REDUCTION OF DISSOLVED ORGANIC MATTER IN CONTAMINATED SHALLOW WELL WATER BY FERRIC CHLORIDE COAGULATION WITH CERAMIC MEMBRANE FILTRATION

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การลดสารอินทรีย์ละลายน้ำในน้ำบ่อตื้นปนเปื้อนโดยการโคแอกกูเลชั่นด้วยเฟอริกคลอไรด์และการกรองเซรามิกเมมเบรน

นางสาวบัณฑิตา ตั้งสุวรรณ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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Thesis Title	REDUCTION OF DISSOLVED ORGANIC MATTER IN CONTAMINATED SHALLOW WELL WATER BY FERRIC CHLORIDE COAGULATION WITH CERAMIC MEMBRANE FILTRATION
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บัณฑิตา ตั้งสุวรรณ์ : การลดสารอินทรีย์ละลายน้ำในน้ำบ่อตื้นปนเปื้อนโดยการโคแอกกูเลชั่นด้วยเฟอริกคลอไรด์และการกรองเซรามิกเมมเบรน. (REDUCTION OF DISSOLVED ORGANIC MATTER IN CONTAMINATED SHALLOW WELL WATER BY FERRIC CHLORIDE COAGULATION WITH CERAMIC MEMBRANE FILTRATION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.สุรพงษ์ วัฒนะจีระ, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: อ. ดร.อรรณพ วงศ์เรือง, 113 หน้า.

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาการลดสารอินทรีย์ละลายน้ำในน้ำบ่อตื้นปนเปื้อนจากหลุมฝังกลบขยะ ตำบลแม่เหียะ อำเภอเมือง จังหวัดเชียงใหม่ โดยการโคแอกกูเลชั่นด้วยเฟอริกคลอไรด์และการกรองเซรามิกเมมเบรนที่มีรูพรุน 0.1 ไมครอน น้ำบ่อตื้นปนเปื้อนมีสารอินทรีย์คาร์บอนละลายน้ำเท่ากับ 12.6 มก./ลิตร และค่าการดูดกลืนแสง UV_{254} เท่ากับ 1.545 ซม.$^{-1}$ โดยที่สารอินทรีย์คาร์บอนละลายน้ำในน้ำบ่อตื้นปนเปื้อน แบ่งออกเป็น 2 กลุ่ม ได้แก่ กลุ่มที่ชอบน้ำ (Hydrophilic) และกลุ่มที่ไม่ชอบน้ำ (Hydrophobic) มีความเข้มข้นเท่ากับ 8.1 และ 3.0 มก./ลิตร ตามลำดับ ปริมาณเฟอริกคลอไรด์และค่าพีเอชที่เหมาะสมในการโคแอกกูเลชั่นคือ 100 มก./ลิตร และพีเอช 6.5 ตามลำดับ ซึ่งสามารถลดสารอินทรีย์คาร์บอนละลายน้ำเท่ากับ 25% จากการศึกษาพบว่า น้ำบ่อตื้นปนเปื้อนที่ผ่านการโคแอกกูเลชั่นด้วยเฟอริกคลอไรด์และน้ำบ่อตื้นปนเปื้อนหลังการโคแอกกูเลชั่นด้วยเฟอริกคลอไรด์ร่วมกับการกรองเซรามิกเมมเบรน 0.1 ไมครอน มีค่าสารอินทรีย์คาร์บอนละลายน้ำไม่แตกต่างอย่างมีนัยสำคัญ

นอกจากนี้ ได้มีการศึกษาค่าการลดลงของสารไตรฮาโลมีเทนทั้งหมด (Total trihalomethane) พบว่า ในน้ำบ่อตื้นปนเปื้อนแห่งนี้มีค่าความเข้มข้นของสารไตรฮาโลมีเทนทั้งหมดเท่ากับ 10.8 ไมโครกรัม/ลิตร หลังจากที่น้ำบ่อตื้นปนเปื้อนได้ผ่านกระบวนการบำบัดโดยวิธีโคแอกกูเลชั่น และวิธีโคแอกกูเลชั่นร่วมกับกระบวนการกรองด้วยเซรามิกเมมเบรน พบว่า ค่าความเข้มข้นของสารไตรฮาโลมีเทนทั้งหมดลดลงเหลือ 6.0 และ 4.5 ไมโครกรัม/ลิตร ตามลำดับ

สาขาวิชา การจัดการสิ่งแวดล้อม

ปีการศึกษา 2556

ลายมือชื่อนิสิต ....

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BANTHITA TANGSUWAN: REDUCTION OF DISSOLVED ORGANIC MATTER IN CONTAMINATED SHALLOW WELL WATER BY FERRIC CHLORIDE COAGULATION WITH CERAMIC MEMBRANE FILTRATION. ADVISOR: ASSOC. PROF. SURAPHONG WATTANACHIRA, D.Eng., CO-ADVISOR: AUNNOP WONGRUENG, Ph.D., 113 pp.

This study presented a reduction of dissolved organic matter in contaminated shallow well water with landfill leachate by coagulation and ceramic microfiltration (CM) membrane. Contaminated shallow well water was collected from an abandon open dump site in Chiang Mai, Thailand. Ferric chloride ($FeCl_3$) was used as a coagulant. CM membrane with nominal pore size 0.1 μm was examined. The results illustrated that the contaminated shallow well water contained dissolved organic carbon (DOC) of 12.6 mg/L and UV_{254} of 1.545 cm^{-1}. In addition, the contaminated shallow well water was fractionated into hydrophilic (HPI) and hydrophobic (HPO) fractions. DOC for HPI and HPO fractions were 8.1 and 3.0 mg/L, respectively. Optimal dosage and pH were observed at 100 mg/L and 6.5, respectively. As a result, DOC was reduced by 25%. Subsequently, supernatant water after coagulation was filtered through CM membrane. The result showed that DOC in the filtrated water was insignificantly different. For chlorination process, total trihalomethane in contaminated shallow well water was 10.8 μg/L and it was reduced to 6.0 and 4.5 μg/L by coagulation process and coagulation combined with CM membrane, respectively.

Field of Study:	Environmental Management	Student's Signature	....
		Advisor's Signature	....
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CHAPTER 1

INTRODUCTION

1.1 Theoretical Background

Thailand has many environmental problems such as air pollution, noise pollution and water pollution. Water pollution was a critical issue in Thailand because water is the main component of daily life and survival. Water was usually contaminated by human and industrial activities, agricultures, and leachate from landfills. Landfill leachate included a large number of organic matter, dissolved organic matter, phenol, ammonical-nitrogen, phosphate, sulphide, acidity, alkalinity, salnity, solids, inorganic salts, and other toxicants and heavy metals (Aziz, Daud, Adlan, & Hung, 2007). Heavy metals that were present in groundwater from landfill site included cadmium (Cd), nickel (Ni) and zinc (Zn), for example, and their potential mobility depended on their properties (J. B. Christensen, Jensen, & Christensen, 1996). The complexity of these characteristics made the leachate more difficult to manage.

Chiang Mai city in 1983 had smell and water quality problems from Mae Hia landfill site that caused from increasing of waste in the municipal area (Osatharayakul, 1999). In 1989, Mae Hia landfill was closed due to the local villagers didn’t allow to enter the landfill site and didn’t allow the Chiang Mai municipality to bring garbage to landfill site (Karnchanawong, 1993).

Disinfection by product (DBP) precursors in term of dissolved organic carbon (DOC) was a classification of organic molecules and compositions in aquatic systems. DOC reacted with disinfectants in water to form harmful disinfection by-products, causing carcinogenic substances that affected human health (Rook, 1974). Moreover, DOC influenced the appearance and color as well as the taste and odor of water (Fan et al., 2012). In addition to dissolved organic nitrogen (DON), DON leaching into streams and drinking water could also affect the environments such as through the eutrophication and acidification of streams (Kessel, Clough, & Groenigen, 2009).

The major chemical methods that were used to treat landfill leachate were coagulation, chemical or electrochemical oxidation and flocculation (Ahn, Yun, & Won, 2002). Later, membrane filtration was used to reduce contaminants in water. A ceramic membrane was long-lasting and reliable throughout its working lifetime and resists to high temperature and corrosion (Luque, Gomez, & Alvarez, 2008). Moreover, the ceramic membrane could work with highly viscous fluids (Luque et al., 2008).

This research combines physical and chemical methods to treat shallow well water contaminated with landfill leachate. $FeCl_3$ coagulation was used for the pretreatment to increase the efficiency of the membrane.

1.2 Objectives

1. To analyze DBP precursors in contaminated shallow well water with landfill leachate
2. To fractionate DBP precursors in contaminated shallow well water
3. To reduce DBP precursors by $FeCl_3$ coagulation and ceramic microfiltration (CM) membrane
4. To investigate a formation of DBP in contaminated shallow well water

1.3 Hypotheses

1. Reduction of DBP precursors in contaminated shallow well water via $FeCl_3$ coagulation can be enhanced by combining with CM membrane.
2. Ferric chloride ($FeCl_3$) coagulation and CM membrane can reduce DBP formation during a chlorination process.

1.4 Scopes of work

1. Contaminated shallow well water with landfill leachate from Mae-Hia dumping site, Chiang Mai, Thailand, was used in this study.
2. Organic matters were fractionated into two portions including hydrophilic group and hydrophobic groups
3. $FeCl_3$ was utilized as a coagulant.

4. Ceramic microfiltration (CM) membrane with a nominal pore size 0.1 µm was tested.
5. Chlorine residual in range 0.1-0.2 mg/L and 24 hours reaction time were applied in this study.

1.5 Benefits of this work

1. The characteristics of the contaminated shallow well water with landfill leachate were found out.
2. Knowledge of removal DBP precursors by $FeCl_3$ coagulation and CM membrane was clarified.
3. The removal efficiency of DBP precursors by $FeCl_3$ coagulation and CM membrane was carried out.

CHAPTER 2

LITERATURE REVIEWS

2.1 Leachate

Leachate was determined as wastewater that contaminated in groundwater by rainwater percolation, biochemical process in waste's cell, and natural water content of wastes themselves (Renou, Givaudan, Poulain, Dirassouyan, & Moulin, 2007). By products in landfill site was caused by degradation reaction. Degradation reaction in landfill site occurred chemical contaminated in groundwater (Alamgir, Mohiuddin, Ahsan, & Roehl, 2006). The critical problem of landfill site of municipal solid waste (MSW) was percolation of leachate into surrounding area (Walker, 1969).

Chemical oxygen demand (COD), ammonia nitrogen (NH_4^+-N), dissolved solids (SD), suspended solid (SS), xenobiotic organic compounds (XOCs), heavy metal and salt were main parameters that used to indicate contaminated landfill site (T. Christensen et al., 2001).

In the previous studies, they demonstrated treatment process to remove contaminated leachate by using coagulation process. Different coagulants were used to demonstrated these are shown in Table 2.1

The leachate from a young landfill was characterized by having a high BOD_5 and COD concentration, a quite high amount of NH_3-N, a high BOD_5/COD ratio, and a pH value that was below 6.5. Leachate from a mature or stabilized landfill usually had a high amount of NH_3-N, a moderately high amount of COD, and a BOD_5/COD ratio that was lower than 0.1 (Rivas, Beltran, Carvalho, Acedo, & Gimeno, 2004). The leachate from a young landfill can control using a biological treatment, but the leachate from a mature or stabilized landfill cannot. A physical-chemical treatment was suitable for leachate from a mature or stabilized landfill (Rivas et al., 2004).

Table 2.1 Different types of coagulants were used in coagulation process

Coagulants	Measured parameters	%of COD removal	References
$FeCl_3$ or $Al_2SO_4$4 (concentration range 0.01–0.07 M)	COD and turbidity	40 -50	Amokrane, Comel et al., 1997
$FeSO_4$ (0.3 g L−1 of Fe)	COD and TOC	70	Wang, Lau et al., 2000
$Ca(OH)_2$ (6 kg m−3)	COD, BOD and metals	57	Keenan, Steuner et al. 1983
$Ca(OH)_2$ + Al_2SO_4(1.5 + 1.0 kg m−3)	COD and BOD	42	Papadopoulos, Fatta et al., 1998
$FeCl_3$ + Al_2SO_4 (concentration range 0.1–1.0 g L−1)	COD, BOD and TOC	53	Welander and Henrysson, 1998
$Ca(OH)_2$ + $FeSO_4$ (concentration range 0.5–4.0 and0.0–0.2 g L−1)	COD and BOD	39	Loizidou, Vithoulkas, 1992
$FeCl_3$ + Al_2SO_4 (concentration range 1.0–5.0 g L−1)	COD, BOD and color	75	Taesi, Zouboulis et al., 2003

Table 2.1 Different types of coagulants were used in coagulation process (continue)

Coagulants	Measured parameters	%of COD removal	References
Struvite ($Mg:NH_4:PO_4$ = 1:1:1) (concentration range 0.1–1.0 g L−1)	COD, NH_4^+, TKN and color	50	Ozturk, Altinbas et al., 2003
$FeCl_3 \cdot 6H_2O$ (concentration range 0.1–1.0 g L−1)	COD and color	24	Wang, Zhang et al., 2003
$FeCl_3$ (concentration range 0.8–1.0 g L−1)	TOC	38 -48	Yoon, Cho et al., 1998
$FeCl_3$ (concentration range 0.2–1.2 g L−1)	COD	39	(Yoo, Cho, & Ko, 2001)

2.2 Natural organic matter (NOM)

Natural organic matter was the major disinfection by products (DBPs) precursors when reacted with chlorine residual in water. Trihalomethane (THMs) included chloroform, bromodichrolomethane, chlorodibromomrthane, and bromoform (Sketchell, Peterson, & Christofi, 1995). THMs had given toxicity to human health because THMs was a carcinogenic substance (Shon & Vigneswaran, 2006). Humic substances, amino acid, sugars aliphatic acids and a large number or organic molecules were compound of DOM (T.F. Marhaba & Pu, 2000). Humic substances included humic and fulvic acids; whereas non-humic substances included hydrophilic acids, proteins, carbohydrates, carboxylic acids, amino acids, and hydrocarbons (Thruman, 1985). NOM can separate into two fractions i.e., humic and non-humic fraction. Non- Humic fraction had less hydrophobic character than humic fraction. The non- humic almost included hydrophilic acid, proteins, amino acids and carbohydrate, while humic fraction included humic and fulvic acid. Nevertheless, the humic substance was the most important in term of their chemical properties and implication for water supply (Owen, Amy, & Chowdhury, 1993). Natural color in water in important that caused from humic and fulvic acids those was compound of DOM (J.K. Edzwald, 1993).

In acidity, humic substance consisted of humic and fulvic acid. Humic acids have molecular weight more than 2000 a.m.u. but less than 100000 a.m.u while, fulvic acids have molecular weight in range 500 – 2000 a.m.u (Thruman, 1985). When measuring

Specific Ultraviolet Absorbance (SUVA) at 254 nm of wavelength, the values of SUVA were in range of 4.8 -7.4 and 2.9 -4.3 L/mg-m of humic and fulvic acids, respectively (Reckhow, Simger, & Malcolm, 1990). When comparison density of charge between humic and fulvic acids, fulvic acids had high density of charge than humic acids. Moreover, fulvic acids were more difficult for charge neutralization by coagulation process than humic acids (Amy, Sierka, Bedessem, Price, & Tan, 1992). Not only fulvic acids were more difficult by coagulation process, but they were also high solubility than humic acid. Range of humic substances concentration in most surface water is 100 μg/L-4 mg/L (Thruman, 1985).

Algae and their extracellular products were non- humic substance. Those had been illustrated to be THMs precursors (Morris & Baum, 1978). In the previous study, they explained the algae in surface water might be a major contributed to THMs formation due to reaction kinetics between chlorine and algae was faster than chlorine and aquatic humic materials (Oliver & Shindler, 1980).

The previous study explained higher humic acids concentration increased THMs formation. This result was investigated by adding concentration of humic acids 3, 5 and 10 mg/L at chlorine dosage 3, 5 and 10 mg/L. The experiment could conclude that THMs was increased when increasing humic acids at the same dosage of humic acids (Muttamara, Sales, & Gazali, 1995).

Moreover, non-specific parameters could characterize humic substance which depended on their organic carbon content. Organic carbon had ability to absorb UV light at wavelength 254 nm. Thus, it was a useful technique to characterize NOM (T.F. Marhaba & Washington, 1998).

2.2.1 Surrogated parameters of natural organic matter (NOM)

Table 2.2 shows surrogate parameters of water quality in water treatment (J.K. Edzwald, Becker, & Wattier, 1985).

Table 2.2 Surrogate parameters of water quality in water treatment

Surrogate Parameters	Measurements
Turbidity	Turbidity parameter was used for measuring suspended particles. Standard of turbidity is 1 NTU.
Color	Color parameter was used for measuring humic matter. There is secondary standard of 15 Pt-Co units and no standard instrument method of measurement .
TOC	TOC parameter was used to collect or group of organic matter. There is not standard.
UV_{254}	UV_{254} parameter was used to indicate TOC and THMs precursor.

Source: (J.K. Edzwald et al., 1985)

2.2.1.1 Dissolved organic carbon (DOC)

Dissolved organic carbon is an organic molecule in aquatic systems. DOC can be divided into two types based on their movement: the first moves horizontally into soil and the second moves vertically with water around a surface area. DOC is usually mobile with heavy metals such as cadmium (Cd), nickel (Ni) and zinc (Zn) contaminated in shallow well and surface water. Heavy metals are harmful to human health. High exposure to cadmium, for example, can cause "itai-itai" disease, had carcinogenic effects in kidneys, generate various toxic effects in the body, disturb bone metabolism, deform the reproductive tract as well as disrupt the endocrine system (Mudgal, Madaan, Mudgal, Singh, & Mishra, 2010).

DOC was difficult to treat because it could react with disinfectants and form harmful disinfection by-products, caused membrane fouling, and reduced the efficiency of activated carbon because DOC competed with target compounds for active adsorption sites. Moreover, DOC influenced the appearance and color as well as the taste and odor of water.

DOC was separated from total organic carbon (TOC) by using 0.45 μm PTFE filter (APHA, AWWA, & WPCF, 1995). DOC was independent of the oxidation state of organic matter. Particulate organic carbon (POC) and dissolved organic carbon (DOC) were the fraction of natural water. There was

DOC approximately 50 -60% of humic substances in surface water (Thruman, 1985).

2.2.1.2 Ultraviolet absorbance at wavelength 254 nm (UV_{254})

Absorbing of UV_{254} had a benefit for using to be an indicator to measure organic matter in water. UV_{254} was used in measuring quality of water treatment and used to evaluate reduction ability of DBPs precursor in coagulation process (APHA et al., 1995). The value of DOC concentration was absorbed by UV light was concerned with DOC concentration in water sample. When concentration of DOC in water sample was high, the value of UV_{254} was also high. UV_{254} can use with aromatic compound due to organic matter that had aromatic compound and had double bond of structure can greatly absorb UV light, whereas simple aliphatic acids alcohol and sugar cannot absorb UV light (Edzwald et al., 1993) Moreover, they explained that pH and turbidity had effected on UV measuring. Therefore, UV_{254} measuring was useful technique to indicate NOM in water (Eaton, 1995). The reason that why needed to measure UV at wavelength 254 (approximately 253.7 nm) nm because in this wavelength, organic matter is the best absorbed and is almost not disturbed from other compounds (Eaton, 1995). Before measuring UV_{254}, water sample was filtrated by filter to remove suspended particles.

2.2.1.3 Specific ultraviolet absorbance (SUVA)

SUVA is the ratio between UVA absorbance and DOC concentration multiply by 100. SUVA value was used to indicate humic content in water Edzwald et al., 1993; Owen et al., 1993). Specific absorbance could suggest the nature of NOM and its consequent THMs formation (Krasner, Croue, Buffle, & Perdue, 1996). Molecular weight of substance was involve in specific absorbance of human due to if the water has high humic content, the value of SUVA is higher (Pettersson, Bishop, Lee, & Allard, 1995). Furthermore, SUVA can be indicator that use in coagulation process to reduce DBPs precursor. Coagulation process was suitable for water sample that had SUVA value more than 3 L/mg-m because it contained organic matter that was more humic-like in character, higher in apparent molecular weight (AMW). While, was water sample had SUVA value less than 3 L/mg-m that means organic matter of lower AMW that was more fulvic-like in character and more difficult to remove (USEPA, 1999). Table 2.3 shows guidelines for SUVA and nature of NOM.

Table 2.3 Guidelines for SUVA and nature of NOM

SUVA	Composition
More than 4	Mostly aquatic NOM, high hydrophobicity and high molecular weight
2-4	Mixture of aquatic NOM and other NOM. Mixture of hydrophobic
Less than 2	Mostly non-humic substances. Low hydrophobicity. Low molecular weight

Source: (Edzwald & Tobiason, 1999)

Cho, Amy & Pellegrino (2002) explained that relationship between NOM removal and SUVA was higher than between NOM removal and molecular weight suggesting that electrostatic repulsion was more important than size exclusion for NOM rejection.

2.3 Coagulation and flocculation

Coagulation and flocculation were the techniques that used to remove the suspended particles or organic matter in the water (Zhao et al., 2012). Coagulants and flocculants made the small suspended particle molecules combined together to form large molecules, called “flocs,” and after that suspended particles or organic matter slow settling to produce a rapid-settling floc (Reynolds & Richards, 1996). Coagulation process was the process that helped suspended particle precipitated that was easily removed. Particle size, shape and density were important in source of suspended particles. Therefore, the selection of a coagulant and flocculant depended on particle size, shape and density.

2.3.1 Coagulation

Coagulation was the process that balanced charge of suspended particle to be neutral charge by adding coagulant that was positive charge to react with negative charge in surface of suspended particle. Repulsion force among small suspended particles was reduced when they formed bigger size.

2.3.2 Flocculation

Flocculation was the process that neutralized suspended particle to form large particle that called “floc” by adding flocculant. After formation of suspended particle, large suspended particle was rapidly sediment.

2.3.3 Coagulant

There were three groups of coagulants. First, inorganic coagulants such as aluminum sulfate or alum, polyaluminum chloride, ferric chloride and poly ferric sulfate. Second, organic synthetic coagulants such as polyacrylamide derivatives and polyethylene imine, and finally naturally occurring coagulants such as chitosan, sodium alginate (SA) and bioflocculant (Zhao et al., 2012).

The abilities of different used coagulants to remove TOC were discussed below:

2.3.3.1 Aluminum Sulfate Coagulant ($Al_2(SO_4)_3$)

Aluminum Sulfate Coagulation has pH range approximately 5.5-6.0. Percentage removal of TOC by ($Al_2(SO_4)_3$) coagulant was 30%. They used optimal dosage of ($Al_2(SO_4)_3$) coagulant was 20 mg/L at pH 5.5 -6.3 to remove THMs precursor in Southern California (Cheng, Krasner, Green, & K.L., 1995).

2.3.3.2 Ferric Sulfate Coagulant ($Fe_2(SO_4)_3$)

$Fe_2(SO_4)_3$ coagulant was used in experiment in previous study with optimal dosage 20 mg/L. $Fe_2(SO_4)_3$ coagulant could remove TOC nearly haft of the beginning. When they increased the dosage of $Fe_2(SO_4)_3$coagulant, the efficiency of TOC removal was increased to 70% at approximately pH 5.0 (Sinsabaugh, Hoehn, Knocke, & Linkins, 1986).

2.3.3.3 Ferric chloride coagulant ($FeCl_3$)

$FeCl_3$ coagulant was used to be a coagulant to reduce disinfection by products (DBPs). $FeCl_3$ has molecular formula $FeCl_3{\bullet}6H_2O$ or $FeCl_3$ anhydrous.

$FeCl_3$ hexahydrate includes of *trans*-$[Fe(H_2O)_4Cl_2]^+$ cationic complexes and chloride anions, with the remaining two H_2O molecules embedded within the monoclinic crystal structure (Lind, 1967). Table 2.4 shows properties of $FeCl_3$.

Table 2.4 Properties of $FeCl_3$

Properties	
Molar mass	162.2 g/mol (anhydrous) 270.3 g/mol (hexahydrate)
Appearance	green-black by reflected light; purple-red by transmitted light hexahydrate: yellow solid aq. solutions: brown
Odor	Slight Hydrochloric acid
Density	2.898 g/cm^3 (anhydrous) 1.82 g/cm^3 (hexahydrate)
Melting point	306 °C (583 °F ; 579 K) anhydrous 37 °C (99 °F; 310K) hexahydrate
Boiling point	315 °C (599 °F; 588K) anhydrous, decomposes) 280 °C (536 °F; 533K) hexahydrate, decomposes partial decomposition to $FeCl_2$ + Cl_2)
Solubility in water	74.4 g/100 mL (0 °C) (Patnaik, 2002) 92 g/100 mL (hexahydrate, 20 °C)
Viscosity	40% solution: 12 cP

When $FeCl_3$ was soluble, $FeCl_3$ was positive charge and after that positive charge of $FeCl_3$ neutralized with negative charge from suspended particle. In the previous study, $FeCl_3$ was used to vary pH in range 5.5 -8.8 to removal contaminated in water (Konieczny, Bodzek, & Rajca, 2006).

A good coagulant for turbidity removal in water treatment was ferric chloride ($FeCl_3$). It was more effective in removing total organic carbon (TOC) than an aluminum-based coagulant, achieving the same removal effects with a lower dosage. The use of aluminum resulted in added health risks (e.g., carcinogenic and mutagenic effects) to living things. Therefore, it was necessary to monitor residuals from the treatment process to keep them below a certain level. Moreover, $FeCl_3$ coagulants were found to be effective in wide ranges of pH and temperature at removing humic substances from water (Shi, Fan, & Brown, 2004).

Moreover, the previous described that $FeCl_3$ had effective for NOM removal. Percent removal of DOC was in range 46% -71% and percent removal of trihalomethane formation potential (THMFP) and haloacitic acid formation potential (HAAFP) was in range 59% -90% (Dryfuse, Miltner, & Summers, 1995). When comparison between iron and aluminum-salt coagulants included the optimum pH values for organics removal, solubility, surface areas, and surface charge, iron had more efficiently to remove precursor than alum (Vilage, Rose, Masion, Laine, & Bottero, 1997).

2.3.3.4 Polyaluminum Chloride Coagulant (PACl)

PACl coagulant enhanced at all pH values above and below those for optimum alum coagulation to remove fulvic acid (Dempsy, Ganho, & O, 1984). Furthermore, there was other study to examine efficiently of PACl. PACl with 30 mg/L can reduce percentage of turbidity and humic acid were 94 -65, respectively (Nagare, Aso, Ebie, & Ebie, 2008).

2.4 Ceramic microfiltration membrane

Membrane filtration is a technique used to separate the molecules of contaminated compounds based on their size. Membranes can be divided into four types, dependent on pore diameter: microfiltration (a diameter of 0.05-10 micrometers); ultrafiltration (a diameter of 0.1–0.001 micrometers); nanofiltration (a diameter of 0.005-0.0005 micrometers); and reverse osmosis (a diameter of less than 0.0005 micrometers) (no ‘‘real’’ pores) (Luque et al., 2008). The efficiency of each type of membrane is shown in Figure 2.1.

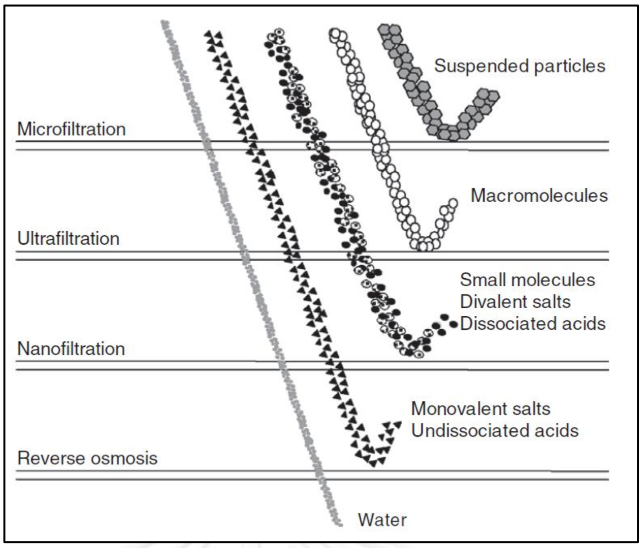


Figure 2.1 Efficiency of each type of membrane (Luque et al., 2008)

A microfiltration membrane (MF) can be used with suspended solids in water or sterilization stages. MF can also be used as a pretreatment before nanofiltration (NF) and reverse osmosis (RO).

Most ceramic membranes were made from oxides such as Al, Si, Ti and Zr. The normal structure of a ceramic membrane had an asymmetrical composition of different porosity levels, at least two or three. Inside this structure of filtration channels, there was an active layer line where directly contacted with the fluid to be treated occurs. A Micro -microporous top layer, a mesoporous intermediate layer used to reduce roughness of the surface of a membrane before applying the active. The macroporous support was the most porous part of the membrane and provides mechanical strength, while minimizing mass transfer resistance.

The important parameters that involved in the efficiency of ceramic membranes were pore size, porosity, surface roughness, and mechanical properties. The reason that why these parameters were important because a ceramic membrane-based system depended on the separation and permeation properties of the membrane as well as its mechanical integrity. These properties depended on the selective top layer and on the support system on which the active separation layer was coated.

Separation of ceramic membrane process was driven by the pressure difference across the membrane and the trans membrane pressure. Nowadays, many industries produced many different structures for uses (see Figure 2.2).

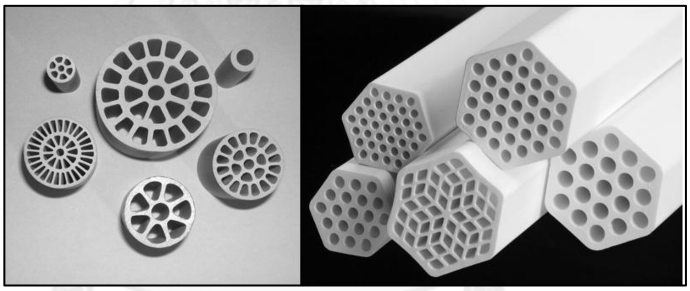


Figure 2.2 Examples of commercial ceramic membranes

Using a ceramic membrane was better than using another membrane because ceramic membranes were long-lasting, reliable and resistance to high temperatures and corrosion. Moreover, a ceramic membrane was compatible with highly viscous fluids (Luque et al., 2008).

The normalized flux of membrane permeation was calculated as follows:

$$\mathrm{QDt} = \frac{\mathrm{Qt}/(\mathrm{A} * \mathrm{Pt})}{Q0/(A * P0)}$$

Where Q_{Dt} is the normalized membrane permeate flux;

Q_0 is the measured flow rate at the start of filtration;

Q_t is the measured flow rate at the time after filtration;

A is the area of membrane;

P_0 is the trans membrane pressure at the start of filtration;

P_t is the trans membrane pressure at the time t after filtration

(Li, Wu, Guan, & Zhang, 2011).

2.5 DAX-8 Resin fractionation

NOM was a heterogeneous mixture comprised of humic and fulvic acids, lignins, carbohydrates, and proteins of various sizes and molecular weight (Hua & Reckhow, 2008). Fractionation was a procedure that was used for dividing dissolved organic matter (DOM) into two fractions, hydrophobic (HPO) DOM fractions that included humic acid and fulvic acid and hydrophilic (HPI) DOM fractions that included non-humic acids, by exchanging ions between a resin and the sample. HPO fractions were aromatic structure more than HPI fraction (T. F. Marhaba, Pu, & Bengraine, 2003).

Natural organic matter fraction and chemical group are shown in Table 2.5 (Leenheer, Noyes, & Steer, 1982).

Table 2.5 Organic matter fraction and chemical group

Fraction	Chemical groups
Hydrophobic	
Acids	
Strong	Humic and fuvic acid, high MW alkyl monocarboxylic and dicarboxylic acids, aromatic acids
Weak	Phenols, tannins, intermediate MW alkyl monocarboxylic and dicarboxylic acids, aromatic acids
Base	Proteins, aromatic amines, high MW alkyl Amines
Neutrals	Hydrocarbon, aldehydes, high MW methyl ketones and alkyl alcohols, ethers, furan, pyrrole
Hydrophilic	
Acids	Hydroxy acids, sugars, sulfonics, low MW alkyl monocarboxylic and dicarboxylic acids
Base	Amino acids, purines, pyrimidines, low MW alkyl amines
Neutral	Polysaccharides; low MW alkyl alcohols, aldehydes and ketones

sources: (Leenheer & Noyes, 1984; Leenheer et al., 1982; Reckhow, Bose, Bezbarua, Hesse, & McKnight, 1992)

The fractionation procedure was based on uses an adsorbing resin and solid-phase extraction ion-exchange (Pohl, 2007). XAD-8 and DAX-8 resins can be used in the fractionation procedure, but this study only concentrated on using the DAX-8 resin.

The first procedure of fractionation was adjusted the pH of the DOM in the water sample to 2.0 and then the water sample was pumped passed the DAX-8 resin in a column (see Figure 2.3). After that, the column was rinsed with 0.01M HCl. The liquid phase that was not sorbed onto the DAX-8 resin was classified as the hydrophilic phase. The phase sorbed by the DAX-8 resin was classified as the hydrophobic phase. The HPO phase can be removed from the resin by rinsing it with 0.1M NaOH (Amery, 2009).

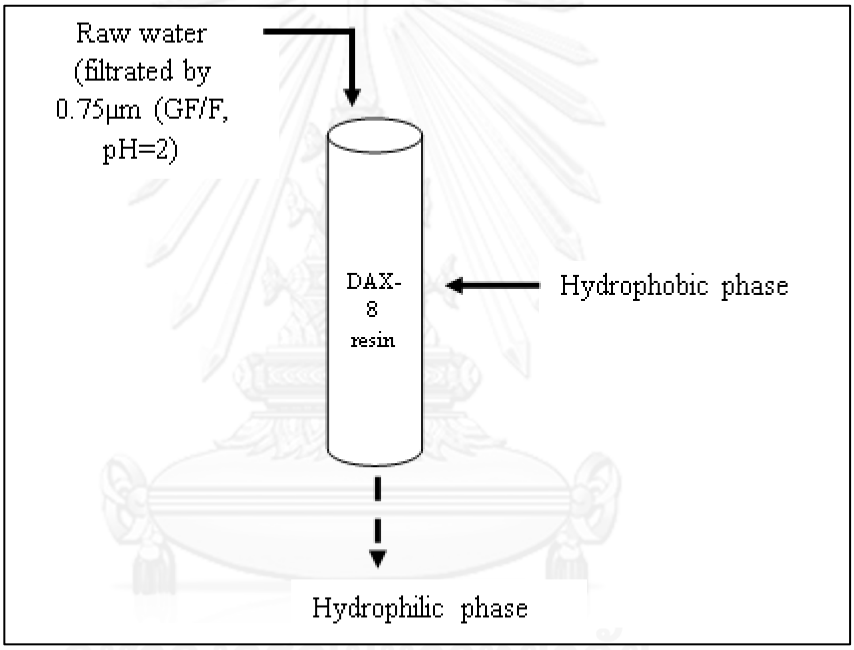


Figure 2.3 Fractionation procedure using DAX-8

Most previous used XAD resin fraction (XAD-2, XAD-4 and XAD-8) and DAX resin fraction (DAX-2, DAX-4 and DAX-8) to fractionate HPI and HPO in DOM fractions. Most research of Thailand used DAX-8 resin fraction due to DAX-8 resin had high force of hydrogen bond that had high ability to exchange ions and had low humidity less than 1 percent by weight (w/w)(Peuravuori, Lehtonen, & Pihlaja, 2002). Table 2.6 shows resins fractionation of DOM.

Table 2.6 Review of resin fractionation in DOM

Water source	Resin	Fraction	Reference
Saguaro Lake, Mexico	XAD-4, DAX-8	Percentage of HPO, HPI and TPI were 22, 31 and 10, respectively.	(Mash, Westerhoff, Baker, Nieman, & Nguyen, 2004)
Sein-Aval wastewater treatment plant,Paris	XAD-4, DAX-8	Percentage of HPO, HPI and TPI were 35, 45 and 20, respectively.	(Benoit et al., 2008)
Bitumen roof runoff,Berlin	XAD-4, DAX-8	Percentage of HPO, HPI and TPI were 65, 17 and 18, respectively.	(Ropru & Martin, 2008)
Waste effluent,USA	XAD-4, DAX-8	Percentage of HPO, HPI and TPI were 29, 36 and 35, respectively.	(Park, Kim, & Cho, 2008; Ropru & Martin, 2008)
Glane River, France	XAD-4, DAX-8	Percentage of HPO, HPI, TPI and HA were 65.5, 16, 13 and 5, respectively.	(Lananowski & Feuillade, 2009)

Table 2.6 Review of resin fractionation in DOM (continue)

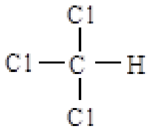
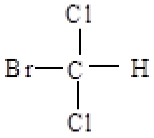
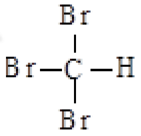
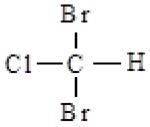
Water source	Resin	Fraction	Reference
Mosina Water Intake (TOC 3.8-6.5 mg/L)	XAD-4, XAD-8, AGMP-50, and Duolite A7	Percentage of humic acid, HPOA, HPON, HPIA, HPIB and HPIN were 19, 54, 12, 7, 5 and 3, respectively.	(Swietlik & Sikorka, 2004)
South Platte River, Colorado,USA (DOC 2.6 mg/L)	XAD-4,XAD-8 and MSC-1H	HPOA, HPON, Transphilic acids, Transphilic neutral, and HPI	(Croue, M.F., Violleau, & Leenheer, 2003)
Nakdong River, Korea (DOC 3.71 mg/L)	XAD-4 and XAD-8	HPO, Transphilic, and HPI	(Lee et al., 2002)
Da Cha creek, Taichung,Taiwan (DOC 2 mg/L)	DAX-4 and DAX-7	Percentage of HPO substance, HPIT and non- acid hydrophilic were 43, 41 and 16, respectively.	(Chang et al., 2001)
Moorabool, Hope Valley, and Wanneroo (Australia)	XAD-4, DAX-8, and IRA-958	Percentage of vary HPOA, slightly HPOA, HPI charged fraction and HPIN were 34-80, 9-21, 9-33 and 1-15.	(Bolto, Abbt-Braun, & Dixon, 1999)

2.6 Formation of DBPs

Disinfection by products precursor are formed by the reaction between organic substances, inorganic compounds, i.e. chloride, bromide and oxidizing agents that used for adding in water treatment process. The major constituent of organic substance and DBP precursors is natural organic matter (NOM). For measuring precursors level, that usually used total organic carbon (TOC), dissolved organic carbon (DOC) and UV_{254} as parameters. The factors that affect to amount and type of DBPs formed are: (1) type of disinfectant dose, dose, residual concentration, (2) concentration and characteristic of precursors, (3) water temperature, (4) water chemistry (i.e. pH, bromide ion concentration, organic nitrogen concentration, and presence of other reducing agents such as iron and manganese), (5) contact time and mixing conditions for disinfectant, coagulant, source water and other treatment chemicals.

Using chlorine compounds to treat water leaves chlorine residuals in water and when chlorine compounds reacted with natural organic matter (NOM), they created disinfection by-products such trihalomethanes (THMs), which were carcinogenic and affect the rectal-intestinal organs, caused bladder cancer and have other mutagenic effects on human health (Shon & Vigneswaran, 2006). There are four species of trihalometane i.e. chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$). The structure of THMs is presented in Table 2.7

Table 2.7 Structure of four types of THMs

Individual, DBPs	Structure
Chloroform ($CHCl_3$)	 $\mathrm{Cl{-}C(Cl)(Cl){-}H}$
Bromodichloromethane ($CHBrCl_2$ or BDCM)	 $\mathrm{Br{-}C(Cl)(Cl){-}H}$
Bromoform ($CHBr_3$)	 $\mathrm{Br{-}C(Br)(Br){-}H}$
Dibromochlromethane ($CHBr_2Cl$ or DBCM)	 $\mathrm{Cl{-}C(Br)(Br){-}H}$

Source: (Rook, 1974)

According to the U.S. Environmental Protection Agency, the standard of level of THMs in drinking water must be below 80 mg/L (Goslana et al., 2009). The disinfection by-product formation potential (DBPFP) test was used to measure and monitor disinfection by-products (DBPs) (Ates, Kitis, & Yetis, 2007; Bougeard, Goslan, Jefferson, & Parsons, 2010). The American Public Health Association (APHA) used the DBPFP test as a standard analysis method to measure chlorinated products from long contact time reactions of chlorine under controlled pH and temperature conditions (Sirivedhin & G., 2004). The ultraviolet absorbance at a wavelength of 254 nanometers (UV_{254}) and specific ultraviolet absorbance at a wavelength of 254 nanometers ($SUVA_{254}$) were used as parameters to predict the DBPFP (Chow, Dahlgren, Zhang, & Wong, 2008; Domino, Pepich, Munch, Fair, & Xie, 2003). But, it was not advantageous to use UV_{254} and SUVA with water samples after pretreatment because the result would indicate the content of DOM absorbed in the ultraviolet region, but the DBP precursors were only part of that DOM. Thus, these methods cannot be used to provide specific precursors. Therefore, a fluorescence-based technique may be used to investigate the formation of DBPs (Hambly et al., 2010; Hudson, Baker, & Reynolds, 2007). Since DOM had different functional groups of aromatic structures, fluorescence spectroscopy should be used to investigate the types of DOM, which would for instance provide information on the chemical structure, the functional groups, the spatial configurations, the intra-molecular and intermolecular kinetic characteristics, and the heterogeneity of components in DOM (Sheng & Yu, 2006).

CHAPTER 3

METHODOLOGY

3.1 Source of Samples

Water sample was collected from a shallow well in the Mae-Hia landfill site. The distance from the Mae-Hia landfill site to Chiang Mai is approximately 5 kilometers (Jiarsirkul, 2003). The Mae-Hia landfill site is located at the western foothill of the Chiang Mai-Lamphun Basin. The location of this landfill site is between a transition zone and clay-rich colluvial deposits and the Ping River alluvial complex. The Mae-Hia landfill site was established in 1958 as an unsanitary landfill on the existing surface without any technical safety measures (see Figure 3.1).

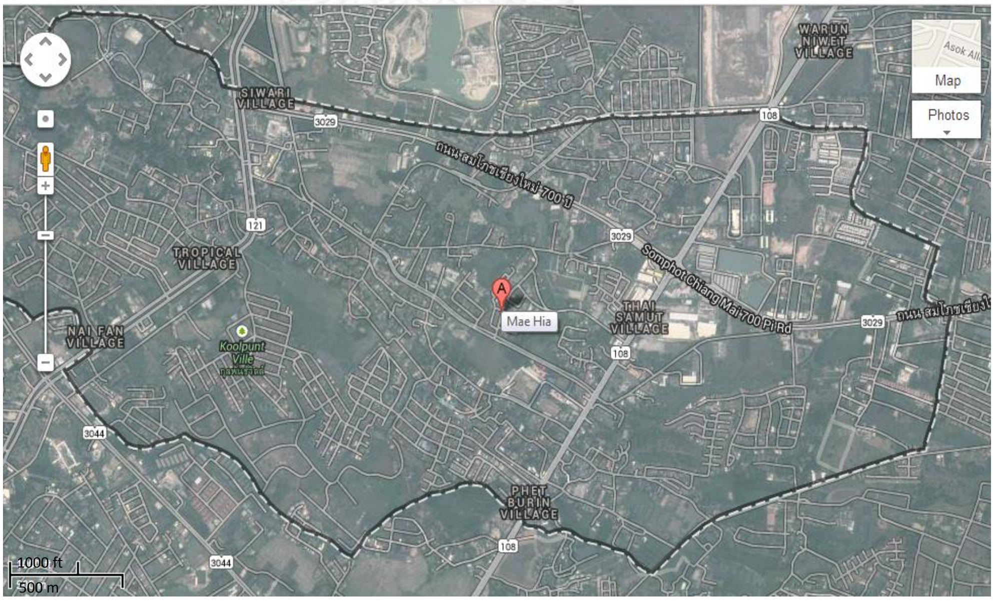


Figure 3.1 Location of the Mae-Hia solid waste dumping site

The Mae-Hia landfill site was closed in 1989 because leachate from the site was degrading water resources in the surrounding area. These problems were caused by the mismanagement of the landfill. The original of Mae-Hia landfill site is from the Doi-Suthep National Park and floe along the western periphery dump. The Mae-Hia landfill site spread organic matter and hazardous chemicals and liquid into the surface water, shallow well and soil.

The water sample was collected from the landfill site and it was kept in controlled room at 4 °C that is shown in Figure 3.2. After that, basic parameters were measured (i.e., pH, temperature, alkalinity, turbidity and electrical conductivity).

Figure 3.2 Water sample

After measuring the basic parameters, the raw water sample was filtrated by using the 0.45 μm-PTFE filter to measure UV_{254}, DOC and Iron. Moreover, after being filtrated by the ceramic membrane, the water sample was separated in term of HPO and HPI fractions by using the DAX-8 resin fractionation technique. The parameters were considered in the ceramic microfiltration (CM) membrane process and resin fractionation process were UV absorbing organic constituents (UV_{254}), dissolved organic carbon (DOC) and Iron those are shown in Figure 3.3.

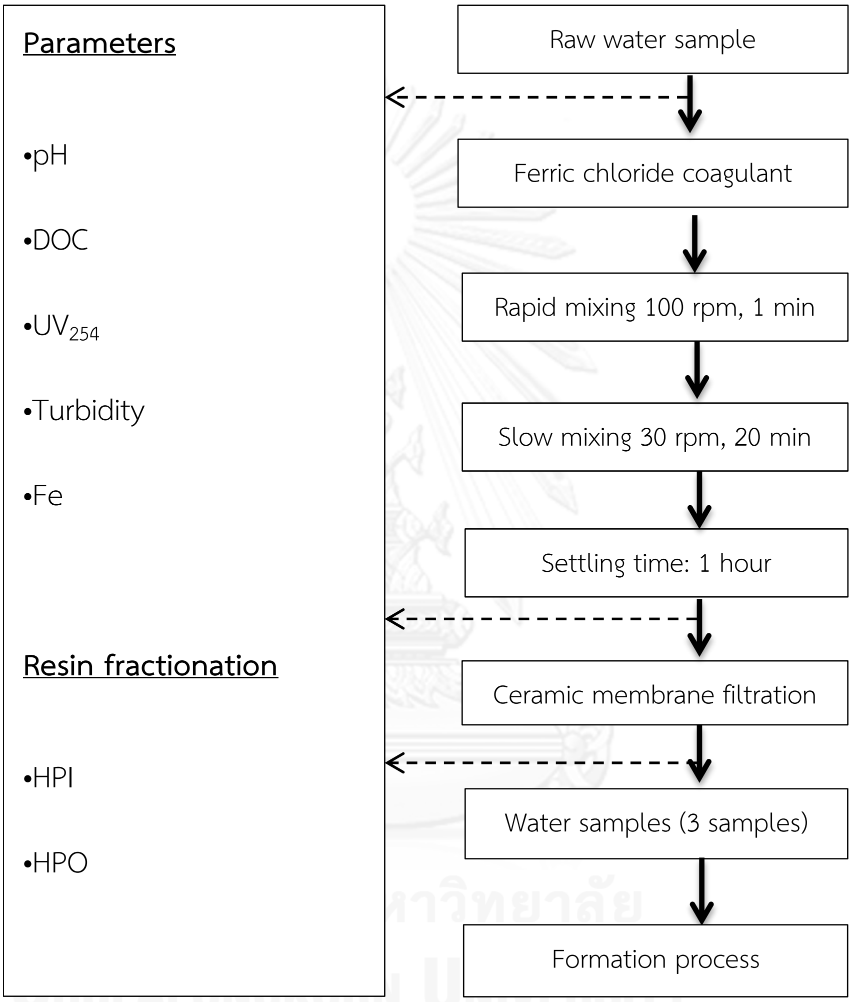


Figure 3.3 Procedure of all treatment

3.2 Coagulation process

3.2.1 Coagulant

Ferric chloride ($FeCl_3 \cdot 6H_2O$) approximately 46% was used to be a coagulant. In this experiment, $FeCl_3$ was prepared the 10000 mg/L as a stock solution.

3.2.2 Optimal dosage of $FeCl_3$ coagulation

This study collected water samples two sampling times (i.e. in November 2013 and January 2014) to investigate optimal condition in coagulation. In November 2013, the coagulation was carried out in fives dosage of $FeCl_3$ i.e. 10, 25, 50, 75 and 100 mg/L, respectively. For January 2014, four dosages of coagulant were tested (i.e. 50, 100, 150, and 200 mg/L, respectively) to select optimal dosage as shown in Figure 3.4. In this process, the water sample was poured 1 liter per beaker without any pH adjustment (see Table 3.1).

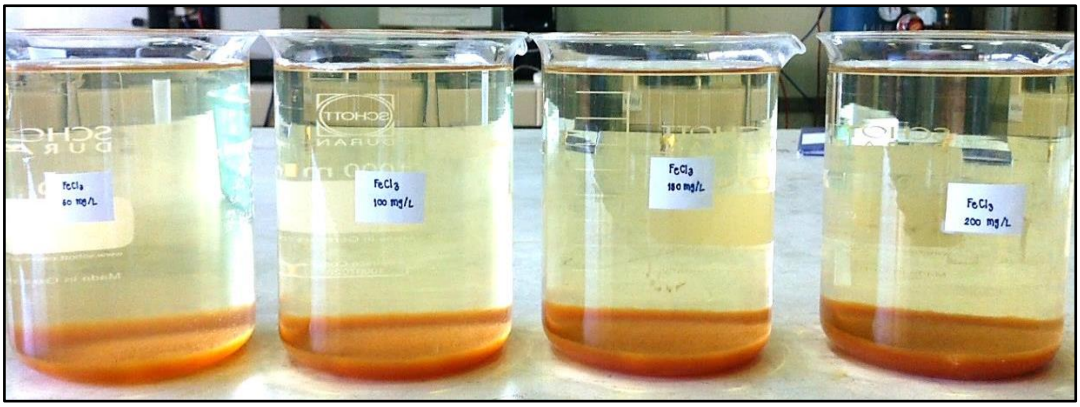


Figure 3.4 Optimal dosage of $FeCl_3$ coagulation

Finally, the optimum dose was determined by measuring DOC and UV_{254} reduction. After that, the optimum pH was determined.

Table 3.1 Optimal dosage of $FeCl_3$ coagulation

$FeCl_3$ concentration (mg/L)	**Beaker**				
	1	**2**	**3**	**4**	**5**
November 2013	10	25	50	75	100
January 2014	50	100	150	200	-

3.2.3 Optimal pH of $FeCl_3$ coagulation

When the optimal dosage was selected, three pH values, i.e. 6.5, 7.5 and 8.5 (see Figure 3.5) were varied to find optimal pH followed Konieczny et al., (2006). The optimum pH was also determined by measuring DOC and UV_{254} reduction.

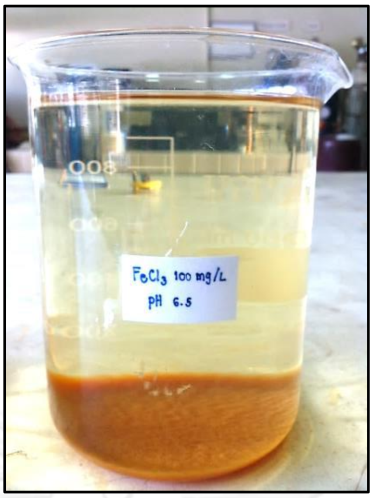


Figure 3.5 Optimal pH of $FeCl_3$ coagulation

In coagulation process, coagulant and water sample were mixed together. The first minute, water sample and $FeCl_3$ was mixed rapidly at 100 rpm. Subsequently, slow mixing at 30 rpm was used in this process for 20 minutes. After that, water sample was settled for 1 hour.

3.3 Membrane process

This stage was carried out with $FeCl_3$ coagulation combined with CM membrane. The CM membrane was obtained from Metawater Co., Ltd., Japan. The supernatant from the coagulation was further filtered with CM membrane with pore size of 0.1 μm, total surface area of 0.0042 m^2, 3 centimeters in diameter, 10 centimeters height and 55 tubular channels (see Figure 3.6). An operating pressure was controlled at 0.1 MPa.

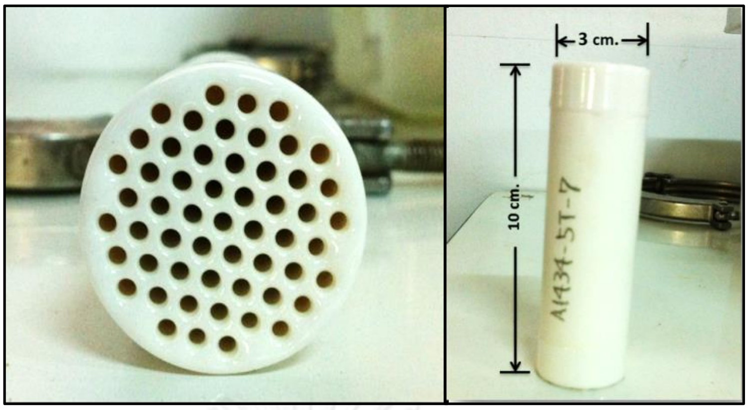


Figure 3.6 Ceramic membrane in this study

Treated water by coagulation was poured into a tank and it was pressurized into CM membrane by air pressure. Treated water was gone out from CM membrane in two streams, the first stream was permeate water (filtrated by filter in CM membrane) that shows in Figure 3.7

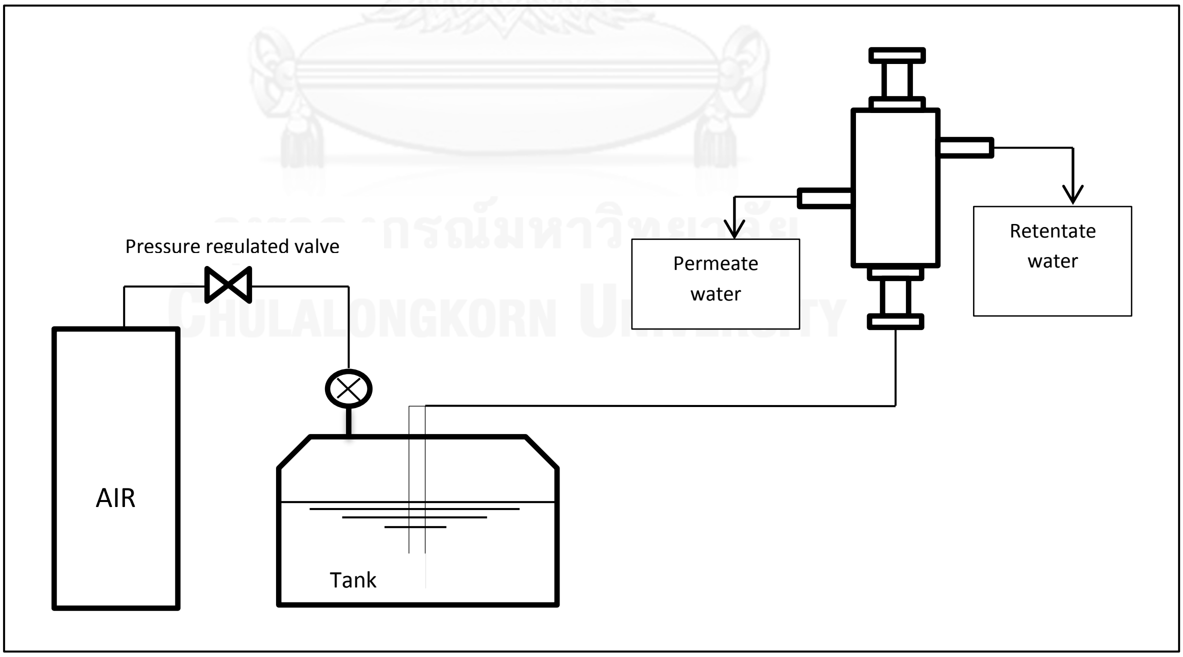


Figure 3.7 Experimental set up

Contaminated shallow well water was also applied in CM membrane to compare water flux with treated water by coagulation. Treated water by CM membrane was measured DOC and UV_{254} to study efficiency of DOC reduction by CM membrane.

Efficiencies of the coagulation and the CM membrane were investigated. Water fluxes during the CM membrane filtration were also observed.

3.4 Resin fractionation process

Contaminated shallow well water, treated water by coagulation process and treated water by coagulation combined with CM membrane were fractioned and measured parameters (i.e. DOC and UV_{254}) to characterize organic matters in water samples.

The resin fractionation technique has three parts (Leenheer, Hsu, & Barber, 2001): (a) Soxhlet extraction of DAX-8 resin, (b) preparation of the DAX-8 resin in a column, and (c) the fractionation process.

3.4.1 Soxhlet extraction of DAX-8 resin

a) DAX-8 resin was soaked in 0.1N of NaOH for 24 hours. After that, NaOH was rinsed from the resin by using milli-Q water.
b) After using milli-Q water to rinse the resin, the resin was put into thimmers and the thimmers was put into soxlet equipment.

c) The resin in the thimmers was soxhlet by using acetone for 24 hours and then the resin was also soxhlet by hexane for 24 hours.

d) The resin was put into beaker and methanol was used to rinse hexane for a period of 24 hours.

NOTE: Observing out of hexane from resin, the resin was sunk in methanol if the resin completely rinse.

3.4.2 Preparing DAX-8 resin in a column

a) The DAX-8 resin was put into a column.

b) 0.1N of NaOH (approximately 250 mL) was used to rinse the resin. And then the resin was also rinsed by using 0.1N of HCl (using the same volume).

c) Milli-Q water was used for rinsing the resin.

d) The liquid phase was collected from the column to measure DOC, which should be below 0.2 mg/L and conductivity, which should be below 10 μs/cm.

3.4.3 Fractionation process

a) The raw water sample was filtered by using a 0.75μm GF/F filter and their pH was adjusted to 2 with conc. H_2SO_4.

b) The filtered and pH adjusted water sample was put into the resin using a flow rate of 1.2 bed volume/hr = 20 mL/min = 3.3 mL/10s (using proximately 3-5 liter of raw water).

c) The liquid phase that is the hydrophilic (HPI) dissolved organic matter (DOM) fraction was collected.

d) For hydrophobic (HPO) fraction, which it was absorpted with resin; it was replaced with 1 bed volume (100 mL) of milli-Q water.

e) After completely rinsing the resin with milli-Q water, the resin in the column was eluted with 0.1N of NaOH 0.25 bed volume (50 mL) and 0.01N of NaOH 1.25 bed volume (250 mL), respectively with flow rate of 2 bed volume/hr = 200 mL/hr = 3.3 min/hr.

f) HPO fraction was collected and then, it was diluted 10x for mass balancing with the beginning.

g) Both of DOM fractions were adjusted to pH 7 by using NaOH.

3.5. Formation process

3.5.1 Investigated optimal dosage of Chlorine (Cl_2)

Contaminated shallow well water was filled into bottles. Each bottle contains 130 mL of water. After that Cl_2 in form hypochlorite was spiked into the bottles with various dosages. The dosages of Cl_2 were used to investigate optimal dosage those are

2, 3 and 4 mg/L. All bottles were kept for 24 hours. Finally, chlorine residual was measured. A dosage that provided chlorine residual of 0.1-0.2 mg/L was identified as the optimal dosage (see Figure 3.8).

Figure 3.8 Investigated optimal dosage of Chlorine (Cl_2)

The optimal dosage that provided chlorine residual of 0.1-0.2 mg/L in this study was 3 mg/L.

3.5.2 Investigated formation of DBPs

HPI and HPO fractions of contaminated shallow well water, treated water by coagulation process and treated water by coagulation combined with CM membrane were filtrated by 0.45 μm-PTFE filters with optimal Cl_2 dosage that was obtained from the previous section. In the end, all water samples were analyzed gas chromatography (GC) to investigate DBPs formation.

3.6 Analytical method

The water sample was measured i.e. pH, Temperature, Alkalinity, Turbidity, TOC, UV_{254} and Iron. Each parameter was measured with difference instruments. These parameters were measured by using instruments that are shown in Table 3.2

3.6.1 pH

pH values of water sample were measured by a Model F21 Horibra pH- meter which was adjusted by buffer at pH 4.0, 7.0 and 9.0

3.6.2 Temperature

Temperature was measured by a model F21 Horibra Thermometer.

3.6.3 Alkalinity

Alkalinity was measured by titration method by following standard method 2320 in part of 2320B titration method without filtration of water sample.

3.6.4 Turbidity (FAU)

Turbidity was measured by the HACH Turbidity meter Model 2100 without filtration of water sample.

3.6.5 DOC

DOC was used standard method 5310C by wet oxidation method. Water sample was filtrated by 0.45 μm-PTFE filter. After that, DOC was measured by O.I. analytical 1010 TOC analyze.

3.6.6 UV_{254}

Water sample was filtrated by 0.45 μm-PTFE filter before it was measured by Perkin-Elmer Model Lambda 25, UV/VIS spectrophotometer instrument by following 5901B standard method.

3.6.7 Iron

Water sample was filtrated by 0.45 μm-PTFE filter before measuring by DR/890 colorimeter.

3.6.8 THMs

Concentrations of trihalomethanes (THMs) i.e. chloroform, bromodichloromethane, dibromochloromethane, and bromoformwere measured by 5710B standard method.

3.6.9 Free chlorine residual

Free chlorine residual was measured by standard method 4500-Cl DPD method. The chlorine residual must have 0.1 -0.2 mg/L.

Table 3. 2 List of parameters and instruments

Parameter	Instrument
pH	A Model F21 Horibra pH- meter
Temperature (°C)	A model F21 Horibra Thermometer
Alkalinity (mL)	Titration
Turbidity (FUA)	The HACH Turbidity meter Model 2100
DOC	O.I. analytical 1010 TOC analyze
UV_{254}	Perkin-Elmer Model Lambda 25, UV/VIS spectrophotometer
Iron	DR/890 colorimeter
THMs	Agilent 6890 Series Gas Chromatographic with ECD detector
Free chlorine	DR/890 colorimeter

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Shallow well water characteristics

Characteristics of contaminated shallow well water from Mae-Hia landfill site in Chiang Mai, Thailand of water sample was collected in November 2013 to January 2014 are reported in Table 4.1.

Table 4.1 Characteristics of contaminated shallow well water

Parameters	Contaminated shallow well water in November 2013	Contaminated shallow well water in January 2014
pH	7.2	7.4
Temperature (°C)	24.9	25.0
Alkalinity (mg/L as $CaCO_3$)	1230	1290
Turbidity (FAU)	14.0	16.0
Electrical conductivity (mS/cm)	5.61	4.26
UV_{254} (cm^{-1})	1.577	1.545
DOC (mg/L)	11.4	12.6
SUVA (L/mg-m)	13.8	12.3

pH of contaminated shallow well water was 7.2 and 7.4. The pH values in this study were basic due to this landfill site was closed for long time (approximately 24 years). Andreottola, Cannas et al. (1990) explained the pH of landfill site, which is close 2- 3 years was acidic because waste degradation by anaerobic caused increase in the solubilization of chemical substances and a decrease in the sorptive capacity of wastes. After that, it become basic due to the destruction of fatty acids caused brought about the increase in pH and alkalinity that agree with the pH values in this study.

The turbidity of contaminated shallow well water was 14.0 FAU and 16.0 FAU of in case of water sample was collected in November 2013 and in January 2014, respectively (approximately 14.0 NTU and 16.0 NTU, respectively). The value of turbidity in this study was higher than the turbidity of the previous study as same as landfill that Jiarsirkul (2003) reported the value of turbidity was 5.9 NTU (approximately 5.9 FAU). In case of EC values, the EC values of contaminated shallow well water were 5.61 and 4.26 mS/cm in case of water sample was collected in November 2013 and January 2014, respectively. The EC value and turbidity of contaminated shallow well water in this study were higher than those of other shallow well water due to this study was collected from landfill site, which is high contaminated.

The alkalinity level indicated the capacity of solutes such as a carbonate, bicarbonate and a hydroxide that contained in natural water to react with acid (Hem, 1985). Moreover, it was described that the principle source of alkalinity was bicarbonate presenting in the most natural water. Alkalinity of contaminated shallow well water was very high (1230 and 1290 mg/L as $CaCO_3$ in case of water sample was collected in November 2013 and January 2014, respectively). If water sample has low alkalinity, the water sample must be added with alkalinity during coagulation process. Because of the reaction of coagulation to produce floc must be neutralized (Homklin, 2004). Thus, this study was not necessary to add alkalinity to contaminated shallow well water during coagulation.

Organic matters of contaminated shallow well water in term of DOC concentrations were 11.4 and 12.6 mg/L in November 2013 and January 2014, respectively. The high DOC concentration in shallow well water might be due to the contaminated from landfill leachate. In addition, since the shallow well was not well protected, leaves fell into the well. Therefore, this also could be resulted in high DOC concentration when compared with the previous study. Jiarsirkul (2003) reported DOC concentration at Mae-Hia landfill site was 9.24 mg/L, that was slightly lower than this study.

Aromatic groups in organic matters were indicated by using UV absorbance at wavelength 254 nm. This was due to organic matters have efficiency to absorb and low disturb from other compounds in this wavelength. UV_{254} in the contaminated shallow well waters were 1.577 and 1.545 cm^{-1} in November 2013 and January 2014, respectively. Thus, the water sample might contain extremely high concentration of aromatic group. The previous study presented UV_{254} of the same shallow well in 2003-2004, which was 15.84 cm^{-1}. It was explained that high values of UV_{254} owing to the contaminated from landfill caused high concentration of aromatic rings (Jiarsirkul, 2003).

SUVA calculated by using UV_{254} divided by DOC concentration and multiplied by 100. In this study, SUVA value of contaminated shallow well water in November 2013 was 13.8 L/mg-m and that of contaminated shallow well water in January 2014 was 12.3 L/mg-m. SUVA was used to be an indicator of the humic content. If SUVA in water sample was high (>3.00 L/mg-m) that meant the water contained primarily humic organic matter (e.g., hydrophobic compounds) and responsive to coagulation process (USEPA, 1999). Aromatic, carboxyl, carbonyl, methoxly and aliphatic units were compounds of humic molecules (Stevenson, 1982). In addition, SUVA was defined as a surrogate parameter, which was used to estimate hydrophobic natural organic matters. It was explained that if water has SUVA values more than 3.00 L/mg-m, it showed more humic -like in character, higher in apparent molecular weight, and more readily removed by coagulation process (Edzwald, 1993). Thus, from the high SUVA value of contaminated shallow well water in this study, it can be indicate that organic matter in this shallow well water had more humic content and appropriated to use coagulation process to remove those compounds.

4.2 Optimal dosage and pH in coagulation process

This study used coagulation as a pre-treatment process. Ferric chloride ($FeCl_3$) was utilized as coagulant. Jar test was used to determine the optimal parameters of coagulation process, i.e. coagulant dosages and pH of water sample. The optimal dosage of $FeCl_3$ was determined from the percent reduction of DOC and UV_{254}. Figure 4.1 shows jar test experiment for finding the optimal dosage of $FeCl_3$.

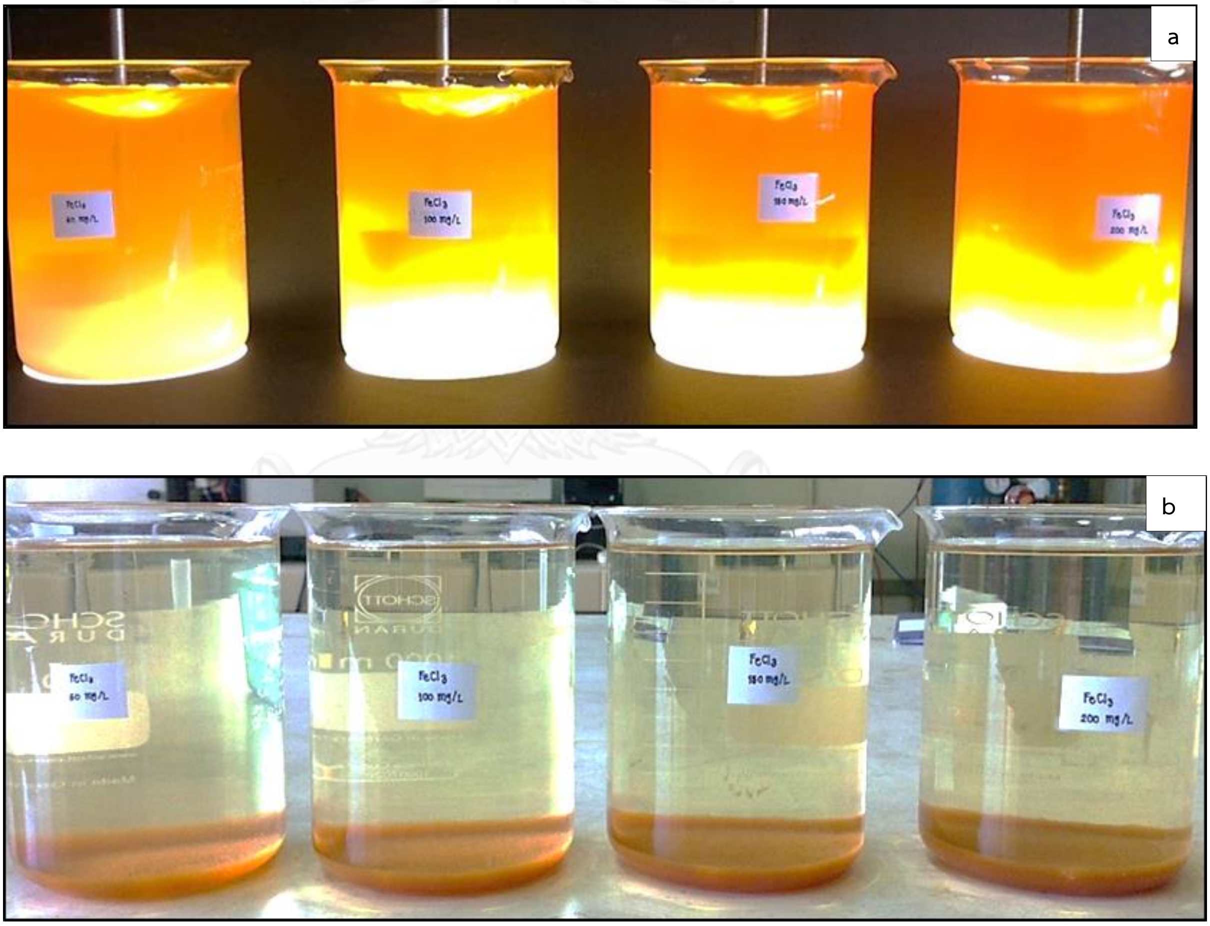


Figure 4.1 Jar test experiment for finding the optimal dosage of $FeCl_3$: (a) mixing period, (b) settling period

After settling for 1 hour, supernatant water was collected to measure parameters (i.e. DOC, UV_{254} and SUVA). The results of DOC, UV_{254} and SUVA of treated water by coagulation for selection optimal dosage for contaminated shallow well water in November 2013 are presented in Tables 4.2.

Table 4.2 The results of DOC, UV_{254} and SUVA of treated water by $FeCl_3$ coagulation for selection optimal dosage for contaminated shallow well water in November 2013

Dosage	DOC (mg/L)	UV_{254} (cm^{-1})	SUVA (L/mg-m)
10 mg/L	9.40	1.594	16.9
25 mg/L	9.60	1.563	16.3
50 mg/L	9.40	1.533	16.3
75 mg/L	9.20	1.506	16.4
100 mg/L	9.10	1.482	16.3

From Table 4.2, DOC concentration in contaminated shallow well water was 11.4 mg/L. After treated water by $FeCl_3$ coagulation, DOC concentration at dosage 10, 25, 50, 75 and 100 mg/L were reduce 9.40, 9.60, 9.40, 9.20 and 9.10 mg/L, respectively. Whereas, the values of UV_{254} in treated water by $FeCl_3$ coagulation at dosage 10, 25, 50, 75 and 100 mg/L were 1.594, 1.563, 1.533, 1.596 and 1.482 cm^{-1}, respectively.

Figure 4.2 shows DOC concentration of $FeCl_3$ coagulation at dosage 10, 25, 50, 75 and 100 mg/L in November 2013. Percent reduction of DOC by $FeCl_3$ coagulation at dosage 10, 25, 50, 75 and 100 mg/L were 18%, 16%, 18%, 19% and 20%, respectively. From this figure, the highest percent reduction of DOC by $FeCl_3$ was found at dosage 100 mg/L that could reduce 20% of DOC.

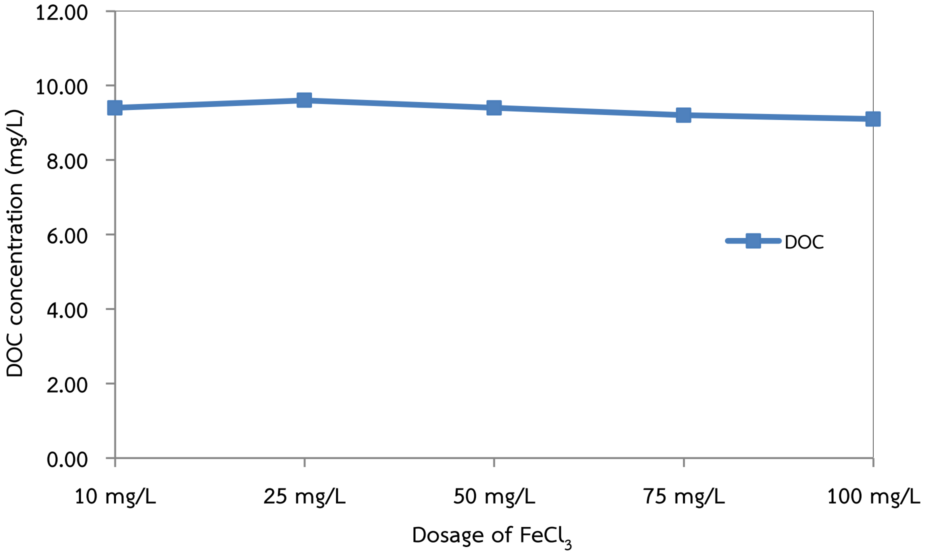


Figure 4.2 DOC concentration of $FeCl_3$ coagulation at different dosage in November 2013

This study not only considered the reduction DOC concentration to select optimal dosage of $FeCl_3$, but also considered the reduction of UV_{254} that is shown in Figure 4.3

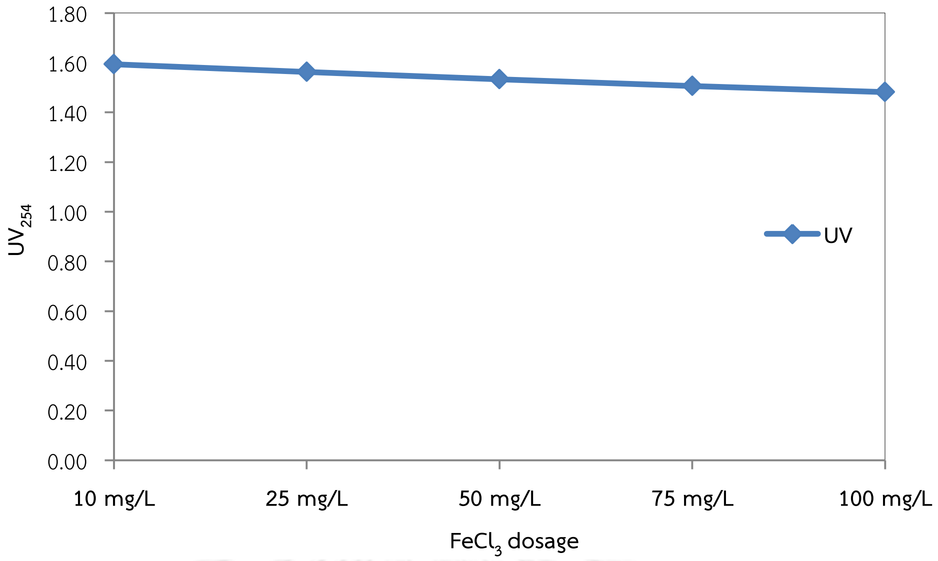


Figure 4.3 UV_{254} of $FeCl_3$ coagulation at different dosage in November 2013

Figure 4.3 illustrates UV_{254} value of $FeCl_3$ coagulation at dosage 10, 25, 50, 75 and 100 mg/L in November 2013. The value of UV_{254} of contaminated shallow well water was 1.577 cm^{-1}. After treated by coagulation, percent reductions of UV_{254} were 1%, 3%, 5% and 6% at dosage 25, 50, 75 and 100 mg/L, respectively. UV_{254} was reduced after coagulation process due to organic matter was removed, which is related with absorbance of UV_{254} (Krutklom, 2013). The highest percent reduction of UV_{254} was dosage 100 mg/L (6%). Therefore, based on the percent reduction of DOC and UV_{254}, the optimal dosage of $FeCl_3$ for contaminated shallow well water in November 2013 was selected at dosage 100 mg/L.

For the contaminated shallow well water which collected in January 2014, the results of DOC, UV_{254} and SUVA of treated water by coagulation are presented in Table 4.3.

Table 4.3 The results of DOC, UV_{254} and SUVA of treated water by coagulation for selection optimal dosage for contaminated shallow well water in January 2014

Dosage	DOC (mg/L)	UV_{254} (cm^{-1})	SUVA (L/mg-m)
50 mg/L	12.3	1.442	11.7
100 mg/L	9.70	1.373	14.2
150 mg/L	10.3	1.296	12.6
200 mg/L	10.3	1.223	11.9

From Table 4.3, DOC concentration in contaminated shallow well water was 12.6 mg/L. After treated water by $FeCl_3$ coagulation, DOC concentration at dosage 50, 100, 150 and 200 mg/L were reduce 12.3, 9.70, 10.3 and 10.3 mg/L, respectively. The values of UV_{254} in treated water by $FeCl_3$ coagulation at dosage 50, 100, 150 and 200 mg/L were 1.442, 1.373, 1.296 and 1.223 cm^{-1}, respectively.

Figure 4.4 shows DOC concentration in treated water of $FeCl_3$ coagulation at dosage 50, 100, 150 and 200 mg/L. The results showed that percent reduction of DOC were 2%, 23%, 18% and 18% at $FeCl_3$ dosage 50, 100, 150 and 200 mg/L, respectively. From this figure, the highest percent reduction of DOC concentration by $FeCl_3$ coagulation was at dosage 100 mg/L that could reduce 23% of DOC.

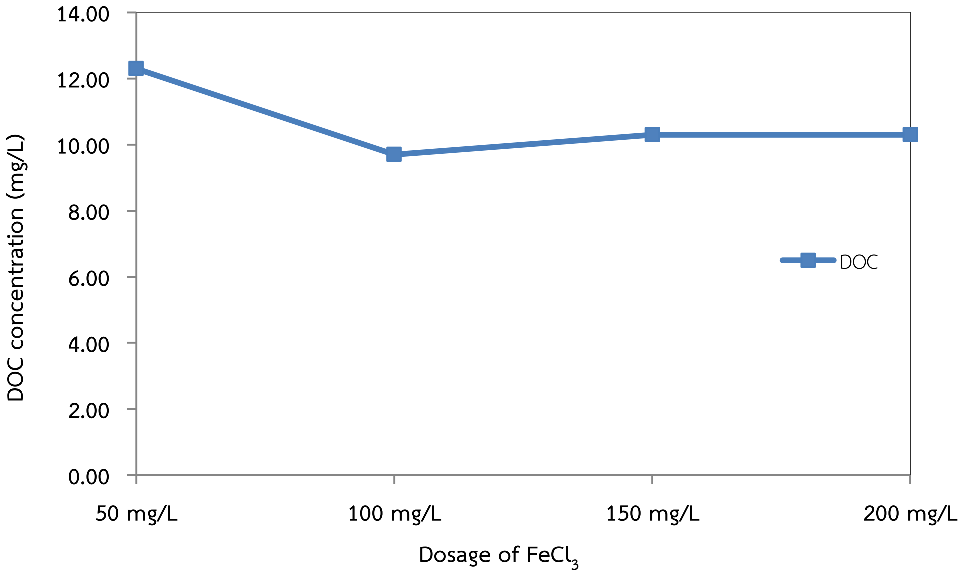


Figure 4.4 DOC concentration of $FeCl_3$ coagulation at different dosage in January 2014

Figure 4.5 presents UV_{254} value of $FeCl_3$ coagulation at dosage 50, 100, 150, and 200 mg/L. The value of UV_{254} of contaminated shallow well water was 1.545 cm^{-1}. After treated by coagulation, percent reductions of UV_{254} were 7%, 11%, 16% and 21% at dosage 50, 100, 150 and 200 mg/L, respectively. UV_{254} was reduced after coagulation process due to organic matter was removed, which is related with absorbance of UV_{254} (Krutklom, 2013).

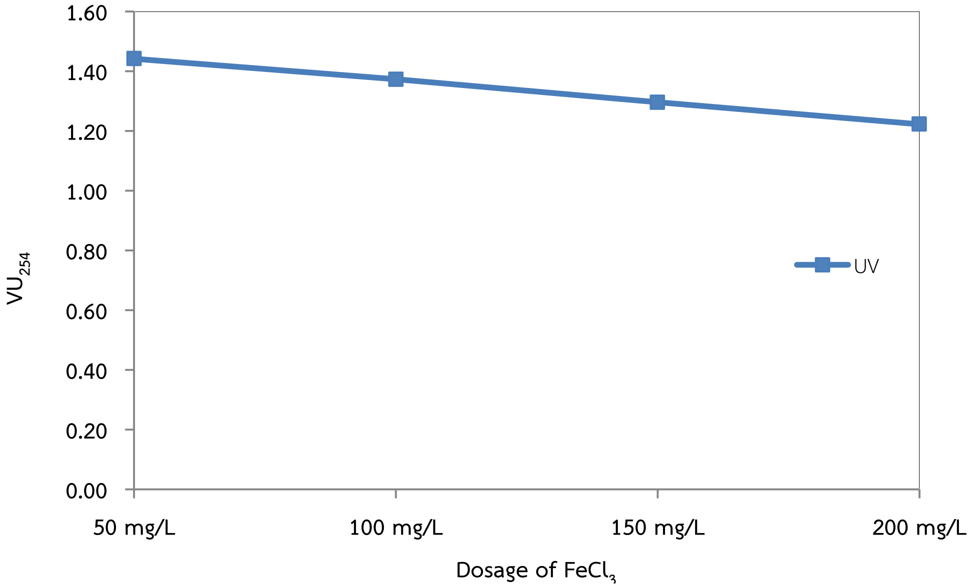


Figure 4.5 UV_{254} of $FeCl_3$ coagulation at different dosage in January 2014

$Fecl_3$ coagulation at dosage 200 mg/L can reduce UV_{254} with the highest percent reduction (21%). Although, $FeCl_3$ at dosage 200 mg/L is the best condition for reduce UV_{254} but this study selected $FeCl_3$ at dosage 100 mg/L because percent reduction of UV_{254} at dosage 100 mg/L and 200 mg/L were slightly different. From this reason, choosing $FeCl_3$ at dosage 100 mg/L is the best condition to remove contaminated in water sample because it utilize lower chemical consumption.

Consequently, it was concluded that the optimal condition of $FeCl_3$ coagulation was 100 mg/L both for contaminated shallow well water in November 2013 and January 2014. Subsequently, the optimal pH was tested by using the $FeCl_3$ coagulation at the optimal dosage that was investigated in the previous section.

Figure 4.6 shows jar test for finding the optimal pH from the optimal dosage that was chosen in the previous section.

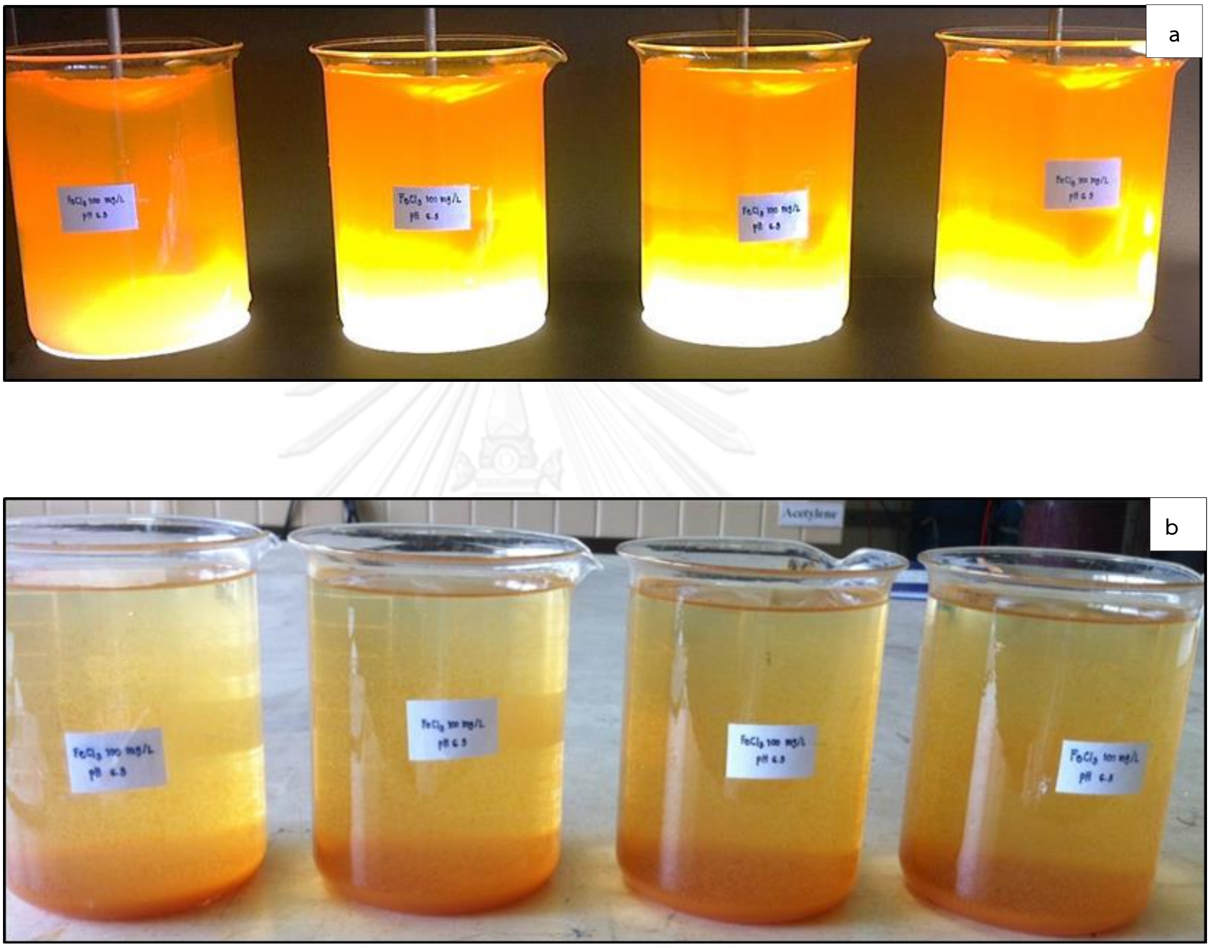


Figure 4.6 Jar tested experiment for finding the optimal pH of $FeCl_3$: (a) mixing period, (b) settling period

After settling for 1 hour, supernatant water was collected to measure parameters (i.e. DOC, UV_{254} and SUVA). The results of optimal pH by $FeCl_3$ coagulation for contaminated shallow well water in November 2013 are presented in Tables 4.4.

Table 4.4 The results of DOC, UV_{254} and SUVA of treated water by coagulation for selection optimal pH for contaminated shallow well water in November 2013

pH	DOC (mg/L)	UV_{254} (cm^{-1})	SUVA (L/mg-m)
6.5	9.20	1.383	15.0
7.5	9.60	1.482	15.5
8.5	10.3	1.522	14.8

From Table 4.4, DOC concentration in treated water by $FeCl_3$ coagulation at pH 6.5, 7.5 and 8.5 were 9.2, 9.60 and 10.3 mg/L, respectively. The values of UV_{254} in treated water at pH 6.5, 7.5 and 8.5 were 1.383, 1.482 and 1.522 cm^{-1}, respectively.

Figure 4.7 displays DOC concentration in treated water by $FeCl_3$ coagulation of $FeCl_3$ coagulation at pH 6.5, 7.5 and 8.5 in November 2013.

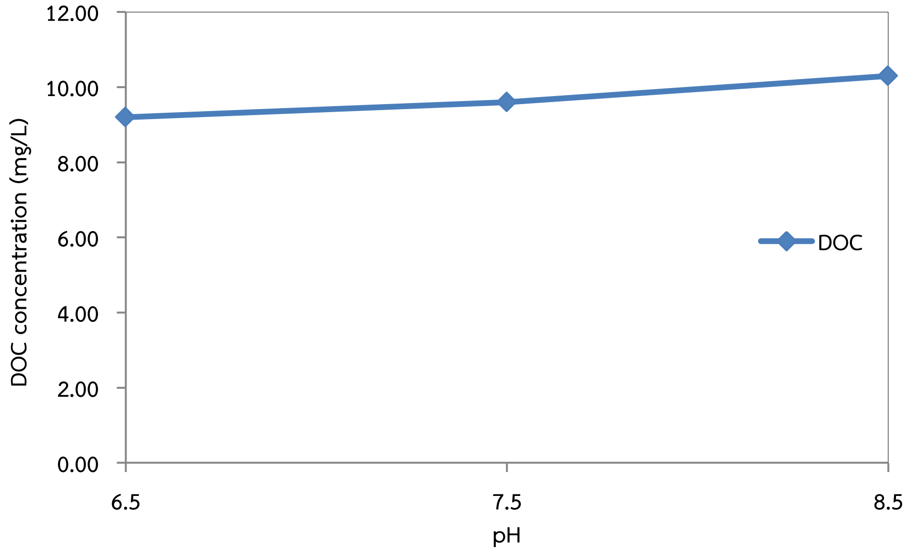


Figure 4.7 DOC concentration of $FeCl_3$ coagulation at different dosage in November 2013

Percent reduction of DOC by $FeCl_3$ coagulation at pH 6.5, 7.5 and 8.5 were 19%, 16% and 10%, respectively. This study not only considered the reduction DOC concentration to select optimal dosage of $FeCl_3$, but also considered the reduction of UV_{254} that is shown in Figure 4.8

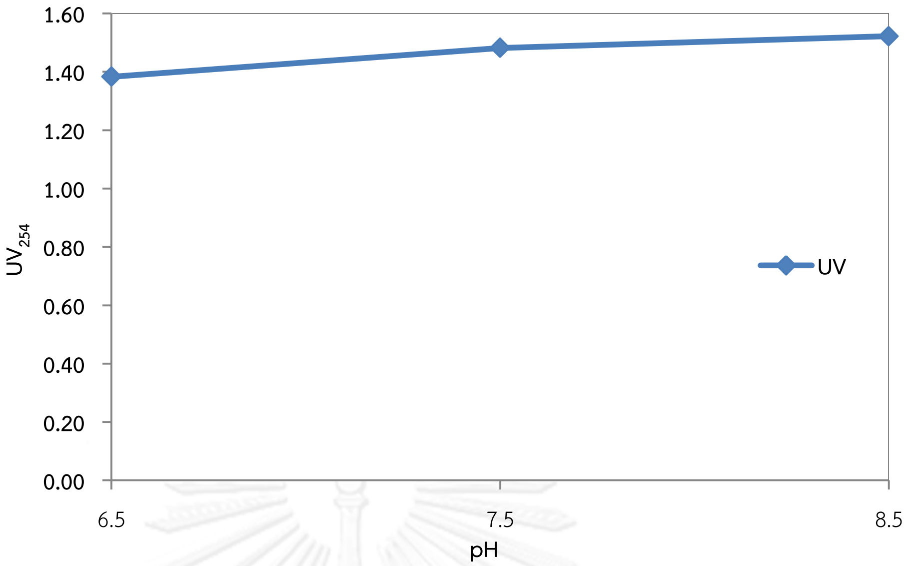


Figure 4.8 UV_{254} of $FeCl_3$ coagulation at different dosage in November 2013

From the results, percent reduction of UV_{254} was 12%, 6% and 4% at pH 6.5, 7.5 and 8.5, respectively. The highest percent reduction of UV_{254} was pH 6.5 (12%). Therefore, based on the percent reduction of UV_{254}, the optimal pH of $FeCl_3$ for contaminated shallow well water in November 2013 was selected at pH 6.5.

For contaminated shallow well water in January 2014, selected optimal pH was concentrated as same as those in November 2013. The results of DOC, UV_{254} and SUVA of treated water by coagulation for selection optimal pH in January 2014 are shown in Table 4.5.

Table 4.5 The results of DOC, UV_{254} and SUVA of treated water by coagulation for selection optimal pH for contaminated shallow well water in January 2014

pH	DOC (mg/L)	UV_{254} (cm^{-1})	SUVA (L/mg-m)
6.5	9.5	1.228	12.9
7.5	9.7	1.373	14.2
8.5	11.6	1.610	13.9

From Table 4.5, DOC concentration by $FeCl_3$ coagulation at pH 6.5, 7.5 and 8.5 were 9.5, 9.70 and 11.6 mg/L, respectively. The values of UV_{254} at pH 6.5, 7.5 and 8.5 were 1.228, 1.373 and 1.610 cm^{-1}, respectively.

Figure 4.9 presents DOC concentration of $FeCl_3$ coagulation at pH 6.5, 7.5 and 8.5 in January 2014. Percent reduction of DOC by $FeCl_3$ coagulation at pH 6.5, 7.5 and 8.5 were 25%, 23% and 8%, respectively.

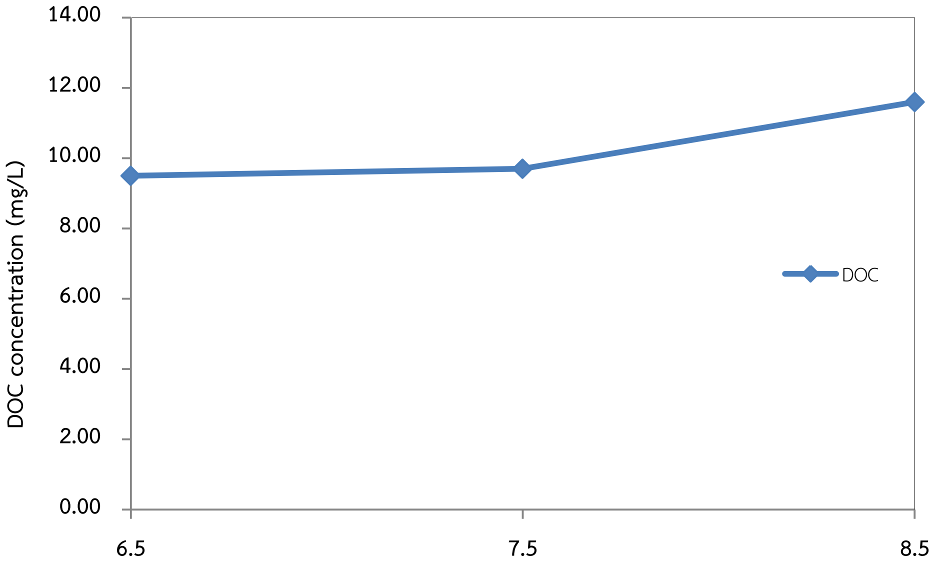


Figure 4.9 DOC concentration of $FeCl_3$ coagulation at different dosage in January 2014

This study not only considered the reduction DOC concentration to select optimal dosage of $FeCl_3$, but also considered the reduction of UV_{254} that is shown in Figure 4.10

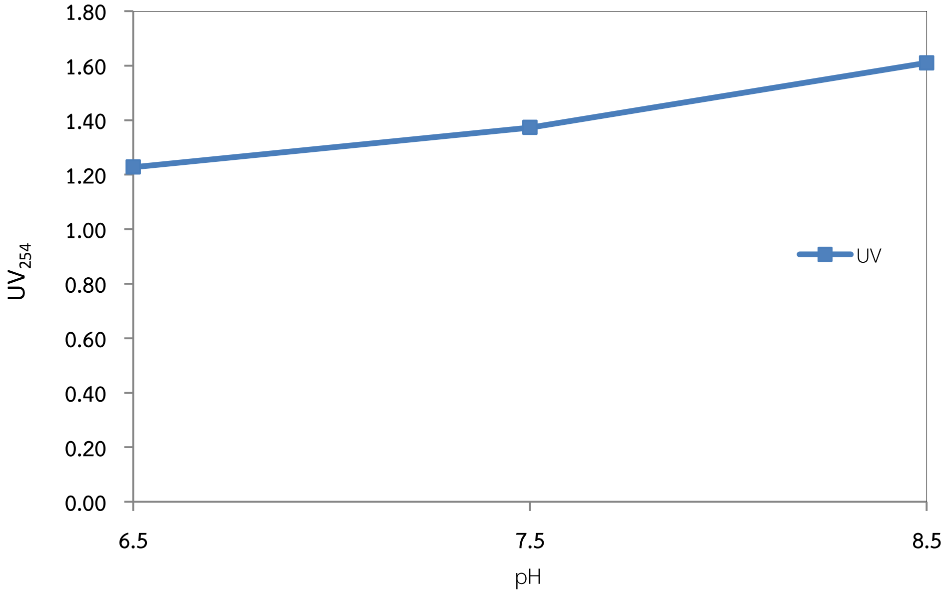


Figure 4.10 UV_{254} of $FeCl_3$ coagulation at different dosage in January 2014

From the results, percent reduction of UV_{254} was 21% and 11% at pH 6.5 and 7.5, respectively. For controlled pH 8.5, it had not efficiently to reduce UV_{254}. The highest percent reduction of UV_{254} was pH 6.5 (21%).

Accordingly, it can be concluded that pH 6.5 was the highest percent reduction of DOC (19% for contaminated shallow well water in November 2013 and 25% for contaminated shallow well water in January 2014) at $FeCl_3$ dosage 100 mg/L. The results was related to the studied of Konieczny, Bodzek et al. (2006) which reported that the optimal pH for $FeCl_3$ coagulation are in a range of 5.5-8.8. Moreover, Edwards (1997) explained efficiency of coagulation to remove NOM fraction is higher under acidic condition in wastewater, whereas coagulation had a high efficiency under basic condition in seawater.

4.3 $FeCl_3$ coagulation combined with CM membrane

$FeCl_3$ coagulation combined with ceramic membrane was conducted with the contaminated shallow well water collected in January 2014. The efficiency of DOC reduction via $FeCl_3$ coagulation combined with CM membrane filtration at the optimal $FeCl_3$ dosage (100 mg/L) and pH 6.5 was elucidated. The results are shown in Table 4.6.

Table 4.6 Water characteristics of contaminated shallow water, treated water by coagulation and treated water by coagulation combined with CM membrane

Water samples	pH	Temp. (°C)	DOC (mg/L)	UV_{254} (cm^{-1})	SUVA (L/mg-m)
Contaminated shallow well water in January 2014	7.4	25.0	12.6	1.545	12.3
Treated water by coagulation Process at $FeCl_3$ 100 mg/L and pH 6.5	6.6	25.0	9.50	1.228	12.9
Treated water by coagulation combined with CM membrane at $FeCl_3$ 100 mg/L and pH 6.5	7.5	25.0	8.90	1.179	13.2

From the results, $FeCl_3$ coagulation could remove DOC by 25% while CM membrane filtration could increasingly remove DOC by 4%. Percent of DOC reduction from coagulation combined with CM membrane is hardly higher than treated water by a unit of coagulation process, it might be due to complete flocculation was unnecessary for membrane filtration (Rakruam & Wattanachira, 2013). Moreover, the result was agreed with the studied of Li, Wu et al. (2011) which reported that the hybrid system of coagulation and membrane filtration had higher percent reduction of DOC (34-54%) than a unit of coagulation or membrane filtration. From the results, it can be indicated that $FeCl_3$ coagulation can employed to use as pretreatment of CM membrane filtration which had the larger pore size for increase the percent DOC reduction and also reduce membrane fouling. Coagulation process can dramatically reduce membrane fouling when using with several coagulants such as aluminum-based and $FeCl_3$ (Lehman, Admam, & Liu, 2008).

Aromatic hydrocarbons in contaminated shallow well water, treated water by coagulation and treated water by coagulation combined with CM membrane were interpreted by using UV_{254}. The result presented that UV_{254} of treated water by coagulation and treated water by coagulation combined with CM membrane were reduced by 20% and 24%, respectively (see Table 4.6). Percent UV_{254} reduction of treated water by coagulation in this study is lower than the study of Musikavong, Wattanachira et al. (2004) that reported that $FeCl_3$ coagulation can reduce UV_{254} with approximately 50-70%. It might be because of the concentration of aromatic group in this study was lower than the study of Musikavong, Wattanachira et al. (2004). In case of SUVA, the value of SUVA in this study is high because this water sample was enriched in humic substances.

The water quality of treated water by coagulation and treated water by coagulation combined with CM membrane compared with water quality of water supply are shown in Table 4.7.

Table 4.7 Treated water compared with water quality of water supply

Parameters	A	B	C	Reference
pH	6.6	7.5	7- 8.5	Newater, 1998
DOC (mg/L)	9.5	8.9	< 0.5	Newater, 1998
Iron (mg/L)	0.04	0.03	< 0.3	WHO, 2006
SUVA (L/mg-m)	12.9	13.2	< 2	USEPA, 1998

A = treated water by coagulation

B = treated water by coagulation combined with CM membrane

C = standard

From the results, it could be explain that treated water by coagulation process and treated water by combined with CM membrane did not have efficiently to remove

DOC and SUVA value to meet the standard of water supply due to DOC concentration and SUVA of treated water were higher than the standard value. In case of iron concentration, treated water by coagulation process and treated water by combined with CM membrane had Iron concentration lower than the standard of iron concentration of water supply from WHO (2006). Therefore, the using of $FeCl_3$ coagulation and coagulation with CM membrane filtration were not appropriate to reduce DOC concentration from shallow well water near landfill site to meet the standard of water supply.

4.4 Trihalomethane (THMs) formation in contaminated shallow well water and their reduction by coagulation and CM membrane

Trihalomethane (THMs) compound concludes four species i.e. chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$). THMs could be detected in water supply during chlorination process due to THMs could form by reaction between chlorine and NOM in water. This study focuses on reducing THMs precursors that the main factor for the formation of THMs. Thus, THMs in water samples including contaminated shallow well water, treated water by coagulation and treated water by coagulation combined with CM membrane filtration was determined. Hypochlorite was applied to examine formation of THMs in this study by adding 3 mg/L of chlorine dosage to water samples that agreed with Muttamara et al. (1995). They added chlorine dosage 3, 5 and 10 mg/L to form THMs.

Reaction time between NOM and chlorine to form THMs was set at 24 hours that followed the Natural Environmental Board studied which adding chlorine 10 mg/L for 24 hours of contact time. Additionally, Jiarsirkul (2003) described THMs formation was occurred within the first 24 hours.

In contaminated shallow well water, treated water by coagulation and treated water by coagulation combined with CM membrane that consist of chloroform, bromodichloromethane and bromoform in this study were shown in Table 4.8

Table 4.8 THMs species in contaminated shallow well water, treated water by coagulation process and treated water by coagulation combined with CM membrane

THMs species	A	B	C
$CHCl_3$ (μg/L)	1.61	0.94	1.16
$CHBrCl_2$ (μg/L)	-	5.09	-
$CHBr_2Cl$ (μg/L)	-	-	-
$CHBr_3$ (μg/L)	9.23	-	3.30
Total (μg/L)	10.84	6.03	4.46

A is contaminated shallow well water, B is treated water by coagulation process

C is treated water by coagulation combined with CM membrane

From the table, Chloroform specie was found in all water samples. For bromodichloromethane specie was found only in treated water by coagulation process. Whereas, dibromochloromethane specie was not found in all water samples.

Bromoform specie was found in contaminated shallow well water and treated water by coagulation combined with CM membrane.

This study focuses on chloroform species because this species is the dominant species (Thacker, Kaur, & Rudra, 2002) and commonly found in natural water. Srimuang (2011) demonstrated that chloroform was largest found among the THMs species. Figure 4.11 presents chloroform concentration of contaminated shallow well water treated water by coagulation process and treated water by coagulation combined with CM membrane filtration and percent reduction of chloroform by coagulation process and coagulation combined with CM membrane filtration.

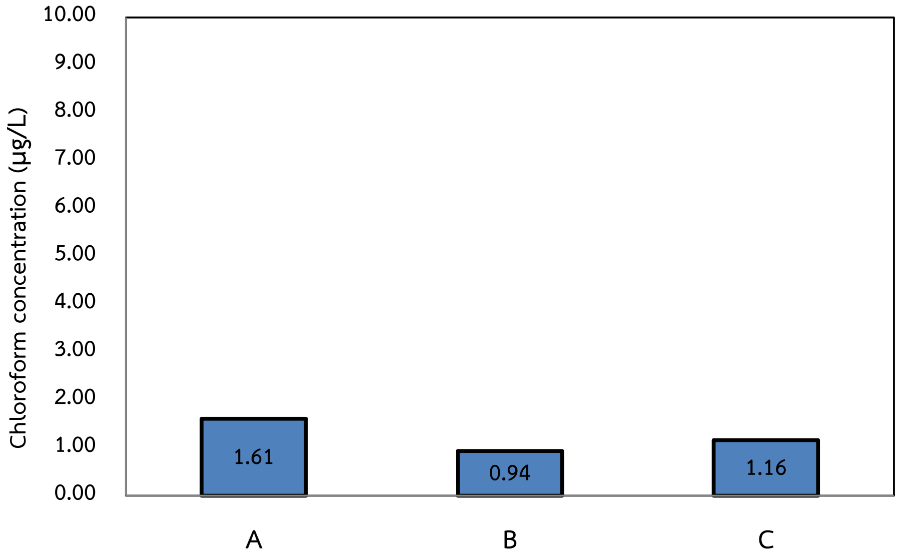


Figure 4.11 Percent reduction of chloroform in water samples

From the figure 4.11, Chloroform concentration in contaminated shallow well water was 1.61 µg/L. The results showed that chloroform in this water source was relatively low when compared to the chloroform in other source and standard in water supply. It might be due to DOC in old landfill was difficult to break down that it was precursor to react with chlorine in water samples.

From the results, coagulation process could reduce THMs in term of chloroform from 1.61 to 0.94 µg/L. For coagulation combined with CM membrane, it could reduce chloroform from 1.61 to 1.16 µg/L. As a result, it could be conclude that the reduction of chloroform concentration by coagulation process was higher than coagulation combined with CM membrane but the residual chloroform concentration of treated water by both process were closely. Furthermore, the results showed that chloroform concentration of contaminated shallow well water after treated by coagulation and coagulation combined with CM membrane filtration was lower than standard of water supply (0.3mg/L) which set by WHO 2006.

The result of reduction of chloroform by $FeCl_3$ coagulation combined with CM membrane filtration was compared with that reduction by using other process. Jutatipatai, Wattanachira, & Wongrueng (2014) reported that the using of powder activated carbon (PAC) absorption combined with CM membrane filtration can reduce chloroform concentration in the same water samples with this study from 1.61 µg/L to 1.30 µg/L. It was found that $FeCl_3$ coagulation combined with CM membrane filtration had a high efficient to reduce chloroform more than PAC combined with CM membrane filtration. Accordingly, this result can predicate that $FeCl_3$ coagulation is better than adsorption by PAC to reduce chloroform.

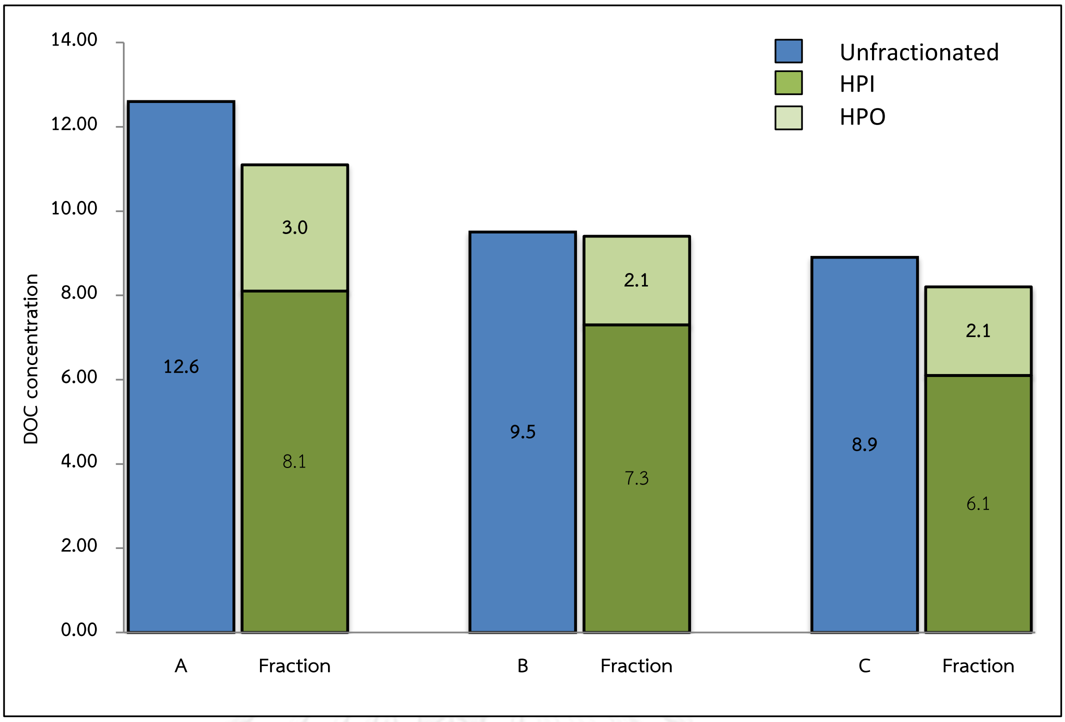
4.5 Organic matter fractionation

The contaminated shallow well water, treated water by coagulation at the optimal dosage of $FeCl_3$ 100 mg/L and pH 6.5 and treated water by coagulation combined with CM membrane at the optimal dosage of $FeCl_3$ 100 mg/L and pH 6.5 were collected and fractionated into hydrophilic (HPI) and hydrophobic (HPO) by using DAX-8 resin fractionation. The result of fractionation was presented in term of DOC concentration that is shown in Table 4.9 and Figure 4.12.

Table 4.9 Results of DOM fractions in term of DOC concentration in water samples

Water samples	**DOM fractions**		**HPI + HPO**	**Unfractionated water**	**% Diff**
	HPI	**HPO**			
Contaminated shallow well water	8.10	3.00	11.1	12.6	12
Treated water by coagulation Process	7.30	2.10	9.40	9.50	1
Treated water by coagulation combined with CM membrane	6.10	2.10	8.20	8.90	8

Note: %Diff = (Unfractionated water – (HPI+HPO)) x 100 / unfractionated



A is contaminated shallow well water.

B is treated water by coagulation process

C is treated water by coagulation combined with CM membrane

Figure 4.12 Proportions of DOC concentrations in water samples

Percent difference of DOC concentration between summarization of each fractionated (HPI and HPO fractions) and unfractionated water in shallow well water, treated water by coagulation process and treated water by coagulation combined with CM membrane were 12%, 1% and 8%, respectively.

The level of inaccuracy was accepted in fractionation process was often reported to give as much 10-15% tolerance recovery (Day, Beckett, Hart, & Mckelvie, 1991). Additionally, percent different was acceptable in the range of 8-12% (Croue, Martin, Simon, & Legube, 1993). The missing of DOC concentration may occur during the elution process in fractionation (Srimuang, 2011). From the obtained results, it can be concluded that percent different from fractionated shallow well water, treated water by coagulation process and treated water by coagulation combined with CM membrane were accepted.

DOC concentration in the contaminated shallow well water was 12.6 mg/L comprising of 8.10 mg/L of HPI fraction and 3.0 mg/L of HPO fraction. The result of this study was lower DOC concentration than the previous study at the same location (Jiarsirkul, 2003). They illustrated that the DOC concentration in shallow well water was 14.5 mg/L comprising of 5.75 mg/L of HPI fraction and 7.10 mg/L of HPO fraction.

DOC concentrations of treated water by coagulation process were 9.50 mg/L which comprising of 7.30 mg/L of HPI fraction and 2.10 mg/L of HPO fraction. Whereas, in treated water by coagulation combined with CM membrane, DOC concentration was 8.90 mg/L comprising of 6.10 mg/L and 2.10 mg/L of HPI and HPO fraction, respectively.

Percent DOC distribution of HPO and HPI in contaminated shallow well water, treated water by coagulation process and treated water by coagulation combined with CM membrane are presented in Figure 4.13

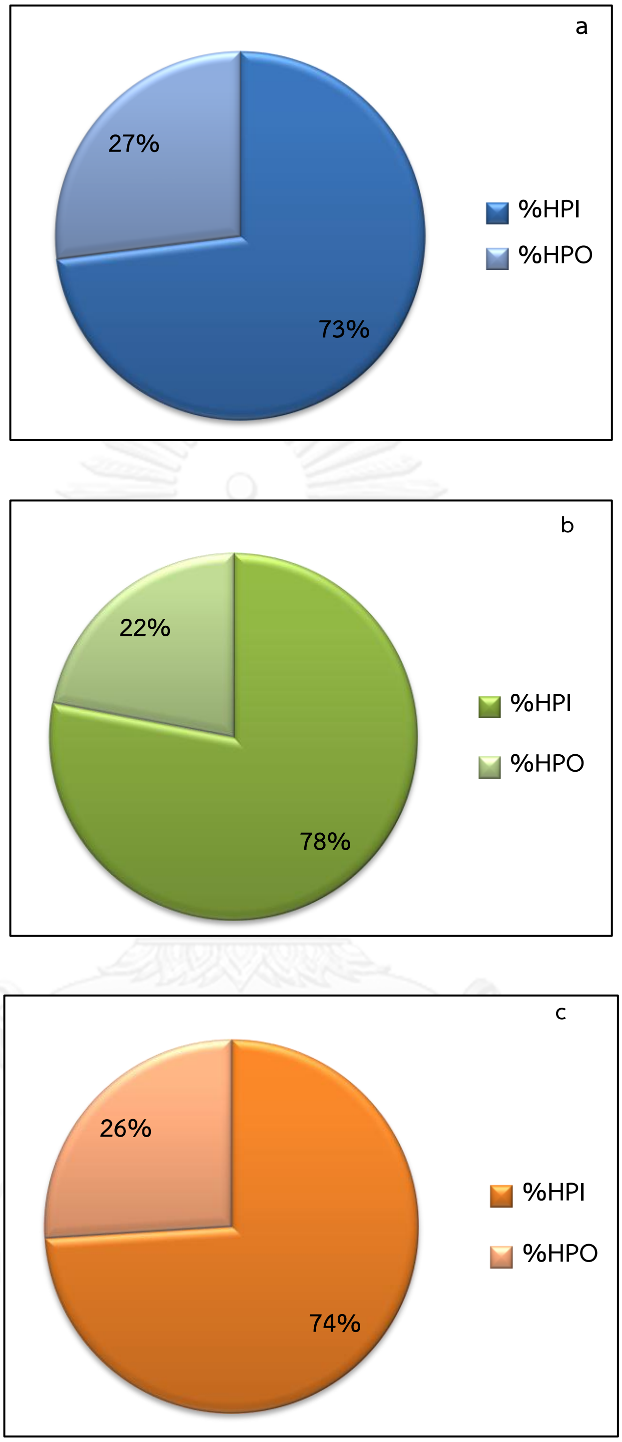


Figure 4.13 Percent DOC distribution of HPO and HPI in water samples: (a) contaminated shallow well water, (b) treated water by coagulation process and (c) treated water by coagulation combined with CM membrane

In contaminated shallow well water, it was observed that percent distribution of DOC concentrations of HPI and HPO fractions were 73% and 27%, respectively. In case of treated water by coagulation process, percent distribution of DOC concentrations of HPI and HPO fractions were 78% and 22%, respectively. And in case of treated water by coagulation combined with CM membrane, percent distribution of DOC concentrations of HPI and HPO fractions were 74% and 26%, respectively.

Percent DOC distribution of contaminated shallow well water obtained from this studied was compared with percent DOC distribution of other water sources which it is presented in Table 4.10.

Table 4.10 Percent DOC distribution of shallow well water compared with other water sources

Water source	DOC (mg/L)	% DOM fraction		References
		HPI	HPO	
Ping River, Chiang Mai Province				
- Cold season	2.30	57	43	Rakruam and Wattanachira, 2013
- Rainy season	2.00	56	44	
- Summer season	2.20	54	46	
Ping River, Chiang Mai Province				
- Raw water	4.77	58	42	Krutklom, 2013
-Treated water by coagulation	3.32	70	30	
-Treated water by in-line coagulation and CM membrane filtration	3.39	66	34	
Chao Phraya River, Bangkok	4.70	60	40	Panyapinyopol, Marhaba et al., 2005

Table 4.10 Percent DOC distribution of shallow well water compared with other water sources (continue)

Water source	DOC (mg/L)	% DOM fraction		References
		HPI	HPO	
Mae Hia reservoir, Chiang Mai Province	6.40	51	49	Phumpaisanchai, 2009
Bhumibol Dam, Tak Province	2.5	51	49	
U-Tapao canal, Songkla Province				Inthanuchit, 2009
- Rainy season	10.7	54	46	
- Dry season	6.9	52	48	
Mae Hia landfill site, Chiang Mai Province				This study
-contaminated shallow well water	11.1	73	27	
-Treated water by coagulation	9.40	78	22	
-Treated water by in-line coagulation and CM membrane	8.20	74	26	

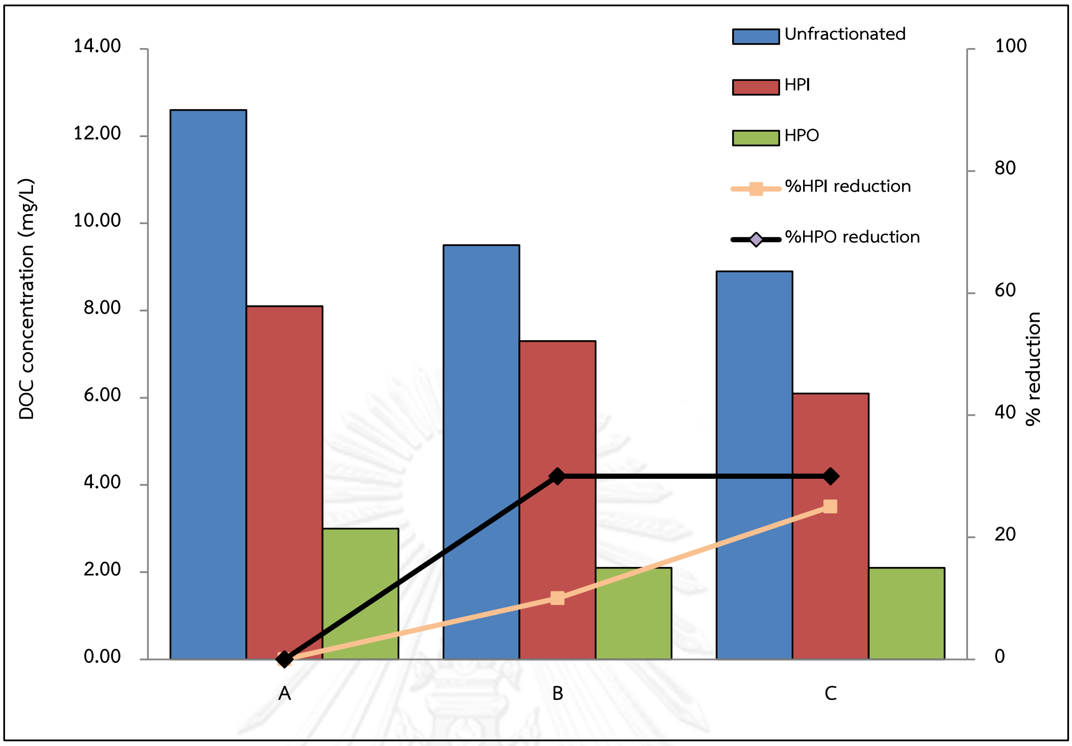
From the comparison between contaminated shallow well water and other water sources, it was found that DOC concentration in contaminated shallow well water was extremely higher than other water sources due to contaminated shallow well water was collected from landfill site. While, other water sources were collected from river, dam and canal, which they were lower contaminated than landfill site. Nevertheless, all of water samples which were included water sample in this study had percent distribution of HPI fractions more than HPO fractions.

In case of Ping river in Chiang Mai Province, Krutklom (2013) reported percent distribution of HPI fraction (70%) was higher than HPO fraction (30%) in treated water by alum coagulation that related with this study (HPI and HPO fractions were 78% and 22%, respectively). For treated water by coagulation combined with membrane process, HPI fraction in this study was higher than HPO (74% and 26%, respectively) that it also agreed with the studied of Krutklom (2013).

Figure 4.15 shows the reduction of DOC concentration by $FeCl_3$ coagulation and coagulation combined with CM membrane. In unfractionated water, coagulation process could reduce DOC concentration from 12.6 mg/L in contaminated shallow well water to 9.50 mg/L which it had percent reduction was 25%. For HPI fraction, coagulation process could reduce DOC concentration of HPI fraction from 8.10 mg/L to 7.30 mg/L which it had percent reduction 10%. For HPO fraction, coagulation process could reduce DOC concentration from 3.00 mg/L to 2.10 mg/L which it had percent reduction was 30%.

For coagulation process combined with CM membrane filtration, DOC concentration of unfractionated water was reduce from 12.6 mg/L in contaminated shallow well water to 8.90 mg/L which it had percent reduction was 29%. While, DOC concentration of HPI fraction was reduced from 8.10 mg/L to 6.10 mg/L which had percent reduction 25%. For HPO fraction, DOC concentration of HPO fraction was reduced from 3.00 mg/L to 2.10 mg/L which had percent reduction 30%.

In both of coagulation process and coagulation combined with CM membrane filtration, the percent reduction of DOC in this study was less than those studied of Jeong, Sathasivan et al. (2013) which reported that DOC reduction of HPI fraction was 55-63% at pH 5.0-6.0 of $FeCl_3$.



A is contaminated shallow well water

B is treated water by coagulation process

C is treated water by coagulation combined with CM membrane

Figure 4.14 DOC concentration of HPO and HPI in water samples and percent reduction of HPI and HPO by coagulation process and coagulation combined with CM membrane

When compared the DOC reduction of HPI and HPO fractions in this study, DOC concentrations of HPO fraction were reduced higher than HPI fractions both of treated water by coagulation process and treated water by coagulation combined with CM membrane filtration. This results was related to the studied of Kruthklom (2013) which reported percent reduction of HPO fraction (49%) was higher than HPI fraction (17%) by using coagulation. HPO fraction was easily to remove by coagulation process than HPI fraction due to HPO fraction was the component of humic substances. Maharba and

Pipada (2000) interpreted the coagulation process had high efficiently to reduce humic substances (HPO fraction) and high molecular weight organic matter than non-humic substances (HPI fraction). From the result in this study, it could conclude that water samples had the large number of humic substance and easily to remove by coagulation process. Thus, HPO fraction could reduce by coagulation process more than HPI fraction Edzwald (1993).

In case of treated water by coagulation combined with CM membrane, the trend of percent HPI and HPO reduction could reduce in both of fractions. From this reason, it could conclude that CM membrane could increase efficiently to reduce HPI which difficult to reduce by coagulation process. As a result, it was agreed with Rakruam and Wattanachira (2013) studied that reported in-line coagulation combined with ceramic membrane could reduce DOC concentration both in HPO fraction (68.5%) and HPI fraction (49.3%). Furthermore, Krutklom (2013) also presented percent reduction DOC in HPO and HPI fraction were 42% and 20%, respectively, by using alum coagulation combined with ceramic membrane.

4.6 Flux measurement

Figure 4.15 shows flux of contaminated of shallow well water and treated water by coagulation during 3 liters of filtered volume compared with deionized water. For the contaminated shallow well water, flux gradually decreased from 31.9 to 25.7 m^3/m^2day and decreased from 34.8 to 26.0 m^3/m^2day of treated water by coagulation process.

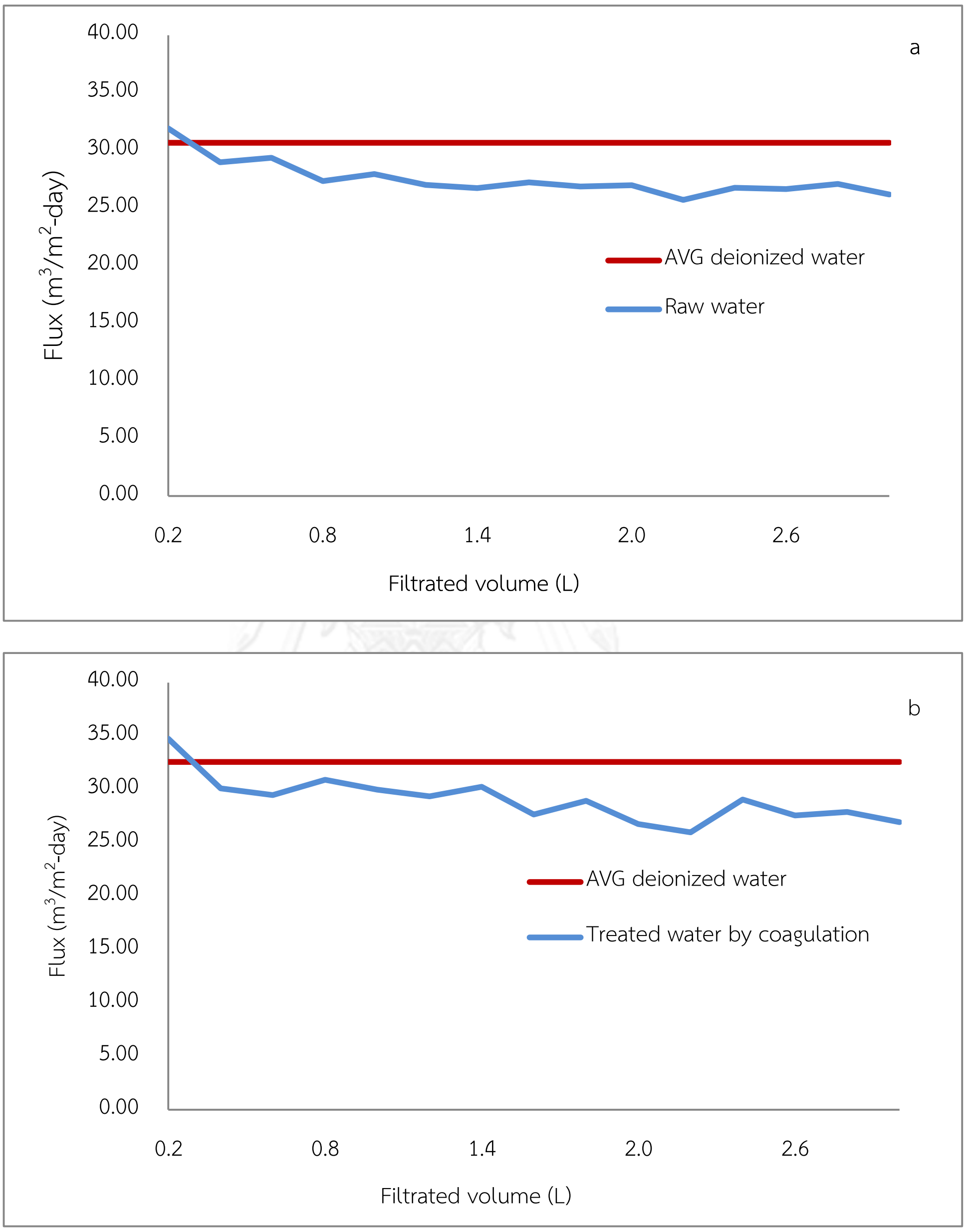


Figure 4.15 Flux (J) of water sample (a) flux of contaminated shallow well water (b) flux of treated water by coagulation process

As a result, it could conclude that treated water by coagulation combined with CM membrane had flux higher than contaminated shallow well water owing to coagulation as a pre-treatment could reduce contaminated in water sample.

The decreasing of flux could be indicated the membrane fouling in this study due to filtration of contaminated shallow water and treated water by coagulation process were carried out with higher content of organic compounds (Konieczny et al., 2006). Consequently, fouling rate could calculate by volumetric flux for contaminated shallow water or treated water by coagulation process divided by the volumetric flux of deionized water. The value from this calculated can call “Normalized flux”

Normalized flux of CM membrane of contaminated shallow well water and treated water by coagulation process during filtration is illustrated in Figure 4.16

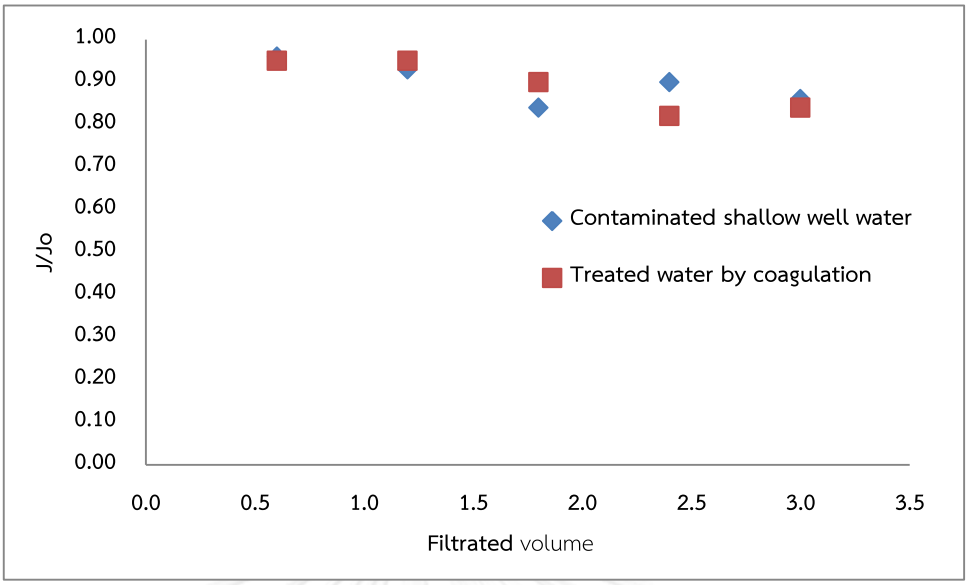


Figure 4.16 Normalized flux of water sample (J/Jo) of contaminated shallow well water and treated water by coagulation process

The value of normalized flux in contaminated shallow well water was within in range 0.79-0.99. In case of treated water by coagulation process, the value of normalized flux was close to contaminated shallow water (0.78-0.99). The value of normalized flux in this study was higher than Konieczny, Bodzek et al. (2006) that they used $FeCl_3$ coagulation combined with 0.1 µm of CM membrane. Their result was reported that the value of normalized flux was in range 0.5 -0.8. Hence, the result in this study could conclude that membrane fouling was not significantly founded during the filtration of this studied due to the values of normalized flux is nearly to 1. The value of normalized flux was related to filtrated volume. In this study, the CM membrane filtration was conducted with few filtrated volume of water sample (3 liters) and short filtrated time. Consequently, membrane fouling did not occur during the experimental period of this study.

Moreover, this study could approve that coagulation process had advantage to be a pre-treatment of CM membrane filtration in water sample with high organic substance (Konieczny et al., 2006).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The main objective of this study was to analyze DBPs precursors in contaminated shallow well water with landfill leachate at Mae Hia landfill in Chiang Mai, Thailand and to reduce DBPs precursors by $FeCl_3$ coagulation and CM membrane. Base on the experimental results, parameters that use to indicate organic matters in water sample were DOC, UV_{254} and SUVA, the following conclusion can be draw.

1. Contaminated shallow well water in this studied was high DOC concentration at 12.6 mg/L that might be contaminated form landfill site and high SUVA value that suitable for using coagulation process in pre-treatment (>3L/mg-m).

2. Optimal dosage of $FeCl_3$ coagulant in coagulation process for reduction of DOC concentration in shallow well water was 100 mg/L at pH at 6.5. At the optimal condition, $FeCl_3$ can reduce DOC concentration 25%.

3. Using coagulation combined with CM membrane was slightly high efficiently than using a unit of coagulation by $FeCl_3$. Percent reduction of DOC concentrations at the optimal dosage of $FeCl_3$ are 29% by using coagulation combined with CM membrane.

4. Chloroform concentration in contaminated shallow well water was 1.61 μg/L. After treated by coagulation and coagulation with CM membrane, the chloroform concentration was reduced to 0.94 and 1.16 μg/L, respectively.

5. Contaminated shallow well water had hydrophilic and hydrophobic fractions 8.1 and 3.0, respectively. Coagulation process and coagulation combined with CM membrane can reduce DOC concentration in term of hydrophobic fraction more than hydrophilic fraction. In addition, the using of CM membrane can increase the reduction of DOC concentration in HPI fraction which difficult to reduce by using coagulation.

6. Flux of treated water by coagulation process and coagulation combined with CM membrane were higher than flux of contaminated shallow well water. This indicates that the using coagulation as pre-treatment could increase the flux during the filtration process. The membrane fouling was

not significantly found during the course of filtration due to the values of normalized flux is nearly to 1.

5.2 Recommendations

In this study used only $FeCl_3$ as a coagulant that cannot compare DOC reduction efficiency with other coagulants. Therefore, the further study should study the DOC reduction by using others types of coagulants. This study mainly investigates the THMs formation in water samples but the THMs in fractionated water were not investigated. So, the further study should be analyzed THMs in fractionated water.

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APPENDIX

Experiment 1 Optimal dosage in coagulation process

1.1 Water sample was collected in November 2013

Table 1 DOC and percent reduction of DOC at $FeCl_3$ coagulation dosage 10, 25, 50 75 and 100 mg/L

Parameters	**$FeCl_3$ dosages (mg/L)**				
	10	**25**	**50**	**75**	**100**
DOC (mg/L)	9.442	9.616	9.354	9.243	9.046
% DOC reduction	18	16	18	19	20

Table 2 UV_{254} and percent reduction of UV_{254} at $FeCl_3$ coagulation dosage 10, 25, 50 75 and 100 mg/L

Parameters	**$FeCl_3$ dosages (mg/L)**				
	10	**25**	**50**	**75**	**100**
UV_{254} (cm^{-1})	1.5943	1.5628	1.5333	1.5064	1.4820
% UV_{254} reduction	-2	0	2	4	5

1.2 Water sample was collected in January 2014

Table 3 DOC and percent reduction of DOC at $FeCl_3$ coagulation dosage 10, 25, 50 75 and 100 mg/L.

Parameters	$FeCl_3$ dosages (mg/L)			
	50	**100**	**150**	**200**
DOC (mg/L)	12.302	9.727	10.302	10.321
% DOC reduction	2	23	18	18

Table 4 UV_{254} and percent reduction of UV_{254} at $FeCl_3$ coagulation dosage 10, 25, 50 75 and 100 mg/L.

Parameters	$FeCl_3$ dosages (mg/L)			
	50	**100**	**150**	**200**
UV_{254} (cm^{-1})	1.4423	1.3732	1.2963	1.2231
% UV_{254} reduction	7	11	16	21

Experiment 2 Optimal pH in coagulation process

2.1 Water sample was collected in November 2013

Table 5 DOC and percent reduction of DOC at $FeCl_3$ coagulation pH 6.5, 7.5 and 8.5

Parameters	**pH**		
	6.5	**7.5**	**8.5**
DOC (mg/L)	9.230	9.578	10.30
% DOC reduction	19	16	10

Table 6 UV_{254} and percent reduction of UV_{254} at $FeCl_3$coagulation pH 6.5, 7.5 and 8.5

Parameters	**pH**		
	6.5	**7.5**	**8.5**
UV_{254} (cm^{-1})	1.3825	1.4824	1.5215
% UV_{254} reduction	12	5	3

2.2 Water sample was collected in January 2014

Table 7 DOC and percent reduction of DOC at $FeCl_3$ coagulation pH 6.5, 7.5 and 8.5

Parameters	pH		
	6.5	**7.5**	**8.5**
DOC (mg/L)	9.502	9.714	11.62
% DOC reduction	25	23	8

Table 8 UV_{254} and percent reduction of UV_{254} at $FeCl_3$ coagulation pH 6.5, 7.5 and 8.5

Parameters	pH		
	6.5	**7.5**	**8.5**
UV_{254} (cm^{-1})	1.228	1.373	1.610
% UV_{254} reduction	21	11	-4

Table 9 SUVA and percent reduction of SUVA at $FeCl_3$ coagulation pH 6.5, 7.5 and 8.5

Parameters	**$FeCl_3$ dosages (mg/L)**		
	6.5	**7.5**	**8.5**
SUVA (L/mg-m)	12.926	14.155	13.879
% SUVA reduction	21	11	-4

Experiment 3 $FeCl_3$ coagulation combined with CM membrane filtration

Table 10 percent reduction of DOC concentration, UV_{254} and SUVA after treatment process

Water samples	DOC (mg/L)	%DOC reduction	UV_{254} (cm^{-1})	% UV_{254} reduction
A	12.6	-	1.545	-
B	9.50	25	1.228	21
C	8.90	29	1.179	24

A is contaminated shallow well water

B is treated water by coagulation process

C is treated water by coagulation combined with CM membrane

Experiment 4 Organic matter fraction

Table 11 Water characteristics of contaminated shallow water, treated water by coagulation and treated water by coagulation combined with CM membrane.

Parameters	A			B			C		
	Unfractionated	HPI	HPO	Unfractionated	HPI	HPO	Unfractionated	HPI	HPO
pH	7.4	7.0	7.0	6.6	7.1	7.0	7.5	7.0	7.2
Temp (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
DOC (mg/L)	12.6	8.10	3.00	9.50	7.30	2.10	8.90	6.10	2.10
UV_{254} (cm^{-1})	1.545	-	-	1.228	-	-	1.179	-	-
SUVA (L/mg-m)	12.3	-	-	12.9	-	-	13.2	-	-
Color (Pt-Co)	87.0	52.0	41.0	60.0	34.0	25.9	59.0	33.0	28.1

A is contaminated shallow well water B is treated water by coagulation process C is treated water by coagulation combined with CM membrane

Table 12 DOC concentration and percent DOC reduction in coagulation process and coagulation combined with CM membrane

Parameters	DOC concentration (mg/L)			% DOC reduction	
Water samples	A	B	C	B	C
HPI	8.10	7.30	6.10	10	25
HPO	3.00	.2.10	2.10	30	30
HPI + HPO	11.1	9.40	8.20	-	-
Unfractionated	12.6	9.50	8.90	25	29
% diff	12	1	8	-	-

% diff = (Unfractionated water – (HPI+HPO)) x 100 / unfractionated

A is contaminated shallow well water

B is treated water by coagulation process

C is treated water by coagulation combined with CM membrane

Experiment 4 Flux measurement

Table 13 Flux of deionized water was filtrated by CM membrane in case of contaminated shallow well water

Volume (L)	Total Time (sec)	Flow rate (L/s)	Flow rate (m^3/day)	Flux (m^3/m^2-day)
0.2	11.63	0.01720	1.48581	35.38
0.4	25.74	0.01417	1.22466	29.16
0.6	39.42	0.01462	1.26316	30.08
0.8	54.32	0.01342	1.15973	27.61
1.0	67.72	0.01493	1.28955	30.70
1.2	81.51	0.01450	1.25308	29.84
1.4	93.72	0.01638	1.41523	33.70
1.6	106.62	0.01550	1.33953	31.89
1.8	120.15	0.01478	1.27716	30.41
2.0	135.33	0.01318	1.13834	27.10
2.2	149.07	0.01456	1.25764	29.94
2.4	162.15	0.01529	1.32110	31.45
2.6	175.51	0.01497	1.29341	30.80
2.8	188.15	0.01582	1.36709	32.55
3.0	202.19	0.01425	1.23077	29.30

Table 14 flux of deionized water was filtrated by CM membrane in case of treated water by $FeCl_3$ coagulation

Volume(L)	Total Time (sec)	Flow rate (L/s)	Flow rate (m^3/day)	Flux (m^3/m^2-day)
0.2	11.72	0.01706	1.47440	35.10
0.4	24.75	0.01535	1.32617	31.58
0.6	37.66	0.01549	1.33850	31.87
0.8	50.49	0.01559	1.34684	32.07
1.0	63.79	0.01504	1.29925	30.93
1.2	76.73	0.01546	1.33539	31.80
1.4	90.23	0.01481	1.28000	30.48
1.6	102.93	0.01575	1.36063	32.40
1.8	115.07	0.01647	1.42339	33.89
2.0	127.65	0.01590	1.37361	32.70
2.2	139.95	0.01626	1.40488	33.45
2.4	152.25	0.01626	1.40488	33.45
2.6	164.73	0.01603	1.38462	32.97
2.8	177.21	0.01603	1.38462	32.97
3.0	189.81	0.01587	1.37143	32.65

Table 15 Flux of contaminated shallow well water was filtrated by CM membrane

Volume(L)	Total Time (sec)	Flow rate (L/s)	Flow rate (m^3/day)	Flux(m^3/m^2-day)
0.2	12.9	0.01550	1.33953	31.89
0.4	27.1	0.01408	1.21690	28.97
0.6	41.12	0.01427	1.23252	29.35
0.8	56.17	0.01329	1.14817	27.34
1.0	70.89	0.01359	1.17391	27.95
1.2	86.13	0.01312	1.13386	27.00
1.4	101.53	0.01299	1.12208	26.72
1.6	116.65	0.01323	1.14286	27.21
1.8	131.97	0.01305	1.12794	26.86
2.0	147.23	0.01311	1.13237	26.96
2.2	163.24	0.01249	1.07933	25.70
2.4	178.62	0.01300	1.12354	26.75
2.6	194.07	0.01294	1.11845	26.63
2.8	209.26	0.01317	1.13759	27.09
3.0	224.98	0.01272	1.09924	26.17

Table 16 Flux of treated water by coagulation combined with CM membrane

Volume(L)	Total Time (sec)	Flow rate (L/s)	Flow rate (m^3/day)	Flux (m^3/m^2-day)
0.2	11.84	0.01689	1.45946	34.75
0.4	25.52	0.01462	1.26316	30.08
0.6	39.48	0.01433	1.23782	29.47
0.8	52.8	0.01502	1.29730	30.89
1.0	66.53	0.01457	1.25856	29.97
1.2	80.55	0.01427	1.23252	29.35
1.4	94.15	0.01471	1.27059	30.25
1.6	109.04	0.01343	1.16051	27.63
1.8	123.26	0.01406	1.21519	28.93
2.0	138.64	0.01300	1.12354	26.75
2.2	154.48	0.01263	1.09091	25.97
2.4	168.65	0.01411	1.21948	29.04
2.6	183.59	0.01339	1.15663	27.54
2.8	198.35	0.01355	1.17073	27.87
3.0	213.62	0.01310	1.13163	26.94

Table 17 Normalized flux of contaminated shallow well water

Filtrated volume (L)	Flux of deionized water (m^3/m^2-day)	Flux of contaminated shallow well water (m^3/m^2-day)	Normalized flux
0.2	35.10	31.89	0.91
0.4	31.58	28.97	0.92
0.6	31.87	29.35	0.92
0.8	32.07	27.34	0.85
1.0	30.93	27.95	0.90
1.2	31.80	27.00	0.85
1.4	30.48	26.72	0.88
1.6	32.40	27.21	0.84
1.8	33.89	26.86	0.79
2.0	32.70	26.96	0.82
2.2	33.45	25.70	0.77
2.4	33.45	26.75	0.80
2.6	32.97	26.63	0.81
2.8	32.97	27.09	0.82
3.0	32.65	26.17	0.80

Table 18 Normalized flux of treated water by coagulation combined with CM membrane

Filtrated volume (L)	Flux of deionized water (m^3/m^2-day)	Flux of contaminated shallow well water (m^3/m^2-day)	Normalized flux
0.2	35.10	34.75	0.99
0.4	31.58	30.08	0.95
0.6	31.87	29.47	0.92
0.8	32.07	30.89	0.96
1.0	30.93	29.97	0.97
1.2	31.80	29.35	0.92
1.4	30.48	30.25	0.99
1.6	32.40	27.63	0.85
1.8	33.89	28.93	0.85
2.0	32.70	26.75	0.82
2.2	33.45	25.97	0.78
2.4	33.45	29.04	0.87
2.6	32.97	27.54	0.84
2.8	32.97	27.87	0.85
3.0	32.65	26.94	0.83

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