

**PERFORMANCE STUDY OF CALCIUM
HYPOCHLORITE ON WASTEWATER TREATMENT
SYSTEM FROM BIOMASS GASIFICATION WATER
SCRUBBER**

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by

LEE SHU XIAN

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LIST OF ABBREVIATIONS

| | |
|------|--|
| AAS | Atomic Absorption Spectrometry |
| ADMI | American Dye Manufacturer's Institute |
| APHA | Standard methods for the examination for water and |
| BGP | wastewaterBiomass Gasification Plant |
| BGW | Biomass Gasification Wastewater |
| BOD | Biochemical Oxygen Demand |
| COD | Chemical Oxygen Demand |
| DOE | Department of Environment |
| HPLC | High Performance Liquid Chromatography |
| ICP | Inductive Coupled Plasma |
| PAHs | Polynuclear Aromatic Hydrocarbon |
| rpm | Rotation per minutes |
| TDS | Total Dissolved Solids |
| TSS | Total Suspended Solids |
| WHO | World Health Organization |

LIST OF CHEMICAL FORMULA

| | |
|-------------------------------|----------------------|
| As (III) | Arsenic ion |
| Ca(OCl) ₂ | Calcium Hypochlorite |
| Cd (II) | Cadmium ion |
| CO ₂ | Carbon dioxide |
| Cr (VI) | Chromium ion |
| Cu (II) | Copper ion |
| DO | Dissolved Oxygen |
| Fe (II) | Iron ion |
| Hg (II) | Mercury ion |
| H ₂ O ₂ | Hydrogen Peroxide |
| Mg (II) | Magnesium ion |
| Mn (II) | Manganese ion |
| NaOCl | Sodium Hypochlorite |
| Na ₂ S | Sodium sulphate |
| NH ₃ | Ammonia |
| NH ₄ -N | Ammonical nitrogen |
| Ni (II) | Nickel ion |
| OCl ⁻ | Hypochlorite ions |
| Pb (II) | Plumbum/ Lead |
| Sr (II) | Strontium ion |
| Zn (II) | Zinc ion |

KAJIAN PRESTASI KALSIMUM HIPOKLORIT DALAM SISTEM RAWATAN AIR SISA DARIPADA PENGEGASAN BIOMASS AIR SCRUBBER

ABSTRAK

Prestasi kalsium hipoklorit [$\text{Ca}(\text{OCI})_2$] telah dikaji untuk menentukan kesesuaian untuk merawat air kumbahan daripada air scrubber pengegasan biomass. Kajian ini juga menentukan kesesuaian teknikal rawatan fizik-kimia untuk menyingkirkan logam berat seperti zink daripada janaan air sisa Biomass Pengegasan Logi (BPL) yang mengandungitar. Tumpuan khusus diberikan untuk memastikan keadaan operasi yang optimum termasuk pH, dos yang diperlukan, kepekatan logam awal dan prestasi rawatan kepada pemendakan kimia melalui Test Jar .Ujian eksperimen dapat membuktikan bahawa kalsium hipoklorit adalah yang paling kerap dikaji dan digunakan secara meluas untuk rawatan yang digunakan untuk disinfektan, pengklorinan, oksida dan penyingkirkan air sisa logam tercemar. 1g / L kalsium hipoklorit telah mampu membasmi zink dengan kepekatan awal 31.5 mg / L sepenuhnya. Keputusan adalah setanding dengan masa tahanan yang berbeza dan suhu. Mengenai kandungan klorin yang ada, rawatan aircenderung untuk menjadi stabil bagisehari penyimpanan apabila disimpan pada 6°C atau pada 20°C kerana haba menyumbang kepada ketidakstabilan terhadap air rawatan itu. Kalsium hipoklorit amat beralkali dan menunjukkan peningkatan pH apabila kepekatan kalsium hipoklorit semakin bertambah. Adalah penting untuk ambil perhatian bahawa kos rawatan keseluruhan air sisa berbeza-beza, bergantung kepada proses yang digunakan, kualiti air sisa dan keadaan tempatan. Secara umum, kesesuaian teknikal, kesederhanaan loji dan keberkesanan kos adalah faktor utama dalam memilih rawatan yang paling sesuai untuk efluen bukan organik.

**PERFORMANCE STUDY OF CALCIUM HYPOCHLORITE ON
WASTEWATER TREATMENT SYSTEM FROM BIOMASS
GASIFICATION WATER**

ABSTRACT

Performance of calcium hypochlorite [Ca(OCl)₂] was investigated to determine the suitability to treat the wastewater from biomass gasifier water scrubber. This research also reviews the technical applicability of physico-chemical treatment for the removal of heavy metal (zinc) from Biomass Gasification Plant (BGP)-generated tar-containing wastewater. A particular focus is given to coagulant precipitation through Jar Test to determine the optimal operating conditions which include pH, dose required, initial metal concentration and treatment performance. It is evident from the experiment that calcium hypochlorite are the most frequently studied and widely applied for the treatment used for disinfectant, chlorination, oxidant and removal of metal-contaminated wastewater. 1g/L of calcium hypochlorite has achieved a complete removal of zinc with an initial concentration of 31.5 mg/L. The results are comparable to that of different retention times and temperature. Regarding the available chlorine content, the treated solutions tend to be stable to 1 days of storage when kept at 6°C or at 20°C as the heat contribute to the instability of the solutions. Calcium hypochlorite solutions are extremely alkaline and showed an increase in pH when the concentration of calcium hypochlorite increase. It is important to note that overall treatment cost of wastewater varies, depending on the process employed, quality of wastewater and the local conditions. In general, the technical applicability, plant simplicity and cost effectiveness are the key factors in selecting the most suitable treatment for inorganic effluent.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Over the last century, rapid industrialization (Valipour, 2015a), population growth (Valipour, 2015b), environmental crisis (Valipour, 2014a) and water resources limitations (Valipour, 2014b; Valipour et al., 2015) have resulted in the deterioration of various ecosystems on which human life relies on (Hu et al., 2013). The primary cause of water pollution is the discharge of inadequately treated industrial wastewater. On initial discharge, these wastewaters contain high levels of inorganic and organic pollutants, (Jern, 2006). Moreover, in the past few decades, the cost of energy experienced great fluctuation, and synchronous energy consumption huge growth with the continue industrialization (Xiao, et al., 2015).

Biomass plays a crucial role in achieving the glowing global energy need, exceptionally in what concerns electricity generation worldwide. In the close decades, the policy modification of energy structure would make the biomass gasification industry more significant in the new clean and renewable energy market. On the other side, producer gas in its untreated form tends to be extremely polluted, containing significant quantities of tars, soot and ash. These contaminants must be eliminated from the producer gas before it enters the internal combustion engine or gas engine, so that engine damage and high degree of engine maintenance may be evaded (Wu et al., 2002). Thus, gas cleaning is an essential component of any biomass gasification plant (BGP). Gas cleaning is implemented in water scrubbers. These systems utilise water for cleaning these contaminants; this, in turn, leads to the generation of wastewater. This wastewater is commonly loaded with various

contaminants and must be treated before being discharged into the environment. Thus, study on wastewater treatment from BGPs is very important and needs attention (Metha et al.,2009).

Wastewater produced from BGPs consists of organic as well as inorganic compounds. The main component of organic contaminants is tar. Tar can be expressed as a mixture of several acidic, basic and neutral compounds. The inorganic compounds include oil and grease, heavy metals and phenol meanwhile basic components include free residual chlorine contents. Since most of heavy metals are non-degradable into non-toxic end products, their concentrations must be reduced to tolerable levels before discharging them into environment. Otherwise these could pose threats to public health and affect the aesthetic character of potable water. According to World Health Organization (WHO) the metals of most concern are chromium, zinc, iron, mercury and lead (Malik et al.,2010).

Due to the growing environmental awareness of the public, environmental groups, international organizations and strict requirements of environmental regulations, this study sharply forward the requirement of acquiesce with the discharge for BGP treatment. A shift in paradigm of wastewater management approach is indeed important. In this view, Biomass Gasification Wastewater (BGW) can be used as a valuable resource after appropriate treatment, since it can be either recycled for the same purpose or reused for several other purposes. Therefore, more attention should be focus towards the physiochemical wastewater treatment technologies, which have the preference of high resources recovery rate and energy saving (Ji et al.,2016).. The selection and development for advanced treatment process is mainly based on the quality of effluent, wastewater discharge standard,

and quality requirements for wastewater reuse. Usually, physical and chemical methods and advanced oxidation processes are used to treat BGW.

In this work, we investigated the coagulation and oxidative potential of calcium hypochlorite in the treatment and discolouration of BGW. This reagent has been generally used as a disinfectant in the tertiary treatment of polluted water loaded with pathogenic microorganisms and in the water of swimming pools, and also as an agent with high bleaching capacity (Shayeb et al., 1998; Lambert, 2006). These effects are due to its oxidizing ability towards organic matter even when barely degradable. Calcium hypochlorite ($\text{Ca}(\text{OCl})_2$) is a white powder used for industrial sterilization, bleaching, and purifying water treatment (Wittaker et al., 2012). It is relatively stable and has higher available chlorine compared with NaOCl (Dutta et al., 2012)

Current process is that effluent is being discharged into streams or canals after retention period of some hours in stabilization pond without any secondary or tertiary treatment. This wastewater has serious adverse impact not only on underground and surface water bodies and land in the surrounding area but also has an adverse effect on the aquatic ecological system. Effluents from BGW also contain heavy metals, which has a cumulative effect, and higher feasibility for entering into the food chain. Effluents are yellowish in colour, which in turn carton the photosynthesis process, causing deviation in the habitat (Pak EPA, 2003).

Calcium hypochlorite as an oxidant has been used to reduce the Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) of industrial wastewater for many years. Calcium hypochlorite due to the redox properties finds utilization in bleaching paper pulp, sugar and textile (Bell, 1965).

Eventually, this oxidising agent is evaluated on the treatment of wastewater and the optimum dosage required.

1.2 Problem statement

Today, part of the entire world is facing drinking water scarcity due to the contamination of ground water and the discharge of untreated or partially-treated industrial wastewater. Portable water demand is increasing day-by-day due to the exponential growth of population and it has become a severe problem to be solved with priority. It has been found that wastewater produced from biomass gasification plant sites contains heavy metals, as well as other substances with concentration exceeding wastewater effluent discharge guideline. From an environmental perspective industrial effluent are very toxic and can be considered both an environmental and health hazard due to its complex chemical composition. The discharge of untreated wastewater would cause significant deterioration of the environment due to the presence of persistent compounds and hazardous substances especially because of its high content in organic and inorganic compound. Moreover, the wastewater also contains some tar components, a major by-product of gas production process. The purpose of this research is to describe a study of the treatability of wastewater by calcium hypochlorite.

Industrial wastewater treatments are faced with extremely stringent discharge limitations for toxic contaminants through the adoption of state water quality human health criteria and limitations of the Department of Environment (DOE) to mitigate the implementation of water quality standards. Various concentrations of different inorganic can be expected in different industrial waste streams, it is not clear what the best dosage of calcium hypochlorite act as disinfectant, coagulant and oxidising

agent in respect of its potency as a synthetic reagent in terms of stability, ease of handling, commercially readily available and inexpensiveness.

1.3 Objectives

The purposes of this study are:

- i. To study the potential usefulness of calcium hypochlorite that conceivably could be used to treat the biomass gasification wastewater.
- ii. To characterize the components and their concentrations typically found in biomass gasification wastewater before and after treatment.
- iii. To optimize the conditions and doses of calcium hypochlorite required in treating the wastewater in order to comply with DOE standard.

1.4 Scope of study

In this work, calcium hypochlorite was utilized to treat BGP-generated tar-containing wastewater. The preparation of treated solution was done via physico-chemical method which applies calcium hypochlorite through Jar Test to improve the dissolution performance of the $\text{Ca}(\text{OCl})_2$ powder dissolved in it. The optimization of the operating conditions was determined for the temperature and retention time.

The optimized dosage of calcium hypochlorite was obtained through the concentration of heavy metal and percentage of reduction. The samples of treated wastewaters were also included for comparison purposes with standard of discharged in DOE. The samples were then used to investigate the effect and behaviour of wastewater after treatment. In order to carry out the analysis study on organochlorine compound was done by examining using gas chromatography to identify the effect of this component towards the environmental impact.

1.5 Organization of thesis

This thesis consists of five main chapters and each chapter contributes to the sequence of this study. The following are the contents for each chapter in this study:

Chapter 1 introduces the usage of calcium hypochlorite in wastewater industries, problem statement, research objectives and organization of thesis.

Chapter 2 discusses the literature review of this study. An insight into calcium hypochlorite, discussion on treating the wastewater from biomass gasification water scrubber, and the guideline for Department of Environment discharged standard are elaborated. Moreover, the parameters on COD, phenol, Dissolved oxygen (DO), free residual chlorine, heavy metals and colour determination are included as well.

Chapter 3 covers the experiment materials and the details of methodology. It discusses on the description of equipment and materials used, jar test experiment, experimental procedure and description of factors affecting the wastewater.

Chapter 4 refers to the experimental results and discussions of the data obtained. Further elaboration on the effect of different factors on Biomass Gasification Wastewater Plant (BGWP), the results on optimal dosage, pH and temperatures are provided in this chapter.

Chapter 5 concludes all the findings obtained in this study. Recommendations are also included as well.

CHAPTER TWO

LITERATURE REVIEW

2.1 Calcium Hypochlorite

In chemistry, hypochlorite is an ion composed of chlorine and oxygen, with the chemical formula OCl^- . It can combine with a number of counter ions to form hypochlorites, which may also be cognized as the salts of hypochlorous acid. Common examples include sodium hypochlorite (household bleach) and calcium hypochlorite (bleaching powder, swimming pool "chlorine"). Hypochlorites are generally quite unstable in their pure forms and for this reason are normally managed as aqueous solutions. Their primary applications are as bleaching, disinfection and water treatment agents but they are also used in chemistry for chlorination and oxidation reactions. Among this class of reagents, calcium hypochlorite, $\text{Ca}(\text{OCl})_2$ has brought only a little attention, irrespective of its potency as a synthetic reagent in terms of stability, ease of handling, commercially ready availability, and inexpensiveness (Hirano et al., 1997).

Calcium hypochlorite is resistant to exothermic, self-propagating decomposition lead to spark, flame or contamination with an organic substance. More notably, this invention concerns a calcium hypochlorite composition containing at least about 55 percent $\text{Ca}(\text{OCl})_2$, preferably about 60 to 70 percent $\text{Ca}(\text{OCl})_2$, on a total weight basis, consisting imperatively of particulate calcium hypochlorite constantly mixed with water-soluble, hydrated inorganic salt in quantity sufficient to equip a water content in said mixture within the range of about 3 percent to about 13 percent by weight. High-grade particulate calcium hypochlorite

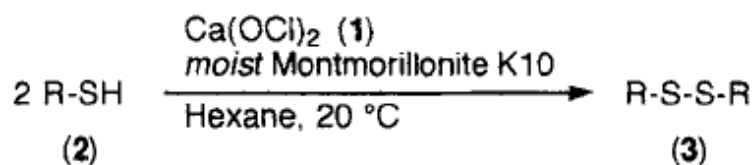
compositions are primarily used for water treatment, especially of swimming pools, where it distributes as a convenient source of chlorine for disinfectant purposes and for public sanitation. Certain commercial processes are presently used for the mass-produce of the so called “high-grade” calcium hypochlorite compositions containing at least about 65 percent $\text{Ca}(\text{OCl})_2$, from which the active and available chlorine for sanitation intent is derived. Calcium hypochlorite ($\text{Ca}(\text{OCl})_2$) is a relatively stable chemical substance that is ordinary used for industrial sterilization and water purification treatments (Zehnder et al., 2002). Besides, this substance shows antibacterial properties (Muhammadi et al, 2008) and (Spano et al., 2001) the ability to boost organic matter dissolution (Clarkson et al., 2001). Calcium hypochlorite has engage only a little attention, irrespective of its potency as a synthetic reagent in terms of stability, ease of handling, commercially ready availability, and reasonable price. The chlorinated products (sodium or calcium hypochlorite) have been used for a long time in the tertiary treatment of urban wastewater, in order to avoid the spread of pathogenic microbes in the environment and typical as an agent of whitening.

$\text{Ca}(\text{OCl})_2$ with no catalyst reacts with substituted molecules. This mechanism seems to be rely on the substrate to be oxidized, the pH and the $\text{Ca}(\text{OCl})_2$ concentration. The overall oxidation kinetics would be 1st order with respect to the substrate provided that $\text{Ca}(\text{OCl})_2$ is available in high excess. Depending on the substrate composition, the reaction steps might include the arrangement of a transition chlorinated intermediate (Eliason et al., 1991). Under neutral to basic pH, the oxidized product does not carry any chloride, the end product is CaCl_2 (Weast and Astle, 1980) and the O atom is transferred to the substrate's end products. On the other hand, organochlorides are incorporate by $\text{Ca}(\text{OCl})_2$ oxidation underacidic pH

(Nadupalli et al, 2011). Most of these general features assuredly apply to $\text{Ca}(\text{OCl})_2$ soil oxidation.

Work is here undertaken to demonstrate the suitability an inexpensive and environmentally friendly reagent system, calcium hypochlorite and Montmorillonite K10 in hexane, for the oxidation of thiols. Calcium hypochlorite (1) was purchased from Kokusan Chemical Works, Ltd. Japan and its purity (available chlorine) was determined by iodometry (65 %) the reagent has a good shelf life without any appropriate care.

Scheme :



Present reactions can be readily carried out only by efficiently stirring a mixture comprising of (1), Montmorillonite K10 preloaded with a small amount of water (moist Mont.; vide infra), and thiol (2) in hexane at 20 °C under inert atmosphere (Scheme). In addition, the heterogeneous system allows a simple work-up to be performed merely by filtering off the insoluble and removing the solvent from the filtrate.

2.2 Biomass Gasification

Biomass gasification permits the production of several products with various end used as fuels or intermediates for chemical synthesis. Biomass gasification with air in downdraft gasifiers coupled to an Internal Combustion Engine (IC-engine) is one of the most common small scale applications due to the low tar

content of the syngas and the high fuel conversion (Martinez et al., 2012). However, tight feedstock specifications such as low moisture and narrow size distribution (Martinez et al., 2012; Simone et al., 2009) limit the reliability and diffusion of this technology. Most studies on downdraft gasifiers involve woody materials as feedstock, cut in distinct shapes such as chips or briquettes. (Sharan et al., 1997) characterized a gasification plant by using certain types of wood as feedstock, demonstrating the feasibility of power production by means of an internal-combustion engine.

On the other hand, some conflicts related to the wastewater disposal were mentioned (Hassler et al., 1997). Zainal et al. (2002) performed a series of experiments in a complete gasifier- IC engine plant and reported the performance of the system for different air–fuel ratios and different woody fuels with cubic shape. Sharma (2011) complete tests with an open-top downdraft gasifier using Acacia briquettes as feedstock; much attention was paid to the gasifier behaviour in terms of pressure drops and gas flowrate. As pointed out by Erlich and Fransson (2011), it is crucial to broaden the range of fuels which can be fed to gasifiers, to overcome supply limitations related to the seasonality of limited biomass feedstock. Besides wood feedstocks, hazelnut shells also prove to be useful for downdraft gasification (Dogru et al., 2002; Midilli et al., 2001). However other agro-industrial residues do not performed the same mechanical properties of chipped wood or nuts. For example Wander et al. (2004) reported operational issues in the gasification of wood sawdust due to the bed mechanic aspects. Consequently these residues need to be conditioned before being processed in downdraft gasifiers. Pelletization is a suitable option for biomass conditioning, allowing production of stable dry fuels of homogenous size from different biomass residues. Erlich and Fransson (2011) carried out a detailed

work to determine the gasification of pelletized agricultural residues, not suitable for gasification as raw material (e.g. bagasse). These authors take into consideration the effect of equivalence ratio and they analyze the evolution of the pelletized material and its influence on the gas pressure drop across the char bed. Some of the aforementioned works were carried out on small scale reactors throughput from 1 to 5 kg h⁻¹ (Dogru et al., 2002; Erlich and Fransson, 2011; Sheth and Babu, 2010). However, the demonstration of technological reliability for downdraft gasification should depend on pilot scale tests (Garcia-Bacaicoa et al., 2008; Pathak et al., 2008; Sharan et al., 1997). In this work gasification tests of two pelletized biomass in a pilot scale downdraft gasifier with a thermal throughput of 200 kW were carried out.

2.3 Water Scrubber

Water scrubber is one of the gas purification techniques consists of a gas flow and a biological engine. In the water-scrubber the components to remove from the gas flow are absorbed in the water. In the biological engine the absorbed pollution in the water is further decomposed biologically (Ofori et al., 2009). The purified water is recycled to the scrubber where it absorbs pollution. Biologically degradable hydrocarbons are converted into the water-scrubber into water and carbon dioxide (Dubey., 2000). The non degradable hydrocarbons remain in the water. Components such as hydrogen sulphide and ammonia are converted into respectively sulfate and nitrate. To keep the salinity and the non-degradable carbon source water scrubber(KWS) low enough, regular ventilation is needed. This can happen on the basis of conduction or by means of a fixed ventilation. The degree of ventilation depends on the finished gas composition. There has been determined that even

salinities that correspond to a conduction of 5 mS/cm still can obtain a stable biological degradation.

A hydraulic stay time of the water for 20 - 40 (maximum) days gives good results. The scrubber must be devised as such that the stay time of the gases in the scrubber is approximately 1 second. Depending on of the solubility of the components this can be more or less. The scrubber must have a special open packing and special spray heads to avoid constipation of the biosilt. The biological system needs beside a carbon source (KWS) also nutrients to survive. For that purpose a nutrient mix is added to water-scrubber (Lantela et al., 2012). This nutrient mix contains nitrogen, phosphorus and track elements. The biological engine contains ventilation to provide the bacteria with sufficient oxygen to break down the components. In the case of a bad soluble and a difficult degradable components the danger for stripping of the components to air is real. To prevent that stripping pollution becomes emitted into the air of the ventilation in these cases can best be recycled back to the water-scrubber. The biological engine can be carried out as an active silt system or biofilmsystem on carrier (Hagen et al., 2001). The systems with carrier generally know a lower silt production. At starts up of scrubber biology is grafted with silt from a biological water purification installation or another scrubber. This silt must adapt to the specific component proposition of the degassing. Especially the adaptation to degradable more with difficulty components can some weeks up to a month last before the postulated.

Water-scrubbers are applied in:

- Cigarette industry for fragrance reduction. The fragrance concentration is reduced of approximately 5,000 ge/m³ to 200 - 300 ge/m³. Solvent problemen where alcohols, ketones, acetates are used.

- Disposal of fragrance components, NH₃, H₂S gas originating from water purification installations
- Remove originating of fragrance from production of enzymes

2.4 Physical and Chemical method

The treatment of BGPW by physical and chemical methods, such as coagulation precipitation (Yalou et al., 2010; Zhao and Gaun., 2010), adsorption (Lianqin et al., 2011), membrane separation (Bhattacharyya et al., 1983; M and Jing., 2009) and combined technologies (Lili et al., 2013) has been widely investigated and applied. It is reported that BGPW treated could meet the wastewater discharged or wastewater reuse standards. However, the main role of physical and chemical methods is to separate the pollutants, but not to degrade them, therefore it is necessary to pay more attention to the transformation of pollutants and take measures to degrade them.

Coagulation–flocculation can be employed to treat wastewater hampered with heavy metals. Principally, the coagulation process destabilizes colloidal particles by adding a coagulant and results in sedimentation (Shammas., 2004). To increase the particle size, coagulation is followed by the flocculation of the unstable particles into bulky floccules (Semerjian et al., 2003). The common approach for this technique includes pH adjustment and involves the addition of ferric/alum salts as the coagulant to overcome the repulsive forces between particles (Licsko., 1997).

After lime precipitation, Chareerntanyarak, (1999) employed consecutive coagulation process to remove Zn(II), Cd(II) and Mn(II) ions from synthetic wastewater in Table 2.1. The ideal pH for coagulation process was found to be 11. At pH 11, the concentration of Zn(II) and Mn(II) in the treated effluent was decreased to

less than 5 mg/L, the limit for the wastewater discharge set by the Pollution Control Department (PCD., 2005). In general, coagulation–flocculation can treat inorganic effluent with a metal concentration of less than 100 mg/L or higher than 1000 mg/L.

Table 2.1 Heavy metal removal using chemical precipitation

| Species | Coagulant | Dose of coagulant (mg/L) | Initial metal concentration (mg/L) | Optimum pH | Removal efficiency |
|---------|---------------------|--------------------------|------------------------------------|------------|--------------------|
| Zn (II) | Ca(OH) ₂ | 10 | 450 | 11.0 | 99.77 |
| Cd (II) | Ca(OH) ₂ | 10 | 150 | 11.0 | 99.67 |
| Mn (II) | Ca(OH) ₂ | 10 | 1085 | 11.0 | 99.30 |
| Cu (II) | Mg(OH) ₂ | NA | 16 | 9.5 | 80.00 |
| Cd (II) | Fe(OH) ₃ | NA | 37 | 11.0 | 96.00 |

Like chemical precipitation, pH ranging from 11.0 to 11.5 (Elimelech et al., 1990) has been found to be adequate to improve the heavy metal removal by the coagulation–flocculation process (Table 2.2). Improved sludge settling, dewatering characteristics, bacterial inactivation capability, sludge stability are reported to be the major dominance of lime-based coagulation (Cheng et al., 1994).

In spite of its advantages, coagulation–flocculation has limitations such as high operational cost due to chemical consumption (Edwards., 1994). The increased volume of sludge generated from coagulation–flocculation may interfere its adoption as a global strategy for wastewater treatment. This can be attributed to the matter that the toxic sludge must be converted into a stabilized product to hamper heavy metals from leaking into the environment (Ayoub et al., 2001).

To overcome such issues, electro-coagulation may be a better choice than the conventional coagulation, as it can remove the smallest colloidal particles and produce just a small volume of sludge (Vik et al., 1984). However, this approach also creates a floc of metallic hydroxides, which requires further purification (Persin et al., 1989), making the recovery of valuable heavy metals impossible.

Table 2.2 Heavy metal removal using coagulation-flocculation

| Species | Coagulant | Dose of coagulant (mg/L) | Initial metal concentration (mg/L) | Optimum pH | Removal efficiency |
|---------|----------------------|--------------------------|------------------------------------|------------|--------------------|
| Zn (II) | Na ₂ S | 100 | 450 | 11.0 | 99.91 |
| Cd (II) | Na ₂ S | 100 | 150 | 11.0 | 99.73 |
| Mn (II) | Na ₂ S | 100 | 1085 | 11.0 | 99.95 |
| Cu (II) | Poly-ferric sulphate | 25 | 20 | 10-11.5 | 99.60 |
| Cu (II) | Poly-acrylamide | 5 | 20 | 10-11.5 | 95.00 |

2.5 Oxidation

In chemical oxidation, organic compounds are oxidized into water and carbon dioxide or some other outputs such as alcohols, aldehydes, ketones and carboxylic acids which are easily biodegradable (Bigda., 1995). Chemical oxidation is carried out by potassium permanganate, chlorine, ozone, hydrogen peroxide (H₂O₂), Fenton's reagent (H₂O₂ and Fe catalyst) and chlorine dioxides (Gogate et al.,2004). The rate of chemical oxidation depends on the nature of oxidants and pollutants (Ternes et al., 2003). Besides, pH, temperature and existence of catalyst also play an essential role in the rate of chemical oxidation (Huber et al., 2005). By this method, pollutants such as ammonia, phenols, dyes, hydrocarbons and other organic pollutants may be eliminated (Zazo et al., 2005). The cost of water production ranges from 100 to 2000 US\$ million liters of clean water (Bautista et al.,2008).

Advanced Oxidation Processes (AOPs) are processes involving the concurrent use of more than one oxidation process, and involve the increase production of the highly reactive hydroxyl free radical (Yoon et al., 2001). These processes include techniques like Fenton's reagent oxidation, ultra violet (UV) photolysis and sonolysis, and are capable of degrading the organic pollutants at surrounding temperature and pressure (Comminellis et al., 2008). The main advantage of the advanced oxidation process is that organic contaminants are typically oxidized

to CO₂ (Chong et al., 2010). High removal rate of COD and chromaticity is the main characteristic of advanced oxidation processes. Compared with Fenton oxidation (Qiang et al., 2011), ozone oxidation process has the preference of not adding chemicals into the wastewater, generating no secondary pollution, and yielding high phenol's removal efficiency, thus been widely investigated (Guotao et al., 2013; Neufeld and Spinola, 1978; Wenqi et al., 2005; Yongqiang et al., 2013). However, high operation costs and poor Ammonical Nitrogen (NH₄-N) removal are the major disadvantages of ozone oxidation process. Ozonation is normally used coupled to biological treatment technology, such as membrane bioreactor (MBR), biological fluidized bed (Ji et al., 2014; Zhang and Xi, 2007), to enhance the biodegradation of pollutants present in BGW, making good use of the advantages of both techniques.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

In this study, 65% purity of calcium hypochlorite powder was provided and mixed with distilled water used to treat the wastewater from biomass gasification pilot plant. Besides, zinc and chromium standard solution are needed to be tested in Atomic Absorption Spectrometry (AAS). The BGP-generated tar-containing wastewater was obtained from Biomass Gasification pilot plant.

3.2 Equipment and instrumentations



Figure 3.1: Equipments and instruments

Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma (ICP), pH meter, BOD and COD equipment, High Performance Liquid Chromatography (HPLC), spectrophotometer, beaker, measuring cylinder, filter paper, burette, stirrer rod, filter funnel, weight balance, thermometer, petri dish, oven, turbidimeter, colorimeter, refrigerator, volumetric flask, conical flask and jar test apparatus.

3.3 Experimental procedures

3.3.1 Wastewater samples preservation

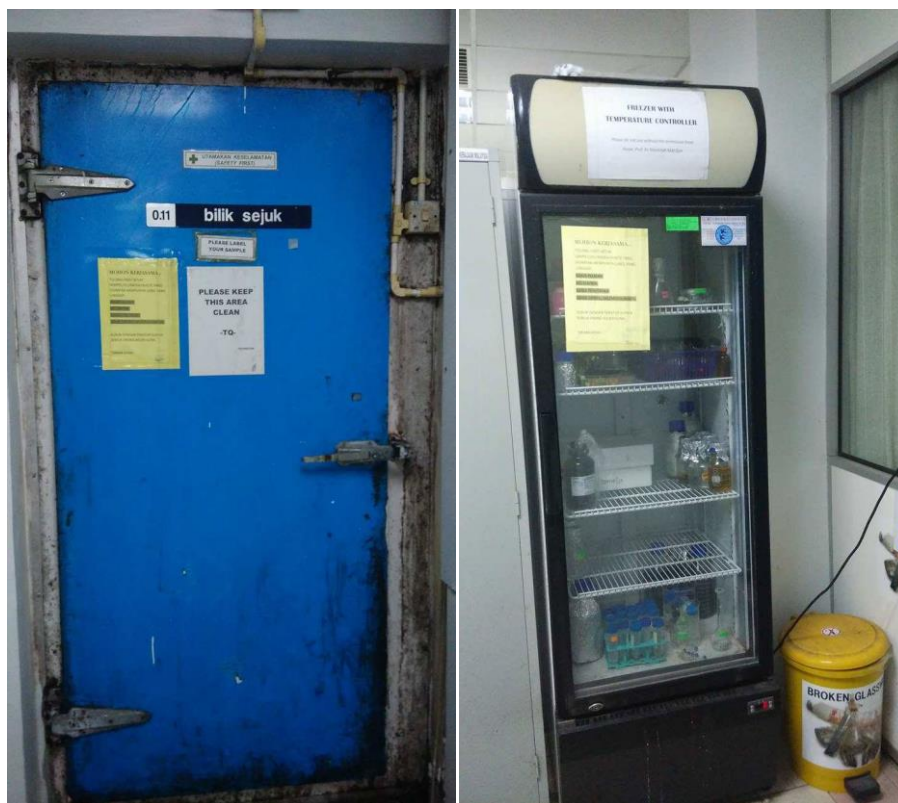


Figure 3.2 Preservation of wastewater samples using cold room and refrigerator

After composite sampling at diverse places, samples were collected in sampling bottles and an average samples were set up for analyses in laboratory. The transport of samples since the taking point and the laboratory is made in an icebox at 4°C to preserve the characteristics of wastewater. When samples are preserved, they were put in the refrigerator and were measured the temperature, pH and turbidity at the spot in unit operation laboratory. At the time of dosages, samples are homogenized before proceeding to the analytical operations.

3.3.2 Analytical methods

BGP production involves a number of wet processes that uses large quantities of water and other chemicals. Process wastewater is a major source of pollutants. It is typically a slightly acid and contains heavy metal wastewater. All these processes

contribute toward toxicity of the wastewater that needs to be characterized for possible treatment. Wastewater was analysed for the BOD, COD, TSS, TDS, pH, turbidity, colour, temperature, oil and grease, Cu, Zn, Cr, Hg, Cd, Pb, Mn, Ni, Mg, Fe, As, Sr, NH₄-N, phenol and free residual chlorine using standard methods (APHA, 2005).

The physicochemical analyses were performed on BGW studied according to standardized methods:

The chemical oxygen demand (COD) is analysed according to the method described in AFNOR (1983) (pp. 90–101) and measured by a spectrophotometer (UNICAM Model 8625 UV/VIS spectrometer). BOD₅ at 20°C was tested using APHA 5210(B). The total suspended solids TSS and TDS were evaluated according to the standard NF pp. 90–105. Discolouration of BGPW was assessed by the difference in optical density, read at 395 nm (Yesilada et al., 1995) between the BGPW before and after hypochlorination. The extraction of the phenolic fraction has been carried out according to the method described by Macheix et al. (1990) and the determination of total phenols was predicted by using the reagent Folin–Ciocalteu (Flouri et al., 1996), the absorbance was read at 760 nm and converted according to an equation into equivalent catechoic acid (g L⁻¹). The phenolic extract was analysed by high performance liquid chromatography (HPLC) at 280 nm on a HPLC Waters 600E device equipped with a photodiode 990 detector and a Millipore software for data analysis. Temperature and pH were measured by digital pH meter and thermometer. Turbidimeter 2100P is used to determine the turbidity. Chlorine levels are measured by a colorimetric method (Rodier, 1984). The effect of the two-stage treatment was evaluated by analysing these five parameters of the effluent: heavy metal concentration, turbidity, colour, the levels of residual chlorine and pH. Other heavy

metals were identified using standard methods for the examination for the water and wastewater through ICP or AAS. These parameters are conducted according to the following procedures.

3.4 Disinfection with Calcium Hypochlorite in the treatment of clarifying

$\text{Ca}(\text{OCI})_2$ powder with 65% purity was weighted in a precision balance. All the solutions were prepared under constant agitation. Twelve samples of BGW were processed by different concentrations of calcium hypochlorite solution (Table 3.1). The jar test assays are realized with MT-S-06 jar test apparatus by arranging 6 1000mL of beaker containing each 500 mL of sample for 2 run. Mixtures were agitated at 200 rpm for 5 min, followed by a flocculation period at 60 rpm for 5 min and then filtered through a filter paper (12.5 cm). After total powder dissolution, the solutions were filtered to remove debris. For storage, volumetric flask with covered were maintained closed in the flask because the solutions can be affected when exposed to light and air, the volumetric flask were covered with the cover and entirely filled with $\text{Ca}(\text{OCI})_2$ so that the space between the solution and the vial cap was minimal. Individual volumetric flasks were used for each test solution in AAS, colorimeter, turbidimeter, spectrophotometer and digital pH meter. All the solutions were stirred before analysis. The results obtained are presented in average values. The tests were applied to treat the percentages of reduction of polluting matters in the study of the treatment with calcium hypochlorite in solution.

Table 3.1 Samples and their concentrations of calcium hypochlorite

| Samples | Ca(OCl) ₂ concentration (g L ⁻¹) |
|---------|--|
| S1 | 0.25 |
| S2 | 0.40 |
| S3 | 0.50 |
| S4 | 1.00 |
| S5 | 1.50 |
| S6 | 2.00 |
| S7 | 2.50 |
| S8 | 3.00 |
| S9 | 4.00 |
| S10 | 6.00 |
| S11 | 8.00 |
| S12 | 10.00 |

3.5 Determination of the Available Chlorine Content and pH measurement

Wastewater samples were taken and mixed with the amount of the Ca(OCl)₂ powder as follows:

1. Ca(OCl)₂ 0.5% : 0.1153 g Ca(OCl)₂ Power + 15 mL wastewater
2. Ca(OCl)₂ 1.0% : 0.2307 g Ca(OCl)₂ Power + 15 mL wastewater
3. Ca(OCl)₂ 2.5% : 0.5769 g Ca(OCl)₂ Power + 15 mL wastewater
4. Ca(OCl)₂ 5.25%: 1.2115 g Ca(OCl)₂ Power + 15 mL wastewater

The beaker were wrapped with parafilm and stored at 6°C in a refrigerator, at 20°C in a air conditional environment and at ambient temperature (around 28°C) inside a cupboard for different periods (1, 3 and 5 days). The pH value and available chlorine content were measured to compare the effect of different retention times and temperature for the treatment of BGP wastewater.

3.6 Experimental activities

The overall experimental activities carried out in this study are presented in the following schematic flow diagram:

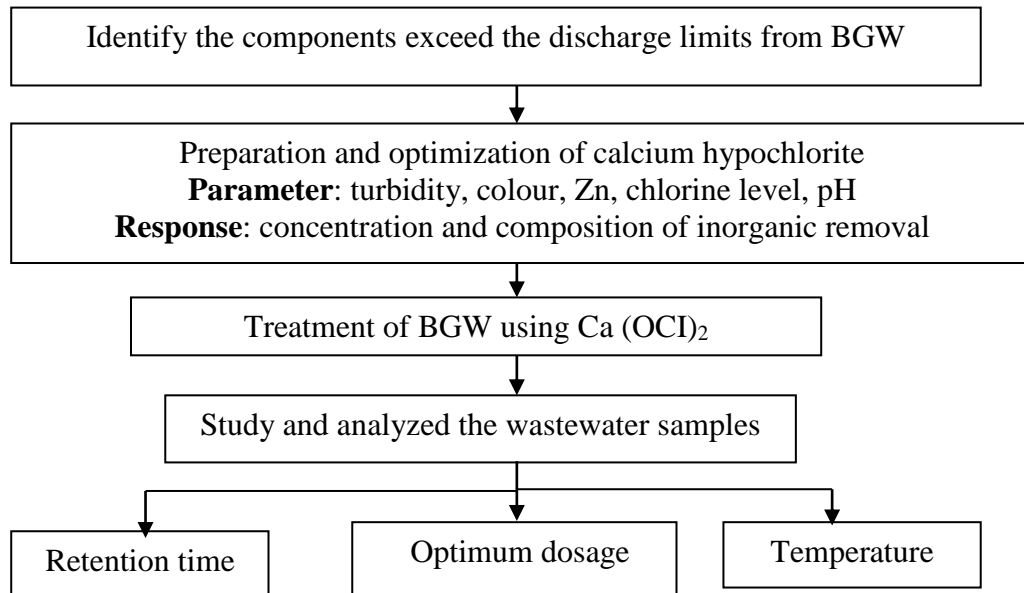


Figure 3.3 Schematic flow diagrams of experimental activities

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of BGP-generated tar-containing wastewater

4.1.1 Characteristics of Wastewater

The characteristic parameters of the physical quality and the composition in organic matters of the analyzed water are presented in Table 4.1. Effluents from BGPs are typically yellowish in colour, with fine particles and exert more oxygen demand.

Table 4.1 Parameters obtained from the analysis of Biomass Gasification Plant effluent

| Parameters | Unit | Raw water |
|---|------|--------------|
| pH | | 5.7 |
| Turbidity | NTU | 9.31 |
| Colour | ADMI | 22 |
| Temperature | (°C) | 30 |
| Total Suspended Solids (TSS) | mg/L | 5 |
| Total Dissolved Solid (TDS) | mg/L | 153 |
| Biochemical Oxygen Demand (BOD ₅) | mg/L | 2 |
| Chemical Oxygen Demand (COD) | mg/L | 28 |
| Mercury (Hg) | mg/L | ND (< 0.002) |
| Ammonical Nitrogen (NH ₄ -N) | mg/L | 4.27 |
| Phenol | mg/L | 0.04 |
| Cadmium (Cd) | mg/L | 0.0035 |
| Lead (Pb) | mg/L | 0.1 |
| Chromium (Cr) | mg/L | 0.04 |
| Manganese (Mn) | mg/L | 0.276 |
| Nickel (Ni) | mg/L | 0.0559 |
| Magnesium (Mg) | mg/L | 1.7149 |
| Zinc (Zn) | mg/L | 31.5 |
| Iron (Fe) | mg/L | 0.2529 |
| Arsenic (As) | mg/L | ND (< 0.002) |
| Strontium (Sr) | mg/L | 0.0484 |
| Dissolved Oxygen | mg/L | 8 |
| Free Residual Chlorine | mg/L | 0 |
| Oil & Grease | mg/L | 0 |

Table 4.1 represents the complete picture of the components obtained from the BGP-generated tar-containing wastewater sample analysis. The BGP water samples were collected after the water scrubbing process. The BGP water samples were stored in recipients of 10 L at 6 °C. The physicochemical components of the studied BGP are grouped in Table 4.1; they are expressed as average of values for three successive trial. Qualitative analysis of the zinc components show that the most abundant compounds, detected at 31.5 mg/L. Other compounds such as turbidity was also identified to be exceeded the standard requirement.

4.1.2 Qualitative Analysis

We can observe that the raw BGP water samples are shady and slightly acid, because certain concentrations of parameters are superior to the DOE standard.

Over the past two decades, environmental regulations have become more stringent, requiring an improved quality of treated effluent. In recent years, a wide range of treatment technologies such as chemical precipitation have been developed for heavy metal removal from contaminated wastewater. The most frightening values are for heavy metals (Zn) and cause a real threat to the environment (CPP, 1999).

Due to the discharge of large amount of metal-contaminated wastewater, inorganic effluent from the BGP-generated tar-containing wastewater contains toxic metals (Kurniawan,2002) which tend to accumulate in the food chain. Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders (Table 4.2). Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment.