REDUCTION OF AMMONIACAL NITROGEN IN SEMICONDUCTOR WASTEWATER USING SEQUENCE BATCH REACTOR BY VERMIWASH-ISOLATED BACTERIA

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by

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16S rRNA	16S ribosomal Ribonucleic Acid
ADMI	American Dye Manufacturers' Institute
Al_2O_3	Aluminium Oxide
APHA	American Public Health Association
ASP	Activated Sludge Process
BOD	Biochemical Oxygen Demand
CeO_2	Cerium Dioxide
CMP	Chemical Mechanical Polishing
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
H_3PO_4	Phosphoric Acid
IC	Integrated Circuit
IMD	Inter-metal Dye Electric
K	Potassium
MBBR	Moving Bed Bioreactor
MBR	Membrane Bioreactor
MIDA	Malaysian Investment Development Authority
N	Nitrogen
N_2	Nitrogen Gas
NA	Nutrient Agar
NB	Nutrient Broth
NH_4^+	Ammonia
NH_4+-N	Ammonium

NH_4-N	Ammoniacal Nitrogen
NH_4OH	Ammonium Hydroxide
NO_2^-	Nitrites
NO_3^-	Nitrates
P	Phosphorous
SAS	Surplus Activated Sludge
SBR	Sequence Batch Reactor
SiO_2	Silicon Dioxide
TKN	Total Kjeldahl Nitrogen
VOC	Volatile Organic Compound

PENGURANGAN AMMONIA NITROGEN DALAM AIR SISA SEMIKONDUKTOR MENGGUNAKAN REAKTOR KELOMPOK BERTURUTAN OLEH BAKTERIA DARI 'VERMIWASH'

ABSTRAK

Air sisa semikonduktor mengandungi banyak bahan kimia refraktori dan juga sebatian organik dan bukan organik serta menunjukkan tahap ammonia, fosfat dan flourida yang tinggi. Walaubagaimanapun, ammonia adalah satu masalah utama di antara bahan pencemar kerana ia memberi kesan yang buruk kepada sistem ekologi. Dalam kajian ini, *Bacillus pumilus*, *Micrococcus luteus* and *Staphylococcus warneri* telah diasingkan daripada 'vermiwash' dan digunakan pada sistem reaktor kelompok berturutan (SBR) untuk mengurangkan ammonia nitrogen dalam sisa air semikonduktor menggunakan tiga jenis kitaran yang berbeza (12jam:12jam, 8jam:8jam dan 6jam:6jam) pada kondisi oksik anoksik masing-masing. *B.pumilus*, *M. luteus* dan *S. warneri* dibiakkan didalam sisa air sintetik yang tinggi ammonia dimana NH_4-N disesuaikan pada permulaannya 1000 mg/L untuk mengetahui kebolehan mereka dalam mengurangkan ammonia nitrogen. Kesemua tiga bakteria menunjukkan pengurangan tahap NH_4-N dalam masa 24 jam. *S. warneri* menunjukkan pengurangan tahap NH_4-N tertinggi iaitu 579 mg/L (57.9 %) diikuti oleh *B. pumilus* 389 mg/L (38.9 %) dan *M. luteus* 303 mg/L (30.3 %). Seterusnya, SBR dioperasikan dalam keadaan 12 jam oksik diikuti 12 jam anoksik sebanyak 4 kitaran untuk mengetahui jumlah pengurangan NH_4-N pada setiap kitaran. Terdapat kecekapan pengurangan tertinggi yang signifikan ($p<0.0001$) dari *S. warneri* (Min$\pm$SD: 27.5$\pm$2.6 mg/L; R: 97.1%), diikuti oleh *B. pumilus* (Min$\pm$SD: 201$\pm$3.7 mg/L; R: 79.9%) dan *M. luteus* (Min$\pm$SD: 406.3$\pm$20.4 mg/L; R: 59.4%). Akhir

sekali, kesan oksik dan anoksik ditentukan menggunakan ‘analisis varian satu arah’ (ANOVA) pada masa tahanan tertinggi iaitu kitaran 12jam:12jam. Pada keadaan anoksik, kecekapan pengurangan (R) adalah signifikan (p<0.0001) pada *B. pumilus* (49.1%) diikuti oleh *S. warneri* (47.8%) dan *M. luteus* (37.6%). Manakala dalam keadaan anoksik, kecekapan pengurangan ditunjukkan secara signifikan (p<0.0001) oleh *S. warneri* (97.3%), diikuti *B. pumilus* (79.9%) dan *M. luteus* (59.4%). Ujian T untuk sampel bebas antara oksik dan anoksik pada setiap jenis bakteria juga menunjukkan perbezaan yang signifikan (p<0.0001). Penemuan ini memberikan informasi yang berguna dimana, adalah penting untuk aplikasi SBR pada industri mendalami metabolism dan ekologi mikroorganisma yang diingini bagi mencapai nitrifikasi yang optima selain dari faktor fizikal yang memberi kesan pada pengurangan ammonia (nitrifikasi) seperti pH, suhu dan masa.

REDUCTION OF AMMONIACAL NITROGEN IN SEMICONDUCTOR WASTEWATER USING SEQUENCE BATCH REACTOR BY VERMIWASH-ISOLATED BACTERIA

ABSTRACT

The semiconductor wastewater contains many refractory chemicals and other organic and inorganic compounds. It presents high levels of ammonia, phosphate and fluoride. However, among the pollutants, ammonia is a major concern because it has harmful effect on the ecology system. In this study, *Bacillus pumilus*, *Micrococcus luteus* and *Staphylococcus warneri* were isolated from vermiwash and used in sequence batch reactor (SBR) system to reduce ammoniacal nitrogen in semiconductor wastewater using three different cycles (12hours:12hours, 8hours:8hours and 6hours:6hours) in oxic-anoxic condition respectively. *B. pumilus, M. luteus* and *S. warneri* were cultivated in synthetic high ammonia wastewater which NH_4-N customized initially at 1000 mg/L to determine their abilities to reduce ammoniacal nitrogen. All three bacteria showed reduction of NH_4-N level within 24 hours. *S. warneri* showed the highest reduction of NH_4-N level to 57.9% (579 mg/L final effluent) followed by *B. pumilus* 38.9% (389 mg/L final effluent) and *M. luteus* 30.3% (303 mg/L final effluent). Next, the SBR was run for 12 hours oxic followed by 12 hours' anoxic condition for 4 cycle to determine total NH_4-N reduction of for each cycle. There was a significant reduction ($p<0.0001$) where highest efficiency by *S. warneri* (Mean$\pm$SD: 27.5$\pm$2.6 mg/L; R: 97.1%), followed by *B. pumilus* (Mean$\pm$SD: 201$\pm$3.7 mg/L; R: 79.9%) and *M. luteus* (Mean$\pm$SD: 406.3$\pm$20.4 mg/L; R: 59.4%). The effect of oxic and anoxic conditions were at the highest retention time which is 12hours:12 hours cycle. During oxic condition, the highest removal

efficiency (R) was significantly ($p<0.0001$) observed in *B. pumilus* (49.1%) followed by *S. warneri* (47.8%) and *M. luteus* (37.6%). While in anoxic condition, the highest removal efficiency was significantly ($p<0.0001$) shown by *S. warneri* (97.3%), followed by *B. pumilus* (79.9%) and *M. luteus* (59.4%). Independent sample t-test within each bacteria strain also showed a significant difference between oxic and anoxic condition ($p<0.0001$). These finding served as useful information where it is important where SBR industrial application to study the metabolism and ecology of the intended microorganism to achieve optimum nitrification apart from physical factors which affect ammonia reduction (nitrification) such as pH, temperature and time.

CHAPTER 1

INTRODUCTION

1.1 Semiconductor wastewater and environmental pollution

Semiconductor manufacturing process generated a significant amount of wastewater due to a huge quantity of ultrapure water utilized during chemical mechanical planarizing (CMP) process (Van Zant, 2000). Direct discharge of the wastewater generated is strictly regulated due to the presence of various organic and/or inorganic compounds (Lai & Lin, 2003). The wastewater generated in the semiconductor manufacturing process may contain non-halogenated solvents, acids, bases, salts and other organic compounds (Lin & Yang, 2004).

A typical semiconductor wastewater obtained from a large manufacturer was strongly coloured since the presence of refractory photoresists, solvents, dyes and salts (Omar et al., 2008). In addition, the wastewater had a high chemical oxygen demand (COD) concentration, frequently exceeding 50,000 mg/l (Lin & Kiang, 2003). Apart from consuming a huge quantity of ultra-pure water, CMP process also utilized high levels of chemicals such as ammonia, phosphate and fluoride (Kim et al., 2011).

Ammonia and phosphate are major concerns among these pollutants. The concentration of ammoniacal nitrogen in semiconductor wastewater is range of

3000 to 6000 mg/L (Lai & Lin, 2003), resulting adverse effect on the environmental ecosystem (Barimo & Walsh, 2005). There are formed from ammonium hydroxide (NH_4OH) and phosphoric acid, which are used as additives in the CMP process (Lin & Yang, 2004). Ammonia and phosphate facilitate O_2 depletion, eutrophication and red tidal phenomena in water courses. In addition to its harmful effect, ammonia can vaporize in the ecology and environment due to its natural gas state. Therefore, the removal of ammonia from wastewater is important before it discharge into aquatic system (Lapointe et al., 2005).

There are a few methods for the ammoniacal nitrogen removal which are chemical, physical and biological treatment like adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination and biological nitrification and denitrification (Sudarsan et al., 2011). However, the chemical and physical methods of treatment produced secondary pollutants which are form through chemical and photochemical reactions and toxic to humans (Oller et al., 2011). Apart from that, the biological treatment is considered the most effective and economic, in the field of wastewater treatment (Arun Mittal, 2011).

1.2 Vermiwash and application

Vermicomposting is one type of biological treatment which are cost-effective and rapid technique for the management of the domestic animals as well as industrial wastes, where organic wastes are converted into homogeneous and stabilized vermicompost by earthworms and associated microbes (Pathma & Sakthivel, 2012).

Vermiwash is a liquid fertilizer collected after the passage of water through a column of vermicomposting substrate in such a way that the water washes the nutrients excreted by the earthworms feeding on the substrate as well as the earthworm's body surface (Ansari & Sukhraj, 2010). In other words, it is a collection of excretory products of earthworms, along with major micronutrients of the soil and soil organic molecules that are useful for plants (Abdullah Adil Ansari, 2008). These bio-liquid is rich in nutrients and plant growth hormones. Vermiwash seems to possess an inherent property of acting not only as a fertilizer but also as a mild biocide (More et al., 2013).

Microbiological study of vermiwash revealed that it contains nitrogen fixing bacteria (nitrifiers) like *Azotobacter* sp., *Azospirilum* and phosphate solubilising bacteria (Pathma & Sakthivel, 2012). The earthworms harbour 'nitrogen-fixing' and 'decomposer bacteria' in their gut and excrete them along with nutrients in their excreta (Singleton et al., 2003).

This nitrogen fixing bacteria in vermiwash is used for nitrification-denitrification process in many applications. Since vermiwash is a huge storage of microorganisms fixing atmospheric nitrogen, it plays a significant role in raising the phosphorus of soil (Jayashree, 2006). One of the application of in pot and field experiments through foliar application led to remarkable improvement in the growth, nutrient contents of shoot and yield of young and mature tea compared to the untreated plants (Islam et al., 2012).

Due to the microbial diversity of vermiwash that has been known to exhibit useful agricultural traits, it is also said to have waste management potential as NH_4-N treatment (Phukan & Savapondit, 2014). However, not many studies have been done and very scarce data were found for vermiwash application in wastewater specifically in semiconductor wastewater.

1.3 Sequence Batch Reactor and biological treatment.

The Sequencing Batch Reactor (SBR) is one of the potential options for aerobic and anaerobic treatment of wastewaters which performs equalization, biological treatment, and secondary clarification in a single tank using timed control sequence (Mane & Munavalli, 2012). Through SBR systems, wastewater is added to a single batch reactor, treated to remove undesirable components, before its being discharged (Jafarinejad, 2017). The major differences between SBR and conventional continuous-flow is their activated sludge system in which, the SBR tank carries out the functions of equalization aeration and sedimentation in a time sequence rather than in the conventional space sequence of continuous-flow systems (Minhas & Bakshi, 2017).

In addition, the SBR system can be designed with the ability to treat a wide range of influent volumes whereas the continuous system is based upon a fixed influent flow rate. Thus, there is a degree of flexibility associated with working in a time rather than in a space sequence. Many studies have been conducted to prove the efficiency of SBR system. One of them is study from Lin and Jiang which reported its capabilities to reduce the COD from 80,000 mg/L to below 100 mg/L, and completely reducing the colour in semiconductor wastewater (Lin & Jiang, 2003). Therefore, ranging from efficacy, economically and its flexibility, SBR can be said to be an outstanding option for aerobic and anaerobic treatment of semiconductor wastewaters.

The operation of an SBR is works by repeating sequences such as filling, aeration, anoxic, sedimentation, and emptying in a set period, and within the same reactor. Each treatment length and both sequences depend on the type of water to be treated and the organic matter or nutrient wanted to be removed. It has been showed 99.8% of nitrogen and 97.8% of phosphate were successfully removed in high ammonia and phosphate from piggery wastewater carried out by biological denitrification using a lab-scale SBR experiment (Obaja et al., 2005).

The biological nitrification and denitrification processes are one of the applications used for wastewater treatment. The process of nitrification-denitrification is a microbial process which comprises of two phase. The first, known as nitrification, is an aerobic process which ammonia is first converted to nitrite and then to nitrate. The second is denitrification, an anaerobic process by which nitrate is converted to nitrogen and other gaseous end products (Wu et al., 2007). The nitrification-denitrification process can be carried out in an SBR which is activated sludge, all performed within the same tank and achieving high nitrogen system used for the treatment of wastewater containing carbon and nitrogen (Kundu et al., 2013).

The nitrification process requires a slow-growing nitrifying bacteria with sludge that has been aged for a long time and high dissolved oxygen concentration (Van Rijn et al., 2006). In addition, they were susceptible to inhibition by a wide range of compounds at concentrations so low as not to affect the heterotrophic bacteria (Yang et al., 1995). Previous study was conducted to treat the industrial wastewater with 300-600 ppm ammonium content using the nitrifying and denitrifying bacteria by applying conventional Sludge Retention Time (SRT) constant at 30 days to promote the slow growth of the bacteria. Since this natural biological process of nitrification requires a long retention time, vermiwash application in SBR were suggested for this present study to minimize the time consumption for the process with the flexibility of SBR system.

1.4 Problem statement

Although ammoniacal nitrogen removal in various type of wastewater has been widely studied, to date, there are few studies on ammoniacal nitrogen removal from semiconductor wastewater. Semiconductor wastewater may contain non-halogenated solvents, acids, bases, salts and other organic compounds. However, little is known about the specific nutrient of semiconductor wastewater for bacterial growth. Thus, the first purpose of this study is to determine the nutrient content of semiconductor wastewater and then acclimized it for vermiwash isolated bacterial growth.

Secondly, despite the application of vermiwash on plant and soils treatment which proven in treating NH_4-N has been widely reported (Zambare et al., 2008), plus its potential in wastewater treatment (Phukan & Savapondit, 2014); to our best knowledge, the application of vermiwash for ammoniacal removal in semiconductor wastewater treatment has never been reported previously. Therefore, this study aim to isolate and characterize the nitrogen fixing bacteria from vermiwash and to examine its ability in removing the ammoniacal nitrogen from the semiconductor wastewater.

Ultimately, the SBR system is chosen in this study for its known flexibility system where the tank carries out its operation in a time manner and can be designed with the ability to treat a wide range of influent volumes (Subbramaiah & Mall, 2015). It also can performs equalization, biological treatment and secondary clarification in a single tank using a timed control sequence (Mahvi, 2008). The suitability of different types of bacteria also has been reported in SBR application (Rodríguez, Ramírez, & Mesa, 2011). However, to the best of our knowledge vermiwash isolated bacteria has never been reported in treating NH_4-N in semiconductor wastewater using SBR system. Therefore, using bacteria from vermiwash, four cycles of time (12 hours oxic:12 hours anoxic, 8 hours oxic:8 hours anoxic, and 6 hours oxic:6 hours anoxic were proposed as to investigate the time consume and the efficiency of the isolated nitrogen fixing bacteria in each cycle and condition.

Overall, this study is to determine the nutrient parameter of semiconductor wastewater and to investigate the removal of ammoniacal nitrogen using isolated bacteria characterized from vermiwash, conducted in SBR system.

1.5 Objectives of the study

There are three objectives in this study:

1. To examine COD, ammoniacal nitrogen: NH_4-N, NO_3-N, Total Kjeldahl Nitrogen (TKN), and pH of semiconductor wastewater.
2. To identify and characterize the ammoniacal nitrogen related bacteria in vermiwash using Gram Staining and 16S rRNA gene sequencing.
3. To determine the reduction of ammoniacal nitrogen in semiconductor wastewater using isolated bacteria from vermiwash in different cycle by using SBR system.

1.6 Significant of the study

Study on reduction of ammoniacal nitrogen by using biological treatment is important due to its ecofriendly and cost effective application. Apart from treating the wastewater and discharge safely into the nearest water source, air and the environment, it may protect human, aquatic ecosystem and environment from toxic and hazardous effect. Furthermore, the research could be useful for in the wastewater treatment for semiconductor industry which currently has been growing rapidly as a result of vast electronic devices application.

1.7 Limitations of the study

One of limitation of the study is the difficulty faced upon sampling to get the same concentration of ammoniacal nitrogen in raw semiconductor wastewater.

To solve this limitation, the synthetic wastewater was used after the nutrient composition of raw semiconductor wastewater has been characterized.

CHAPTER 2

LITERATURE REVIEW

2.1 Semiconductor industry

The semiconductor industry has been a fast developing and growing sector of economy in many countries around the world including Malaysia for the past several decades (Hsu et al., 2011). According to the Investment Performance Report in 2012 by the Malaysian Investment Development Authority (MIDA), the semiconductor sector has become one of the top eight new and emerging technologies in the manufacturing industries and has been seen to continue its accelerated growth in the future (Fatehah et al., 2013). The semiconductor is used in computers and their peripherals, communication equipment, consumer electronic products, electronic control devices, scientific and medical test equipment (Wong et al., 2013).

The semiconductor manufacturing involves many complex and highly delicate processes including silicon growth, oxidation, doping, photolithography, etching, stripping, dicing, metallization, planarization, cleaning, and so on (Lai & Lin, 2003; Lin & Yang, 2004). There are over two hundred types of organic and inorganic compounds (proprietary and generic) involved in the manufacturing processes of semiconductor integrated circuits (IC) which is also known as IC fabrication (Wong et al., 2013). Integrated circuits fabrication is a multiple-step sequence of photo lithographic and chemical processing steps during which electronic circuits are gradually created on a wafer made of pure semiconducting material (Drouiche et al., 2013).

A schematic representation of the overall process flow in the manufacture of IC devices illustrate in Figure 2.1. Single crystalline silicon wafers are manufactured from raw polysilicon for use as substrates for the various semiconductor devices. The IC is then manufactured by repeatedly processing the substrates through a cycle of three basic unit operations: film deposition, lithography, and etching. This cycle builds up the patterned layers (semiconductors, conductors, and insulators) required to make a final device. The overall cycle may be repeated as many as 20 to 30 times depending on types of devices (Barrett, 1997).

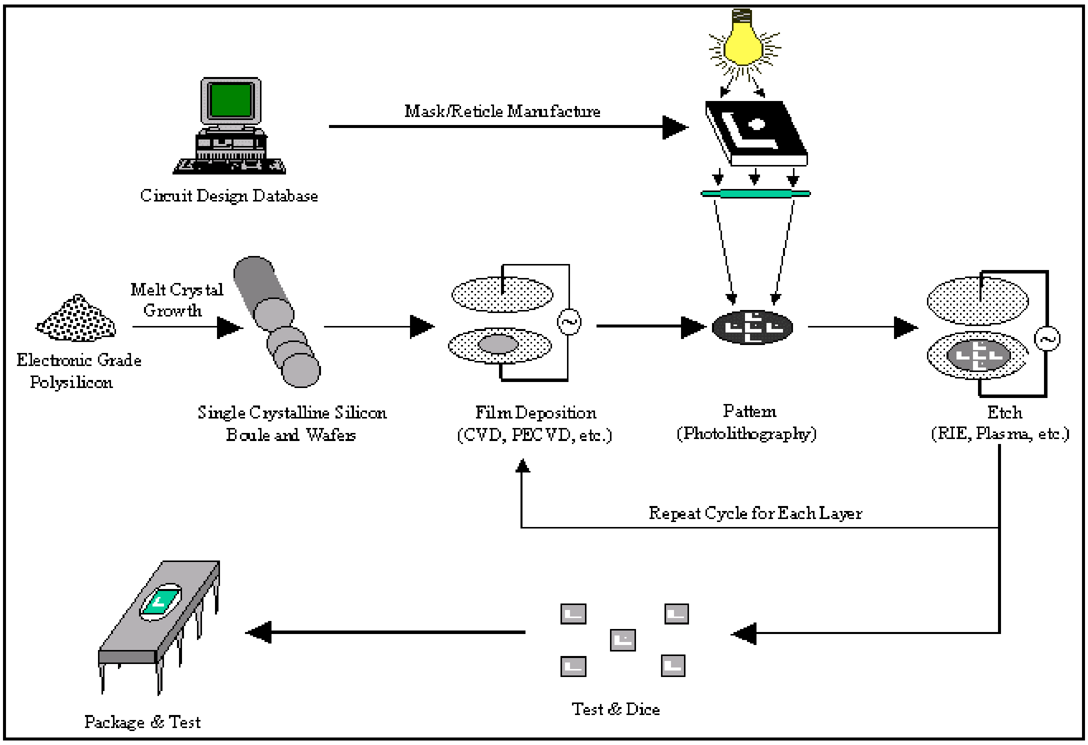

Figure 2.1: Simplified overall process flow for the manufacture of semiconductor integrated circuit devices (Barrett, 1997).

2.1.1 Chemical mechanical planarizing process

Chemical mechanical planarizing (CMP) also known as chemical mechanical polishing is a major semiconductor IC fabrication process. It is a smoothing and planning surfaces with the combination of chemical and mechanical forces. It can, in a way, be thought of as a hybrid of chemical etching and free abrasive polishing (Dornfeld et al., 2004). The CMP entailing micro-polishing used to obtain uniform surfaces of inter-metal dielectrics (IMD) or inter-level dielectrics (ILD) during semiconductor IC fabrication (Chou et al., 2010). The surface must go through mechanical downward force of an abrasive chemical liquid known as slurry and the chemical oxidation to ensure the flatness of semiconductor surface (Xie, 2007).

The basic operation of the CMP process composed of a polishing pad loaded on a rotating table, a wafer carrier, a conditioner, and a slurry feeder (Choi et al., 2011). A wafer is mounted at the bottom of the wafer carrier under rotation and pushed down against the rotating pad. Slurry including abrasive particles (~100 nm) is dispensed onto the pad surface, creating chemical reaction with the wafer material and then, the weakened layer is removed by the rotating pad. The rotating conditioner with metallic or diamond grit on it breaks up the surface of the pad, restoring the pad surface roughness which is smoothed due to the polishing work (Choi et al., 2011). This basic operation of CMP process is ilustrates in Figure 2.2.

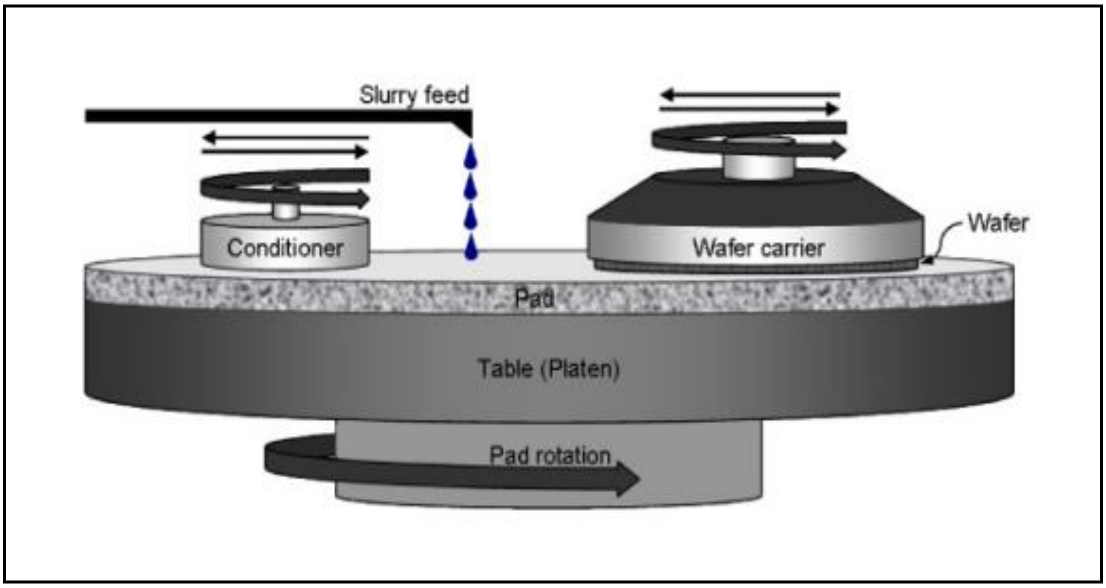

Figure 2.2: Basic operation of the CMP process (Woo et al., 2011).

A large amount of water which formulated with NH_4-N is required to wash out the slurry abrasives that have adhered to the wafer surface (Chou et al., 2010). Thus, correspondingly large quantities of semiconductor wastewater and sludge are produced and released into the environment.

2.2 Semiconductor wastewater

Semiconductor wastewater is characterized as strongly dark in colour, highly turbid, with high chemical oxygen demand (COD) concentration, low biodegradability, various solvents, acids, bases, salts, fine oxide particles and may contain the presence of inorganic and organic contaminants depending on the nature of CMP application (Fatehah et al., 2013). The inorganic and organic contaminants derive primarily from the CMP slurry. In general, inorganic contaminants may include suspended solids of silicon dioxide (SiO_2), aluminium oxide (Al_2O_3) or cerium dioxide (CeO_2) with concentrations ranging from 50 to 500 mg/L (Lin &

Yang, 2004). In addition, high levels of ammonia and phosphate are also presented in semiconductor wastewater range from 3000 to 6000 mg/L (Lai & Lin, 2003).

Among these inorganic pollutants, ammonia and phosphate are major concerns because of their harmful effect on the environment and ecosystem. Ammonia and phosphate are formed from ammonium hydroxide (NH_4OH) and phosphoric acid (H_3PO_4), which are used as chemical oxidation in the CMP process (Lee et al., 2005). Ammonia and phosphate have adversely affects the quality of water bodies and causes several environmental problems such as surface-water eutrophication, reduced disinfection efficiency, increased dissolved oxygen consumption and has toxic effect on aquatic population (Lapointe et al., 2005). Despite of its harmful effect, ammonia can vaporize in the ecology and environment due to its natural gas state. Therefore, the removal of ammonia from wastewater is accomplishable before its being discharge into aquatic system.

Another problem caused by semiconductor wastewater is the organic contaminant which may include metal complexing agents, surfactants, stabilizers and rheology control agents (Lin & Yang, 2004). Semiconductor wastewater especially contaminant from CMP slurry contains suspended particles with highly negative surface charges which repel adjacent particles when they are immersed in alkaline solutions (Den et al., 2005). Because of these characteristics of CMP slurry, removing such Nano-sized particles by conventional chemical treatment is not ideal (Huang et al., 2011). As consequences, untreated semiconductor wastewater which is rich in organic contaminants leads to an increased concentration of microorganisms. High concentration of microorganism will subsequently escalting the level of COD as pollution parameter for the semiconductor wastewater (Chou et al., 2010).

Chemical oxygen demand is a measure of the amount of oxygen used in chemical oxidation of inorganic and organic matter contained in wastewater (Bahadori & Smith, 2016). Although COD is not the only parameter to measure pollution, it is considered an indicator of the degree of pollution in the effluent and of the potential environmental impact of wastewater discharge (Emongor et al., 2005). Ergo, there is an urgent need to develop more efficient techniques for the treatment of CMP slurry in semiconductor wastewater.

Considering the semiconductor industry has become a representative and major industry in Malaysia, the rapid development of semiconductor industry also results in some environmental problems including the difficulty on its wastewater treatment and high water demand (Fatehah et al., 2013). Many highly sophisticated and delicate processes involved in semiconductor IC fabrication which requires abundant of organic and inorganic material, needs much pure water for rinsing and cleaning operation (Huang et al., 2011). Due to the shortage of water supply, higher cost of wastewater treatment and the upward trend of water price; wastewater reclamation and reuse have become an important task for semiconductor industry from the sustainable development point of view (Yang et al., 2007).

2.2.1 Semiconductor wastewater treatment for ammoniacal nitrogen

During the past few years, a wide range of wastewater treatment technologies to remove the ammonia and phosphorus have been applied. Ammoniacal nitrogen (NH_4-N), is a measure used for the amount of ammonia in a waste products such as wastewater and leachate (Lin et al., 2009). Chemical treatment; such as struvite precipitation, adsorption, chemical precipitation and physical treatment; like membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination are some of the treatment methods for the ammoniacal nitrogen removal in wastewater (Sudarsan et al., 2011). Despite of being uneconomical; chemical and physical methods of treatment produced secondary pollutants which form through chemical and photochemical reactions are toxic to humans (Oller et al., 2011).

In principle, contaminant of CMP slurry in semiconductor wastewater possess highly negative surface charges and repel adjacent particles when they are immersed in alkaline (Den et al., 2005). Therefore, removing such Nano-sized particles by conventional chemical treatment is not effective. Chemical treatment must be combined together with physical treatment leading to the invention of physiochemical treatment for semiconductor wastewater (Ocansey, 2005).

Numbers of studies were reporting on effectiveness of physiochemical treatment for sewange wastewater (Connor, 2008), synthetic wastewater (Hussain et al., 2007), chemical fertilizer industries (Rafie et al., 2013; Suthar & Chokshi, 2011), acid wastewater (Li et al., 2012) and landfill leachate waste (Poveda et al., 2016). Nevertheless, not much studies can be found concentrating on their effectiveness in semiconductor wastewater. However, one study applying physiochemical treatment method on semiconductor wastewater has demonstrated its ineffectiveness due to the formation of condensed slurry at the bottom of their designed vertical-flow electro-chemical cell, causing an operational problems (Den & Huang, 2006). Hence, biological treatment has been considered as a better alternative for semiconductor wastewater treatment (Hsu et al., 2011).

2.3 Biological treatment on semiconductor wastewater

Biological wastewater treatment is the largest biotechnological industry in the world, essential for protecting human health and the environment (Mielczarek et al., 2012). In recent years, biological processes have been considered to be a significant importance for the treatment of organic wastewater because of cost-effective and environmentally sustainable alternative technology (Abdel-Raouf et al., 2012).

The principle of all biological wastewater treatment is to introduce contact with microorganism which feed on the organic materials in the wastewater, thereby reducing its biochemical oxygen demand (BOD) content (Von Sperling, 2007). The BOD is the amount of dissolved oxygen needed by aerobic organism to breakdown organic material at certain temperature over specific time. BOD is similar in function to COD in that both measure the amount of organic compounds in water (Clair N. Sawyer; Perry L. McCarty; Gene F. Parkin, 2003). However, COD is less specific, since it measures everything that can be chemically oxidized, rather than just levels of biodegradable organic matter thus more suitable to be used as the parameter for semiconductor wastewater which contains over two hundreds types of organic and inorganic substances (Wong et al., 2013).

There are two types of biological wastewater treatment; aerobic and anaerobic (Oller et al., 2011). Aerobic means in the presence of air (oxygen); while anaerobic means in the absence of air (oxygen). These two terms are directly related to the type of bacteria or microorganisms that are involved in the degradation of organic impurities in a given wastewater (Von Sperling, 2007). Aerobic treatment processes take place in the presence of oxygen and utilize aerobic microorganisms, which use free oxygen to assimilate organic impurities and convert them in to carbon dioxide, water and biomass. The anaerobic treatment processes, on other hand, take place in the absence of oxygen by anaerobic microorganisms to assimilate organic impurities and mostly time consuming. The final products of organic assimilation in anaerobic treatment are methane and carbon dioxide gas and biomass (Arun Mittal, 2011).

Conventional activated sludge process (ASP) is the common system of biological treatment in the industrial application followed by their upgraded version which require smaller space called moving bed bioreactor (MBBR), membrane bioreactor (MBR), oxidation ponds, and the latest technology named sequence batch reactor (SBR) which many of them can utilized aerobic and anaerobic types of treatment depending on the types of wastewater (Arun Mittal, 2011).

The ASP is a biological treatment process where it required multiple large tank to be operated thus only suitable when land is at a premium (Ahansazan et al., 2014). The term ‘activated’ comes from the fact that the sludge teem with bacteria, fungi, and protozoa that can feed on the incoming wastewater (Akshey Bhargava, 2016). The sludge are aerated to promote the growth of microorganism that gradually consume the organics in the wastewater thus settling to the bottom of the tank, leaving a relatively clear liquid free of organic material and suspended solids in which drastically reduced the BOD content (Ahansazan et al., 2014). This mixture is then passed through a clarifier (settling tank) where the sludge is separated from the water (Mielczarek et al., 2012).

Moving bed bioreactor is a two-stage biological treatment comprising of trickling filter in ASP based aeration tank and proceed to secondary clarifier in a single tank or bio-tower (Minhas & Bakshi, 2017). This hybrid process of fluidized media and ASP taking place in a single aeration tank (Arun Mittal, 2011). The advantages of MBBR configurations as compared to conventional ASP is the fixed film media provides additional surface area for biofilm to grow on it and degrade the organic impurities that are resistant to biodegradation or may even be toxic to some extent in which provide a better biotreatment system than ASP alone (Minhas & Bakshi, 2017). However, ASP and its upgrade version MBBR have shown limited success in removing potentially toxic substances and may not be suitable for semiconductor wastewater (Abdel-Raouf et al., 2012).

Membrane Bioreactor is the latest technology for biological degradation of soluble organic impurities and has been in extensive usage for treatment of domestic sewage, but limited in industrial waste treatment applications (Arun Mittal, 2011). The MBR process is very similar to the conventional ASP, in that both have mixed liquor solids in suspension in an aeration tank. The difference in the two processes lies in the method of separation of bio-solids (Sinha et al., 2014). In the MBR process, the bio-solids are separated by means of a polymeric membrane based on microfiltration or ultrafiltration unit, as against the gravity settling process in the secondary clarifier in conventional ASP (Gander et al., 2000).

The advantages of MBR system over conventional ASP are the membrane filtration provides a barrier to suspend bio-solids that they cannot escape the system unlike gravity settling in ASP (Arun Mittal, 2011). As a result, the bio-solids concentration can be maintained at 3 to 4 times in an MBR process (~ 10,000 mg/l) in comparison to the ASP (~2500 mg/l) leading to smaller aeration tank size which can be one-third the size of the aeration tank in an ASP (Sinha et al., 2014). Due to the requirement of smaller space, it significantly reducing the concrete work and overall foot-print. However, MBR required skilled operators compared to other system and have poor ability to deal with ingress of roily contaminat (Gander et al., 2000) such as semiconductor wastewater.

While oxidation ponds are time consuming for the industries (Butler et al., 2015), SBR is likely to be more suitable for semiconductor wastewater since it required smaller space, time and cost effective plus operator friendly. The overall comparison for the semiconductor biological treatment system were tabulated in Table 2.1.