped with platinum on vulcan carbon cloth was used as electrodes, with each working area of 63 cm^2. The result showed that a three chambers MSC was able to generate electricity and at the same time removed the salinity. The degree of electricity generation and salinity removal was influenced by initial substrate concentration in the anode chamber. The higher substrate concentration, the better performance of the MSC. The best performance of the MSC was achieved when the initial substrate was 2034 mg/L as COD, lead to a maximum voltage of 0.44 V, and maximum current density of 0.29 mA/m^2. With %CE was 5.4%. The maximum conductivity upsurge in salinity chamber was from 11.2 µS/cm to 1027 µS/cm (corresponding to salinity of 0.57% ppt).

1. INTRODUCTION

The fish processing industry generates liquid wastewater contains high organic matter and salinity (Lefebvre & Moletta, 2006). The conventional biological treatment is used to treat this type of wastewater (Aloui, Khoufi, Loukil, & Sayadi, 2009). However, some issues, such as high salinity, hindered the performance of the conventional technology. In order to treat and at the same time to utilized this wastewater into more sustainable way, the microbial salinity cell was introduced. The objective of this technology was to simultaneously remove organic material and to convert it into electricity and to remove salt in the wastewater. The similar mechanisms, Microbial Desalination Cell (MDC), also can harvest electricity and perform desalination at the same time (Gude, 2016; Kim & Logan, 2013; Lefebvre, Tan, Kharkwal, & Ng, 2012; Mehanna, Kiely, Call, & Logan, 2010). However, MDC can only be used for drinking water desalination, not for real high salinity wastewater. Therefore, for more applicable technology to treat high salinity wastewater, microbial salinity cell (MSC) system concept was introduced.

A Microbial Salinity Cell (MSC) system consists of three chambers, which are anode, salinity and cathode chamber. Between anode and salinity chamber, cation exchange membrane (CEM) is installed, and between salinity and cathode chamber, anion exchange membrane is installed. Anode chamber is filled with a high salinity

*Correspondence author. Tel. : +6281288581633
E-mail : rustianay@kemenperin.go.id

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substrate. When biofilm oxidize the substrate, the proton will drift to the salinity chamber, and the electron will transfer to the external circuit (producing currents). While in the cathode, negative ions will drift into the salinity chamber. The flow of ions will increase the conductivity in the salinity chamber.

This study aimed to identify the effect of substrate concentration on the performance of a Three chambers Microbial Salinity Cell (a three chambers MSC), using synthetic wastewater containing glucose.

2. METHODS

2.1 Reactor Configuration

A three chambers MFC system was built, consisting of anode, salinity chamber and cathode chamber (as shown in Figure 1). Each chamber was made of plexy glass bottle filled with solution of 200 ml. Both anode and cathode were made of aluminum wrapped with platinum on vulcan carbon cloth (fuellcellstore.com, USA). The anode had a working area of 63 cm^2. A Cation Exchange Membrane (CEM) (Nafion 117, Chemours, USA) was attached to separate anode and salinity chamber. An Anion Exchange Membrane (AEM) (Fumasep FAS-30, Fuma-tech, USA) was installed to separate salinity and cathode chamber. Platinum wires were mounted in the electrodes, used as current collectors. Temperature in the anode chamber was maintained at 37^0C using hot plate. The cathode chamber was continuously sparged with oxygen.

2.2 Inoculum and substrate

Inoculums were a mix cultures, generated from inactive Aerobic Granular Sludge (AGS) (Figure 2). Selective Pressure mechanism was done to ensure that mixed culture was dominated by *Geobacter sulfurreducens* species by doing inoculation in a sealed bottle with growth medium for specific *Geobacter sulfurreducens* (DSMZ medium No. 826, Germany) for 73 hours. The growth of the inoculum was monitored using Optical Density (OD 600) methods (Figure 2).

Anolyte was made of a mixture of substrate (glucose), 40 ml seed mix microorganisms, 140 ml *Geobacter sulfurreducens* (DSMZ medium No. 826, Germany), 10 ml trace element and 10 ml vitamin (which both referred to DSMZ medium 141, Germany). The addition of glucose was varied, the first phase was 201 mg/L (as COD) and the second phase was 2034 mg/L (as COD). Salinity (middle) chamber was filled with 200 ml demineralized water. Catholyte was consisted of 200 ml of phosphate buffer (50 mM).

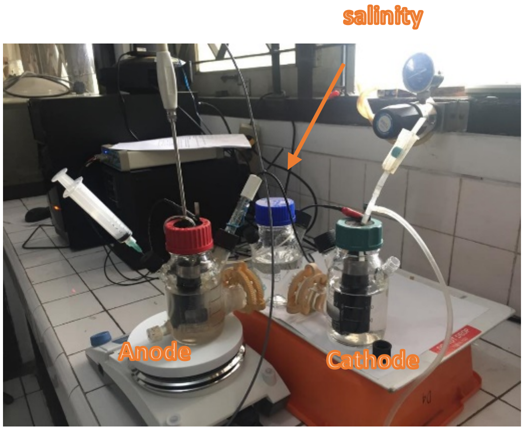
2.3 Operational Condition

The Microbial Salinity Cell (MSC) was operated using glucose as substrate, with two different concentrations: 201.2 mg/L (known as 1^{st} stage) and 2034 mg/L (known as 2^{nd} stage), analysed as COD. In the first stage, 201.2 mg/L glucose was used as substrate. Initial conductivity in the anode chamber was 15.09 mS/cm and the experiment was run for 6 days. In the second stage, after the MSC solution from the first stage was emptied, anode chamber was filled with new glucose-medium with a concentration of 2034 mg/L, salinity was 11 mS/cm and the experiment was run for 7 days. The MSC experiment was run as batch mode. During the experiment, the salinity increase was monitored in the salinity chamber along with the current and voltage.

2.4 Analysis and Calculation

The current dan voltage was observed using a potentiostat (Digi-IVY, Model DY 2023) or sometimes using a voltmeter (Hantek, 365), and recorded for every 100 s. The COD was measured using standard methods and the conductivity was measured using a conductivity meter (TES-1381). The optical density $(OD)_{600}$ was measured by scanning absorbance using a spectrophotometer at 600 nm.

Coulombic Efficiency (%CE) is defined as the fraction of electrons transferred to the anode among the total electron, released by substrate oxidation. %CE was calculated as in (Min & Logan, 2004). Salinity has derived by converting the conductivity value into salinity (ppt).



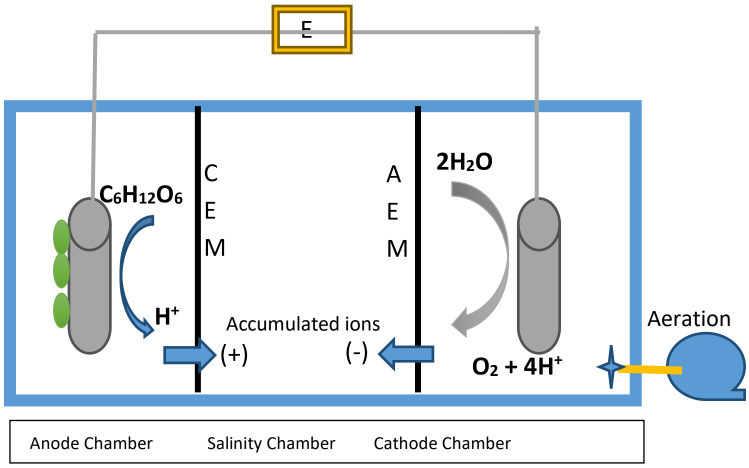


Figure 1. A reactor three chambers MSC (left) MSC scheme (right)

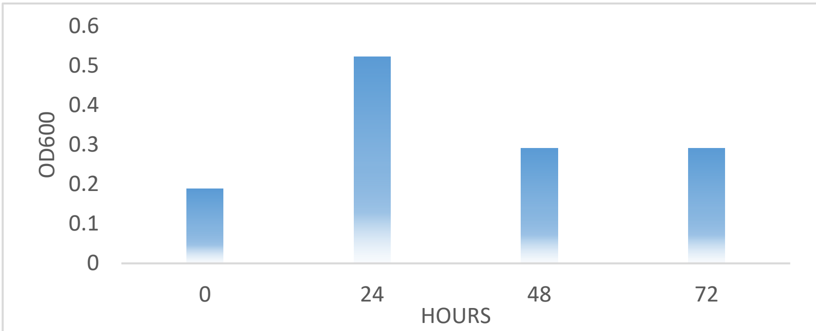


Figure 2. Inactive Aerobic Granular Sludge seed (left). Optical density of inoculum (at 72 h) before added to the MSC system (right).

3. RESULT AND DISCUSSION

3.1 MSC performance as a function of electricity generation: voltage and current response

In the first stage period, 201.2 mg/L glucose (concentration analysed as COD) was used as substrate. Initial conductivity in the anode chamber was 15.09 mS/cm and the experiment lasted for 5 days. The currents were recorded for every 100 s continuously for 6 days using a potentiometer (data were not shown), while voltage could only be recorded for 1 hour maximum because of technical limitation. The voltage profile only be recorded on day 1 and could not be recorded at day 6 because of the technical error from voltmeter, but judging from the currents data which did not show variation significantly, it also can be concluded that voltage will also do not variate significantly because normally currents were responded accordingly to voltage.

However, the Coulombic Efficiency (%CE) still can be calculated in this stage. Figure 3 shows the profile of voltage versus current density. Figure 3 shows that at the beginning, the voltage was 0.283 V and then dropped to 0.135 V while the currents could drop until $1.56 x 10^{-4}$ mA/m^2 but increase again for maximum 4.5 x10^{-4} mA/m^2. The graph pattern (only for currents) keep repeated during 6 days observation using a potentiostat (data are not shown). And the maximum current density achieved during stage 1 was 4.5 x10^{-4} mA/m^2, while the maximum voltage was 0.283 V. According to theoretical calculation using glucose as substrate, the maximum voltage reached in the system was 1.14V, thus in order to achieve the desirable voltage or current for practical purposes, the MSC should be stacked

(Aelterman, Rabaey, The Pham, Boon, & Verstraete, 2006). Compared to the theoretical calculation, the voltage and current produced in this study were still low, because of the wide distance between anode and cathode creates high over-potential of the system which inhibits the flows of the electron from anode to cathode (Fan, Hu, & Liu, 2007). Moreover, the low generation of both voltage and current (from Figure 3,4, and 5) can be also because of the energy that comes from the oxidation of glucose is used to drive the ions into salinity chamber rather than to produce electricity, the similar mechanism that also occurs in MDC system (Chen, Liang, Wei, Zhang, & Huang, 2012). To boost the capability of the anode to capture the electron from the system, polarization should be done. Unfortunately, because of the limitation of potentiostat model device, polarization was not possible to be done.

In the second stage, after the MSC solution from the first stage emptied, anode chamber was filled with new glucose-medium with concentration 2034 mg/L as COD, salinity was 11 mS/cm and experiment was run for 7 days. Because of the limitation ability of potentiometer to simultaneously measure current and voltage, for measuring voltage, another portable voltmeter was used (Hantex). Currents were continuously recorded for every 100 seconds, from day 1 to day 7 using a potentiometer (data are not all shown here). However, because the voltmeter could not observe currents for 24 hours continuously, the voltage was measured only for 1 hour at the beginning (day 1) and the ending of the cycle (day 7). Therefore, the data presented in Figure 4 and Figure 5 were data from day 1 and day 7 and only were measured for 1 hour, so that we could get a correlation between current and voltage.

Stage 2, with substrate concentration 2034 mg/L, at day 1 observation, the initial voltage was higher than at first stage. The maximum voltage was 0.44 V, with corresponding current density was 3.9 x 10^{-4} mA/m^2. However, the voltage then dropped at day 7 to a minimum of 0.15 but then raised again to 0.23 V, with corresponding current density was 0.29 mA/m^2. The average voltage during stage 2 was about 0.2 to 0.44 V, and the maximum current density was 0.29 mA/m^2 (in which 1000x higher than first stage). The rise of the current density and voltage was explainable, due to higher substrate concentration.

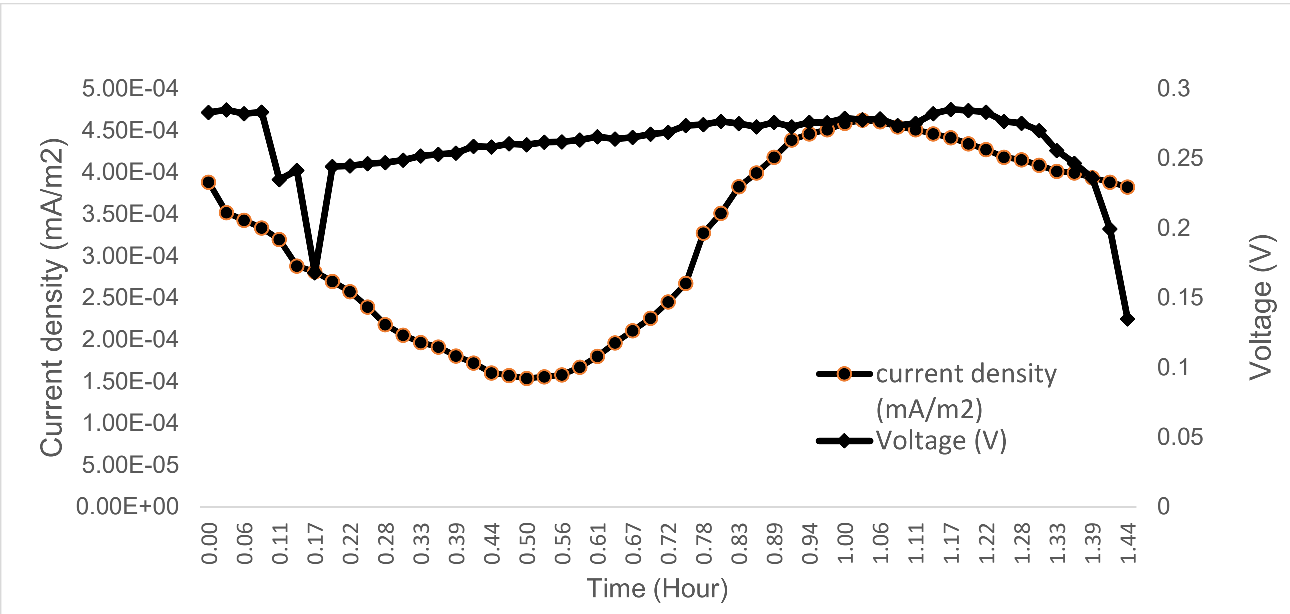


Figure 3. The voltage versus current density profile when the initial substrate concentration was 201.2 mg/L for day 1

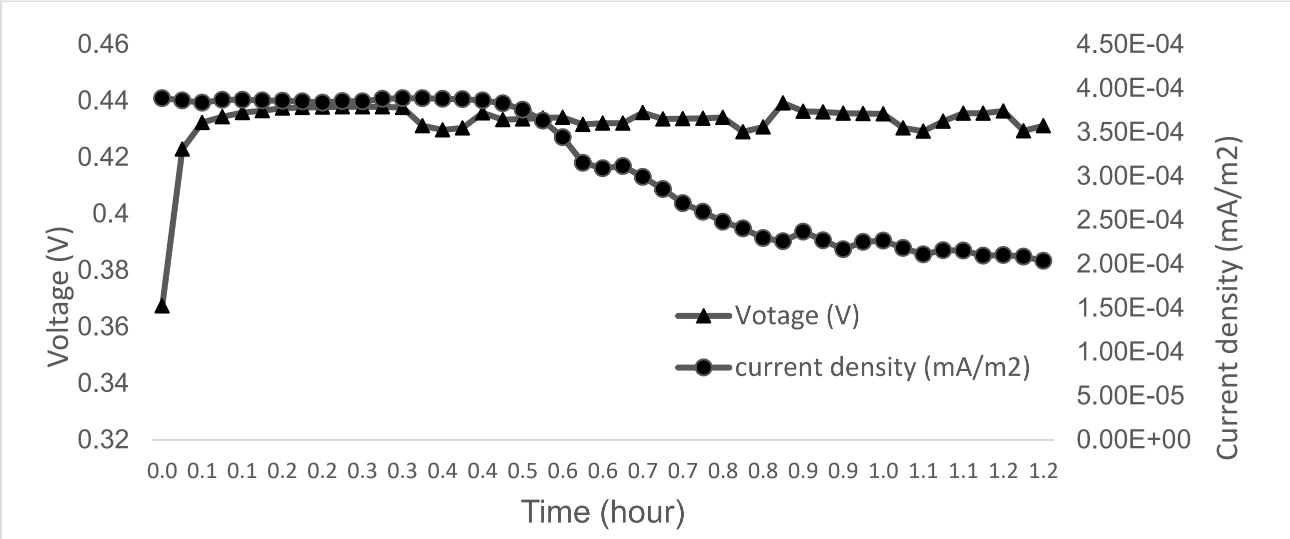


Figure 4. The voltage versus current density after MSC run for 1 day, when the initial substrate concentration 2034 mg/L (measured current and voltage continuously observed for 1 hour)

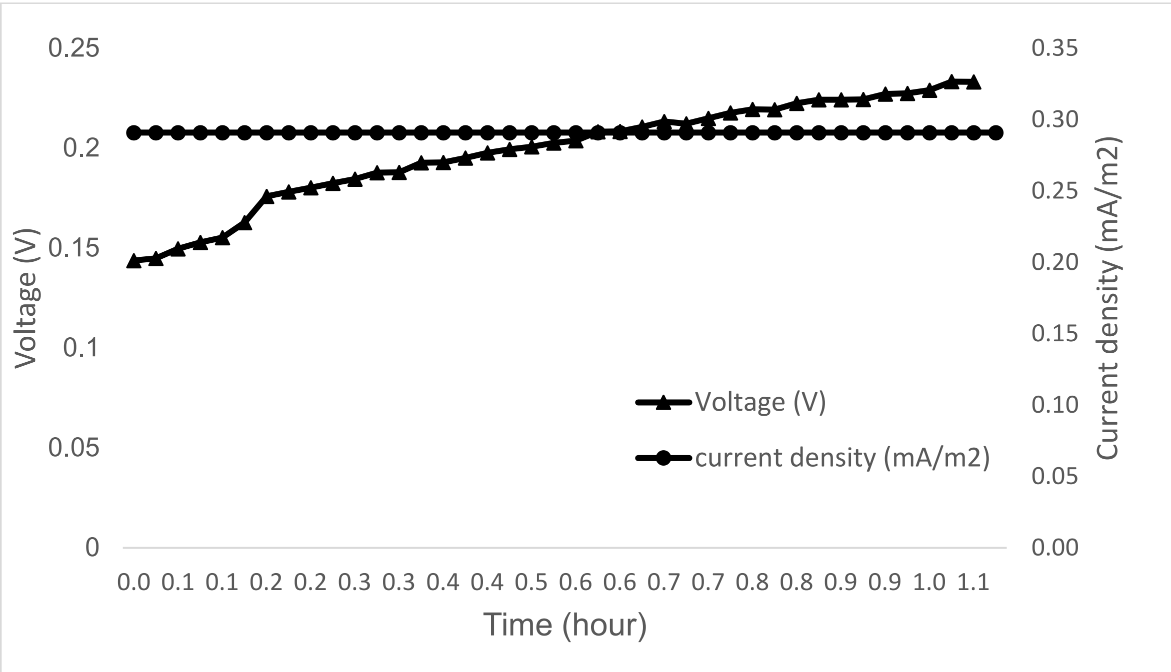


Figure 5. The voltage versus current density after MSC run for 7 day, with the initial substrate concentration 2034 mg/L (measured current and voltage continuously observed for 1 hour)

To measure the MSC performance, Coulombic Efficiency (written as %CE), was calculated as in Min & Logan, 2004. %CE was described as the ratio between electricity produced (as currents) versus substrate utilization (as COD). In stage 1, %CE was only 0.59% while in stage 2 %CE increased to 5.4%. These results showed that higher substrate concentration resulted in higher electricity produced per COD consumed. At low COD, the biofilm that consisted of different types of organisms compete for substrate (Jadhav & Ghangrekar, 2009). The heterotrophic microorganisms that have faster growth will outcompete slow growth microorganisms (such as G. *sulfurreducence* or any electroactive microorganism) (Logan & Regan, 2006). The limited electron donor also affected the type of microorganism that growing in the anode chamber (Santoro, Arbizzani, Erable, & Ieropoulos, 2017).

3.2 MSC performance in terms of substrate utilization and increasing conductivity in salinity chamber

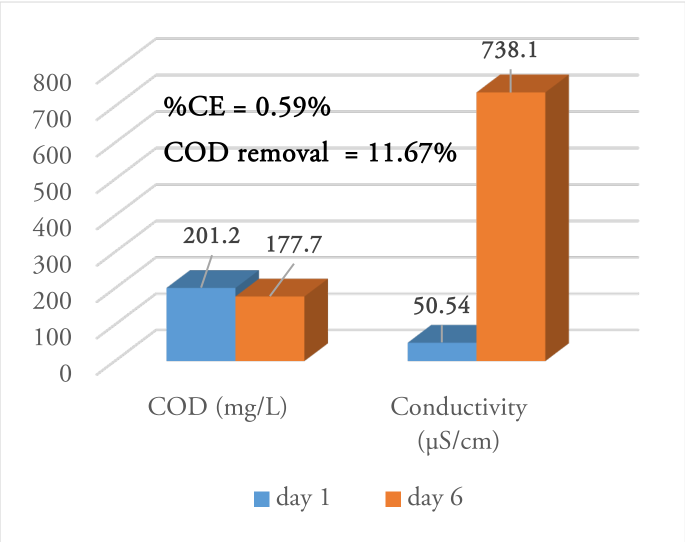


Figure 6. Substrate utilization versus conductivity increase in the first stage (when the initial substrate 201.2 mg/L)

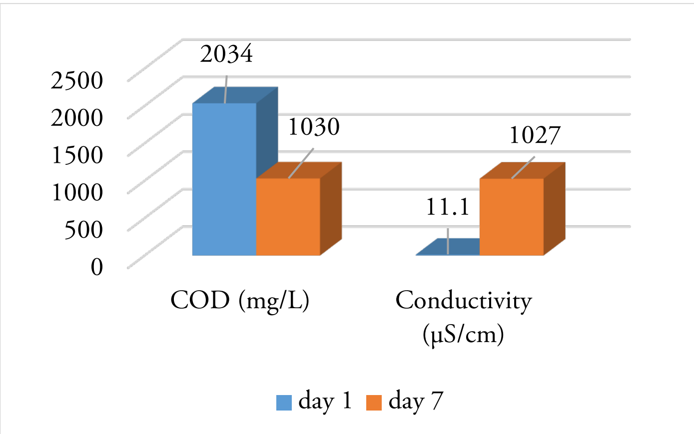


Figure 7. Substrate utilization versus conductivity increase in the second stage (when the initial substrate 2034 mg/L)

In this section, the effect of substrate utilization versus the amount of conductivity increase in the middle chamber was discussed. In stage 1, COD removal was 11.67% with corresponding conductivity increase in the salinity chamber was from 50.54 µS/cm to 738.1 µS/cm (equal to salinity = 0.36 ppt), and %CE was 0.59%. That means that the amount of substrate which can be converted into electricity was only 0.59%, the rest energy derived from the oxidation of organic substrate went for driving the ions from anode to salinity chamber, resulting in the increase of conductivity. In stage 2, COD removal was 49.36% with corresponding conductivity rise in the salinity chamber was from 11.2 µS/cm to 1027 µS/cm (salinity 0.57% ppt), and %CE was 5.4%. %CE gathered in this study was lower than (Zhang, Min, Huang, & Angelidaki, 2011), because of the relatively higher initial conductivity in the anode chamber that might be hindered microorganisms metabolism (Grattieri & Minteer, 2018). It can be concluded that the higher initial substrate concentration could lead to higher conductivity rise in the salinity chamber and the higher electricity generation. Higher COD means higher electron donor and energy, and could drive more salt ions from anode chamber into salinity chamber, and at the same time produce currents (Pant, Van Bogaert, Diels, & Vanbroekhoven, 2010).

4. CONCLUSION

This study showed that the performance of a three chambers Microbial Salinity Cell (MSC) was influenced by initial substrate concentration in the anode chamber. The best performance of MSC achieved when COD was 2034 mg/L, which simultaneously produced voltage of 0.44 V, current density of 0.29 mA/m^2 and %CE of 5.4%. Furthermore, conductivity concentration in the salinity chamber increased from 11.2 µS/cm to 1027 µS/cm (salinity 0.57% ppt). To improve the performance of MSC, anode polarization and shortened distance between anode and cathode should be done. For a more practical purpose of further full-scale application in order to achieve the desirable voltage or current, the MSC should be stacked.

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REFERENCES

Aelterman, P., Rabaey, K., The Pham, H., Boon, N., & Verstraete, W. (2006). Continuous electricity generation at high voltages and currents using stacked microbial fuel cells. *Communications in Agricultural and Applied Biological Sciences*, *71*(1), 63–66.

Aloui, F., Khoufi, S., Loukil, S., & Sayadi, S. (2009). Performances of an activated sludge process for the treatment of fish processing saline wastewater. *Desalination*, *246*(1–3), 389–396. https://doi.org/10.1016/j.desal.2008.03.062

Chen, X., Liang, P., Wei, Z., Zhang, X., & Huang, X. (2012). Sustainable water desalination and electricity generation in a separator coupled stacked microbial desalination cell with buffer free electrolyte circulation. *Bioresource Technology*, *119*, 88–93. https://doi.org/10.1016/j.biortech.2012.05.135

Fan, Y., Hu, H., & Liu, H. (2007). Enhanced Coulombic efficiency and power density of air-cathode microbial fuel cells with an improved cell configuration. *Journal of Power Sources*, *171*(2), 348–354. https://doi.org/10.1016/j.jpowsour.2007.06.220

Grattieri, M., & Minteer, S. D. (2018). Microbial fuel cells in saline and hypersaline environments: Advancements, challenges and future perspectives. *Bioelectrochemistry*, *120* (2018), 127–137.

Gude, V. G. (2016). Wastewater treatment in microbial fuel cells - An overview. *Journal of Cleaner Production*, *122*, 287–307. https://doi.org/10.1016/j.jclepro.2016.02.022

Jadhav, G. S., & Ghangrekar, M. M. (2009). Performance of microbial fuel cell subjected to variation in pH, temperature, external load and substrate concentration. *Bioresource Technology*, *100*(2), 717–723.

Kim, Y., & Logan, B. E. (2013). Simultaneous removal of organic matter and salt ions from saline wastewater in bioelectrochemical systems. *Desalination*, *308*, 115–121. https://doi.org/10.1016/j.desal.2012.07.031

Lefebvre, O., & Moletta, R. (2006). Treatment of organic pollution in industrial saline wastewater: A literature review. *Water Research*, *40*(20), 3671–3682. https://doi.org/10.1016/j.watres.2006.08.027

Lefebvre, O., Tan, Z., Kharkwal, S., & Ng, H. Y. (2012). Effect of increasing anodic NaCl concentration on microbial fuel cell performance. *Bioresource Technology*, *112*, 336–340. https://doi.org/10.1016/j.biortech.2012.02.048

Logan, B. E., & Regan, J. M. (2006). Electricity-producing bacterial communities in microbial fuel cells. *Trends in Microbiology*, *14*(12), 512–518. https://doi.org/10.1016/j.tim.2006.10.003

Mehanna, M., Kiely, P. D., Call, D. F., & Logan, B. E. (2010). Microbial electrodialysis cell for simultaneous water desalination and hydrogen gas production. *Environmental Science and Technology*, *44*(24), 9578–9583. https://doi.org/10.1021/es1025646

Min, B., & Logan, B. (2004). Continous Electricity Generation from DOmestic Wastewater and organic substrate in a flat Microbial Fuel Cell. *Environ. Sci. Technol.*, *38*(21), 5809–5814.

Pant, D., Van Bogaert, G., Diels, L., & Vanbroekhoven, K. (2010). A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production. *Bioresource Technology*, *101*(6), 1533–1543.

Qu, Y., Feng, Y., Wang, X., Liu, J., Lv, J., He, W., & Logan, B. E. (2012). Simultaneous water desalination and electricity generation in a microbial desalination cell with electrolyte recirculation for pH control. *Bioresource Technology*, *106*, 89–94. https://doi.org/10.1016/j.biortech.2011.11.045

Santoro, C., Arbizzani, C., Erable, B., & Ieropoulos, I. (2017). Microbial fuel cells: From fundamentals to applications. A review. *Journal of Power Sources*, *356*,225–244. https://doi.org/10.1016/j.jpowsour.2017.03.109

Zhang, Y., Min, B., Huang, L., & Angelidaki, I. (2011). Electricity generation and microbial community response to substrate changes in microbial fuel cell. *Bioresource Technology*, *102*(2), 1166–1173. https://doi.org/10.1016/j.biortech.2010.09.044.

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Full Scale Application of Integrated Upflow Anaerobic Filter (UAF) - Constructed Wetland (CWs) in Small Scale Batik Industry Wastewater Treatment

Novarina Irnaning Handayani[1*], Rustiana Yuliasni[1], Nanik Indah Setianingsih[1], Agung Budiarto[1]

[1]The Centre of Industrial Pollution Prevention Technology, Jalan Ki Mangunsarkoro No. 6, Semarang, Central Java

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Azo dyes

ABSTRACT

This research was aimed to evaluate the implementation of integrated Upflow Anaerobic Filter (UAF)-Constructed Wetlands (CWs) in real condition of wastewater treatment plant in batik small scale industry. The full-scale reactor consisted of equalization chamber with Hydraulic Retention Time (HRT) of 2 days; Upflow Anaerobic Filter (UAF) with HRT of 6 days, and Horizontal Subsurface Constructed Wetlands (HSSCWs) with HRT of 1.5 days. The UAF - CWs integrated technology was used to treat batik wastewater with Chemical Oxygen Demand (COD) inlet of 1339 – 2034 mg/L and pH of 9.0 – 9.4. This study showed that single UAF technology alone was able to reduced COD 56 – 78%, while the integration UAF–CWs technology improved the performance to 85% and reduced the pH into 7.5 – 7.8.

1. INTRODUCTION

Batik small scale industry discharges specific wastewater that contains paraffin, dyes (synthetic and natural dye), starch, and caustic soda. It makes the wastewater characteristic with a high load of COD and pH. The major pollutants of wastewater come from dyeing and paraffin removal process (Yuliasni et al., 2017). Recently, the commonly applied technology in small scale industry is coagulation-flocculation (Acquabella, 2006; Mehta, 2012; Rodrigues, Madeira, & Boaventura, 2012). However, the trouble of coagulation-flocculation process are their inability to meet the effluent standard requirement as well as still generates a high amount of toxic sludge. There are other alternative technologies in batik wastewater treatment at laboratory scale such as decolorization white root fungi (Subarno, 2007), membrane nanofiltration (Rashidi, Sulaiman, & Hashim, 2012), photocatalytic for decolorization and demineralization (Wan Mohd Khalik et al., 2015), and phytoremediation (Setiyono & Gustaman, 2017). However, due to still having many drawbacks such as durability, feasibility and effectiveness, those technologies are not quite familiar for full-scale application on treating high strength batik wastewater.

Many studies reported that one of the reasons for high concentration of COD batik or textile wastewater is of high amount azo dyes concentration that inhibits removal of COD biologically. Azo dyes are relatively non-biodegradable compounds but the double-azo linkage can be easily cut under anaerobic condition, transformed into

*Correspondence author. Tel. : +628112710098
E-mail : novarina947@gmail.com

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toxic aromatic amine. Toxic aromatic amine compounds are completely demineralized under aerobic condition. Demineralized aromatic amines are proven to be environmentally friendly. The combination of biological technology which involves anaerobic and aerobic organisms as catalysts for the oxidation-reduction reaction of azo dyes degradation can be an alternative to a more sustainable way of wastewater treatment technology. Therefore the development of this technology has gone rapidly (Beydilli & Pavlostathis, 2005; Himanshu, 2011; Van Der Zee & Villaverde, 2005) (Figure 1).

The combination of anaerobic-aerobic technology for biologically removing azo dyes in the form of unbiodegradable COD is an integrated technology Upflow Anaerobic Reactor (UAR)-Activated Sludge (AS). Integration technology of UAR-AS has been tried in the laboratory scale to treat batik wastewater without chemical pretreatment and could remove COD in wastewater up to 74.98 – 91.66% % (Yuliasni et al., 2017). Thus, the idea of this study is to combine the Upflow Anaerobic Filter (UAF) - Wetland in a full-scale application and to evaluate its use. Upflow Anaerobic Filter (UAF) is an anaerobic reactor that contains baffle and filter technology to create physical (depositional) and biological mechanism. Water-resistant compartments contain several layers of submerged media, become settlement surface area for bacteria. Wastewater flow in anaerobic filter reactors is from the bottom up (up-flow), aiming to make contact between wastewater and biomass in the filter to increase anaerobic degradation (Morel and Diener 2006). For Aerobic, the utilization of Horizontal Subsurface wetland system (Wetland) can not only oxidize azo dyes but also other organic pollutants such as COD, Ammonia and phosphorous (Geovana et al., 2016).

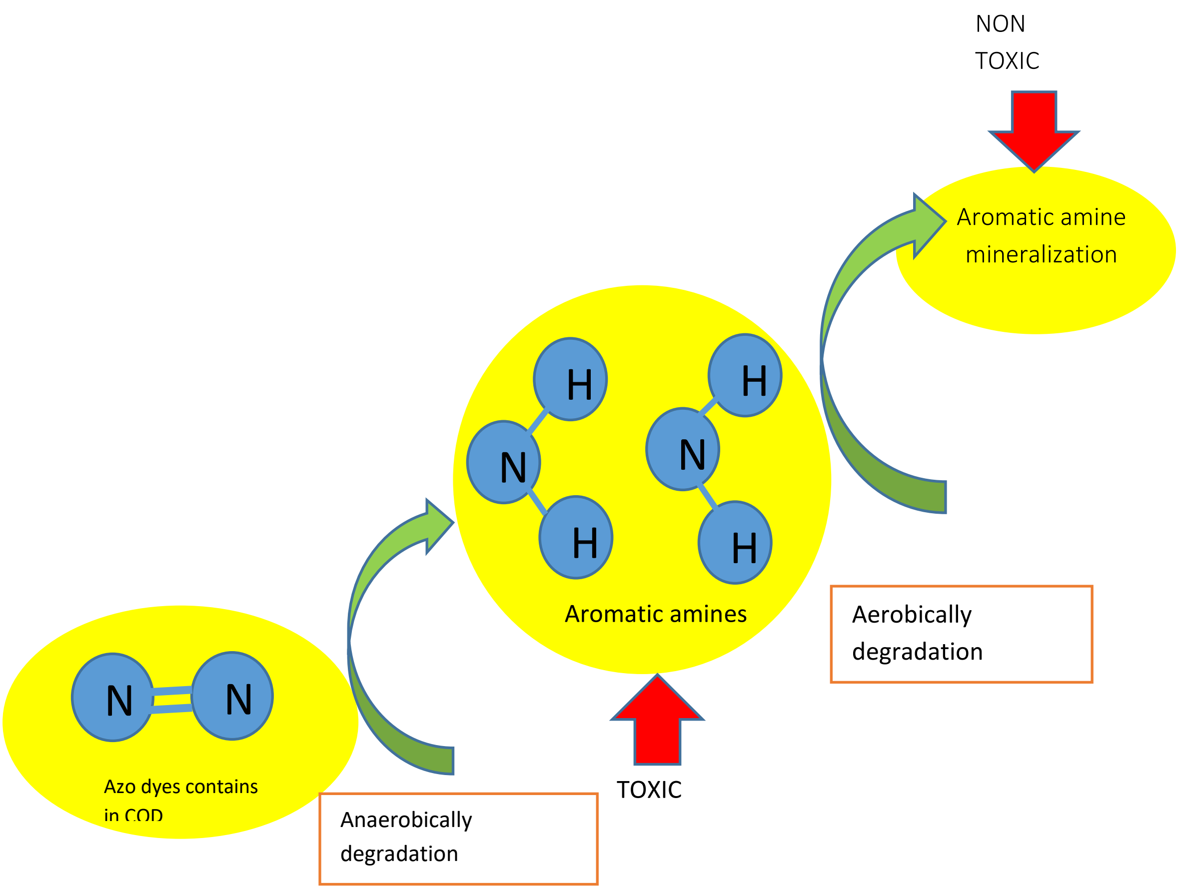

Figure 1. An illustration of biologically azo dyes removal that contained in COD

Constructed wetland is a complex system that includes natural treatment, sedimentation, filtration, gas transfer, adsorption, chemical and biological processing activities, due to microorganism activity in soil and plant activities. Soil, rock, or gravel media provide a surface for attaching microorganisms, contribute to macrophytic growth, and also as a filtration media and contaminant absorber (Alireza Valipour & Ahn, 2016). Rhizomes and roots will provide substrate for bacteria that attach and aerated the root area, and absorb Nitrogen (N), Phosphorus (P) pollutants taken through the root epidermis and vascular, and then transported up to the stems and leaves (A Valipour, Azizi, Raman, Jamshidi, & Hamnabard, 2014). Horizontal Subsurface Constructed Wetland (HSSCWs) was used in this study because of its robust construction and low operational cost (Leady, 1997). Heliconia, Typha, Papyrus were used as plant in this study because of their effectiveness to remove pollutant, their compatibility to the tropical weather and their aesthetical look (Sandoval, Zamora-Castro, Vidal-Álvarez, & Marín-Muñiz, 2019; Vymazal, 2013).

This study aims to evaluate the performance and effectiveness of COD and pH reduction in the application of the combined Upflow Anaerobic Filter (UAF) technology followed by Constructed Wetlands (CWs) using *Heliconia sp, Typha latifolia,* and *Cyperus papyrus* plants in real conditions in the wastewater treatment plant at a small batik industry.

2. MATERIAL AND METHODS

2.1 Material

Batik wastewater, with characteristic written in Table 1, was used. Upflow Anaerobic Filter (UAF) was made of concrete bricks. The liquid capacity was 24 m^3. Overall volume was divided into 6 equal compartments. Honeycomb filters made of plastics were attached inside of the compartment no.2 to compartment no.5, while compartment no.1 and no.6 were only chambers with no filter in it. All compartments were filled with microorganisms seed (sludge). Microorganisms seed was derived from anaerobic mix cultures from the tofu industry. The addition of the initial seed was 30% of total volume of the UAF reactor. Sugar, Starch and micronutrient were used to ensure the development of anaerobic mix cultures in the UAF (see Figure 2 (A) chamber B1 to B6).

Constructed Wetlands (CWs) model was referred to Horizontal Subsurface Constructed Wetlands (HSSCWs) model. Typha *(Typha Latifolia)*, Papirus *(Cyperus papirus)*, dan Heliconia *(Heliconia sp)* were used. CWs was also made of concrete bricks. Gravels with gradual size in diameters were filled in it. Gavels volume occupied 65% of the total volume of CWs. (See Figure 2 (A), chamber C1 and C2).

Batik wastewater inlets were collected in two periods, first period was collected when the industry generated high strength wastewater (referred as Sampling 1 in Table 1), the second period was collected when industry generated low strength wastewater (referred as Sampling 2 in Table 1).

Tabel 1. Batik Wastewater Characteristics

No	Parameter	Unit	Sampling 1	Sampling 2
1	Temperature	°C	29,0	29,0
2	TSS	mg/L	2461	815,0
3	BOD_5	mg/L	1105	762,5
4	COD	mg/L	7858	4466
5	Phenol	mg/L	0,058	0,022
6	Crom	mg/L	<0,010	<0,010
7	Amonia	mg/L	1.725	1,125
8	Sulfide (S^{2-})	mg/L	5,030	3,520
9	Fat and Grease	mg/L	2,50	1,40
10	MBAS	mg/L	0,383	0,185
11	pH	-	9,1	8,5

2.3 Methods

2.3.1. Reactor construction

The full scale reactor consisted of equalization chamber (Dimension = : 4.0 m; W: 2.0 m; H: 1.0 m, designed HRT: 2 days), UAF (Dimension: L: 7.5 m (6 compartements total) x W: 1.0 m; H: 3.85, HRT 6 days), HSSCW compartement 1 dimension L:7.10m; W: 1.00 m: H: 1.00); HSSCW compartement 2 dimension L: 8.25 m; W: 0.8 m: H: 1.00 m). The reactor scheme is shown in Figure 2.

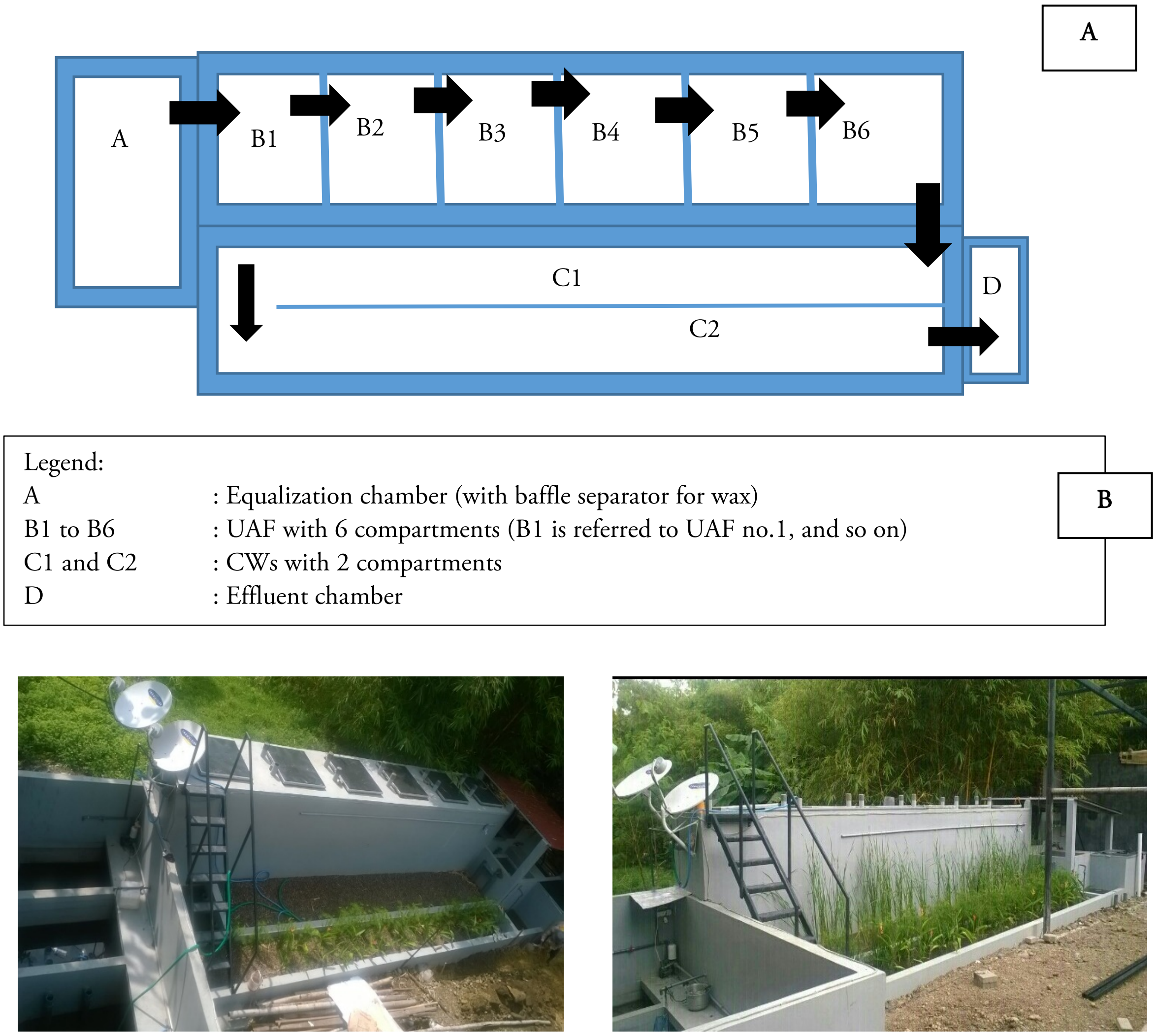

Figure 2. Scheme diagram (A) and real image (B) of full-scale integrated UAF-CW technology

2.3.2 Operational condition

There were 3 stages have been done, namely seeding, acclimatization and continue application. Seeding was done by adding anaerobic mix cultured seed derived from tofu WWTP to occupy 30% of total UAF volume, while 70% was occupied by water. Starch, sugar and micronutrient were added and then UAF was left for 7 days. During that time, pH, and gas formation were monitored. Afterwards, the acclimatization stage was done by adding batik wastewater with gradual concentration 30%, 50%, 70%, 85%, and 100%. In theacclimatization stage, pH, COD inlet and outlet were monitored. Lastly, for continue application, 100% of wastewater was added continuously. Complete textile wastewater standard parameters were analyzed (i.e: BOD, COD, pH, temperature, ammonia, sulfide, total chrom, color and oil and grease).

2.3.3 Evaluation of wastewater treatment plant performance

Evaluation conducted by observing the performance of the system consisting of equalization unit, anaerobic units, and wetland in COD degradation and pH condition. After each unit works optimally, the performance of all existing units were observed. The calculation performance of the technology using equation:

$$\{(Ci - Ce)/Ci\}*100\%$$

Ci : influent/inlet concentration
Ce : effluent/outlet concentration

2.3.4 Analysis

Complete textile wastewater standard parameters were analyzed using the methodology described in Standard Methods (SM) for the Examination of Water and Waste Water (APHA) and SNI (Standar Nasional Indonesia) : COD (APHA 23nd, 5220 D), BOD_5 (APHA 22nd, 5210 B), TSS (APHA 22nd, 2540 A.D), oil and grease (APHA 22nd, 5520 A,C), Cr total (APHA 22nd, 3111 B), phenol (APHA 22nd 5330 B, C, D), ammonia (APHA 22nd 4500 NH_3), sulfide (APHA 22nd, 4500 S^{2-}) temperature (SNI 06-6989.23-2005) and pH (SNI 06-6989.11.2004).

3. RESULT AND DISCUSSION

Batik wastewater is mainly containing of wax and azo dyes that would completely biodegradable using the combination of anaerobic-aerobic technology (Yuliasni et al., 2017). Thus, in this study, the integrated technology that consists of Upflow Anaerobic Filter (UAF) - Constructed wetland (CWs) was used. In UAF chamber, most biological organic, either biodegradable or recalcitrant, would be anaerobically reduced. Double-bond azo would be cut into aromatic amines single bond, then mineralized by aerobic microorganisms that plenty occurred in CWs (Beydilli & Pavlostathis, 2005; Van Der Zee & Villaverde, 2005; Yemashov a & Kalyuzhnyi, 2006).

As also shown in Figure 2, raw wastewater was collected in the equalization chamber with retention time (HRT) of 1 day. In the equalization chamber, the soluble organic (soluble COD) and insoluble organic (wax) were separated using a baffle. Insoluble organic such as wax was collected in another chamber and soluble organic wastewater was pumped from the equalization chamber into UAF chamber. UAF was consisted of pipe that planted vertically inside of the chamber and was used upflow model as in (Chowdhury, Viraraghavan, & Srinivasan, 2010) to allow liquid equally distributed inside the chambers. UAF was consisted of 6 compartments with filters, to allow a plug flow flowrate and to achieve a long solid retention time (SRT) (Drtil, Bod, & Herdov, 2002).

3.1 The performance of Upflow Anaerobic Filter

Due to the utilization of anaerobic microorganisms and the high strength COD concentration of influent wastewater (COD: 1000 - 2300 mg/L) and also high pH (pH > 9), to boost and maintain the growth of microorganism, three stages were done namely: seeding, acclimatization and continuous application.

3.2 Seeding

In this research seeding process is carried out by adding anaerobic microbes of 1200 kg (to reach 30% of the building height) each compartment in the UAF unit. The UAF unit consists of 6 compartments with each volume 4 m^3. Microorganisms were added with 300 mg/L sugar nutrient and clean water until the reactor was full and observed the emergence of gas bubbles as a visual indicator of the formation of hydrogen or methane gas resulted from the anaerobic bacteria metabolic process.

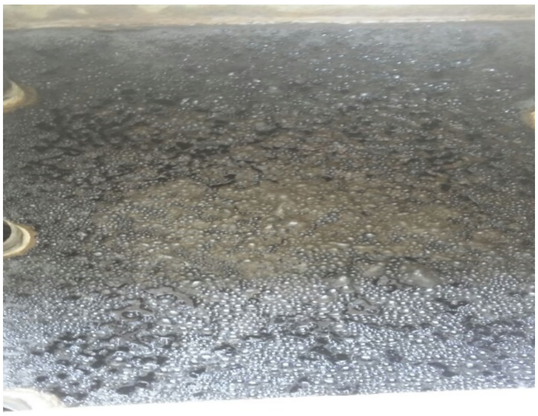

Figure 3. Microbial visual activity observation

3.3 Acclimatization

The acclimatization process was carried out by feeding wastewater at a certain concentration which is gradually increased to each compartment in batch system. The concentration of wastewater fed to UAF unit starts from concentration of 30% (wastewater: clean water ratio = 30:70); 50%; 70%; 85% and 100%. Because of the variation of the wastewater inlet, the gradual increase of COD concentration was not achieved. The COD inlet increased gradually at 30% to 75%, but because of the change of the production process of batik wastewater, at 85% and 100%, the inlet COD were lower than usual value. For each concentration, the wastewater was allowed to stand for 6 days for microbial adaptation to the concentration of wastewater. As an additional carbon source, sugar and starch of 125 mg/L were added. To evaluate the results of the acclimatization process, dissolved COD and pH parameters were observed. Sampling for dissolved COD and pH was carried out only in compartment 1, assuming the compartment 1 condition was representative of the other 5 compartments. The results of the acclimatization process are presented in Figure 4.

As shown in Figure 4, the COD inlet (day 0) initially was around 375 mg/L. There was no significant decrease in COD in the variation at 30% and 50% concentration of wastewater. This condition was probably due to microbes in initial stages of acclimatization were not fully active yet. When wastewater concentrations were increased at 70% and 85% (COD 623.7 and 395 mg/L), COD degradation reached on 58.8% and 45.7%, respectively, indicate that microbes were already active and degrade pollutants. However, when wastewater concentration increased at 100%, with COD value of only about 275.5 mg/L, the efficiency of COD reduction decreased only 15%, with visual observations that there was reducing of active microbes. To ensure that microbes did not collapse, MLSS analysis was performed in UAF reactor with a result of 448 mg/L.

3.4 Continous UAF operation

The next stage was the continuous UAF reactor operation carried out by feeding wastewater from equalization tank 1.5 m^3 for 2 hours per day (Q = 12 L/min). Nutrient of sugar and starch 125 mg/L respectively were also added to help lower the pH due to the ability of sugar and starch to anaerobically produce VFA that slightly acidic (Feijoo, Soto, Mndez, & Lema, 1995). Observation was carried out every day for 17 days, with observed parameters were COD and pH. All samples were analyzed once. pH was also observed because ph inlet is too high and high pH was regarded as inhibition factor for the growth of both anaerobic and aerobic microorganisms (Jung, Lee, Shin, & Chung, 2000). The result of observation can be seen in Figure 5.

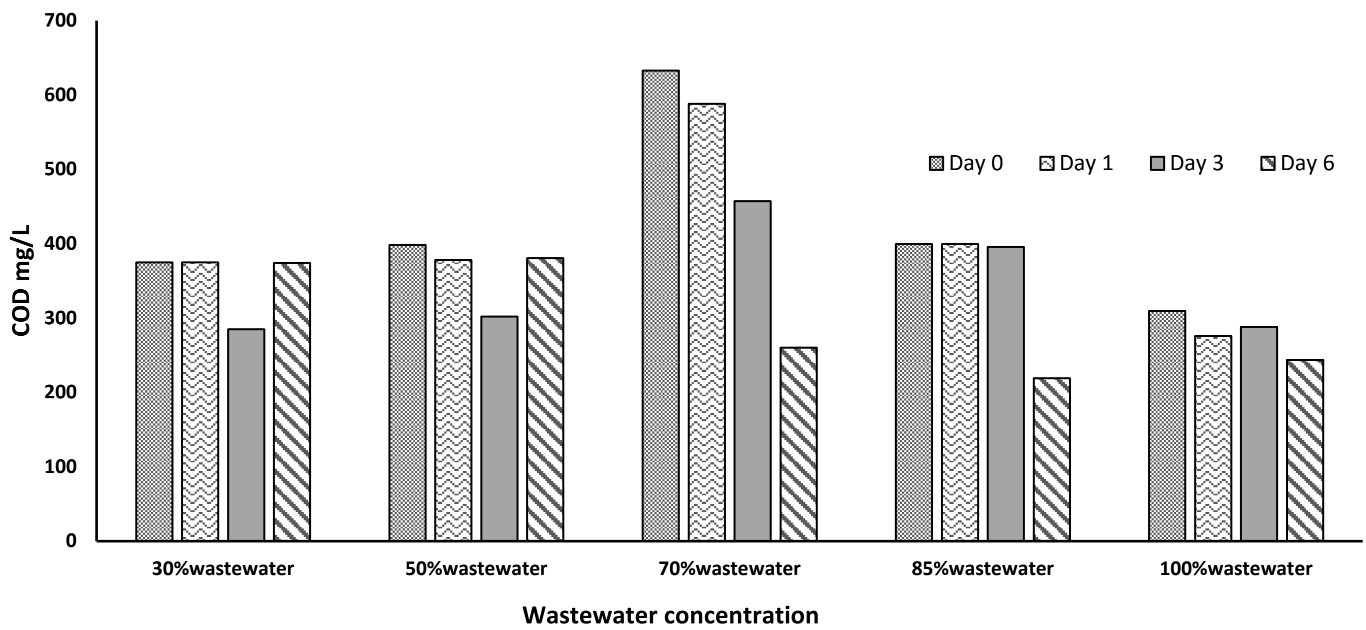

Figure 4. COD degradation profile in the acclimatization process

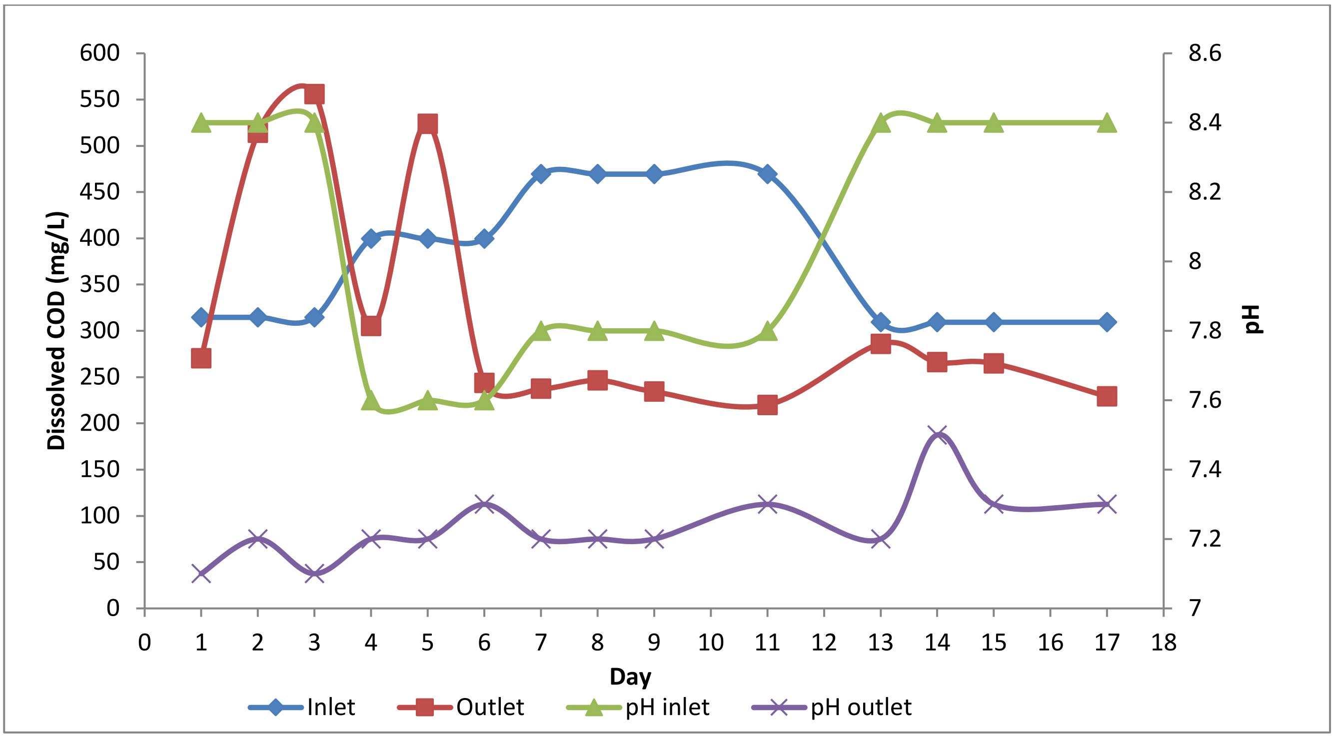

Figure 5. Soluble COD and pH profile in UAF

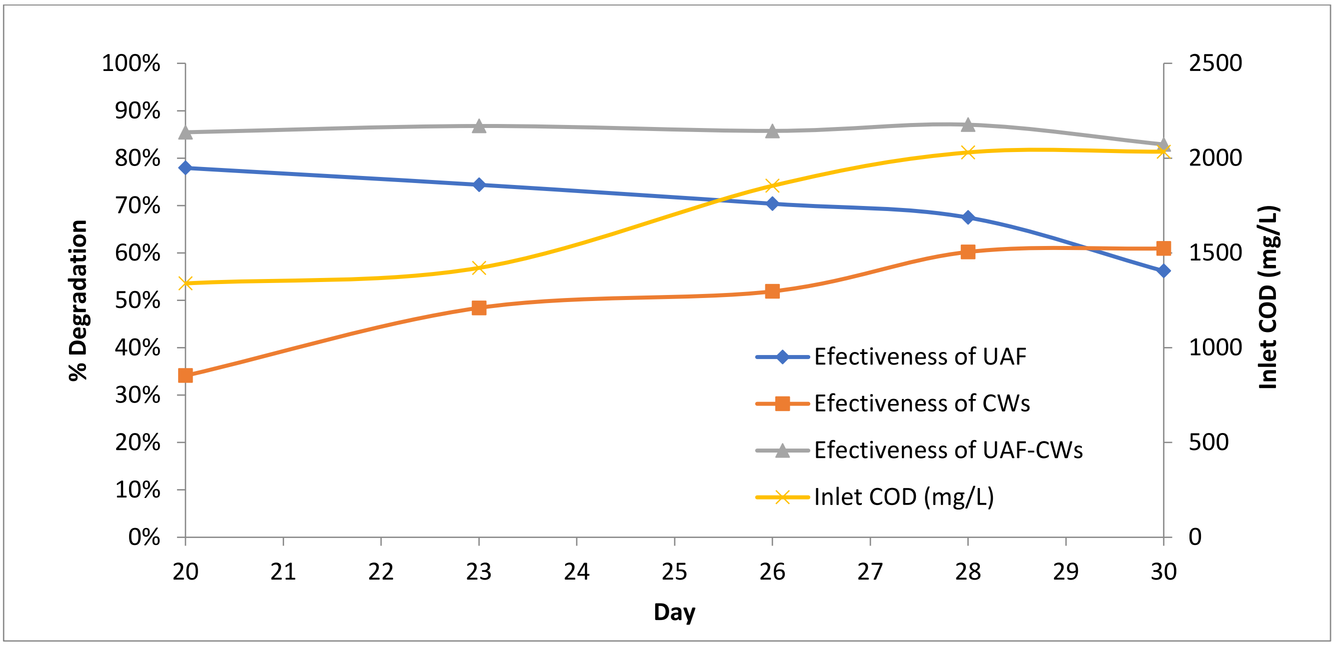

Figure 6. Effectiveness in UAF, Costructed Wetlands (CWs) dan UAF-CWs

Figure 4 shows that COD inlet ranges from 300 - 469 mg/L. COD outlet fluctuate in the first 6 days, even COD outlet tends to be higher than COD inlet. However after day 6 to day 17, COD outlet tends to be stable in the range of 220 - 280 mg / L. pH inlet tends to fluctuate in the range of 7.6 - 8.4, but pH outlet tends to be stable in the range of 7.1 - 7.5. This phenomena proved that the system could lower the pH. Furthermore, decreased pH can also be an indication of degradation process in UAF, which in VFA's were present as a reduction/ degradation products of complex organics pollutant, in this case, COD that contains in azo dyes.

3.5 The performance of integrated UAF – CW technology

Performance of UAF unit and wetland observed starting from day 20. The observation was conducted in 10 days continuous operation reactor, and the observed parameters were COD and pH with periodically sampling period. The observations are presented in Figure 6.

In the observation performance of combined UAF-CW, inlet COD values range from 1339 to 2034 mg/L. Average percentage COD reduction in the UAF system is 69.26% while in CWs system is 51.1%. pH inlet is high, ranging from 9.0 - 9.4, outlet pH from UAF system is between 7.4 - 8.1 and from the CWs system is between 7.5-7.8. Although the effectiveness in UAF reactor tends to decrease, the effectiveness in wetland unit tends to increase, so that effectiveness in the combined UAF-wetland tends to be stable at around 85%. Figure 7 is presented to observe the visual effect of the degradation of COD in the system in line with data in Figure 6. The intensity of the color and turbidity were gradually decreased, from inlet to the wetland outlet, which also an indication of azo dyes degradation/ removal (measured as COD).

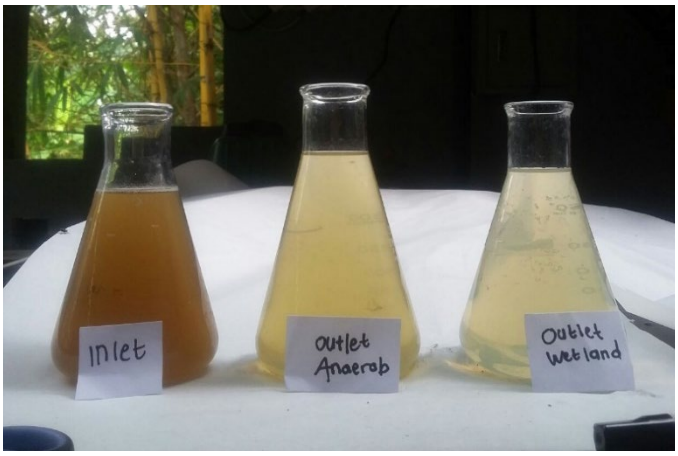

Figure 7. Visual of wastewater from inlet, UAF, and wetland

4. CONCLUSION

Complex unbiodegradable organics pollutant contains in batik wastewater could be biologically degraded by the combination of the technology UAF and CWs (HSSCW). UAF technology can anaerobically degrade organic pollutant, and at the same time lowering the pH. CWs can aerobically complete the biological degradation. The combination technology can be an alternative for full-scale application for treating batik wastewater.

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REFERENCES

Acquabella. (2006). Coagulation and Flocculation Process Fundamentals, 199–206.

APHA, AWWA. WEF.(2012)." *Standard methods for the examination of water and wastewater* 22nd (2012).

Beydilli, M. I., & Pavlostathis, S. G. (2005). Decolorization kinetics of the azo dye Reactive Red 2 under methanogenic conditions: Effect of long-term culture acclimation. *Biodegradation*, *16*(2), 135–146. https://doi.org/10.1007/s10532-004-4875-y

Chowdhury, P., Viraraghavan, T., & Srinivasan, A. (2010). Biological treatment processes for fish processing wastewater - A review. *Bioresource Technology*, *101*(2), 439–449. https://doi.org/10.1016/j.biortech.2009.08.065

Drtil, M., Bod, I., & Herdov, B. (2002). The use of upflow anaerobic filter and AnSBR for wastewater treatment at ambient temperature, *36*, 1084–1088.

Feijoo, G., Soto, M., M??ndez, R., & Lema, J. M. (1995). Sodium inhibition in the anaerobic digestion process: Antagonism and adaptation phenomena. *Enzyme and Microbial Technology*, *17*(2), 180–188. https://doi.org/10.1016/0141-0229(94)00011-F

Geovana, P. G., Dinara, G. A., Marcos, F. J., Alexandre, L. N., Camila, F. de P., Leonardo, D. B. da S., & Antônio, C. F. de M. (2016). Removal of nitrogen and phosphorus from cattle farming wastewater using constructed wetland system. *African Journal of Agricultural Research*, *11*(44), 4542–4550. https://doi.org/10.5897/AJAR2016.11425

Himanshu, B. (2011). Bacterial degradation of Azo Dyes and its derivatives. *Thesis PhD, Saurashtra University*.

Jung, J.-Y., Lee, S.-M., Shin, P.-K., & Chung, Y.-C. (2000). Effect of pH on phase separated anaerobic digestion. *Biotechnology and Bioprocess Engineering*, *5*(6), 456–459. https://doi.org/10.1007/BF02931947

Leady, B., 1997, Constructed Subsurface Flow Wetlands For Wastewater Treatment, Purdue University.

Mehta, P. (2012). Treating textile effluents by coagulation - flocculation method using different dosing compositions, *3*(4), 2514–2517.

Rashidi, H. R., Sulaiman, N. M. N., & Hashim, N. A. (2012). Batik Industry Synthetic Wastewater Treatment Using Nanofiltration Membrane. *Procedia Engineering*, *44*, 2010–2012. https://doi.org/10.1016/j.proeng.2012.09.025

Rodrigues, C. S. D., Madeira, L. M., & Boaventura, R. a. R. (2012). Treatment of textile dye wastewaters using ferrous sulphate in a chemical coagulation/flocculation process. *Environmental Technology*, (May 2015), 1–11. https://doi.org/10.1080/09593330.2012.715679

Sandoval, L., Zamora-Castro, S., Vidal-Álvarez, M., & Marín-Muñiz, J. (2019). Role of Wetland Plants and Use of Ornamental Flowering Plants in Constructed Wetlands for Wastewater Treatment: A Review. *Applied Sciences*, *9*(4), 685. https://doi.org/10.3390/app9040685

Setiyono, A., & Gustaman, R. A. (2017). PENGENDALIAN KROMIUM (CR) YANG TERDAPAT DI LIMBAH BATIK DENGAN METODE FITOREMEDIASI. *Unnes Journal of Public Health*, *6*(3), 155. https://doi.org/10.15294/ujph.v6i3.15754

Subarno, S. (2007). Dekolorisasi Limbah Pabrik Cair Industri Tekstil dengan Miselium omphalina SP. A-1 Amobil. *Dinamika Kerajinan Dan Batik: Majalah Ilmiah*. https://doi.org/10.22322/DKB.V24I1.999

Valipour, A, Azizi, S., Raman, V. K., Jamshidi, S., & Hamnabard, N. (2014). The Comparative Evaluation of the Performance of Two Phytoremediation Systems for Domestic Wastewater Treatment. *Journal of Environmental Science & Engineering*, *56*(3), 319–26. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/26563084

Valipour, Alireza, & Ahn, Y. H. (2016). Constructed wetlands as sustainable ecotechnologies in decentralization practices: a review. *Environmental Science and Pollution Research*, *23*(1), 180–197. https://doi.org/10.1007/s11356-015-5713-y

Van Der Zee, F. P., & Villaverde, S. (2005). Combined anaerobic-aerobic treatment of azo dyes - A short review of bioreactor studies. *Water Research*, *39*(8), 1425–1440. https://doi.org/10.1016/j.watres.2005.03.007

Vymazal, J. (2013). Emergent plants used in free water surface constructed wetlands: A review. *Ecological Engineering*, *61*, 582–592. https://doi.org/10.1016/j.ecoleng.2013.06.023

Wan Mohd Khalik, W. F., Ho, L.-N., Ong, S.-A., Wong, Y., NIK YUSOFF, N. I. K. N. A., & Ridwan, F. (2015). Decolorization and Mineralization of Batik Wastewater through Solar Photocatalytic Process. *Sains Malaysiana*, *44*, 607–612. https://doi.org/10.17576/jsm-2015-4404-16

Yemashova, N., & Kalyuzhnyi, S. (2006). Microbial conversion of selected azo dyes and their breakdown products. *Water Science and Technology*, *53*(11), 163–171. https://doi.org/10.2166/wst.2006.349.

Yuliasni, R., Setyaningsih, N. I., Handayani, N. I., & Budiarto, A. (2017). The performance of combined technology Upflow anaerobic reactor (UAR)-activated sludge (AS) for treating batik wastewater. *Advanced Science Letters*, *23*(3), 2246–2250. https://doi.org/10.1166/asl.2017.8725

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DOAS Calibration Technique for SO_2 Emission Measurement Based on H_2SO_4 and Na_2SO_3 Reaction

Januar Arif Fatkhurrahman[1,2*], Ikha Rasti Julia Sari[2], Yose Andriani[2], Moh Syarif Romadhon[2,3], Nur Zen[2], Adi Prasetio[2], Ali Murtopo Simbolon[2,4]

[1]Environmental Engineering, Institut Teknologi Bandung, Jalan Ganesha 10, Bandung

[2]The Centre of Industrial Pollution Prevention Technology, Jalan Ki Mangunsarkoro No. 6, Semarang, Central Java

[3] Atmospheric, Oceanic and Planetary Physics Department, University of Oxford

[4]Departement of Environmental Engineering, Diponegoro University, Jl. Prof. H. Soedarto, S.H, Tembalang, Semarang

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ABSTRACT

The coal used as a primary fuel in an Indonesian power plant produces sulfur dioxide emission from its burning process. Several testing and monitoring methods developed, from laboratory analysis, CEMs based instrument, and absorption spectroscopy method developed for this purpose. Differential Optical Absorption Spectroscopy (DOAS) method based on Lambert-Beer law used as emission quantification. DOAS instrumentation developed in this research to measure sulfur dioxide as one of the emission parameters. Sulfur dioxide generated from the reaction between the sulfuric acid and dilute sodium sulfite. CCD spectrometer used to measure sulfur dioxide spectrum intensity at 260 to 350 nm absorption cross-section. There is a high correlation between sulfur dioxide gas produced by that reaction to spectrum intensity, with coefficient determination (r^2) 0.978, 0.982, 0.987, 0.993 or coefficient correlation (r) 0.989, 0.991, 0.993, and 0.996 from lowest range concentration to highest range concentration. Precision analysis from gas calibration standard using Horwitz ratio indicates instrument setup precise enough with 0.504 Horwitz ratio, according to its acceptable range. The suspended particulate matter may interfere with UV penetration into CCD detector in emission simulation test using gasoline generator exhaust that causes 2.5 times deviation error between typical 800 ppm concentrated sulfur dioxide from chemical reaction and gasoline generator exhaust.

1. INTRODUCTION

Several power plants in Indonesia use coal as the primary fuel for power generation. As coal burned for generating steam, it releases a massive amount of emission into the atmosphere. Sulfur dioxide was a significant emission pollutant that releases as coal burned in the power plant industry (Lin et al., 2018). Different coal types contain different sulfur content. Low-sulfur coal contains less than 1% sulfur, and medium sulfur will have approximately 1% to 3% sulfur content. High-sulfur coal will have more than 3% sulfur content (Chou, 2012). By 2020, power plants in Indonesia will use more than 200 million tons of coal per year and increase continuously year by year progressively based on ministry of energy data on 2019. It will impact on sulfur dioxide emission escalation in

*Correspondence author. Tel. : +62816655080
E-mail : januarfa@gmail.com@gmail.com

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the atmosphere. Sulfur dioxide pollution can address the damaging effect on human health like respiratory problems and cardiovascular (Shepherd, Haynatzki, Rautiainen, & Achutan, 2015). It also develops acid rain in the environment (Sudalma, Purwanto, & Santoso, 2015; Wang, Xing, Zeng, Ding, & Chen, 2005). It increases the acidity of the soil lead to soil microbial activity degeneration (Mohajan, 2019). It also affects the dissolution of limestone in wall building lead to integrity losses of the wall.

Regulation of Ministry of Environment Number 21 of 2008 limits sulfur dioxide below 750 mg/Nm^3 before safely released into the atmosphere. To fulfill this regulation, the coal power plant uses a testing laboratory to measure air quality releases into the atmosphere by using a stack sampling method. It is an accurate method based on chemical absorption reagent (US EPA, 2017). This data hardly to be evaluated as a continuous emission profile from the coal power plant. Another coal power plant might have a continuous emission monitoring system (CEMs) to monitor its emission based on electrochemiluminescence or non-dispersive infrared (NDIR) instrument. At the same time, it can be an expensive application as high as USD 90000 per unit installed (Clapsaddle, 2002).

In this research, we arrange an experimental design of sulfur dioxide emission measurement based on differential optical absorption spectroscopy (DOAS), produced sulfur dioxide from sulfuric acid, and sodium sulfite reaction used as calibration. Typically, DOAS is a method to determine concentrations of trace gases by measuring their specific narrow band absorption structures in the UV and visible spectral region (Platt & Perner, 1983). Generally DOAS instrument following Lambert-Beer Law in absorption spectroscopy, it states that the radiant intensity traversing a homogeneous medium decreases exponentially with the product of the extinction coefficient and the path length (Furukawa & Fukuda, 2012),(Mellqvist & Rosén, 1996), in the mathematic formula we can describe as below;

$$I(\lambda) = I_0 e^{\left(-\sum_{j=1}^{n} S^j(\lambda) C_j\right)} \quad \ldots\ldots (1)$$

Where;

I_0 : spectrum intensity without air contaminant

I : measured spectrum intensity in existing air contaminant

Sj : absorption cross-section of the species j, with wavelength-dependent structures [cm2/molecules]

Cj : column density of the species j [molecules/cm2]

The variation of the absorbed light intensity $I(\lambda)$ with wavelength can be though as the sum of two parts, one that varies fast and the other is slowly varying. The fast part is due to the fast varying absorption cross-section of gas molecules, while the slowly varying part is due to slow varying absorption cross-section of gas molecules. DOAS can extract the fast part from the overall spectrum, making it a compassionate technique to determine specific molecules (Platt, 2017). DOAS allows the quantitative determination of atmospheric trace gas concentrations by recording and evaluating the characteristic absorption structures (lines or bands) of the trace gas molecules along an absorption path of known length in the open atmosphere. The DOAS technique characterized by the following: (1) measuring the transmitted light intensity over a relatively (compared to the width of an absorption band) broad spectral interval; (2) high-pass filtering of the spectra to obtain a differential absorption signal and eliminating broad-band extinction processes such as Rayleigh and Mie scattering and (3) quantitative determination of trace column densities by matching the observed spectral signatures to prerecorded (reference) spectra by, for instance, least-squares methods (Platt, 2006).

DOAS method work in a wide range of wavelength from UV-wavelength area to visible-wavelength area. Based on (Hu, Wen, & Wang, 2016) NO_3 can be detected in 220-230 nm absorption cross-section in water species, chemical oxygen demand (COD) and total organic carbon (TOC) detected in 280-290 nm absorption cross-section, while watercolor, turbidity, and total suspended solids (TSS) measured in the visible-wavelength area. According to (Zhang, Fang, & Zhao, 2013) they develop a portable spectroscopy method to measure ammonia nitrogen, nitrite nitrogen, hexavalent chromium, and arsenide in water using a multiwavelength LED. (Theys et al., 2015) develop sulfur dioxide retrieval from ozone DOAS monitoring with Linear

Fit and Principal Component Analysis algorithms. These algorithms calculate sulfur dioxide concentration based on ozone concentration monitoring; this method reads the noise spectrum intensity of ozone in 270 nm to 500 nm wavelength based on (Levelt et al., 2006). (Theys et al., 2019) also, develop sulfur dioxide monitoring for volcano's sulfur dioxide emission using TROPOspheric Monitoring Instrument (TROPOMI). Many researchers develop DOAS monitoring based on existing and fabricated instruments. There is a possibility for emission monitoring using cheap and simple setup based on the DOAS method that this research work on. In this research, LED-UV with 285 nm wavelength used as a continuous light source specific for sulfur dioxide detection (Platt & Stutz, 2008). In this range, DOAS is very sulfur dioxide selective as there are no significant interferences due to the absorption from gases commonly existing in the air (Platt & Stutz, 2008). As the optical pathway, we use a clear acrylic tube, and for spectrum intensity detector, we use CCD spectrometer (Poole, 2015). Quantification of spectrum emission conducted by the least square analysis using gas standard calibration (Margelli & Giovanelli, 2002). Another calibration method could be conducted by on the fly correlation with a calibrated gas analyzer (Hasenfratz, Saukh, & Thiele, 2012; Rivera et al., 2009). (Al-Jalal, Al-Basheer, Gasmi, & Romadhon, 2019) set DOAS experiment for nitrogen dioxide measurement using chemical reaction preparation for its nitrogen dioxide calibration, by reacting copper wire with nitric acid. In this research, we adopt this method by reacting H_2SO_4 and Na_2SO_3 solution that would produce sulfur dioxide gases, sodium sulfate and amount of water, following this reaction (Abrash, 2020);

$$20\ Na_2SO_3 + 10\ H_2SO_4 \rightarrow 20\ Na_2SO_4 + H_2O + 10\ SO_2 \quad .....(2)$$

Produced sulfur dioxide then quantified using a gas analyzer, which correlated with sulfur dioxide spectrum intensity, which is the cheapest and straightforward DOAS calibration technique and will be analyzed by the least square method analysis.

2. METHODS

Figure 1 shows the schematic diagram of the employed experimental setup. The output light of UV LED taken from Tao Yuan 285 nm wavelength LED, this LED built-in lens, reflector, and protective window are removed. The circuitry used to enlighten LED from battery also removed, and the LED connected directly to 3 volts regulated DC power supply. UV light from LED emitted directly into the closed channel to eliminate possible light interference from the ambient light into a 30 cm acrylic tube, as an optical pathway with 40 mm od and 36 mm id. Each end of the acrylic tunnel windowed by 1.5 mm Azom thick fused silica glass, with 98% UV light transmittance. At the end of the optical pathway, Round-to-Linear Bundle, 7 x Ø105 µm optical fiber connected to Thorlabs CCS 200 CCD Spectrometer as spectrum intensity detector. The spectrum digitized by the line CCD camera is acquired to a personal computer using Thorlabs OSA software. The gas inlet of the optical pathway connected to the dilution chamber that produces sulfur dioxide, while its outlet line connected to a bacharach PCA 3 gas analyzer with 0.5 liters per minute flow as a quantitative measurement correlating instrument.

Sulfur dioxide gas prepared by reacting 5 mL, 0.5 M (171.5 mg/L) sulfuric acid with 5 mL sodium sulfite in different concentration, pipetting 3, 4, 5, and 10 mL from 1 gram sodium sulfite diluted to 100 mL as variable to produce different sulfur dioxide gas concentration. 50 ppm gas calibration standard used as a replicability analysis and instrumentation precision test. Prepared gasoline generator exhaust will be used as a stationary emission source to simulate measurement from the emission source. In the simulation test, inlet sulfur dioxide from the dilution chamber replaced by gasoline generator exhaust using stainless steel tube connected with gas hose. Sulfur dioxide produced from the chemical reaction, 50 ppm gas calibration standard, and gasoline generator emission compared with spectrum analysis using Thorlabs OSA software. Each test will take 5 minutes continuous spectrum reading data from CCD Spectrometer and gas analyzer directly saved as a CSV file format.

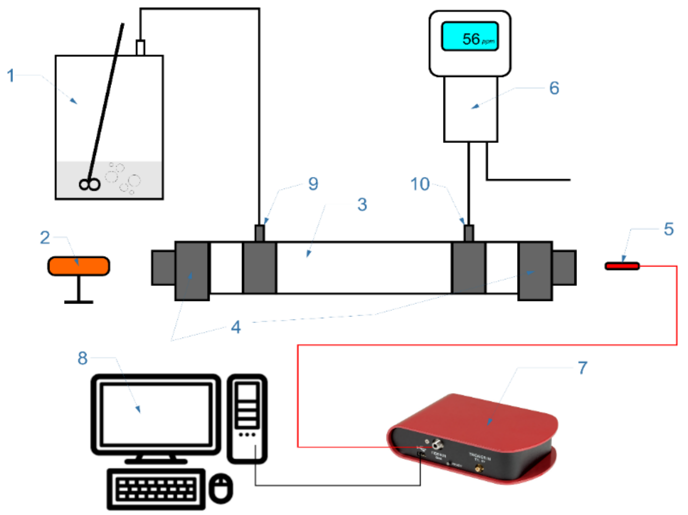

Figure 1. Instrument Setup for SO2 Spectrum Intensity Measurement (1. Dilution chamber, 2. LED-UV, 3. Optical Pathway, 4. Fused Silica Window, 5. Optical Fiber, 6. Gas Analyzer, 7. CCD Spectrometer, 8. PC, 9. Gas Inlet, 10. Gas Outlet)

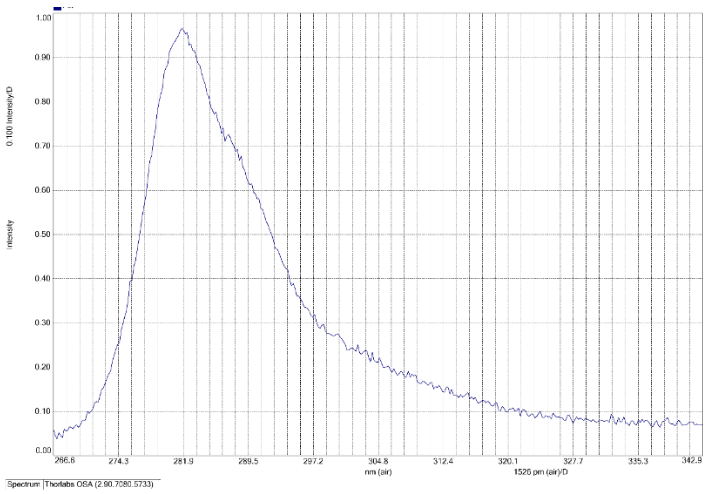

Figure 2. Typical Measured Spectrum Intensity of UV LED in Sulfur Dioxide Absorption Cross Section

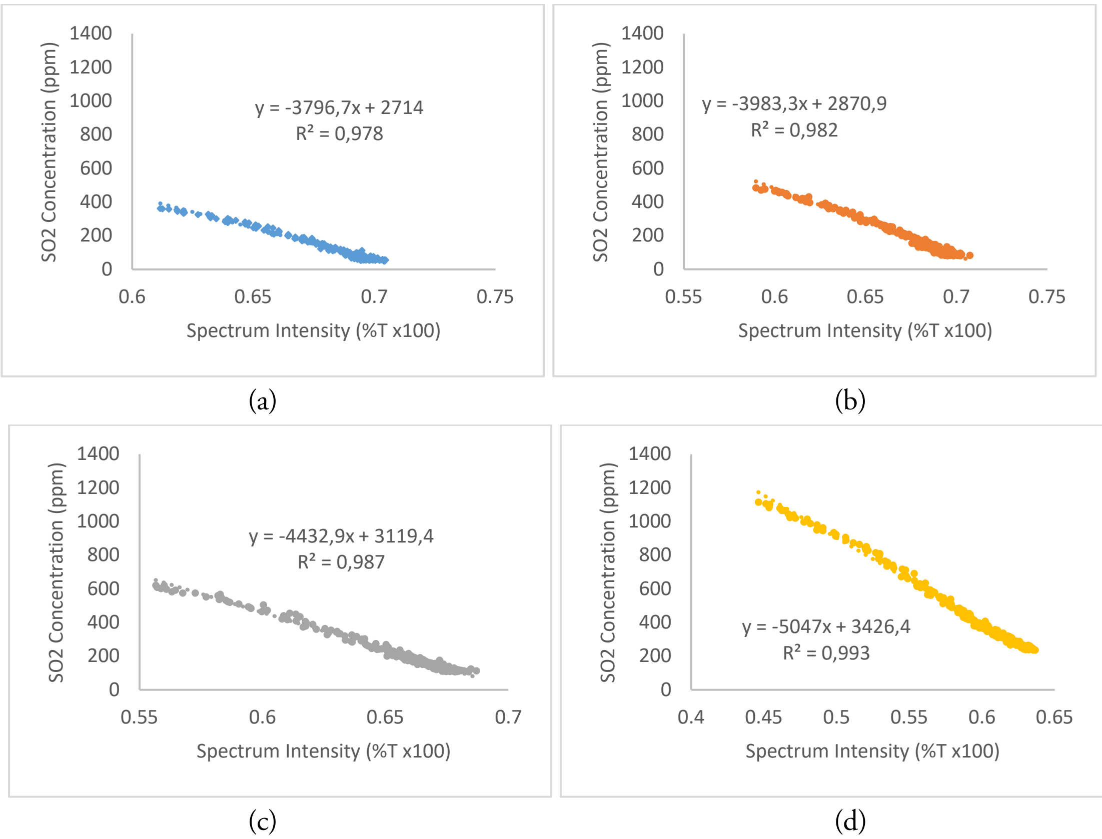

Figure 3. Spectrum Intensity Correlation to sulfur dioxide Concentration for variation of sodium sulfite (a) 3mL, (b) 4mL, (c) 5mL, and (d) 10mL

3. RESULT AND DISCUSSION

Figure 2 shows the measured intensity spectrum of the emitted light from UV LED and sulfur dioxide high-resolution absorption over the UV region from 255 to 345 nm. The LED intensity spectrum has a broad and smooth peak located around 280 nm. Based on (Platt & Stutz, 2008), sulfur dioxide has absorption cross-section around 260 to 350 nm.

Peak intensity of sulfur dioxide spectrum analyzed as peak value versus sulfur dioxide concentration read by bacharach PCA 3 gas analyzer. Both spectrum intensity and gas analyzer data reading saved every second for 5 minutes running time, CSV file contains raw data tabulated into an Excel spreadsheet for correlating between sulfur dioxide spectrum intensity and gas analyzer concentration reading. Each sodium sulfite volume variation then corresponds to sulfur dioxide spectrum intensity and gas analyzer concentration reading, list as follows.

When sulfuric acid begins to react with sodium sulfite, sulfur dioxide starts to produce, and it slowly lowers the % transmintance of spectrum intensity. It raises sulfur dioxide concentration read by the gas analyzer. Both spectrum intensity and concentration lapse through running time shown strong correlation, to convince this correlation a statistical analysis investigates the significance of the relationship, the study was done with SPSS software and Pearson Correlation as seen as table 1.

Table 1. Significance Test using Pearson Correlation

		Intensity	Concentration
Intensity	Pearson Correlation	1	-.981**
	Sig. (2-tailed)		0.000
	N	824	824
Concentration	Pearson Correlation	-.981**	1
	Sig. (2-tailed)	0.000	
	N	824	824

*****. Correlation is significant at the 0.01 level (2-tailed).***

Table 1 from the statistical analysis shown significance level between spectrum intensity and sulfur dioxide concentration based on this hypothesis;

H_0 : There is no strong correlation between spectrum intensity and sulfur dioxide concentration

H_1 : There is a strong correlation between spectrum intensity and sulfur dioxide concentration

If Sig > 0.05, then H_0 accepted, else if Sig < 0.05 H_0 rejected, then from that analysis Sig < 0.05, so we should reject H_0, there is a strong correlation between spectrum intensity and sulfur dioxide concentration (Mukaka, 2012). Hence, we could use linear formula $y = a + bx$ from Figure 3 as a calibration factor for sulfur dioxide measurement based on sulfur dioxide spectrum intensity. Each sodium sulfite variation generates variation sulfur dioxide concentration, for 3, 4, 5, and 10 mL variation approximately will generate maximum sulfur dioxide concentration of 350 ppm, 475 ppm, 650 ppm, and 1150 ppm. Linearity test from lowest concentration range to highest concentration range shows coefficient determination (r^2) 0.978, 0.982, 0.987, 0.993 or correlation coefficient (r) 0.989, 0.991, 0.993, and 0.996. According to (Akoglu, 2018; Fatkhurrahman & Juliasari, 2016; Ratner, 2009) and another DOAS experiment (Chan et al., 2012; Romadhon, 2015) this indicates a strong correlation between sulfur dioxide spectrum intensity and measured concentration.

Measurement precision by replication analysis done by comparing spectrum intensity to sulfur dioxide generated by chemical reaction since there is unhomogenized concentration through time. 50 ppm gas calibration standard used as precision analysis, figure 4 shows measured sulfur dioxide concentration using linear formula between 2% calibration error requirement as stated in (US EPA, 1995, 2018)

Average sulfur dioxide concentration from data, as seen in Figure 4, is 49.992 ppm, then standard deviation (SD) 0.280, coefficient variance (RSD) can be calculated by equation 3.

$$RSD = \frac{SD}{Average} \times 100\% \qquad .....(3)$$

Based on equation (3), the RSD value is 0.560. Concerning among-laboratory precision, the acceptability of the methods calculated using Horwitz-ratio (Horrat) (Horwitz & Albert, 2006). While predicted RSD (PRSD) computed using equation (4).

$$PRSD = 2^{1-0.5logC} \qquad .....(4)$$

Acceptance limit evaluated by using Horrat equation below;

$$Horrat = \frac{RSD}{PRSD} .....(5)$$

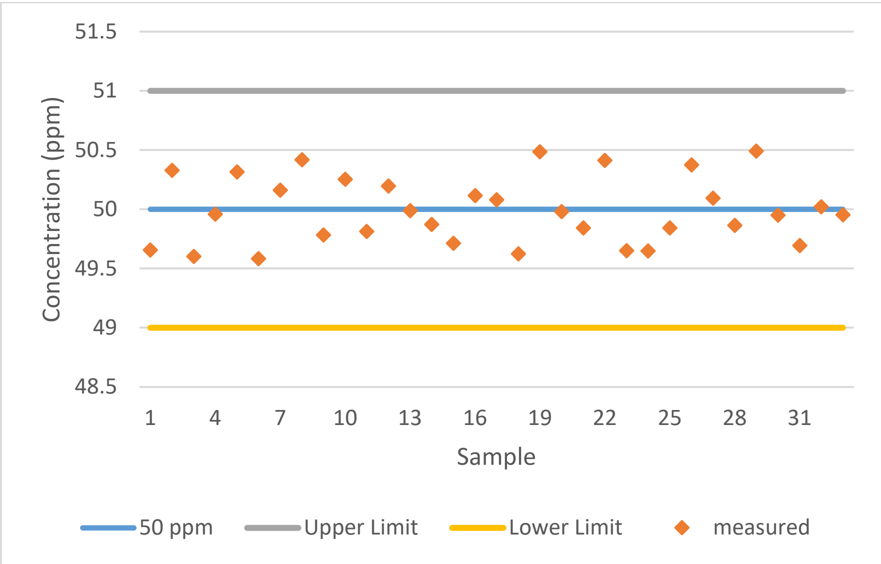

Figure 4. Measured sulfur dioxide between USEPA calibration error requirement

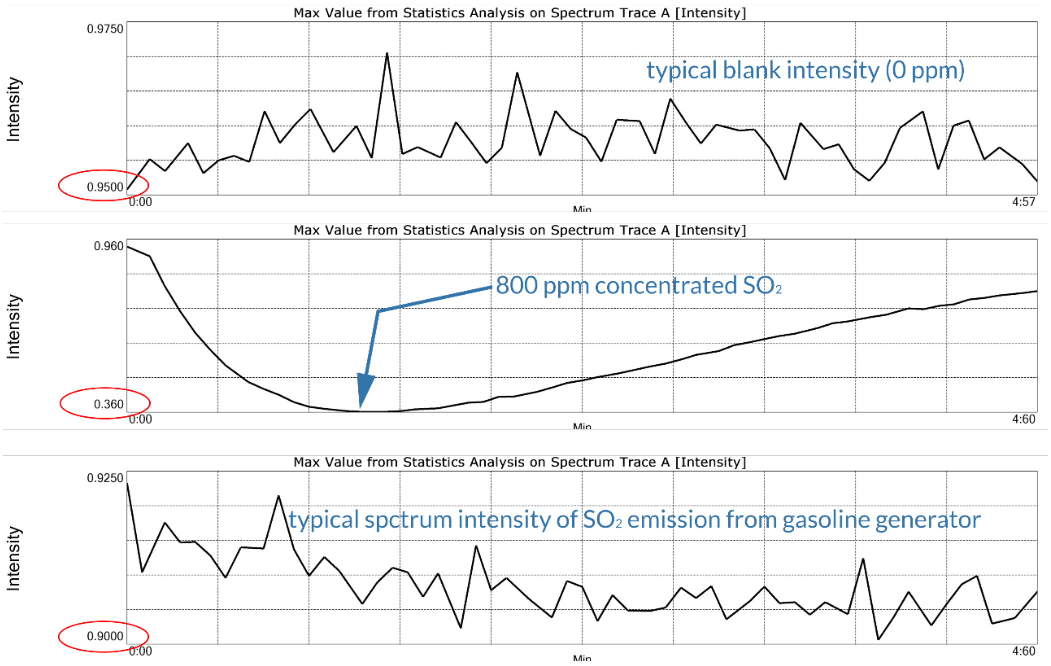

Figure 5. Spectrum intensity of sulfur dioxide from 0 ppm Concentration (up), 800 ppm Maximum Concentration of generated sulfur dioxide from H_2SO_4 and Na_2SO_3 reaction (middle), sulfur dioxide from gasoline generator emission (bottom)

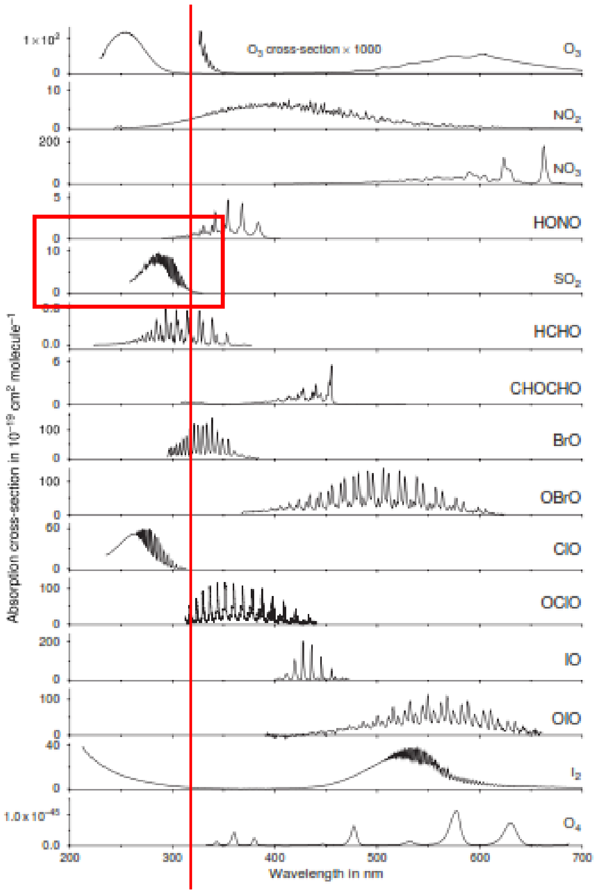

Figure 6. Absorption cross-section features of several species as a function of wavelength (in nm); picture from (Platt & Stutz, 2008)

Calculation from equation 5, Horrat from this precision analysis is 0.504, The precision is better than expected if the ratio is less than 1, and poorer if greater than 1, while the acceptable empirical range is 0.5 to 2.0.

Prepared gasoline generator then tested for emission simulation test through DOAS instrument with the same procedure as spectrum intensity measurement in sulfur dioxide from chemical reaction and gas calibration standard method. As shown in Figure 5, there is a large deviation error comparing typical 800 ppm concentrated sulfur dioxide with 0.360 (36%) transmittance intensity than 0.900 (90%) transmittance intensity when conducted simulation test using gasoline generator exhaust. It indicated 2.5 times deviation error that needs identifications.

According to (Emmerich, Wang, & Persily, 2017), (Souza et al., 2016), (Peterka, Pexa, Čedík, Mader, & Kotek, 2017) gasoline generator will emit SO_2, NO_x, CO, CO_2, hydrocarbon, and several suspended particulates (Emmerich et al., 2017), (Souza et al., 2016), (Peterka et al., 2017). Based on Figure 2, the only change is sulfur dioxide from the dilution chamber replaced with gasoline generator exhaust inlet using stainless steel pipe for emission stream into DOAS acrylic chamber as an optical pathway. Sulfur dioxide spectrum intensity from gasoline generator emission reveals some anomalies compare with spectrum intensity from H_2SO_4 reaction with Na_2SO_3. According to (Platt & Stutz, 2008), typically, sulfur dioxide absorption cross-section did not have substantial interference with any other gases in 250 to 300 nm UV range, shown in Figure 6.

There is sulfur dioxide, ClO, O_3, and a small section of NO_2 in the 250 to 300 nm absorption cross-section. Still, there is no possibility that species exist in gasoline generator exhaust according to (Elliott, Nebel, & Rounds, 1955). There is the only possibility of suspended particulate matter from gasoline generator emission that could obstruct UV light penetration from 285 nm LED-UV into CCD Spectrometer detector. Hence we could not analyze the spectrum intensity of sulfur dioxide from gasoline generator emission (Caro, Mateo-Martí, & Martínez-Frías, 2006; Christensen & Linden, 2003). This suspended particulate matter interference needs to be eliminated before it gets through the optical pathway, a dust filter will be a good point for this instrument development, and it needs another study of filtering effect on the DOAS instrument.

4. CONCLUSION

We develop DOAS calibration technique for sulfur dioxide using a reaction between H_2SO_4 and Na_2SO_3 that produce several sulfur dioxide gases. There is a high correlation between sulfur dioxide gas produced by that reaction to spectrum intensity, with coefficient determination (r^2) 0.978, 0.982, 0.987, 0.993 or correlation coefficient (r) 0.989, 0.991, 0.993, and 0.996 from lowest range concentration to highest range concentration, also compared with another DOAS experiment. Precision analysis from gas calibration standard using Horwitz ratio indicates instrument setup precise enough with 0.504 Horwitz ratio, according to its acceptable range. 2.5 times huge deviation error in emission simulation test using gasoline generator exhaust exist between typical 800 ppm concentrated sulfur dioxide from a chemical reaction and gasoline generator exhaust. Since there is no possibility ClO, O_3, and NO_2 exist in gasoline generator exhaust, the suspended particulate matter may interfere UV penetration into CCD detector that needs to be eliminated before emission gas stream flowed into the acrylic chamber as an optical pathway.

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REFERENCES

Abrash, S. A. (2020). *Preparation and Properties of Pollutant Gases*. Richmond, Virginia. Retrieved from https://facultystaff.richmond.edu/~sabrash/

Akoglu, H. (2018, September 1). User's guide to correlation coefficients. *Turkish Journal of Emergency Medicine*. Emergency Medicine Association of Turkey. https://doi.org/10.1016/j.tjem.2018.08.001

Al-Jalal, A. A., Al-Basheer, W., Gasmi, K., & Romadhon, M. S. (2019). Measurement of low concentrations of NO2 gas by differential optical absorption spectroscopy method. *Measurement: Journal of the International Measurement Confederation*, *146*, 613–617. https://doi.org/10.1016/j.measurement.2019.07.022

Caro, G. M. M., Mateo-Martí, E., & Martínez-Frías, J. (2006). Near-UV Transmittance of Basalt Dust as an Analog of the Martian Regolith: Implications for Sensor Calibration and Astrobiology. *Sensors (Basel, Switzerland)*, *6*(6), 688.

Chan, K. L., Pöhler, D., Kuhlmann, G., Hartl, A., Platt, U., & Wenig, M. (2012). NO2 measurements in Hong Kong using LED based long path differential optical absorption spectroscopy. *Atmospheric Measurement Techniques*, *4*, 901–912. https://doi.org/10.5194/amt-5-901-2012

Chou, C. L. (2012, October 1). Sulfur in coals: A review of geochemistry and origins. *International Journal of Coal Geology*. Elsevier. https://doi.org/10.1016/j.coal.2012.05.009

Christensen, J., & Linden, K. G. (2003). How particles affect UV light in the UV disinfection of unfiltered drinking water. *Journal / American Water Works Association*, *95*(4), 179–189. https://doi.org/10.1002/j.1551-8833.2003.tb10344.x

Clapsaddle, C. (2002). Continuous Particulate Matter Emission Monitoring Using PM CEMs. In *EMC 2002 Workshop*. Retrieved from https://www3.epa.gov/ttn/emc/meetnw/2002/clapsaddle.pdf

Elliott, M. A., Nebel, G. J., & Rounds, F. G. (1955). The composition of exhaust gases from diesel, gasoline and propane powered motor coaches. *Journal of the Air Pollution Control Association*, *5*(2), 103–108. https://doi.org/10.1080/00966665.1955.10467686

Emmerich, Wang, & Persily. (2017). Measured carbon monoxide concentrations from stock and reduced-emission prototype portable generators operated in an attached garage. *Journal of the Air & Waste Management Association*, *67*(8), 889–898. https://doi.org/10.1080/10962247.2017.1300202

Fatkhurrahman, J. A., Julia Sari, I. R., & Zen, N. (2016). Verifikasi Low Cost Particulate Sensor Sebagai Sensor Partikulat Pada Modifikasi Teknologi Wet Scrubber. *Jurnal Riset Teknologi Pencegahan Pencemaran Industri*, *7*(1), 31–38.

https://doi.org/10.21771/jrtppi.2016.v7.no1.p31-38.

Furukawa, H., & Fukuda, T. (2012). In vivo absorption spectroscopy for absolute measurement. *Biomedical Optics Express*, *3*(10), 2587. https://doi.org/10.1364/boe.3.002587

Hasenfratz, D., Saukh, O., & Thiele, L. (2012). On-the-fly calibration of low-cost gas sensors. In *Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics)* (Vol. 7158 LNCS, pp. 228–244). https://doi.org/10.1007/978-3-642-28169-3_15

Horwitz, W., & Albert, R. (2006). The Horwitz ratio (HorRat): A useful index of method performance with respect to precision. *Journal of AOAC International*, *89*(4), 1095–1109.

Hu, Y., Wen, Y., & Wang, X. (2016). Detection of water quality multi-parameters in seawater based on UV-Vis spectrometry. In *OCEANS 2016 - Shanghai*. Institute of Electrical and Electronics Engineers Inc. https://doi.org/10.1109/OCEANSAP.2016.7485737

Levelt, P. F., Van Den Oord, G. H. J., Dobber, M. R., Mälkki, A., Visser, H., De Vries, J., … Saari, H. (2006). The ozone monitoring instrument. *IEEE Transactions on Geoscience and Remote Sensing*, *44*(5), 1093–1100. https://doi.org/10.1109/TGRS.2006.872333

Lin, C. K., Lin, R. T., Chen, P. C., Wang, P., De Marcellis-Warin, N., Zigler, C., & Christiani, D. C. (2018). A global perspective on sulfur oxide controls in coal-fired power plants and cardiovascular disease. *Scientific Reports*, *8*(1), 1–9. https://doi.org/10.1038/s41598-018-20404-2

Margelli, F., & Giovanelli, G. (2002). Calibration And Validation Methods For DOAS Remote Sensing Systems. *WIT Transactions on Ecology and the Environment*, *53*. https://doi.org/10.2495/AIR020381

Mellqvist, J., & Rosén, A. (1996). DOAS for flue gas monitoring - II. Deviations from the Beer-Lambert law for the U.V./visible absorption spectra of NO, NO2, SO2 and NH3. *Journal of Quantitative Spectroscopy and Radiative Transfer*, *56*(2), 209–224. https://doi.org/10.1016/0022-4073(96)00043-X

Mohajan, H. (2019). Acid Rain is a Local Environment Pollution but Global Concern, *3*, 47–55.

Mukaka, M. M. (2012). Statistics corner: A guide to appropriate use of correlation coefficient in medical research. *Malawi Medical Journal*, *24*(3), 69–71.

Peterka, B., Pexa, M., Čedík, J., Mader, D., & Kotek, M. (2017). Comparison of exhaust emissions and fuel consumption of small combustion engine of portable generator operated on petrol and biobutanol. *Agronomy Research*, *15*, 1162–1169.

Platt, U. (2006). Differential Optical Absorption Spectroscopy, Air Monitoring by. In *Encyclopedia of Analytical Chemistry*. Chichester, UK: John Wiley & Sons, Ltd. https://doi.org/10.1002/9780470027318.a0706

Platt, U. (2017). Air Monitoring by Differential Optical Absorption Spectroscopy. In *Encyclopedia of Analytical Chemistry* (pp. 1–28). Chichester, UK: John Wiley & Sons, Ltd. https://doi.org/10.1002/9780470027318.a0706.pub2

Platt, U., & Perner, D. (1983). MEASUREMENTS OF ATMOSPHERIC TRACE GASES BY LONG PATH DIFFERENTIAL UV/VISIBLE ABSORPTION SPECTROSCOPY. *Springer Series in Optical Sciences*, *39*, 97–105. https://doi.org/10.1007/978-3-540-39552-2_13

Platt, U., & Stutz, J. (Jochen). (2008). *Differential optical absorption spectroscopy : principles and applications*. Springer Verlag.

Poole, C. F. (2015). Mahmood Barbooli (Ed.): Environmental Applications of Instrumental Chemical Analysis. *Chromatographia*, *78*(21–22), 1415–1416. https://doi.org/10.1007/s10337-015-2945-4

Ratner, B. (2009). The correlation coefficient: Its values range between 1/1, or do they. *Journal of Targeting, Measurement and Analysis for Marketing*, *17*(2), 139–142. https://doi.org/10.1057/jt.2009.5

Rivera, C., Garcia, J. A., Galle, B., Alonso, L., Yan, Z., Johansson, M., … Gangoiti, G. (2009). Validation of optical remote sensing measurement strategies applied to industrial gas emissions. *International Journal of Remote Sensing*, *30*(12), 3191–3204. https://doi.org/10.1080/01431160802558808

Romadhon, M. S. (2015). *Development Of A Detector For Trace Amount Of Nitrogen Dioxide Using Light Emitting Diode*. King Fahd University of Petroleum dan Minerals.

Shepherd, M. A., Haynatzki, G., Rautiainen, R., & Achutan, C. (2015). Estimates of community exposure and health risk to sulfur dioxide from power plant emissions using short-term mobile and stationary ambient air monitoring. *Journal of the Air & Waste Management Association*, *65*(10), 1239–1246. https://doi.org/10.1080/10962247.2015.1077174

Souza, S. n. M. De, Lenz, A. M., Werncke, I., Nogueira, C. e. C., Antonelli, J., & Souza, J. de. (2016). Gas emission and efficiency of an engine-generator set running on biogas. *Engenharia Agrícola*, *36*(4), 613–621. https://doi.org/10.1590/1809-4430-eng.agric.v36n4p613-621/2016

Sudalma, S., Purwanto, P., & Santoso, L. W. (2015). The Effect of SO2 and NO2 from Transportation and Stationary Emissions Sources to SO42– and NO3– in Rain Water in Semarang. *Procedia Environmental Sciences*, *23*, 247–252. https://doi.org/10.1016/j.proenv.2015.01.037

Theys, N., De Smedt, I., van Gent, J., Danckaert, T., Wang, T., Hendrick, F., … Van Roozendael, M. (2015). Sulfur dioxide vertical column DOAS retrievals from the Ozone Monitoring Instrument: Global observations and comparison to ground-based and satellite data. *Journal of Geophysical Research: Atmospheres*, *120*(6), 2470–2491. https://doi.org/10.1002/2014JD022657

Theys, N., Hedelt, P., De Smedt, I., Lerot, C., Yu, H., Vlietinck, J., … Van Roozendael, M. (2019). Global monitoring of volcanic SO 2 degassing with unprecedented resolution from TROPOMI onboard Sentinel-5 Precursor. *Scientific Reports*, *9*(1). https://doi.org/10.1038/s41598-019-39279-y

US EPA, O. EMC Conditional Test Methods (CTM-022), Pub. L. No. CTM-022 (1995). United States. Retrieved from https://www.epa.gov/emc/emc-conditional-test-methods

US EPA, O. (2017). *Method 6 - Sulfur Dioxide*. Retrieved from https://www.epa.gov/emc/method-6-sulfur-dioxide

US EPA, O. Method 7E - Nitrogen Oxide - Instrumental Analyzer (2018). United States. Retrieved from https://www.epa.gov/emc/method-7e-nitrogen-oxide-instrumental-analyzer

Wang, C., Xing, D., Zeng, L., Ding, C., & Chen, Q. (2005). Effect of artificial acid rain and SO2 on characteristics of delayed light emission. *Luminescence*, *20*(1), 51–56. https://doi.org/10.1002/bio.806

Zhang, X., Fang, Y., & Zhao, Y. (2013). A Portable Spectrophotometer for Water Quality Analysis. *Sensors and Transducers*, *148*, 47–51.

9 772503 501001
9 772087 096504