FERROUS SULPHATE FROM TITANIUM DIOXIDE INDUSTRY FOR THE TREATMENT OF PETROLEUM REFINERY WASTEWATER

By

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LIST OF ABBREVIATIONS

$Al_2(SO_4)_3$	Aluminum sulphate
Al^{3+}	Aluminium (III)
$AlCl_3$	Aluminum chloride
ANOVA	Analysis of variance
AOPs	Advanced oxidation processes
API	American Petroleum Institute
Ca^{2+}	Calcium (II)
$CaCl_2$	Calcium chloride
CaO	Calcium oxide/ Lime
COD	Chemical oxygen demand
DAF	Dissolved air flotation
DO	Dissolved oxygen
DOC	Dissolved organic carbon
EDX	Energy dispersive X-ray spectroscopy
FCCD	Face centered composite design
FSH	Ferrous sulphate heptahydrate
Fe(II)	Iron (II)
Fe(III)	Iron (III)
$Fe(OH)_2$	Iron (II) hydroxide
$Fe(OH)_3$	Iron (III) hydroxide
$Fe_2(SO4)_3$	Ferric sulphate
Fe^{2+}	Iron (II)
Fe^{3+}	Iron (III)
$FeCl_2$	Ferrous chloride
$FeCl_3$	Ferric chloride
$FeSO_4$	Ferrous sulphate
$FeSO_{4.}7H_2O$	Ferrous sulphate heptahydrate
H^+	Hydrogen ion
H_2SO_4	Sulfuric acid
HCl	Nitric acid
$HgSO_4$	Mercury sulphate
$K_2Cr_2O_7$	Potassium dichromate

Mg^{2+}	Magnesium (II)
min	Minutes
NaOH	Sodium hydroxide
NTU	Nephelometric Turbidity Units
OFAT	One-factor-at-a time
OH^-	Hydroxide ion
PACl	Polyaluminium chloride
ppm	Parts per million
PRW	Petroleum refinery wastewater
rpm	Revolutions per minute
RSM	Response surface methodology
SEM	Scanning electron microscope
TOC	Total organic carbon
TSS	Total suspended solids
WWTPs	Wastewater treatment plants

LIST OF SYMBOLS

t	Time
x_i	Variables/input factors
y	Response of the system
x_1	pH
x_2	Dosage of $FeSO_4$
U_E	Electrophoretic mobility
ε	Dielectric constant
ξ	Zeta potential
η	Viscosity
κ	The Debye–Hükel parameter
a	Particle radius
d_H	Z-average hydrodynamic diameter
k	Boltzmann’s constant
T	Absolute temperature
D	Transitional diffusion coefficient

FERUS SULFAT DARI INDUSTRI TITANIUM DIOKSIDA UNTUK RAWATAN AIR SISA KILANG PENAPISAN PETROLEUM

ABSTRAK

Kaedah rawatan penggumpalan dan pengelompokan digunakan secara meluas dalam proses industri. Kecekapan proses penggumpalan dan pengelompokan ditentukan oleh dos penggumpal, pH, suhu, kekuatan ionik, kepekatan bahan organik, caj permukaan dan beberapa faktor lain. $FeSO_4$ (penggumpal) tidak didokumentasikan dengan baik dalam rawatan air sisa kilang penapisan petroleum (PRW). Oleh itu, dalam kajian ini, keupayaan $FeSO_4$ dalam rawatan PRW telah dikaji. Kecekapan penyingkiran/pengurangan warna, jumlah pepejal terampai (TSS), kekeruhan dan keperluan okisigen kimia (COD) telah dikira. Penggumpalan dan pengelompokan boleh dipantau melalui pengukuran kegerakan elektroforetik dan penentuan potensi zeta. Dalam kajian ini, interaksi antara $FeSO_4$ dengan zarah koloid bercas negatif dalam PRW dan mekanisme yang terlibat dalam proses penggumpalan dan pengelompokan dikaji. Tingkah laku zarah PRW yang berbeza terhadap $FeSO_4$ bergantung kepada pH dan dos $FeSO_4$ telah ditunjukkan. Didapati bahawa pada pH yang sangat rendah (pH 2), peneutralan bertanggungjawab dalam pengagregatan zarah dan pada pH yang tinggi ($pH > 8$), mekanisme menyapu pengelompokan bertanggungjawab dalam pengagregatan zarah. Pada pH dan dos penggumpal yang tinggi, $FeSO_4$ membentuk pepejal besi (II) hidroksida dan zarah koloid akan 'disapu keluar' dari PRW dan mengendap ke bawah. Kaedah respon permukaan telah digunakan dengan menggunakan muka reka bentuk komposit berpusat (FCCD) untuk mencari kombinasi terbaik pH dan dos penggumpal yang menyebabkan penyingkiran maksimum warna, TSS, kekeruhan dan pengurangan maksimum COD. Model-model kuadratik menunjukkan keadaan operasi yang optimum untuk WW16 ialah 623 mg/L

$FeSO_4$ pada pH 11, dengan 73.2% penyingkiran warna, 96.6% penyingkiran TSS, 79.4% penyingkiran kekeruhan dan 42.7% pengurangan COD. Keadaan operasi optimum untuk T1269 ialah pH 12 dan 1088 mg/L $FeSO_4$. Penyingkiran warna sebanyak 72.6%, pembuangan TSS sebanyak 56.4%, penyingkiran kekeruhan sebanyak 88.0% dan pengurangan COD sebanyak 16.3% telah ditunjukkan.

FERROUS SULPHATE FROM TITANIUM DIOXIDE INDUSTRY FOR THE TREATMENT OF PETROLEUM REFINERY WASTEWATER

ABSTRACT

Coagulation-flocculation treatment method is widely used in industrial processes. The efficiency of coagulation-flocculation process is determined by the coagulant dosage, pH, temperature, ionic strength, nature and concentration of organic matter, the surface charge and several other factors. $FeSO_4$ (coagulant) is not well documented in the treatment of petroleum refinery wastewater (PRW). Therefore, in this research, capability of $FeSO_4$ in the treatment of PRW was studied. The removal/reduction efficiencies for color, total suspended solids (TSS), turbidity and chemical oxygen demand (COD) were calculated. The coagulation-flocculation process can be monitored through the measurement of the electrophoretic mobility and the determination of zeta potential. In this study, the interaction between $FeSO_4$ and the negatively charged colloidal particles in PRW and the mechanisms involved in the coagulation-flocculation process were studied. Different behaviors of PRW particles with $FeSO_4$ depending on the pH and the dosage of the $FeSO_4$ were demonstrated. It was found out that at very low pH (pH 2), charge neutralization is responsible for the particle aggregation and at high pH (pH > 8) sweep flocculation mechanism is responsible for the particle aggregation. At high pH and high coagulant dosages, $FeSO_4$ formed solid iron(II) hydroxide and colloidal particles were 'swept out' from PRW and settled to the bottom. Response surface methodology was applied by using face centered composite design (FCCD) to find the best combination of pH and coagulant dosage that result in maximum color removal, TSS removal, turbidity removal and COD reduction. The quadratic models developed indicated the optimum operating conditions for WW16 to be 623 mg/L of $FeSO_4$ at pH 11, with 73.2% color removal, 96.6% TSS removal, 79.4% turbidity removal and 42.7% COD reduction. The optimum operating conditions for T1269 to be pH 12 and 1088 mg/L of $FeSO_4$. The color removal of 72.6%, TSS removal of 56.4%, turbidity removal of 88.0% and COD reduction of 16.3% were demonstrated.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

The main sources of energy supply in Malaysia are crude oil and petroleum products, which accounted for 44.7% of the total energy supply in year 2010. Thus, Malaysia is investing in the crude oil refining activities. The average oil production of Malaysian for 2010 was 664,827 bbl/d (Rahim and Liwan, 2012). The refining processes of crude oil produce a significant amount of wastewater and the treatment of wastewater is one of the major problems faced by the petroleum and petrochemical industries. These make crude oil processing and the production of petroleum refinery wastewater (PRW) an important issue. The study on the petroleum refining processes revealed that the production of petroleum products involved many complicated processes. The complexity of the units and processes make the PRW consist of many types of pollutants (Coelho et al,. 2006; Alva-Arg´aez et al., 2007; El-Naas et al., 2014).

Malaysia is still greatly dependent on non-renewable fuel as a source of energy. Being a developing country, Malaysia will have to cope with the increasing demands for energy. The production of energy will however have to be conducted in a cost effective manner while ensuring its sustainability (Rahim and Liwan, 2012). In the petroleum and petrochemical industries such as in petroleum refineries, large volumes of wastewater are generated leading to great concerns in improving the management of wastewater (Saien and Nejati, 2007; El-Naas et al., 2014). Generally, petroleum refinery wastewater or PRW contains many different contaminants, such as Mg^{2+}, Ca^{2+}, S^{2-}, Cl^{-}, SO_4^{2-}, emulsified oil and grease, phenols, cresols, sulfides, ammonia and cyanides. All of these pollutants contribute to the high chemical oxygen demand (COD) (Yan et al., 2010; El-Naas et al., 2014).

In petroleum refining, the major sources of wastewater are from the different petroleum refining units, such as crude desalting, crude oil distillation, thermal cracking, catalytic cracking, hydrocracking, polymerization, alkylation, isomerization, reforming and hydrotreating (Alva-Arg´aez et al., 2007). The mixture of these processes and products create a wastewater containing a multitude of pollutants, resulting in the complexity of the wastewater to be discharged. As a result, an effective approach should be developed to face stringent environmental regulations as per the requirements of Environmental Quality (Industrial Effluent) Regulations 2009 of Malaysia on the quality of effluent discharged (Appendix B). The effluents are only allowed to be discharged into the inland waters if specific parameters met the regulatory limits. However, there are inherent problems with certain PRW parameters that are harder to comply with the two water standards, Standard A and Standard B. The water quality standards are graded based on the purpose of consumption. In Malaysia, the primary drinking water standard (Standard A) relates directly to health, where it is for the purpose of human consumption; while secondary standard (Standard B) relates more to the appearance and non-consumptive uses of water. Hence, it is essential for continuing research and study on wastewater treatment, in order to discover treatment methods that can sustain this industry.

1.2 Problem Statement

The quality of water for the purpose of human consumption has been of interest since its effects on health was first discovered. Concerning the increase in water demand and the decrease in resources, water as the essential fluid of life is a scarce commodity. Hence, public awareness of the need to better manage and protect water has grown over the last decade; water supply and treatment are now critical needs of the society.

The refining processes of crude oil generate a wastewater containing multi contaminants which can be difficult to treat (Sun et al., 2008). This wastewater can cause serious environmental problems due to their high organic substances, large amount of suspended solids, which contribute to high chemical oxygen demand (COD) in a natural environment (Sun et al., 2008; Yan et al., 2014). The standard discharge limits of effluent are becoming more stringent, creating problems for the industries to comply. With the remarkable economic growth in the world, concerns are raised about many environmental challenges. Industries face challenges to reduce the amount and quality of wastewater generated while trying to attain sustainable standards of operation (Alva-Arg´aez et al., 2007; El-Naas et al., 2014). Therefore, there is an urgent need to develop efficient treatment methods to remove contaminants from PRW ensuring its reuse and/or decreasing the pollution to acceptable levels before discharging into the receiving water bodies (Mansouri et al., 2014).

The PRW generated by petroleum refineries usually require treatment before its discharge or reuse. The discharge of untreated PRW into freshwater, estuarine or marine ecosystems may change/affect the aquatic life and the habitats and also has adverse effects on human health (Barceló, 2005). On the other hand, the treatment of wastewater is costly and is a burden to many industries. As a result, a cost effective wastewater treatment method should be developed in order to obtain effluent with better quality while comply with the stringent environmental regulations.

At the present time, there is no single process capable of adequately treating PRW, and this is mainly due to the complex nature of PRW (AECOM, 2010). Hence, a combination of different processes is used to overcome the drawback of individual unit process as well as attain desired water quality in an economical way (Benyahia et al., 2006; Diya’uddeen et al., 2011; El-Naas et al., 2014). Generally, PRW is treated based on an initial step consists of physicochemical and mechanical treatments and further advanced treatment of the pretreated effluent (e.g. Biological treatment in the integrated activated sludge treatment unit) (Shahrezaei et al., 2012).

Numerous treatment methods are proposed including electrocoagulation (Yavuz et al., 2010), photocatalytic oxidation (Shahrezaei et al., 2012), photodegradation (Stepnowski et al., 2002), catalytic vacuum distillation (Yan et al., 2010), coagulation and flocculation (Santo et al., 2012), fenton oxidation (Hasan et al., 2012), adsorption (El-Naas et al., 2010), biodegradation (Tyagi et al., 1993), membrane bioreactor (Shariati et al., 2011), ultrasound (Rasheed et al., 2011) and microwave-assisted catalytic wet air oxidation (Sun et al., 2008). Generally, after the physical treatment, PRW undergoes chemical treatment for the removal of pollutants. The chemical treatment of PRW is either by coagulation-flocculation or by coagulation-dissolved air flotation processes. Both the processes are widely used in water treatment plants and have been found to be desirable for the treatment of PRW (Verma et al., 2010; Santo et al., 2012).

Coagulation-flocculation treatment technology is extensively used in many water and wastewater treatment facilities. Coagulation and flocculation help in removing/separating organics/inorganics dissolved/suspended colloids in wastewater (Verma et al., 2010). Coagulation-flocculation is popular as a pre-treatment step for the removal of turbidity, organic matter, color, and microorganism in the wastewater (Zheng et al., 2011). The increasing popularity of using chemical treatment in coagulation-flocculation can be rationalized by the fact that the chemical treatment is fast (due to the chemical reaction involved), predictable and controllable by simple techniques. Moreover, it need only lower operating space, plants are flexible and readily modified without the change in the basic structure. The chemical processes can also be designed to produce useful by-products (Semerjian and Ayoub, 2003).

In recent years, Ayeche (2012), Alkarkhi et al. (2013), Lakshmanan and Rajarao (2014), Teh et al. (2014) and Amor et al. (2015) have used coagulation and flocculation in the removal of pollutants from wastewaters from the dairy industry, textile industry, sewage plant, palm oil mill and landfill leachate respectively. However, only few studies are found in the literature for the treatment of PRW with coagulation and flocculation. Coagulation–flocculation is one of the fastest ways to remove organic matter, by integrating into existing treatment process of PRW, the treatment efficiency may improve.

Most frequently used coagulants are aluminum sulphate, ferric chloride, ferric sulphate, lime and polyaluminum chloride (Corbitt, 1999; Tchobanoglous et al., 2003; Irfan et al., 2013). However, commercially available coagulants are relatively expensive. Hence, there is a growing interest in using coagulants with a lower cost. In the present study, ferrous sulphate, $FeSO_4$ (a by-product from the sulphate process of titanium dioxide pigment) is used as a coagulant in the treatment of PRW. The

$FeSO_4$ from titanium dioxide industry is used in a range of applications. For instance, Su and Ludwig (2005) used $FeSO_4$ (as a reluctance) to treat hexavalent chromium, Cr (VI) during the chromite ore processing, where Fe(II) was used to reduce Cr(VI) (carcinogen) to Cr(III) (essential micronutrient for living organisms). Besides that, $FeSO_4$ is also used (as an iron supplement) to treat iron deficiency in the blood. $FeSO_4$ supplies iron to the body to produce haemoglobin, which is needed to help the blood to carry oxygen (Zariwala et al., 2013). Apart from that, $FeSO_4$ also has been employed in the purification of water by flocculation (Aziz et al., 2007; Kushwaha et al., 2010; Rodrigues et al., 2013), as well as the removal of phosphate in municipal and industrial sewage treatment plants to prevent eutrophication (Gázquez et al., 2014). However, $FeSO_4$ is not well documented in the treatment of PRW. Therefore, in this research, capability of $FeSO_4$ in the treatment of PRW was studied. Since $FeSO_4$ is relatively cheaper compared to other coagulants, it's also beneficial to coagulation removal in terms of lower cost.

The present case study is on wastewater from a local refining company located in Port Dickson, Malaysia. In this study, the suitability of inorganic coagulant ($FeSO_4$) was evaluated for the treatment of PRW. The efficiency of coagulation and flocculation is determined by pH, coagulant dosage, temperature, ionic strength, total dissolved solids, concentration of organic substances, distribution and the size of colloidal particles in suspension and some other factors (Santo et al., 2012). Therefore, the effect of different parameters, such as initial pH and coagulant dosage, on the treatment efficiency was assessed in terms of color removal, turbidity removal, total suspended solids (TSS) removal and chemical oxygen demand (COD) reduction were studied.

1.3 Research Objectives

The objectives of this study are as follows:

i. To determine the removal/ reduction efficiency of color, TSS, turbidity and COD as a function of pH and $FeSO_4$ dosage.

ii. To study the mechanism involved in coagulation-flocculation process with the aid of zeta potential measurement.

iii. To optimize the coagulation-flocculation process using response surface methodology (RSM).

CHAPTER TWO

LITERATURE REVIEW

2.1 Titanium Dioxide Industry

Titanium dioxide (TiO_2) is a simple inorganic compound produced as a pure white powder and it is non-hazardous (McNulty, 2007; Huntsman Pigments, 2008). The main uses of TiO_2 are in coatings (such as paints), plastics, papers and printing inks. There is also a wide range of minor uses, such as pharmaceuticals, cosmetic industries, textiles and food Industry (McNulty, 2007; Gázquez et al., 2014). In year 2013, the world production of titanium mineral concentrates was 7.6 million tonnes. Almost 95% of the concentrates are consumed in the production of titanium dioxide pigment (Gambogi, 2014). Titanium dioxide has worldwide sales of around 4.5 million tonnes (McNulty, 2007).

The overall process of manufacturing TiO_2 is to convert an impure titanium mineral concentrates into pure white TiO_2 pigment. Traditionally, there are two distinct processes of the TiO_2 manufacturing: the sulfate process and the chloride process. Both routes start with impure TiO_2 based mineral feedstocks. The chloride process used chlorine gas. The main chemical reactions of chloride process can be represented as (McNulty, 2007; Gázquez et al., 2014):

$$TiO_{2\ (impure)} + C + 2Cl_2 \rightarrow TiCl_4 + CO + CO_2 \text{ (Chlorination)} \qquad (2.1)$$

$$TiCl_4 + O_2 \rightarrow TiO_{2\ (pure)} + 2Cl_2 \text{ (Oxidation)} \qquad (2.2)$$

The pure titanium dioxide produced is then undergone a range of chemical surface treatments, milling and drying operations to give a range of products with specific properties which are suitable to use in particular applications.

For the sulphate process, normally the feedstock is ilmenite with 50- 60% of TiO_2, 15-25% of FeO and 15-25% of Fe_2O_3. The overall chemistry of the sulphate process can be represented as (McNulty, 2007; Gázquez et al., 2014):

$FeTiO_3 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + H_2O$ (Digestion) (2.3)

$TiOSO_4 + H_2O \rightarrow TiO_2n.H_2O + H_2SO_4$ (Hydrolysis) (2.4)

$TiO_2n.H_2O \rightarrow TiO_2 = n.H_2O$ (Calcination) (2.5)

The sulphate process is a complicated process as shown in Figure 2.1. The feedstock used is ilmenite ($FeTiO_3$). Firstly, ilmenite is digested in concentrated sulphuric acid and converts the titanium components into titanyl sulphate ($TiOSO_4$) and the iron into sulphates. Then, a reduction step (where iron is added) is needed to convert any ferric ions (Fe^{3+}) to ferrous ions (Fe^{2+}). This is to aid the separation process later. After that, followed by a clarification step, in which the undigested material is allowed to settle and remove from the liquor. Next, followed by crystallization which separates out by-product, ferrous sulphate heptahydrate ($FeSO_4.7H_2O$, FSH) (McNulty, 2007; Huang et al., 2015). In China, 98% of the TiO_2 is manufactured using the sulphate process route, thus producing over 7 million tons of FSH waste annually (Zhu et al., 2011a). FSH is used in a range of applications including water treatment, agriculture (fertilizer) and cement manufacturing (Gázquez et al., 2014). The remaining liquor undergoes hydrolysis in which the $TiOSO_4$ is reacted with water to form hydrated titanium dioxide ($TiO_2n.H_2O$) and sulphuric acid is released. After filtration, the hydrated titanium dioxide slurry is then passed to a rotary kiln where it is calcined (heated to high temperatures in air or oxygen) to produce titanium dioxide product in anhydrous form. The finishing process is similar to the chloride process including chemical surface treatments, milling and drying operations. About one ton of raw material (ilmenite or ilmenite +

slag) is required to produce 0.5 tons of titanium dioxide pigment. The sulphuric acid that is released at hydrolysis process is not strong enough to be used directly in the digestion process. Hence, it is subjected to either acid concentration (to increase the acid strength) or neutralization where gypsum ($CaSO_4{\cdot}2H_2O$) is produced (McNulty, 2007; Gázquez et al., 2014).

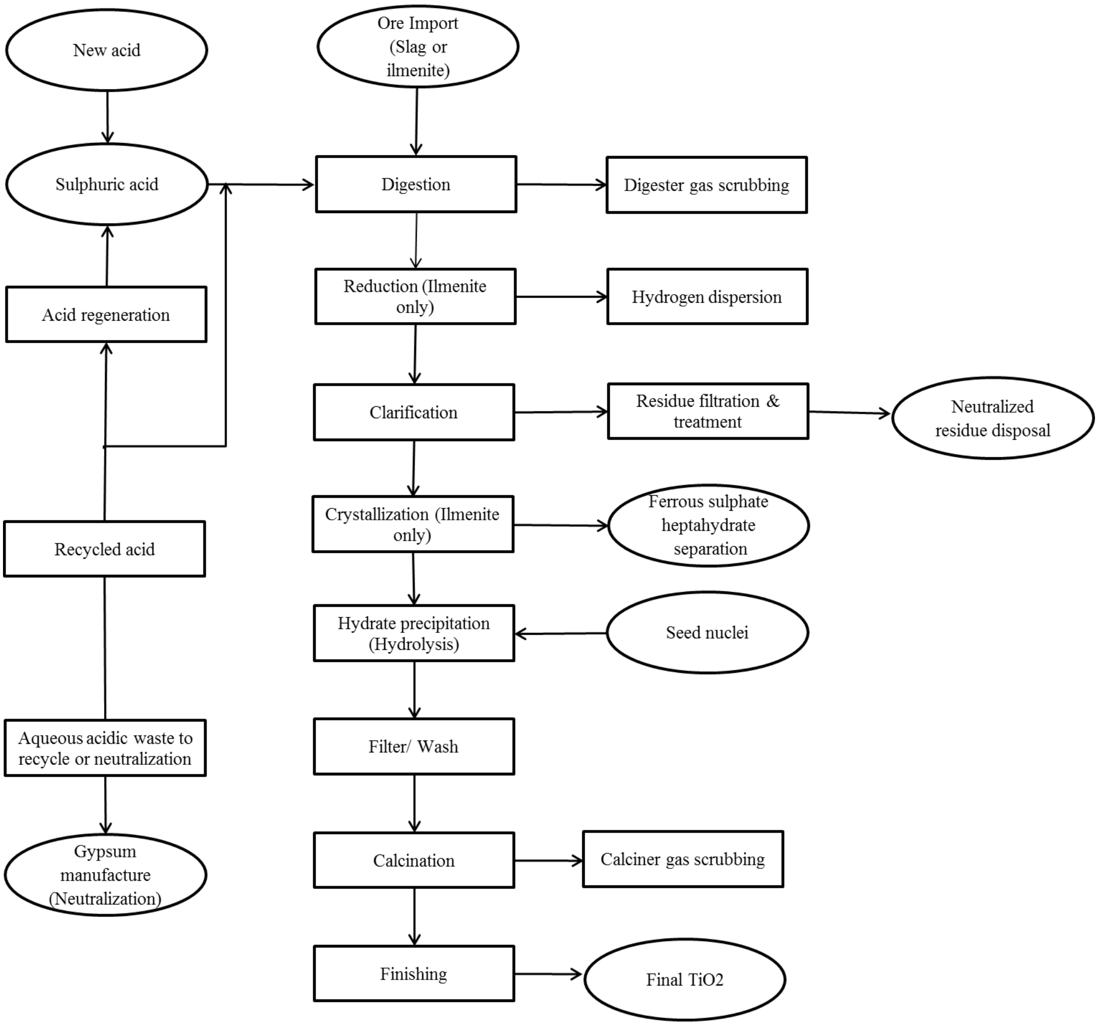

Figure 2.1: The sulphate process route of TiO_2 production (McNulty, 2007).

2.2 Petroleum Refinery Wastewater

Petroleum refinery consists of multiple operations, which depend on the type of crude refined and the products. Petroleum refinery is a large water consumer, depending on the crude, products, size and complexity of the unit operations (AECOM, 2010). Petroleum refining is a vital process, where crude oil is converted into useful petroleum products. Crude oil is converted into over 2,500 useful petroleum products, comprising of liquefied petroleum gas, kerosene, gasoline, diesel fuel, aviation fuel, lubricating oils and fuel oils (Benyahia, 2006; Santo et al., 2012). In 2014, the global production of oil averaged 93 million barrels per day (mbpd), which was actually a huge amount (United States Energy Information Administration, 2015).

The crude oil refining process consumes great volume of water, thus the volume of wastewater generated are large. The process wastewater, utilities operation wastewater, laboratory wastewater, refinery storm water, sewerage and sanitary waste and miscellaneous contaminated streams contribute significantly to the total volume of the petroleum refinery wastewater (PRW) (Al Zarooni and Elshorbagy, 2006; Coelho et al., 2006; AECOM, 2010; Santo et al., 2012). PRW is a kind of wastewater that produced mainly by the industries that involved in refining crude oil and manufacturing petrochemical intermediates, fuels and lubricants. Thus, PRW generally composed of oil and grease along with many other toxic organic compounds (Diya'uddeen et al., 2011).

Coelho et al. (2006) reported that the volume of PRW generated was about 0.4 to 1.6 times the volume of the crude oil processed. The discharges of PRW into the natural water body will contaminate the water with numerous pollutants such as petroleum hydrocarbons, sulphur compounds, nitrogen compounds, inorganic substance (sulfides, cyanides, Mg^{2+}, Ca^{2+}, S^{2-}, Cl^{-} and SO_4^{2-}) and dissolved or particulate organic (phenols, cresols) (Santo et al., 2012; El-Naas et al., 2014). Table 2.1 summarizes the main pollutants in several petroleum refining units.

Table 2.1: Major pollutants in petroleum refining units (Alva-Arg´aez et al., 2007).

Unit	**Wastewater main pollutants**
Crude desalting	Free oil, ammonia, sulfides and suspended solids
Crude oil distillation	Sulfides, ammonia, phenols, oil, chlorides, mercaptans
Thermal cracking	H_2S, ammonia, phenols
Catalytic cracking	Oil, sulfides, phenols, cyanide, ammonia
Hydrocracking	High in sulfides
Polymerization	Sulfides, mercaptans, ammonia
Alkylation	Spent caustic, oil, sulfides, suspended solids
Isomerization	Low level of phenols
Reforming	Sulfide
Hydrotreating	Ammonia, sulfides, phenol

In crude desalting, the crude oil is dehydrated and salts are separated from the oil either in the presence of chemicals or under the influence of high voltage electrostatic fields that agglomerate the dispersed droplets. The wastewater of crude oil distillation unit comes from overhead accumulators, oil sampling lines, barometric condensers, overhead reflux drum and overhead product drum. In thermal cracking, the major source of wastewater is from the overhead accumulator on the fractionator, where water is separated from the hydrocarbon vapor. In a refinery, the catalytic cracking units are among the biggest sources of sour and phenolic wastewaters. Hydrocracking is a catalytic cracking process in the presence of hydrogen. In polymerization, acid is used as a catalyst, however, the waste generated is alkaline. This is because, the acid catalyst is recycled and removed by caustic washing. In alkylation, the major pollutant is the spent caustics from the neutralisation stage. The isomerization wastewaters contain low levels of phenols and oxygen demand. Reforming is a relatively clean process where none of the waste streams have high concentrations of pollutants (Alva-Arg´aez et al., 2007).

PRW can differ depending on the type of oil being processed, the unit operations and plant configuration involved at any specific time, therefore the exact composition of PRW cannot be generalized (Wake, 2005; Saien and Nejati, 2007). There are various refinery configurations, each one is designed to transform crude oil into useful petroleum products (Diya'uddeen et al., 2011). Al Zarooni and Elshorbagy (2006) categorized refineries into either a hydro-skimming unit or a complex unit, which combines an additional catalytic cracking unit into the hydro-skimming unit. The hydro-skimming unit consists of three sub-units (a crude distillation unit, which fractionates crude oil into various components, a desulphurising unit, which reduces the sulphur content of some fractions such as kerosene and naphtha and a reforming unit, which produces reformate). Each PRW generated depends on the refinery configurations and the number of units, as a result, there is a lack of uniformity in the PRW composition (Diya'uddeen et al., 2011). In petroleum and petrochemical industries, in order to conserve water, there is a great interest in improving the wastewater management. Wastewater management can be improved through optimizing the water use and introducing recycling technologies within the production units (Saien and Nejati, 2007). Improved water management in a petroleum refinery can decrease the volume and cost of raw water used in the operations. By optimizing water management, it may also reduce the mass of contaminants in the treated effluent, thus improving the quality of the effluent discharge and ultimately reduce the environmental impact (AECOM, 2010).

2.2.1 Wastewater Characteristics and Impact on Environment

PRW is one of the major sources of aquatic environmental pollution. PRW consists of a wide range of chemicals at different concentrations, including hydrocarbons, ammonia, sulphides, phenol and cyanides that have detrimental and harmful effects on plant, aquatic life, surface of soil as well as surface and ground water resources (Wake, 2005; Sun et al., 2008; El-Naas et al., 2009). The high polycyclic aromatics contents in PRW are toxic and persistent in the environment (Mrayyana and Battikhi, 2005; Wake, 2005). The nitrogen and sulphur components in PRW are toxic and usually exist in the form of ammonia and hydrogen sulphide (H_2S), respectively. In an aqueous solution, H_2S exists in equilibrium with bisulphide (HS^-) and sulphide (S^{2-}), or volatilize as H_2S gas. H_2S is highly toxic to aquatic animal. Once the threshold limit surpasses 0.5 mg/L, it causes mass fish mortality in saltwater or freshwater fish (Altas and Büyükgüngör, 2008). Cyanides are very toxic to marine organisms as it affects the transport of oxygen from the blood to the tissues (Wake, 2005).

According to Wake (2005), the different components of the PRW can have varying effects and toxicities to phytoplankton, algae, invertebrates and fish. Marine /estuarine species are more sensitive than freshwater species and larvae be likely to be more sensitive than adults are. PRW not only can be lethal, it also has effects on reproduction and growth of aquatic life. The minimum amount of dissolved oxygen

(DO) essential to support life in an aquatic environment is approximately 2 mg/L (Attiogbe et al., 2007). The discharge of wastewater high in organic matter in water bodies will cause the increase in oxygen consumption by the bacteria. This is an attempt to oxidize the effluent, thus depleting oxygen from the water faster than it dissolves back from the air (Attiogbe et al., 2007). This leads to the inadequate oxygen to support higher life forms. Furthermore, oxygen is important because the end products of chemical and biochemical reactions in anaerobic systems often produce aesthetically displeasing odors, colors and tastes in water (Attiogbe et al., 2007). Besides that, in PRW receiving water bodies, decreased in productivity of algae (primary producer, an important link in the food chain) were observed (Hansson et al., 1998; El-Naas et al., 2009). Reduced productivity of phytoplankton and/or algae will have a knock on effect to the other organisms in the environment, such as crustaceans and fish (Wake, 2005).

Oil and grease are stable organic substances, they are sticky and tend to aggregate. Oil and grease tend to (1) clog drain pipes and sewer lines, causing unpleasant odors (2) corrode sewer lines under anaerobic conditions. Oil and grease also caused problems in municipal wastewater treatment plants because they tend to float on top of the water, stick on to pipes and walls, subsequently blocking strainers and filters and interfering with the treatment unit operations (Chen et al., 2000; Xu and Zhu, 2004). The oil in PRW can affect marine organisms in a number of different ways. Oil can kill marine organisms directly through contact poisoning or coating (Wake, 2005).

2.3 Treatment of Petroleum Refinery Wastewater (PRW)

There are three main types of water and wastewater treatment technologies, including physical, chemical and biological treatments. Physical treatment involves few basic processes like screening, aeration, sedimentation, filtration, flotation and skimming in order to separate floating and settleable particles and microbes from water. Coagulation, chlorination, ozonation, neutralization, adsorption and ion exchange are examples of chemical treatment. In chemical treatment, chemicals are added to remove suspended solids and dissolved solid. Biological treatment (Aerobic or anaerobic) uses microorganisms to remove the organic matter in water (Corbitt, 1999; Tchobanoglous et al., 2003; Davis and Cornwell, 2008).

Typical petroleum refinery wastewater treatment plants (Figure 2.2) consist of primary and secondary oil/water separation, followed by biological treatment, and tertiary treatment (AECOM, 2010). The refining process usually produces wastewater that requires chemical or physicochemical treatment and biological treatment before it is discharged into the water bodies (Santo et al., 2012). The refinery wastewater treatment plants (WWTPs) used gravity separation (API separators, tank separation), physico-chemical processes (Flocculation, sedimentation, filtration) to attain effluents with acceptable oil content so that it can be further treated with biological processes (Biofilters, activated sludge, aerated ponds) (Wake, 2005; Santo et al., 2012).

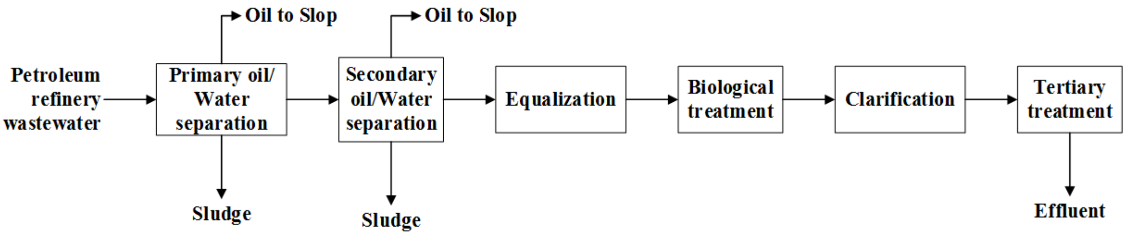

Figure 2.2: Typical PRW treatment (AECOM, 2010).

According to Diya'uddeen et al. (2011), PRW treatment is accomplished in two stages. The first stage comprises of mechanical and physical-chemical treatments (in which suspended matter, oil and grease are reduced) followed by the second stage, the advanced treatment of the pre-treated primary effluent. Figure 2.3 demonstrates sequence for treating PRW. The first stage treatment step is vital as it determines the efficiency and prolonged use of the secondary treatment unit.

In the first stage, oil, immiscible liquids, solid particles and suspended substances (colloids or dispersions) are mechanically separated/ reduced (Renault et al., 2009) from PRW by gravity in the American Petroleum Institute (API) separators (Diya'uddeen et al., 2011; Santo et al., 2012). Without the primary treatment, the concentration of salts and sulphide over 20 mg/L can strongly hinder the following biological treatment (Altas and Büyükgüngör, 2008). Generally, after the mechanical step (API), the wastewater treatment followed by the physiochemical step, in which pollutant concentration is decreased and suspended solids are removed through agglomeration by forming larger floc particles to ease the removal by means of filtration, sedimentation or floatation (El-Naas et al., 2009; Santo et al., 2012). Mostly, the chemical treatment of wastewater is carried out by coagulation-flocculation or coagulation-dissolved air flotation processes. Dissolved air flotation (DAF) is necessary to remove free and emulsified hydrocarbons from PRW before the biological processes (Santo et al., 2012).

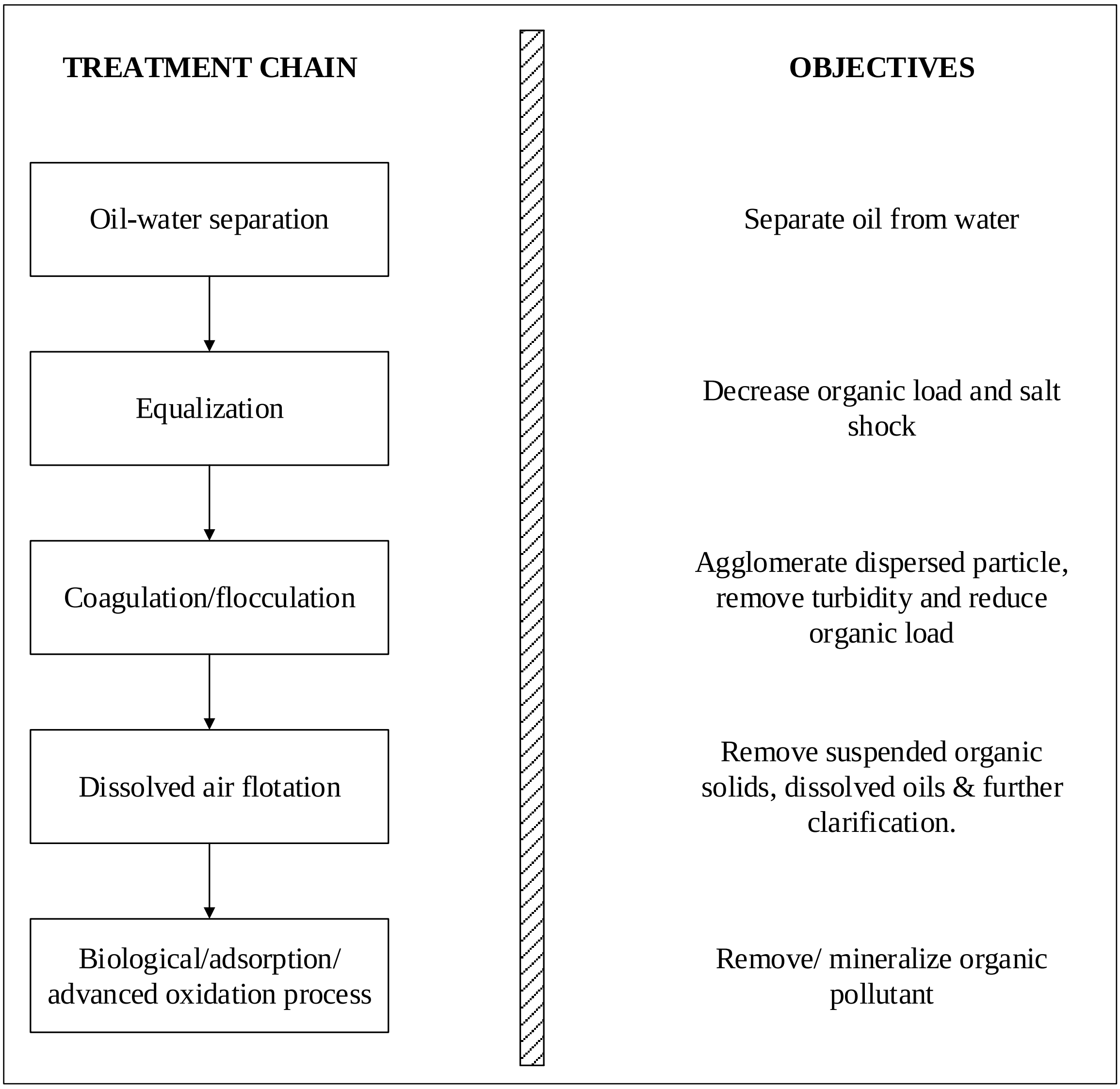

Figure 2.3: Schematic diagram of PRW treatment (Adapted from Diya'uddeen et al., 2011).

Numerous methods are applied as advanced treatment methods, namely bioremediation, advanced oxidation processes (AOPs) and adsorption. The objective of this stage is to reduce the effluent pollution level to an allowable limit to be discharged into receiving water bodies (El-Naas et al., 2009). The most widely used treatment method is bioremediation. Although biological technique is capable of removing most of the dissolved organic matters, however, recalcitrant components are not sufficiently removed (Diya'uddeen et al., 2011). Among AOPs, heterogeneous photocatalytic degradation has been found to be an effective treatment method by Li and Yue (2003). Table 2.2 demonstrates the advantages and disadvantages of numerous treatment methods available for PRW.

Table 2.2: Advantages and disadvantages of treatment methods available for PRW (Yan et al., 2010; Diya'uddeen et al., 2011; Shah, 2014).

Treatment methods	Advantages	Disadvantages
Coagulation	Economically feasible. Require short detention time and satisfactory removal of contaminants.	Removal is pH dependent. Voluminous sludge production. May not not suitable to treat the high-polluting wastewater, such as COD over 4000 mg/L.
Electrocoagulation	Effective removal of contaminants; reduction of COD. Not affected by the presence of salt in wastewater	Sludge production and secondary pollution (from chlorinated organics, heavy metals) are associated with electrocoagulation. High cost of electricity.
Photocatalytic oxidation	No sludge production. Faster reaction rates. Lower cost. Potential use of solar light.	Light penetration limitation, fouling of catalysts, and problem of fine catalyst separation from the treated effluent.
Fenton oxidation	Complete mineralization of organic matter. No harmful byproducts. Simple equipment and easy implementation.	Effective within a narrow pH range of < 3.5 and involves sludge generation. Comparatively longer reaction time required.
Adsorption	Good removal of organic matter.	Removal is pH dependent. Regeneration is expensive and involves adsorbent loss.
Membrane bioreactor	High COD reduction.	May not suitable to treat large volumes of wastewater.
Wet air oxidation	Effective COD reduction.	Uneconomical. Require high energy and high pressure.

2.4 Coagulation-flocculation Process

The particles in wastewater can be categorized as colloidal and suspended particles. Suspended particles are generally larger than 1 µm thus can be removed by gravity sedimentation. Typically, colloidal particles have a net negative surface charge and the size ranging from 0.01-1 µm, such that the attractive forces between colloidal particles are less than the electrical repulsive forces (Tchobanoglous et al., 2003). Under these conditions, the colloidal particles repel each other and the Brownian motion keeps the colloidal particles remain stable in the suspension. As colloidal particles cannot be removed by means of sedimentation or filtration, thus coagulants and or flocculants are added to help in the removal of these particles (Tchobanoglous et al., 2003; Davis and Cornwell, 2008).

Coagulation-flocculation, a well-established physical–chemical process in water and wastewater treatment, it is used to remove colloidal, suspended and dissolved particles by aggregating small particles into large aggregates (Ghafari et al., 2009; Ho et al., 2010; Oriekhova and Stoll, 2014). Coagulation refers to the process of reducing or neutralizing the negative charge on the particles, thus overcoming or neutralizing the electrical repulsive forces on suspended particles. This allows the van der Waals attractive forces to initiate the aggregation of colloidal and suspended particles to form microfloc (Ebeling et al., 2003; Ho et al., 2010; Lee et al., 2012).

Flocculation is a process after coagulation, bringing the microfloc particles together to form large aggregates by either physically mixing or through the binding action of polymeric materials (flocculants) (Ho, 2009; Lee et al., 2012). The purpose of flocculation is to produce large particles that can be removed by inexpensive particle-separation process such as filtration and sedimentation. There are two types of flocculation (1) Perikinetic flocculation (Where particles form aggregates by the

Brownian motion of fluid molecules) or orthokinetic flocculation (where particles form aggregates by physical mixing) (Tchobanoglous et al., 2003).

According to Ebeling et al. (2003), a conventional unit process of coagulation-flocculation consists of three separate stages (Figure 2.4):

1) Rapid mixing (coagulation): Chemicals (Coagulants, flocculants or pH adjusters) are added and mixed uniformly with a high mixing speed.

2) Slow mixing (flocculation): The wastewater is agitated at low speed. This is to ensure the formartion of large flocs, which can be easily settle out.

3) Sedimentation: Flocs formed during flocculation are allowed to settle down and removed from the effluent.

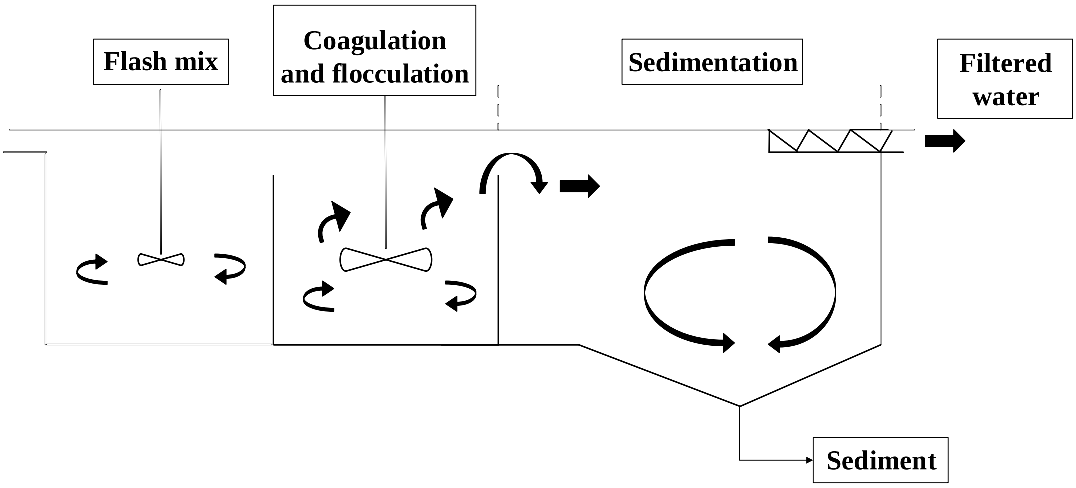

Figure 2.4: The coagulation-flocculation unit process (Ebeling et al., 2003).

Usually inorganic coagulant such as aluminum (e.g. Alum, aluminum chloride and polyaluminum chloride) and iron (e.g. Ferric Chloride, ferric sulphate and ferrous Sulphate) based chemicals are introduced in wastewater treatment. These coagulants play an important role in neutralizing the surface charge of suspended or colloidal particles and assisting the particle aggregation and settling under the influence of gravitational force (Ebeling et al., 2003; Ho et al., 2010; Lee et al., 2012). At a fixed final pH with hydrolyzing metal salt as coagulant, four zones, namely stabilization, charge neutralization, destabilization and sweep flocculation, normally occur in sequence with the increase of coagulant dosage (Wei et al., 2015). The selection of proper coagulant (type and dosage) has to be made through experimentation, commonly by Jar test (Corbitt, 1999). Various inorganic coagulants are listed in Table 2.3. Aluminum sulphate, ferric chloride and ferrous sulphate are discussed in the following sections as they are frequently used inorganic coagulants in wastewater treatment.

Table 2.3: Inorganic coagulants (Corbitt, 1999; Tchobanoglous et al., 2003; Bratby, 2006).

Chemical name	Formula
Aluminum chloride	$AlCl_3$
Aluminum sulphate	$Al_2(SO_4)_3$
Calcium chloride	$CaCl_2$
Calcium oxide	CaO
Ferrous chloride	$FeCl_2$
Ferric chloride	$FeCl_3$
Ferrous sulphate	$FeSO_4$
Ferric sulphate	$Fe_2(SO4)_3$

2.4.1 Aluminum Sulphate

Aluminum Sulphate, known as alum probably the most commonly used coagulant, and has been in use for waswater treatment for several centuries (Bratby, 2006). Alum is effective at pH values range between 5 to 8 under some conditions (Corbitt, 1999; Davis and Cornwell, 2008). The coagulation–flocculation mode of action of alum can typically be explained in terms of two different mechanisms: charge neutralization of negatively charged colloids by cationic hydrolysis products or incorporation of impurities in an amorphous hydroxide precipitate (sweep flocculation (Duan and Gregory, 2003). The coagulation diagram of alum is shown in Figure 2.5, indicates the regions where each mechanism dominates based on the pH and alum dosage.

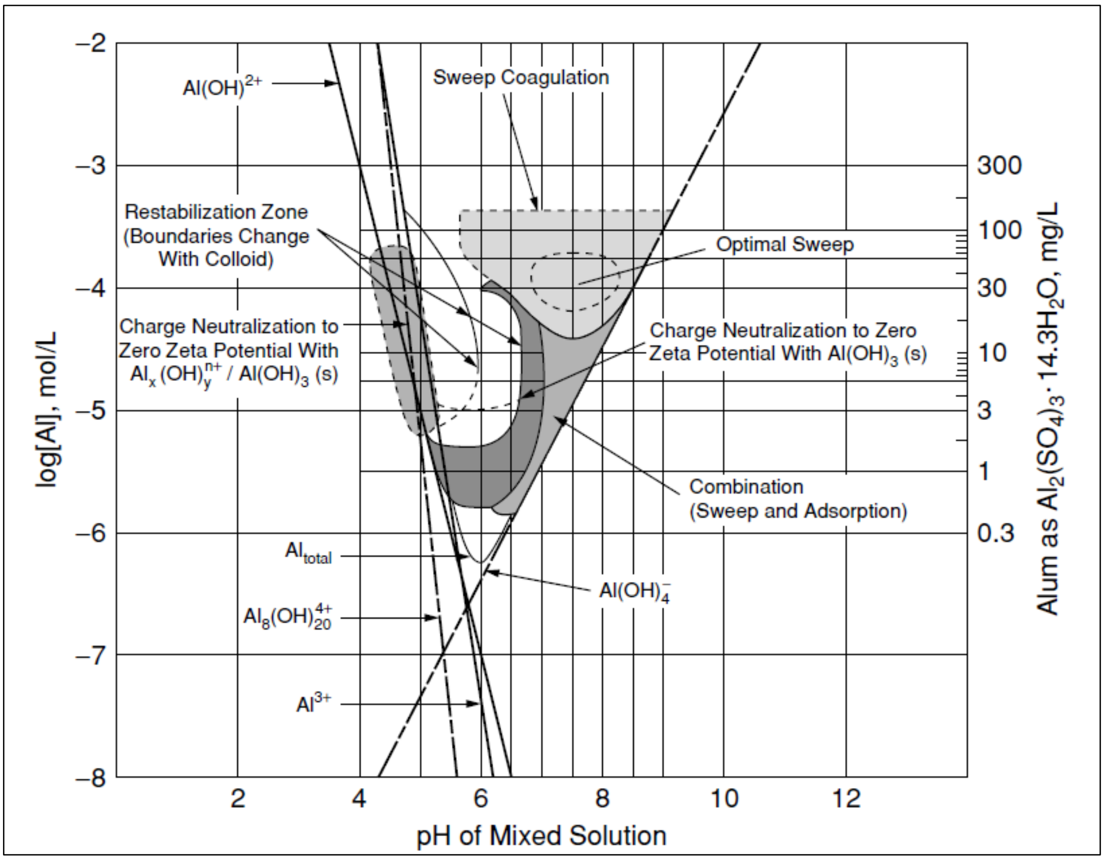

Figure 2.5: Typical operating ranges for alum coagulation (Amirtharajah and Mills, 1982).

The interaction between aluminium species and negatively charged colloidal particles is presented in Figure 2.6. Initially, negatively charged colloidal particles are stable, they become destabilized after the adsorption of positively charge aluminium species (Charge neutralization). At higher coagulant dosages colloidal particles can become restabilized by charge reversal or incorporated in an amorphous hydroxide precipitate (Sweep flocculation) (Duan and Gregory, 2003).

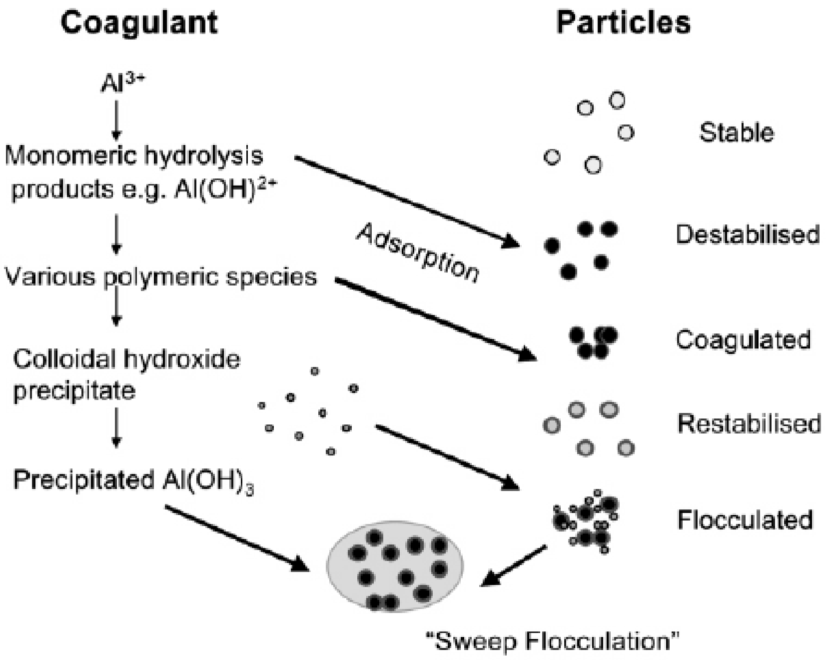

Figure 2.6: Schematic diagram showing the interaction between aluminium species and negatively charged colloidal particles in water (Duan and Gregory, 2003).

Treatment of tannery wastewater was investigated by Haydar and Aziz (2009) using ferric chloride, alum and ferrous sulfate. Alum was reported to be the suitable coagulant at a dose of 200–240 mg/L. The percentage turbidity, COD and TSS removal was 99, 57 and 96% respectively. In another study, alum was used for the impurities removal from pulp and paper mill wastewater (Ahmad et al., 2008). At an optimum pH of 6 and optimum alum dosage of 1,000 mg/L, the turbidity, TSS and COD reduction/removal are found to be 99.8%, 99.4% and 91% respectively. Verma et al. (2010) studied the pretreatment of petrochemical wastewater by coagulation–flocculation. Their analysis revealed that alum reduced the COD by 33.1% at an optimum pH value of 8.5 and optimum dosage of 3,500 mg/L.