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ชื่อโครงการ **Removal efficiency of 0.3 to 4 millimeters microplastics in raw water via coagulation and flocculation process**

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Removal efficiency of 0.3 to 4 millimeters microplastics in raw water via coagulation and flocculation process

Paranee Wattanarojruang

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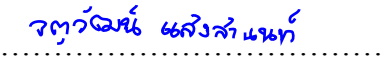
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บทคัดย่อ

ไมโครพลาสติกเป็นปัญหาที่กำลังได้รับความสนใจจากทั่วโลก ในปัจจุบันมีการตรวจพบไมโครพลาสติกในน้ำประปาและแหล่งน้ำจืดที่ใช้ในการผลิตน้ำประปาเพิ่มขึ้นอย่างต่อเนื่อง ก่อให้เกิดความกังวลด้านสุขภาพเพราะไมโครพลาสติกสามารถถูกย่อยและสะสมอยู่ในร่างกายได้ ในงานนี้ได้ทำการศึกษาเกี่ยวกับประสิทธิภาพการกำจัดไมโครพลาสติกขนาด 0.3 ถึง 4 มิลลิเมตร ในน้ำดิบ ด้วยกระบวนการสร้างและรวมตะกอน โดยใช้สารส้มเป็นสารสร้างตะกอนและใช้โพลีอะคริลาไมด์ชนิดประจุลบ เป็นสารช่วยรวมตะกอน จากการศึกษาพบว่า การใช้ปริมาณสารส้ม 15 มิลลิกรัมต่อลิตร ให้ประสิทธิภาพในการกำจัดความขุ่นในน้ำดิบสูงสุดร้อยละ 98.07±0.02 ในขณะที่ต้องใช้ปริมาณสารส้ม 40 มิลลิกรัมต่อลิตร จึงให้ประสิทธิภาพในการกำจัดความขุ่นในน้ำดิบที่มีไมโครพลาสติกผสมอยู่ สูงสุดร้อยละ 97.77±0.02 และ ที่ปริมาณสารส้ม 40 มิลลิกรัมต่อลิตร ยังให้ประสิทธิภาพในการกำจัดไมโครพลาสติกสูงสุดร้อยละ 80.00±0.00 หลังจากที่ทราบปริมาณสารส้มที่เหมาะสมแล้ว โพลีอะคริลาไมด์ชนิดประจุลบจะถูกเติมลงไปเพื่อช่วยเพิ่มประสิทธิภาพการกำจัดความขุ่นและไมโครพลาสติก โดยปริมาณโพลีอะคริลาไมด์ชนิดประจุลบ 0.06 มิลลิกรัมต่อลิตร ให้ประสิทธิภาพสูงสุดในการกำจัดความขุ่นในน้ำดิบที่มีไมโครพลาสติกที่ร้อยละ97.88±0.02 และปริมาณโพลีอะคริลาไมด์ชนิดประจุลบ 0.04 มิลลิกรัมต่อลิตร ให้ประสิทธิภาพสูงสุดในการกำจัดไมโครพลาสติก ที่ร้อยละ 85±0.00 ซึ่งผลที่ได้จากการศึกษานี้สามารถนำไปประยุกต์ใช้เพื่อเป็นแนวทางในการกำจัดไมโครพลาสติกผ่านกระบวนการสร้างตะกอนและรวมตะกอนในโรงบำบัดน้ำที่ผลิตน้ำประปาต่อไป

คำสำคัญ: ไมโครพลาสติก, กระบวนการสร้างตะกอน, กระบวนการรวมตะกอน, ประสิทธิภาพการกำจัด, น้ำดิบ

Project Title   Removal efficiency of 0.3 to 4 millimeters microplastics in raw water via coagulation and flocculation process

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Abstract

Microplastics (MPs) have attracted worldwide attention. MPs are gradually detected in freshwater and tap water. In terms of human health risks, MPs as contaminants represent a concern because they can be ingested and accumulated in the body. In this study, the removal efficiency of 0.3 – 4 mm MPs was investigated during traditional coagulation and flocculation processes using aluminum sulphate (alum) as a coagulant and anionic polyacrylamide (APAM) as a coagulant aid. Results showed that the optimum alum dose of 15 mg/L showed maximum turbidity removal efficiency (98.07±0.02%) in non-added MPs raw water. Whilst, 40 mg/L of alum was the optimum dose for highest turbidity removal efficiency (97.77±0.02%) in added MPs raw water and also greatest MPs removal efficiency (80.00±0.00%). After obtained the optimizing alum dose, APAM were added to enhance the removal efficiency of turbidity and MPs. 0.06 mg/L of APAM was the optimum dose for highest turbidity removal efficiency (97.88 ± 0.02%) and 0.04 mg/L was the optimum dose for maximum MPs removal efficiency (85± 0.00%). Based on this investigation, the MPs removal behaviors during coagulation and flocculation processes will have potential application in tap water treatment.

Keywords: Microplastics, Coagulation, Flocculation, Removal efficiency, Raw water

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

1.1   Background and the significance of the research

Plastics are synthetic or semi-synthetic organic polymers that have been applied worldwide for different purposes. The world had produced 7.8 billion tonnes of plastics cumulatively since 1950 to 2015. The annual global plastic production had already reached 381 million tonnes in 2015 (Geyer et al., 2017). These plastics can be broken down into smaller pieces by mechanical action, biodegradation and photooxidation over a long period of time. When the particle size of plastics is below 5 millimeters, they are commonly defined as microplastics (Wright et al., 2013; Rocha-Santos and Duarte, 2015). Microplastics are stable and highly durable in environment because of their chemical stability (Lusher, 2015). So far, the presence of microplastics has been demonstrated that it can cause various environmental and health problems because they can carry the persistent organic pollutants (POPs) easily (Mizukawa et al., 2013). Heavy metals and nanoparticles can also be adsorbed onto the surface of microplastics (Ashton et al., 2010; Fries et al., 2013). As a result, human health and marine organisms can be threatened by microplastics through the food chain. Consequently, microplastics are known as a new kind of emerging pollutant (Rocha-Santos and Duarte, 2015).

Many kinds of microplastics have been detected in water. Most studies reported most of them were polyethylene and polypropylene polymers (Hiddalgo-Ruz et al., 2012). It has been reported that the proportion of PE and PP production are higher than the other plastics because they are the classes of plastics that are used in packaging (Andrady, 2011). Additionally, the density of PE ($0.92 - 0.97$ g/cm^3) and PP (0.85 to 0.94 g/cm^3) are close to the density of natural water (Hiddalgo-Ruz et al., 2012). As a result, their particles are easily suspended in water, resulting in more severe potential hazards to the water treatment process (Bordós et al., 2019). Additionally, MPs in the size range between 0.1 to 5 mm were almost detected in tap water (Kosuth et al., 2018). Thus, PP and PE particles with the size range between 0.3 to 4 mm were chosen in this study.

The water from raw water sources often have high level of turbidity and need to be treated to remove the turbidity by water treatment process. Conventional water treatment process consists of the following unit processes: screening, grit removal, coagulation,

flocculation, sedimentation, filtration, and disinfection. The main process which can improve to higher particle removal is coagulation-flocculation process. In coagulation, a positively charged coagulant such as aluminum sulfate ($Al_2(SO_4)_3$) is added to raw water and mixed in the rapid mix chamber to destabilize negative charge of colloidal, particulate, and dissolved contaminants in raw water. Coagulant aid or polymers may also be added in flocculation to enhance the coagulation process (United States Environmental Protection Agency, 2006). Up to now, microplastics have been detected gradually in freshwater and other raw water sources for drinking water and tap water production (Pivokonsky et al., 2018), however, no studies have been conducted to examine the microplastics removability at drinking water treatment plant. Therefore, the distribution of microplastics in raw water sources and lack of microplastics removal information have raised the question if pollution of drinking water and tap water occurs. With these gradual detections of microplastics in raw water sources, it is necessary to investigate their behaviors and removal efficiency. In water treatment processes i.e., screening, grit removal, sedimentation, filtration, and disinfection, they have been designed construction to fit with water production capacity and no chemical used in these processes. This means it is difficult to modify the system to use for other purposes (remove microplastics). However, coagulation-flocculation process that use $Al_2(SO_4)_3$ and polyacrylamide (PAM) to mainly remove suspended particle can easily adjust the amount of chemical for suitable remove other contaminants.

Thus, this study systematically investigated the microplastics removal performance of conventional water treatment in the presence of microplastics in the size range 0.3 to 4 millimeters using $Al_2(SO_4)_3$ and anionic PAM as a coagulant and coagulation aid in coagulation-flocculation process. Furthermore, the information about the removal of microplastics from water in this study will be useful for the potential application in water treatment process.

1.2 Objectives

1.2.1 To determine the optimum dose of aluminum sulfate (alum) and anionic polyacrylamide (APAM) for the removal of turbidity and microplastics 0.3 to 4 millimeters in size in raw water by coagulation and flocculation processes.

1.2.2 To compare the turbidity removal efficiency between the raw water with and without microplastics condition in coagulation and flocculation processes.

1.2.3 To investigate the 0.3 to 4 millimeters MPs removal efficiency in raw water via coagulation and flocculation processes.

1.3   Expected Outcomes

The findings had potential to apply in removal of microplastics during drinking water or tap water treatment.

CHAPTER 2

THEORETICAL BACKGROUNDS
AND LITERATURE REVIEW

2.1   Microplastics background and definition

Over the past years, microplastics contamination in marine and freshwater system has become an emerging issue. In the 1980 s, microplastics were first noted as spherules in plankton tows along the coast of New England in North America. Nowadays, microplastics been gradually found in oceans, seas, lakes and rivers (Arthur et. al., 2009).

Microplastics are plastic particles range from 0.1 to 5,000 μm. In the field, the 333 μm mesh neuston nets is commonly used to collect the floating debris that range between 5 mm and 333 μm because there is no lower bound of size requirement. Smaller particles (1.6μm) have been also detected, but no standard procedure for sampling these small particles in seawater has been developed (EFSA CONTAM Panel, 2016; Ng and Obbard, 2006).

2.2   Microplastic types

Microplastics can be divided by usage and sources into 2 main categories as:

1) Primary microplastics

Primary microplastics are produced for indirect use as precursors for the polymer consumer products production, or for direct use, such as in scrubs, cosmetics, and abrasives.

2) Secondary microplastics

Secondary microplastics are particles that result from the breakdown of larger plastic material into smaller fragments. Fragmentation is caused by a combination of mechanical forces, e.g. waves or photochemical processes triggered by sunlight (Arthur et. al., 2009).

Furthermore, in some studies further categorize pieces to describe microplastics, as seen in the Table 2.1.

Table 2.1 Categories used to describe microplastics **(Hidalgo-Ruz et al., 2012)**

Categories	Description
Type	Plastic fragments, pellets, filaments, plastic films, foamed plastic, granules and styrofoam
Shape	- For pellets: cylindrical, disks, flat, ovoid, spheruloids - For fragments: rounded, subrounded, subangular, angular - General: irregular, elongated, degraded, rough and broken edges
Erosion	Fresh, unweathered, incipient alteration, and level of crazing (conchoidal fractures), weathered, grooves, irregular surface, jagged fragments, linear fractures, subparallel ridges and very degraded
Color	Transparent, crystalline, white, clear-white-cream, red, orange, blue, opaque, black, grey, brown, green, pink, tan, yellow and pigmentation

2.3   Environmental fate and transport of microplastics

The transport behaviors of microplastics are the essential information to understand the environmental fate of microplastics. Nowadays, it is well recognized that water, air, and soil are common pathways for microplastics transport (Figure 2.1). Area of water surface, depth, surface current, prevailing wind and density of microplastic particles are all important factors determining microplastics transport in aquatic environment (Fischer et al., 2016; Free et al., 2014). Microplastics are often buoyant at the water surface, transported with water along rivers and into oceans, which is known as surface transport (advective transport). Because most of microplastics density are lower than that of fresh or sea water (Andrady, 2011).

There are researchers who calculated the transport of spherical particles (i.e. microbeads with size range 100 nanometers to 10 millimeters) in freshwater systems and found the 99% retention distance (RD99) to be around 200 kilometers and up to > 900 kilometers for nanoplastics and microplastics, respectively. They suggested that the intermediate size class of microplastics may be transported downstream preferentially. The bigger plastics are generally easier to drift in the uppermost layer (Besseling et al., 2017); thus, microplastics are less affected by stoke drift resulted from surficial water wind waves so they are more likely to be carried offshore (Isobe et al., 2014). Additionally, there are

some vertical transports in the water column because the turbulence in the upper-water layer can mix buoyant microplastics vertically.

For the microplastics with higher density, they are more probable to retain in soils and be transported to deeper soil layer; while the microplastics with lower density are more susceptible to surface runoff and wind to reach the surface of terrestrial and aquatic systems (Zylstra, 2013). On the other hand, microplastics may enhance the transport of persistent, toxic, and bio-accumulative substances. These microplastics can be a transport carrier of toxic metals (Brennecke et al., 2016) and persistent organic pollutants (POPs) (Gouin et al., 2011). Some of these compounds are added into MPs during manufacture, while others adsorb on MP surfaces. Previous study has demonstrated the transfer of contaminants from MPs to organisms (Browne et al., 2007).

Weathering processes including oxidative, photo-oxidation, hydrolytic degradation, and biodegradation processes can affect the fate of plastic debris in the aquatic environment. Plastic fragmentation can be turned into smaller particles by these processes (Barnes et al., 2009; Lambert and Wagner, 2016). Furthermore, biofilm formation and hetero-aggregation also play important roles in affecting the aqueous microplastics fate (Rummel et al., 2017; Woodall et al., 2014). The biofilm formation and hetero-aggregation may cause an increase of microplastics density and a decrease of their buoyancy (Lagarde et al., 2017). For smaller microplastics, they tend to reach a significant precipitation density in a faster way (Chubarenko et al., 2016). Meanwhile, this biofilm formation can make microplastics become sticky because of the promoting of hetero-aggregates formation by the extracellular polymeric substances matrix.

Microplastics can be also trapped in sediments over a long time. This affected by wave action, bioturbation or currents, and other disturbances. These trapped microplastics can be resuspended from sediments because of their smaller size and lower density compared to natural sediments (Kershaw and Rochman, 2015). Microplastics can be ingested by organisms and excreted as waste and retained or translocated into tissues, causing trophic transfer and accumulating in food chain.
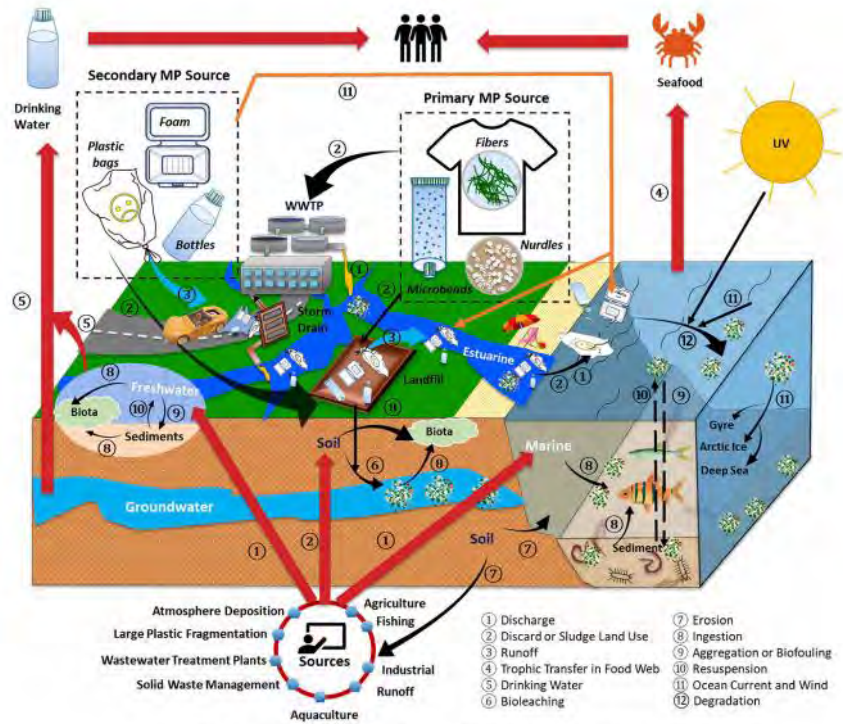
Fig. 3. Sources, transport, accumulations, and fate of MPs in the environment.

Figure 2.1 Sources, transport, accumulations, and fate of microplastics in the environment (Wu et al., 2019)

2.4 Microplastics contamination in natural freshwater systems and water supply systems

An increasing number of microplastics distribution studies show that microplastics are pervasive in all environmental compartments. Microplastics have been detected not only in sediments, soils, water columns, and surface layers in fresh water and marine system, but also tap water bottle water, salt and beer (Li et. al., 2016; van Sebille et. al., 2015; Kosuth et. al., 2018). As a result, the microplastics contamination in consumption products issue has increasingly gained public interest and media attention. This leads to numerous publication deliberating about the human health after effects of microplastics exposure.

1) Microplastics contamination in natural freshwater systems

Wang et al. (2017) investigated the levels of microplastics in surface water of 20 urban lakes and urban reaches of the Hanjiang River and Yangtze River of Wuhan, the largest city in central China. Microplastics concentration ranged from 1660.0 ± 639.1 to 8925 ± 1591 pieces/m^3. Microplastics, smaller than 2 mm in size, were detected more than

80%. Polyethylene terephthalate and polypropylene were the dominant polymer types of microplastics analyzed.

Wang et al. (2018) investigated the occurrence of microplastics in surface waters of two important lakes in the middle reaches of the Yangtze River. The average concentration of microplastics in Dongting Lake and Hong Lake were 1191.7 piece/m^3 and 2282.5 piece/m^3, respectively. The major components of the selected particles were identified as polyethylene (PE) and polypropylene (PP).

Di and Wang (2018) reported the abundance of microplastics in surface waters, from the Three Gorges Reservoir, ranged from 1597 to 12,611 pieces/ m^3. The average abundance was 4703 ± 2816 pieces/ m^3. Polystyrene (PS) was the most common type detected (38.5%), followed by polypropylene (PP) for 29.4% and polyethylene (PE) for 21%.

Pivokonsky et al. (2018) investigated the content of microplastic particles in freshwater. Microplastics were found in all water samples and their average abundance ranged from 1473 ± 34 to 3605 ± 497 pieces/L in raw water. This study determined microplastics down to the size of 1 μm, while microplastics smaller than 10 μm were the most abundant in both raw and treated water. The dominant shape of microplastics was fragments and the dominant types were PET, PP, and PE.

Di et al. (2019) investigated the abundance of microplastics in surface water from Danjiangkou Reservoir. The abundance of microplastics ranged from 467 to 15,017 pieces/ m^3. The average abundance was 2594 ± 3875 pieces/ m^3. Microplastics with a size of less than 2 mm were most frequently detected. The composition of the identified microplastics was polypropylene (PP) as the largest chemical composition (44.9%), followed by polystyrene (PS) for 34.7% and 20.3% of polyethylene (PE).

Microplastics contamination in natural freshwater systems are summarized in Table 2.2.

2) Microplastics contamination in tap water, drinking water and water supply systems

Kosuth et al. (2018) investigated the presence of anthropogenic particles in 159 samples of tap water. 81% were found to contain anthropogenic particles. The major shapes were fibers (98.3%) between 0.1–5 mm in length. The abundance range was 0 to 61 pieces/L, with an overall mean of 5.45 pieces/L.

Pivokonsky et al. (2018) investigated the content of microplastic particles in drinking water in three water treatment plants that supplied by different kinds of water

bodies. Microplastics were found in all water samples and their average abundance ranged from 338 ± 76 to 628 ± 28 pieces/L in treated water. This study determined microplastics down to the size of 1 µm, while microplastics smaller than 10 µm were the most abundant. The dominant shape of microplastics was fragments and the dominant types were PET, PP, and PE.

Strand et al. (2018) investigated the microplastics contamination in drinking water from 17 sites in Denmark. The average abundance of microplastics was 15.6 particles/50 L. The dominant size detected was bigger than 100 µm. The major shapes were fibers. The dominant types were PET, PP, and PS.

Wang et al. (2020) investigated the microplastics contamination in treated water from drinking water treatment plants (DWTPs) where located in the Yangtze River Delta. The average of microplastics abundance was 930 ± 72 particles/L. The major size was 1–5 µm (84.4–86.7%). The dominant shape was fiber (51.6–78.9%). The main types detected were PET, PE, and PP.

Microplastics contamination in tap water, drinking water and water supply systems are summarized in Table 2.3

2.5   Concerned problems of MPs

The presence of microplastics has been demonstrated that it can cause various environmental and health problems because they can carry the persistent organic pollutants (POPs). It has been reported that POPs on the surface of microplastics have been detected in many coastal zones, such as along the USA, UK, Japan, China, etc. (Mizukawa et al., 2013). Heavy metals and nanoparticles can be also adsorbed onto the surface of microplastics, including Pb, Zn, Cu, Al, Fe, and TiO_2 (Ashton et al., 2010; Fries et al., 2013). In terms of human health risks, microplastics as contaminants represent a concern because it has been shown that they can be ingested by a wide range of aquatic organisms and have the potential to accumulate through the food chain (Galloway, 2015).

2.6   Water treatment Processes

Rivers, lakes, streams, and underground aquifers are potential sources of potable water. The raw water obtained from surface sources must be treated to remove turbidity and harmful bacteria. The conventional treatment is known as the most common treatment process for surface water supplies. The conventional water treatment consists of

coagulation, flocculation, sedimentation, filtration, and disinfection. Conventional treatment is often preceded by pre-sedimentation and pre-oxidation. The water treatment process for tap water production can be divided into 5 processes:

1) **Coagulation**

Coagulation is a process used to neutralize charges on non-settleable solid. When the charge is neutralized, the small suspended particles are capable for sticking together forming the slightly larger particles called microflocs, but they are still too small to be visible to the naked eye. Therefore, rapid mixing is needed to increase the collision between coagulant and particles or microflocs to achieve good coagulation and formation of the microflocs. Therefore, coagulation can remove dissolved organic and inorganic compounds from raw water. Contact time in the rapid-mix chamber is typically 1 to 3 minute(s). The most common coagulating agents or coagulants are hydrolyzing metal salts, most notably alum [$Al_2(SO_4)_3 \cdot 14H_2O$], ferric sulfate [$Fe_2(SO_4)_3$], and ferric chloride ($FeCl_3$). Their highly charged ions neutralize the suspended particles when added to water. The short polymer chains are formed by the inorganic hydroxides which enhance microflocs formation (Massachusetts Water Resources Authority, 2012). Basic stoichiometric reaction occurs during the coagulation process for aluminum sulfate (Alum) is given below:

$$Al2(SO_4)_3 \cdot 14H_2O + 6HCO^{3-} \rightleftharpoons 2Al\,(OH)_3 + 8H_2O + 3H_2SO_4$$
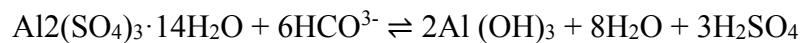
Underdosing, as well as overdosing, of coagulants may lead to the reduction of solids removal efficiency. Thus, condition may be corrected by performing jar tests and verifying solids removal performance after making any change in the coagulation process (United States Environmental Protection Agency, 2006).

2) **Flocculation**

Flocculation is a slow mixing stage which increases the particle size from microfloc particles to visible suspended particles by contact with other microflocs. The floc size continues to build through additional collisions and interaction with inorganic polymers formed by the coagulant or with organic polymers added. Then, macroflocs are formed. Coagulant aids or high molecular weight polymers may be added during this step to bridge macroflocs and increase settling rate. These polymers (high-molecular-weight and long-chained organic chemicals) become more widely used as coagulant aids along with the

inorganic coagulants. Anionic polymers or negatively charged polymers are often used with metal coagulants, such as aluminum sulfate and ferric chloride. Cationic polymers or positively charged polymer, which have low-to-medium weight, may be used alone, or in combination with alumor ferric coagulants to attract suspended solids and neutralize their surface charge. These polymers are effective in wide pH range. Furthermore, they can be applied at lower doses, and do not consume alkalinity. They produce more rapidly settling flocs. However, the poor macroflocs formation can be occurred when the mixing is ineffective because the flocculated particles can be torn apart. These polymers are several times more expensive in price per pound than inorganic coagulants. Selection of the proper polymer requires considerable jar testing under simulated plant conditions, followed by pilot or plant-scale trials.

The contact times for flocculation process range from 15 or 20 minutes to an hour or more. The minimum detention time recommended for flocculation ranges from 5 to 20 minutes for direct filtration systems and up to 30 minutes for conventional filtration. Then, the water is ready for the separation process after the floc has reached optimum size and strength (United States Environmental Protection Agency,2006; Massachusetts Water Resources Authority, 2012).

3) Clarification

Clarification is the process which remove suspended solids and flocs from chemically treated water, before its application to filters. After flocculation, the water flows into the sedimentation tanks. During sedimentation, the flow of the water is slowed to imitate a calm environment. Then, the large flocs that have been formed settle to the bottom of the sedimentation basin. The clarified water passes over a system of weirs and moves to the filtration process (United States Environmental Protection Agency, 2006).

4) Filtration

Filtration removes virtually all particles carried over from the sedimentation process through filters. The filters have different pore sizes and varying compositions such as sand, gravel, and charcoal for dissolved particles removal. Suspended particles are trapped within the pores of the filter media, which also remove harmful protozoa and natural color. After filtration, the water will flow to the disinfection unit.

5) Disinfection

After filtration process, a disinfectant such as chlorine and chloramine may be added in order to kill the remaining parasites, bacteria, and viruses, and to protect the water from germs during the water distribution. Many of these disinfectants can react with the organic and inorganic precursors and bring the formation of disinfection by-products (DBPs) with adverse health effects if they are overdosed or used inappropriately (Collivignarelli et al., 2017).

2.7   Jar test

The jar test is a laboratory procedure that simulates the coagulation and flocculation processes to determine the optimum pH and the optimum coagulant dose for the removal of suspended solids in water. The jar test is often used for the design of treatment facilities and in the routine operation of treatment plants. (Yapsakli K., 2014).

Jar tests apparatus as shown in Figure 2.2, can be used to study the effects of chemicals, coagulant dose, and pH on settled water quality. The sample pH can be adjusted if necessary. For coagulant dose, it can be added to one jar with doses slightly above and below in the jars on either side and the test is run as described in the parts of coagulation and flocculation process. The results should confirm that the current coagulant dose is the optimum dose.
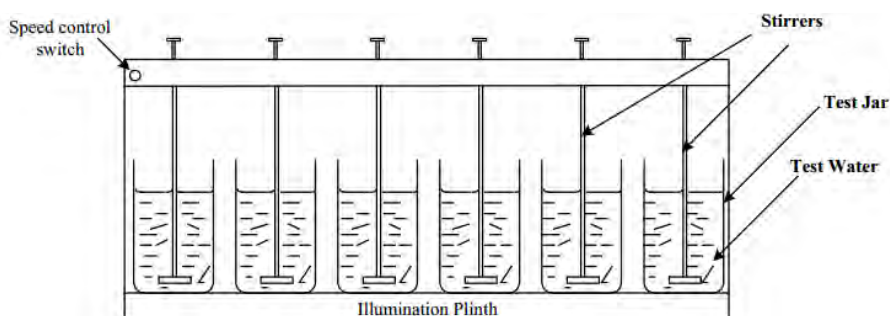

Figure 2.2 Apparatus for conducting jar tests

(United States Environmental Protection Agency, 2017)

2.8   Factors affecting coagulation process

1) Particle size

The smaller size of solid particles, the more surface zone per unit weight of solids, so it is not a typical to see an increase in the coagulant dose to coagulate these fine particles. However, this increase is not a linear; therefore, the small decrease of solid particles size can cause the dramatic increase in coagulant dose requirements (Pillai, 2004).

2) Surface charge

The surface charge density of solid particles also affects the coagulant dose because more coagulant is required to neutralize the surface charge when the surface charge density of solid particles increases. However, the over-addition of coagulant may cause the reversal of surface charge and result in inter-particle repulsion (Pillai, 2004).

3) Water chemistry

Ca^{2+}, Mg^{2+}, Fe^{2+} and Fe^{3+} or other dissolved species can neutralize the surface charge and reduce the coagulant requirements. These ions increase the conductivity of the water after treatment. Determining of coagulant demand can be assisted by determining the water conductivity. Magnesium and calcium ions can also determine the water hardness, the higher hardness of the water leads to the lower coagulant demand (Pillai, 2004).

4) pH and alkalinity

During the destabilization process, pH has an influence on the effectiveness because it controls the speciation of the coagulant and the solubility. Furthermore, it also affects the speciation of the contaminants. An excessive amount of coagulant may be required to lower the pH to the optimal pH ranges (alum pH 6 to 7, iron 5.5 to 6.5) in high alkalinity water (United States Environmental Protection Agency, 2017).

5) Temperature

Temperature also impacts the coagulation process because it affects the viscosity of the water; therefore, the hydrolysis and precipitation kinetics may decrease because of the lower temperature of water.

2.9   Factors affecting flocculation process

1) Polymer types

The copolymer variations can behave very differently in different systems. The main molecular groups in these types of polymer are amide and carboxylate which can adsorb onto the mineral surface. In copolymers, the primary function of the amide group is to adsorption by hydrogen bonding. For the carboxylate group, the primary function is to extend the polymer chain by electrostatic repulsion and enable bridging effect. Copolymers of acrylamide and sodium acrylate are generally more active than nonionic acrylamide polymers because most particles carry a negative charge. Thus, acrylamide and sodium acrylate become widely used copolymers. (Pillai, 2004).

2) pH

As the pH ranges from 0 to 14, the choice of flocculant ranges from nonionic to highly anionic. Nonionic polymers show the greatest activity at pH of 4 and below. On the other hand, anionic polymers are coiled up like the nonionic polymers but they show little activity at this pH range. Because the amide groups in anionic flocculants are replaced by carboxylate groups which reduce the available sites of hydrogen bonding in the flocculants. For the moderate pH range, the activity of anionic flocculants increases. And at a pH range of 6 to 8, a moderate anionic flocculant shows a better activity than nonionic flocculants. Furthermore, highly anionic flocculants perform the best at pH levels over 9.5 (Pillai, 2004).

3) Slurry solids

Adsorption will take place rapidly when a fully activated flocculant is added to a slurry. The concentration of solids in the feed particle size and the slurry has a strong influence on the flocculant distribution in the slurry. The higher the concentration of solids causes the more difficult to distribute the flocculant uniformly through the slurry. The smaller particle size causes the larger surface area. Consequently, when the solids concentration increases, flocculant demand increases (Pillai, 2004).

4) Shear

Flocs can be torn apart by excessive shear or other mechanical actions. Therefore, a balance should be tested between distribution and floc shear (Pillai, 2004).

5) Molecular weight

The molecular weight can affect the performance. The higher molecular weight results in better activity in most thickener applications. However, there are instances in which increasing molecular weight results in loss of activity. The number of polymer chains per unit of weight decreases due to the molecular weight increase. Because the solution does not have enough polymer molecules to flocculate all the solids in high solids slurries (Pillai, 2004).

2.10   Optimum conditions in jar test

Metropolitan Waterworks Authority (Thailand) conducted jar test experiment to find the optimum condition for raw water treatment. They found that the most suitable pH for turbidity removal (optimum pH) is 6.55. The optimum dosage of alum was 32 mg/L. In this experiment, the mixing speed were 200 rpm (1 minute) for the rapid mixing and 40 rpm (20 minutes) for the slow mixing. The water turbidity decreased from 93.8 to 4.38 NTU. Therefore, the removal efficiency of this condition was 95.3%.

Baghvand et al. (2010) determined the alum capability to reduce turbidity of drinking water. In this experiment, the water turbidities were 0, 50, 100, 200, 500 and 1000 NTU. Results showed that turbidity removal is dependent on pH, coagulant dosage, and initial water turbidity for both coagulants. The optimum alum dose and the optimum pH range were 10-20 mg/L and 6.0 to 7.0, respectively. Highest turbidity removal efficiency was within 82.9-99.0%.

Kalavathy et al. (2017) evaluated the effectiveness of alum at different pH values of 5, 7, 9 and coagulant dosage 10 mg/L to 60 mg/L to find optimal operational conditions for turbidity of 50, 100, and 250 NTU turbid waters. Results showed that coagulation process could remove turbidity effectively, using relatively low doses of alum (20-40 mg/L). The highest turbidity removal efficiency was within 66-76 %.

Poonsawatt and Ratpukdi (2019) conducted jar test experiment to find the optimum condition for high-turbidity water treatment. The alum optimum dose for 3,000 NTU and 5,000 NTU removal was 50 mg/L and 90 mg/L, respectively. The optimum pH of both conditions was 7.0. There were 50 and 100 mL of sediment after coagulation, flocculation, and sedimentation.

The optimum conditions in jar test are summarized in Table 2.4.

Table 2.2 Microplastics contamination in freshwater systems

Area	Microplastics abundance (Mean ± S.D.)	Microplastics dominant size	Microplastics dominant type	References
Urban lakes in Wuhan, China	1660.0 ± 639.1 to 8925 ± 1591 piece/m^3	< 2 mm	PE, nylon, PS	Wang et al., 2017
Dongting Lake, China	1191.7 piece/m^3	< 2 mm	PP, PE, PS	Wang et al., 2018
Hong Lake, China	2282.5 piece/m^3	< 2 mm	PP, PE, PS	Wang et al., 2018
Three Gorges Reservoir, China	4703 ± 2816 piece/m^3	<0.5 mm	PS, PP, PE	Di and Wang., 2018
Three drinking water treatment plants, Czech Republic	$(1473 \pm 34) \times 10^3$ to $(3605 \pm 497) \times 10^3$ piece/m^3	<10 μm	PET, PP, PE	Pivokonsky et al., 2018
Danjiangkou Reservoir, China	2594 ± 3875 piece/m^3	< 2 mm	PP, PS, PE	Di et al., 2019

Table 2.3 Microplastics contamination in tap water, drinking water and water supply systems

Area	Microplastics abundance (Mean ± S.D.)	Microplastics dominant size	Microplastics dominant type	References
Tap water from 14 countries	5.45 particles/L	0.1–5 mm	Fiber shape	Kosuth et al., 2018
Three drinking water treatment plants, Czech Republic	338±76 to 628±28 particles/L	1–5 µm	PET, PP, PE	Pivokonsky et al., 2018
Denmark	15.6 particles/50 L	> 100 µm	PET, PP, PS	Strand et al., 2018
Drinking water treatment plants, China	6614 ± 1132 particles/L	1–5 µm	PET, PE, PP	Wang et al., 2020

Table 2.4 The optimum conditions for removal of turbidity

Parameter		Coagulant concentration	Coagulant aid concentration	Mixing speed		Optimum condition		Turbidity removal efficiency	References
pH	Initial turbidity			Rapid mixing	Slow mixing	pH	Chemical dose		
4.0 – 8.0	0, 50, 100, 200, 500 and 1000 NTU	Alum 1 %	Lime 5 mg/L	350 rpm 1 min	30 rpm 20 min	6.0-7.0	Alum 10-20 mg/L	82.9-99.0%	Baghvand et al., 2010
6.5-8.5	93.8 NTU	Alum 1%	Anionic PAM 1%	200 rpm 1 min	40 rpm 20 min	6.55	Alum 32 mg/L APAM 0.03 mg/L	95.3%	Metropolitan Waterworks Authority
7.0	3000 NTU	Alum 1%	-	100 rpm 1 min	30 rpm 10 min	7.0	Alum 50 mg/L	-	Poonsawatt and Ratpukdi, 2019

Table 2.4 The optimum conditions for removal of turbidity (Cont.)

Parameter		Coagulant concentration	Coagulant aid concentration	Mixing speed		Optimum condition		Turbidity removal efficiency	References
pH	Initial turbidity			Rapid mixing	Slow mixing	pH	Chemical dose		
5.0-9.0	~80 NTU	Alum 0, 50, 70, 100 mg/L	-	161 rpm 2 min	25 rpm 30 min	7.0	Alum 100 mg/L	76%	Kalavathy et al., 2017
5.0-9.0	50 NTU	Alum 1%	-	150 rpm 2 min	15 rpm 20 min	7.0	Alum 30 mg/L	97.4%	Mohsinkhan et al., 2016
	100 NTU	Alum 1%	-	150 rpm 2 min	15 rpm 20 min	7.0	Alum 30 mg/L	98.8%	
	250 NTU	Alum 1%	-	150 rpm 2 min	15 rpm 20 min	7.0	Alum 20 mg/L	98.64%	

CHAPTER 3

MATERIALS AND METHODS

3.1 Research Materials

3.1.1 Laboratory instruments

1) Jar tester
2) pH meter (Milwaukee Model pH55 /pH66)
3) Turbidity meter (Hach Model 2100P)
4) Conductivity meter (Hach 5465010 Sension 156)
5) Stereo microscope
6) Fixed microscope adapter (FMA050)
7) Hot plate
8) Laboratory fume hood
9) Drying oven
10) Air pump

3.1.2 Chemical reagents

1) 1% Aluminum sulfate (Alum)
2) Anionic polyacrylamide (APAM)
3) Phenolphthalein indicator
4) Methyl orange indicator
5) Methyl red indicator
6) 95% Ethyl alcohol
7) 0.02 N H_2SO_4
8) 50% HCl
9) 0.05 N Na_2CO_3
10) Conc. NH_4OH
11) NH_4Cl
12) 0.01 M Standard EDTA
13) Eriochrome Black T
14) Hydroxylamine hydrochloride
15) 0.01 M Standard calcium Solution

16) Buffer pH 10

17) FeSO$_4$

18) 30% H$_2$O$_2$

19) NaCl

3.1.3 Materials and equipment

1) 300 μm, and 4 mm stainless steel sieves

2) Polyethylene and polypropylene beads

3) Glass microfiber filters (GF/C Dia.47 mm.)

4) Watch glass

5) Standard Metal Forceps

6) 50 mL, 150 mL, 250 mL, 500 mL, 1L, and 2 L glass beakers

7) Analytical balance (precise to 0.1 mg)

8) Metal spatula

9) Stir bar

10) Retort stand

11) Aluminum foil

12) Distilled water

13) 1 mL, 2 mL, 5mL, 25 mL, and 100 mL glass pipettes

14) Pipettes bulb

15) 100 mL, 200 mL, 250 mL, 1 L, and 2 L Volumetric flasks

16) Büchner funnel

17) Reagent bottles

18) Glass bottles

19) Stirring rod

20) Burettes

21) 5 mL and 250 mLglass cylinder

22) 250 mL Erlenmeyer flask

23) Glass funnel

24) Amber bottle

25) Dropper

26) 25 mL Syringe

27) Desiccator

28) 12 μm polycarbonate Whatman nuclepore track-etch membrane

29) Density separator

3.2   Research methods

The experimental procedure in this study was divided into 2 main parts. Firstly, the raw water without microplastics addition, were conducted via coagulation and flocculation processes to determine the optimum dose of alum and anionic PAM. Then, the removal efficiency of turbidity was calculated. Secondly, the raw water with microplastics addition, was conducted via coagulation and flocculation processes for the optimum alum dose and anionic PAM dose. Then, the removal efficiency of turbidity and microplastics were calculated. The overview of experimental procedure is shown as a flow chart in Figure 3.1.
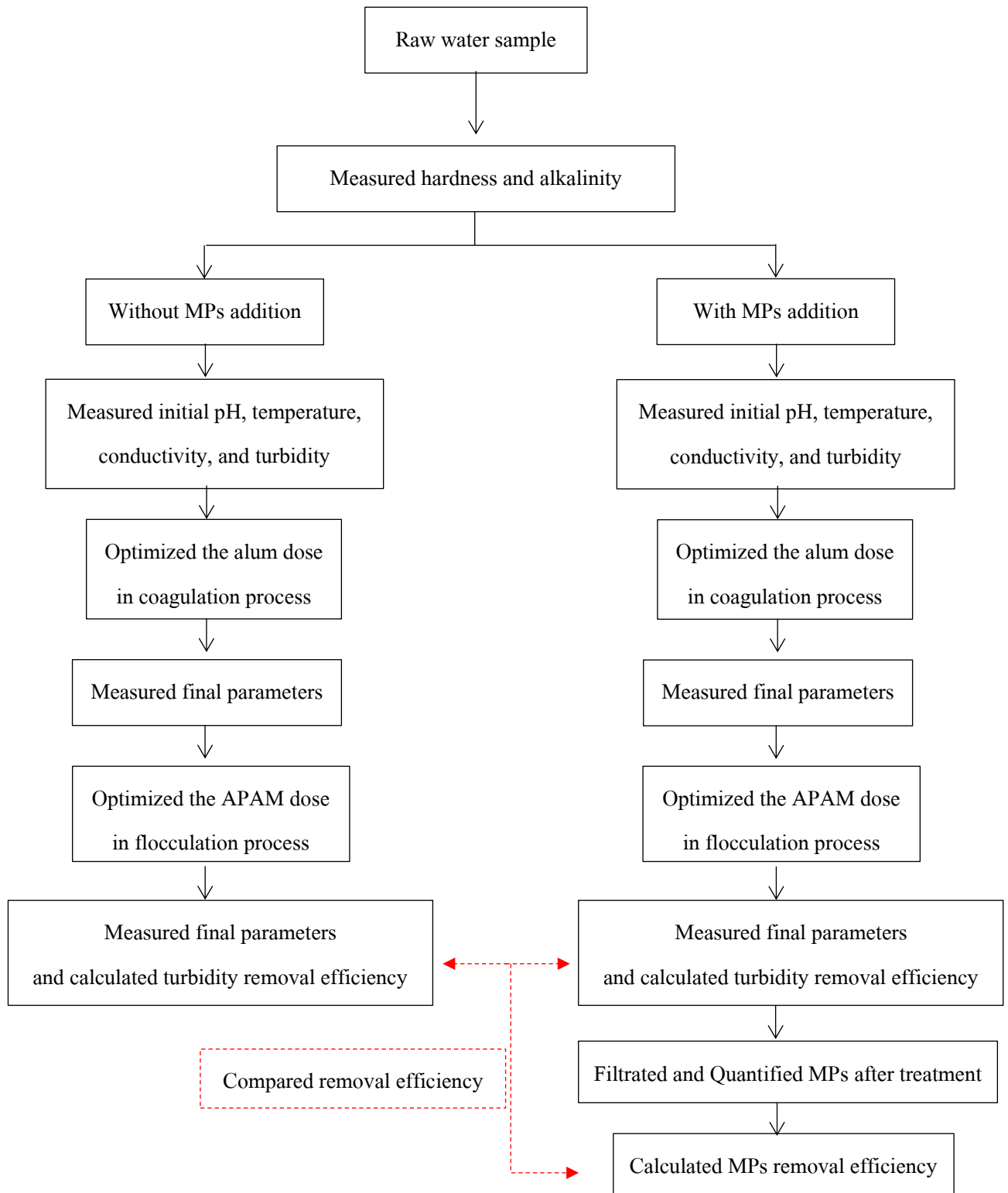
Figure 3.1 Experimental procedure flow chart

3.2.1 Water sample

80 L of raw water was sieved at sampling site, using 300 μm, and 4 mm stainless steel sieves. Then, 28 L of raw water was collected using stainless bucket, from water supply canal, Don Muang, Bangkok, Thailand (Figure 3.2).

Figure 3.2 Raw water sampling point in the canal for water supply

3.2.2 Water quality measurement

All standard methods for water quality measurement were shown in Table 3.1.

Table 3.1 Measurement of the water sample quality (National Environmental Methods Index (NEMI), Tuntoollavest, 2008)

Parameter	Unit	Standard Method
Alkalinity	mg/L as CaCO$_3$	Indicator method
Hardness	mg/L as CaCO$_3$	2340B Hardness in Water by EDTA Titration
pH	-	4500-H+B pH Value in Water by Potentiometry Using a Standard Hydrogen Electrode
Temperature	°C	2550B Temperature of Water
Turbidity	NTU	2130B Nephelometric Method
Conductivity	μS/cm	2510B Conductivity

Figure 3.3 pH meter (Milwaukee Model pH55/pH66)

Figure 3.4 Conductivity meter (Hach 5465010 Sension 156)

Figure 3.5 Turbidity meter (Hach Model 2100P)

3.2.3   Quantifying of microplastics in raw water

1)   Suspended solids in raw water

1.1)   80 L of raw water was sieved, using 300 μm, and 4 mm stainless steel sieves. After that, all solids were collected into a 250-mL beaker.

1.2)   The sieved solids in beaker was dried at 60 ºC overnight.

2)   Wet peroxide oxidation (WPO)

2.1)   20-mL $FeSO_4$ solution and 20-mL 30% H_2O_2 were added.

2.2)   The solution was mixed by stir bar and left in room temperature for 5 minutes. The beaker was covered by a watch glass while mixing.

2.3)   The solution was heated to 75ºC on a hotplate in fume hood for 30 minutes.

2.4)   If gas bubbles was observed at the surface, removed the beaker from the hot plate and added distilled water to slow the reaction.

2.5)   6 g of NaCl was added per 20 mL of sample.

2.6)   The mixture was heated until the NaCl dissolves.

3)   Density separation

3.1)   The WPO solution was transferred to the density separator.

3.2)   The beaker was rinsed with NaCl solution to transfer all remaining solids to the density separator.

3.3)   The density separator was covered with aluminum foil and left overnight.

3.4)   The settled solids was drained from the density separator.

3.5)   The remaining solids on density separator surface was rinsed with NaCl solution.

3.6)   Drained and rinsed until the supernatant layer under the floating solids was clear.

4)   MPs filtration

4.1)   The floating solids was filtered with 12 μm polycarbonate Whatman nuclepore track-etch membrane, using Büchner funnel equipped with suction flask and air pump.

4.2)   The density separator was rinsed with distilled water to remove the remaining solids during the filtration process.

5)   Microscope exam

A stereomicroscope with 30X magnification was used for identifying suspected microplastics.

3.2.4 Preparation of water samples with microplastics addition

PP and PE particles were added into raw water to investigate the removal efficiency of microplastics using coagulation and flocculation processes as follows.

1) Plastic beads were grinded into small particles and soaked in wastewater from sugar industry for 1.5 month to provide more weight and surface charge.
2) Plastic particles were sieved with a series of sieves with mesh sizes of 4 and 0.3 mm.
3) Microplastic particles were counted under the stereomicroscope equipped with fixed microscope adapter.
4) 20 microplastic particles were added into each beaker.
5) 250 mL of water sample was pipetted into each beaker.
6) The procedure in 3.2.3 was conducted to determine the optimum chemicals dose for the treatment of raw water with microplastics.

3.2.5 Coagulation and flocculation procedure
1) Determination of optimum alum dose

1.1) The initial pH, temperature, conductivity, and turbidity of samples were measured.

1.2) 0, 5, 10, 15, 20, 25, 30, 35, 40, and 45 mg/L of alum were pipetted into each water samples. All doses were conducted 3 times.

1.3) The mixing speed of jar test apparatus was adjusted to 200 rpm for 1 minute (rapid mixing).

1.4) The mixing speed was adjusted to 40 rpm for 20 minutes (slow mixing).

1.5) Jar test apparatus was turned off for sedimentation for another 10 minutes.

1.6) The final pH, temperature, conductivity, and turbidity of samples were measured.

The optimum dose of alum, which provided the highest percentage of turbidity removal efficiency, was selected to repeat the steps 1.1) to 1.6) with the narrow range of alum dose.

Figure 3.6 Jar test apparatus

2) Determination of optimum anionic PAM dose

The optimum alum dose from narrow range was selected to determine the optimum anionic PAM as follows.

2.1) The initial pH, temperature, conductivity, and turbidity of samples were measured.

2.2) The optimum dose of alum was pipetted into each sample.

2.3) The mixing speed of jar test apparatus was adjusted to 200 rpm for 1 minute (rapid mixing).

2.4) 0.02, 0.04, and 0.06 mg/L of anionic PAM were added into each sample. All doses were conducted 3 times.

2.5) The mixing speed was adjusted to 40 rpm for 20 minutes (slow mixing).

2.6) Jar test apparatus was turned off for sedimentation for another 10 minutes.

2.7) Measured the final pH, temperature, conductivity, and turbidity of the sample solution.

3.2.6 Microplastics quantification after treatment

1) After step 3.2.3, 25 mL of supernatant was transferred to glass bottles.

2) The solution was filtered through a glass microfiber filter using Büchner funnel and air pump.

3) Microplastic particles on the filter were counted under the stereomicroscope equipped with fixed microscope adapter.

3.2.7 Analytical methods

1) The turbidity removal efficiency (%) was calculated via Eq. (3.1)

$$\text{Turbidity removal efficiency (\%)} = \frac{T_i - T_f}{T_i} \times 100 \qquad \text{Eq. (3.1)}$$

Where T_i represent the initial turbidity (NTU)

T_f represent the turbidity after treatment (NTU)

2) The MPs removal efficiency (%) was calculated via Eq. (3.2)

$$\text{MPs removal efficiency (\%)} = \frac{N_i - N_f}{N_i} \times 100 \qquad \text{Eq. (3.2)}$$

Where N_i represent the quantity of MPs before treatment (pieces)

N_f represent the quantity of MPs after treatment (pieces)

3.2.8 Statistical analysis

The data analysis was conducted using IBM SPSS Statistics version 22. Statistical significances of means were tested with a model of One-Way ANOVA followed by Scheffe and Dunnett's T3 test at significance level of 0.05.

CHAPTER 4

RESULTS AND DISCUSSION

In this study, raw water from canal for water supply was collected to use in the jar test experiment. Current MPs in raw water were quantified before experiment. 250 pieces/m^3 of MPs were detected in raw water, but only 250 mL of raw water was used in each sample. Thus, we assumed that no MPs contamination was found in each sample.
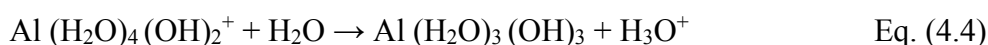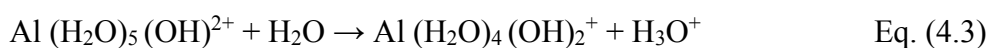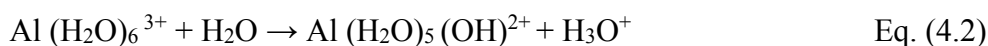
Hardness and alkalinity of raw water were measured to ensure that they are appropriate to be used in coagulation and flocculation processes without causing extreme drops in pH after treatment. The average alkalinity and hardness of raw water were in the range of 109.60-124.45 mg/L as $CaCO_3$ and 102.50-107.03 mg/L. The conductivity and pH of raw water were measured before and after treatment as well. Then, jar test experiments were conducted in order to determine the optimum dose of alum and APAM for the removal of turbidity and microplastics (MPs) via coagulation and flocculation processes. After treatment, the removal efficiencies were calculated and compared. The results were divided into 4 main parts and each section presents a discussion as follows.

4.1   pH before and after coagulation and flocculation processes

The initial pH values of raw water were within the range of 7.4 to 8.2. After treatment via coagulation and flocculation processes, the final pH values slightly decreased in the range of 7.1 to 7.9. The decrease of pH values is caused by the acid production during coagulation process. In water, the aluminum cations are presented in hydrated form. The formation of this hydrated form can be described with the chemical reaction in Eq. (4.1).

$$Al_2(SO_4)_3 + 12H_2O \rightarrow 2Al\,(H_2O)_6{}^{3+} + 3SO_4{}^{2-} \qquad \text{Eq. (4.1)}$$
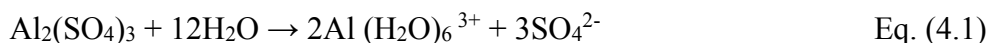
After alum addition, proton occurs because hydrated aluminum ions are proton donors. This can be demonstrated by Eqs. (4.2) to (4.4).

$$Al\,(H_2O)_6{}^{3+} + H_2O \rightarrow Al\,(H_2O)_5\,(OH)^{2+} + H_3O^+ \qquad \text{Eq. (4.2)}$$

$$Al\,(H_2O)_5\,(OH)^{2+} + H_2O \rightarrow Al\,(H_2O)_4\,(OH)_2{}^+ + H_3O^+ \qquad \text{Eq. (4.3)}$$

$$Al\,(H_2O)_4\,(OH)_2{}^+ + H_2O \rightarrow Al\,(H_2O)_3\,(OH)_3 + H_3O^+ \qquad \text{Eq. (4.4)}$$

As shown in the above reactions, it can be seen that the concentration of hydronium ions increases due to the increase in dissolution of alum in water. As a result, the net effect is a drop in pH.

4.2 Conductivity before and after coagulation and flocculation processes

The initial conductivity values were within the range of 356 to 565 µS/cm and slightly increased after treatment in the range of 361 to 574 µS/cm. The increase of conductivity is affected by the presence of aluminum salts in the water which is the inorganic dissolved solids. After the dissolution of aluminum salts, the aluminum ions can carry the positive charge and the sulphate ions can carry the negative charge. These ions lead to the increase in capacity of water to conduct the electrical currents.

4.3 Removal efficiencies of MPs and turbidity in added and non-added MPs using alum as a coagulant.

In this study, jar test experiment was conducted using alum as a coagulant to investigate the removal efficiencies of turbidity and microplastics in raw water. The analysis was performed with One-Way ANOVA followed by a post hoc analysis using Scheffe multiple comparison test to determine the optimum dose of alum. The optimum doses were considered significant difference when $p \leq 0.05$ for 95% confidence interval. The removal efficiencies were reported as mean ± SEM. The results are presented in Figure 4.1.
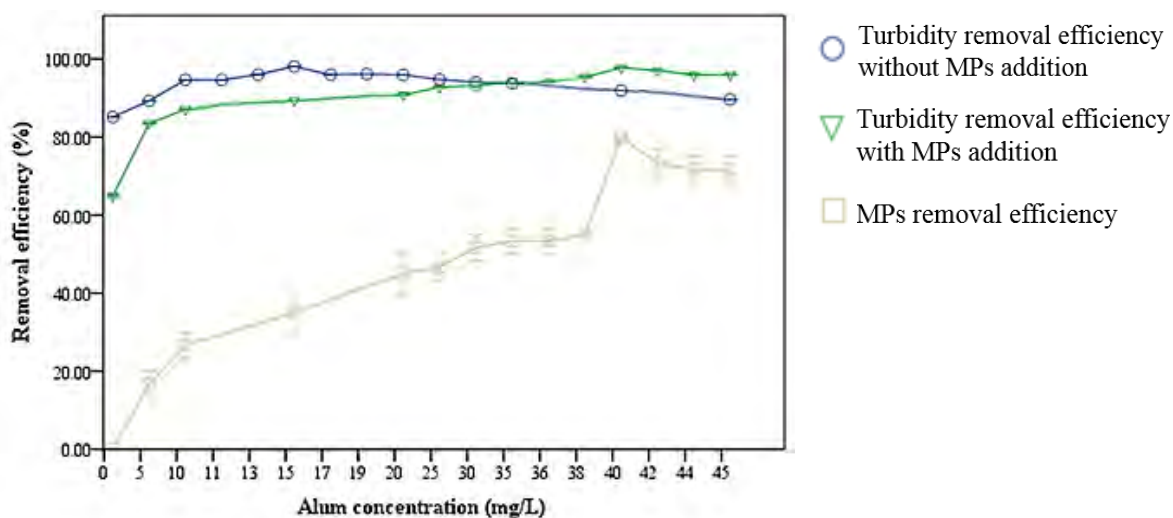

Figure 4.1 Removal efficiencies of MPs, turbidity (with MPs addition) and turbidity (without MPs addition) using alum as a coagulant (N=3)

4.3.1 The optimum dose of alum for the removal of turbidity in raw water without MPs addition

The initial turbidity of raw water was in the range of 23 to 32 NTU. The removal efficiencies (%) of turbidity in the non-added MPs gradually increased from 85.12±0.04 to 98.07±0.02 for 0-15 mg/L of alum. Then, the removal efficiency (%) slightly decreased from 98.07±0.02 to 89.60±0.03 after adding 20-45 mg/L of alum. Thus, 15 mg/L of alum provided 98.07±0.02% of turbidity removal which is the highest removal efficiency. After that, the optimum dose of alum from wide range (15 mg/L) was varied into a narrow range to determine more actual value of optimum alum dose. For the narrow range, the turbidity removal efficiency (%) slightly increased from 94.64±0.04 to 98.07±0.02 for 11-15 mg/L of alum. Then, the removal efficiency (%) slightly decreased from 98.07±0.02 to 96.14±0.02 after adding 17-19 mg/L of alum. The result confirmed that 15 mg/L of alum is the actual optimum dose which provided the highest turbidity removal efficiency (98.07±0.02%) in the non-added MPs.

4.3.2 The optimum dose of alum for the removal of turbidity in raw water with MPs addition

Due to the flotation of new MPs before coagulation process, these MPs were soaked in the wastewater from sugar industry to increase the mass of MPs by attachment of organics on MPs surface. The initial turbidity was not much change after MPs addition. Then, these MPs suspended in water. After that, 0.3-4 mm MPs were added in raw water sample for conducting coagulation and flocculation processes. The removal efficiencies (%) of turbidity in the added MPs condition gradually increased from 64.89±0.16 to 97.77±0.02 for 0-40 mg/L of alum. Then, the removal efficiency (%) slightly decreased from 97.77±0.02 to 95.93±0.02 after adding 45 mg/L of alum. Thus, 40 mg/L of alum provided 97.77±0.02% of turbidity removal which is the highest removal efficiency. After that, the optimum dose of alum from wide range (40 mg/L) was varied into a narrow range to determine more actual value of alum optimum dose. For the narrow range, the turbidity removal efficiency (%) slightly increased from 94.15±0.04 to 97.77±0.02 for 36-40 mg/L of alum. Then, the removal efficiency (%) slightly decreased from 97.77±0.02 to 95.93±0.01 after adding 42-44 mg/L of alum. The results revealed that 40 mg/L of alum was the actual optimum dose which provided the highest turbidity removal efficiency (97.77±0.02%) in the added MPs condition.

4.3.3 The optimum dose of alum for the removal of MPs

The MPs removal efficiencies (%) increased from 0 to 80.00±0.00 for 0-40 mg/L of alum. Then, the removal efficiency (%) slightly decreased from 80.00±0.00 to 71.67±1.67 after adding 42-45 mg/L of alum. The results revealed that 40 mg/L of alum was the optimum dose which provided the highest MPs removal efficiency (80.00±0.00%).

4.3.4 Comparisons of the removal efficiencies

According to Figure 4.1, the results indicated that the removal efficiency of turbidity and 0.3-4 mm MPs were affected by doses of alum. The overview results revealed that removal efficiency increased by increasing alum concentration. In this study, 15 mg/L of alum provided the highest removal efficiency of turbidity and 40 mg/L of alum provided the highest removal efficiency of 0.3-4 mm MPs.

The increase of alum dose and SS removal efficiency, including turbidity and MPs, can be explained by the charge neutralization and sweep coagulation mechanisms. In charge neutralization, the positive charge (Al^{3+}) occurs after adding alum in raw water. Then the positive charge is attracted to the negatively charged colloids via electrostatic interaction. After particle collisions, the small flocs (neutral charge) start to form during the neutralization step.

After charge neutralization, sweep coagulation mechanism occurs during coagulation process. The sweep flocs can be described as large aggregates of aluminum hydroxide compounds which are formed when Al salt (alum) is added to water as shown in Eqs. (4.1) to (4.5). After that, colloidal particles are attached to the sweep flocs. Thus, the increase of alum dose provided more sweep flocs to attach with colloidal particles. Then, the flocs stick together and become larger in size. As a result, the flocs have more ability to settle, resulting in high removal efficiency of turbidity and MPs.

However, the removal efficiency did not increase by increasing alum concentration in all cases. According to the results in Figure 4.1, the removal efficiency of turbidity and MPs slightly dropped after reaching their optimum doses. This can be occurred because of alum overdosing. Adding excessive doses of alum can cause charge reversal, resulting in re-stabilization of the suspended solids. Consequently, lower of turbidity and MPs removal efficiency had occurred.

$$Al_2(SO_4)_3 \cdot 14H_2O + 6HCO^{3-} \rightleftharpoons 2Al(OH)_3 + 8H_2O + 3H_2SO_4 \qquad \text{Eq. (4.5)}$$

Furthermore, the overview result revealed that the removal efficiency of turbidity was higher than MPs. While the average turbidity removal efficiency (without MPs addition) was 93.56%, the average turbidity and MPs removal was 90.83% and 48.5% in added MPs condition. The decrease of removal efficiency in added MPs condition can also be explained by charge neutralization and sweep coagulation. The increase of alum dose provides more positive charge and sweep flocs to attach with colloidal particles to form larger flocs. However, the neutral charge on MPs surface cannot be attached by the positively charged coagulant. As a result, the removal efficiency decreased after MPs addition. However, the MPs in this study were the deteriorative microplastics and covered with organic solid particles on the surface, resulting in the attachment between positively charged coagulant and negatively charged colloidal on MPs surface. Thus, the MPs particles covered with negatively charged particles can be attached. However, the positive charged coagulant can only attach some areas on MPs surface, resulting in the decrease of removal efficiency. Thus, the size of MPs became an important role in removal efficiency. It had been noticed that the residual MPs in supernatant were more large size (4 mm) than small size (0.3<d<4 mm). This can be described by the effect of surface area. MPs with larger size can be attached more difficult compared to smaller size of MPs. In another word, less of surface area to attach leads to less removal. This finding conforms with the result of Ma et al. (2019) which studied characteristics of microplastic removal via coagulation and ultrafiltration during drinking water treatment and found that the smaller size of MPs provided higher removal efficiency.

To conclude, MPs required more coagulant (alum) dose to make themselves destabilized and stick together to settle when compared to natural colloid.

4.4 Removal efficiencies of MPs and turbidity (with MPs addition), using APAM as a coagulant aid

After alum optimization was discovered, APAM at different concentrations were added to investigate the removal efficiency of turbidity and microplastics. The analysis was performed with One-Way ANOVA followed by a post hoc analysis using Scheffe multiple comparison test to determine the optimum dose of APAM. The tests were considered statistically significant difference when $p \leq 0.05$ for 95% confidence interval. The removal efficiencies were reported as mean ± SEM. The results are presented in Figure 4.2.
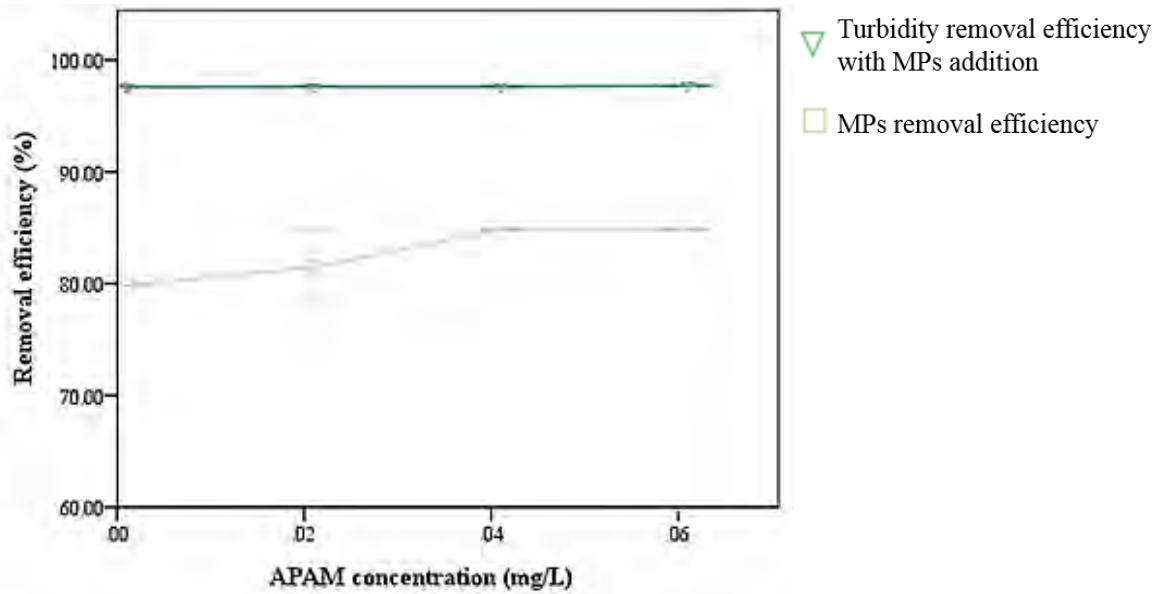
Figure 4.2 Removal efficiency of turbidity and MPs, using APAM as a coagulant aid

(N=3)

4.4.1 The optimum dose of APAM for the removal of turbidity in raw water with added MPs

The removal efficiencies (%) of turbidity in the added MPs condition were not significantly different in the range of 97.77 ± 0.02 to 97.79± 0.00 for 0 - 0.04 mg/L of APAM. Moreover, the results revealed that 0.06 mg/L APAM was the optimum dose which provided highest turbidity removal efficiency (97.88 ± 0.02%) compared to other APAM dose.

4.4.2 The optimum dose of APAM for the removal of MPs

The removal efficiencies (%) of MPs slightly increased from 80.00± 0.00 to 85.00± 0.00 for 0 - 0.06 mg/L of APAM. The results revealed that 0.04 mg/L APAM was the optimum dose which provided the highest removal efficiency (85± 0.00%).

4.4.3 Comparisons of the removal efficiencies

According to Figure 4.2, the result indicated that the removal efficiency of MPs was affected by APAM doses. The overview results revealed that removal efficiency slightly increased by increasing APAM concentration. The increase of APAM dose and SS removal efficiency, including turbidity and MPs, can be explained by polymer bridging mechanism. APAM, the polymer used in bridging flocculation, is high molecular weight

linear-chain compounds. Polymer molecules can bind to other particles or adhere to the colloidal particles in many positions due to the free ends. Thus, the surface of MPs flocs can be attached by these free ends of APAM, resulted in greater settleability. However, the overview of results revealed that the trends of both MPs and turbidity removal efficiency were not much change. This might be caused by the diluted concentration of APAM did not provide free ends adequately to adhere to the flocs surface.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

With the gradual increase of microplastics (MPs) in surface water, water treatment plants, and tap water, MPs have become a great concern worldwide. However, most of the research has focused on their sources, distributions, toxicological effects, and detection methods, especially in the marine systems. Thus, understanding the MPs removal characteristics in the current tap water treatment processes is necessary. Hence, the removal efficiency of 0.3 − 4 mm. MPs was investigated during traditional coagulation and flocculation processes in this study, with the main conclusions as follows.

15 mg/L of alum was the optimum dose which provided the highest turbidity removal efficiency (98.07±0.02%) for non-added MPs condition whereas 40 mg/L of alum was the optimum dose which provided the highest removal efficiency of both turbidity (97.77±0.02%) and MPs (80.00±0.00%) in raw water with MPs addition.

After alum optimization was discovered, APAM at different doses were added to enhance the removal efficiency of turbidity and MPs. 0.06 mg/L APAM was the optimum dose for turbidity removal in added MPs condition (97.88 ± 0.02%). 0.04 mg/L APAM was the optimum dose for MPs removal (85± 0.00%). However, the overview of results revealed that the trends of both MPs and turbidity removal efficiency were not much change after APAM addition.

The results revealed that MPs can be removed via coagulation and flocculation process. In coagulation process, it can be seen that MPs required more alum dose compared to natural colloidal particles. Furthermore, the small number of MPs were removed with the low dose of alum. However, the removal efficiency increased after increasing alum dose, especially for the small MPs particles which are more easily adsorbed than larger MPs particles.

5.2   Recommendations

5.2.1   pH of raw water should be varied and investigated to find the most optimal conditions for water treatment.

5.2.2   Zeta potential should be measured to investigate the colloid stability during coagulation process.

5.2.3   The larger sample size (quantity of MPs before treatment) should be considered to increase because larger the sample size leads to the more accurate results.

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Appendix A

Table A.1 MPs removal efficiency using alum as coagulant

Alum Concentration (mg/L)	MPs Before (pieces)	MPs After (pieces)	MPs Removal Efficiency (%)	Average (%)	Std. Dev.
0	20	20	0		
0	20	20	0	0.00	0.00
0	20	20	0		
5	20	17	15		
5	20	17	15	16.67	2.89
5	20	16	20		
10	20	15	25		
10	20	14	30	26.67	2.89
10	20	15	25		
15	20	13	35		
15	20	14	30	35.00	5.00
15	20	12	40		
20	20	12	40		
20	20	11	45	45.00	5.00
20	20	10	50		
25	20	11	45		
25	20	11	45	46.67	2.89
25	20	10	50		
30	20	10	50		
30	20	10	50	51.67	2.89
30	20	9	55		
35	20	10	50		
35	20	9	55	53.33	2.89
35	20	9	55		
36	20	10	50		
36	20	9	55	53.33	2.89
36	20	9	55		
38	20	9	55		
38	20	9	55	55.00	0.00
38	20	9	55		
40	20	4	80		
40	20	4	80	80.00	0.00
40	20	4	80		
42	20	5	75		
42	20	6	70	73.33	2.89
42	20	5	75		
44	20	6	70		
44	20	5	75	71.67	2.89
44	20	6	70		
45	20	6	70		
45	20	6	70	71.67	2.89
45	20	5	75		

Table A.2 MPs removal efficiency using APAM as coagulant aid

APAM concentration (mg/L)	MPs Before (pieces)	MPs After (pieces)	MPs Removal Efficiency (%)	Average (%)	Std. Dev.
0.00	20	4	80		
0.00	20	4	80	80.00	0.00
0.00	20	4	80		
0.02	20	4	80		
0.02	20	3	85	81.67	2.89
0.02	20	4	80		
0.04	20	3	85		
0.04	20	3	85	85.00	0.00
0.04	20	3	85		
0.06	20	3	85		
0.06	20	3	85	85.00	0.00
0.06	20	3	85		

Appendix B

Figure B.1 MPs before treatment

Figure B.2 MPs after treatment

Figure B.3 New MPs

Figure B.4 Raw water sampling area

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