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COAGULATION AND FLOCCULATION OF METALWORKING FLUID WASTEWATER BY POLYACRYLAMIDE AND POLYALUMINUM CHLORIDE

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ศึกษาการบำบัดน้ำเสียจากของไหลตัดกลึงโลหะด้วยกระบวนการจับก้อน โดยใช้พอลิอะคริลาไมด์ชนิดประจุบวก (CPAM) หรือ พอลิอะลูมินัมคลอไรด์ (PAC) เป็นสารก่อการจับก้อน ตามด้วยการจับกลุ่มด้วยพอลิอะคริลาไมด์ชนิดประจุลบ (APAM) ประสิทธิภาพของการบำบัดน้ำเสียสังเคราะห์ของของไหลตัดกลึงโลหะ และน้ำเสียจริงจากอุตสาหกรรมตัดกลึงโลหะพิจารณาจากการลดค่าความขุ่น ค่าซีโอดี และค่าของแข็งแขวนลอยทั้งหมด รวมทั้งค่า pH หลังการบำบัด ผลการทดลองพบว่าประสิทธิภาพในการลดค่ามลพิษดังกล่าว เพิ่มขึ้นตามปริมาณสารก่อการจับก้อนที่สูงขึ้น โดยน้ำเสียสังเคราะห์ที่มีความเข้มข้นของไหลตัดกลึงโลหะ 10% โดยปริมาตร ต้องใช้ปริมาณสารก่อการจับก้อนทั้งสองชนิดสูงกว่าที่ความเข้มข้น 3% โดยปริมาตร แต่ปริมาณของสารก่อการจับกลุ่มไม่ค่อยมีผลกระทบมากต่อการลดค่ามลพิษ แต่ทำให้ตะกอนที่ได้มีขนาดใหญ่ขึ้นโดยเฉพาะการจับก้อนตะกอนจาก PAC การใช้ CPAM ร่วมกับ APAM บำบัดน้ำเสียสังเคราะห์ที่ความเข้มข้น 3% และ 10% โดยปริมาตร สามารถลดค่าความขุ่น ค่าซีโอดี และค่าของแข็งแขวนลอยทั้งหมดได้มากกว่า 96% สำหรับ PAC เมื่อใช้ร่วมกับ APAM สามารถลดค่าความขุ่น ค่าซีโอดี และค่าของแข็งแขวนลอยทั้งหมดได้มากกว่า 97% นอกจากนี้ pH ของน้ำเสียมีผลกระทบต่อประสิทธิภาพการบำบัดน้ำเสียด้วย PAC แต่ไม่มีผลสำหรับการบำบัดด้วย CPAM โดยการใช้ PAC เป็นสารก่อการจับก้อนให้ประสิทธิภาพที่ดีในช่วงค่า pH 6-9 นอกจากนั้นค่า pH ของน้ำเสียหลังการบำบัดด้วย PAC จะมีค่าลดลงแต่ไม่เปลี่ยนแปลงเมื่อใช้ CPAM ในกรณีน้ำเสียจริงการใช้ PAC ให้ประสิทธิภาพในการกำจัดค่ามลพิษต่างๆ สูงกว่าการใช้ CPAM อย่างไรก็ตามตะกอนที่เกิดขึ้นโดยใช้ PAC ไม่เสถียรและมีขนาดเล็กกว่าการจับก้อนด้วย CPAM

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต....................
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WORATAT SATHIRASATHAPORN: COAGULATION AND FLOCCULATION OF METALWORKING FLUID WASTEWATER BY POLYACRYLAMIDE AND POLYALUMINUM CHLORIDE. THESIS PRINCIPAL ADVISOR: PUTTARUKSA VARANUSUPAKUL, Ph.D., THESIS COADVISOR: ASST.PROF. NATTAYA PONGSTABODEE, Ph.D., 83 pp.

A coagulation/flocculation process was studied for treatment of metalworking fluid (MWF) wastewater, using cationic polyacrylamide (CPAM) or polyaluminum chloride (PAC) as coagulant with the flocculant, anionic polyacrylamide (APAM). The removal efficiency of turbidity, chemical oxygen demand (COD) and total suspended solid (TSS) as well as the effluent pH were the main evaluating parameters for the treatment of synthetic and real MWF wastewater. The results revealed that all removal increased as coagulant dose increased. For synthetic wastewater at 10% oil-in-water (O/W) emulsion, the optimum doses of both coagulants used were higher than at 3% O/W emulsion. Flocculant dose showed slight effect but beneficial of floc size, especially coagulated by PAC. At the optimum CPAM dosage for synthetic wastewater at 3% and 10% O/W emulsion, removal of turbidity, COD and TSS were higher than 96%. While at optimum PAC dosage, removal of turbidity, COD and TSS were higher than 97%. The pH of wastewater showed a marked effect on PAC performance but practically not affected on CPAM performance. The optimum efficiency was achieved at pH range 6-9. Moreover, pH of the effluent treated by PAC led to a pH decrease but was not changed when treated by CPAM. For real wastewaters, the use of PAC appeared more efficient than CPAM. However, the flocs formed using PAC were unstable and smaller than that using CPAM.

Field of study: Petrochemistry and Polymer Science Student's signature: ....
Academic year: 2008 Principal Advisor's signature: ....
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LIST OF ABBREVIATIONS

APAM	=	Anionic polyacrylamide
ASP	=	Activated sludge plants
BOD_5	=	Biochemical oxygen demand at 5 days
COD	=	Chemical oxygen demand
CPAM	=	Cationic polyacrylamide
EPA	=	Environmental protection agency
FAS	=	Ferrous ammonium sulfate
HLB	=	Hydrophilic/lipophilic balance
mg/L	=	Milligram per litre
MWF	=	Metalworking fluid
NTU	=	Nephelometric turbidity units
O/W	=	Oil-in-water
PAA	=	Polyacrylic acid
PAC	=	Polyaluminum chloride
ppb	=	Parts per billion
SCWO	=	Supercritical water oxidation
SUS	=	Saybolt universal seconds
TSS	=	Total suspended solids

CHAPTER I

INTRODUCTION

1.1 General Introduction

Now water pollution is still a vital environmental problem. Wastewater from metalworking fluid (MWF) is one of that. MWF has used in a wide range of industrial such as automobile part, aeronautical industrial, mould for plastic injection, etc. MWF use for metal removal as known as cutting and grinding fluids. The chemical additives used to formulate MWF serve various functions. These include emulsification, corrosion inhibition, lubrication, microbial control, pH buffering, cooling, defoaming, dispersing and wetting [1]. The worldwide annual usage of MWF is estimated to exceed $2x10^9$ L and use in manufacturing operation in the automotive industry; typically results in wastewater flows ranging from 76 to 2,839 m^3/day (20,000 to 740,000 gal/day) [1-2].

Efforts must be made to reduce the discharge of used MWF on external environment. Wastewaters containing large concentrations of oil and grease as well as complex organics can present several problems when received by the municipal treatment plant [1]. For UK industry, the disposal cost is estimated to be up to £16 million per year [2]. The treatment of MWF wastewater has been addressed by several techniques. Advances have been made in the use of membrane technologies such as utrafiltration for treatment of MWF wastewater. However, this technique was generally limited to small flow (less than 76 m^3/day or 20,000 gal/day). Evaporation has been used as a method of reducing the water content of spent MWF in small scale systems. The energy requirement and disposal costs of the concentrate are major barrier in using this approach on a large scale of MWF wastewater [1]. Now biological treatment is being increasingly adopted as it seems to offer the potential of cost saving. However, there are significant difficulties in operating bioreactors, such as maintenance of the stability of the microbial communities in activated sludge plants

[2]. This tends to cause deterioration in fluid performance, and induces all sorts of other problems such as corrosion, odor generation and health risks for the workers [3]. Above techniques have drawbacks from membrane fouling and unsuitable for MWF wastewater with high volume. Coagulation and flocculation processes have been widely used for the wastewater effluents, such as domestic rejection and various industrial wastewaters. For the emulsified effluents, the principle of the method consists on the destabilization of the colloidal state of the emulsion by canceling the electrostatic or/and Van der waals forces, existing between the surface active and the dispersing medium [4]. The electrical charges on the emulsified droplet are neutralized by introducing an opposite charge through the addition of chemical emulsion breakers. The dielectric characteristics of water and oil droplets to carry negative charges, thus a cationic or positive charge emulsion breaker is required.

The most widely used coagulants are aluminium or iron salt base such as aluminum sulfate and ferric chloride. However, the formation of a precipitate of aluminium hydroxide with the release of some acidity and the liquid or crystal forms of ferric chloride are very corrosion and must be handled in a similar fashion to hydrochloric acid [5, 6]. Moreover, the existence of which trivalent metal ions act as primary coagulants for neutralizing electrostatic surface charge on colloids is very short lived under neutral pH conditions. High concentrations of coagulant chemical would be required, along with very slow addition of chemical, to supply enough coagulant metal ions to do a complete job of colloid destabilization [7].

Alternative coagulants, based on prehydrolysed forms of aluminium and iron are often found to be considerably more effective than the traditional coagulants. Polyaluminum chloride products seem to give better coagulation than 'alum' at low temperatures and are also claimed to produce lower volumes of residual solids (sludge). Because they are already partially neutralised, they have a smaller effect on the pH of water and so reduce the need for pH correction [5, 8]. Organic polymers are also the alternative used as primary coagulants. The polymer acts as a destabilizing agent via a charge neutralization precipitation mechanism, and is also an agent for floc growth [6, 9].

Avoiding the use of an inorganic coagulant has the advantage that a smaller amount of sludge is produced in a system less sensitive to pH, and that there is less dissolved salt present. Cationic polyelectrolytes have a distinct advantage over the metal salts which are commonly used in this procedure, cause from charge neutralization without the formation of additional solids in the form of metal hydroxide precipitate. Polymers give the advantage of a deformable floc, extend filter runs and decrease sludge volume from filter backwashing. The small floc formed by coagulation can be built up into larger agglomerates by flocculation with polymer. With flocs of slightly positive character an anionic polymer is appropriate [9]. By performing either as primary coagulants or as particle binding agents, polyelectrolytes are used successfully in settling operation [7].

Polyelectrolyte and polyaluminum chloride have many advantages for wastewater treatment. Therefore, this research was used cationic polyacrylamide and polyaluminum chloride as a primary coagulant with anionic polyacrylamide as flocculant in coagulation/flocculation process for treatment of MWF wastewater.

1.2 Literature Reviews

Many researchers focus on purify wastewater in various industries through coagulation process by coagulant such as aluminium sulfate, ferric chloride and polyaluminum chloride. The small particles formed by coagulation were enlarging with flocculation process by flocculant such as nonionic polyelectrolyte, cationic polyelectrolyte and anionic polyelectrolyte. Each types of polyelectrolyte can received from natural polymer or synthetic polymer such as chitosan and polyacrylamide. However, these coagulants and flocculants have different advantage and drawback to each types of wastewater on treatment. Normally for MWF wastewater treatment, coagulation/flocculation process using inorganic salts such as calcium chloride and aluminium chloride as coagulant were favored [10]. Nevertheless, the remaining aqueous phase after treatment has turbidity between 100 and 200 NTU, which indicates that its oil content is still high. Pakawan et al. [11] reported the use of ferric chloride and aluminium sulfate to destabilize waste coolant emulsions by coagulation process. They found that ferric chloride has precipitated faster than aluminum sulfate with similar quality of water after treatment. Kridsana et al. [12] reported the use of ferric chloride or aluminium sulfate with bentonite as flocculant for treatment of emulsion coolant wastewater. The results showed bentonite can increase turbidity removal but lower the pH values after treatment.

Badaway and Alii [13] used ferric chloride with various coagulant aids. Powdered activated carbon was added to enhance the color removal of various industrial wastewaters. Polyacrylamide, bentonite and powdered activated carbon increased the efficiency of the treatment as well as the color removal. However, high amount of sludge was produced by bentonite and powdered activated carbon when compared with sludge from polyacrylamide.

Polyaluminum chloride has been used as coagulant for many years at water purification plants and many researches of wastewater treatment [14-16]. The advantages of polyaluminum chloride compared to a conventional aluminium salts are faster floc formation, lower dosage rates, lower acidity and smaller effect on the pH of water [5, 8, 16-18]. Aquilar et al. [19] used polyaluminum chloride, ferric sulphate and aluminium sulphate as coagulants with anionic polyacrylamide as coagulant aid applied to a slaughterhouse wastewater treatment. The use of polyaluminum chloride with anionic polyacrylamide can reduce amount of anionic polyacrylamide that evaluated from removal efficiency of chemical oxygen demand (COD), biochemical oxygen demand at 5 days (BOD_5) and total suspended solids (TSS). For the effect of pH, the optimal pH range of polyaluminum chloride was between 5 and 8. This wider pH range than observed for the other two coagulants. Morover, the used of polyaluminum chloride with anionic polyacrylamide not only reduced suspended solid but also removed 95% of oil in oily wastewater [20]. However, only polyaluminum chloride as coagulant can increase oil removal efficiency up to 90% for wastewater treatment from oil refinery [17].

Pan et al. [21] used chitosan mixed with polyaluminum chloride as coagulants. Coagulation of synthetic and real water, the efficiency was evaluated by the factor of setting rate, floc diameter and residual turbidity. Satisfactory results were obtained from the mixed coagulant and better than using chitosan alone.

Polyelectrolyte has been used as flocculant indicated that can improve efficiency of wastewater treatment by coagulation/flocculation process. However, polyelectrolyte can not only used as flocculant but also as primary coagulant. For example, Fan et al. [22] reported the use of combination of the anionic form of a polyacrylic acid (PAA) as coagulant and cationic copolymer of acrylamide (Percol) as flocculant in coagulation/flocculation process of alumina fines. When Percol was added to the suspension, flocculation process was found to improve markedly after treatment by PAA in coagulation process. In addition sequential addition of the two polymers produced better flocculation than co-addition. Pinotti and Zaritzky [23] compared the performance of aluminum sulfate with natural and synthetic polyelectrolytes (chitosan and polyacrylamide) for treatment of emulsified oil in wastewater. Polyelectrolytes can reduce turbidity and pH had no significant effect of wastewater pH. For aluminum sulfate, the pH showed a marked effect on the treatment performance. In addition to pollutants removal, sludge production was less when used polyelectrolyte as primary coagulant or flocculant. For example, Aboulhasson et al. [24] improved the coagulation/flocculation process for a paint wastewater by adding polyelectrolyte as flocculant with ferric chloride as coagulant. The addition of polyelectrolyte produced a lower volume of decanted sludge compared that using ferric chloride alone.

From the above advantages, it is interesting to study the coagulation/flocculation process by polyaluminum chloride with polyelectrolyte or combination of oppositely charged polyelectrolyte. In this research polyaluminum chloride or cationic polyacrylamide as coagulant with anionic polyacrylamide as flocculant was applied to MWF wastewater.

1.3 Objective

The aim of this work was to investigated the effectiveness of cationic polyacrylamide and polyaluminum chloride as a coagulant and use anionic polyacrylamide as flocculant in coagulation/flocculation process for treatment of MWF wastewater. The effects of pH, coagulant and flocculant dosage were evaluated in term of percent removal of chemical oxygen demand (COD), total suspended solids (TSS) and turbidity.

CHAPTER II

THEORY

2.1 Metalworking Fluid (MWF)

Metalworking fluid is best defined by what they do. Metalworking fluid is engineering materials that optimize the metalworking process. Metalworking is commonly seen as two basic processes, metal deformation and metal removal or cutting. Comparatively recently, metal cutting has also been considered a plastic deformation process–albeit on a sub microscale and occurring just before chip fracture [1].

In the manufacturing and engineering communities, metalworking fluid was used for metal removal are known as cutting and grinding fluids. Fluids used for the drawing, rolling, and stamping processes of metal deformation are known as metalforming fluids. However, the outcome of the two processes differs. The processes by which the machines make the products, the mechanics of the operations, and the requirements for the fluids used in each process are different.

The mechanics of metalworking govern the requirement demanded of the metalworking fluid. As all tool engineers, metalworking fluid process engineers, and machinists know, the fluid must provide a layer of lubricant to act as a cushion between the workpiece and the tool in order to reduce friction. Fluids must also function as a coolant to reduce the heat produced during machining or forming. Otherwise, distortion of the workpiece and changed dimensions could result. Further, the fluid must prevent metal pick–up on both the tool and the workpiece by flushing away the chips as they are produced. All of these attributes function to prevent wear on the tools and reduce energy requirements. In addition, the metalworking fluid is expected to produce the desired finish on an accurate piece–part. Any discussion of metalworking fluid requirements must include the fact that the manufacturing impetus since the days of the industrial revolution is to machine or form parts at the highest rate of speed with maximum tool life, minimum downtime, and the fewest possible part rejects (scrap), all while maintaining accuracy and finish requirements [1].

2.1.1 The Chemistry of Metalworking Fluid

Throughout the twentieth century, metalworking chemistry has evolved from simple oils to sophisticated water–based technology. The evolution of these products is shown in figure 2.1 between 1910 and 1920, soluble oils were initially developed to improve the cooling properties and fire resistance of straight oils. By emulsifying the oil into water, smoke and fire were greatly reduced in the factories, thus improving working conditions. With the presence of water in the fluid, tool life was extended by reducing wear since the fluid kept the tools cool. However, water–diluted fluids caused rust on the work piece, thereby creating the need for rust inhibition [1].

Synthetic fluids were first marketed in the 1950s because of better cooling and rust protection compared to soluble oils in grinding operations. In the early 1970s, oil shortages encouraged compounders of cutting fluids to formulate synthetic oil-free products that could replace oil – based fluids in all metalworking operations. Synthetic fluids offer benefits over soluble oil technology. These benefits include better cooling and longer tank life because of good hard–water stability and resistance to microbiological degradation. However, soluble oils, while indeed more susceptible to bacteria growth, provide better lubricity and easier waste treat ability than synthetic fluids. These trade–offs encouraged the development of semi synthetic fluids. These water–based fluids contain some oil – based additives emulsified into water to form a tight micro emulsion system. These semi synthetic fluids are an attempt to reap the benefits of oil–soluble technology while retaining the good microbial control and long tank life of synthetic fluids.

In the 1980s, synthetic and semi synthetic fluids were growing in a mature market, displacing oil – based technology. However, in the early 1990s oil prices dropped, placing oil technology at the forefront in pricing. With increasing waste treatment costs, easier to waste – treat soluble oils gained market share over synthetics. Additionally, hazard regulations on ethanolamines commonly used in synthetic fluids for corrosion control further encouraged the use of soluble oils. Therefore, mature straight and soluble oil technology has held its 65% market share.

The chemistry of metalworking fluids is as diverse as a library of cookbooks. Each formulating chemist will develop his own fluid formula to meet the performance criteria of the metalworking operation. But like lasagna, each "recipe" will have common ingredients or raw materials: noodles, cheese, meat, sauce, etc. That is why fluids are at times called "black box chemical blend." No user is fully aware of the exact composition of the fluid used, but the user knows whether it meets certain performance criteria (tastes good). There are many additive blends that will function as metalworking fluids and there is no assurance of the "perfect" fluid for an operation. Misapplication of that perfect fluid could render it unacceptable [1].

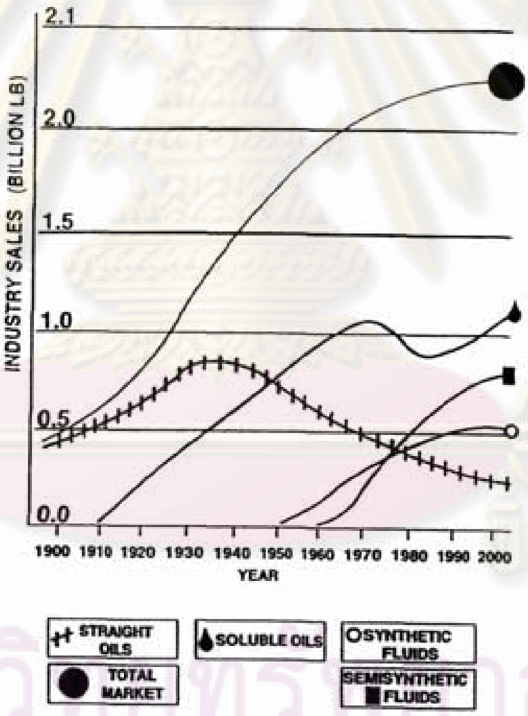


Figure 2.1 Evolutionary product life cycle [1].

The chemical additives used to formulate metalworking fluids serve various functions. These include emulsification, corrosion inhibition, lubrication, microbial control, pH buffering, coupling, defoaming, dispersing and wetting.

Most of the additives used are organic chemicals that are anionic or nonionic in charge. Most are liquids, used for ease of blending by the compounder. Some of the basic chemical types utilized are fatty acids, fatty alkanolamides, esters, sulfonates, soaps, ethoxylated surfactants, chlorinated paraffins, sulfurized fats and oils, glycol esters, ethanolamines, polyalkylene glycols, sulfated oils, fatty oils, and various biocide/fungicide chemical entities.

The functional additives used in metalworking fluids each contribute to the total composition. The effect of the addition of an additive is tested by the chemist to ensure that optimal properties of a fluid are maintained. In general, a fluid should be stable, low foaming, and waste treatable. Many of the properties of additives are mutually exclusive. Typically, if a fluid has excellent biological and hard – water stability, it may be difficult to waste treatment. Or if it provides excellent lubricity, it may be difficult to clean. The following reviews the typical properties of additives and the significance to the formulator and user [1].

Stability

The fluid concentrate must be stable without clouding or separating for a minimum of six months storage. The fluid may be tested in cold and hot atmospheres to assess the effect of shipment or storage in winter and summer climates. Some chemists check for gelling, freezing, or "skinning" of the fluid, which may signify handling problems.

Oxidative Stability

Some consider the oxidative stability of the additives are important. Aerating and heating the coolant can accelerate any destructive oxidation of the chemical additive.

Emulsion Stability

In soluble oils, emulsion stability is the most critical property. The emulsifier system must be balanced based on its alkalinity, acidity, and HLB (hydrophilic/

lipophilic balance) to ensure a white emulsion with no cream or oil forming at the surface of the fluid.

Hard – Water Stability

All fluid types are tested for hard – water stability because of the progressive increase in hard – water salts in the used fluid. As the fluid evaporates, only deionized water is removed, leaving behind water salts like calcium and magnesium. Carry – out of the fluid on the parts also depletes the fluid volume. As more water and fluid concentrate is added, more salts are accumulating in the tank. Calcium and magnesium cations build up in the fluid. Therefore, in soluble oils, the sodium sulfonate emulsifier is changed to calcium sulfonate, an additive that is not an emulsifier. This destabilization of the emulsion causes oil separation and loss of fluid concentration. In synthetic fluids, hard-water stability problems are visible as soap scum formation on the surface of the fluid. Typically, anionic additives may have hard-water stability problems, whereas nonionic-type additives are stable to hard-water salts.

Mixability of Fluid Concentrate

The ease of dilution of the fluid concentrate is important from a practical perspective. The oil must "bloom" into the water without gelling to ensure fast and complete mixing. Many times fluid concentrate is not premixed and is added at a point in the tank where there is little agitation. Without good mix ability, the fluid concentrate could sink, thereby not contributing to the fluid concentration intended. High soap components cause mix ability problems.

Foam

Because of constant agitation, spraying, and recirculation of metalworking fluids, foam can easily form in the tank. Besides being a nuisance, foam interferes with the lubricity and cooling functions of the fluid. Air does not lubricate, so air entrained in the fluid renders a fluid ineffective. Foam also interferes with the worker's view of the work piece, affecting machining accuracy and measurements. Many emulsifiers and lubricity additives may serve their function very well in a stagnant system but may be marginally useful if they foam excessively.

Residue/Cleanability

The fluid should not leave a sticky or hard-to-clean residue on the parts or equipment. Some boron-based corrosion inhibitors can leave a sticky-residue. Chlorinated paraffins and pigmented lubricant additives can be difficult to remove in cleaning operations.

Corrosion Inhibition

Fluids are tested for their corrosion-inhibiting properties. Since water is the diluent for the majority of fluids, corrosion inhibition is critical. Some additives are film forming (amine carboxylate), some are more like vapor phase inhibitors (monoethanolamine borates), while others actually form a matrix with the metal surface to provide protection (azoles).

Lubricity

Additives tested for lubricity can be combined to obtain various types of lubricity, depending on the fluid requirements.

Boundary lubricants like lard oil, over based sulfonates, esters, soaps, and sulfated oils provide a boundary between the work piece and tool. This slipperiness is ideal for all systems, especially when machining aluminum. Soft metals need boundary lubricants to allow metal removal with good tolerance by inhibiting the tool from welding onto the aluminum work piece.

Extreme-pressure additives like sulfur, chlorine, and phosphorus actually form metal complexes with the metal surface at elevated temperatures. Chlorinated additives are the most effective with typically 40-70% chlorine in the product compared to sulfurized additives with 10-15% sulfur, or phosphate esters with 5-15% phosphorus. Each has its problems. Chlorinated additives in general are under scrutiny because of their hazardous nature. Sulfurized materials can be stain.

2.1.2 Types of Metalworking Fluid

2.1.2.1 Soluble Oils

With the changeover to carbide tooling and increased machine speeds, water-diluted metalworking fluids were developed. Soluble oils or emulsifiable oils are the largest type of fluid used in metalworking. The product concentrate, oil fortified with emulsifiers and specialty additives, is diluted at the user's site with water to form oil-in-water emulsions. Here the oil is dispersed in a continuous phase of water.

Dilutions for general machining and grinding are 1-20% in water, with 5% being the most common dilution level. Drawing compounds are diluted with less water-typically 20-50%. At rich 50% dilutions, an invert emulsion is often purposely formed with the oil as the continuous phase. This thickened lubricant has superb lubricating properties and clinging potential on the metal to avoid run-off prior to the draw [1].

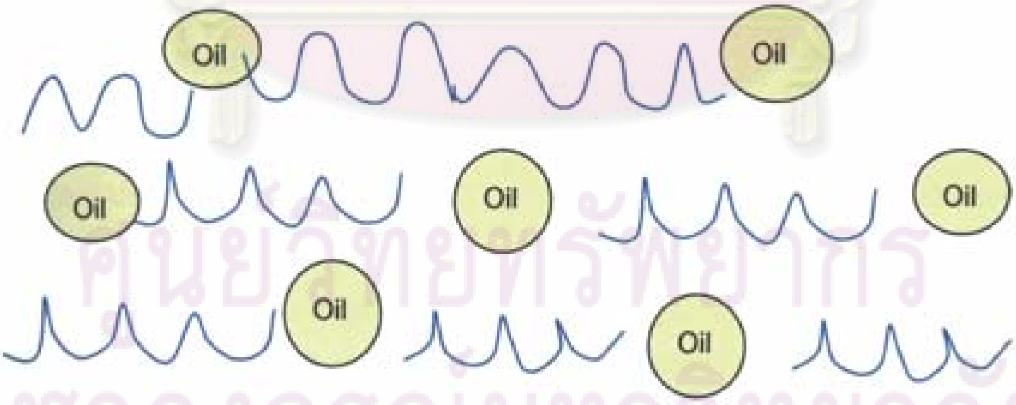


Figure 2.2 Oil–in–water emulsions [1].

The major component of soluble oils is either a naphthenic or paraffinic oil with viscosities of 100 SUS (Saybolt universal seconds) at 100°F, sometimes termed a 100/100 oil. Higher-viscosity oils can be used with greater difficulty in emulsification, but with possibly better lubricity. Naphthenic oils have been predominantly used because of their historically lower cost and ease of emulsification. Today, naphthenic oils are hydrotreated or solvent-refined to remove potential carcinogens known as polynuclear aromatics.

The next major class of additives in soluble oil is the emulsifiers. These chemicals suspend oil droplets in the water to make a milky to translucent solution in water. Some compounders relate the effectiveness of the two types of emulsions to comparing basketballs to small ball bearings. One can visualize more ball bearings entering a tight metal/tooling interface for lubrication than basketballs. Others agree that biostability can be enhanced with a microemulsion. Advantages of a standard milky emulsion are large oil droplet size for forming operations, ease of waste treat ability, and lower foam than with microemulsions.

The predominant emulsifier is sodium sulfonate, which is used with fatty acid soaps, esters, and coupling agents to provide a white emulsion with emulsion with no oil or cream separating out after mixing with water. Nonionic emulsifiers like nonylphenol ethoxylates, PEG esters, and alkanolamides are also used when hard water stability or microemulsion systems are desired. Many basic soluble oils are complete with this combination of oil and emulsifier system.

Many specialty compounders include other additives to add further value to the product. Since the fluid will be diluted with water, the possibility of rust forming is introduced. Normal rust control is usually satisfactory, but this depends on the emulsifier. Some added rust inhibitors used include calcium sulfonate, alkanolamides, and blown waxes. To impart biostability along with rust inhibition, boron containing water – soluble inhibitors are coupled into the formulation. The pH of the diluted fluid should be 8.8-9.2 to ensure rust protection, metal safety, and rancidity control. This pH should be buffered so the pH is maintained upon recirculation of the fluid. This is more attainable with amines as alkaline sources rather than caustic soda or potash. To further control rancidity of the fluid from bacteria growth; biocides are often added to the oil. Further tank side additions will be necessary to prolong bacteria control. The lubricity of soluble oil comes from the oil emulsion. Because the viscosity of waterdilatable fluids is almost equal to that of water, the film strength or hydrodynamic lubrication potential is negated compared to straight oils. Lubricant additives are commonly added for medium to heavy duty operations. Boundary lubricant like lard oil, eaters, amides, soaps, and rapeseed oil are used just as they were in straight oils. Likewise, chlorinated, sulfurized, and phosphorus-based extreme-pressure additives discussed earlier are popular value lubricant additives.

Defoamers are sometimes added if the product foams excessively due to the emulsifier system's properties. The advantages of soluble oils over straight oils include lower cost, since they are diluted with water, heat reduction; and the ability to run at higher machining speeds. Soluble oils are also cleaner, cooler, and more beneficial to the health of the workers because oil mists are no longer inhaled. The advantages of straight oils over soluble oils include no rancidity, good wet ability of the metal surface, good rust protection, and no destabilization problems from emulsions oiling out from hard-water buildup and bacterial attack.

2.1.2.2 Semisynthetic Fluids

Many users like the semisynthetic fluids nature of these fluids because of the advantages of both soluble oils and synthetics without many of their individual disadvantages. The advantages of semisynthetic fluids are rapid heat dissipation, cleanliness of the system, resistance to rancidity, and bioresistance. The bioresistance is due to the small emulsion particle size and small amount of oil in the fluid for anaerobic bacteria to feed on. Rust protection and lubricity are better than in a synthetic fluid because the oil and oil-soluble additives provide a barrier film that protects from corrosion and adds lubricity. The disadvantage is foam in griding operations, acceptance of tramp oil, and less lubricity than soluble oils.

2.1.2.3 Synthetic Fluids

Synthetic metalworking fluids are water-based products containing no mineral oil. The particle size of a synthetic fluid is typically 0.000000125 in. in diameter [1].

Much new product development is centered on synthetic products in order to produce additive systems that provide optimal lubricity and rust protection in an easily disposed fluid. One such concept is the marriage of semisynthetic technology with synthetic chemistry. By using multiple emulsifiers to couple synthetic water-insoluble lubricants into water, a waste-treatable system is created with petroleum oil absent from the formula.

Synthetic fluids have found widespread use in multiple machining, grinding, and forming operation. They are the products of choice where clean fluids with long tank life and modest lubrication is needed.

2.1.2.4 Straight Oils

Straight oil is a petroleum or vegetable oil that is used without dilution with water. It can be alone or oil compounded with various polar and/or chemically active additives. Light solvent, neutral oils, and heavy bright and refined stocks are among the petroleum oils used. Paraffinic oils offer better oxidative stability and less smoke during cutting than naphthenic oils. However, most compounded oils contain naphthenic oils because the lubricant additives are more soluble and compatible in naphthenic oils [1]. For environmentally favorable requirement, vegetable oils are the oil of choice. Although considerably more expensive than petroleum oils, they are easily biodegraded for disposal. If follows then that they are more prone to biological deterioration than petroleum oils. Nondrying oils like rapeseed, castor and coconut oil are best. Straight oils provide hydrodynamic lubrication. When compounded with lubricant additives, they are useful for severe cutting operations, for machining difficult metals, and for ensuring optimal grinding wheel life.

2.2 Treatment of Metalworking Fluid Wastewater

Environmental consciousness in manufacturing operations is becoming increasingly important and is receiving greater attention at all levels. In the past, the environmental impact of industrial practices was not considered as a significant factor in technical decision for making and manufacturing plant practices. This has changed as a result of public opinion and government regulation, prompting industry to take into account the environmental impact of manufacturing practices such as waste reduction and recycling and reuse of materials. As a result, industrial decision is increasingly accommodation environmental concerns [1].

An environmental problem of major concern is the proper disposal of unwanted waste oils and the treatment of wastewater containing oils from manufacturing operations. There are thousands of sources of oily wastewater. The largest volumes result from metalworking, food processing, and vehicle cleaning operations but those operations account for less than half of the total volume. Oily wastewater is generated by virtually every major industry including paper products companies, glass manufacturers, tobacco companies, and of course oil refiners. The manufacturing plants within these industries range from small to large but there are a larger number of small plants generating oily wastewater volumes in the range from 2 to 189 m^3 /day (500 to 50,000 gal /day). The use of metalworking fluids in manufacturing operations in the automotive industry typically results in wastewater flows ranging from 76 to 2839 m^3 /day (20,000 to 740,000 gal /day).The worldwide annual usage is estimated to exceed $2x10^9$ l and the waste could be more than ten times the usage, as the MWF have to be diluted prior to use. For UK industry the disposal cost is estimated to be up to £16 million per year. Used MWF causes high levels of contamination and rancid odors due to the presence of complex chemicals, biocides, etc., so that their treatment and final disposal must be handled carefully [2].

Efforts must be made to reduce the discharge of used metalworking fluids from manufacturing plants in order to reduce the impact of metalworking fluids on the external environment. In this respect, maximizing the recycle and reuse of the metalworking fluids can be very cost effective and is commonly practiced. This can substantially reduce the amounts of used metalworking fluids that have to be discharged into the external environment. Apart from the discharge of used metalworking fluids, parts washing operations also lead to the discharge of wastewaters containing metalworking fluid.

Straight oils and soluble oil-in-water emulsions were the primary metalworking fluids used in the automotive and other manufacturing industries until the late 1960s. The hydrocarbons contained in these products are normally refined paraffins or unsaturated with straight or branched carbon atoms. The carbon number is normally in the 10 to 20 range, representing a low viscosity to heavy oil. A dispersant in the form of a surfactant is normally dissolved in the oil resulting in a white or gray-colored stable suspension when the solution is added to water. Viscosity modifiers, corrosion inhibitors, and biocides are often included in these fluid mixes [1].

Historically, manufacturing plants, when possible, have discharged their process wastewaters into the local sanitary sewer system believing that the municipal wastewater treatment plant at the end of the sewer line could handle the discharged materials. Wastewaters containing large concentrations of oil and grease and complex organics can present several problems when received by the municipal treatment plant. The oil and grease can:

1. Present a fire and explosion hazard.
2. Impact on the mechanical operating equipment in the plant, clogging screens, fouling instrumentation equipment, and interfering with skimming operations.
3. Inhibit biological treatment processes when present above a threshold concentration.

The complex organics:

1. Represent a significant oxygen demand to the treatment plant impacting its performance.
2. Can be the source of toxic chemicals impacting on both the operation of the treatment plant and its effluent quality.

The deleterious effects that oily wastewaters have on municipal treatment plants led in the past to the development of local pretreatment ordinances limiting the discharge of oil and grease to concentration typically less than 100mg/l. more recently, when the effects of discharges of toxic chemicals to the treatment plants were recognized, the federal regulatory body, the U.S. Environmental Protection Agency (EPA), issued regulations governing industrial discharges to municipal severs. These "pretreatment regulations" limit industrial discharges of not only oil and grease, but heavy metals, acid and bases, and toxic organic chemicals. The regulations became effective on August 25, 1978 [1].

Technologies for treating industrial wastewaters can be divided into three categories: chemical methods, physical methods, and biological methods. Chemical methods include chemical precipitation, chemical oxidation or reduction, formation of an insoluble gas followed by stripping, and other chemical reactions that involve exchanging or sharing electrons between atoms [25].

Figure 2.3 presents a categorization of the components of industrial wastewater and preliminary selections of treatment technologies, based on the appropriateness of the mechanism of each technology compared to the fundamental properties of the pollutants. Different versions of Figure 2.3 could be generated by beginning with a characterization other than dissolved or undissolved; for instance, organic or inorganic, but all versions would ultimately result in the same list of appropriate treatment technologies.

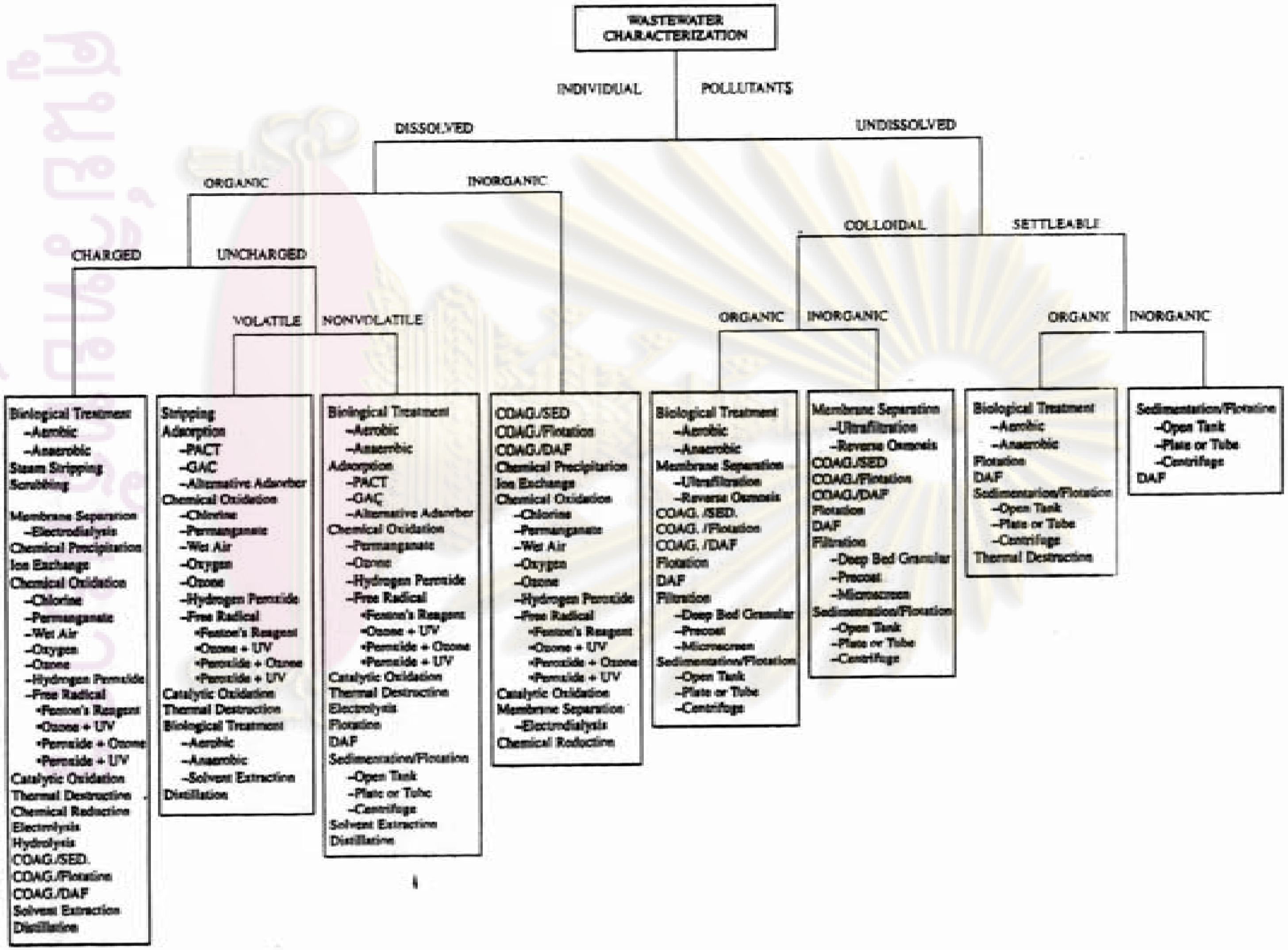


Figure 2.3 Candidate treatment technologies, based on fundamental characteristics of pollutants [25].

2.2.1 Physical Treatment

Ultrafiltration

Ultrafiltration is a pressure-driven membrane filtration process which uses molecular size pores to separate emulsions and macromolecules from a solution. It has been applied for oil recovery from wastewaters in many industries including adhesives and sealants, commercial laundries, synthetic rubber manufacturing, timber products processing, and metalworking operations. Unlike reverse osmosis, which provides separation down to the ionic level, ultrafiltration consists of a more open membrane and lower pressures are employed. Ultrafiltration membranes will reject solutes greater than approximately 0.001 μm in effective diameter. The size of a bacterial cell is typically greater than 0.5 μm. Ultrafiltration membranes cannot retain lower molecular weight soluble organic and inorganic compounds.

Determining the ultrafiltration membrane area requirement relies on specifying an operating liquid throughput or membrane flux. In treating oily emulsions, the flux normally depends on such factors as the concentration of oil and suspended solids in the feed stream, the membrane surface velocity, temperature, transmembrane pressure drop, surface fouling, and the extent of concentration polarization. Concentration polarization arises from the accumulation of solutes on the membrane surface. Solutes reach the membrane surface by convective transport of the solvent, a portion of which passes through the membrane. The rejected solutes often form a viscous gel layer on the membrane. This gel layer acts as a secondary membrane reducing the flux and often reducing the passage of low molecular weight solutes. Surface fouling is a result of the deposition of submicron particles on the surface as well as the accumulation of smaller solutes because of crystallization and precipitation. Modifying the membrane surface by chemical or physical methods can significantly improve its flux characteristics [1].

Reverse Osmosis

Reverse osmosis membranes provide a barrier to the transfer of small molecular weight, dissolved organics and inorganics and thus are used to remove such contaminants as water-soluble organics, chlorides, and phosphates. Reverse osmosis membranes are easily fouled and as such the feed must be relatively free of oil and suspended solids [1].

Evaporation

Evaporation has been used as a method of reducing the water content of spent metalworking fluids in small scale systems. The energy requirements and disposal costs of the concentrate are major barriers in using this approach on a large scale to deal with wastewaters containing spent metalworking fluids [1].

2.2.2 Biological Treatment

Biological systems are the most popular method of treatment of metalworking fluid wastewaters containing water-soluble organics. Biological process reactors can be classified according to the nature of their biological growth. Those in which the active biomass is suspended as free organisms or microbial aggregates can be regarded as suspended growth reactors, whereas those in which growth occurs on or within a solid media can be termed supported attached growth reactors. Both suspended and supported growth reactors have been utilized to treat metalworking fluid wastewaters, following secondary treatment, for removal of the remaining five-day biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD), and for ammonium oxidation or nitrification [1]. Now, biological treatment is being increasingly adopted as it seems to offer an alternative with the potential for significant cost saving. However, there are significant difficulties in operating bioreactors, such as maintenance of the stability of the microbial communities present in activated sludge plants (ASP) [2].

2.2.3 Chemical Treatment

Chemical Emulsion Breaking

In order to break an oil-water emulsion chemically, the stabilizing factors must be neutralized to allow the emulsified droplets to coalesce. The electrical charges on the emulsified droplet are neutralized by introducing an opposite charge through the addition of chemical emulsion breakers. The dielectric characteristics of water and oil cause emulsified oil droplets to carry negative charges thus a cationic or positive charge emulsion breaker is required. Once the oil-water emulsion is broken, ideally two distinct layers are formed, and oil layer and a water layer. In actual practice, a scum or "rag" layer normally forms at the interface where solids and the neutralized emulsifier collect. The process usually consists of rapidly mixing the emulsion breaking chemicals with the wastewater followed by flocculation, and flotation or settling [1].

In breaking the emulsion, it is common to use sulfuric acid to lower the pH of the wastewater, followed by addition of an emulsion-breaking chemical such as alum and/or a polyelectrolyte. This emulsion-breaking process is usually conducted batch wise and involves the determination of the correct dosages of the treatment chemicals required for each batch of wastewater by laboratory analyses. The sulfuric acid converts the carboxyl ion in surfactants to carboxylic acids, allowing the oil droplets to agglomerate.

The addition of an inorganic coagulating chemical such as alum as an alternative to, or after sulfuric acid addition, aids in the agglomeration of the oil droplets. It has been claimed that organic demulsifies such as polyamines are effective emulsion-breaking agents. Lower dosages of the organics are often required and less chemical solids are produced. Alternative chemical demulsifying processes include:

- Addition of coagulating salts (e.g., aluminum, iron)
- Addition of acids
- Addition of salts and heating the emulsion
- Addition of coagulating salts and treatment by electricity
- Addition of acids plus organic cleaving agents

Chemical treatment followed by gravity sedimentation is employed in a number of industries including those involving metalworking operations. One company reported treating oily wastewater from a ball and roller-bearing plant by coagulation with sodium carbonate, lime, and a polyelectrolyte flocculating agent to achieve oil and grease reduction from 302 mg/l to 28 mg/l representing 90% removal in the treatment of up to 227 m^3/day (60,000gal/day). Other industry results are presented in Table 2.1.

Table 2.1 Oil and grease removal by chemical treatment plus gravity sedimentation [1].

Industry	Treatment Chemical	Oil and Grease (mg/l)		
		Influent	Effluent	% Removal
Paint manufacture	Sodium aluminate	1260	22	98
	Alum	1810	11	99
	Alum + lime	830	16	98
	Alum + lime + ferric chloride	393	91	77
	Alum + lime + polymer	980	22	98
	Alum + polymer	1700	880	48
	Alum + polymer	642	8	99
	Alum + polymer	1200	153	87
Commercial laundry	Alum + polymer	15	4	73
Steel pickling	Lime	3	1	66
Steel pickling	Lime + polymer	650	6	99
Steel pipe fabrication	Lime + polymer	5	4	20
Paint manufacture	Polymer	1100	22	98

Hydrothermal Oxidation

Hydrothermal oxidation processes have been widely studied and applied to an extensive variety of wastewaters. Aqueous oxidation at high pressure and temperature can be operated at conditions below or above the vapor-liquid critical point of water

(374.2 C and 22.1 MPa). The former, known as wet air oxidation (WAO), is typically operated at temperatures and pressures ranging from 200 to 330 C and from 2 to 20 MPa, respectively. The latter, often referred to as supercritical water oxidation (SCWO), is carried out at pressures and temperatures above the critical point for pure water, usually ranging from 400 to 650 C and from 25 to 35 MPa, respectively [26].

2.3 Coagulation - Flocculation

Coagulation and flocculation is and area of water treatment that developed greatly over the last 20 – 30 years of the twentieth century [18]. Of the many unit processes and operations used in water treatment, coagulation and flocculation require a unique combination of chemical and physical phenomena for producing water acceptable for human consumption. These are essential pretreatment processes for the removal of finely divided particulate matter which, due to its small size (usually less than 10 μm), will not settle out of suspension by gravity in an economical time frame. Aggregation of fine particulate matter into larger particulates by the use of coagulation and flocculation facilities permits cost effective removal in subsequent solids separation processes [27].

It is convenient to think of solids as being present in water in three main forms: suspended particles, colloids, and DS (molecules). Suspended particles may be coarse or fine particles of, for example, sand, rocs, or vegetable matter. They range in size from very large particles down to particles with a typical dimension of 10 μm. suspended particles will under quiescent conditions either settle or float. Colloids are very fine particles; typically between 10 nm and 10 μm. finally there are DS that are present as individual molecules or as ions. Figure 2.4 shows the size ranges of materials present in water. These size bands are approximate and some sources quote slightly different ranges. The colloid size range includes large organic molecules.

Coarse or fine particles are generally relatively simple to remove by either settlement or filtration. DS cannot be removed by physical treatment save by reverse osmosis (although they may be removed after precipitation). Thus removal of colloids is often the main objective and most difficult aspect of conventional water treatment.

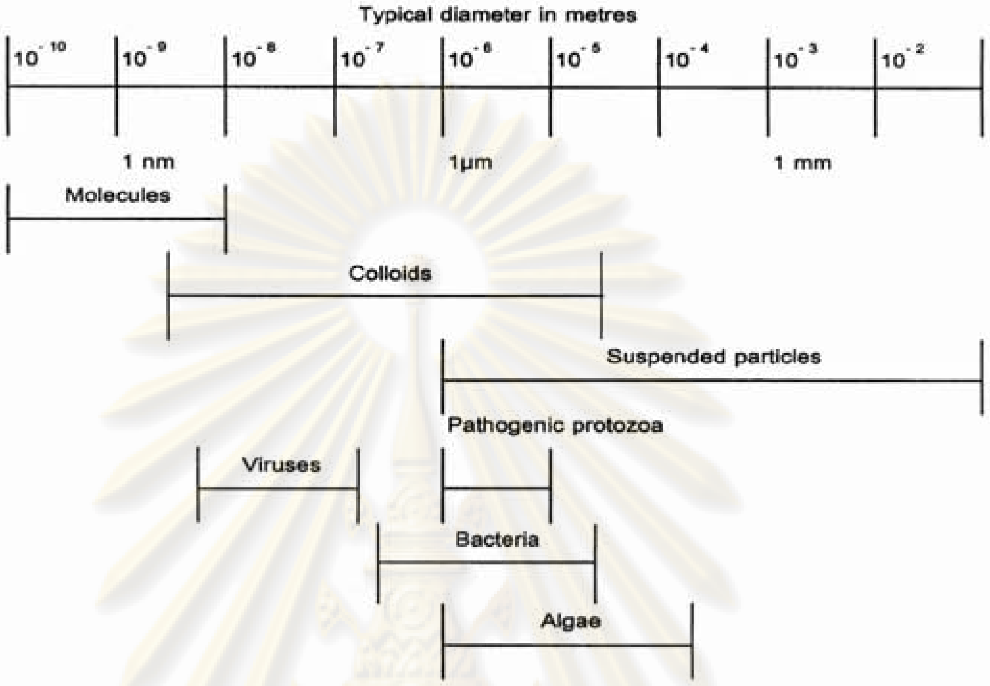


Figure 2.4 Size ranges of particles of concern in water treatment [18].

Because the size of colloidal particles is so small they have significantly different characteristics to larger particles. If a 1 m cube of material were to be divided into cubes with a side of 10 nm, the surface area of the material would increase from 6 m^2 to 6000 km^2. A cubic centimeter of material would have an area of 600 m^2. As a result of the large surface area associated with small particles surface phenomena predominate and gravitational effects are unimportant.

Colloids themselves are split into two types: hydrophilic or water-loving colloids, and hydrophobic or water-hating colloids, hydro phobic colloids are unstable; once the particles aggregate they do not easily reform as colloids. Examples are some clay particles and non-hydrated metal oxides. Other common examples of hydrophobic systems, although of liquid/liquid colloids, are emulsion paint and mayonnaise. Hydrophilic colloids include soap and wallpaper paste. When these materials are mixed with water they form colloidal solutions, which cannot be destabilized [18].

The reason that colloids stay as such small particles is that the particles have similar negative electrical charges, meaning that electrical forces keep the individual particles separate. The importance of surface electrical charge is associated with the very large specific surface area of the particles.

In order to remove colloids it is necessary to form larger particles that can then be removed by physical treatment. For hydrophobic colloids it is necessary to overcome the forces keeping the particles apart; once this has been done the particles coalesce into larger particles that do not reform into colloids. This process of particle destabilization and formation of larger particles is called coagulation. Flocculation is the process of mixing which results in further collisions between the particles formed by coagulation, and results in the formation of relatively large particles that can be more easily removed. Hydrophilic colloids cannot be destabilized in the same way as they would simply reform as colloids. They normally have to be removed by chemical precipitation, filtration, or adsorption. However, some hydrophilic colloids can be removed from water by flocculation, specifically those composed of long organic molecules with multiple charges.

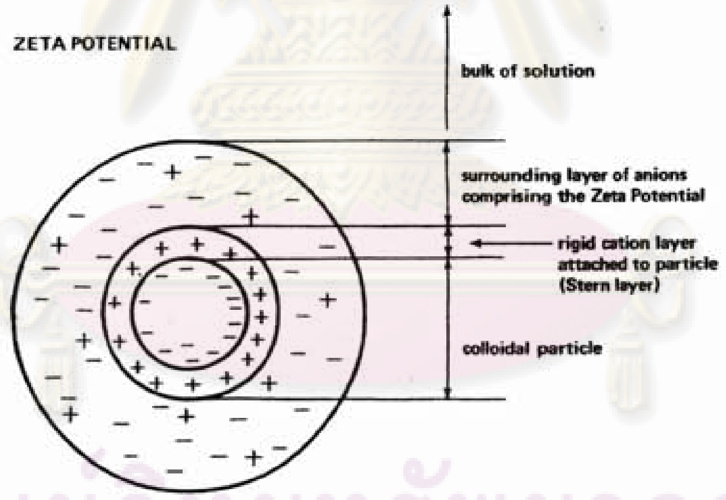


Figure 2.5 Representation of a colloid suspended in a solution, showing the electric double layer [7].

Table 2.2 Materials with their size and an indication of the time needed for these particles to settle vertically through one metre of water, at 20 °C, under the influence of gravity alone [5].

Table 2.2 Settling time for various particles [5]. (According to Stokes' law)

Particle diameter			**Type of particle**	**Settling time through 1 m of water**	**Specific area $m^2.m^{-3}$**
mm	**µm**	**Å**			
10	10^4	10^8	Gravel	1 second	6.10^2
1	10^5	10^7	Sand	10 seconds	6.10^3
10^{-1}	10^6	10^6	Fine sand	2 minutes	6.10^4
10^{-2}	10	10^5	Clay	2 hours	6.10^5
10^{-4}	10^{-1}	10^3	Colloid	2 years	6.10^7
10^{-5}	10^{-2}	10^2	Colloid	20 years	6.10^8
10^{-6}	10^{-3}	10	Colloid	200 years	6.10^9

The table also shows that the smaller the particle, the larger its specific area. Thus colloids are particles that cannot settle naturally and for which surface area factors are most important. These factors determine the stability of colloidal suspensions. In fact, colloids are subject to two major forces: Van der Waals attraction, which relates to the structure and form of colloids as well as to the type of medium (E_A), the electrostatic repulsive force, which relates to the surface charges of the colloids (E_B).

The stability of a colloidal suspension depends on the balance between the forces of attraction and repulsion, the energy level of which is:

$$E = (E_A) + (E_B)$$

In order to destabilize the suspension, it is necessary to overcome the energy barrier E_S. To accomplish this and, thereby, promote the agglomeration of the colloids, it is necessary to reduce the electrostatic repulsive forces. This destabilization is brought about by coagulation [5].

2.3.1 Types of Destabilization

There are four main methods of destabilizing colloid systems [18].

Double layer compression –involves the addition of an electrolyte to water to increase the concentrations of ions. This has the effect of decreasing the thickness of the electrical double layer that surrounds each colloidal particle. This allows the particles to move closer to each other, meaning attractive forces have more chance of overcoming the electrical forces that keep them apart. The effectiveness of the coagulant depends on the change in ionic concentration and also exponentially on the charge on the ions added. Thus, ions with a charge of +3 are around 1000 times more effective than ions with a charge of +1. There are three points to note. Firstly, this method of destabilization only work when ions are present and thus where a metal salt is added which subsequently precipitates as a hydroxide floc, the effect is only present before the insoluble hydroxide is formed. Secondly, the effect is independent of the concentration of colloidal material. Finally, the effect is proportional to the change in ionic concentration.

Charge neutralization –adding ions with a charge opposite to that on the colloidal particles can lead to adsorption of the ions on to the colloidal material and reduction of surface charge. This reduces the electrical forces keeping particles apart and allows easier agglomeration. There are two points to note: the dose needed is proportional to the quantity of colloidal material present, and it may be possible, with some colloids, to overdose, leading to charge reversal on the colloidal matter.

Entrapment in a precipitate –if soluble aluminium or iron salts are added to water at the correct pH value, they will precipitate as hydroxide flocs. If colloids are present then the hydroxide will tend to precipitate using colloid particles as nuclei, forming floc around colloid particles. Once the hydroxide floc has formed it may physically entrap other colloidal particles, particularly during subsequent flocculation. The point to note is that there is often an inverse relationship between the concentration of colloidal material to be removed and the coagulant does required. This is explained by the concept that at high colloid concentrations the colloidal particles act as nuclei on to which the coagulant precipitates. On the other hand at low colloid concentration an excess of precipitated coagulant is required to entrap the colloid particles. The optimum coagulation pH value is dependent on the pH/solubility characteristics of the coagulant used.

Particle bridging –large organic molecules with multiple electrical chares are often effective as coagulants. In water treatment such chemicals are normally referred to as anionic or cationic polymers. These are believed to work by bridging between particles. It is interesting to note that both anionic and cationic polymers are often found to be capable of coagulating negatively charged colloid particles. Polymers are also often used during flocculation to aid in particle formation when they are referred to as coagulant aids. Excessive agitation of flocs formed using a polymer coagulant can lead to the flocs breaking up.

2.3.2 Coagulant and Flocculant

2.3.2.1 Aluminium and Iron Salts

The commonly used metal coagulants fall into two general categories: those based on aluminium and those based on iron. The aluminium coagulants include aluminium sulphate, aluminium chloride, polyaluminum chloride and sodium aluminate. The iron coagulants include ferric sulphate, ferrous sulphate, chlorinated copperas and ferric chloride [6]. In the part the common iron and aluminium coagulants were the trivalent compounds.

The addition of a ferric or aluminium coagulant to water sets in motion a complex series of reactions. Initially trivalent ferric or aluminium ions are formed. These then hydrate to form complexes of the metal with water molecules. In a series of further reactions the water molecules are replaced by hydroxide ions giving rise to a further series of complexes. Dependent on pH values and concentrations the iron and aluminium will eventually largely precipitate as a hydroxide floc. The points to note are that many of the intermediate complexes are very effective in double layer compression and in charge neutralization, and they also have a short life. This explains the importance of proper mixing when iron or aluminium salts are used as coagulants. If there is not effective mixing then higher doses of coagulant may be required [18].

pH control during coagulation with iron and aluminium is most important. The solubility of ferric hydroxide and aluminium hydroxide is lowest at particular pH values for given water, and above these values concentrations of soluble iron and aluminium higher than the minimum will be carried forward to clarification and filtration. The floc formed by the hydroxides is important in enmeshment and it is normally most effective to maximize its formation during coagulation. However, the salts used for coagulation are strongly acidic, being salts formed from weak bases and strong acids. This makes control of coagulation pH complicated for most waters, and very difficult for un-buffered soft waters [18].

2.3.2.2 Polyaluminum Chloride (PAC)

As well as traditional coagulants, based on Al and Fe salts, there are now many commercial products that contain pre–hydrolysed forms of the metals, mostly in the form of polynuclear species. In the case of Al, most materials are formed by the controlled neutralization of aluminium chloride solutions and are generally known as polyaluminum chloride (PAC) [8].

It is believed that many of these products contain substantial proportions of the tridecamer Al_{13}. PAC products seem to give better coagulation than 'alum' at low temperatures and are also claimed to produce lower volumes of residual solids (sludge). Because they are already partially neutralized, they have a smaller effect on the pH of water and so reduce the need for pH correction. However, the mechanisms of action of PAC and similar products are still not well understood [8].

Most explanations are in terms of the high charge associated with species such as Al_{13} and the consequent effectiveness in neutralizing the negative charge of colloids in water. The relatively high stability of Al_{13} means that it should be more readily available for adsorption and charge neutralization at around neutral pH, whereas conventional 'alum' undergoes rapid hydrolysis and precipitation. PAC is more expensive than alum but normally have a number of advantages:

- more effective at low temperatures.
- faster floc formation.
- lower dosage rates.

- savings in pH adjustment chemicals.
- possibly more effective with algae.

These chemicals can offer significant benefits at plants where there are poor dosing and flocculation facilities; the replacement of alum by a polymeric aluminium salt may greatly improve flocculation and overall treatment efficiency [18].

Approximately half the dosage is required for turbidity removal, but more or less the same dosage as aluminium sulphate is required for predominantly colored waters. In cases where waters are predominantly turbid, therefore, use of this coagulant may significantly reduce sludge disposal problems [6].

2.3.2.3 Polyelectrolyte

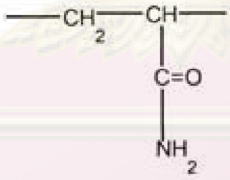
The term polyelectrolyte, as used here, refers to a large variety of natural or synthetic water soluble, macromolecular compounds which have the ability to destabilize or enhance flocculation of the constituents of a body of water. Strictly speaking, the term polymeric flocculants is more appropriate as a general description, polyelectrolyte being perhaps better reserved for those carrying ionized groups. However, because of its widespread usage, the term polyelectrolyte will be taken as including those polymeric flocculants which are essentially non-ionic [6].

A polymer molecule may be described as a series of repeating chemical units held together by covalent bond. If the repeating units are of the same molecular structure, the compound it termed a homopolymer. However, if the molecule is formed from more than one type of repeating chemical unit, it is termed a copolymer. The individual repeating units are called monomers and the molecular weight of the polymer molecule is the sum of the molecular weights of the individual monomers. The total number of monomer units is referred to as the degree of polymerization.

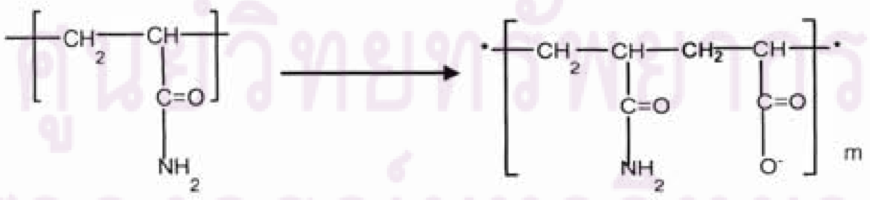
Polyelectrolytes are special classes of polymers containing certain functional groups along the polymer backbone which may be ionizable. If present, when the ionizable groups dissociate, the polymer molecules become charged either positively or negatively, depending on the specific functional groups present, and are thus referred to as cationic or anionic polyelectrolytes respectively. Polyelectrolytes that possess both positively and negatively charged sites are referred to as ampholytic, whereas those that possess no ionizable functional groups are termed nonionic polyelectrolytes.

All polyelectrolytes are typical hydrophilic colloids. They have molecular weights generally in the range 10^4 to 10^7 and are soluble in water due to hydration of functional groups [6].

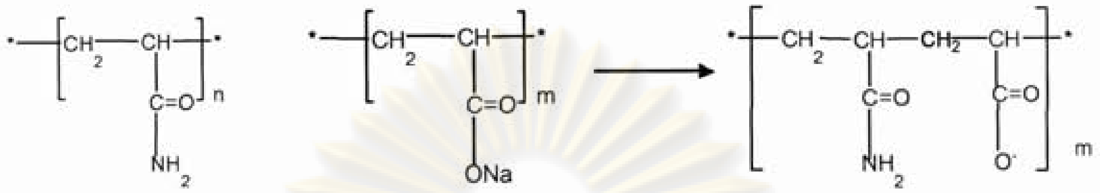
A very high proportion of synthetic polyelectrolytes are based on polyacrylamide and its copolymers with polyacrylic acid. The acrylamide monomer, making up the units of the polymer, is prepared by reacting natural gas and methane at high temperatures in the presence of controlled amounts of oxygen and ammonia to for hydrocyanic acid and acetylene followed by catalysis with cuprous chloride [6]. The acrylonitrile which results is then acid hydrolyzed to the acrylamide monomer using sulphuric acid. The acrylamide is then polymerized by catalysis. Polyacrylamide itself is nonionic but on hydrolysis the macromolecule aquires carboxyl groups and assumes an anionic character. Increased negativity is usually accomplished by copolymerizing acrylamide with acrylic acid. The structure of nonionic polyacrylamide is shown below:



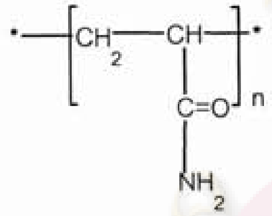
The structure of anionic hydrolysed polyacrylamide is as follows:



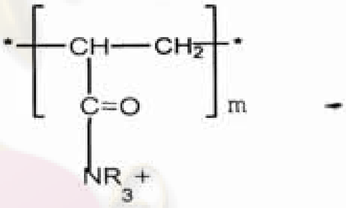
The structure of anionic polyacrylamide formed by copolymerization with sodium (or potassium or hydrogen) acrylate is as shown below:



The structure of anioninic polyacrylamide formed by hydrolysis, and by copolymerization with acrylate is seen to be identical. However, with copolymerization more control over molecular weight distribution and charge density is possible [6]. The percentage of acrylate units copolymerized is referred to as the percent hydrolysis; the higher the degree of hydrolysis, the higher is the overall ionic charge. Typically, percent hydrolysis ranges from zero to 30%. Cationic derivatives of polyacrylamide are available: for example, those produced by acrylamides, as shown below:



and



where R is usually a CH_4 or $CH_3 CH_2$ [6]

The main applications of organic polyelectrolytes in the water industry are in coagulation and flocculation, and in sludge treatment. The first two processes are usually followed by sedimentation and filtration, although with only slightly contaminated waters the sedimentation step can be omitted [9]. Flotation is an option instead of sedimentation, especially for algae-laden waters or for oil-and grease-contaminated wastes. The sludge obtained from the various separation processes have very high water contents and must be further concentrated to minimize transportation costs; polymers have a role in this sludge conditioning.

For oil and grease emulsions an inorganic coagulant is not required, the necessary effect being obtained with the medium–CD, high–MW copolymer of acrylamide and quaternized dimethylaminoethyl acrylate or methacrylate, which adequately neutralizes the negatively charged organic phase [9].

2.3.3 Coagulation of Emulsions

The coagulation process for these emulsions includes, just as in the case of colloidal particles, neutralization of the zeta potential. However, a coalescence mechanism may predominate in the case of mechanical emulsions. The treatment of the latter may include a phase of destabilization or partial coagulation directly followed by a coalescent filtration process. The treatment of chemical emulsions must include a complete coagulation process followed by flocculation and separation by settling or dissolved air flotation [5].

The flocculation conditions for the emulsions of hydrocarbons or oils depend on the nature of these substances. They are found in two main forms: mechanical emulsions which are relatively unstable and, after preliminary static settling for one hour, feature a micelle size of a dozen to a hundred microns and concentrations of about 100 to 500 mg/L, chemical emulsions that are relatively stable, which is due either to the nature of the hydrocarbons (asphaltenes, naphthenates), to the simultaneous presence of dispersing agents (alkaline salts, detergents, etc.). Following static settling for one hour, they have a micelle size of 0.1 micron (micro–emulsions) to one dozen microns, and feature a widely variable hydrocarbon concentration that ranges from 100 mg/L (petrochemical complex effluents) to 50 mg/l (aqueous cutting fluids).

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Coagulant

Two coagulants used in this research were commercial grade.

1) Cationic polyacrylamide (CPAM) was supplied by Bornnet Company Limited. CPAM with high molecular weight-medium charge and bulk density approximate 0.75-0.95 g/cm^3 was used.
2) Polyaluminum chloride (PAC) was supplied by Thai PAC Industry Company Limited.

3.1.2 Flocculant

Anionic polyacrylamide (APAM, commercial grade) was supplied by Bornnet Company Limited. APAM with high molecular weight-medium charge and bulk density approximate 0.80-1.00 g/cm^3 was used.

3.1.3 Synthetic Metalworking Fluid (MWF) Wastewater

Synthetic metalworking fluid (MWF) wastewaters were prepared by mixing the cutting oil supplied by Iida-Seven Suns Company Limited with water. The cutting oil used in this research was a high stable oil-in-water (O/W) emulsion type.

3.1.4 Real Metalworking Fluid (MWF) Wastewater

Real MWF wastewaters were collected from three industrial sources. Each sample of MWF wastewater was O/W emulsion type. The wastewater was sampling from MWF wastewater reservoir tank.

3.2 Experimental Procedure

3.2.1 Analytical Methods for Determination of Turbidity, COD, TSS and pH

Turbidity of sample was measured using turbidimeter (Eutech, TN-100). COD and TSS were determined according to the APHA method [28].The pH value was measured by pH meter (Metrohm, 744).

3.2.2 Determination of the Optimum Coagulants Dose for Synthetic MWF Wastewater

Preliminary experiments of MWF wastewater treatment were carried out for synthetic MWF wastewater at 3% and 10% by volume of O/W emulsion. As a result, different ranges of dosage of CPAM and PAC were varied for coagulation/flocculation process at 3% and 10% O/W emulsion as shown in Table 3.1. The dosage of 200 mg/L of APAM as flocculant was used which was a recommended value for sludge conditioning in wastewater [9]. Coagulation and flocculation experiments were carried out by first adding the coagulant into MWF wastewater and stirred at 300 rpm for 20 min. Then, the flocculant was added and stirred at 250 rpm for 20 min. The mixture was allowed to settle down. After setting time of 30 min, the effluent was taken to determine turbidity, COD, TSS and pH values. The floc formations, pH, and percent removal of turbidity, COD, and TSS of the effluent were evaluated to obtain the optimum dosage of coagulant.

Table 3.1 Coagulant dosage for each % O/W emulsion.

%O/W emulsion	Coagulant Dose (mg/L)	
	Cationic polyacrylamide (CPAM)	**Polyaluminum chloride (PAC)**
3	100, 300, 400, 600, 800	100, 300, 400, 600, 800
5	400, 600, 800, 1000	400, 500, 600, 700
7	800, 1000, 1200, 1400, 1600	400, 500, 600, 700
10	400, 900, 1200, 1600, 1800, 2400	300, 400, 600, 700, 800, 1300

3.2.3 Determination of the Optimum Flocculant Dose for Synthetic MWF Wastewater

Pre-determined optimum dosage of CPAM or PAC in section 3.2.2 was used to determine the optimum dosage of APAM. The dosage of APAM was varied for 100, 200, 400, 600 and 800 mg/L. Coagulation and flocculation process was performed as described in section 3.2.2. The optimum flocculant dosage was determined from percent removal of turbidity, COD, TSS and pH values.

3.2.4 Effect of pH of MWF Wastewater on Coagulation/Flocculation Performance

The pH of MWF wastewater was varied within a range of 4-9 (adjusted by 1 M H_2SO_4 and 1 M NaOH). The dosage of coagulant and flocculant were applied at optimum values determined from section 3.2.2 and 3.2.3 for each concentration of O/W emulsion. Percent removal of turbidity, COD and TSS as well as the effluent pH was evaluated.

3.2.5 Relationship between Turbidity and Optimum Coagulant Dose

Relationship between turbidity and optimum coagulant dose were investigated at 3%, 5%, 7%, and 10% synthetic O/W emulsion. The coagulation/flocculation process at 5% and 7% were performed as described in section 3.2.2. The coagulant dosages were varied as shown in Table 3.1. The optimum coagulant dose at various O/W emulsion concentration was plotted versus their turbidity. Optimum dosages were selected from percent removal of turbidity only. Calibration curve from this relation will use for selected optimum dose of coagulant for the treatment of real MWF wastewater.

3.2.6 Treatment Ability Test for Real MWF Wastewater

The real MWF wastewaters were obtained from KTT Machinery Company Limited., Tue Parknum Company Limited and Otachai Industry Company Limited. The wastewaters were taken to measure turbidity, COD, TSS and pH value. The dosage of coagulants and flocculant was selected based on the turbidity of the wastewater and the concentration of O/W used in MWF from the industry. Coagulation/flocculation process for real wastewater was performed as same as synthetic wastewater. The clarification zone of water after treatment was withdrawn to determine the percent removal of turbidity, COD, TSS and pH values.

CHAPTER IV

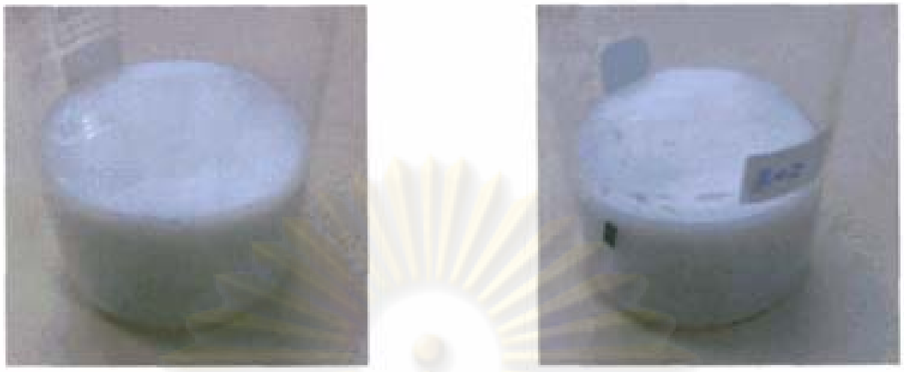
RESULTS AND DISCUSSION

4.1 Characteristics of Synthetic MWF Wastewater

Synthetic MWF wastewaters were prepared at 3% and 10% O/W emulsion which is favorite concentration used in many industries. However, working concentration can be varied according to machining operation. The characteristics and appearance of synthetic MWF wastewater were presented in Table 4.1 and Figure 4.1, respectively. The turbidity, COD and TSS were proportional to the oil concentration (% O/W). These parameters increased gradually as the %O/W emulsion increased. Although turbidity and TSS values were not objectionable in standard values of industrial effluent by Ministry of Science, Technology and Environment, No. 3, B.E. 2539, high values of turbidity and TSS could imply for the high content of organic matters and suspended particles which indicate the poor quality of wastewater. In addition, COD of synthetic MWF wastewater was exceeded the regulated value (120 mg/L). Hence, pretreatment of the effluent from MWF wastewater was necessary.

Table 4.1 Characteristics of synthetic MWF wastewaters used in this study.

% O/W	Turbidity (NTU)	COD (mg/L)	TSS (mg/L)	pH
3	3411	13067	377	7.68
10	12178	25333	680	8.43



(a) (b)

Figure 4.1 Appearance of synthetic MWF wastewater at (a) 3% O/W and (b) 10% O/W.

4.2 Effect of Coagulant Dosage on Coagulation of Synthetic MWF Wastewater

Percent removal of turbidity, COD and TSS of the synthetic wastewater at 3% O/W and 10% O/W using various doses of CPAM and PAC were presented in Figures 4.2 and 4.3. The values of turbidity, COD and TSS after treatment were also tabulated in Appendix A.

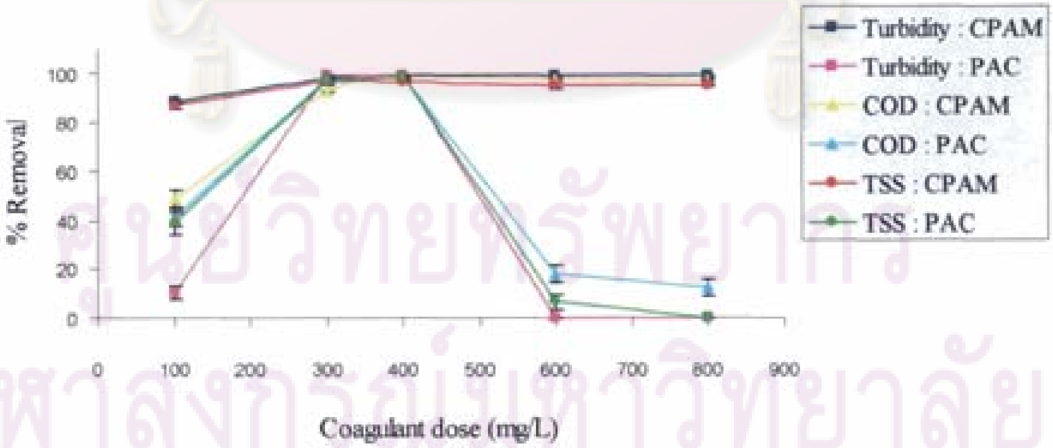


Figure 4.2 Removal efficiency of turbidity, COD and TSS using different doses of CPAM or PAC as primary coagulant for synthetic wastewater at 3% O/W.

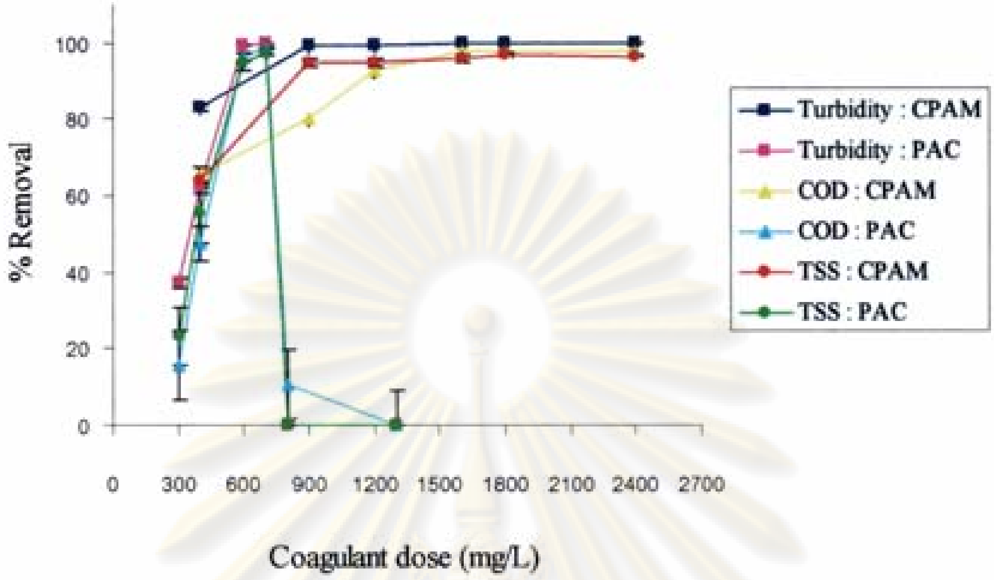


Figure 4.3 Removal efficiency of turbidity, COD and TSS using different doses of CPAM or PAC as primary coagulant for synthetic wastewater at 10% O/W.

Figure 4.4 Flocs formed using optimum doses of (a) CPAM and (b) PAC for synthetic MWF wastewater at 3% O/W emulsion.

(a) **(b)**

Figure 4.5 Flocs formed using optimum doses of (a) CPAM and (b) PAC for synthetic MWF wastewater at 10% O/W emulsion.

4.2.1 Effect of CPAM Dosage on Coagulation

For synthetic wastewater at 3% O/W, the turbidity, COD and TSS removal efficiencies increased as the dosage of CPAM increased up to 99%, 98% and 96%, respectively. The maximum removal of turbidity, COD and TSS were obtained at 400 mg/L of CPAM and above. The removal of turbidity, COD and TSS at CPAM dosage below 400 mg/L were not efficient enough due to under feeding of coagulant to destabilize all particles [7, 9]. Addition of the coagulant above 400 mg/L resulted in similar removal efficiency. That meant coagulant dose was sufficient for destabilize stable particles and overdosing CPAM was not affected the coagulation efficiency. Therefore, dose of CPAM was selected at 400 mg/L for further study.

Similar results were observed for synthetic wastewater at 10 % O/W. The turbidity, COD and TSS removal efficiencies increased up to 99 %, 97% and 96%, respectively, with the use of 1800 mg/L of CPAM. Addition of the CPAM above 1800 mg/L did not increase the removal efficiency to appear constant. Therefore, optimum dosage of CPAM was selected at 1800 mg/L for 10% O/W synthetic MWF wastewater. Here, the efficient mechanisms of CPAM are electrostatic patch and bridging. These two mechanisms have effect from concentration of particles. Both mechanisms used adsorption phenomenon on particles and reduced the potential energy of repulsion between particles. The high concentration of O/W emulsion means high stable colloid particles in solution. Therefore, the optimum dosage of CPAM was increased as concentration of O/W emulsion increased.

4.2.2 Effect of PAC Dosage on Coagulation

The optimum turbidity, COD and TSS removal efficiencies using PAC were obtained at critical PAC dosage. For synthetic wastewater at 3% O/W, the optimum turbidity, COD and TSS removal efficiencies were 99%, 98% and 98% respectively, with the use of 400 mg/L of PAC. For the dosage below 400 mg/L, the removal efficiencies of turbidity, COD and TSS increased gradually with increasing of PAC dosage. This referred that PAC dosage below 400 mg/L did not reach the sufficient point of destabilization of oil emulsion in water. However, the removal efficiency also decreased in a diminishing fashion with increasing dose of PAC above the optimum (400 mg/L). This may be as a result of overdosing of PAC leading to a charge reversal of particles by access PAC and re-suspension of colloidal material [8, 18]. As a result, the maximum removal of turbidity, COD, and TSS was achieved at 400 mg/L of PAC.

The similar results were observed for synthetic wastewater at 10 % O/W. The turbidity, COD and TSS removal efficiencies were optimum at 99%, 98% and 97% respectively, with the use of 700 mg/L of PAC. Above this point all removal percentage decreased for the reason as explained at 3% O/W. Higher use of coagulant dosage for high concentration of O/W emulsion was noticed. This effect was similar to the coagulation using CPAM. Therefore, high amount of hydrolysis species from PAC was required to destabilize the particles.

4.2.3 Effectiveness of Coagulation by CPAM and PAC

The coagulation-flocculation process by CPAM or PAC with 200 mg/L of APAM as flocculant had different advantages and disadvantages. The similar efficiency was obtained with the use of optimum dosage of CPAM and PAC. However, in case of 10 % O/W emulsion the dosage of PAC was a lot lower than CPAM. These results can be explained based on different mechanisms of colloid destabilization by CPAM and PAC. For PAC, different hydrolysis species of PAC give many mechanisms for destabilization of negative colloids as presented in Figure 4.6. Species of PAC proposed to form during hydrolysis are commonly the monomeric hydrolysis products such as Al^{3+}, $Al(OH)_2^+$, $Al(OH)^{2+}$, $Al(OH)_3$ (amorphous aluminium hydroxide) and $Al(OH)_4^-$, as well as a dimer $Al_2(OH)_2^{4+}$, a trimer $Al_3(OH)_4^{5+}$, and a tridecamer $Al_{13}O_4(OH)_{24}^{7+}$ (often denoted by Al_{13}). The main mechanism of PAC is not only charge neutralization mechanism from cationic species but also sweep coagulation mechanism (enmeshment) from amorphous aluminium hydroxide [29-35]. These caused a low optimum dosage of PAC. CPAM has two principles destabilization mechanisms which are electrostatic patch and bridging. The bridging mechanism which the principle lies in the ability of charged polyelectrolyte to destabilize particles bearing the same charge [6, 36] has been accepted for some circumstances. The electrostatic patch is the main mechanism for destabilized opposite charge of colloids by polyelectrolyte, especially at high dosage of CPAM. High dosage of CPAM increased the amount of charge density from chains of polymer. The higher the charge density, the more effective the destabilization of high particle. In addition, the higher of charge density was given more effective in bringing model due to larger loops. However, upper limit dictated by electrostatic repulsion between polyelectrolyte and surface of particles, where respective charges were similar during adsorption. Regarding electrostatic patch and bridging mechanism, the optimum dosage appears to increase in proportional to the concentration of particulates present [27]. The high concentration of O/W emulsion means high stable colloid particles in solution. Therefore, the optimum dosage of CPAM was increased as concentration of O/W emulsion increased. In spite of that, time and speed of mixing in coagulation/flocculation process were important for polyelectrolyte to be adsorbed evenly on particles. Mixing should be short and vigorous at the time of polyelectrolyte addition. If mixing too vigorous for too long, a period desertion and/or rearrangement of adsorbed chain could give rise to restabilization [6].

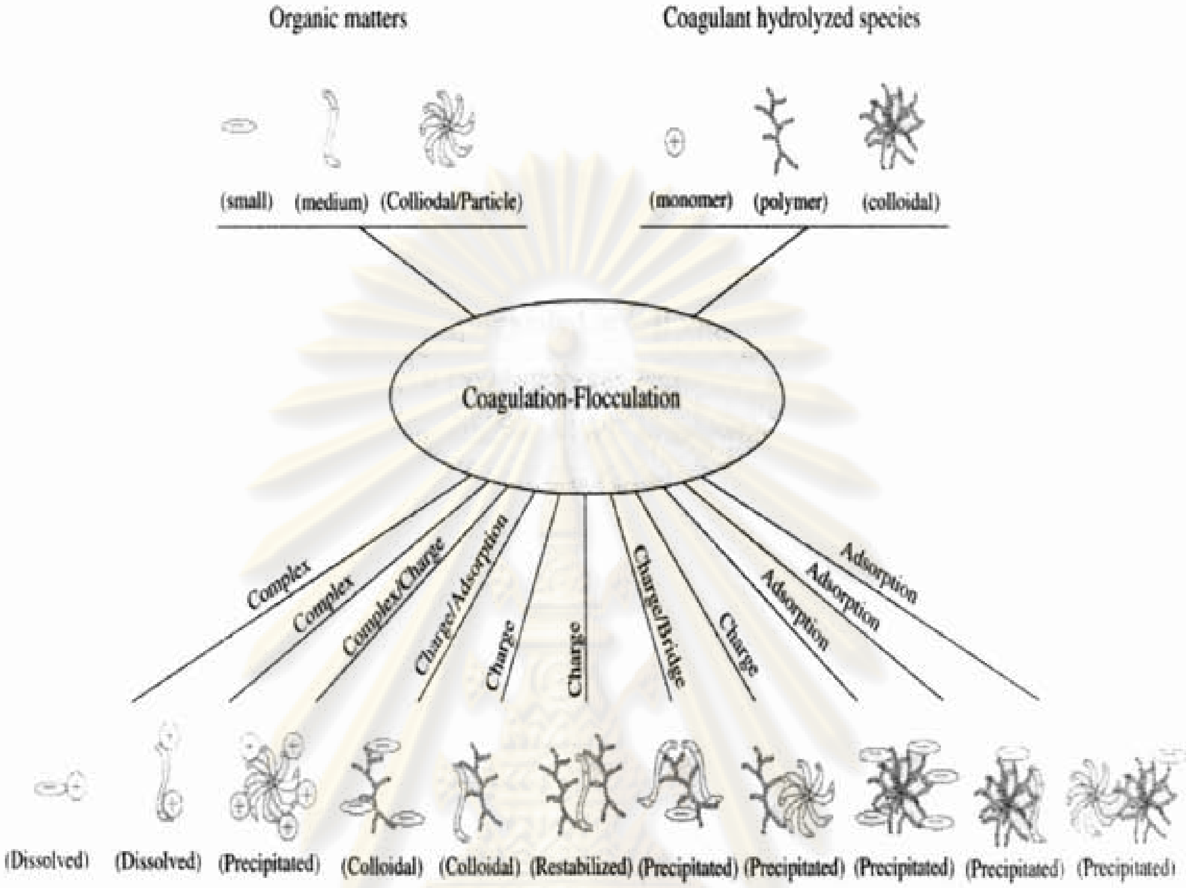


Figure 4.6 Model of interaction of coagulant hydrolyzed species and organic matters [41].

Nevertheless, in the case of 3% O/W emulsion the best removal efficiency use the similar dosage of PAC and CPAM. This may be as a result of limited large particle aggregation at 3% O/W emulsion.

Because of the increase of O/W concentration, the collision efficiency between particles during the coagulation process will increase. An increase of collision efficiency will improve the particle-aggregation induced by charge neutralization [35]. Therefore, high stable colloid particles in O/W emulsion hardly affected for selected high optimum PAC dosage. However, this advantage can overturn at over O/W concentration. The charge neutralization ability of PAC was deprived, because from large amount of particles at 10% O/W emulsion. This phenomenon disappeared when the dosage was increased [35].

Although dosage PAC was used lower than CPAM, PAC still found problem from restabilization of colloidal suspensions. Therefore, the working dosage of CPAM was more tolerance than PAC for MWF wastewater treatment. Furthermore, the flocs using CPAM formed more firmly, largely and tightly than using PAC as shown in Figures 4.4 and 4.5. This might due to the bridging mechanism of CPAM. Therefore, CPAM with APAM promoted the aggregation of colloid bridges between the dispersed oil droplets and suspended solid, and conduced the particles to form larger size, which can easily to flocs separate.

The pH values of synthetic MWF wastewater after treatment by various dosages of CPAM and PAC were presented in Figure 4.7. In case of PAC, the effluent pH was decreased to pH 4-5 for both O/W concentrations. Since aluminum hydrolysis products of PAC are positively charge ion like $Al(OH)^{2+}$, $Al_3(OH)_4^{5+}$or Al_{13} and hydrogen ion (H^+), the pH of solution was decreased when applied PAC into wastewater. However, the pH value of the wastewater after treated was still higher than treated with aluminum sulfate and ferric chloride [11-12, 23]. For CPAM, pH values were not changed because CPAM has a high molecular weight and destabilized mechanism was not involved the hydrogen ion. Therefore, final pH after coagulation by CPAM was unchanged. However, the pH of wastewater after coagulation by CPAM or PAC was in range 4-9 which is a regulated value for industrial effluent. Therefore, it was unnecessary to adjust the wastewater pH before discharge.

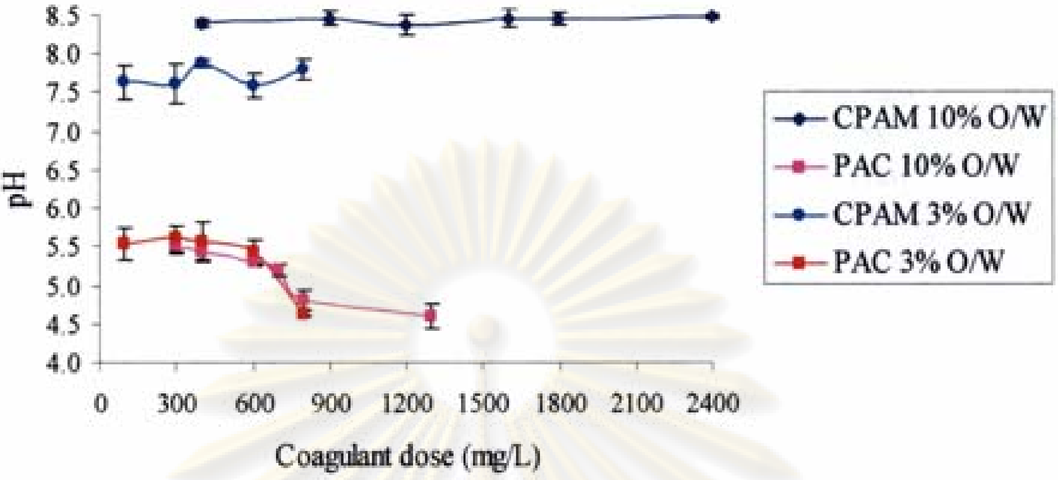


Figure 4.7 The pH values after treatment using different dosages of CPAM or PAC as primary coagulant with 200 mg/L of APAM as flocculant for synthetic wastewater at 3% and 10% O/W.

4.3 Effect of Flocculant Dosage on Flocculation for Synthetic Wastewater

The dosage of APAM was varied from 0 to 800 mg/L for both coagulants, CPAM and PAC. The experiments were performed with the optimum dose of CPAM and PAC which were 400 mg/L of CPAM and 400 mg/L of PAC for 3% O/W wastewater and 1800 mg/L of CPAM and 700 mg/L of PAC for 10 % O/W wastewater. The effect of APAM dosage as flocculant on the turbidity, COD and TSS for the synthetic wastewater at 3% O/W were presented in Figure 4.8 and 10 % O/W in Figure 4.9.

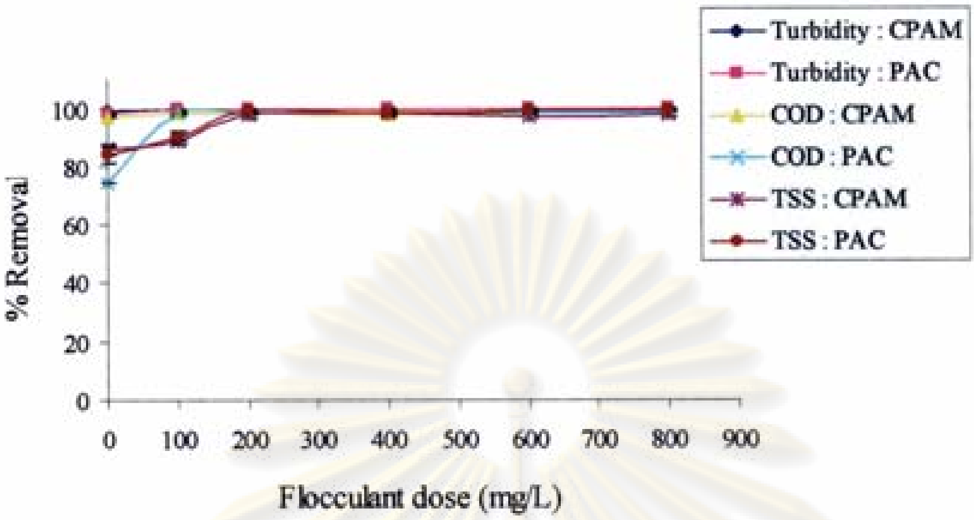


Figure 4.8 Removal efficiency of turbidity, COD and TSS using different doses of APAM as flocculant for synthetic wastewater at 3% O/W.

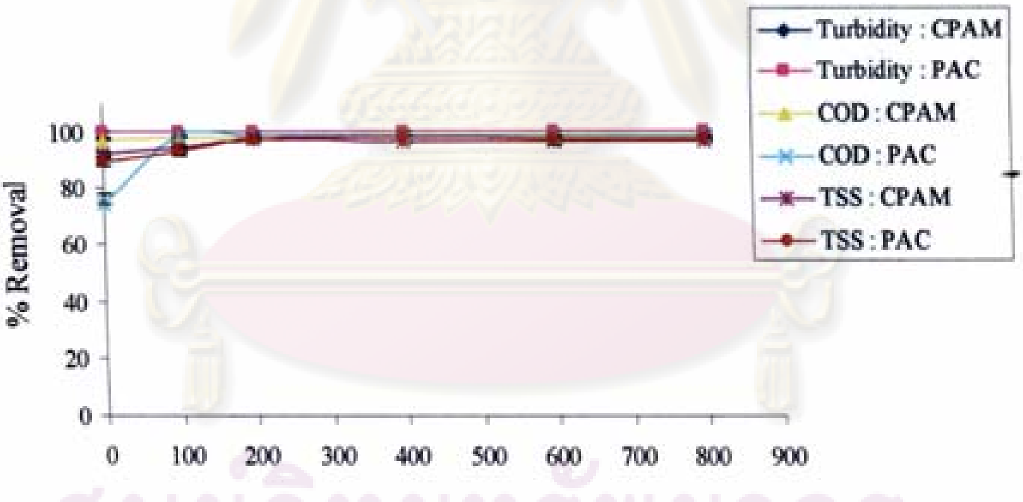
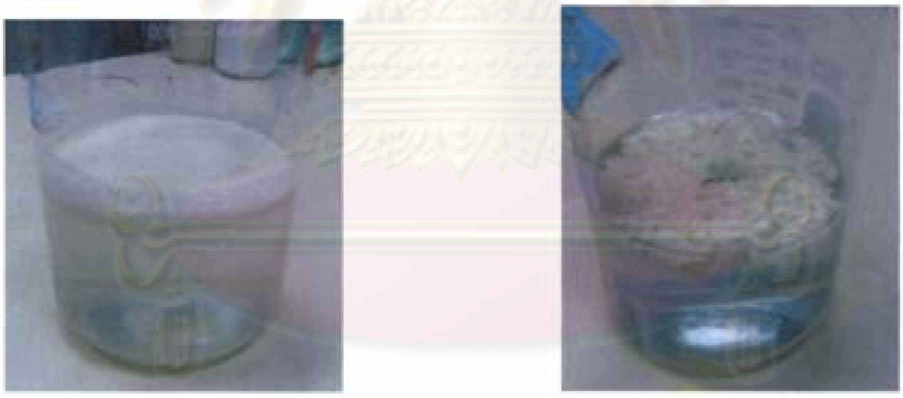


Figure 4.9 Removal efficiency of turbidity, COD and TSS using different doses of APAM as flocculant for synthetic wastewater at 10% O/W.

(a) (b)

Figure 4.10 Flocs formed using (a) optimum dosage of CPAM alone and (b) optimum dosage of CPAM with 200 mg/L of APAM for synthetic wastewater at 3% O/W.



(a) (b)

Figure 4.11 Flocs formed using (a) optimum dosage of PAC alone and (b) optimum dosage of PAC with 200 mg/L of APAM for synthetic wastewater at 3% O/W.

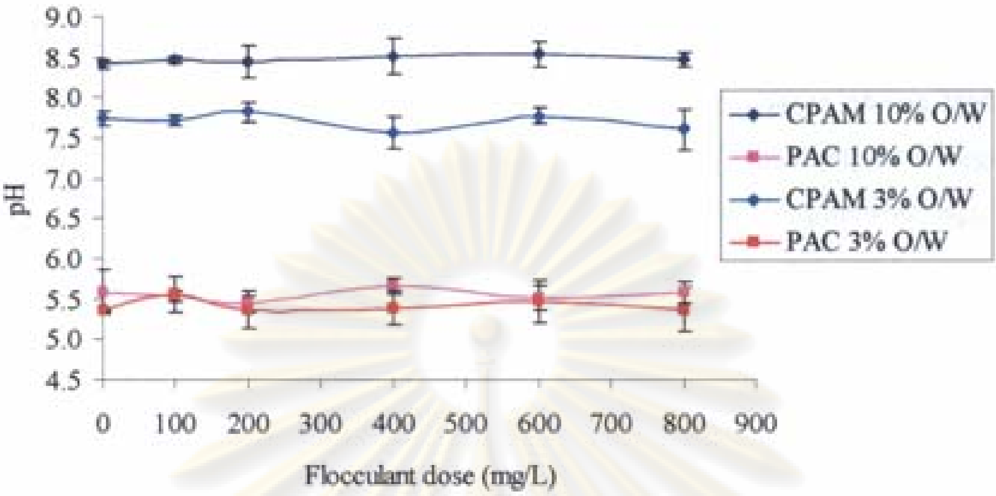


Figure 4.12 The pH values after treatment using optimum doses of CPAM or PAC as primary coagulant and different doses of APAM as flocculant for synthetic wastewater at 3% and 10% O/W.

From Figures 4.8 and 4.9, the removal efficiency of turbidity, COD and TSS using APAM above 100 mg/L was not significantly different or imperceptible when different doses of APAM were added. However, with the addition of APAM to the synthetic wastewater, flocculation was improved markedly as shown in Figures 4.10 and 4.11. The small flocs formed by coagulation with CPAM or PAC can be built up into larger agglomerates. The flocculation process with APAM involved the polymer bridging mechanism, in which polyelectrolyte bounded to a particle, looped and dangled chains to nearby particles [9]. In the other word, CPAM or PAC which added first was proposed to serve as the anchor for the adsorption of the second polymer. The addition of CPAM or PAC alone produced primary flocs and formed binary flocs when APAM was added, particularly for PAC coagulant. The result indicated that CPAM produced bigger primary flocs than PAC, which required a smaller amount of the tethering APAM to form binary flocs. Nonetheless, APAM was needless if flocs size in water treatment process was not emphasized. After flocculated by APAM, the pH values were not significant different as presented in Figure 4.12. This maybe as a result from stable structure of APAM [9] with high molecular weight of polymer in specific products.

In overall, the coagulant dose plays an important role in treatment of MWF wastewater due to the high stability of colloidal particles. The flocculant doses had slight effect for the treatment process. Normally, the net charge on the flocs after coagulation was close to zero, in which the number of positively and negatively charged site is almost equal [9]. Moreover, APAM was not required as high as the dosage of CPAM or PAC in coagulation process.

4.4 Effect of pH on Coagulation/Flocculation Process

The effect of wastewater pH in coagulation/flocculation process was conducted by adjusting the pH from 4 to 9. With the previously established optimum coagulant and flocculant doses for 3% and 10% O/W emulsion, the results corresponding to the removal efficiency of turbidity, COD and TSS at various pH of wastewater for each coagulant used were shown in Figures 4.13 and 4.14.

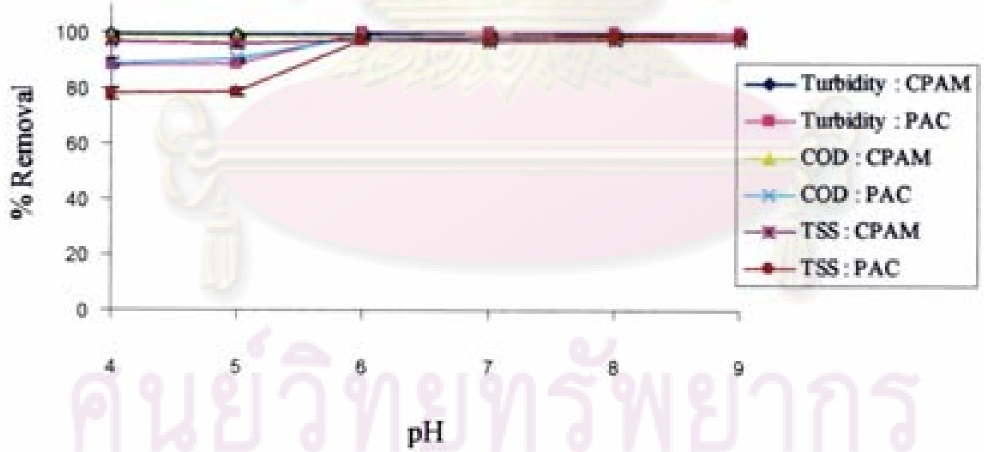


Figure 4.13 Removal efficiency of turbidity, COD and TSS using CPAM or PAC as coagulants and APAM as flocculant for synthetic wastewater at 3% O/W emulsion, when the wastewater pH was varied.

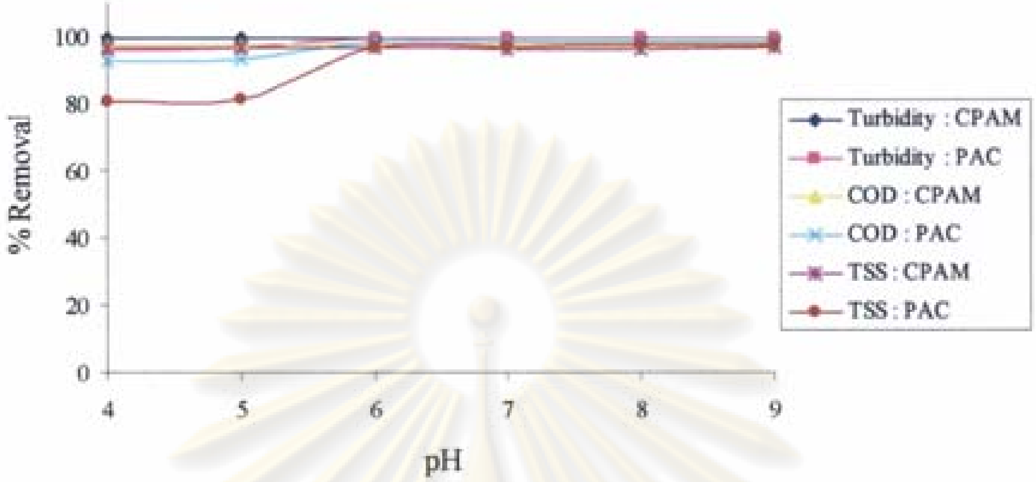


Figure 4.14 Removal efficiency of turbidity, COD and TSS using CPAM or PAC as coagulants and APAM as flocculant for synthetic wastewater at 10% O/W emulsion, when the wastewater pH was varied.

In case of CPAM, the removal efficiency was not changed within studied pH. The coagulation/flocculation process took place with relatively independent of the pH. This indicated that the coagulation by CPAM can be worked in wider pH range of wastewater in comparison with the use of inorganic coagulant as in ref. [11], which the optimum pH of $FeCl_3$ and $Al_2(SO_4)_3$ were 6 and 6.5, respectively.

In case of PAC, at low pH (4-6), the removal efficiency of turbidity, COD and TSS were lower than at high pH (6-9). The performance increased to reach maximum values at pH above 6. This may be a result from the Al species distributions [29, 38] which significantly depend on the pH value. Since many kinds of hydrolyzed species were occurred, the hydrolysis of PAC could produce a series of products ranging from monomeric Al species, $Al(OH)^{2+}$ and $Al(OH)_2^{+}$, dimer $Al_2(OH)_2^{4+}$, trimer $Al_3(OH)_4^{5+}$ and tridecamer $Al_{13}O_4(OH)_{24}^{7+}$, (often denoted by Al_{13}), and consequently caused destabilization and aggregation of colloids particle [30,41]. Many researchers believed that Al_{13} was the most effective polymeric Al species in PAC composition for wastewater treatment [29, 31, 41] because Al_{13} species has a high stability of positive electric charge and a better opportunity to adsorb on negative colloids [8, 41].

At low pH, the Al_{13} fraction was lower than in neutral pH region [29, 38]. Therefore, the optimum pH for PAC was observed around 6-9.

4.5 Relationship between Optimum Coagulant Dose and Turbidity

The values of turbidity, COD and TSS of MWF wastewater were proportional to the O/W concentration as shown in Table 4.1. Among these parameters of wastewater, the turbidity was the most convenient to measure and used to predict the optimum dose of coagulant. As shown in Figure 4.15, the turbidity of O/W emulsion showed a linear relationship with the concentration of O/W emulsion. Therefore, the study of turbidity removal for synthetic MWF wastewater at 3%, 5%, 7% and 10% O/W was constructed. The coagulant dosage for optimum removal efficiency of turbidity was increased as the concentration of O/W emulsion increase (Figures 4.16 and 4.17). As a consequence, the optimum dosage of coagulants, both CPAM and PAC gave a good linear relationship with % O/W emulsion and turbidity as shown in Figure 4.18 and Figure 4.19. Therefore, the condition used for real wastewater can determined from either the turbidity or % O/W.

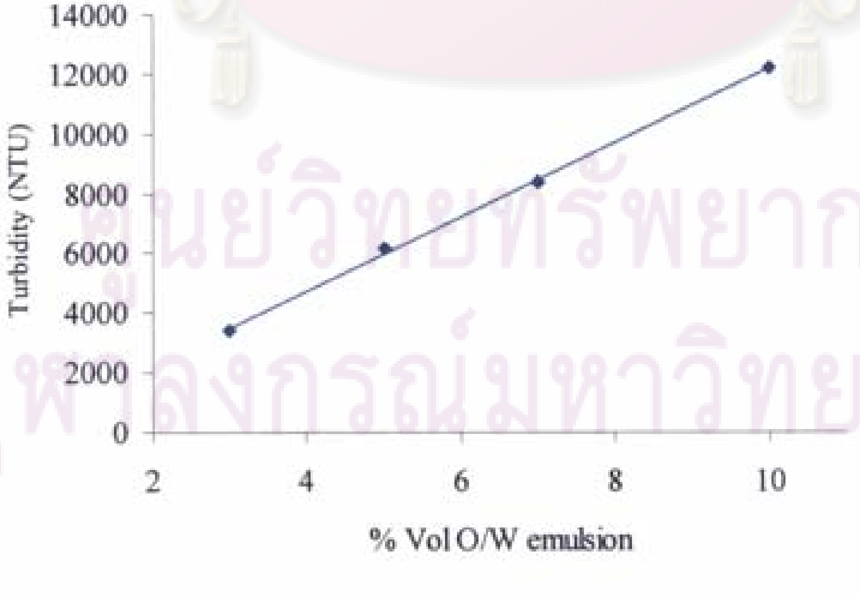


Figure 4.15 Relationship between turbidity and % Vol O/W emulsion.

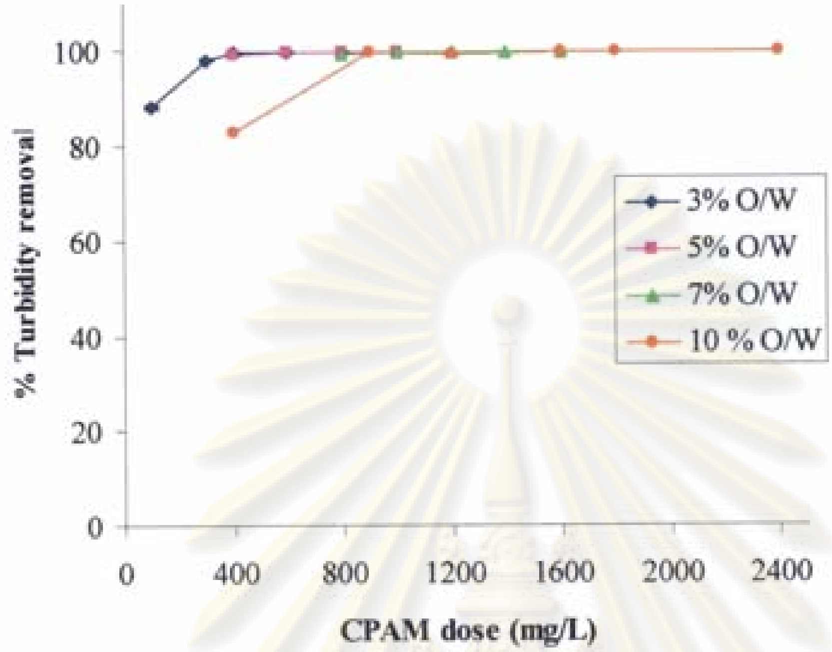


Figure 4.16 Removal efficiency of turbidity using different dosages of CPAM as coagulant for synthetic wastewater at 3%, 5%, 7% and 10% O/W.

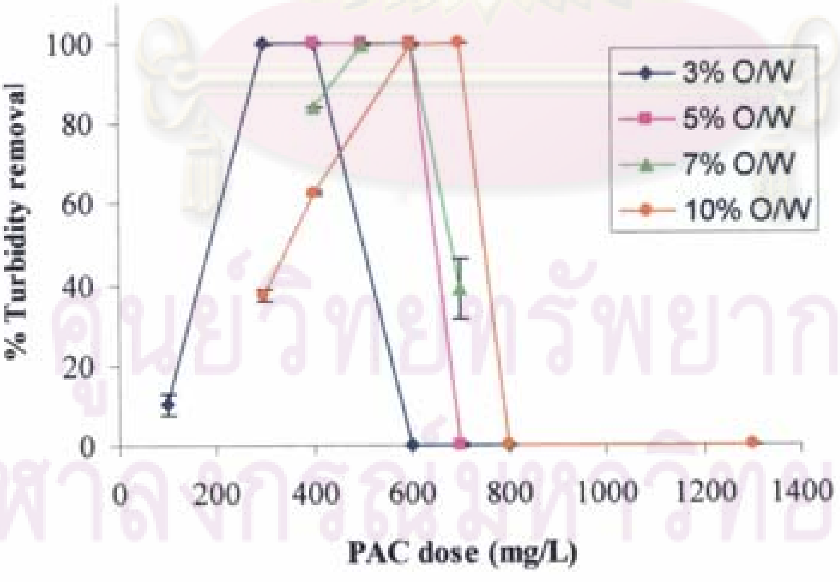


Figure 4.17 Removal efficiency of turbidity using different dosages of PAC as coagulant for synthetic wastewater at 3%, 5%, 7% and 10% O/W.

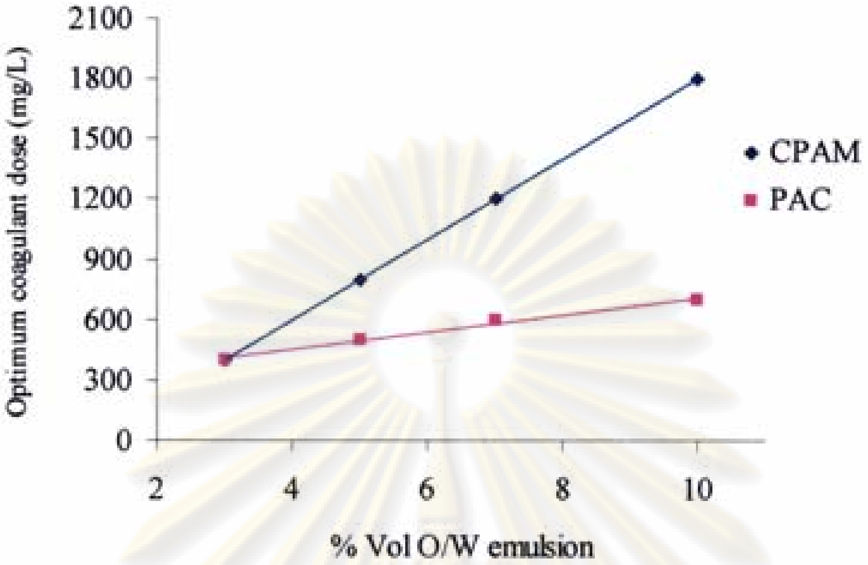


Figure 4.18 Relationship between optimum coagulant dose and % Vol O/W emulsion.

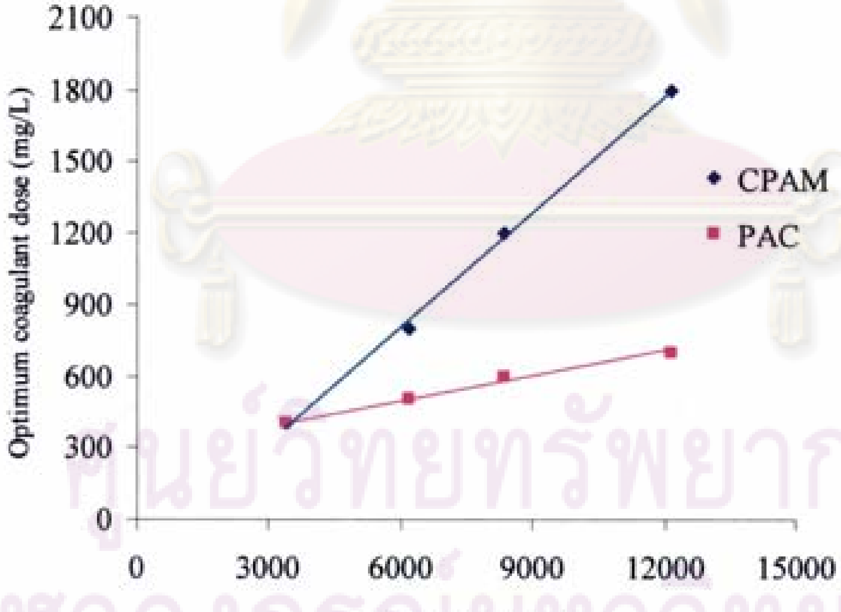


Figure 4.19 Relationship between optimum coagulant dose and turbidity.

4.6 Effectiveness of Coagulation on Real MWF Wastewaters

The real MWF wastewaters collected from three factories contained high turbidity, COD and TSS as shown in Table 4.2. Since the concentration of O/W in real sample can be varied from the machining operation, the coagulant was applied at the dosage determined by % O/W concentration data from MWF factory compared with the dosage by the relation between turbidity and optimum coagulant dose in Figure 4.19.

Table 4.2 Characteristics of real MWF wastewaters used in this study.

	Characteristic				
Source	Turbidity (NTU)	COD (mg/L)	TSS (mg/L)	pH	Appearance
Industry I	5343	18667	299	7.36	
Industry II	8611	22667	543	7.91	
Industry III	7525	38667	493	7.42	

Table 4.3 Characteristics of real MWF wastewaters after treatment.

			Dose from %O/W data		Dose from turbidity data	
Source	% O/W	Removal %	CPAM (400 mg/L)	PAC (400mg/L)	CPAM (696.6 mg/L)	PAC (474.1 mg/L)
Industry I	3	Turbidity	81.5±0.1	99.6±0.0	90.5±0.2	99.8±0.0
		COD	77.1±2.5	99.0±0.5	90.0±2.5	99.6±0.2
		TSS	79.5±0.8	98.4±0.4	85.1±0.8	98.9±0.4
		pH	7.21	5.89	7.43	5.68
Source	% O/W	Removal %	CPAM (800 mg/L)	PAC (500mg/L)	CPAM (1224.1 mg/L)	PAC (587.5 mg/L)
Industry II	5	Turbidity	95.6±0.2	99.8±0.0	96.9±0.1	99.9±0.0
		COD	72.9±2.0	98.6±0.1	74.1±2.0	98.8±0.1
		TSS	87.5±2.6	98.3±0.8	93.6±0.6	99.7±0.2
		pH	7.92	5.78	7.84	5.92
Source	% O/W	Removal %	CPAM (800 mg/L)	PAC (500mg/L)	CPAM (1048.8 mg/L)	PAC (549.8 mg/L)
Industry III	5	Turbidity	81.4±0.4	99.9±0.0	86.7±0.1	99.9±0.0
		COD	65.5±1.2	98.9±0.1	76.5±1.2	99.0±0.1
		TSS	78.5±0.7	98.6±0.2	81.9±0.6	99.1±0.2
		pH	7.34	5.41	7.28	5.29

It was clear from the results in Table 4.3 that the coagulation/flocculation efficiency using PAC either selected the coagulant dose from %O/W data or turbidity data was higher than using CPAM. Interestingly, the coagulant dose selected from turbidity data gave better removal efficiency than actual concentration data. However, the coagulation of O/W in real MWF wastewater using PAC was as good as observed in synthetic MWF wastewater. Nonetheless, the removal efficiency of all pollution was not as high as in synthetic MWF wastewater in case of CPAM coagulant. This may be as a result of high organic matter and suspended particle in real MWF wastewater. In the fact of that destabilization mechanism of CPAM were patch mechanism (main mechanism) and polymer bridging mechanism. In patch mechanism case, the optimum dose appears to increase in proportional to the surface area concentration of particles. Moreover, because polymer bridging is an adsorption phenomenon, the optimum dose will generally be proportional to the concentration of particulates present [27].

Nevertheless, the high pollution in real MWF wastewater did not affect the removal efficiency of PAC coagulant. This may be as a result from sweep coagulation (entrapment in a precipitate) mechanism of destabilization. The mechanism is often an inverse relationship between the concentration of colloidal material to be removed and the coagulant dose required. This is explained by the concept that colloidal particles act as nuclei at high colloid concentrations in which the coagulant precipitates on to. On the other hand, an excess of precipitated coagulant is required to entrap the colloid particle [18] at low colloid concentrations. These results agree with those previously reported in ref. [39].

Although the high colloid concentration has supported sweep coagulation mechanism, higher coagulant dose was given better efficiency than lower dose. It can be attributed to the fact that the coagulant concentration is not high enough to destabilize the negative charge of organic matter and colloidal particles.

Considering either from advantages or economy, there was no profit to use CPAM massively. The heavy pollution in real MWF wastewaters was higher than in synthetic wastewater and destabilized mechanism of CPAM unable to support them. However, the form of flocs using CPAM was large and stable. For PAC, despite the fact that PAC had the advantages of inexpensive price and high pollution removal for MWF wastewater, it had the disadvantages of producing tiny, unstable and loose flocs which was easy to disperse even a slight vibration. These drawbacks were the common problem existing in inorganic coagulants [40]; the obstacle of separation in the detailed operation.

Although flocs from PAC process were hardly removed, combining PAC with APAM can improve flocs size. This may be as a result from the small flocs can be built up into larger agglomerates by flocculation with APAM. The larger particles formed in this way was giving accelerated rate of separation. The nature of the surface charge on the coagulation flocs will depend on the dose of coagulant used, but the net charge is normally close to zero. Often an anionic polymer will increase the size of the flocs by interaction with the positive sites on the flocs surface [9]. Nonetheless, the flocs size coagulated by CPAM was bigger than that from PAC. Furthermore, the solution pH after coagulated dropped to acidic range with a dosage of PAC and slightly changed with a dosage of CPAM as observing in synthetic MWF wastewater.

In selecting the best coagulant system (CPAM alone, PAC alone, CPAM with APAM or PAC with APAM), the effluent quality, sludge volume, flocs size and overall operating cost are the key factors.

If the operating cost is a major consideration, the least expensive coagulant system that produces acceptable effluent quality and sludge volume should be used. At high O/W concentration, PAC with APAM would be the best system since a low dosage of PAC was used to achieve the effective coagulation. At low O/W concentration, CPAM or PAC with APAM would be a suitable system because a similar satisfied performance was achieved. In actually, the cost of PAC is lower than CPAM. Therefore, PAC should be investigated if it was desired to keep costs and operational handling at reasonable levels. Even though low dosage of PAC was used in coagulation, flocculation using APAM was needed to increase flocs size. In spite of the fact that the cost of CPAM is high, it was claimed to be offset by the saving in pH adjustment and the production of larger flocs and fast setting. Moreover, the use of APAM was needless in the use of CPAM if flocs size in water treatment process was not emphasized. The operating cost from chemical expense can be saved.

In awareness of environmental pollution, CPAM and PAC have given advantages over conventional coagulant (i.e. alum and ferric salts) including acidity reduction, low contamination of Al species in effluent (cause of Alzheimer disease) and low sludge volume. All advantages may significantly reduce sludge disposal problems and the chemical costs associated with the use of many conventional coagulants.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusions

Coagulation/flocculation process was conducted for the treatment of MWF wastewater to achieve optimum removal of turbidity, COD, TSS and pH. Coagulant dose, flocculant dose and pH of solution were investigated and found to be important parameters for the treatment of MWF wastewater.

In the case of 3% O/W emulsion, the optimum doses of coagulants were 400 mg/L for both CPAM and PAC with 200 mg/L of APAM. In case of 10% O/W emulsion, the optimum doses of coagulants were 1800 mg/L and 700 mg/L for CPAM and PAC, respectively with 200 mg/L of APAM. The application of PAC lower or higher than the optimum values resulted an inefficient coagulation/flocculation because of insufficient dosage or emulsion restabilization which did not observe in case of CPAM overdosing. The use of APAM was beneficial the flocculation efficiency, particularly for PAC. In addition, wastewater pH markedly affected the coagulation using PAC. The optimum pH was 6-9 and the pH after treatment decreased to 5-6. The removal efficiency was not significant different within pH range 4-9 for CPAM coagulation and the pH after treatment did not changed.

In case of real MWF wastewater, the coagulation performance of both CPAM and PAC with APAM was as good as in synthetic wastewater. However, the removal efficiency using CPAM with APAM was not as high as in synthetic wastewater. The results suggest that PAC performed better than CPAM. However, flocs from PAC were unstable and smaller than those from CPAM.

5.2 Suggestion for the Future Work

Since there are many types of MWF such as semi-synthetic or synthetic, the application of CPAM or PAC should be investigated. Moreover, mixing rate and time as well as operating temperature also affect the coagulation/flocculation process. The performance of PAC and CPAM as coagulant under these conditions are of interested.

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APPENDICES

APPENDIX A

Table A-1 Removal efficiency of turbidity, COD, TSS and pH after treatment using different doses of CPAM or PAC as primary coagulant with 200 mg/L of APAM as flocculant for synthetic wastewater at 3% O/W.

Sample	Dose of Coagulant (mg/L)	Turbidity (NTU)	COD (mg/L)	TSS (mg/L)	pH
Wastewater before treatment	-	3411±41	13067±462	377±46	7.68
Wastewater after treatment using CPAM	100	404.0±16.4	6667±462	50±4	7.64
	300	56.5±2.0	973±23	12±5	7.61
	400	8.4±0.8	240±40	11±3	7.88
	600	12.8±0.6	240±40	17±5	7.59
	800	13.7±0.3	293±61	18±3	7.79
Wastewater after treatment using PAC	100	3083±96	7733±462	231±17	5.53
	300	7.2±0.9	213±23.1	9±2	5.60
	400	4.5±0.5	173±23	5±3	5.57
	600	5091±187	10667±462	351.7±11.1	5.42
	800	5837±250	11467±462	605.7±64.9	4.63

Table A-2 Removal efficiency of turbidity, COD, TSS and pH after treatment using different doses of CPAM or PAC as primary coagulant with 200 mg/L of APAM as flocculant's for synthetic wastewater at 10% O/W.

Sample	Dose of Coagulant (mg/L)	Turbidity (NTU)	COD (mg/L)	TSS (mg/L)	pH
Wastewater before treatment	-	12178±365	25333±2309	680±55	8.43
Wastewater after treatment using CPAM	400	2078±76	8667±1155	245±24	8.40
	900	54.0±2.3	5067±462	35±6	8.46
	1200	58.0±2.8	1867±462	35±6	8.38
	1600	10.5±1.4	587±46	28±8	8.46
	1800	8.2±0.8	533±23	21±4	8.45
	2400	14.2±0.8	547±46	23±3	8.47
Wastewater after treatment using PAC	300	7705±166	21333±2309	523±51	5.51
	400	4543±64	12667±1155	303±55	5.44
	600	78.4±1.8	933±231	33±15	5.31
	700	9.1±0.9	320±40	17±6	5.23
	800	1936±380	22667±2309	760±90	4.87
	1300	19862±246	25333±2309	797±188	4.65

Table A-3 Removal efficiency of turbidity, COD, TSS and pH after treatment using optimum doses of CPAM or PAC as primary coagulant and different doses of APAM as flocculant for synthetic wastewater at 3% O/W.

Sample	Dose of Flocculant (mg/L)	Turbidity (NTU)	COD (mg/L)	TSS (mg/L)	pH
Wastewater after treatment using CPAM	0	30.1±1.9	360±40	53±6	7.74
	100	8.3±0.8	253±23	42±6	7.72
	200	7.1±0.3	240±40	10±3	7.82
	400	8.3±0.4	267±23	7±4	7.56
	600	7.9±0.5	253±23	11±3	7.77
	800	7.9±0.3	240±0	9±2	7.62
Wastewater after treatment using PAC	0	59.7±2.3	4000±0	60±10	5.35
	100	6.6±0.6	187±23	36±6	5.56
	200	4.8±0.3	173±46	5±2	5.37
	400	10.3±0.8	187±61	7±2	5.39
	600	8.2±0.7	187±61	4±2	5.47
	800	8.5±1.2	187±23	5±1	5.37

Table A-4 Removal efficiency of turbidity, COD, TSS and pH after treatment using optimum doses of CPAM or PAC as primary coagulant and different doses of APAM as flocculant for synthetic wastewater at 10% O/W.

Sample	Dose of Flocculant (mg/L)	Turbidity (NTU)	COD (mg/L)	TSS (mg/L)	pH
Wastewater after treatment using CPAM	0	14.6±1.2	640±80	53±6	8.42
	100	8.4±0.5	560±40	40±6	8.47
	200	7.2±0.2	507±23	21±4	8.44
	400	7.9±0.2	533±23	26±3	8.52
	600	10.9±0.4	547±23	25±7	8.54
	800	11.8±0.2	547±23	22±5	8.47
Wastewater after treatment using PAC	0	24.3±0.6	6400±800	70±10	5.59
	100	21.2±0.3	387±46	48±9	5.53
	200	13.3±1.2	333±23	19±6	5.44
	400	13.2±1.4	320±0	14±2	5.66
	600	17.5±1.2	360.0±40.0	17.0±5.3	5.52
	800	14.5±0.9	373.3±40.0	18.0±3.6	5.58

Table A-5 Removal efficiency of turbidity, COD and TSS using CPAM or PAC and APAM for synthetic wastewater (3% O/W emulsion) at pH 4-9.

Sample	pH	Turbidity (NTU)	COD (mg/L)	TSS (mg/L)	pH
Wastewater after treatment using CPAM with APAM	4	13.1±2.7	200±40	12±4	4.27
	5	14.3±1.0	200±40	15±4	5.31
	6	18.3±1.5	200±40	10±3	6.20
	7	9.9±1.6	187±23	14±3	7.14
	8	12.8±1.5	240±80	10±4	8.26
	9	7.5±2.3	213±61	10±3	9.12
Wastewater after treatment using PAC with APAM	4	398.0±23.5	1467±231	83±7	4.28
	5	374.0±16.1	1200±0	80±6	5.17
	6	3.7±1.0	133±23	10±2	5.32
	7	3.6±0.8	173±23	7±2	5.81
	8	7.2±2.4	160±0	6±2	6.02
	9	9.1±1.3	173±23	5±2	7.29

Table A-6 Removal efficiency of turbidity, COD and TSS using CPAM or PAC and APAM for synthetic wastewater (10% O/W emulsion) at pH 4-9.

Sample	pH	Turbidity (NTU)	COD (mg/L)	TSS (mg/L)	pH
Wastewater after treatment using CPAM with APAM	4	11.4±1.8	482±22	20±4	4.15
	5	9.0±0.6	520±22	22±7	5.25
	6	12.7±3.6	495±38	22±4	6.23
	7	11.2±2.8	482±22	24±4	7.21
	8	13.8±2.4	520±58	25±5	8.11
	9	11.1±1.9	520±44	23±5	9.08
Wastewater after treatment using PAC with APAM	4	451.7±46.7	1777±220	132±10	4.13
	5	396.3±78.2	1650±220	125±21	4.82
	6	4.5±2.3	343±38	21±7	5.38
	7	6.6±2.1	406±58	20±3	5.92
	8	8.4±0.9	419±38	19±2	5.60
	9	12.1±3.0	394±44	18±5	7.10

APPENDIX B

(a) (b)

Figure B-1 Appearance of flocs after treatment using optimum doses of (a) CPAM and (b) PAC at 3 % O/W emulsion for real wastewater from Industry I.

(a) (b)

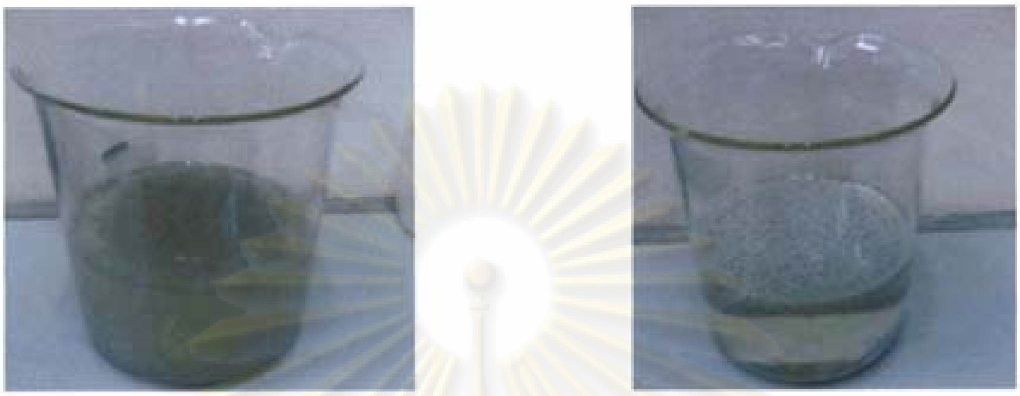
Figure B-2 Appearance of flocs after treatment using optimum doses of (a) CPAM and (b) PAC by calibration curve for real wastewater from Industry I.

(a) (b)

Figure B-3 Appearance of flocs after treatment using optimum doses of (a) CPAM and (b) PAC at 5 % O/W emulsion for real wastewater from Industry II.

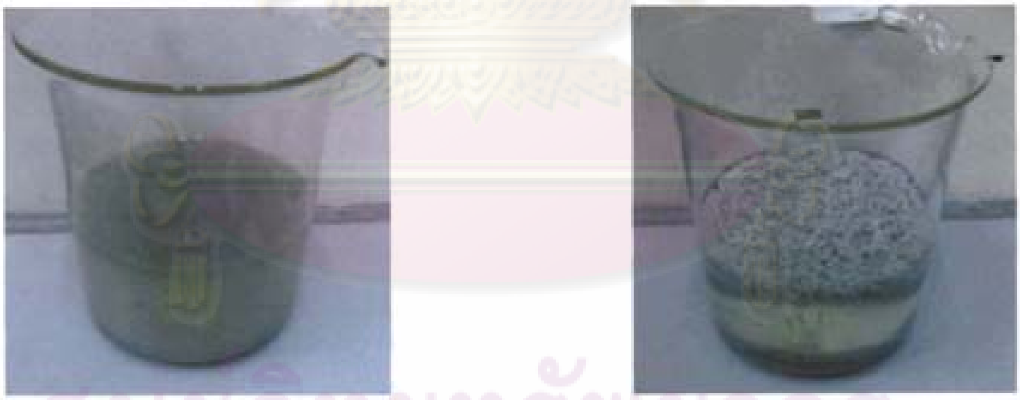
(a) (b)

Figure B-4 Appearance of flocs after treatment using optimum doses of (a) CPAM and (b) PAC by calibration curve for real wastewater from Industry II.



(a) (b)

Figure B-5 Appearance of flocs after treatment using optimum doses of (a) CPAM and (b) PAC at 5 % O/W emulsion for real wastewater from Industry III.



(a) (b)

Figure B-6 Appearance of flocs after treatment using optimum doses of (a) CPAM and (b) PAC by calibration curve for real wastewater from from Industry III.

APPENDIX C

C Standard Methods for the Examination of Wastewater

C.1 Total Suspended Solids

Total nonfiltrable residue is the retained material on a standard glass-fiber filter after filtration of a well-mixed sample. The residue is dried at 103 to 105 °C. If the suspended material clogs the filter and prolongs filtration, the difference between the total residue and the total filtrable residue provides an estimate of the total nonfiltrable residue.Volatile nonfiltrable residue and fixed nonfiltrable residue can be determined on the material retained on the glass-fiber filters in the Gooch crucibles on completion of the drying at 103 to 105 °C [28].

C.1.1 Procedure

a. Preparation of glass-fiber filter: Place filter either on membrane filter apparatus or the bottom of a suitable Gooch crucible. Apply vacuum and wash filter with three successive 20-mL portions of distilled water. Continue suction to remove all traces of water, and discard washings. Remove filter from membrane filter apparatus and transfer to an aluminum or stainless steel planchet as a support. Remove crucible and filter combination if a Gooch crucible is used. Dry in an oven at 103 to 105 °C for 1 hr. Store in desiccator until needed. Weigh immediately before use.

b. Sample treatment: Because excessive residue on the filter may entrap water and extend drying time, take for analysis a sample volume that will yield between 2.5 mg and 200 mg total nonfiltrable residue. As a practical limit, filter 100 mL of well-mixed sample under vacuum. Wash filter with three successive 10-mL portions of distilled water. Carefully remove filter from membrane filter funnel assembly and transfer to an aluminum or stainless steel planchet as a support. Alternatively remove crucible and filter combination from crucible adapter if a Gooch crucible is used. Dry for at least 1 hr at 103 to 105 °C, cool in a desiccator to balance temperature, and weigh. Repeat drying cycle until a constant weight is attained or until weight loss is less then 4% of previous weight, or 0.5 mg, whichever is less.

C.1.2 Calculation

$$\text{mg total nonfiltrable residue/L} = \frac{(A-B)\times 1{,}000}{sample\ volume, mL}$$

Where:

A = weight of filter + residue, mg, and
B = weight of filter, mg.

C.2 Chemical Oxygen Demand

The chemical oxygen demand (COD) is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source, COD can be related empirically to BOD, organic carbon, or organic matter content [28].

The dichromate reflux method is preferred over other methods using oxidants because of superior oxidizability, applicability to a wide variety of samples, and ease of manipulation. The test is most useful for monitoring and control, especially after correlations with constituents such as BOD and organic carbon have been developed. For most organic compounds oxidation is 95 to 100% of the theoretical value. Pyridine is not oxidized. Benzene and other volatile organics are oxidized if they have sufficient contact with the oxidants. While the carbonaceous portion of nitrogen-containing organic matter is oxidized, no oxidation of ammonia, either present in a waste or liberated from the nitrogen-containing organic matter, takes place in the absence of significant chloride concentrations.

C.2.1 Dichromate Reflux Method.

a. Principle: Most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acids. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulfate (FAS), the amount of $K_2Cr_2O_7$ consumed is determined, and the amount of oxidizable organic matter is calculated in terms of oxygen equivalent [28].

b. Interferences and limitations: Volatile straight-chain aliphatic compounds are not oxidized to any appreciable extent. This failure occurs partly because volatile organics are present in the vapor space and do not come in contact with the oxidizing liquid. Straight-chain aliphatic compounds are oxidized more effectively when silver sulfate (Ag_2SO_4) is added as a catalyst. However, Ag_2SO_4 reacts with chloride, bromide, and iodide to produce precipitates that are oxidized only partially. The difficulties caused by the presence of halides can be largely, though not completely, overcome by complexing with mercuric sulfate ($HgSO_4$) before the refluxing procedure. Do not use the test for samples containing more than 2,000 mg chloride/L.

Nitrite (NO_2^-) exerts a COD of 1.1 mg O_2/mg NO_2^--N. Because concentrations of NO_2^- in polluted waters rarely exceed 1 or 2 mg NO_2^--N/L the interference is considered insignificant and usually is ignored. To eliminate a significant interference due to NO_2^- , add 10 mg sulfamic acid/mg NO_2^--N present in the refluxing flask. Also add the same amount of sulfamic acid to the reflux flask containing the distilled water blank.

Reduced inorganic species such as ferrous iron, sulfide, manganous manganese, etc., are oxidized quantitatively under the test conditions. For samples containing significant levels of these species, stoichiometric oxidation can be assumed from known initial concentration of the interfering species and corrections can be made to the COD value obtained.

c. Minimum detectable concentration: Determine COD values of > 50 mg/L using 0.250 N $K_2Cr_2O_7$. With 0.025N $K_2Cr_2O_7$, COD values from 5 to 50 mg/L can be determined but with lesser accuracy.

C.2.2 Procedure

a. Treatment of samples with $\geq$ 50 mg COD/L: Place 50.0 mL sample (for samples with COD>900 mg COD/L, use a smaller sample portion diluted to 50.0 mL) in the 500-mL refluxing flask. Add 1 g $HgSO_4$, several glass beads, and very slowly add 5.0 mL sulfuric acid reagent, with mixing to dissolve $HgSO_4$. Cool while mixing to avoid possible loss of volatile materials. Add 25.0 mL 0.250N $K_2Cr_2O_7$ solution and mix. Attach flask to condenser and turn on cooling water. Add remaining sulfuric acid reagent (70 mL) through open end of condenser. Continue swirling and mixing while adding sulfuric acid reagent. CAUTION: Mix reflux mixture thoroughly before applying heat to prevent local heating of flask bottom and a possible blowout of flask contents. If sample volumes other than 50 mL are used, keep ratios of reagent weights, volumes, and strengths constant. See Table 508:I for examples of applicable ratios. Maintain these ratios and follow the procedure as outlined above.

Use 1 g $HgSO_4$ with a 50.0-mL sample to complex up to a maximum of 100 mg chloride (2,000 mg/L). For smaller samples use less $HgSO_4$, according to the chloride concentration; maintain a 10:1 ratio of $HgSO_4$:C1. A slight precipitate does not affect the determination adversely. Generally, COD cannot be measured accurately in samples containing more than 2,000 mg chloride/L.

Reflux mixture for 2 hr. Use a shorter period for particular wastes if it has been shown that the shorter period yields the same COD as that found by 2-hr refluxing. Cover open end of condenser with a small beaker to prevent foreign material from entering refluxing mixture. Cool and wash down condenser with distilled water.

Disconnect reflux condenser and dilute mixture to about twice its volume with distilled water. Cool to room temperature and titrate excess $K_2Cr_2O_7$ with FAS, using 0.10 to 0.15 mL (2 to 3 drops) ferroin indicator. Although the quantity of ferroin indicator is not critical, use the same volume for all titrations. Take as the end point of the titration the first sharp color change from blue-green to reddish brown. The blue-green may reappear.

Reflux and titrate in the same manner a blank containing the reagents and a volume of distilled water equal to that of sample.

b. Alternate procedure for low-COD samples: Follow the above procedure, with two exceptions: (i) Use standard 0.025N $K_2Cr_2O_7$, and (ii) titrate with 0.025N FAS. Exercise extreme care with this procedure because even a trace of organic matter on glassware or from the atmosphere may cause gross errors.

If a further increase in sensitivity is required, concentrate a larger volume of sample before digesting under reflux as follows: Add all reagents to a sample larger than 50 mL and reduce total volume to 150 mL by boiling in the refluxing flask open to the atmosphere without the condenser attached. Compute amount of $HgSO_4$ to be added (before concentration) on the basis of a weight ratio of 10:1, $HgSO_4$: Cl, using the amount of chloride present in the original volume of sample. Carry a blank reagent through the same procedure.

This technique has the advantage of concentrating the sample without significant losses of easily digested volatile materials. Hard-to-digest volatile materials such as volatile acids are lost, but an improvement is gained over ordinary evaporative concentration methods.

c. Determination of standard solution: Evaluate the technique and quality of reagents by testing a standard potassium hydrogen phthalate solution.

C.2.3 Calculation

$$\text{mg COD/L} = \frac{(A-B)\times N\times 8{,}000}{mL\ Sample}$$

Where:

A = volume FAS used for blank, mL,
B = volume FAS used for sample, mL, and
N = normality of FAS.

CURRICULUM VITAE

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Presentation

Woratat Sathirasathaporn, Puttaruksa Varanusupakul and Nattaya Pongstabodee, Coagulation and Flocculation of Metalworking Fluid by Polyacrylamide. (Poster Session): 10th National Graduate Research Conference, 11-12 September 2008. Sukhothai Thammathirat Open University, Nonthaburi, Thailand.