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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

DEVELOPMENT OF FILTER MODIFIED BY POLYELECTROLYTE MULTILAYERS AS
ADSORBENT FOR HERBICIDES

Mr. Tana Suksawang



A Thesis Submitted in Partial Fulfillment of the Requirements
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ธนา สุขสว่าง : การพัฒนาตัวกรองดัดแปรด้วยพอลิอิเล็กโทรไลต์มัลติเลเยอร์เป็นตัวดูดซับสารฆ่าวัชพืช (DEVELOPMENT OF FILTER MODIFIED BY POLYELECTROLYTE MULTILAYERS AS ADSORBENT FOR HERBICIDES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ดร.ลักษณา ดุบาส, 73 หน้า.

สารฆ่าวัชพืชถูกใช้กำจัดวัชพืชในการเกษตรเพื่อให้ได้ผลผลิตที่เพิ่มขึ้น แต่การใช้สารฆ่าวัชพืชนี้อาจปนเปื้อนในสิ่งแวดล้อมได้ ในการศึกษานี้ได้มีการดัดแปรตัวกรองและไส้กรองน้ำด้วยพอลิอิเล็กโทรไลต์มัลติเลเยอร์ เพื่อเพิ่มประสิทธิภาพในการดูดซับสารฆ่าวัชพืชที่ปนเปื้อนในน้ำได้แก่ พาราควอท และไกลโฟเสท เทคนิค layer-by-layer ถูกนำมาใช้ในการสร้างฟิล์มพอลิอิเล็กโทรไลต์มัลติเลเยอร์ โดยใช้พอลิไดอะเมทิลเอมีนไฮโดรคลอไรด์ (PDADMAC) เป็นพอลิอิเล็กโทรไลต์ที่มีประจุบวก ส่วนพอลิสไตรีนซัลโฟนิคแอซิดโคมาเลอิกแอซิด (PSSMA) เป็นพอลิอิเล็กโทรไลต์ที่มีประจุลบ และกรดฮิวมิก (HA) ซึ่งเป็นโมเลกุลขนาดใหญ่ ในการศึกษาได้ศึกษาความเข้มข้นของโซเดียมคลอไรด์ และค่าพีเอชของสารละลายที่เหมาะสมต่อการสร้างมัลติเลเยอร์นี้ โดยติดตามโดยใช้เทคนิค Uv-Vis, FT-IR SEM และ AFM จากผลการศึกษาพบว่าภาวะที่เหมาะสมในการสร้างฟิล์ม PDADMAC/PSSMA และ PDADMAC/HA ได้แก่ โซเดียมคลอไรด์ที่ค่าความเข้มข้นเท่ากับ 1 M ค่าพีเอชของสารละลายกรดฮิวมิกมีค่าเท่ากับ 7 และสารละลาย PSSMA มีค่าเท่ากับ 5.5 ฟิล์ม PDADMAC/HA สามารถดูดซับสารฆ่าวัชพืชได้มากกว่าฟิล์ม PDADMAC/PSSMA ดังนั้นฟิล์ม PDADMAC/HA เป็นฟิล์มที่เหมาะสมสำหรับในการใช้ในการศึกษาต่อไป ซึ่งจากผลการทดลองพบว่าจำนวนชั้น PDADMAC/HA ที่เหมาะสมคือ 16 ชั้น และอัตราการไหลผ่านของสารฆ่าวัชพืชที่จะทำให้มีประสิทธิภาพที่ดีที่สุดในการดูดซับ เท่ากับ 0.5 มิลลิลิตร/นาที ในกรณีการกำจัดสารพาราควอท ความจุสูงสุดของตัวกรองที่ไม่ได้ดัดแปร เท่ากับ 8.24 ± 0.37 ไมโครกรัม ขณะที่ความจุสูงสุดของตัวกรองที่ผ่านการดัดแปรด้วยฟิล์ม PDADMAC/HA เท่ากับ 16.89 ± 0.45 ไมโครกรัม (2.05 เท่าที่เพิ่มขึ้น) ส่วนกรณีการกำจัดสารไกลโฟเสท พบว่าความจุสูงสุดของตัวกรองที่ไม่ได้ดัดแปร เท่ากับ 56.32 ± 0.54 ไมโครกรัม ขณะที่ความจุสูงสุดของตัวกรองที่ผ่านการดัดแปรด้วยฟิล์ม PDADMAC/HA เท่ากับ 64.43 ± 0.26 ไมโครกรัม (เพิ่มขึ้น 1.14 เท่า) ในศึกษานี้ทำการสร้างฟิล์ม PDADMAC/HA บนไส้กรองที่ใช้ในเครื่องกรองน้ำบ้าน โดยใช้ภาวะที่หาได้จากการศึกษาบนตัวกรอง ในตัวอย่างน้ำประปา เมื่อเปรียบเทียบประสิทธิภาพการกำจัดสารฆ่าวัชพืชของไส้กรองที่มีและไม่มีการดัดแปรด้วยฟิล์ม PDADMAC/HA พบว่าปริมาณการกำจัดสารพาราควอทมีค่าเพิ่มขึ้นจาก 0.20 ± 0.37 เป็น 0.67 ± 0.45 มิลลิกรัม (3.35 เท่าที่เพิ่มขึ้น) และสำหรับการกำจัดสารไกลโฟเสท เพิ่มขึ้นจาก 1.03 ± 0.26 เป็น 1.49 ± 0.34 มิลลิกรัม (1.45 เท่าที่เพิ่มขึ้น) ส่วนในน้ำบาดาล เมื่อเปรียบเทียบประสิทธิภาพการกำจัดสารฆ่าวัชพืชของไส้กรองที่ไม่มีและมีการดัดแปรด้วยฟิล์ม PDADMAC/HA พบว่าปริมาณการกำจัดสารพาราควอทมีค่าเพิ่มขึ้นจาก 0.15 ± 0.42 เป็น 0.55 ± 0.26 มิลลิกรัม (3.67 เท่าที่เพิ่มขึ้น) และสำหรับการกำจัดสารไกลโฟเสท เพิ่มขึ้นจาก 0.69 ± 0.25 เป็น 1.26 ± 0.44 มิลลิกรัม (1.83 เท่าที่เพิ่มขึ้น) การศึกษานี้แสดงให้เห็นถึงความสำเร็จในการสร้างฟิล์มพอลิอิเล็กโทรไลต์มัลติเลเยอร์บนตัวกรองรับทุกชนิดและตัวกรองที่ดัดแปรนี้สามารถเพิ่มประสิทธิภาพในการดูดซับสารฆ่าวัชพืชที่ปนเปื้อนในน้ำได้

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

ลายมือชื่อนิสิต

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TANA SUKSAWANG: DEVELOPMENT OF FILTER MODIFIED BY POLYELECTROLYTE MULTILAYERS AS ADSORBENT FOR HERBICIDES. ADVISOR: LUXSANA DUBAS, Ph.D., 73 pp.

At present, herbicides are used in agriculture in order to obtain higher production yields. Unfortunately, their chemical residues contaminate environment. In this study, polyelectrolyte multilayer was used to modify polypropylene membrane and water filter cartridge to enhance the effectiveness on the removal of water contaminated with paraquat and glyphosate. Poly(diallyl dimethyl ammonium chloride) (PDADMAC) as a polycations and poly(styrene sulfonic acid-co-maleic acid) (PSSMA) as polyanions and humic acid (HA) as a macromolecule were fabricated using layer-by-layer (LbL) technique. Sodium chloride concentration and pH solution were optimized to achieve the best film growth condition. The growth was monitored via Uv-Vis, FT-IR, SEM and AFM. The optimized fabrication condition delivering the thickest PDADMAC/PSSMA and PDADMAC/HA multilayers film were 1 M NaCl, HA pH 7 and PSSMA pH 5.5. However, the PDADMAC/HA could remove more herbicides comparing to PDADMAC/PSSMA. Thus, the PDADMAC/HA multilayers film was used in the performance study of the modified filters on the herbicides removal. The optimum number of the polyelectrolyte multilayers was 16th layers and flow rate was found to be at 0.5 mL/min as the best performance. Regarding paraquat removal, the maximum capacity of non-modified membrane is $8.24 \pm 0.37 \mu\text{g}$, while PDADMAC/HA modified membrane is $16.89 \pm 0.45 \mu\text{g}$ (2.0-fold increase). For glyphosate removal, maximum capacity of non-modified membrane is $56.32 \pm 0.54 \mu\text{g}$ and PDADMAC/HA modified membrane is $64.43 \pm 0.26 \mu\text{g}$ (1.1-fold increase). The water filter cartridge was fabricated with the optimized condition previously found. For tap water, the amount of herbicides removal was increased from 0.20 ± 0.37 to $0.67 \pm 0.45 \text{ mg}$ (3.4-fold increase) for paraquat and from 1.03 ± 0.26 to $1.49 \pm 0.34 \text{ mg}$ (1.5-fold increase) for glyphosate. For groundwater, the amount of herbicides removal was increased from 0.15 ± 0.42 to 0.55 ± 0.26 (3.7-fold increase) in paraquat spiked sample and from 0.69 ± 0.25 to $1.26 \pm 0.44 \text{ mg}$ (1.8-fold increase) for glyphosate. This study showed the success on the fabrication of polyelectrolyte multilayers films on all types of substrates and the effectiveness on the removal of water contaminated with herbicides.

Field of Study: Petrochemistry and Polymer Student's Signature

Science Advisor's Signature

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LIST OF ABBREVIATIONS

HA	=	Humic acid
L	=	Liter
LbL	=	Layer-by-layer technique
LOD	=	The limit of detection
LOQ	=	The limit of quantitation
μg	=	Microgram
mg	=	Milligram
min	=	Minute
mL	=	Milliliter
mM	=	Millimolar
nm	=	Nanometer
PDADMAC	=	Poly(diallyldimethyl ammonium chloride)
PEMs	=	Polyelectrolyte multilayers films
pK_a	=	Acid dissociation constant
PP	=	Polypropylene
ppm	=	Part per million
PSSMA	=	Poly(4-styrene sulfonic acid-co-maleic acid, sodium salt)

CHAPTER I

INTRODUCTION

Currently, herbicides are used in the current market competition, higher than the past. Herbicides, such as glyphosate, paraquat, 2,4-D dimethyl ammonium and atrazine, are most used in agriculture in most countries in order to prevent weeds from growing. Unfortunately, herbicide contaminates the natural water resources and soils. This can be harmful to our health.

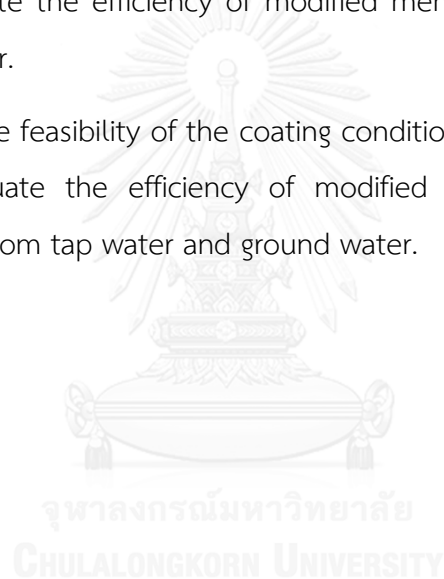
The glyphosate and paraquat are herbicides, which the most volume imported to Thailand. Because there herbicide have high efficiency to prevent weeds from growing. The report of Office of Agricultural Economics in 2014 showed that the amounts of glyphosate and paraquat imported to Thailand were 63,166,212 and 21,325,348 kg, respectively [1]. The maximum residue limits (MRLs) of glyphosate and paraquat in drinking water set by the Environmental Protection Agency (EPA) are 0.7 and 0.02 mg/L, respectively [2]. The European Union (EU) limit of any herbicides in drinking water has been set at 0.1 µg/L irrespective of their toxicological effects [3].

To remove the herbicides from natural resources, many methods were used and developed such as liquid-liquid extraction (LLE) and solid phase extraction (SPE) but there methods are tedious and expensive [4]. Several studies using layer-by-layer (LbL) technique in surface modification of membranes filter for removing chemical residues from water were reported [5]. The advantages of this technique are simple and low cost. This technique was based on alternating adsorption of polycations and polyanions on substrate. Since the fabrication of polyelectrolyte multilayer films (PEMs) were previously prepared on various substrates for herbicides adsorption studies [6]. In the light of information, there is no study on the modification of polypropylene (PP) membrane and fibrous filters with PEMs for herbicides removal.

The research is to modify PP filters with polyelectrolyte multilayers film to enhance the effectiveness on the removal of glyphosate and paraquat contamination of membrane filter and water filter cartridge.

1.1 Research objectives

1. To modify the membrane filters by polyelectrolyte multilayer and study the factors controlling the growth of polyelectrolyte multilayers on membrane.
2. To evaluate the efficiency of modified membrane for herbicide removal from water.
3. To test the feasibility of the coating condition on the water filter cartridge and evaluate the efficiency of modified filter cartridge for herbicide removal from tap water and ground water.



1.2 Scope of the research

The scope of this work is to develop a membrane filter that can absorb glyphosate and paraquat from water by modifying PP membranes with polyelectrolyte multilayer film using layer-by-layer (LbL) technique. Poly(diallyldimethyl ammonium chloride (PDADMAC) as polycations, while poly(4-styrene sulfonic acid-co-maleic acid (PSSMA) as polyanions and humic acid (HA) as a macromolecule were used in this study. PP substrates were used in this study because it is commonly used in household water filter unit. The polyelectrolyte multilayer films were fabricated on substrates, quartz slides and polypropylene (PP) membrane filters with pore sizes of 0.2 and 0.2-0.6 micron. The fabrication parameters, concentration of sodium chloride and pH of polyelectrolyte solution, were optimized. The parameters affecting the glyphosate and paraquat removal efficiency of PEMs modified membrane, which are numbers of depositing layer and flow rate of glyphosate and paraquat solutions, were studied. Based on our finding on the optimized fabricating condition and the best polymer pair, the fabrication of PEMs on water filter cartridge was demonstrated. The efficiency of modified filters cartridge for glyphosate and paraquat removal from tap water and ground water were studied.

1.3 Benefits of research

The modified membranes by polyelectrolyte multilayers can enhance the herbicides removal from water.

CHAPTER II
THEORY AND LITERATURE REVIEW

2.1 Polyelectrolytes

Polyelectrolytes are polyions which are soluble in water. The polyelectrolytes can be classified to strong and weak polyelectrolytes. The strong polyelectrolyte dissociates completely in solution for all pH values. For the weak polyelectrolyte, the dissociation depends on pH value. In some pH values, it will be partially dissociated in solution. Some of polyelectrolytes were shown in Table 2.1 and 2.2.

Table 2.1 Cationic polyelectrolytes and their chemical structures

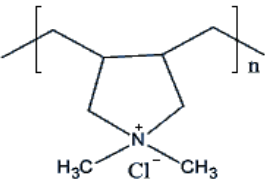
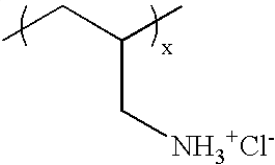
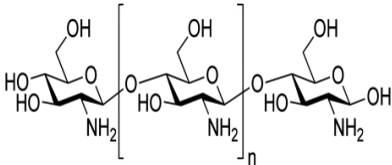
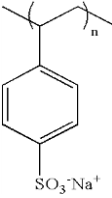
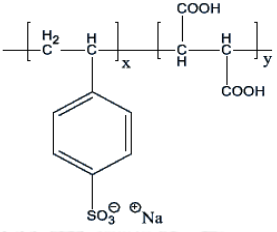
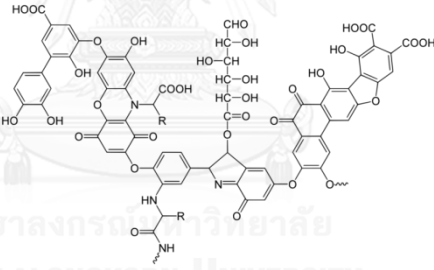
Name	Chemical structures	Classification
Poly(diallyldimethyl ammonium chloride), PDADMAC		Strong
Poly(allylamine hydrochloride), PAH		Weak $pK_a = 8.7$ (amino groups)
Chitosan		Weak $pK_a = 6.2-7.0$ (amino groups)

Table 2.2 Anionic polyelectrolytes and their chemical structures

Name	Chemical structures	Classification
Poly(sodium 4- styrene sulfonate), PSS		Strong
Poly (4-styrene sulfonic acid-co-maleic acid), PSSMA		Weak $pK_{a1} = 2.8$ $pK_{a2} = 8.3$ (carboxylic group)
Humic acid		Weak $pK_{a1} = 4-5$ (carboxylic group) $pK_{a2} = 8-10$ (phenol group)

2.2 Polyelectrolyte multilayers

Polyelectrolyte multilayers have been proposed to modify the surface of materials by sequential adsorption of polycations and polyanions on various substrates. The polyelectrolytes was used in the assembly such as polymers, proteins, nanoparticles, macromolecule, clay and metallic colloids [7, 8]. The method which widely used in fabrication of polyelectrolyte multilayer is layer-by-layer (LbL) technique [9]. This technique can be used to change substrate surface such as silicon wafer, membrane, glass slide and wood [10]. The advantages of layer-by-layer technique are simple to perform and low production cost. Moreover, polyelectrolyte multilayer films are widely applied in various fields such as medicine, dentistry, engineering and industry.

The layer-by-layer (LbL) technique was based on alternating adsorption of polycations and polyanions. The process of fabrication is shown in figure 2.1. At first the negatively charged substrate was dipped in polycations solution. Next, the substrate was rinsed with water or buffer solution to remove the excess polycations on substrate. At this step the surface of substrate was coated with a positive layer of the polycations as the first layer. After the first layer, the substrate was dipped into polyanions and then rinsed with water or buffer solution to remove the excess polyanions on substrate. Now, the substrate coating with the first layer was modified with a negative layer of the polyanions as the second layer. The charge on the surface was reversed. The dipping cycle was repeated until the desired number of layers.

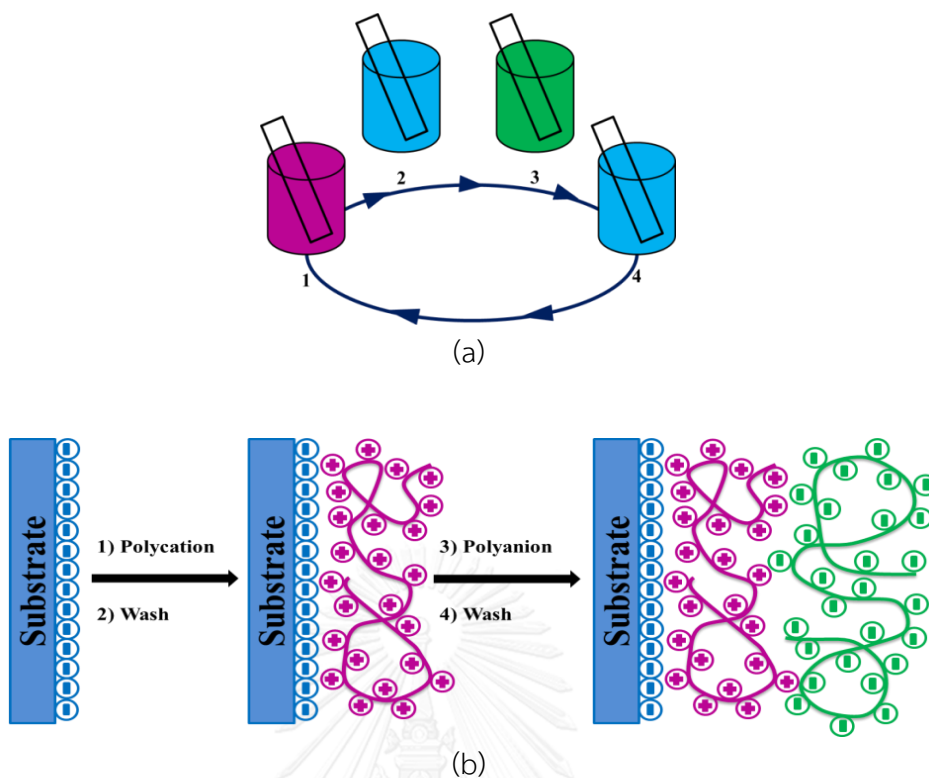


Figure 2.1 (a) The formation process of polyelectrolyte multilayer films. (b) The electrostatic self-assembly of polyelectrolyte multilayer films on substrate. The figure was adapted from Decher and co-workers [9].

2.3 Factors controlling the growth of polyelectrolyte multilayers

2.3.1 The major factors

2.3.1.1 Number of layers

Several previous studies have reported that the increase in the number of layer resulted in the increase in the film thickness [11]. In figure 2.2, the formation of PSS/PDADMAC multilayer thin film on silicon wafer was demonstrated. Initially, the thickness of first bilayers is quite small because of the low charge density on surface. After many coating layers, the charge density on the modified surface increases as it eases the deposition of polyelectrolytes in the later layers. This gives the thicker film in the growth process.

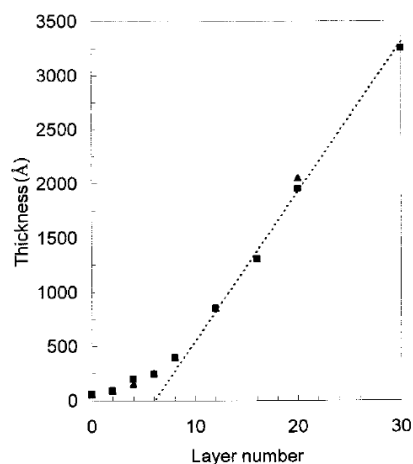


Figure 2.2 Thickness as a function of the number of layers for a PSS/PDADMAC multilayer deposited on silicon wafer. The polyelectrolyte concentration is 10 mM and 1 M of NaCl [11].

2.3.1.2 Sodium chloride concentration (ionic strength)

The effect of sodium chloride salt concentration as a function of thickness of polyelectrolyte multilayer was reported [12]. At low salt concentration, the thin PEMs films were observed due to the weak shielding effect. However, at higher sodium chloride concentration, the thickness was increased due to the increase in the shielding effect.

2.3.1.3 pH of polyelectrolyte solution

The pH of polyelectrolyte solution affects the weak polyelectrolyte adsorption because it relates to the degree of ionization. In the other hand, pH does not affect the adsorption of strong polyelectrolyte because it can be ionized in all pH values. The structure and ionization degrees of weak polyelectrolytes can be tuned by controlling pH values. Figure 2.3 shows the thickness of PDADMAC/PSSMA (3:1) was fabricated from pH 2, 5.8 and 11. The result showed that the thickness decreased when pH of the PSSMA solution was increased from pH 5.8 to pH 11 ($pK_{a,s}$ of PSSMA: 2.8 and 8.3) [13]. At high pH, a greater proportion of carboxylic groups on

PSSMA were ionized, leading to the increase in the charge density of the polymer. When the charge density of the polyelectrolyte increases, the repulsive force between the charged groups also increases (extended chains). Therefore, this conformation causes the thinner PEMs layers. At pH 5.8, the negative charges on the polymer decrease, leading to the change of the polyelectrolytes conformation to a coil conformation resulting to the thicker film. In other hand, the decrease in pH value from 5.8 to 2 causes the polymer to be in a non-ionized form, resulting in the lower charge density on the polymer chains. Then, the lower charge density of PSSMA causes the decrease in the adsorbed PDADMAC resulting in thinner film.

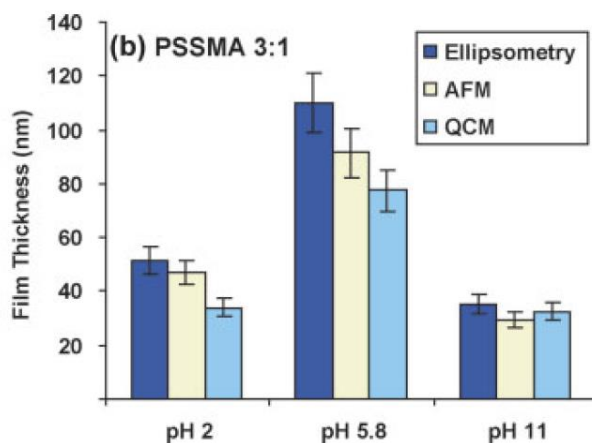


Figure 2.3 Thickness of (PDADMAC/PSSMA)₁₀ multilayer films fabricating using various pH values and 0.5 M NaCl [13].

2.3.2 The minor factors

2.3.2.1 Dipping time

The relationship between dipping time as a function of thickness of polyelectrolyte multilayers shown in figure 2.4 [11]. In the low time of the dipping process, the polyelectrolyte adsorption on surface is the fast process resulting to the large polymer growth. At the longer dipping time, the thickness was slowly increased because the polyelectrolytes were adsorbed on surface and forming a similar charged wall, which prevents more polyelectrolyte depositing on surface.

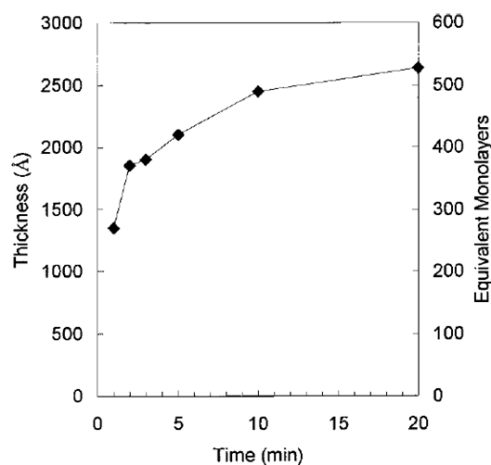


Figure 2.4 Thickness of PSS/PDADMAC (10 bilayers) as a function of dipping time [11].

2.3.2.2 Polymer concentration

The polymer concentration influences the thickness of polyelectrolyte multilayers in only low concentration and then approach to constant value at high concentration as shown in figure 2.5. At low concentration, the surface of substrate has more charge for adsorption resulting to the thickness was increased when the concentration increase. But at high concentration the thickness was constant due to the limit of charge on surface of substrate for adsorption.

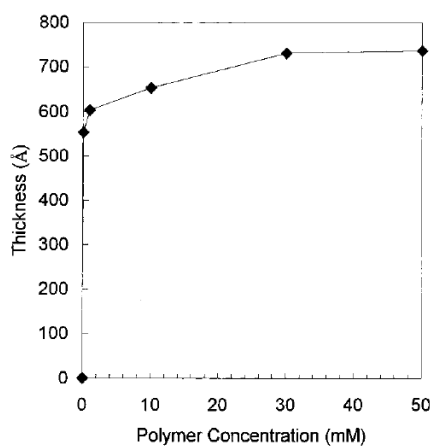


Figure 2.5 Thickness of PSS/PDADMAC (5 bilayers) as a function of polymer concentration [11].

2.4 Herbicides

Humic acid (HA) are organic macromolecules, which result from the microbiological decomposition of animals and vegetables. They can be found in water and soil. Humic acid can interact with herbicides due to their hydrophilic and hydrophobic sites [5, 14, 15]. The structure of humic acid is a wide functional groups, such as carboxyl (COOH), carbonyl (C=O), and hydroxyl (OH). The structure of humic acid was showed in figure 2.6.

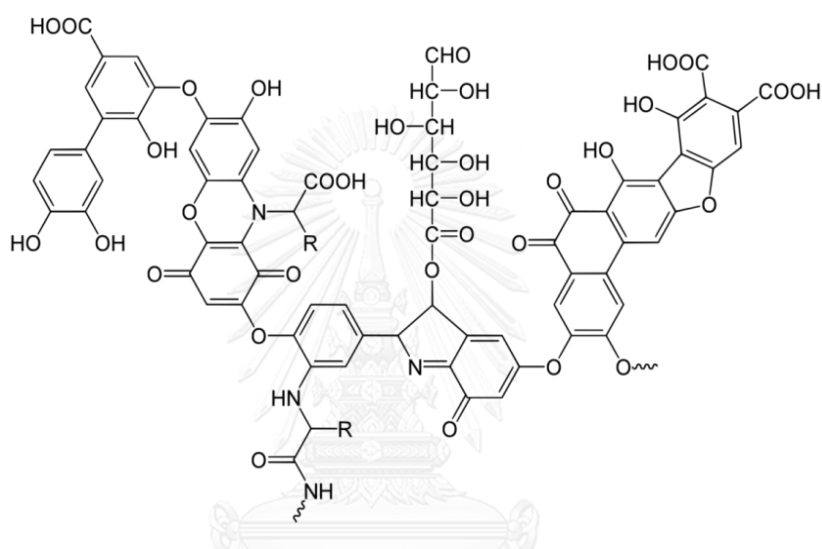


Figure 2.6 The structure of humic acid [5, 14, 15].

Paraquat dichloride (1,10-dimethyl-4,4'-bipyridinium dichloride hydrate) is the heterocyclic organic compound in group of bipyridium herbicide or quaternary ammonium herbicide [16]. The chemical structure of paraquat dichloride was shown in figure 2.7. Molecular structure composes of two pyridium rings which exhibit cationic characteristic for all pH values.

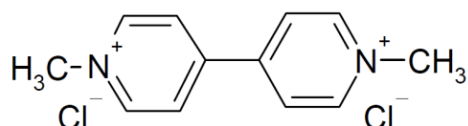


Figure 2.7 Chemical structure of paraquat dichloride [16].

The dissociation species and related ionization constants were shown on figure 2.8 [17]. The acid dissociation constants for glyphosate are $pK_{a1} = 0.8$ (First phosphonic), $pK_{a2} = 2.6$ (Carboxylate), $pK_{a3} = 5.6$ (Second phosphonic) and $pK_{a4} = 10.6$ (Amine).

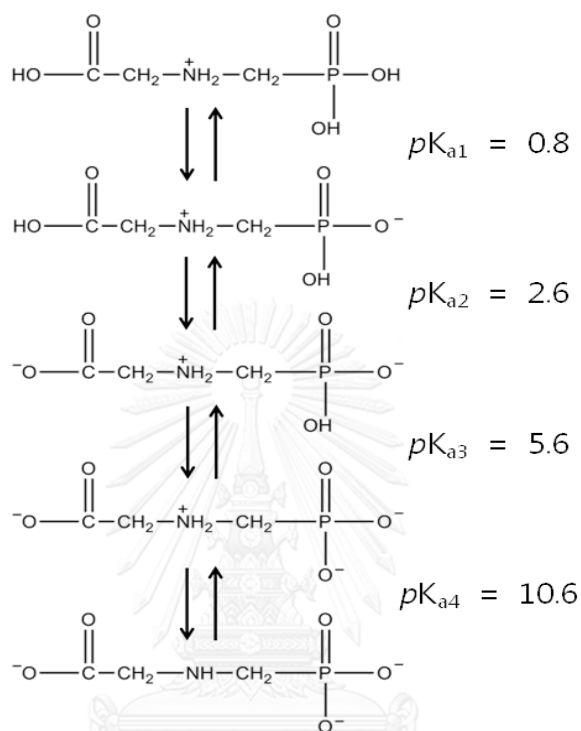


Figure 2.8 Proposed dissociation diagram and ionization constants for glyphosate. The figure was adapted from Paul and co-workers [17].

Due to the low molar absorptivity in UV range of glyphosate, , glyphosate was reacted with ninhydrin and sodium molybdate forming a product with purple color with the maximum absorbance at 570 nm [18]. The mechanism of reaction was shown in figure 2.9. The advantage of this method is selective to react with only glyphosate but not react with paraquat.

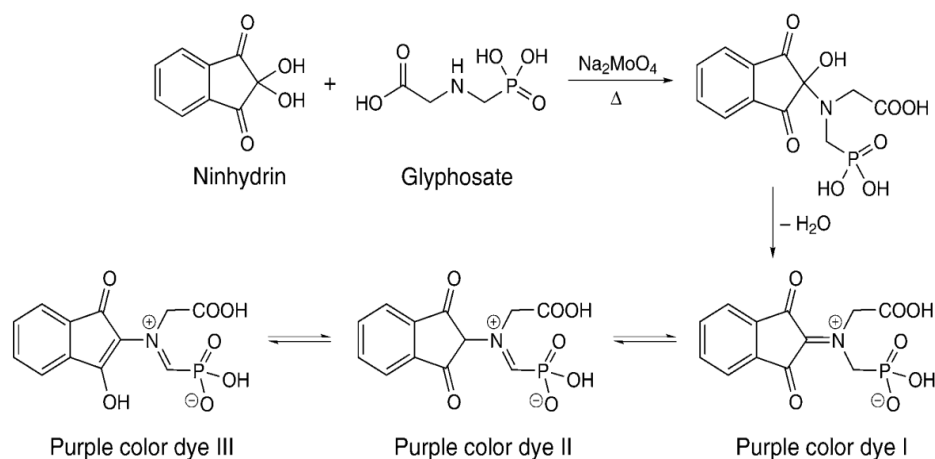


Figure 2.9 Mechanism of reaction of glyphosate with ninhydrin in the presence of sodium molybdate [18].

2.5 Literature reviews

Several studies have reported about modified or prepared materials with polyelectrolyte multilayer for herbicides removal.

In 2005, Frank et al prepared nanostructured thin films of 25 PAH/HA bilayers were assembled on hydrophilic glass, ITO-covered glass, and silicon wafers as substrates [5]. PAH/Humic acids PEMs were fabricated. The films use as modified electrodes for detecting a pesticide via electrochemical sensing.

In 2008, Odilio and Douglas prepared polyelectrolyte complex membrane from chitosan as a polycations and carboxymethylcellulose as a polyanions onto a porous of glass membrane for atrazine recovery from aqueous solution [19]. The filtration tests of chitosan/carboxymethylcellulose bilayer complex membrane which carboxymethylcellulose was the outermost layer and pure chitosan membrane were performed. The chitosan membrane showed the best performance. The chitosan has more unsaturated end groups to interact with atrazine via electrostatic interactions, hydrogen bonds and hydrophobic interaction, while these affinity sites are available less in the polyelectrolyte complex membrane.

In 2012, Daniela et al. prepared polyelectrolyte complex membrane of alginate as polyanions and chitosan as polycations for paraquat removal from water [16]. The herbicide adsorption experiments were performed using three different membranes, consisting of pure alginate, pure chitosan and a chitosan/alginate bilayer, which alginate was outermost layer. The highest paraquat adsorption capacity was observed with the alginate membrane ($77.76 \mu\text{mol/L/g}$ of membrane). This observation might be caused by the large amount of carboxylate groups on alginate chains, which can form electrostatic interaction with paraquat molecule (cations). In 2013, Daniela et al. study the adsorption diquat, difenzoquat and clomazone from water by using the same three membranes [20]. Diquat and difenzoquat were only adsorbed on the alginate and chitosan/alginate membranes. At a concentration of $50 \mu\text{M}$, diquat adsorption reaches 95% after 120 min on both the alginate and chitosan/alginate membranes. The adsorption of difenzoquat reaches 62% after 120 min on pure alginate membranes and 12% on chitosan/alginate bilayer membranes. They suggested that alginate was a good biopolymer for the adsorption of diquat and difenzoquat. This is due to the possible electrostatic interactions between the carboxyl groups of alginate and the positive charges of these herbicides.

In 2015, Rafael et al. prepared biopolymer membranes with chitosan, alginate and chitosan/alginate bilayer which alginate is the outermost layer in order to adsorb glyphosate in water [21]. The results of kinetics experiments showed that adsorption equilibrium was reached within 4 hours. The chitosan membrane presented the best adsorption ($10.88 \text{ mg of glyphosate/g of membrane}$), followed by the chitosan/alginate bilayer ($8.70 \text{ mg of glyphosate/g of membrane}$). The alginate membrane did not show any adsorption capacity for this herbicide. The affinity between glyphosate and chitosan and alginate/chitosan membranes indicates that the interaction between this herbicide and chitosan is via electrostatic interactions.

Because the pH of water used in the tests was around 6.5 which made chitosan shows positive charge due to the $pK_a = 6.2-7.0$. While glyphosate has $pK_{a3} = 5.6$ with the structure was showed three negative charge and one positive charges in molecule.

In this research, the fabrication of polyelectrolyte multilayers film on water filter cartridge as a substrate has never been reported. The humic acid was used as a polyanion in fabrication polyelectrolyte multilayers film via layer-by-layer technique. Although, humic acid was mostly used as an adsorbent for herbicide removal but the incorporation of HA in PEMs used in the removal of glyphosate and paraquat contamination in water has never been studied.



CHAPTER III

EXPERIMENTAL

3.1 Materials and chemicals

3.1.1 Substrates

1. Quartz slides were purchased from Electron Microscopy Sciences and size 50 × 25 mm was prepared.
2. Polypropylene (PP) membrane filter, 47 mm diameter and 0.2 and 0.2-0.6 micron pore size, were purchased from Merck.
3. A 10" water filter cartridge made of polypropylene fiber and 5 micron pore size, was purchased from Promine.

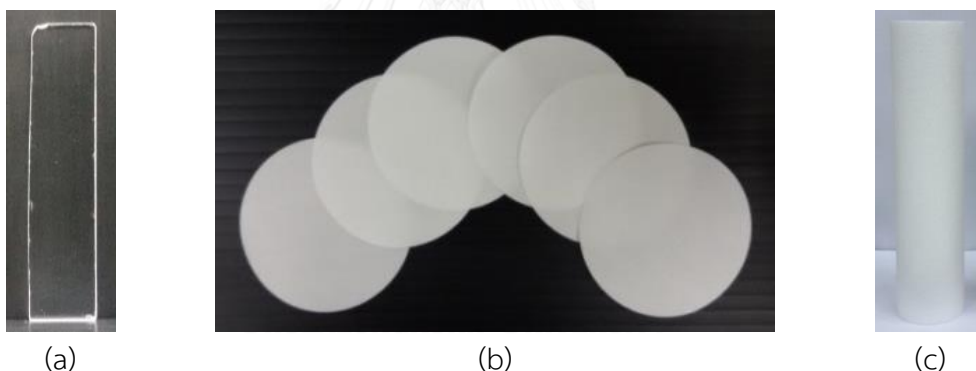


Figure 3.1 (a) Quartz slides, (b) Polypropylene (PP) membrane filter and (c) Water filter cartridge

3.1.2 Chemicals

All chemicals were listed in Table 3.1. Chemicals were used without further purification. Deionized water (DI) was used for the preparation of chemicals and reagent solutions.

Due to the difference in the ions content in DI water and ground water, which could affect the interaction between paraquat and glyphosate and HA, tap water were chosen as solvent for all herbicide solutions.

Table 3.1 List of Chemicals list and suppliers

Chemicals	Suppliers
1. Poly(diallyldimethyl ammonium chloride) (PDADMAC) medium molecular weight, 20 wt% in water	Sigma-Aldrich
2. Poly(4-styrene sulfonic acid-co-maleic acid, 3:1 SS:MA), sodium salt , average MW ~20,000	Sigma-Aldrich
3. Humic acid (HA) sodium salt, Technical Grade	Sigma-Aldrich
4. Sodium tetraborate, A.R. Grade	Ajax Finechem
5. Di-sodium hydrogen phosphate anhydrous, A.R. Grade	Carlo Erba
6. Potassium dihydrogen phosphate, A.R. Grade	Carlo Erba
7. Acetic acid, ACS reagent grade	Merck
8. Sodium acetate, ACS reagent grade	Carlo Erba
9. Hydrochloric acid, ACS reagent grade	Merck
10. Sodium chloride, A.R. Grade	Carlo Erba
11. Ninhydrin, ACS reagent grade	Sigma-Aldrich
12. Sodium molybdate, ACS reagent grade	Sigma-Aldrich
13. Paraquat dichloride, Analytical Standard	Sigma-Aldrich
14. Glyphosate, Analytical Standard	Sigma-Aldrich

3.2 Apparatus

The apparatuses used shown in Table 3.2

Table 3.2 Apparatus list and suppliers

Apparatus	Suppliers
1. UV-visible spectrophotometer	Hewlett Packard 8453
2. Attenuated Total Reflectance Fourier transform Infrared Spectrometer (ATR-FTIR)	Nicolet 6700
3. Atomic Force Microscopy (AFM)	Nanoscope IV
4. Scanning Electron Microscope (SEM)	JEOL, JSM 6400
5. pH meter	Mettler Toledo
6. Syringe pump	QIS, model NE1000
7. Filter holder	Millipore
8. Syringe 50 mL	Nipro
9. Household water filter unit	Pett Filter
10. Vacuum pump	Imperial
11. Water pump	Clinton

3.3 Preparation of solutions

3.3.1 10 mM buffer solutions pH 5, 5.5, 7 and 9 (stock solutions)

The 10 mM buffer solutions with various pH values were prepared in 1000 mL-volumetric flask. The pH 5 was prepared by mixing 3.6 mM and 6.4 mM of acetic acid and sodium acetate, respectively. The pH 5.5 of buffer solution was prepared by mixing 9.6 mM potassium dihydrogen phosphate and 0.4 mM of di-sodium hydrogen phosphate solutions. A 7.6 mM sodium hydrogen phosphate and 2.4 mM hydrochloric acid were used to prepare pH 7. Last, pH 9 buffer was prepared from 10 mM of sodium tetraborate. Then, all buffer solutions were diluted to 1 mM in order to be used as solvent in the working polyelectrolyte solutions.

3.3.2 Polyelectrolyte solutions 100 mM (stock solution)

The 1000mL of 100 mM PDADMAC and PSSMA solutions were prepared by weighing 80.77 ± 0.05 g for PDADMAC and 34.40 ± 0.03 g for PSSMA in 1000 mL-volumetric flask.

3.3.3 A 10 ppm standard herbicides solution (stock solution)

A 1000.00 mL of 10 ppm stock solution of either paraquat or glyphosate was prepared by dissolving 10.00 ± 0.02 mg in tap water. The final volume was adjusted using tap water.

3.3.4 A 5% (w/v) ninhydrin and sodium molybdate solutions

Each solution was prepared with the same method. A 5.00 ± 0.10 g of either ninhydrin or sodium molybdate was dissolved in 100.00 mL volumetric flask with deionized water.

3.4 Optimization of polyelectrolyte multilayers (PEMs) film fabrication process on membrane filter

In this section, the studied substrates were quartz slides and polypropylene (PP) membrane filters (0.2 and 0.6 micron pore size). All substrates were coated with polyelectrolyte multilayers by the same process in this study. Before starting the coating process, quartz slides were cleaned in the piranha solution (conc. H_2SO_4 : 30% H_2O_2 , 3:1) in order to clean organic residues off substrates for 30 minutes [11]. Then, the substrates were rinsed with deionized water several times and dried by an air dryer. For polypropylene (PP) membrane filters, deionized water was used to remove grime on surface several times.

3.4.1 Fabrication process of polyelectrolyte multilayers (PEMs) film

For all working pH conditions (pH 5, 5.5, 7 and 9), the concentration of all polyelectrolyte solution was fixed at 10 mM, which was prepared by diluting the polyelectrolyte stock solution with 1 mM buffer solutions. Polyelectrolyte multilayers were deposited on substrate using the layer-by-layer technique. First, substrate was dipped into a polycation solution for 5 minutes. After that, the substrates were rinsed 3 times with appropriate buffer solution. Next, air was blown to dry the substrate using a hair dryer. Then, substrates were dipped into a polyanion solution for 5 minutes and rinsed 3 times with appropriated buffer solution. Finally, the substrates were dried. Then, the substrates were dipped alternately until the desired number of layers obtained.

3.4.2 Effect of sodium chloride concentration

The sodium chloride concentration was reported to be an important factor on the thickness of PEMs film. Therefore, the studied concentration were varied as 0.5, 1 and 1.5 M. Appropriate mass of sodium chloride was added into a polyelectrolyte solution and diluted with the desired buffer solution. The PEMs were fabricated to 20th layer on studied substrates. The film growth was monitored by Uv-Vis spectrophotometer.

3.4.3 Effect of pH of polyelectrolyte solution

The thickness and PEMs film formation depends on charge density that the charge densities of weak polyelectrolyte molecules and humic acid change with pH solution. Therefore, the optimized pH value of humic acid with various sodium chloride concentrations was evaluated. The pH of humic acid was kept at various pH values: 5, 7 and 9 using 1 mM buffer. However, the pH of PSSMA was fixed at pH 5.5 in the fabrication process of PDADMAC/PSSMA multilayer film due to previous work [22]. At this pH, the thickest PEMs film was achieved. The PEMs were fabricated to 20th layer on studied substrates. The film growth was monitored by Uv-Vis spectrophotometer.

3.4.4 Characterization of filter modified with polyelectrolyte multilayers film

3.4.4.1 Ultraviolet/Visible spectrophotometer

The build-up of polyelectrolyte multilayer on quartz slides were monitored using UV-Vis spectrophotometer. The growth of PDADMAC/PSSMA film was monitoring at characteristic UV absorption band of the styrene group of PSSMA is approximately 227 nm [13]. The PDADMAC/HA film was monitoring at characteristic UV absorption band of humic acid [23]. The evaluation was repeated on three different samples of non-modified and PEMs modified quartz slides. The reported values were the average of these data.

3.4.4.2 Attenuated Total Reflectance Fourier Transform Infrared Spectrometer (ATR-FTIR)

ATR-FTIR was used to monitor the PEMs growth of membrane filter by monitoring characteristic of specific functional groups on each polyelectrolyte. The functional groups were identified with ATR-FTIR within the wavenumber range of 400 to 4000 cm^{-1} and 32 scans in transmittance mode. Estimated peak area of each functional group deposited on membrane filter was measured using OMNIC PROGRAM.

The PEMs growth were evaluated on three pieces of each substrate both modified and non-modified surface under the same fabrication condition. For each sample, the three measurements were performed at three different positions on the surface of both non-modified and modified substrates. The reported peak areas were calculated from the integration of measured peak area, which relates to the functional group of PSSMA and humic acid.

3.4.4.3 Scanning Electron Microscope (SEM)

The surface morphology of non-modified and PEMs modified membranes was investigated by SEM using 15,000 magnification.

3.4.4.4 Atomic Force Microscopy (AFM)

AFM was used to measure the film thickness, surface morphology and roughness. Non-modified and modified membranes with polyelectrolyte multilayer films were measured in air with a scan rate of 0.03 Hz at 256 x 256 resolution in tapping mode. The film thickness was identified from the distance between two peaks on surface of membrane. Roughness reported in the term of Root-mean-square (rms) was determined from 50 μm x 50 μm images. The evaluation was repeated on three different samples of non-modified and PEMs modified membrane. The reported values were the average of these data.

3.5 The study of herbicide removal efficiency of PEMs modified membrane

The efficiency of membrane filter modified with PEMs using the optimized fabricating condition on herbicide removal was evaluated in this section.

3.5.1 The setup of flowing process

The membrane was put into the filter holder, which was connected with syringe pump as shown in figure 3.2. The herbicide solution filled into a 50 mL syringe was pumped into filter holder using syringe pump.

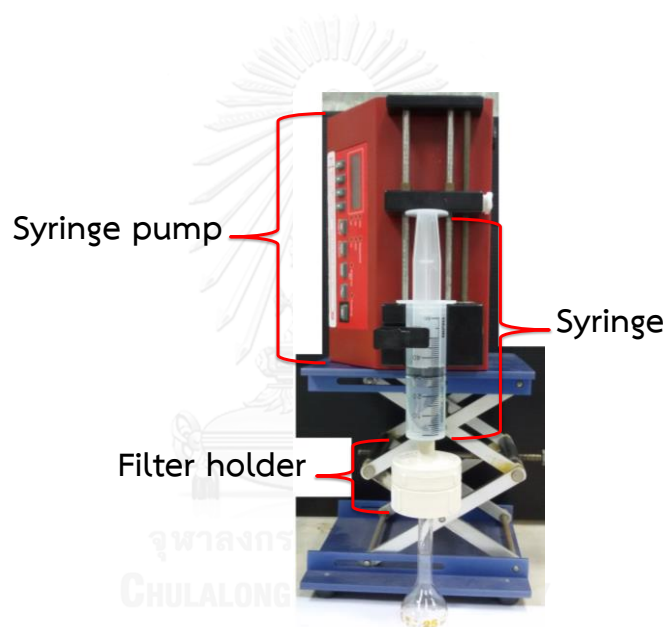


Figure 3.2 The setup of filtration unit

3.5.2 Calibration curves of herbicides

The concentration of herbicides left in the filtrate after filtration process were determined using the calibration curves of these standard solutions as described below. The herbicide concentration left after each filtration was determined three times and the reported values were the average of these data.

3.5.2.1 Paraquat

A calibration curve was prepared from a stock solution of 10 ppm paraquat. The stock solution was diluted with tap water to achieve the final concentration ranging from 0.1 to 5 ppm. Paraquat was performed by Uv/Vis spectrophotometer at 257 nm [24].

3.5.2.2 Glyphosate

A calibration curve of 0.1 to 5 ppm glyphosate was prepared from a stock solution (10 ppm glyphosate) by adding between 0.1 to 5 mL into 10 mL test tube. Then, 1 mL of 5% ninhydrin and 1 mL of 5% sodium molybdate were added to the test tube. The uncapped test tubes were kept in an oven at 95° C for 40 minutes. Then, the samples were cooled to room temperature and transferred to 10 mL volumetric flasks by rinsing all solutions out. The final volume was adjusted with deionized water. Then, the reading was performed by Uv/Vis spectrophotometer at 570 nm [18].

The blank solution was prepared by adding only 1 mL of 5% ninhydrin and 1 mL of 5% sodium molybdate in a test tube. After the reaction time is finished, the solution was transferred and diluted in the same manner.

Although the test tubes were not capped, the evaporation of solvent was not a concern because the solution was completely transferred to a 10 mL volumetric flask, which the final volume was adjusted to be 10.00 mL equally in every analysis.

3.5.3 Herbicides removal efficiency

The herbicide content after filtration was investigated using Uv/Vis spectrophotometer to evaluate the removal efficiency of non-modified and modified by polyelectrolyte multilayer film. From the calibration curve of each herbicide, the amount of herbicides presenting in each sample was determined. The removal efficiency was calculated using equation 3.1

$$\text{Herbicides removal} = A_1 - A_2 \quad (3.1)$$

Where A_1 is amount of added herbicides and A_2 is amount left in filtrate.

In general, a 10 mL of 5 ppm herbicides solution was used in this study. The setup of flowing process was described in the section 3.5.1 which the pumping flow rate was fixed at 1 mL/min. The quantification of herbicides after filtration process was explained in the section 3.5.3. The herbicides removal efficiency was calculated using equation 3.1.

3.5.4 Study of parameters affecting the herbicide removal efficiency of PEMs modified membrane

First, preliminary study on the removal herbicides efficiency of the two polyelectrolyte pairs, PDADMAC/PSSMA and PDADMAC/HA multilayers films fabricating using the optimized condition from section 3.4, were conducted to select only the best polymer pair for further studies.

3.5.4.1 Effect of numbers of depositing layer

In this study, the herbicides removal efficiencies of PEMs modified membrane as a function of deposition layers (6, 10 16 and 20) were investigated. For each condition, the evaluation was repeated on three different membrane filter samples. The reported values were the average of these data.

3.5.4.2 Effect of pumping flow rate

The adsorption kinetic of herbicides on the modified membrane is also a factor affecting the removal efficiency. Then, the impact of its flow rate was evaluated. The flow rates were controlled at 0.5, 1, and 1.5 mL/min. The number of coating layer showing the best herbicide removal efficiency obtaining from section 3.5.4.1 was used in this study. The studies in each condition were conducted on three modified membranes and non-modified membranes. The reported values were the average of these data.

3.6 Study of maximum capacity of modified membrane

The maximum capacities of modifying layer were determined. The 25 mL of herbicides with concentration between 1 and 10 ppm were used in this study, whereas the number of layer and flow rate found in the section 3.5.4.1 and 3.5.4.2 were used. The setup of flowing process was described in the section 3.5.1 and detection and quantification of herbicides after adsorption process were explained in the section 3.5.3. The removal efficiency was calculated using equation 3.1. The evaluation was repeated on three different samples of non-modified and PEMs modified membrane. The reported values were the average of these data.

3.7 Study of the adsorptive competition of herbicides on modified membrane

The effects of the coexisting of paraquat on glyphosate adsorption and vice versa were evaluated in this study. To evaluate the effect of paraquat (an interference) on the removal performance of filter on glyphosate, the concentration of glyphosate was fixed at 5 ppm, while the concentrations of paraquat were varied at 3 and 5 ppm. The volume of the mixture solution was fixed at 25 mL. Also, to evaluate the coexisting of glyphosate on the removal of paraquat, the studied solutions were prepared in the same manner.

The optimized number of layer and flow rate found in the section 3.5.4.1 and 3.5.4.2 were used. The setup of flowing process was described in the section 3.5.1 and detection and quantification of herbicides after adsorption process explained in the section 3.5.3. The removal efficiency was calculated using equation 3.1. The studies in each condition were conducted on three modified membranes and non-modified membranes. The reported values were the average of these data.

3.8 Stability of polyelectrolyte multilayers film

One concern in developing the polyelectrolyte multilayer films is their stabilities on the working condition. The stability of PEMs multilayers deposited on a membrane was evaluated by dipping into tap water for 4 weeks. The ATR-FTIR spectrum of PEMs was evaluated in each week. The peak area of functional groups before and after dipping was compared.

3.9 The modification of PEMs on water filter cartridge

3.9.1 The coating unit

The household water filtration unit was modified as shown in figure 3.3. The unit is composed of housing, vacuum gauge, valves No 1, 2 and 3, which are the inlet valves of buffer, polycation and polyanion solutions, respectively. Valve No 4 was connected to a vacuum pump, while valves No 5 and 6 are outlet valve to drain solution from the housing.

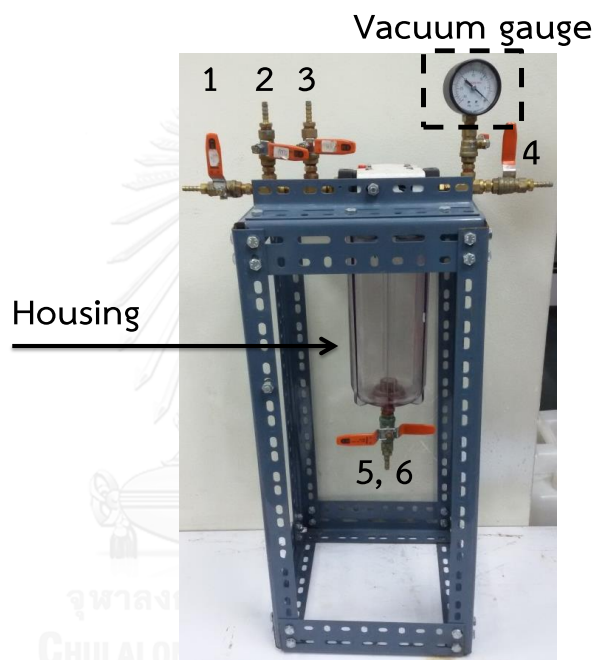


Figure 3.3 Modified household water filtration unit

3.9.2 Fabrication process of polyelectrolyte multilayers (PEMs) film on water filter cartridge

The optimized fabricating condition of polyelectrolyte multilayers on membrane found in section 3.4 was used in this study. The system of fabrication process was shown in figure 3.4. The modification of polyelectrolyte multilayer films on water filter cartridge was investigated by ATR-FTIR.

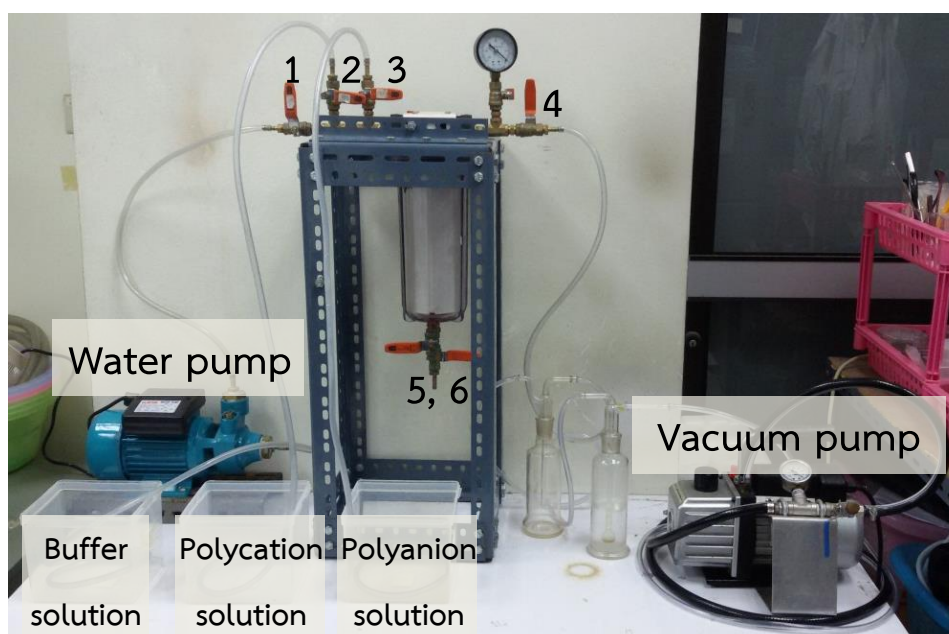


Figure 3.4 The system of fabrication process

The process for fabrication water filter cartridge was described as follow :

1. The water filter cartridge was put inside the household unit.
2. All valves except valve No 4 were closed. Vacuum pump was turned on and held at -25 inHg. Then, valve No 4 was closed as well as vacuum pump was off.

3. The water filter cartridge was coated with polycation solution by gradually opening valve No 2 which is connected with a plastic tube immersing in a bucket containing polycation solution until solution completely filled inside the unit. The system was kept for 5 minutes. Then, valve No 2 was closed.
4. Valves No 5 and 6 were opened to drain the solution into a waste container and were closed again after emptying liquid from the unit.
5. The water filter cartridge was washed with a buffer by opening valve No 1, which is connected to water pump pumping rinsing buffer solution. Valves No 5 and 6 were reopened to drain the buffer solution into a waste container. Then, the rinsing steps were repeated for remove the excess polycations on water filter cartridge. At this step, the surface of water filter cartridge was coated by polycation as the first layer.
6. Steps 2 to 5 were repeated for coating polyanion as the second layer on water filter cartridge by opening valve No 3 to bring polyanion solution into the filter unit.
7. Steps 2 to 6 were repeated until the desired number of layers obtained.

3.10 The efficiency of PP fiber filter cartridge modified with PDADMAC/HA on herbicide removal

3.10.1 The setup of filtration process

The performance of non-modified and modified water filter cartridge with PEMs film on the herbicide removal was evaluated. The modified household water filtration unit was also used in this study as shown in figure 3.5. Water pump was used to pump water sample. The flow rate is 2000 mL/min. The 400-mL spiked water sample was pumped through the system.

After passing the filtration unit, water was collected in a container for determining the herbicides removal efficiency in next step.

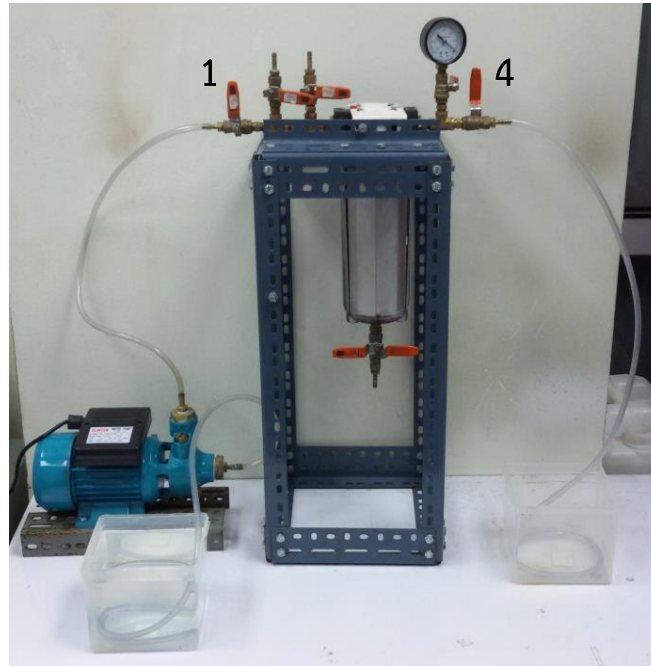


Figure 3.5 The system of filtration process

3.10.2 Herbicides removal efficiency in real water samples

Tap water and ground water were used in this study. The non-modified and modified water filter cartridge were evaluated by flowing 400 mL of 5 ppm herbicide.

The removal efficiency was calculated as described in section 3.5.3. The evaluation was repeated on three different samples of non-modified and PEMs modified water filter cartridge. The reported values were the average of these data.

CHAPTER IV

RESULTS AND DISCUSSION

In our study, there are three major parts. The first part was to optimize the PEMs fabrication condition using layer-by-layer technique on the membrane filter. The studied parameters affecting the fabrication of polyelectrolyte multilayer thin films are pH and concentration of sodium chloride in polyelectrolyte solution. The second part was to employ the membrane filter modified with PEMs in the herbicide removal process and its performance was evaluated. The modification condition of these filters was the optimized condition found in the first step. Studied parameters affecting the herbicide removal efficiency of PEMs modified membrane were number of coating layers and flow rate of herbicides solution. Moreover, the study of the maximum capacity of modified membranes and the adsorptive competition of herbicides on modified membranes were also evaluated. Finally, the feasibility study of this coating on household water filter unit for herbicide removal was also tested.

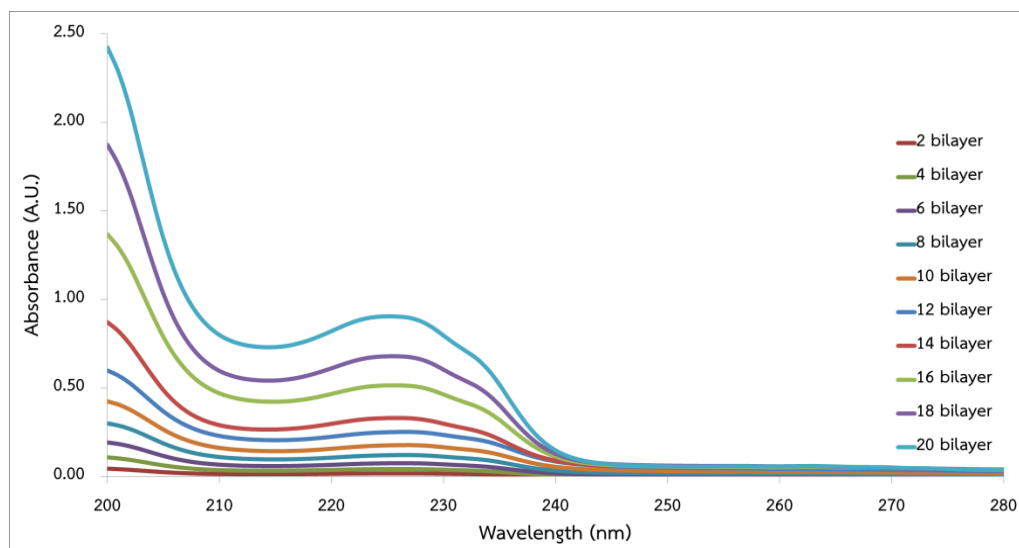
4.1 Optimization study of parameters affecting the fabrication of polyelectrolyte multilayer films

The fabrication of polyelectrolyte multilayer, PDADMAC/PSSMA and PDADMAC/HA, on quartz slides and polypropylene (PP) membrane filter 0.2 and 0.2-0.6 micron pore size as a function of concentration of sodium chloride and pH of solution. The concentration of sodium chloride of 0, 0.5, 1 and 1.5 M were used. The studied pH values of HA solution were 5, 7 and 9, while the pH of PSSMA solution was fixed at pH 5.5 due to previous work at this pH, the thickest PEMs film was achieved [22].

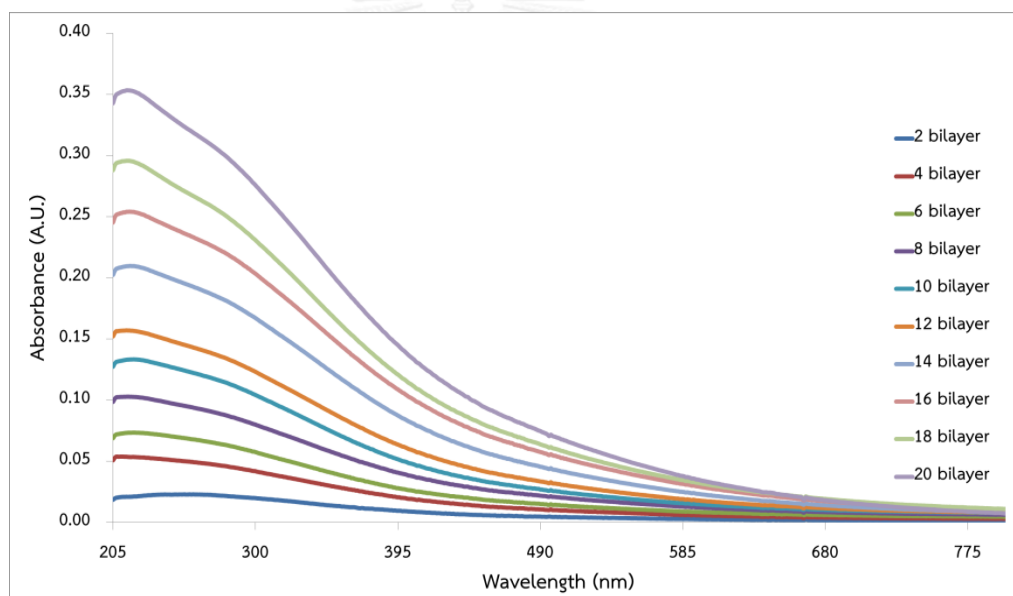
4.1.1 The build-up of polyelectrolyte multilayer films on substrates

In this study, quartz slides were chosen to be one of the studied materials because it is easy to monitor the behavior of PEMs growth by using UV-Vis spectrophotometer. The absorbance values from UV spectra of PEMs provided information on the amount of polyelectrolyte incorporated into the films. The absorbance value of PDADMAC/PSSMA was investigated at 227 nm, which a characteristic UV absorption band of the styrene group of PSSMA [13]. Absorbance value of PDADMAC/HA was investigated at 300 nm, which a characteristic UV absorption band of the carbonyl group of HA [23].

The PDADMAC/PSSMA film with fabrication condition of pH 5.5 and 1 M NaCl and PADMAC/HA film with fabrication condition of pH 7 and 1 M NaCl were represented for all conditions because the growth behavior of all polyelectrolyte multilayer films in all conditions were similar. The UV spectra of polyelectrolyte multilayer films were showed in figure 4.1. From the UV-Vis spectra, the absorbance of both multilayer films increased with the number of deposition layers, indicating the amount of polyelectrolyte incorporated into the film increased. Moreover, the result of UV-Vis spectra shows the success of the PDADMAC/PSSMA and PDADMAC/HA multilayer films fabrication on quartz slides.



(a)

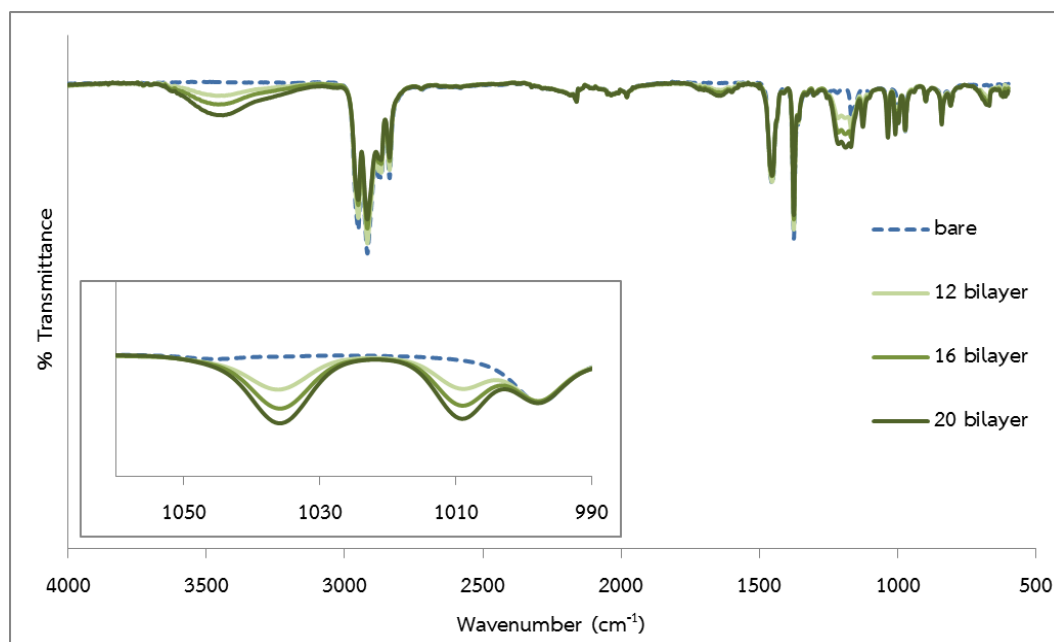


(b)

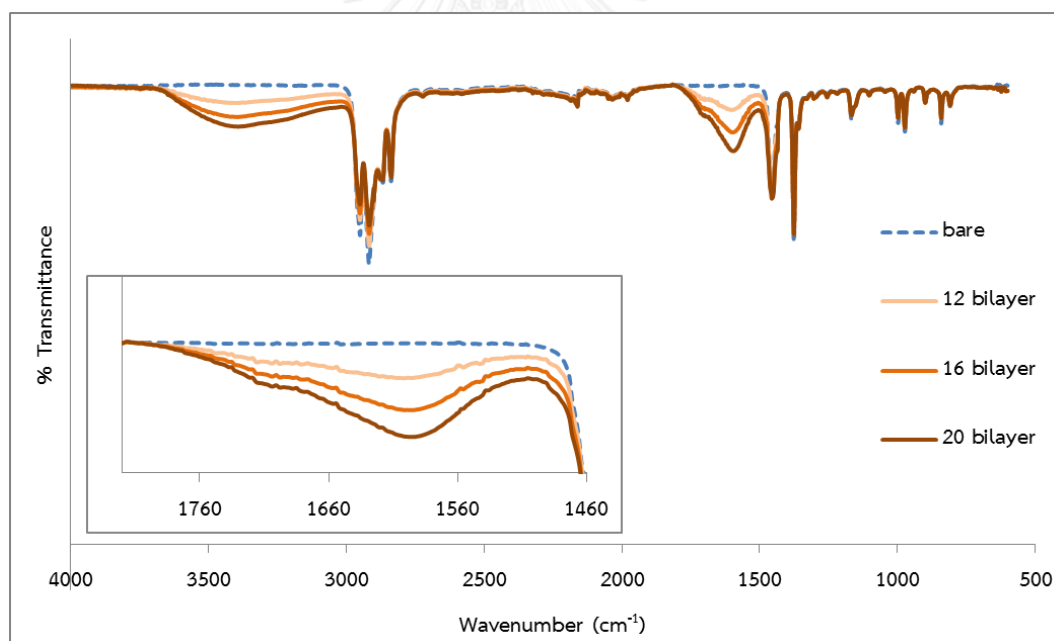
Figure 4.1 Absorption spectra of polyelectrolyte multilayers growth on quartz slides from 2nd to 20th layers. (a) PDADMAC/PSSMA with fabrication condition of pH 5.5 and 1 M NaCl and (b) PADMAC/HA fabrication condition of pH 7 and 1 M NaCl.

Polypropylene (PP) membrane filter 0.2 and 0.2-0.6 micron pore size were chosen to be one of the studied materials because the composition of material similar with water filter cartridge, which was used in next study, and membrane filter easy to investigation the behavior of PEMs growth by using ATR-FTIR. The ATR-FTIR spectra of PDADMAC/PSSMA multilayer films was monitored at 1011 and 1130 cm^{-1} , which are sulfonate group (SO_3^-) on PSSMA [25]. For PDADMAC/HA multilayer films, the characteristic peaks at 1720 and 1580 cm^{-1} , which are assigned for carbonyl ($\text{C}=\text{O}$) stretching of carboxyl groups (COOH) and asymmetric of (COO^-), respectively [23]. The peak areas of functional groups of PEMs provided information on the amount of polyelectrolyte incorporated into the films. The reported peak areas were calculated from the integration of peak areas which relate to the functional group of PSSMA and HA on ATR-FTIR spectra of PDADMAC/PSSMA and PDADMAC/HA multilayer films, respectively.

The PDADMAC/PSSMA film with fabrication condition of pH 5.5 and 1 M NaCl and PADMAC/HA film with fabrication condition of pH 7 and 1 M NaCl were represented for all conditions as well. The ATR-FTIR spectra of polyelectrolyte multilayer films were showed in figure 4.2. The result obtaining from membrane filters with different pore sizes shows the same growth behavior of polyelectrolyte multilayers film thus the result from each condition to fabrication of PEMs was shown on one pore size. From the ATR-FTIR spectra, the peak areas of functional group of both film increased with the number of the coating layers, indicating the amount of polyelectrolyte incorporated into the film increased. Moreover, the result of ATR-FTIR spectra shows the success of the PDADMAC/PSSMA and PDADMAC/HA multilayer films fabrication on membrane filter.



(a)



(b)

Figure 4.2 ATR-FTIR spectra of polyelectrolyte multilayers growth on membrane filter 0.6 micron pore size. (a) PDADMAC/PSSMA (Inset shows the increase SO₃⁻ peak) and (b) PDADMAC/HA (Inset shows the increase C=O stretching peak) multilayers assembled using 1 M NaCl concentration and pH 5.5 PSSMA and pH 7 HA.

4.1.2 Effect of sodium chloride concentration on the build-up of PDADMAC/PSSMA

The concentration of sodium chloride of 0, 0.5, 1 and 1.5 M were used for fabrication PDADMAC/PSSMA multilayer thin films on quartz slides and membrane filters at 20th layer. The absorbance values of PEMs growth on quartz slides were monitored from UV-Visible spectra shown in figure 4.3. The peak areas values of functional groups of PEMs growth on membrane filters were calculated from ATR-FTIR spectra of PEMs shown in figure 4.4.

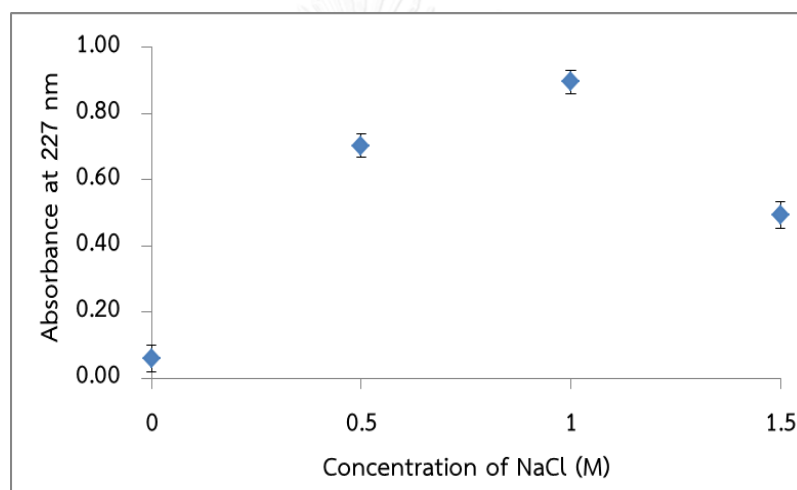


Figure 4.3 Absorbance values of PDADMCA/PSSMA (20th layer) at 227 nm fabricated on quartz slides as a function of concentration of sodium chloride.

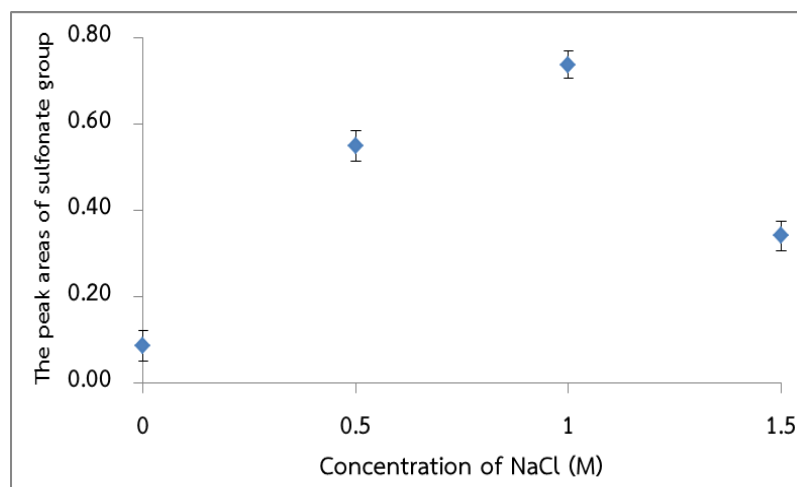


Figure 4.4 Peak areas values of sulfonate group of PDADMCA/PSSMA (20th layer) fabricated on membrane filter 0.2 micron pore size as a function of concentration of sodium chloride.

From our result, similar growth trends were observed that the amount of depositing polyelectrolyte on both substrates was increased with sodium chloride concentration. In case of no added sodium chloride, the polymer charged segments were compensated by other polymer charges resulting thinner film. Under 0.5 M sodium chloride, the polymer charged segments were compensated by some of sodium chloride ions causing polymer chain became more extended resulting to thicker film than in case of no added sodium chloride. At 1 M sodium chloride, sufficient sodium chloride ion was more compensate to polymer charged segments and the polymer chain conformation changes to coil or loop conformation causing thicker film [12, 26]. However, increasing to the 1.5 M sodium chloride, thickness was decreased. Because polymer segments were over extended due to more sodium chloride ion compensate to polymer charged segments [27, 28].

The result found in this section showed the best fabrication condition gaining the thickest PDADMAC/PSSMA multilayers film is 1 M NaCl and pH 5.5 of solution, on both substrates.

4.1.3 Effect of sodium chloride concentration and pH of solution on the build-up of PDADMAC/HA

The studied pH values as 5, 7 and 9 of HA solution and concentration of sodium chloride of 0, 0.5, 1 and 1.5 M were used for fabrication PDADMAC/HA multilayer thin films. The absorbance values of PEMs growth on quartz slides were monitored from UV-Visible spectra shown in figure 4.5. The peak areas values of functional groups of PEMs growth on membrane filter were calculated from ATR-FTIR spectra of PEMs shown in figure 4.6.

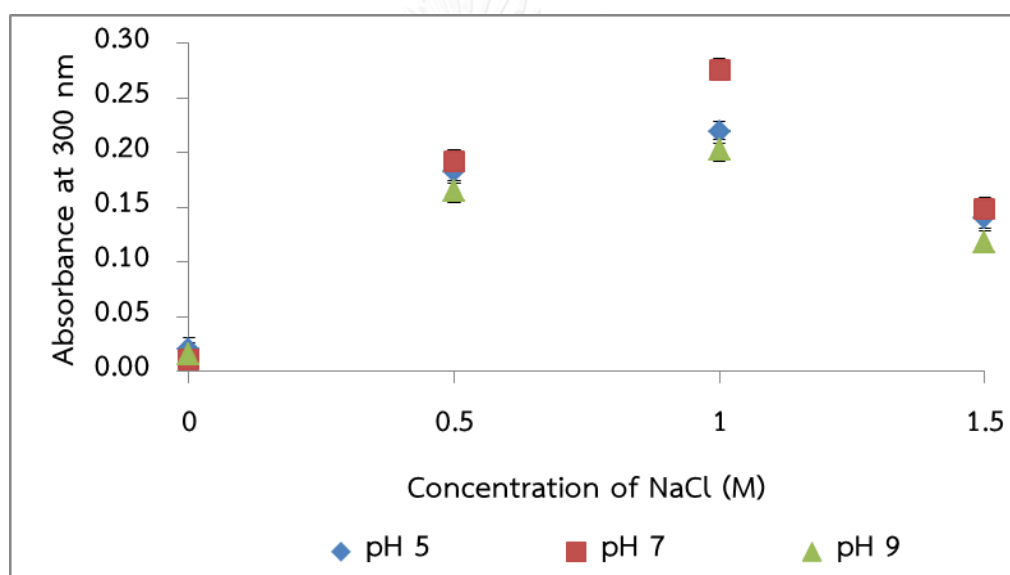


Figure 4.5 Absorbance values of PDADMCA/HA (20th layer) at 300 nm fabricated on quartz slides as a function of concentration of sodium chloride and pH of solution.

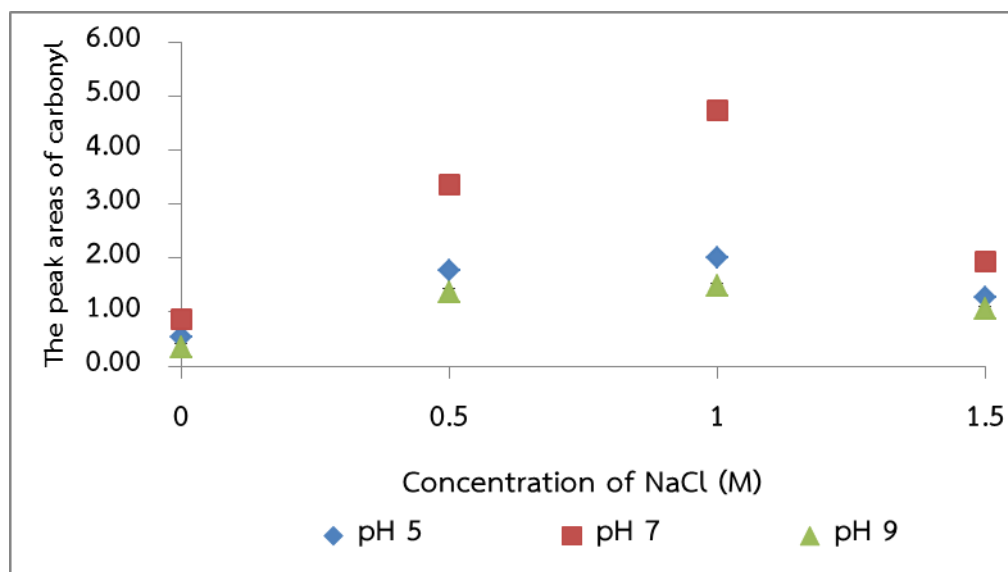


Figure 4.6 Peak areas values of carbonyl group of PDADMCA/HA (20th layer) fabricated on membrane filter 0.2 micron pore size as a function of concentration of sodium chloride and pH of solution.

From our results, similar growth trends on both substrates with function of sodium chloride concentration and pH of HA solution were observed. The 1 M NaCl delivers the highest absorbance values and peak areas values of functional groups of PEMs on all pHs. Moreover, the best pH value was found to be at 7. The effect of sodium chloride concentration on PEMs growth showed similar trend as in PDADMAC/PSSMA study.

The PEMs growth using pH 9 HA solution was poor. It is because at this pH higher than pKa of carboxylic groups (pKa = 4–5) and phenol groups (pKa = 8–10) [29, 30], all weak acid functional groups in macromolecule of HA are deprotonated resulting in the highly negative charged density on the HA molecules [31, 32]. HA are expected to strongly contact with PDADMAC, which always be positive charges [33], mainly by electrostatic interaction and hydrogen bonding. At pH 7, the degree of dissociation of weak acid groups on HA is smaller. Therefore, lowering the ionization leads to a decrease in the negative charge density that decrease repulsive force between the negative charged molecules. HA molecules

might form hydrogen bondings between molecules into aggregate, which is bulky [34]. Therefore, lowering the negative charge density of HA results in the formation of thicker films. At pH 5, HA molecules has less negative charge density. Then, it can form less interactions with PDADMAC. In conclusion, the highest adsorption was gained at pH 7.

The result found in this section showed that the best fabrication condition gaining the thickest PDADMAC/HA multilayers film is 1 M NaCl and pH 7 of solution on both substrates.

4.1.4 Film thickness and surface morphology

The AFM images of polyelectrolyte multilayer (PEMs) films fabricating under 1 M NaCl and various pH values were shown in figure 4.7. The image shows the smooth surface area of unmodified polypropylene (PP) membrane filter while the surface of membrane modified by polyelectrolyte multilayer films are rougher. The thicknesses values of each polyelectrolyte multilayers film were shown in figure 4.8. For PDADMAC/HA pair, the fabrication condition delivering the thickest film were pH 7. The cause of PDADMAC/HA fabricating with all pHs having thicker film than PDADMAC/PSSMA film might be because of the bulky structure of HA molecules [31].

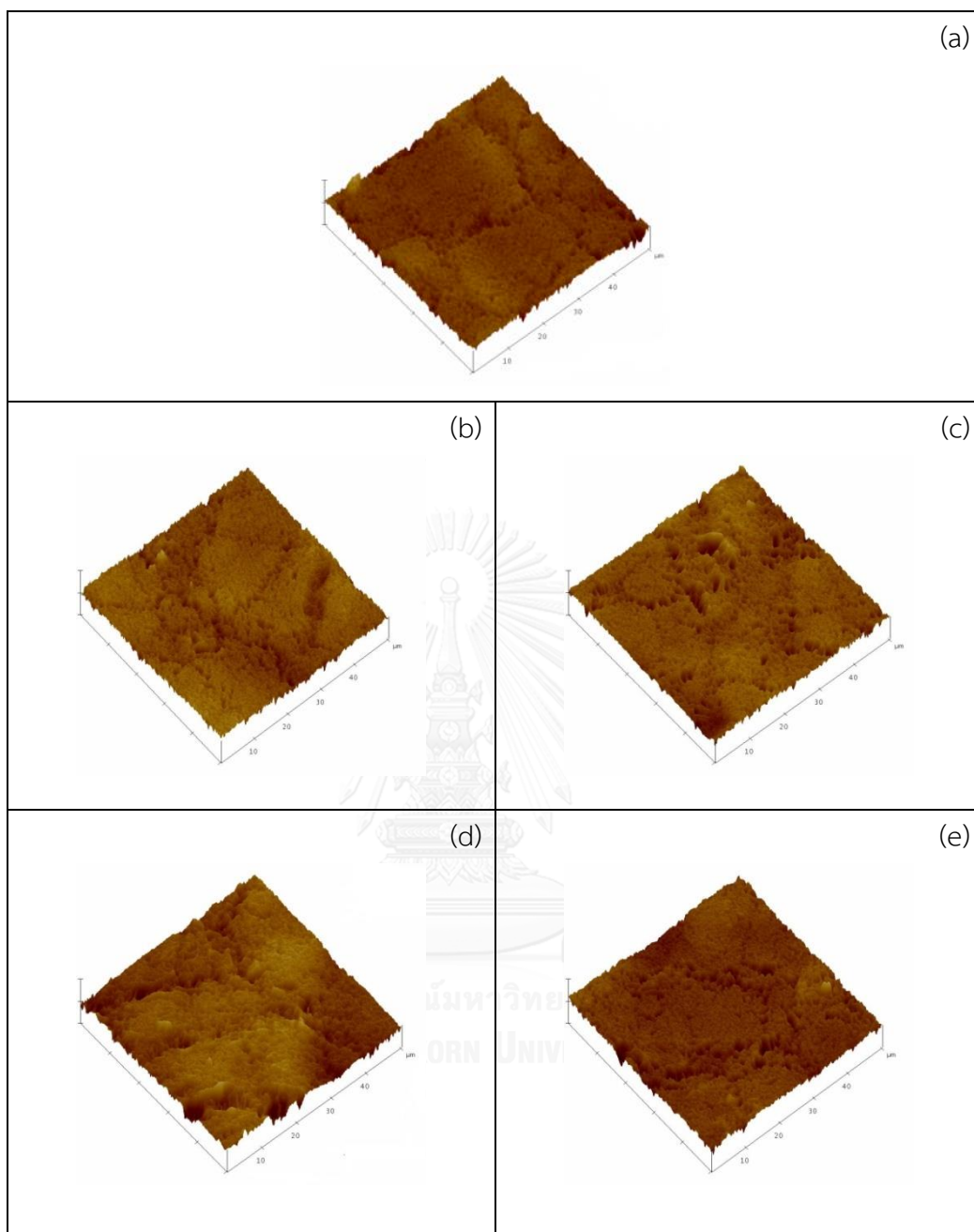


Figure 4.7 AFM images of polypropylene (PP) membrane filter 0.2 micron pore size with (a) unmodified membrane and modified membrane with (b) 6 layers of PDADMAC/PSSMA using buffer pH 5.5 while (c - e) 6 layers of PDADMAC/HA multilayers films using buffer pH 5, 7 and 9, respectively. All films were fabricated using 1 M NaCl.

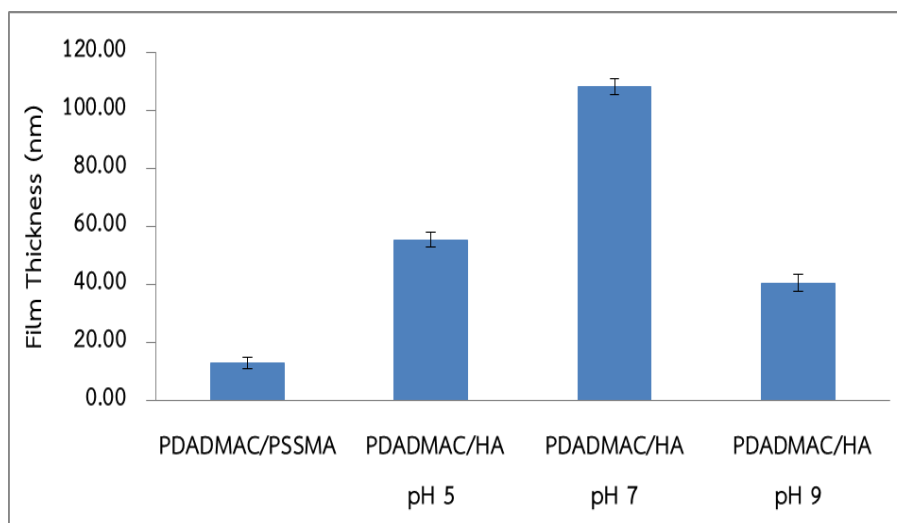


Figure 4.8 Thickness value of PDADMAC/PSSMA and PDADMAC/HA multilayers films after the deduction of the unmodified membrane thickness (274.72 nm).

The surface morphology of the unmodified, PDADMAC/PSSMA and PDADMAC/HA modified membranes, fabricating using the optimized condition (pH 7 and 1 M NaCl) was examined using SEM (Figure 4.9). In comparison with unmodified membrane, the porosity of modified membrane decreased.

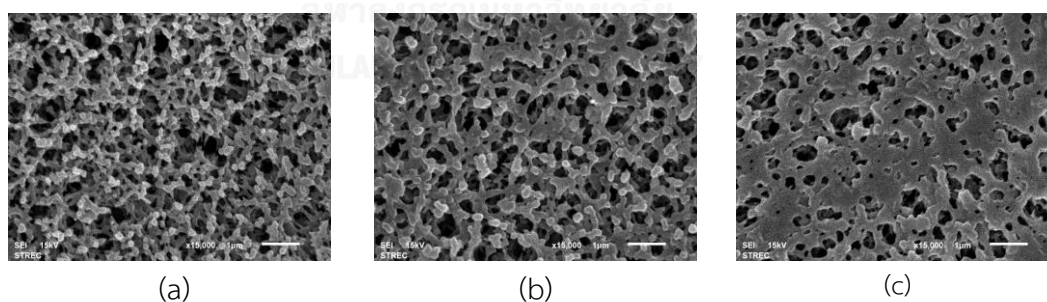


Figure 4.9 SEM images of polypropylene (PP) membrane filter 0.2 micron pore size with (a) unmodified and modified membrane with 6th layer of (b) PDADMAC/PSSMA and (c) PDADMAC/HA.

The result found in section of optimization study of parameters affecting the fabrication of polyelectrolyte multilayer films showed the success on the fabrication of polyelectrolyte multilayers film on all types of substrates. The growth behavior of polyelectrolyte multilayers film is independent from types of substrate which is in agreement with the previous study [10]. These results confirmed that the best fabrication condition gaining the thickest are PDADMAC/HA multilayers film fabricating using 1 M NaCl and pH 7 HA solution.

4.2 Study of parameters affecting the herbicide removal efficiency of PEMs modified membrane.

The removal amount of herbicides after filtration was calculated from calibration curve of each herbicide. The removal amount was calculated from the subtraction between amount of herbicides, which was spiked in tap water and left in the filtrate.

Paraquat concentration was investigated using UV/Vis spectrophotometer. The calibration curve shown in figure 4.10 was plotted between the absorbance at 257 nm [24] and concentration of paraquat ranging from 0.1 to 5 mg/L. The limit of detection (LOD) is 0.03 mg/L and the limit of quantitation (LOQ) is 0.06 mg/L.

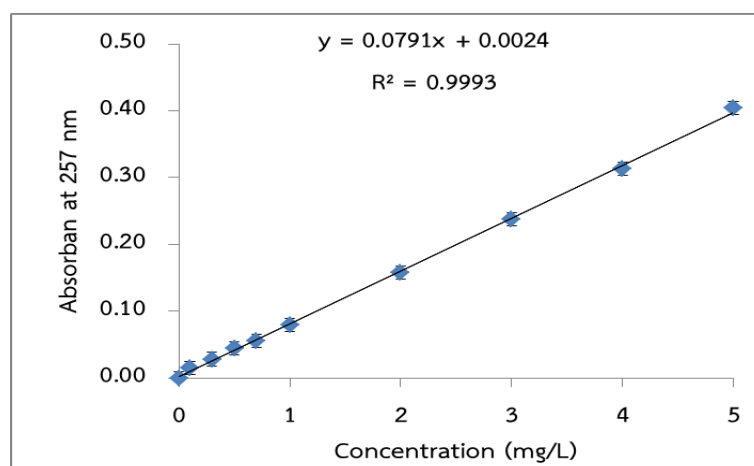


Figure 4.10 Calibration curve of paraquat

The figure 4.11 shows that the linear relationship was observed over the glyphosate concentration range of 0.1 to 5 mg/L. The limits of detection (LOD) and quantitation (LOQ) are 0.03 mg/L and 0.17 mg/L, respectively.

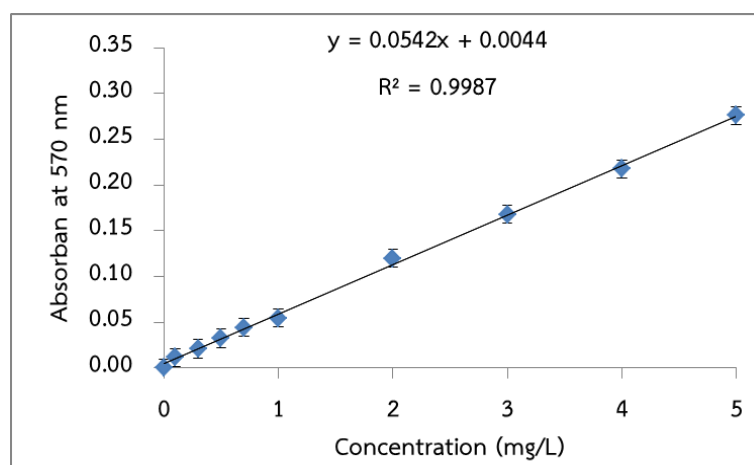


Figure 4.10 Calibration curve of glyphosate with ninhydrin and sodium molybdate

4.2.1 Preliminary study of the polyelectrolyte type on the herbicide removal efficiency

The performance of each pair, PDADMAC/PSSMA and PDADMAC/HA multilayers films, on the herbicide removal was studied to select the best pair for further studies. The PDADMAC/HA removed larger amount of paraquat and glyphosate than PDADMAC/PSSMA could (Figure 4.11). This might be because HA molecules can form stronger electrostatic interaction and hydrogen bond with herbicides [31]. Thus, the PDADMAC/HA multilayers film was selected in for the next studies.

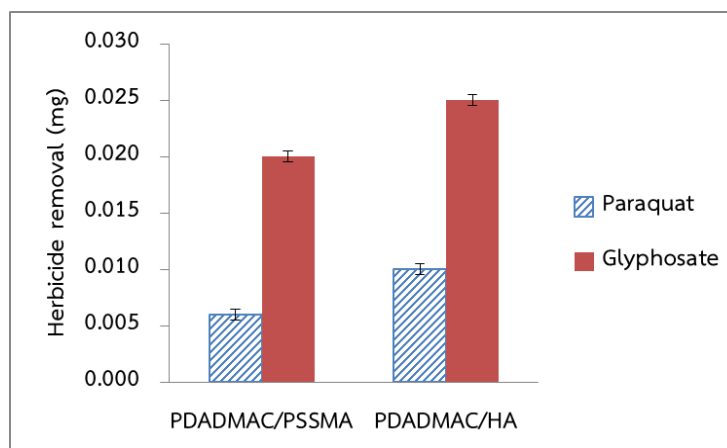
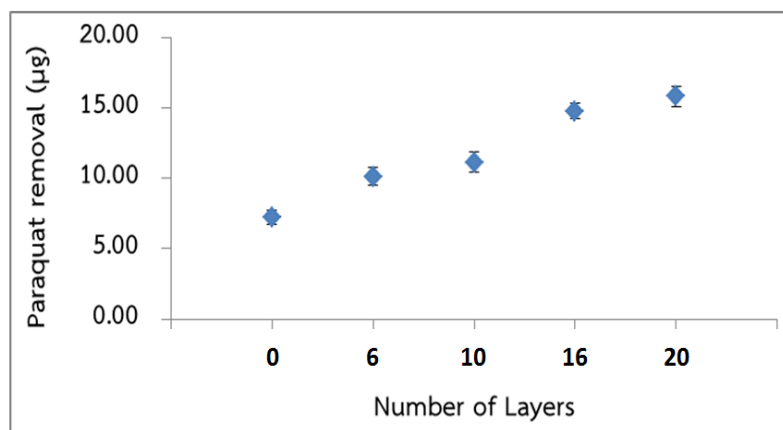


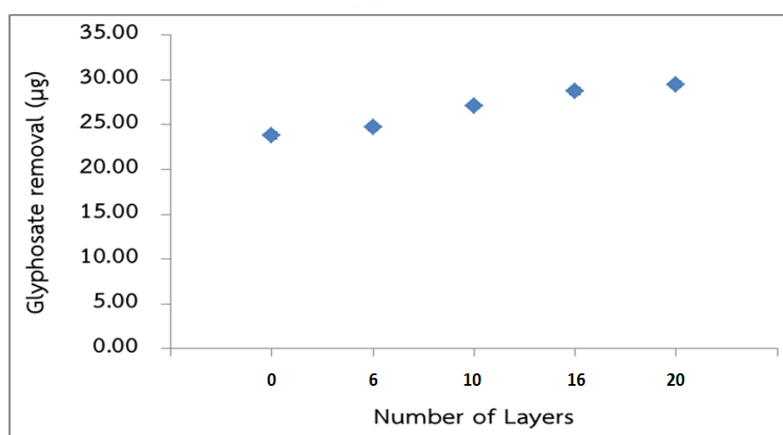
Figure 4.11 Herbicide removal by PDADMAC/PSSMA and PDADMAC/HA multilayers films.

4.2.2 Effect of number of depositing layer

From the preliminary study, only membrane modified with PDADMAC/HA was used in this study. A 10 mL of 5 ppm of paraquat and glyphosate, and flow rate of 1 mL/min were used. The result showed that the removal of herbicides increased with increasing numbers of coating layer (figure 4.12). Due to the PEMs modified membrane thicker than 20 layers, the solution could leak from the filtration unit. Therefore, the highest number of coating layers on the membrane filter in this study was 20 layers. However, after 16 coating layers, the removal values were relatively constant. Thus, in the next study the 16 coating layers were used.



(a)

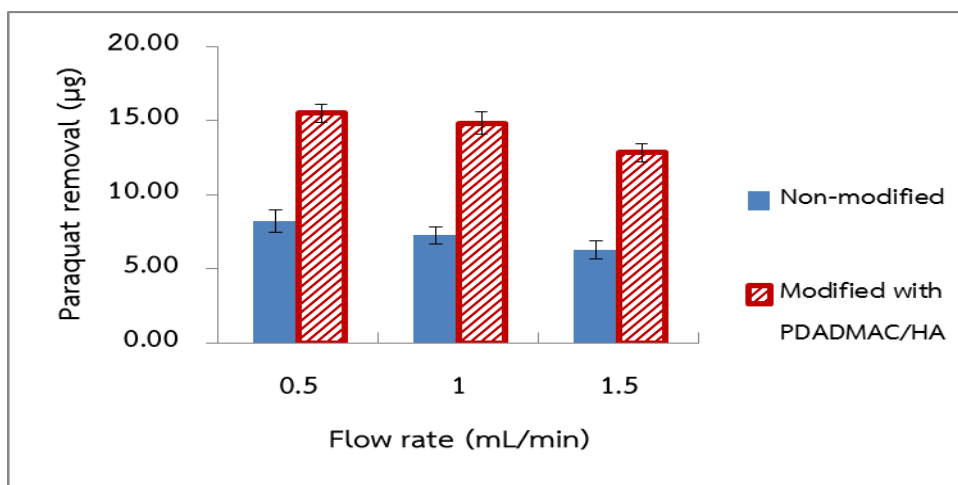


(b)

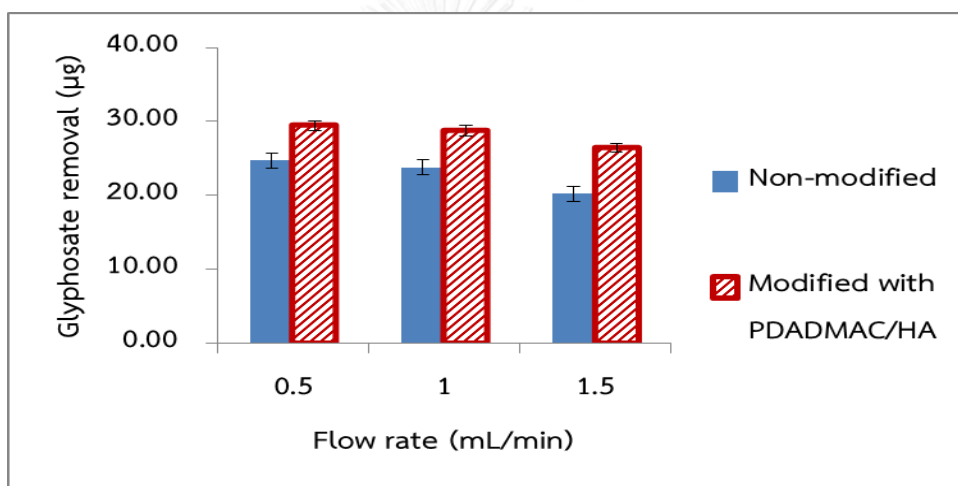
Figure 4.12 Herbicide removal of non-modified and modified membranes with various the numbers of PDADMAC/HA layers. (a) paraquat and (b) glyphosate

4.2.3 Effect of flow rate

The adsorption of herbicides on modified membrane depends on sample flow rate. Then, the optimized sample flow rate was studied. The result showed that when flow rate was increased, the herbicides removal was decreased. This may be because the interaction time between herbicides and PEMs are too little (figure 4.13). Moreover, the modified membrane delivered better performance on the removal herbicides than non-modified membrane for all flow rates. Therefore, flow rate 0.5 mL/min will be used in next studies.



(a)



(b)

Figure 4.13 Herbicide removal of non-modified and modified membrane with various flow rates: (a) paraquat and (b) glyphosate

4.3 Study of maximum capacity of modified membrane

The maximum capacity of non-modified and modified membrane with PDADMAC/HA at 16th layer were determined. The 25 mL of herbicides with concentrations of 1, 2, 3, 4, 5, 8 and 10 ppm were used in this section. The similar trends were observed in both non-modified and modified membrane that paraquat removal was relatively constant with the increase in concentration, while glyphosate removal increased with the increase in concentration and then leveled off.

The maximum herbicide capacity of membranes both non-modified and modified with PDADMAC/HA can be found from the 2nd derivatives of the plot between herbicide removal versus various concentrations (figure 4.14 and 4.15). The lowest point of the curve was used to find the maximum herbicide content. The result was shown in figure 4.14 and 4.15. The maximum capacity of non-modified membranes for paraquat is $8.24 \pm 0.37 \mu\text{g}$, while modified membrane with PDADMAC/HA is $16.89 \pm 0.45 \mu\text{g}$ (2.0-fold increase). For glyphosate removal, maximum capacity of non-modified membrane is $56.32 \pm 0.54 \mu\text{g}$ and modified membrane with PDADMAC/HA is $64.43 \pm 0.26 \mu\text{g}$ (1.1-fold increase).

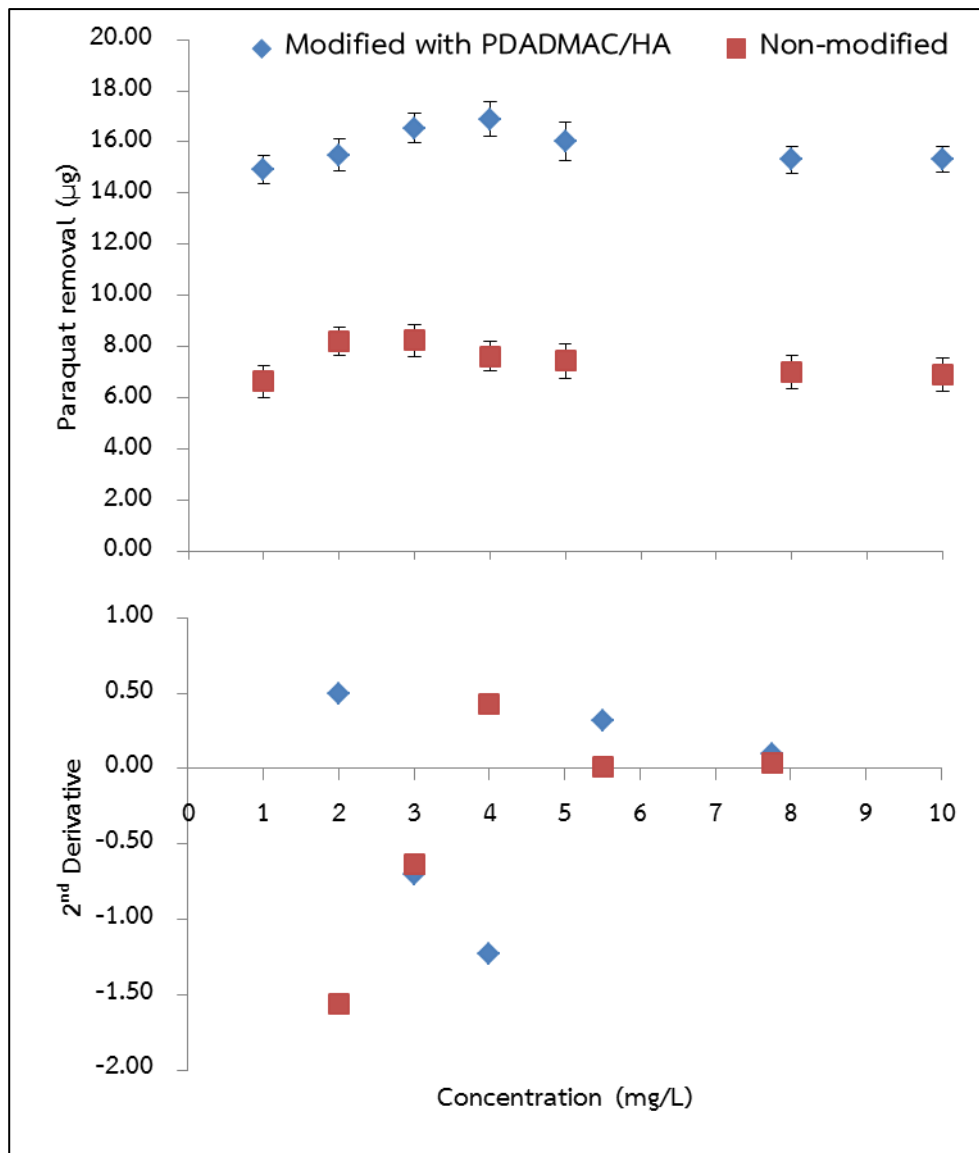


Figure 4.14 Herbicide removal and 2nd derivative of non-modified and modified membranes with various concentrations of paraquat.

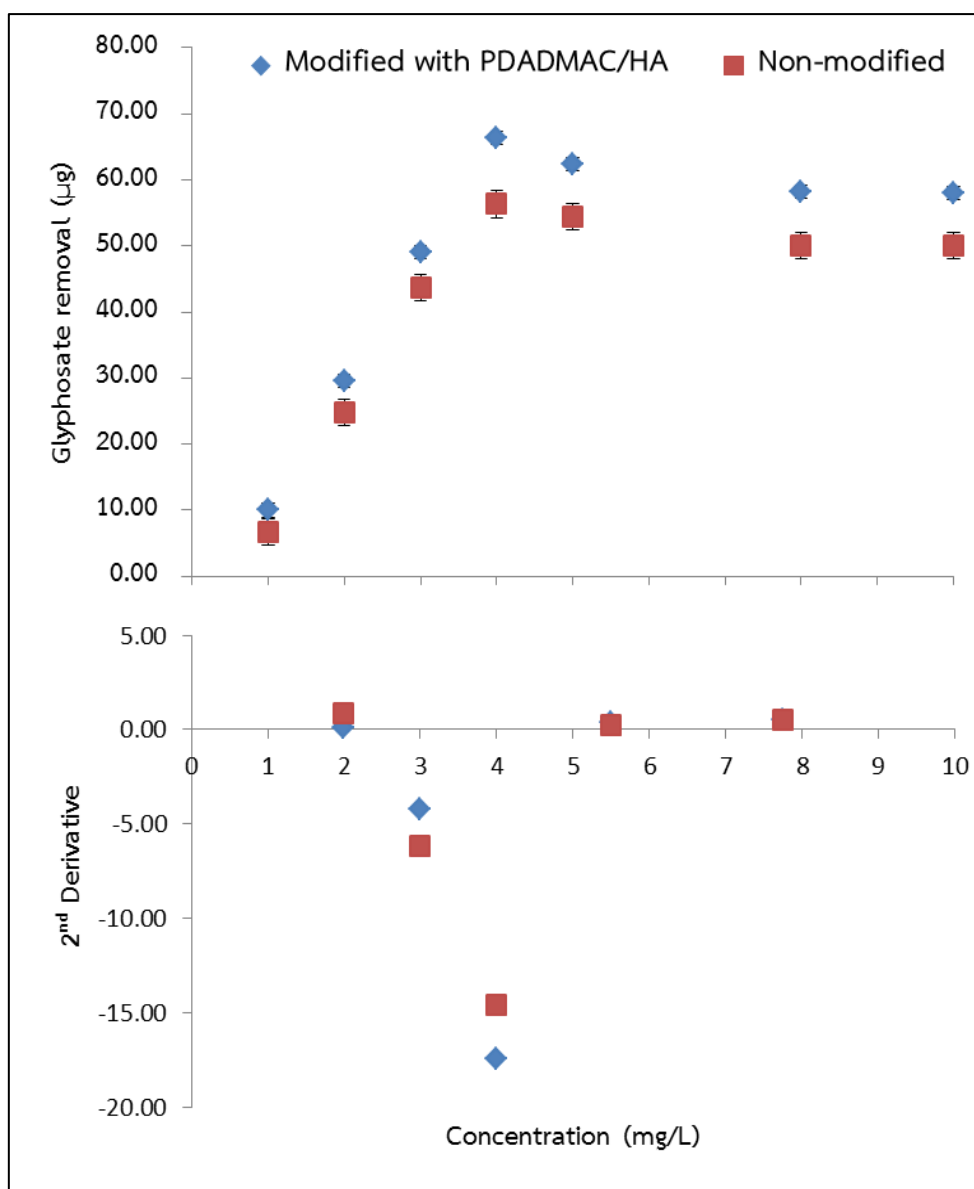


Figure 4.15 Herbicide removal and 2nd derivative of non-modified and modified membranes with various concentrations of glyphosate.

The modified membrane with PDADMAC/HA enhances the herbicides removal especially for paraquat although the thickness of PEMs is in nanometer scale.

The herbicide adsorption on the PDADMAC/HA modified membrane can be depicted into 2 main parts, which are PP material within membrane and PEMs (PDADMAC/HA) layer. Because the adsorption of both paraquat and glyphosate on non-modified membrane should be occurred only on PP membrane, the difference between adsorbed herbicides content on modified membrane could indicate the adsorbed amount in PEMs film. Table 4.1 shows the calculated amount of both paraquat and glyphosate within PEMs layers.

Table 4.1 The adsorbed herbicide content on modified membrane

Herbicide	Herbicide removal of PDADMAC/HA modified membrane (μg)		
	PP membrane	PDADMAC/HA	Total herbicide removal (Maximum capacity)
Paraquat	8.24 ± 0.37	8.65 ± 0.08	16.89 ± 0.45
Glyphosate	56.32 ± 0.54	8.11 ± 0.28	64.43 ± 0.26

The amount of paraquat adsorption on PEMs and PP membrane was insignificant difference. The adsorption between paraquat and PEMs should be via electrostatic interactions. The pH of solution influences the charges on HA molecules. The pH value of paraquat solution was found to be around 6.8 ± 0.15 in all concentrations, which HA possesses partially negative charges due to $pK_a = 4-5$ of carboxylic group and $pK_a = 8-10$ of phenol [29, 30]. Owing to its cationic character, paraquat interacts greater with humic acid which enhances paraquat removal efficiency. The electrostatic interaction between humic acid and paraquat are shown in figure 4.16.

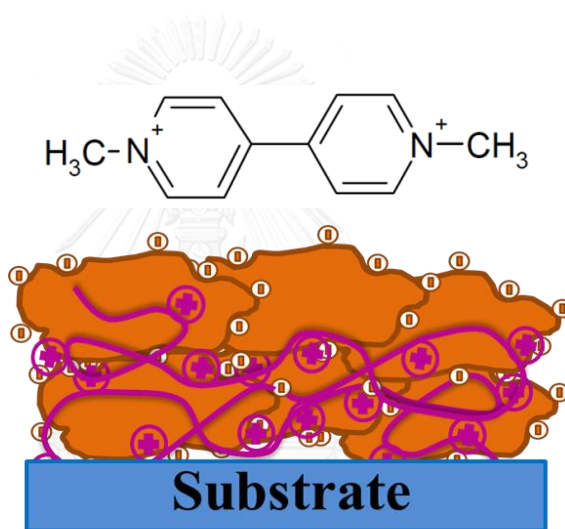


Figure 4.16 The electrostatic interaction between humic acid and paraquat

From Table 4.1, the amount of glyphosate adsorption on PP membrane was larger than the one adsorbed on PEMs. For the glyphosate adsorption, the pH value of glyphosate solutions was around 7.3 ± 0.12 in all concentrations. From the values found in the literature corresponding to the acid dissociation constants of glyphosate are $pK_{a1} = 0.8$ (first phosphonic acid group), $pK_{a2} = 2.6$ (carboxylic acid), $pK_{a3} = 5.6$ (second phosphonic acid) and $pK_{a4} = 10.6$ (amino group) [17], the structure of glyphosate with the acid dissociation constants was shown in figure 4.17.

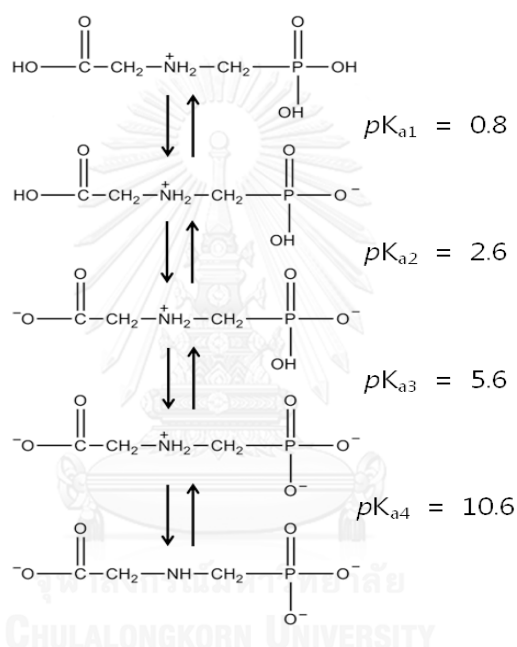


Figure 4. 17 Proposed dissociation diagram and ionization constants for glyphosate [17].

Thus, at $pH = 7.3 \pm 0.12$ of solution, glyphosate possesses three negative charges and one positive charge ($pK_{a3} = 5.6$). The present of both positive and negative charges resulted in the aggregation of glyphosate molecules. This may cause the decrease in the net charges of molecule allowing HA molecules forming interaction with PP membrane via Van der Waals forces. Simultaneously, the electrostatic interactions between humic acid and glyphosate occurred in figure 4.18.

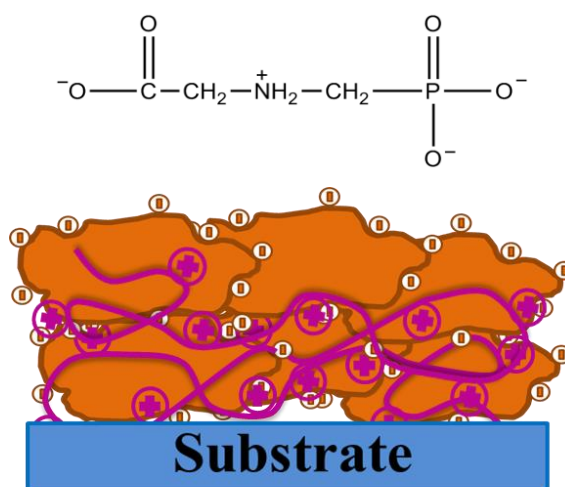


Figure 18 The electrostatic interaction between humic acid and glyphosate

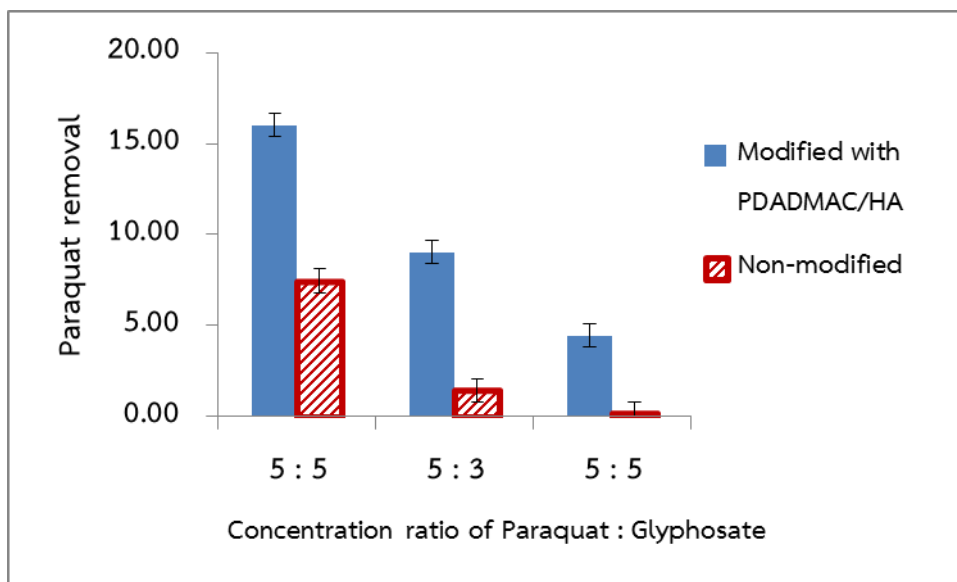
From table 4.1, the maximum capacity of 16th layer PEMs (PDADMAC/HA) on the paraquat and glyphosate adsorption are $8.65 \pm 0.08 \mu\text{g}$ and 8.11 ± 0.28 , respectively. It indicates that the ability of PEMs is not selective to types of herbicides and PEMs shows the maximum capacity around $8 \mu\text{g}$.

In comparison with other reports, the percentage of removal efficiency was calculated from amount of herbicide removal and the spiked content (100 mg of herbicide) [4]. The reported percentage of removal efficiency for paraquat was 5%, whereas in our study the percentage removal was found to be 17%. However, the percentage of removal efficiency for glyphosate reported in previous study was more than 60% [35], whereas in our study the percentage removal was found to be 66%. In summary, our developed membrane filter can deliver better removal efficiency for paraquat but show similar performance for glyphosate.

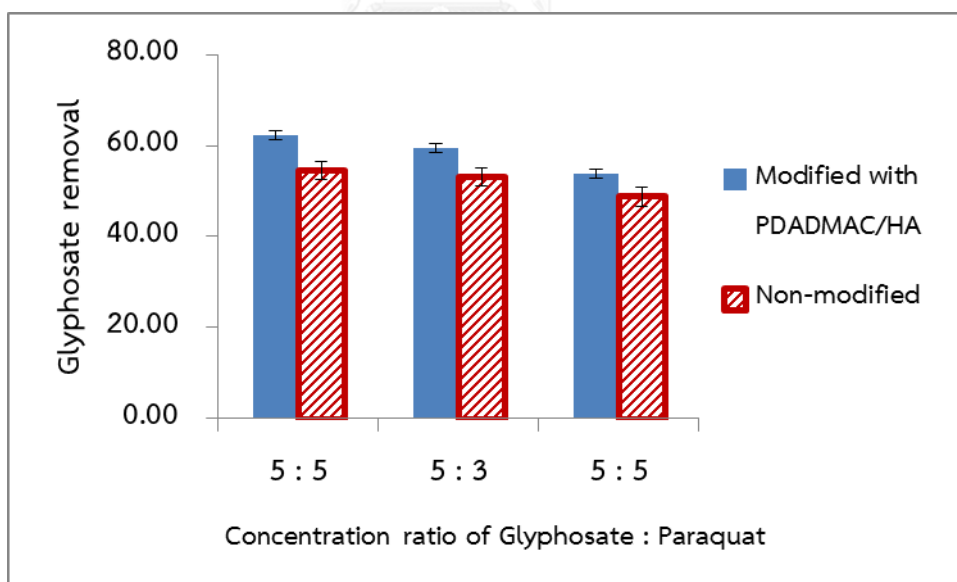
4.4 Study of adsorptive competition of herbicide on membrane

The effects of the coexisting of paraquat on glyphosate adsorption and vice versa on membrane with non-modified and modified with PDADMAC/HA were studied. The concentrations ratios (mg/L:mg/L) of paraquat to glyphosate and vice

versa were 5:0, 5:3 and 5:5 in 25 mL of mixture solution. The result was shown in figure 4.19.



(a)



(b)

Figure 4.19 The competitive adsorption of herbicides with various concentrations ratios of (a) paraquat to glyphosate and (b) glyphosate to paraquat.

In figure 4.19(a), the concentrations ratios of paraquat to glyphosate. When glyphosate, as interference was added in a paraquat solution, the paraquat removal was decreased. As discussed in section 4.3, paraquat is mainly adsorbed on PEMs layer where glyphosate could be adsorbed as well. So these compounds compete to bind with the active site within PEMs

In other hands, in figure 4.19(b) shows the slightly decrease of glyphosate removal when paraquat was added because the glyphosate is mainly adsorbed on PP membrane, while paraquat is adsorbed less in this area. Thus, the coexisting of paraquat has no impact on the glyphosate adsorption in all concentrations.

Moreover, in this study the maximum capacity of PEMs on the herbicide removal was confirmed to be around 8 μg due to the total amount of herbicide on PEMs of all concentration ratios of paraquat to glyphosate (Table 4.2) and glyphosate to paraquat (Table 4.3).

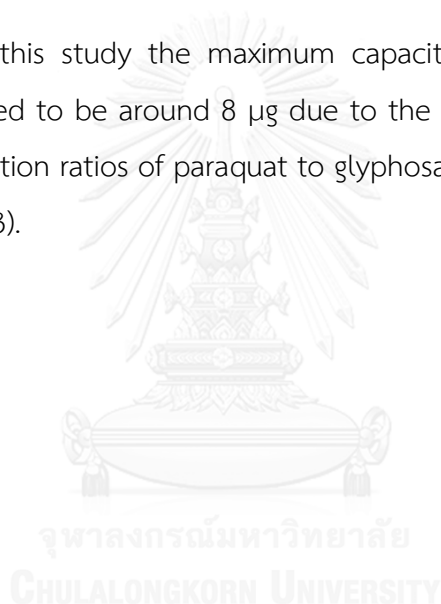


Table 4.2 The adsorbed herbicide content on modified membrane with PDADMAC/HA with the coexisting of glyphosate on paraquat adsorption.

PDADMAC/HA modified membrane	Ratio of paraquat : glyphosate ($\mu\text{g} : \mu\text{g}$)					
	5 : 0		5 : 3		5 : 5	
PP membrane	7.45 ± 0.18	-	1.41 ± 0.56	34.30 ± 0.47	0.15 ± 0.32	48.73 ± 0.29
PDADMAC/HA	8.56 ± 0.16	-	7.63 ± 0.32	2.87 ± 0.29	4.30 ± 0.11	5.03 ± 0.24
Total amount of herbicide	16.01 ± 0.34	-	9.04 ± 0.88	37.17 ± 0.76	4.45 ± 0.43	53.76 ± 0.53
Total amount of herbicide on PDADMAC/HA	8.56 ± 0.16		10.50 ± 0.61		9.33 ± 0.35	

Table 4.3 The adsorbed herbicide content on modified membrane with PDADMAC/HA with the coexisting of paraquat on glyphosate adsorption.

PDADMAC/HA modified membrane	Ratio of glyphosate : paraquat removal ($\mu\text{g} : \mu\text{g}$)					
	5 : 0		5 : 3		5 : 5	
PP membrane	54.44 ± 0.38	-	52.99 ± 0.62	0.09 ± 0.33	48.73 ± 0.29	0.15 ± 0.32
PDADMAC/HA	7.89 ± 0.14	-	6.54 ± 0.27	1.16 ± 0.07	5.03 ± 0.24	4.30 ± 0.11
Total amount of herbicide	62.33 ± 0.52	-	59.53 ± 0.89	1.25 ± 0.40	53.76 ± 0.53	4.45 ± 0.43
Total amount of herbicide on PDADMAC/HA	7.89 ± 0.14		7.70 ± 0.34		9.33 ± 0.35	

4.5 Stability of polyelectrolyte multilayers

The film stability after soaking in tap water was evaluated by monitoring the peak area of humic acid IR spectra at 1720 and 1580 cm^{-1} which was assigned to the COOH and COO^- , respectively. After soaking membrane modified with PEMs in tap water for 4 weeks, the membrane still showed the excellent stability of PEMs film coated on membrane (Table 4.4).

Table 4.4 The peak areas of carboxyl groups of HA with various weeks.

Weeks	The peak areas of carboxyl groups
1	4.7 ± 0.3
2	4.7 ± 0.3
3	4.7 ± 0.3
4	4.7 ± 0.3

The stability of the film after being pressurized was also evaluated by measuring thickness of polyelectrolyte multilayers film before and after flowing tap water through membranes filters by AFM. The AFM image was shown in figure 4.20. The thickness values of PEMs before and after flowing tap water through membranes filter are 682.85 ± 0.42 and 671.09 ± 0.34 , respectively. From these results, the polyelectrolyte multilayers film were not desorbed or torn after being pressurized.

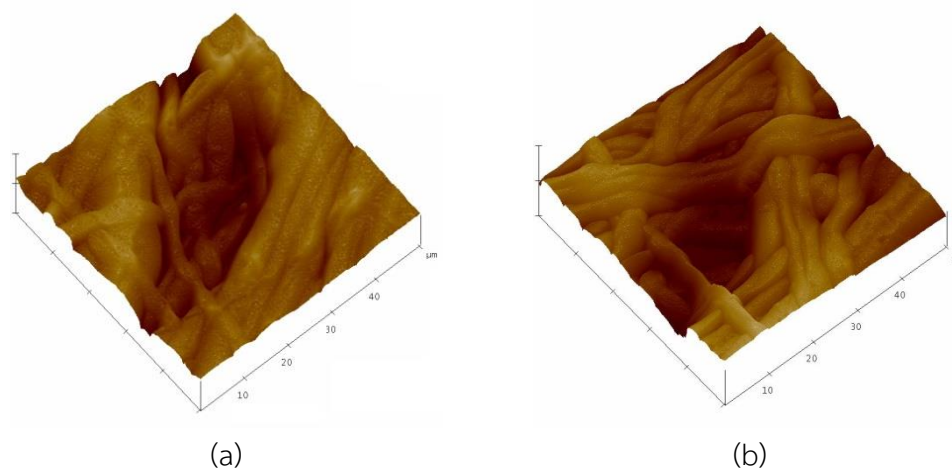


Figure 4.20 AFM images of HA modified membrane (a) before and (b) after flowing tap water through the membranes filter.

4.6 The modification of PEMs on household water filter unit.

Based on our finding on the optimized fabricating condition and the best polymer pair, the fabrication ability of PEMs on membrane was demonstrated on PP fibrous water filter cartridge. The 16th layers of PDADMAC/HA were coated on the fibrous filter cartridge shown in figure 4.21. The step for fabrication was described in section 3.5.7. The images and ATR-FTIR spectra of filter cartridge before and after fabricating were shown in figure 4.22. It can be seen that the polyelectrolyte multilayers was successfully fabricated on filter based on the characteristic peaks at 1720 and 1580 cm^{-1} , which are assigned to the COOH and COO^- on humic acid molecules.

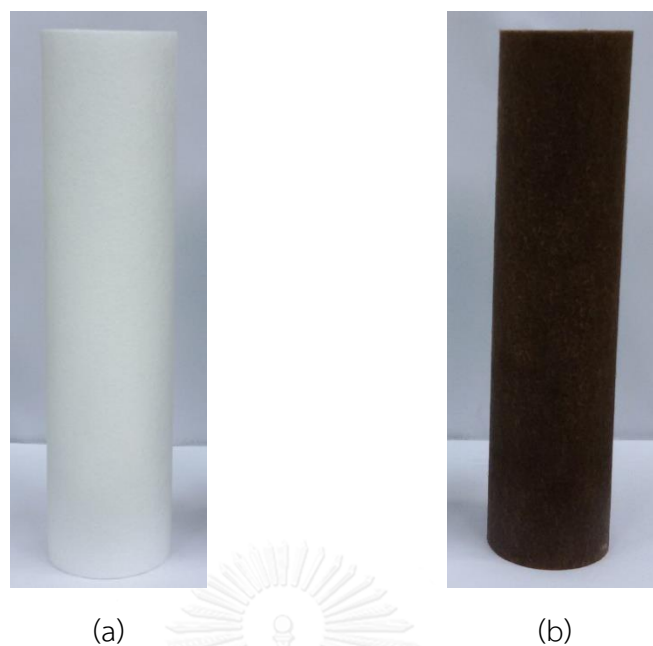


Figure 4.21 (a) filter and (b) modified filter cartridge with 16th layers of PDADMAC/HA.

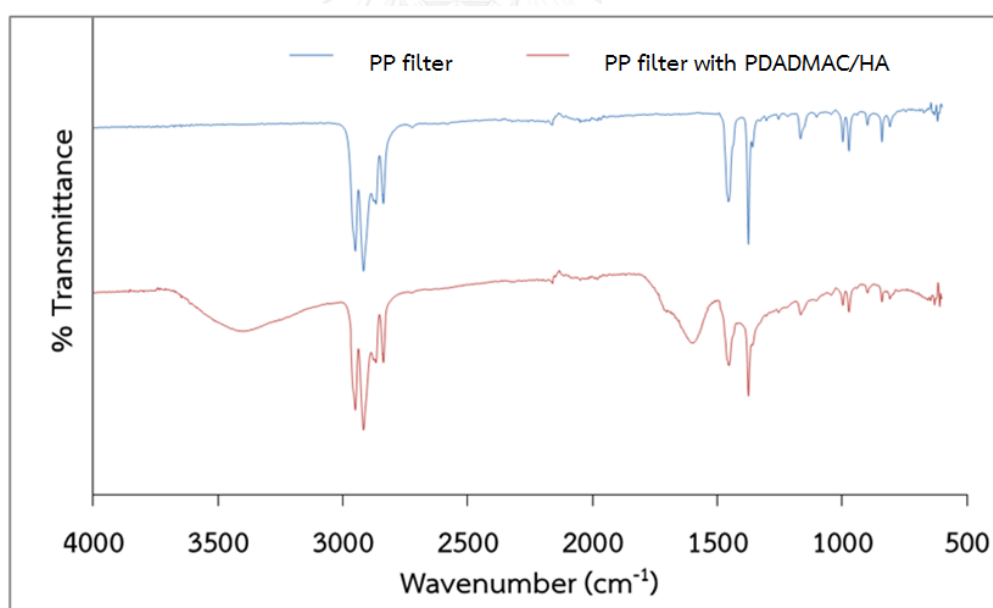


Figure 4.22 ATR-FTIR spectra for (a) Polypropylene (PP) filter cartridge and (b) 16th layers PDADMAC/HA modified PP cartridge.

4.7 The filtration by household water filter unit.

In this part, two types of spiked water samples: tap water and ground water were used to test the modified water filters cartridge. The non-modified and modified filters cartridge were evaluated by flowing 400 mL of 5 ppm paraquat and glyphosate spiked in water samples using the water pump at flow rate of 2000 mL/min. The herbicide content after filtration was investigated using Uv/Vis spectrophotometer to evaluate the removal efficiency.

4.7.1 Spiked tap water sample

In comparison study with unmodified PP, the PDADMAC/HA modified filter cartridge improved the removal efficiency, which amount of herbicides removal was increased from 0.20 ± 0.37 to 0.67 ± 0.45 mg (3.4-fold increase) for paraquat and from 1.03 ± 0.26 to 1.49 ± 0.34 mg (1.5-fold increase) for glyphosate (figure 4.23).

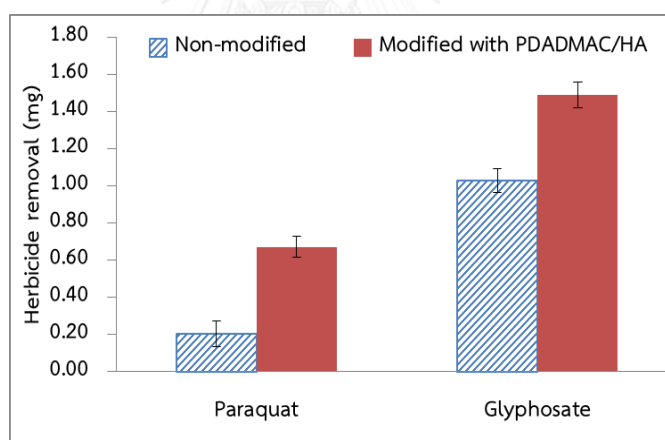


Figure 4.23 Herbicide removal of non-modified and modified filter cartridge with PDADMAC/HA

4.7.2 Ground water sample

In ground water, the new calibration curves were prepared using ground water as solvent. The calibration curve of paraquat was shown in figure 4.24. The limit of detection (LOD) is 0.04 mg/L and the limit of quantitation (LOQ) is 0.09 mg/L.

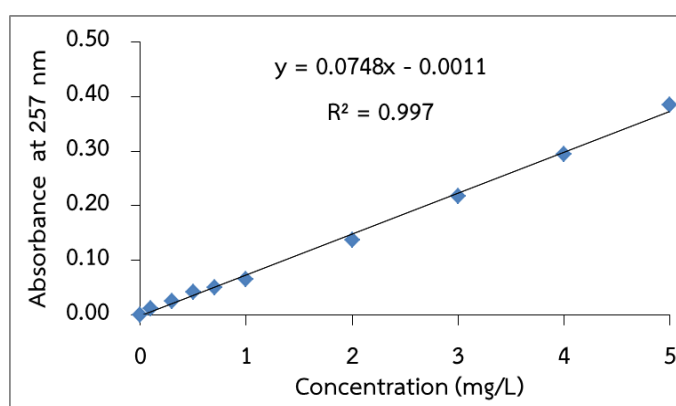


Figure 4.24 Calibration curve of paraquat

The calibration curve of glyphosate was shown in figure 4.25. The limit of detection (LOD) is 0.04 mg/L and the limit of quantitation (LOQ) is 0.21 mg/L.

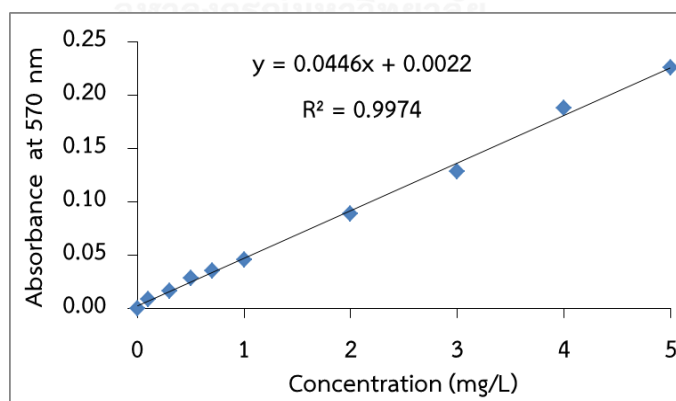


Figure 4.25 Calibration curve of glyphosate with ninhydrin and sodium molybdate.

In comparison study with unmodified PP filter, the PDADMAC/HA modified filter cartridge improved the removal efficiency, which amount of herbicides removal was increased from 0.15 ± 0.42 to 0.55 ± 0.26 mg (3.7-fold increase) for paraquat and from 0.69 ± 0.25 to 1.26 ± 0.44 mg (1.8-fold increase) for glyphosate (figure 4.26).

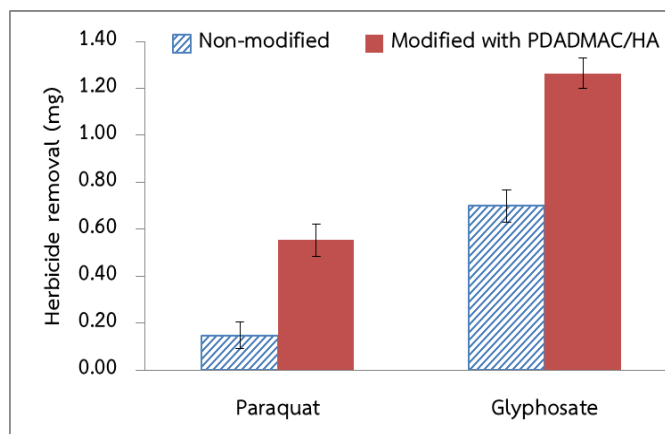


Figure 4.26 Herbicide removal of non-modified and modified filter cartridge

From the result, the herbicides removal efficiency of ground water is better than the spiked tap water. This might be because the ions in the spiked ground water could increase the HA layer thickness; more amount of herbicides were adsorbed.

CHAPTER V

CONCLUSION

In this study, we aimed to modify a polypropylene membrane filter with polyelectrolyte multilayers to enhance the effectiveness on the removal of water contaminated with herbicides, paraquat and glyphosate. Polyelectrolyte multilayers were fabricated using poly(diallyl dimethyl ammonium chloride), (PDADMAC) as a polycations and either poly(styrene sulfonic acid-co-maleic acid), (PSSMA) as a polyanions and humic acid (HA) as a macromolecule via layer-by-layer (LbL) technique. The factors affecting fabrication film were concentration of sodium chloride and pH of humic acid solution to achieve the best film growth condition were studied. The growth of multilayer films on substrates, quartz slides and polypropylene (PP) membrane filters (0.2 and 0.2-0.6 micron pore size) were monitored via Uv-vis, ATR-FTIR, SEM and AFM. The result showed the success on the fabrication of polyelectrolyte multilayers film on all types of substrates with difference morphology. The growth behaviour of polyelectrolyte multilayers film is independent from type and morphology of substrate. The optimized fabrication condition delivering the thickest film is PDADMAC/HA multilayers film, 1 M NaCl and pH 7 of solution. The evaluation the efficiency of modified membrane for herbicides removal from water was studied through the factors: number of layer and flow rate of herbicides solution. The optimized number of the depositing layers was sixteen layers and the flow rate at 0.5 mL/min was the best condition. Regarding paraquat removal, the maximum capacity of non-modified membranes is $8.24 \pm 0.37 \mu\text{g}$, while PDADMAC/HA modified membrane with PDADMAC/HA multilayers film is $16.89 \pm 0.45 \mu\text{g}$ (2.0-fold increase). For glyphosate removal, maximum capacity of non-modified membrane is $56.32 \pm 0.54 \mu\text{g}$ and modified membrane with PDADMAC/HA multilayers film is $64.43 \pm 0.26 \mu\text{g}$ (1.1-fold increase).

The fabrication of polyelectrolyte multilayers film on household water filter unit was successful. The water filter cartridge was fabricated with the optimized condition previously found. In tap water sample, in comparison study with unmodified PP filter, the PDADMAC/HA modified filter improved the removal efficiency. The amount of herbicides removal was increased from 0.20 ± 0.37 to 0.67 ± 0.45 mg (3.4-fold increase) for paraquat and from 1.03 ± 0.26 to 1.49 ± 0.34 mg (1.5-fold increase) for glyphosate. For ground water sample, PDADMAC/HA modified filter improved the removal efficiency over unmodified PP filter, which amount of herbicides removal was increased from 0.15 ± 0.42 to 0.55 ± 0.26 (3.7-fold increase) for paraquat and from 0.69 ± 0.25 to 1.26 ± 0.44 mg (1.8-fold increase) for glyphosate. From the all results obtained, the modified membrane by polyelectrolyte multilayers can enhance the efficiency to herbicides removal from water.

Suggestion of future work

Suggestion for the further work is to optimize flow rate to use with water filter cartridge unit and find the maximum capacity of filter on the herbicides removal and life time of PEMs coated filter cartridge. The final study is to apply our modified filter cartridge with another water samples.

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APPENDIX

จุฬาลงกรณ์มหาวิทยาลัย
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VITA

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