APPLICATION OF COPPERAS AND SAGO STARCH IN DOMESTIC WASTEWATER TREATMENT BY COAGULATION FLOCCULATION PROCESS

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by

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LIST OF ABBREVIATIONS

WHO	World Health Organisation
APHA	American Public Health Association
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
SEM-EDX	Scanning Electron Microscopy and Energy Dispersive X-ray
FTIR	Fourier Transform Infrared
IEP	Isoelectro Static Point
pH	pondus Hidrogen
RPM	Rotation Per Minute
TKN	Total Kjehdahl Nitrogen
TOC	Total Organic Carbon
CPP	Copperas
AFS	Analytical Ferrous Sulfate
SG	Sago starch

APLIKASI KOPERAS DAN KANJI SAGU DALAM OLAHAN AIR SISA DOMESTIK SECARA PROSES PENGGUMPALAN DAN PENGGELOMPOKAN

ABSTRAK

Olahan air sisa domestik secara konvensional melibatkan pelbagai proses seperti proses secara fizikal, kimia dan biologi. Penggumpalan dan pengelompokan adalah salah satu kaedah yang biasanya digunakan dalam olahan air dan air sisa. Koperas (CPP) dan kanji sagu (SG) sebagai bahan penggumpal dikaji dalam penyelidikan ini. CPP yang digunakan merupakan bahan sampingan yang terhasil dari salah sebuah kilang pemprosesan ilmenite di Malaysia. Sebelum ini ia hanya dibuang di tapak pelupusan tanpa olahan. Ciri-ciri serta potensi CPP diuji dalam olahan air sisa domestik dan keputusannya dibandingkan dengan ferum sulfat analitikal (AFS). SG adalah kanji komersial yang sering digunakan dalam industri pembuatan makanan, bioteknologi dan kosmetik. Kegunaannya dalam olahan air sisa domestik belum pernah lagi diuji setakat ini. Air sisa domestik yang digunakan dalam kajian ini diperoleh daripada Loji Olahan Air sisa Berpusat (JRSTP) yang terletak di Juru, Pulau Pinang, Malaysia. Proses pesampelan dilakukan selama setahun iaitu dari April 2014 hingga April 2015. Sampel air sisa didapati mengandungi kandungan keperluan oksigen kimia (COD), kekeruhan, pepejal terampai, ammonia dan warna yang agak tinggi. Dalam kajian ini, kedua-dua bahan penggumpal (CPP dan SG) telah diuji menggunakan kaedah ujian jar standard. Keadaan optimum bagi eksperimen melibatkan CPP adalah pada pH 9, kepekatan 150 mg/L dengan aplikasi 1 min untuk pengadukan laju (100 rpm), 20 min pengadukan perlahan (60 rpm) dan 18 min untuk masa enapan. Untuk ujian menggunakan SG, keadaan optimum berlaku pada pH 7, kepekatan 2000 mg/L dengan aplikasi 1 min pengadukan laju (100 rpm), 30 min untuk pengadukan perlahan (20 rpm) dan 18 min masa enapan. Hasil kajian menunjukkan bahawa koperas berjaya mengurangkan 88% kekeruhan, 79% warna, 92% pepejal terampai, 83% keperluan oksigen kimia, 98% fosforus, 24% ammonia serta 44% Kjeldahl Nitrogen Jumlah. Manakala untuk AFS, 83% kekeruhan, 82% warna, 95% pepejal terampai, 79% keperluan oksigen kimia, 99% fosforus, 16% ammonia dan 12% jumlah Kjehdahl Nitrogen Jumlah. Olahan menggunakan SG pula mencatatkan penyingkiran 82% kekeruhan, 71% warna, 82% pepejal terampai, 73% keperluan oksigen kimia, 57% fosforus, 38% jumlah Kjeldahl Nitrogen Jumlah dan 6% ammonia. Dapat disimpulkan melalui kajian ini bahawa CPP, AFS serta SG mempunyai potensi besar dalam mengolah air sisa domestik.

APPLICATION OF COPPERAS AND SAGO STARCH IN DOMESTIC WASTEWATER TREATMENT BY COAGULATION FLOCCULATION PROCESS

ABSTRACT

Conventional treatment of domestic wastewater involves various processes which include physical, chemical and biological method. Coagulation and flocculation is one of the methods normally applied for water and wastewater treatment. In this study, copperas (CPP) and sago starch (SG) were used as coagulant. CPP used is a by-product of one of an ilmenite processing factories in Malaysia. Previously, it has been dumped in the landfill, untreated. The characteristics and its potential in treating domestic wastewater were investigated and the performances were compared with analytical ferrous sulfate (AFS). SG is a common starch commercially available. It has been used in food, biotechnology and cosmetic industries. Its usage as coagulant in domestic wastewater treatment has not been investigated to date. The domestic wastewater used in this research was collected from Juru Regional Sewage Treatment Plant (JRSTP) at Juru, Penang, Malaysia. Sampling process was conducted for one year (April 2014 to April 2015). The raw sample contains high concentration of COD, turbidity, suspended solids, ammoniacal nitrogen and colour. In this study, both coagulants (CPP and SG) were examined in standard jar test method. The optimum experimental conditions for CPP was pH 9, 150 mg/L of dosage with 1 min of rapid mixing (100 rpm), 20 mins of slow mixing (60 rpm) and 18 mins of settling. For test using SG, the optimum conditions occurred at pH 7, 2000 mg/L of dosage with 1 min of rapid mixing (100 rpm), 30 mins of slow mixing (20 rpm) and 18 mins of settling. It was found that, CPP removed 88% of turbidity, 79% of colour, 92% of suspended solids, 83% of COD, 98% of phosphorus, 24% of ammonia and 44% of TKN. On the other hand, AFS removed 83% of turbidity, 82% of colour, 95% of suspended solids, 79% of COD, 99% of phosphorus, 16% of ammonia and 12% of TKN. Besides that, the treatment using SG obtained the removal of 82% of turbidity, 71% of colour, 82% of suspended solids, 73% of COD, 57% of phosphorus, 38% of TKN and 6% of ammonia. As a conclusion, CPP, AFS and SG have good potential to be used as coagulant in domestic wastewater treatment.

CHAPTER ONE

INTRODUCTION

1.1 Background of Study

Uncontrolled discharge of domestic and industrial wastewaters into the environment causes severe pollution problems such as eutrophication or oxygen depletion in receiving water bodies and toxicity to aquatic organisms which makes wastewater treatment mandatory (Cai et. al., 2013; Moharram et al., 2015). Almost 2.5 billion people stay in developing countries have lacked access to a basic sanitation system nowadays. Hence, more than 40% population in the world dumps their wastewater improperly in watercourses (WHO, 2012). This improper dumping generates environmental problems that directly affect public health and increases the cost water treatment for public supply (Von Sperling, 2005; Wang et al., 2007). Domestic wastewater consists of nutrients, organic matter and other chemicals such as PAHs and phthalates (Huang et al, 2010). Thus, the untreated wastewater can lead to spreading of disease in the form of several types of endemic and epidemic illnesses (Ahmad et al., 2008).

Currently, there are many types of wastewater treatment which can be applied ranging from modest, low priced and less efficient processes to very advanced, highly efficient and pricey operations. The factors influence the selection of the treatment applied are the local area circumstances, such as climate and the weather, social attributes, economy, availability of enforceable standards, availability of land and power, demanded operation skills and its availability, monitoring actions, effluent discharge options as well as effluent reuse applications and conditions (Ahmad et al, 2008). Conventional wastewater treatment technologies are claimed to have some techno-economic limitations (Godos et al., 2009). Thus, currently there are several types of widely-used wastewater treatment technologies include activated sludge process (ASP), sequencing batch reactor (SBR), up-flow anaerobic sludge blanket reactors associated with facultative aerobic lagoon (UASB-FAL) and constructed wetlands (CWs) (Kalbar et al, 2012).

Coagulation and flocculation method is widely used to treat water and wastewater for particle removal (Al-Mallack et al., 1999; Wang et al., 2008). This method is relatively a simple physical chemical technique and commonly used for water and wastewater treatment. Mechanism to remove in this process is mainly consist of charge neutralization of negatively charged colloids by cationic hydrolysis products, followed by incorporation of impurities in an amorphous hydroxide precipitate through the flocculation process (Ghafari et al., 2009). Generally inorganic metal salts used in coagulation-flocculation are aluminium (alum), ferrous sulphate, ferric chloride and chloro-sulfate. Iron salts are often and more efficient than aluminium among these inorganic coagulants (Amokrane et al., 2007). However, the appropriate implementation of coagulation-flocculation method depends on the correct pH and coagulant dosage which are chosen. Therefore, the conventional of trial and error to optimize these variables has been practicing for this method (Ghafari et al., 2009).

Various flocculants categories have been developed recently; there are inorganic flocculants, organic flocculants and composite flocculants (Wang et al., 2008). Metallic compounds such as iron (Fe^{2+}, Fe^{3+}) and aluminium (Al^{3+}) salts are often used as coagulants. Iron salts coagulate in a wider range of pH, forming heavier flocs are less harmful in the event of an overdose compared to aluminium salts (Rennio et al., 2008). This research aimed to investigate the use of alternative coagulant from waste (copperas from ilmenite processing factory) in combination of a natural polymer made of sago starch.

1.2 Problem Statements

Domestic wastewater usually contains high amount of phosphorus (Wang et al., 2007) which comes from the major sources of residences, schools, hospitals, agricultural and commercial buildings (Thongtha et al., 2014). This phenomenon will lead to serious problems of eutrophication in ponds, rivers and seas (Wang and Wang, 2009) caused by enriched nutrients and increased biomass (Posadas et al., 2013). It also causes many water quality problems, including water spoilage and algal toxins (Barat et al., 2011). Usually, these contaminants of anthropogenic input, especially nitrogen (N) and phosphorus (P), were mainly from domestic wastewater uncontrolled discharge in rural areas (Kiedrsyn' ska et al., 2014). Colour in wastewater will damage the aesthetic nature, reduces light penetration and also the photosynthetic activity of aquatic organisms in the water body (Zheng et al., 2013).

Current domestic wastewater treatment in Malaysia normally involved various conventional processes include screening, grit and grease removal, pumping sedimentation, biological system and gravitational clarifier. The treated effluent normally complies with the standard discharge limit of effluent in terms of the main parameters such BOD, COD, and suspended solids. However, the parameters such as Total Kjehdahl Nitrogen (TKN), phosphorus and colour are not given much attention as they are still not degraded and appear in the form of the compound. These advanced parameters are important to be treated as they pose risks to harm aquatic life. These parameters are usually not well treated with conventional treatment processes. Additional treatment by chemical precipitation, settling and coagulation are always necessary.

One of the pigment producing factories in Malaysia produces by-product of copperas or ferrous sulphate heptahydrate ($FeSO_2.7H_2O$). Ferrous sulphate is extracted from the main production process (sulphate process) and sent to the copperas production loop. However, over the years the production of copperas increases from the existing capacity of 41,000 tonnes/annum to 220,000 tonnes/annum. They are currently dumped and dried unused. Its usage as coagulant has not been investigated for details.

Malaysia is the largest exporter of sago starch to the world with an annual production of approximately 51,000 tonnes of dry starch (Yunus et al., 2014). Currently sago starch is an important agricultural commodity in Malaysia, ranking fifth highest in terms of agricultural revenue after pepper, palm oil, cocoa and rubber (Othman et. al., 2015). Sago starch accumulates in the stem of the sago palm, which is a species of Metroxylon. It is the most important food resource and industrial raw material used throughout the world. Starch also is widely used as pharmaceutical excipient, primarily in tablet formulation, functioning as diluent, disintegrant and binder (Widodo and Hassan, 2015). In addition, the price of sago starch nowadays is very cheap (Qudsieh et. al., 2008). It is a natural, non-toxic and biodegradable polymer. Starch, chemically, is a homopolymer made up of basically two molecular species which are amylopectin and amylase. Amylopectin makes up the outer skin and contains combined species of phosphorus while amylase constitutes the inner part without any phosphorus (Nanji et. al., 2014). This characteristic shows the potential of sago starch as a coagulant in treating wastewater trough coagulation flocculation process. Qudsieh et al. in 2008 stated the potential of turbidity removal for kaolin water using sago starch as coagulant. The result was so impressive with over than 90% of turbidity removal obtained from the study. This research proved that sago starch has the potential to be used in wastewater treatment. To date, limited data is available on the application of $FeSO_4$ in domestic wastewater. In addition, no studies have been reported in the use of sago starch as a coagulant in treating domestic wastewater.

Hence this research aimed to investigate and compare the possibility of using two types of alternative coagulants namely copperas produced from ore of the ilmenite processing factories in Malaysia and sago starch in removing selected parameters in domestic wastewater. These parameters include turbidity (NTU), suspended solids (SS), colour, ammonia (NH_3-N), Total Kjeldahl Nitrogen (TKN), phosphorus and Chemical Oxygen Demand (COD).

1.3 Research Objectives

The main objective of this research was to investigate the potential use of copperas and sago starch as alternative coagulant in removing colour, SS, COD, turbidity, ammonia, TKN and phosphorus from domestic wastewater.

The specific objectives are:

i- To characterize and compare copperas, analytical ferrous sulphate and sago starch as coagulants.

ii- To determine the optimum operating conditions in the coagulation experiments which include pH, dosage, speed (rpm) and time (min).

iii- To investigate the sludge properties of domestic wastewater using copperas and sago starch as coagulants.

1.4 Scope of Study

This study focused on the application of standard coagulation and flocculation process to treat domestic wastewater using copperas compared with a laboratory standard of analytical ferrous sulfate as coagulant. Then, sago starch was also tested as polymeric coagulant through the same sample and treatment method. The targeted parameters include SS, colour, turbidity, ammonia, TKN, phosphorus and COD. The experiments covered the variation of optimum pH, dosages and lastly the optimum condition for every coagulants series in terms of speed and time duration of the mixing process. Domestic wastewater used in this research was collected from Juru Regional Sewage Treatment Plant (JRSTP) at Juru, Penang, Malaysia. Sampling process was conducted and characterized for one year (April 2014 to April 2015). Copperas in this study was collected from an ilmenite processing factory and sago starch was sponsored by a ‘keropok lekor’ factory in Terengganu.

1.5 Thesis Layout

There are five chapters covering all the information in this current research study. Chapter 1 is the brief introduction of the study. It explains about the background of the study, problem statement, objectives, scopes of study and the rationale of research study. Then, Chapter 2 focuses on the development of similar studies done by other researchers before. It explains about the overview, definitions, factors, mechanism and application about the current research. Chapter 3 is concerned with the methodologies used in this study. It gives the details of information on the research design and testing flow procedures employed. Next in Chapter 4, the results and findings of the study with the details of discussion are reported. Finally, in Chapter 5 states the conclusion of the overall research done. Suggestions of research work furtherance and refinement are also propounded in this chapter.

CHAPTER TWO

LITERATURE REVIEW

2.1 Wastewater

Wastewater is the water that has been adversely affected in quality by anthropogenic influence. It can be a combination of domestic, industrial, commercial or agricultural activities, storm water or surface runoff, and from sewer inflow or infiltration. Monitoring and treatment of its sources has become extremely important, particularly to prevent excess discharge of toxic substances and nutrients (nitrogen and phosphorus) in the aquatic systems that can affect the structure and functioning of ecological communities (Libralato et. al., 2016). European Inventory of Existing Commercial Chemical Substances in 2013 reported that the point of sources can contain more than 100,000 substances and their relative by-products. Usually, the information to identify the compounds present in wastewater is limited as well as their possible biological effects such as toxicity, genotoxicity or estrogenic potential (Newman and Unger, 2003). The same problem is also faced in the case of nutrient concentration, which it varies in accordance with the density of human activities (in the catchment basin or along the coast), locations and route of discharge. The nutrient enrichment can lead to nuisance of algal bloom under suitable light and temperature condition (Newman and Unger, 2003). Discharging control has been traditionally carried out using the measurements of global parameters (dissolved organic content, chemical oxygen demand) and methods that provide non-specific responses, which providing limited information on biological effects (Farré and Barceló, 2003). Recycled water quality can be assessed by some pollution parameters such as the content of colloidal particles, SS, natural organic matter (NOM) and other soluble. So, an appropriate treatment is considered necessary to meet the standards (Wei et al., 2015) and sustainability in the urban water cycle is increasingly at the forefront of discussion on new treatment technologies due changes in climate, regulation and population (Guest et al., 2009). However, they have substantial impacts towards the environment during their life cycle due to energy consumption, gas emissions and sludge generation (Piao et al., 2015).

2.2 Domestic wastewater

Domestic wastewater is the water contains all the materials added to the water during its use by a community. It contains a composed of a human body waste (faeces and urine) together with the water used for flushing toilets, and sullage, which is the wastewater resulting from personal washing, laundry, food preparation and the cleaning of kitchen utensils (Mara, 2013). Discharging of domestic wastewater that is insufficiently treated to aquatic receptors whether by direct discharge or baseflow, may lead to excess nutrient enrichment, algal blooms and eutrophication (Gill et al., 2009; Palmer-Felgate et al., 2010; Withers at al., 2011, 2012). This bad habit also will lead to waterborne disease and numerous significant outbreaks have been attributed to domestic wastewater treatment effluent ingress to drinking water sources (Karanis et al., 2007; Borchardt et al., 2011).

Fresh domestic wastewater contains large floating and suspended solids (such as faeces, rags, plastic containers and maize cobs), smaller suspended solids (such as partially disintegrated faeces, paper, vegetable peel) and very small solids in colloidal (i.e non-settleable) suspension, as well as pollutant in true solution. Hence, it is a grey turbid liquid that has an earthy with inoffensive odour. It has objectionable in appearance and hazardous in content; mainly because of the number of potential disease that can be caused by the organisms ('pathogenics') it contains (Mara, 2013). The composition of human urine and faeces are stated in Table 2.1.

Table 2.1 Composition of human urine and faeces

	Faeces	Urine
Quantities		
Quantity (wet) per person per day	135-270 g	1.0-1.3 kg
Quantity (dry solids) perperson per day	35-70 g	50-70 g
Approximate composition (%)		
Moisture	66-80	93-96
Organic matter	88-97	65-85
Nitrogen	5.0-7.0	15-19
Phosphorus (as P_2O_5)	3.0-5.4	2.5-5.0
Potassium (as K_2O)	1.0-2.5	3.0-4.5
Carbon	44-55	11-17
Calcium (as CaO)	4.5	4.5-6.0

(Source : Mara, 2013)

The main objective of wastewater treatment is to remove pollutants that can affect the aquatic environment before discharge. Historically, engineers focused on the removal of pollutants that would deplete the dissolved oxygen (DO) in the receiving water for the deleterious effects of low dissolved oxygen concentration on aquatic life (Moharram et al., 2015). Pollutants that demand oxygen are organic compounds. However, in this case, ammonia nitrogen is also an important paremeter that demanding the oxygen. Thus, in the early stage of wastewater treatment systems, it was designed to remove organic matter and to oxidize ammoniacal nitrogen to nitrate nitrogen. This is the goal of many wastewater treatment systems built nowadays (Junior et al., 2011).

Treatment of wastewater is a removing process of biological and chemical pollutants from water. Since the past years, water treatment plants have been developing the adopted technologies to increase the efficiency of reclamation so that it can comply with the discharge limits imposed by the law, which became more restrictive year by year (Panepinto et. al., 2016). Chemical analysis is an approach which was adopted for assessing the environmental impact of discharges. Therefore this technique is not suitable for certain wastewater. Hence, integrated assessment of wastewater is essential to ascertain the potential hazard (Libralato et. al., 2016). Hence, a few authors suggested combining different standard chemical analyses of target compound for toxicity assays to identify the main components of toxic effluents and sludge (Burkhard and Durhan, 1991; Fernández et al., 1995; Tothill and Turner, 1996). On the other hand, separation process has been proved by coagulation and flocculation technique. The process does not only separate suspended solids from water, but also remove color and certain organic matters from diverse sources of water such as paper industry wastewater, micro-polluted water, textile wastewater, municipal sewage and oily wastewater (Verma et al., 2012; Ugurlu et al., 2008; Theepharaksapan et al., 2012; Zhua et al., 2011; Zheng et al., 2009; Wei el al., 2009). Based on that factor, studies on improving the behavior of the coagulation-flocculation process have attracted great attention (Ugurlu et al., 2008; Theepharaksapan et al., 2012; Zhua et al., 2011; Zheng et al., 2009; Wei el al., 2009).

One of the main problems in domestic wastewater is the content of phosphate in the effluent. Wastewater treatment plant that released high concentration of phosphate (PO_4^{3-}) in the effluent can cause negative impact on aquatic ecosystems and human health (Fulazzaky et al., 2014). Phosphorus is an essential nutrient. It is required for many metabolic roles and needed for plant growth. However, the excessive amount of phosphorus enter the water can potentially lead to eutrophication problem (Anderson et al., 2002). Eutrophicated of a water body can create a green layer on the water surface. This condition contributes to the loosing of the water body primary function and subsequently influences the sustainable development of economy and society (Yang et al., 2008). Contaminate water occurred when oxygen is depleted when many plants die and decomposed; decaying organic matter produces unpleasant odours and makes the water cloudy simultaneously increase the turbidity (Conley et al., 2009).

River water clarification to produce potable water requires treatment to remove the suspended particles. Suspended particles in water can give negative effects in the light absorption of the aquatic life. The bluegreen of algae on the surface of the water disrupts the photosynthesis process and produces a negative aesthetic effect on the water (Lima et al., 2009). It usually shows a high degree of photostability. Turbidity can slow the photosynthesis and diffuse sunlight. When plant die, it reduces the amount of dissolved oxygen and increases the acidity (decaying organic material produces carbonic acid, which lowers pH level), both of these effects and harm the aquatic life (Kefford et al., 2012; Ferrari et al., 2010). In addition, the high level of turbidity may also stimulate the growth of microorganisms adsorbed from the particles. Thus, this condition affects the disinfection process by protecting the organisms within the flocs of the suspended matter. Therefore, suspended particles may also act as carriers of metal contamination (Devesa-ray et al., 2009; Devesa-ray et al., 2010) because of their high surface areas. Normally, suspended materials are removed with synthetic flocculant, which reduce or neutralize the electrostatic forces between charges particles in the water, thus leading to their aggregation and sedimentation (Devesa-rey, 2011).

In accelerating the removal of COD, colour and other contaminants present, it is important to determine the optimum conditions for the growth of microorganisms (Ghosh et al., 2014). Biomass can degrade the biodegradable of COD in the presence of oxygen. So the oxygen supply, which is a major factor that affecting the cost of wastewater treatment operation can be determined (Eddy and Metcalf, 2002). The biodegradable amount can determine the nitrogen removal potential of biological nutrient removal process (Kruhne et al., 2003; Ubay-Cokgor et al., 2005). COD is an important parameter for rapid measurement of industrial wastewater studies and control of wastewater treatments. It measures the relative oxygen depletion effect of waste contaminant and has been widely adopted as a measure of pollution effect (Lokhande et al., 2011).

2.3 Coagulation and flocculation

The main objective of wastewater management is the protection of the environment with public health and socio-economic concerns (Al-Saraway, 2001). There are many types of wastewater treatments used worldwide. All of them have the advantages and disadvantages in terms of construction costs, operational costs, operational complexity, energy consumption, effluent quality, land requirements, reliability and environmental impacts. Currently, a few of modern technologies were reported for wastewater treatment such as up flow anaerobic sludge blanket (USAB) (Tawfik et al., 2006), fixed film anaerobic filter (AF) (Renault et al., 2009), multi stage bubble column reactor (El-Hallwany, 2005), sequential batch reactor (SBR) (EPA, 2004), expanded granular sludge bed (EGSB), which is a modification to UASB, up-flow septic tank/baffled reactor (USBR) (Yu et al., 2010), submerged membrane hybrid system (Sahu et al., 2009) and anaerobic-anoxic-aerobic bioreactor (Kemira, 1990).

One of the most important physicochemical operations used in water and wastewater treatment is coagulation (Pernitsky and Edzwald, 2006). It can be used as pre-treatment, post treatment or even a main treatment (Rizzo et al., 2008). Coagulation and flocculation occurs in continuous steps aiming to overcome the forces stabilizing the suspended particles, allowing particle collision and growth to the floc (Sahu and Chaudhari, 2013). Methods of physical-chemical and biological are the treatment processes with their own traits. Biological treatment is economical but not so effective in refractory organic wastewater (Brian et al., 2008).

Coagulation-flocculation is a separation of solid-liquid process in the wastewater treatment (Zou et al., 2011; Maldonado and Guzman, 2014). Coagulation is the addition of a positively charged ion of metal salt or catalytic polyelectrolyte that results in particle destabilization and charge neutralization. The colloid particles of size target by coagulation process are 10^{-7} to 10^{-14} cm in diameter. This colloids particles exhibit Brownian movement through the water, their surface is negatively charged so they repel each other and form a stable dispersed suspension. The electric negative charged will be neutralized if colloid particles or ions of positive electric charge are being added together (Sahu and Chaudhari, 2013). Besides, in the coagulation process, colloidal substances in wastewater essentially are dissolved according to Derjaguin-Landau-Verwey-Overbeek theory (DLVO theory), whereby coagulation refers to the process of overcoming the interparticle repulsive energy barrier by simply increasing its ionic strength (Addai-Mensah and Prestidge, 2005).

Then, flocculation process is the addition of floc-forming chemical reagent usually after coagulation to agglomerate non-settable and slow-settling colloidal solids and it plays a major role in the fate and transport of contaminant in aquatic environments by bridging the aggregated flocs to form larger agglomerates in the presence of polymeric materials (Natalia and Olli, 2006; Somasundaran et al., 2005). In addition, flocculation is the successful collision that occurs when destabilized particles are driven towards each other by hydraulic shear force in the rapid mixing and flocculation basin. A few colloids will agglomerates then quickly bridge together to form microflocs which is turned into visible floc masses (Gregory, 2006). This step is one of the important steps in most wastewater treatment because it separates the particulate matter from the liquid phase. Generally in all waters, especially in surface waters contains both dissolved and suspended particles. However, until this moment, there is no physicochemical method to find the optimal dose for each contaminant removal by coagulation-flocculation, except the jar test (Lopez et al., 2013). Moreover, the major advantages of coagulation process is that most of the COD and turbidity substances are being reduced during this process and some colour can also be removed for effluent, thus leading to it being more cost efficient before secondary treatment. Besides, coagulation is one of the key methods in treating some industrial wastewaters, which are difficult to be treated by biological technologies (Fu et al., 2014).

The potential of coagulation in wastewater treatment depends on the coagulating agent used, the pH solution, the dosage, the concentration and the nature of the organic compound present in the water (Dominguez et al., 2007). The widely and mostly used coagulants are iron and alum salts. These types of coagulants encourage particles to agglomerate by reducing the electrostatic particle surface charge in the acidic pH region, prominently where hydrolysed metal species are abundant (Santo et al., 2012). Common coagulant used in wastewater treatment is the aluminium salts (Meghzili et al., 2008). Aluminium sulphate (alum) is one of the most widely used coagulants due to its low cost. The alum is also easy to use, handle, store, and mix. (Renault et al., 2009).

2.4 Types of Coagulants

Coagulants are chemicals added into water or wastewater to perform coagulation in the treatment. They are broadly classified into three types i.e. metallic salts (hydrolysing metallic salts), polymeric metallic salts (pre-hydrolysed/ pre-polymerised metallic salts) and polymers. Polymeric coagulant can be divided by both natural and synthetic polymers (Rui, 2013). A few chemicals such as ferric chloride, ferrous sulphate, aluminium chloride and hydrated lime have been conventionally used as coagulants in water and wastewater treatment (Al-Mallack et. al., 1999).

Recently, a lot of materials have been developed for coagulation and flocculation purposes. They are inorganic based coagulants, organic-based flocculants as well as hybrid materials (Moussas and Zouboulis, 2009). Besides that, polyacrylamide-based material is also used, however, the possible release of monomers is now considered harmful because they can enter the food chain and effect the health (e.g carcinogenic effects) (Bolto and Gregory, 2007). Nevertheless, the priorities in every research of coagulants are availability, low cost and safety.

Iron salts are found to be effective with a lower dosage compared to aluminium salts. It coagulates in a wider pH range and form heavier flocs (Li et al., 2010; Maranon et al., 2008). Furthermore, aluminium salts have long been suspected of being both carcinogenic and mutagenic as conventional coagulants. Meanwhile, iron-based coagulants pose less health risk than their aluminium counterparts in the event of an overdose. Therefore, using iron-based coagulants in place of aluminium-based one is obviously an advantage (Liu et al., 2012).

In flocculation process, the flocculation effects mainly depend on the choice of flocculants directly. A lot of flocculants are commercially available, but some of them have been received attention for their negative environmental consequences and potential health impacts (Yang, 2010). The use of inorganic salts such as aluminium chloride or aluminium sulphate for example, is now disputed due to their potential contribution to Alzheimer’s disease (Li et al., 2013) and the monomer of the polyacrylamide may cause the poisonous effect on the nerve system (Arezoo, 2002; Dearfield et al., 1988) besides produced a large scale of sludge (Renaut el al., 2009). Thus, the search for a better substitute to conventional flocculants has become an important challenge in the water treatment process with the objective of minimizing detrimental effects associated with the use of such flocculants (Li et al., 2013).

2.4.1 Inorganic Coagulant

Metal coagulants that are commonly used can be categorized into two general categories: aluminum based and iron based. The iron coagulants include ferric sulfate, ferrous sulfate, ferric chloride, ferric chloride, ferric chloride sulfate, poly-ferric sulfate and ferric salts with organic polymers. Aluminum coagulants include aluminum sulfate, aluminum chlorohydrate, poly-aluminum chloride, poly-aluminum sulfate chloride, poly-aluminum silicate chloride and forms of poly-aluminum chloride with organic polymers. Hydrated lime and magnesium carbonate are the other used of chemical coagulants (Bratby, 2006).

The principal of efficiency for these types of coagulants are their ability to form multicharged polynuclear complexes in solution, which enhanced adsorption characteristics. Metal of ions (Al^{3+} and Fe^{3+}) hydrolyzes rapidly when metal coagulants were added to the water. However, in some uncontrolled manner, it formed a metal hydrolysis species. The factors such as rapid mixing, pH and coagulant dosage determine which hydrolysis species is effective for the treatment (Bratby, 2006). In addition, the use of metallic coagulants such as alum and ferrous sulfate is a common practice to coagulate the suspended solids present in sewage wastewater. These kinds of coagulants are also cheap and safe, besides produce an easily handled sludge (Ismail et al, 2012). The advantages and disadvantages of inorganic coagulant are listed in Table 2.2.

Table 2.2 The advantages and disadvantages of inorganic coagulants.

Type of Coagulant	Advantages	Disadvantages
Aluminium based (ex:alum)	➢ Easily dissolved with water ➢ Does not cause reddish brown staining on floors, walls and equipment like ferric sufate of ferric chloride ➢ Less acidic ➢ Relatively low cost	➢ Works effectively at certain pH range ➢ Good coagulation may not be possible with alum in some waters.
Iron based (ex: ferric chloride, Ferric sulfate)	➢ Works well within all temperature range of treated water ➢ Ferric sulfate is able to promote oxidation of organic compounds. ➢ High solubility compared to aluminium based coagulant ➢ The floc formed with ferric coagulant is heavier than the alum floc ➢ Best removal for organic compounds ➢ Low cost	➢ Unsuitable doses cause reddish colour and high iron residual in treated water ➢ High iron residual clogs the filters as well as causes stain on cloth during laudry ➢ Very acidic ➢ Corrosive
Pre-polymerized metal coagulant (ex: PACL)	➢ Allows full charge neutralization before sweep floc formation due to its hydrolysis which is rather slow ➢ Produces less sludge due to lower consumption in coagulant compared to alum ➢ Able to coagulate the particles and colloids even at the lower tempareture ➢ Produces lower metal residuals	➢ The cost is three times greater than that of other coagulants(expensive)

(Source : Palaniandy, 2011; Bratby, 2006; Braul and Leader, 2001; Stephenson and Duff, 1996)

2.4.2 Copperas

Ferrous sulfate is also formerly known as copperas. It is a kind of interesting compound due to the presence of reactive Fe (II) cations that can be applied as anionic pollutant reducers, catalysts, adsorbents and ion exchangers besides sharing the general formula of $FeSO_4.nH_2O$ (Zhao et al., 2015). It is available in crystal or granules containing 20% Fe, both are readily soluble in water (Bratby, 2006). Ferrous sulfate is one of the iron-based coagulants. Wang et al. in 2008 reported that iron-based coagulants are synthesized by oxidation of ferrous sulfate to ferric sulfate, and then carrying out a controlled partial hydrolysis of ferric sulfate to produce a heterogeneous mixture of ferric, Fe (III)) ion hydrolysis species. The family of ferrous sulfate with exact crystal structures include ferroalumen $FeSO_4$, szomolnokite $FeSO_4 \cdot H_2O$, rozenite $FeSO_4 \cdot 4H_2O$ and melanterite $FeSO_4 \cdot 7H_2O$. Ferrous sulfate is commonly discovered in minerals that crystallized from solution of acidmine-waters. The solution becomes saturated in sulfate and Fe^{2+}. It has been used widely as raw materials in large amount of industrial production and chemical experiments (Zhao et al., 2015).

This species will react to many chemical additives forming a high polymer that enhances the aggregating power of flocculants by increasing the ratio of effective component and positive electric charge of the flocculants (Wang et al,. 2008). Ferrous sulfate can react either with natural alkalinity or added alkalinity to form ferrous hydroxide is relatively soluble. It must be oxidized to ferric hydroxide in order to be useful. Oxidation may be accomplished by aeration, dissolved oxygen in water, or adding chlorine, or if without chlorine, lime must be added to obtain sufficient alkalinity (Bratby, 2006). Performance of hydrolyzing metal salts in coagulation is strongly influenced by aqueous chemistry and raw water characteristics. Therefore, variables such as pH, coagulation type and dose, are well recognized as significant influential factors. Besides that, rapid mixing is the most important parameters that are suggested in the whole coagulation step as well (Liang et al., 2009).

Largely used of metallic compound coagulants are iron (Fe^{2+}, Fe^{3+}) and aluminum (Al^{3+}) salts. Iron salts coagulate in a wider pH range, form heavier flocs and are less harmful in the event of an overdose compared to aluminum salts (Rennio et al., 2008). In general, ferric iron is more advantageous and effective in the removal of colour, turbidity and total carbon and presents no problems of toxicity. Aziz et al. in 2007(a) studied the treatment of leachate using ferrous sulfate. The result obtained shows the different percentage removals at pH 4, pH 6 and pH 12. The suspended solids, colour and COD denoted the highest removals at pH12 (81.6%, 63% and 14.9%, respectively). While in the other study using ferrous sulfate as a coagulant, Aziz et al. in 2007(b) obtained the highest removal of colour at pH12 (77%). From these studies, it can be concluded that ferrous sulfate is superiorly react at higher range of pH effectively compared to lower pH.

2.4.3 Organic/ Natural Coagulant

Conventional coagulants in water and wastewater treatment operation used are metal and polymer based materials. The challenges of wide applicability usage of these general coagulants have been assisted with the various research efforts towards the development of green bio-based coagulants. This bio-based coagulant is applicable for obviating the challenges of the conventional coagulants usage. The aspects of green bio-based coagulants that need to be considered are the background information of the material, the economic importance, application of mode extraction as coagulant, underlying coagulating mechanism and the shortcoming of the usage in water and wastewater treatment operation (Oladoja, 2015). The green coagulants are varied from the most widely known seeds of different plants species to bone shell extract, ashes, bark resins, exoskeleton of shellfish extract and natural mineral soils (Ali et al., 2004).

Over the recent years, natural polymeric materials have been used and tested in water treatment with the purpose of volarization of the available biological resources and the elimination of the possible negative impacts of the synthetic polymers on human health. Synthetic polymers contain the presence of residual monomers from the manufacturing process and reaction by-product (Devrimci et al., 2012). Polymers made up of a long chain of smaller molecules, which are man-made organic compounds. It can be either cationic (positively charged), anionic (negatively charged) or non-ionic (neutrally charged) (Sahu and Chaudhari, 2013).

Some of the natural polymers like polysaccharides have been suggested to be moderately efficient due to their low molecular weight besides cheap and easily available from reproducible farm and forest resources. The advantages of these natural polyelectrolytes include safety for human health, wider effective dose range of flocculation for various colloidal suspensions and biodegradability. Hence, many studies have been done towards natural organic polymers for their flocculating ability to replace inorganic coagulants in recent years (Devrimci et al., 2012).

Natural coagulants extracted from plants have been introduced to solve these problems (Vieira at al., 2010). Polysaccharides and proteins are contained in the plant-based. Polysaccharides are a family of carbohydrates made from sugar rings linked by glycosidic bonds and various side functions. Polysaccharides behave as polyelectrolytes when charges are present. Positively charged groups are ammonium groups while negatively charged groups are carboxylic groups or sulphate groups (Crouzier at al., 2010). Organic polymeric coagulants have the inherent advantages of higher molecular weight, less pH dependence and increased aggregation capacity compared with inorganic coagulants (Sun et al., 2011).

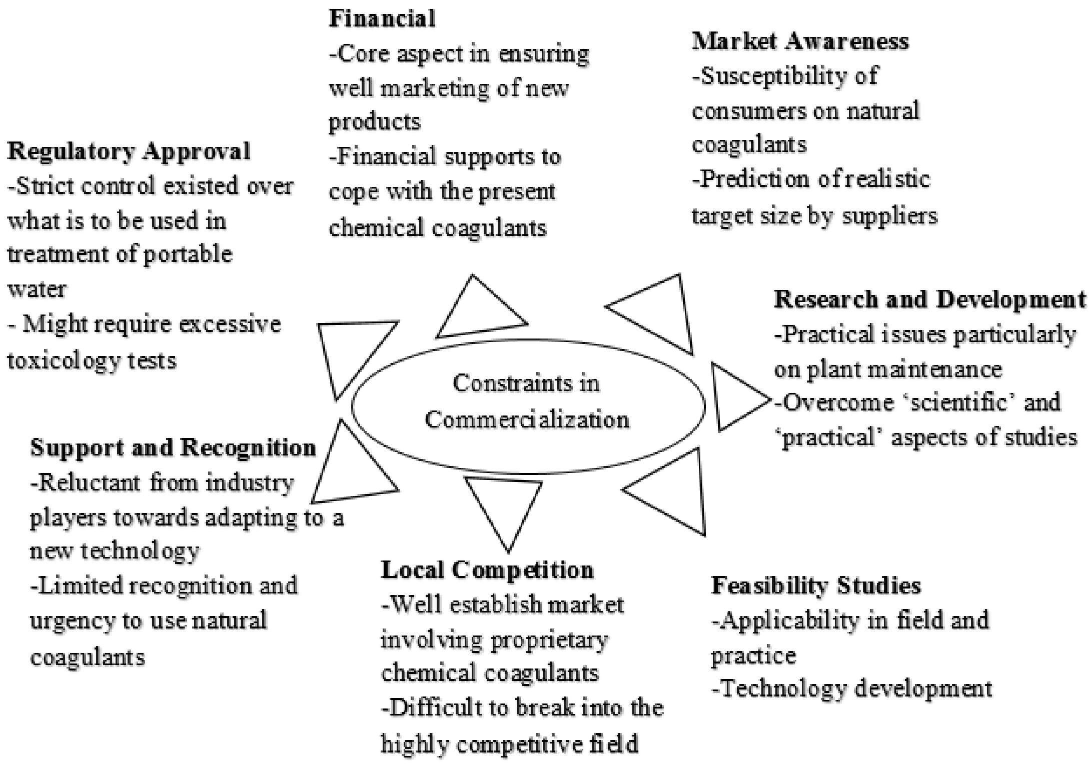

Figure 2.1 Factors hindering the commercialization of natural coagulation. (Source : Choy et al., 2014)

Choy et al. in 2014 stated the factors that hindering the commercialization of natural coagulant (Figure 2.1). The factors are categorized as financial, market awareness, research and development, feasibility studies, local competition, support and recognition and regulatory approval. All these factors restraint the natural coagulants to develop further in the industries. Besides that, Choy et al. in 2014 also denoted the benefits of using natural coagulants as shown in Figure 2.2. In most cases natural coagulant can be used as traditional medicine and it generally non-toxic. Then, it also can reduce the volume of sludge, biodegradable, and produce nutritious sludge that can be used as steel plant. In the cost side, it is normally possess low procurement cost, abundant in source and locally available. Moreover, the most important benefit is the sustainability. It is a plant based source, hence more environmental friendly, thus reduces chemical dependency.