

**DEVELOPMENT OF COMPOSITE POLYELECTROLYTE COMPLEX  
MEMBRANE FOR CATIONIC DYE AND HEAVY METAL SORPTION**

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Membrane for Cationic Dye and Heavy Metal Sorption  
**By:** Wanwanut Chueasupcharoen  
**Program:** Polymer Science  
**Thesis Advisor:** Asst. Prof. Stephan Thierry Dubas

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## ABSTRACT

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The sorption process is most useful in water treatment because it provides high sorption efficiency, low cost and rapid method. Polyelectrolyte complex (PECs) is a novel polymeric membrane prepared by mixing between oppositely charged polyelectrolyte solution of PDADMAC and PSS. Activated carbon (ACs) is used to improved adsorption efficiency in PECs. Non-stoichiometric PDADMAC/PSS membrane were prepared by mixing excess PSS concentration to get the negative charges on the membrane surface. Sorption efficiency was evaluated by methylene blue, cationic dye and heavy metal ions based on the same material, the difference sorption mechanism were observe. In the cationic dye, the adsorption mechanism operated by excess PSS on membrane surface via electrostatic interaction. The maximum adsorption capacity occur in a removal salt 1:2 PDADMAC:PSS mole ratio (R-1:2) without AC which is  $4.9 \text{ mg g}^{-1}$  with  $10 \text{ mg l}^{-1}$  of methylene blue concentration. Furthermore, R-1-2 fitted with pseudo-second order kinetic model and Temkin isotherm model with physical adsorption type and also regenerated by salt solution. In contrast, the heavy metal ions sorption operated ion exchange mechanism, 1:2 PDADMAC:PSS without AC show highest sorption capacity which is  $30 \text{ mg g}^{-1}$  with  $50 \text{ mg l}^{-1}$  of  $\text{Cu}^{2+}$  ions concentration. The mechanism occur between  $\text{Na}^+$  on PSS chain and  $\text{Cu}^{2+}$  ions in solution. The metal ions sorption fitted with pseudo-second order kinetic model and Freundlich isotherm model with chemical sorption type and bilayer surface sorption and shows high selective of  $\text{Pb}^{2+}$  and  $\text{Cr}^{3+}$  metal ions.

## บทคัดย่อ

วรรณวนิช เชื้อทรัพย์เจริญ : การพัฒนาไฮบริด โพลีอิเล็กโทรไลต์ /คาร์บอนกัมมันต์ เมมเบรน สำหรับการดูดซับสีย้อมและโลหะหนัก ( Development of Hybrid Polyelectrolyte Complex/Activated Carbon Membrane for Dye and Heavy Metal sorption)

อ. ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร. สเตฟาน เฮียร์ ดูบาส 107 หน้า

กระบวนการดูดซับมีประโยชน์มากในการบำบัดน้ำเนื่องจากมีประสิทธิภาพในการดูดซับสูง ต้นทุนต่ำและเป็นวิธีการที่รวดเร็ว โพลีอิเล็กโทรไลต์เชิงซ้อน (Polyelectrolyte Complex) เป็นเยื่อพอลิเมอร์ที่เตรียมโดยการผสมระหว่างสารละลายที่มีประจุไฟฟ้าตรงข้ามกัน โดยใช้ถ่านกัมมันต์ (ACs) เพื่อเพิ่มประสิทธิภาพการดูดซับในเมมเบรน การเพิ่มประจุไฟฟ้าลบส่วนเกินบนพื้นผิวของเมมเบรนสามารถทำได้โดยผสมสารละลายประจุลบในสัดส่วนที่มากกว่าสารละลายประจุบวกซึ่งการมีประจุลบบนพื้นผิวจะช่วยเพิ่มประสิทธิภาพในการดูดซับ การปรับพื้นผิวเมมเบรนใช้สำหรับการดูดซับเมทิลีนบลู (สีย้อมประจุบวก) และไอออนโลหะหนัก ในกระบวนการดูดซับเมทิลีนบลู กลไกการดูดซับที่ดำเนินการโดยประจุลบส่วนเกินบนพื้นผิวเมมเบรนผ่านปฏิกิริยาไฟฟ้าสถิต ความจุในการดูดซับสูงสุดเกิดขึ้นในตัวอย่างที่ถูกกำจัดเกลือของ 1: 2 อัตราส่วนโดยโมล (R-1: 2) โดยไม่มีถ่านกัมมันต์เท่ากับ 4.9 มิลลิกรัมต่อกรัม นอกจากนี้ ตัวอย่าง R-1-2 ยังเหมาะสมกับแบบจำลองทางจุลภาคเทียมแบบที่สองและแบบจำลองไอโซเทอมของ เทมกิน (Temkin) แสดงถึงการดูดซับแบบกายภาพและยังสามารถฟื้นฟูได้ด้วยสารละลายเกลือ ในทางตรงกันข้ามไอออนโลหะมีกลไกการดูดซับแบบดำเนินการแลกเปลี่ยนไอออนหนักโดย ตัวอย่าง 1: 2 อัตราส่วนโดยโมลแบบไม่มีถ่านกัมมันต์แสดง ความจุการดูดซับสูงสุดคือ 30 มิลลิกรัมต่อกรัม กลไกเกิดขึ้นระหว่าง โซเดียม ( $\text{Na}^+$ ) ไอออนบนสายโซ่พอลิเมอร์ประจุลบและ ทองแดง ( $\text{Cu}^{2+}$ ) ไอออนในสารละลาย การดูดซับไอออนโลหะเหมาะสมกับแบบจำลองทางจุลภาคเทียมแบบที่สอง และรูปแบบไอโซเทอมของ เฟรทลิช (Freundlich) แสดงถึงประเภทการดูดซับแบบเคมีและการดูดซับบนผิวแบบหลายชั้น นอกจากนี้เมมเบรนยังชอบในการดูดซับ ตะกั่ว และโครเมียมไอออน มากกว่าไอออนชนิดอื่น

## Graphical Abstract

Dye adsorption and heavy metal sorption



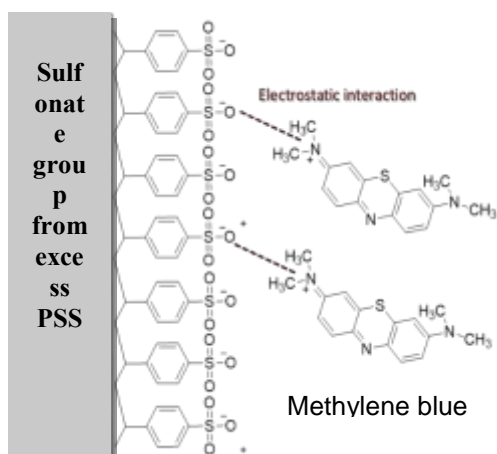
Salt removal by rinse step



Dye adsorption



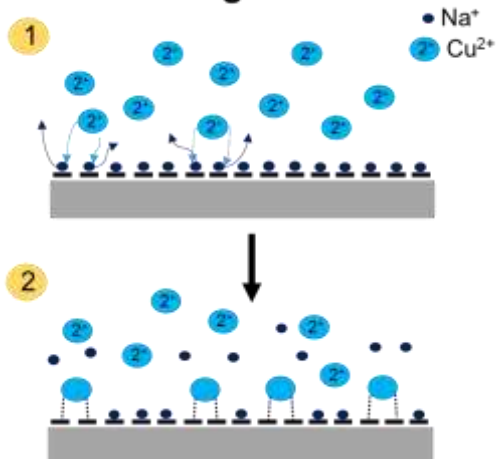
Heavy metal sorption



Dye adsorption:

Electrostatic interaction adsorption

### Ion Exchange mechanism



Heavy metal sorption:

Ion exchange sorption

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## **CHAPTURE I**

### **INTRODUCTION**

Water pollutant is concerning problem because it is one of the provenances of illness in humans. That problem comes from the ignore activities of humans such as sewage, garbage and liquid waste of households, agricultural lands, and factories, it liberates into lakes and rivers without treatment. Wastewater contains excessive hazardous substances consists of volatile organic compounds (VOCs), chemical wastes, heavy metals, dyes, and so on (Saad, 2017). In this study, dyes and heavy metals are the main focus. The production of dyes in the industries relate waste dye in water more than  $7 \times 10^5$  metric tons per year and 5–10% of dyes are drain into the river (Rafatullah, Sulaiman, Hashim, & Ahmad, 2010). Moreover, it have another substrate are concern which is heavy metal because there are high soluble in the aquatic environments that can absorbed into human bodies (Barakat, 2011), it is very toxic to humans organ (brain, heart). The heavy metals can be find in industries wastewater are cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), arsenic (As), lead (Pb), and zinc (Zn). Many research are interesting to find the technique and material to solve this problem.

Currently, the techniques are treat or remove the hazardous component include precipitation, membrane filtration, ion exchange, and adsorption. The adsorption is a physical process of one molecule attracts with another molecule. This process is commonly used because it obtain high efficiency adsorption (Hegazi, 2013). This process requires two components which are an adsorbent and an adsorbate. The adsorbent are common use in adsorption process consist of silica gel, activated alumina, carbons, zeolites, clay, and polymeric adsorbent (Babel & Kurniawan, 2003). It provide high adsorption efficiency in heavy metals and dyes (adsorbate).

Polyelectrolyte complex is polymer from the association of opposite charged polyelectrolytes to obtain the complexes. Strong polyelectrolytes are mostly used to form the complexes because it receive high yield. Poly (sodium styrenesulfonate) (PSS) and poly (diallyldimethylammonium chloride)

(PDADMAC) are examples of synthetic polyelectrolytes as well as pectin and chitosan are examples of natural polyelectrolytes. Polyelectrolyte complex can be applied in many applications such as biological applications for bone tissue and drug delivery (Coimbra et al., 2011), fuel cell applications to be used in pervaporation and nanofiltration (Zhao, An, Ji, Qian, & Gao, 2011) and membrane sorption/separation applications (D'Alessandro et al., 2010). The membranes are preferable as adsorbents because they are low cost, biodegradable, water-based, and easy to remove from the system.

Stoichiometric and non-stoichiometric polyelectrolyte complexes membrane are interested to be used as adsorbents. As the complex formations can be altered by changing the ratio or the concentration of polyelectrolytes. Different complex formations affect the adsorption ability because of the dissimilar formation of ion sites produces different adsorption effects (Kurokawa & Sasaki, 1982) due to the excess charges on the surface from non-stoichiometric complexes (Sean M. Hartig, 2007). As a result, polyelectrolyte complexes are potentially good candidates as dye and heavy metal adsorbents.

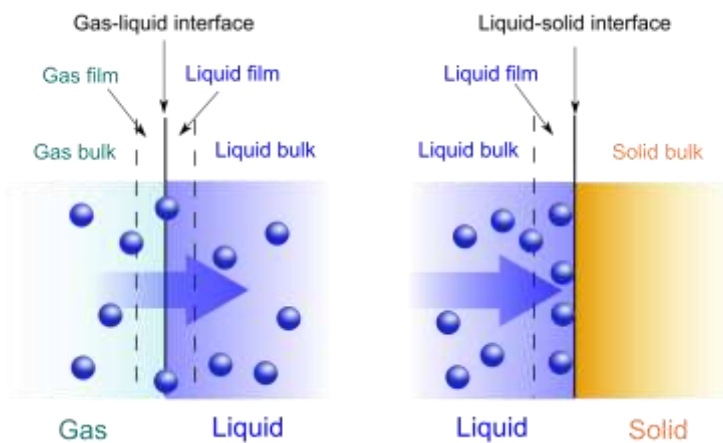
In this work, PSS and PDADMAC were used to prepare polyelectrolyte complexes with stoichiometric and non-stoichiometric ratio. The membrane applied to the dye and heavy metal adsorption. The addition of filler, activated carbon (ACs), used to improve the adsorption efficiency of PECs membrane. Furthermore, the effect of salt concentration and polyelectrolyte concentration were studied. The solution after adsorbed were test by UV-Visible spectroscopy (for dye) and atomic adsorption spectrophotometry, AAS (for heavy metal).

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Adsorption

Adsorption is a mass transfer process which involves the accumulation of substance at the interface of two phases, such as liquid-liquid, gas-liquid, gas-solid and liquid-solid interface.

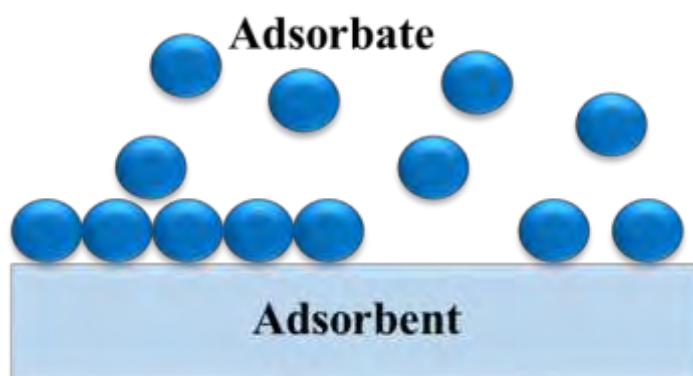


**Figure 2.1** The accumulation of substance at the interface of two phases which are gas-liquid and liquid-solid interface.

The process of adsorption occur due to presence of unbalanced the surface of liquid or solid phase. These unbalanced incline to attract and retain the molecular species which it comes in contact with the surface. So the adsorption can called in another word is surface sorption phenomenon.

Adsorption is completely different from Absorption .While, absorption means uniform distribution of the substance throughout the bulk but adsorption essentially happens at the surface of the substance. When both Adsorption and Absorption processes take place simultaneously, the process is called sorption.

Adsorbent and Adsorbate are two component involve in adsorption process. Adsorbent is the substance which adsorption takes place and adsorbate is the substance adsorbed on the surface of adsorbent.



**Figure 2.2** Adsorbate adsorbed on surface of adsorbent

### 2.1.1 Adsorption mechanism

The amount of heat grew during one mole of the adsorbate is adsorbed on adsorbent is called enthalpy of adsorption. Adsorption is an exothermic process and enthalpy change is always negative. Meanwhile, adsorbate molecules are adsorbed on the surface, free movement of molecules become bound and this results in decreasing of entropy.

Moreover, adsorption is a spontaneous process at constant pressure and temperature, hence Gibb's free energy is also decreased.

Many process represented thermodynamic theory under constant of Temperature (T) and Pressure (P):

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

Where  $\Delta G$  is Gibbs free energy

$\Delta H$  is enthalpy

$T$  is temperature

$\Delta S$  is entropy

Adsorption is spontaneous process, it is decreases in the free energy of system. At constant of temperature and pressure:

$$(\Delta G = \Delta H - T\Delta S) < 0$$

As translational freedom of adsorbate is reduced when it is adsorbed, thus

$$\Delta S < 0 \text{ or negative}$$

$$\Delta G = \Delta H + T\Delta S$$

For spontaneous the  $\Delta G < 0$ , therefore  $\Delta H$  should be negative

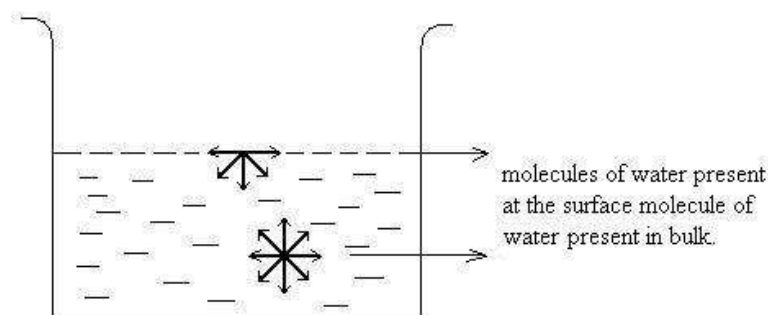
### 2.1.2 The principle of adsorption

Adsorption is the surface phenomenon and consequence of surface energy. The surface of the liquid or solid is in a state of unsaturation which results in unbalanced residual force at the surface. This unbalanced residual force results in higher surface energy. Consequently, the surface of liquid/ solids always has a tendency to attract and retain the molecular species with which it comes in contact. This tendency is responsible for the mass transfer phenomenon, the theory for explain the diffusion were occurred across an interface of substrate (Cussler, 1997).

### 2.1.3 Adsorption in liquid – solid

#### 2.1.3 A. Liquid

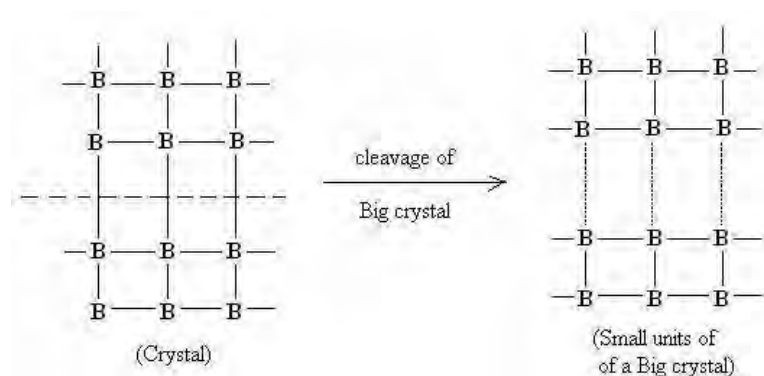
A molecules in the interior of a liquid is completely surrounded by other molecules so on the average, it is attracted equally in all directions. On a molecule in the surface. However, there is a resultant attraction inwards because the number of molecules per unit volume is greater in bulk of the liquid than in the vapor, this gives rise to surface tension. Hence, particles at surface and particles at the bulk are in different environment thus giving rise to difference in free energy at the surface and in bulk.



**Figure 2.3** The adsorption in liquid

### 2.1.3 B. Solid

The cleavage of a big crystal of solid surface area. Due to cleavage of big crystal into smaller units, residual force or vacancies generated on the surface of the solid. Occupation of these vacancies by some other molecular species results in adsorption.



**Figure 2.4** The adsorption in solid

### 2.1.4 Type of adsorption

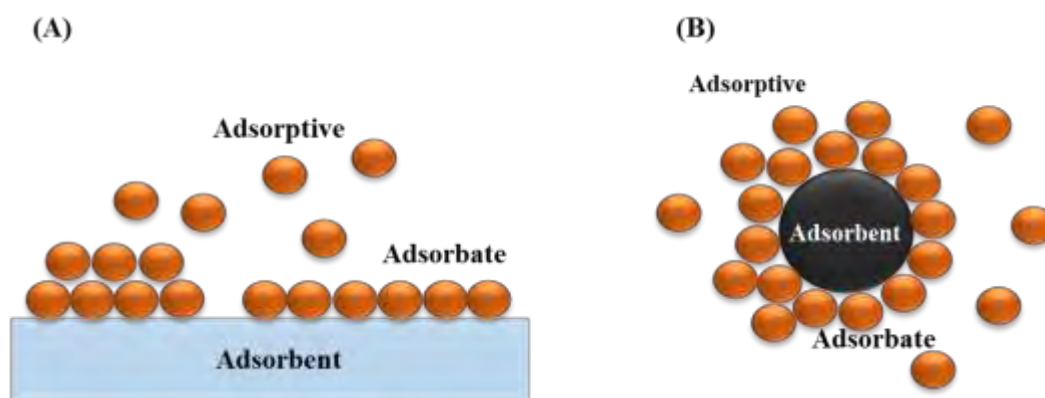
Forces of attraction survive between adsorbate and adsorbent. The attraction force can be due to Vander Waal forces which are weak forces or due to chemical bond which are strong forces of attraction. On the basis of the type of forces of attraction between adsorbate and adsorbent, adsorption can be classified into two types: Physical Adsorption or Chemical Adsorption.



#### 2.1.4.1 Physical adsorption

Physical adsorption or Physisorption, there is van der Waal interaction between the adsorbate and the substrate, for example, the dispersion or dipolar-dipolar interaction. Van der Waal interaction is long range but weak. The physical adsorption is not had specific for adsorbed but the bulk molecule was adsorbed on the surface only (figure 2.4).

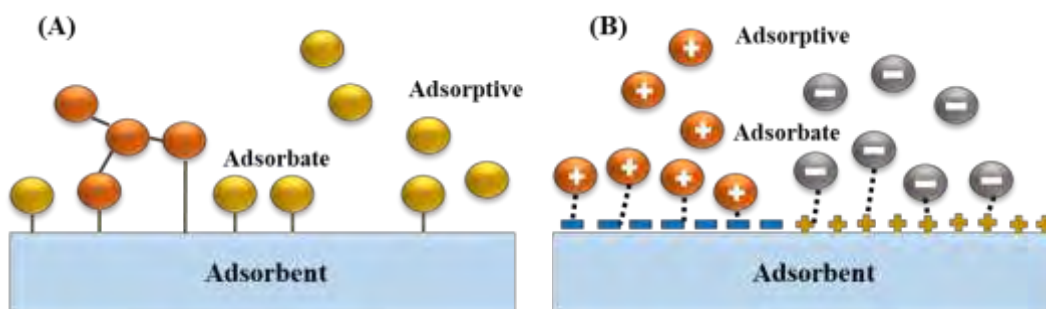
Normally, the Physisorption is reversible in nature so the desorption can operate when the environment changes such as temperature and pressures.



**Figure 2.5** The physical adsorption on membrane (A) and particle (B)

#### 2.1.4.2 Chemical adsorption

Chemical adsorption or Chemisorption is the molecule or atom stick on the surface of adsorbent by forming the chemical bond normally is covalent bond and tent to find the site that maximizes coordinated with the substrate. The distance of the bond between adsorbent surface and the polar molecule is smaller. The chemisorption operated the bond so that become exothermic process. Furthermore, chemisorption operated the unimolecular layer in the process (figure 2.5).

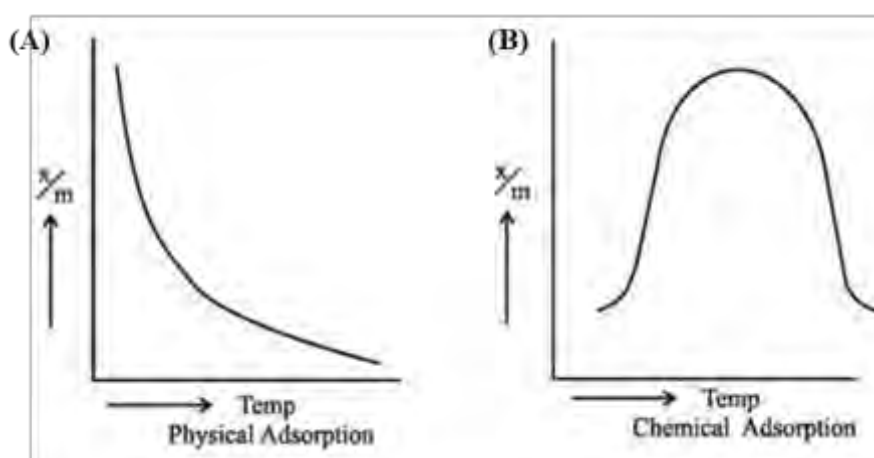


**Figure 2.5** The chemical adsorption on membrane with (A) covalent interaction and (B) electrostatic interaction

### 2.1.5 The parameter affect with adsorption

#### *2.1.5.1 Temperature*

Adsorption is an exothermic process. Accordance with Le Chatelier's principle, the magnitude of adsorption should increase with decreases the temperature. It is in the case of physical adsorption. In contrast, chemisorption increased at first and then start to decreases.



**Figure 2.6** The graphic diagram of temperature dependence in (A) Physical adsorption and (B) Chemical adsorption

#### *2.1.5.2 Pressure / Concentration*

The increasing of pressure operated the adsorption also increased and increased up to certain saturated adsorption. This behavior show in both physical and chemical adsorption.

#### *2.1.5.3 Surface area*

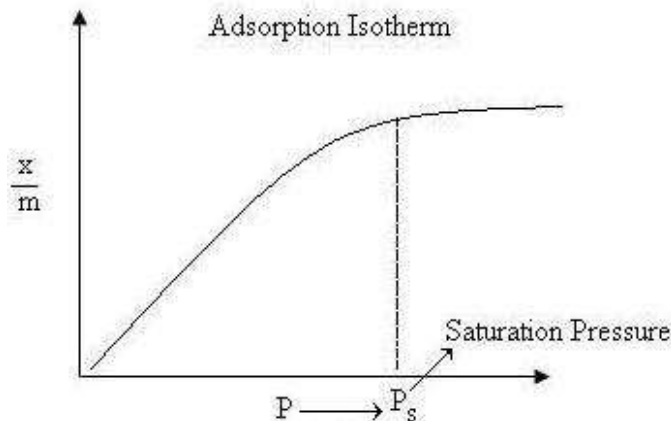
The surface area phenomenon in adsorption, it's directly affected by adsorption capacity. When the adsorbent increases, the adsorption capacity also increases. The surface area increased, it operated high surface interface to attack with adsorbate molecules.

#### *2.1.5.3 Activation of solid adsorbent*

Activation of the adsorbent surface provides more vacant site on the surface. This can be done by breaking the adsorbent to small crystal or small powder.

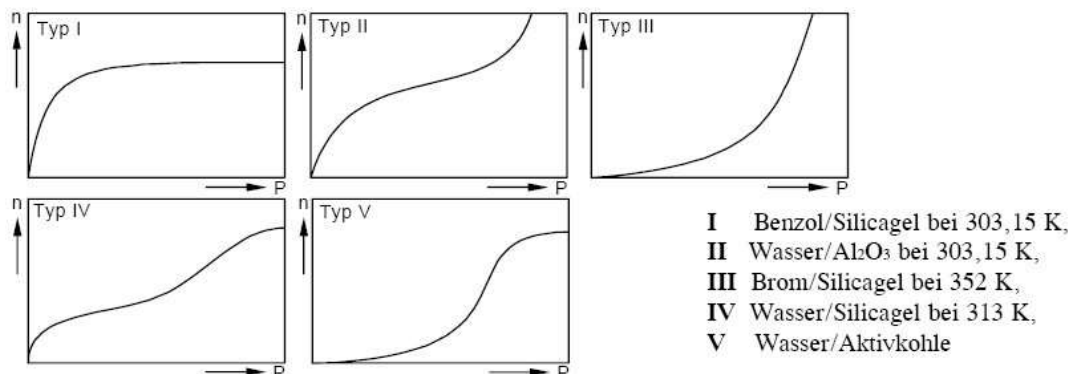
#### 2.1.6 Isotherm of adsorption

The adsorption process is always studied in term of a graph, which is adsorption isotherm. The adsorption isotherm useful studies the behavior of the material in the adsorption process. The amount of adsorbate on the adsorbent as a function when pressure (in gas) or concentration (in liquid) is constant. The example is studies in term of pressure (in concentration is the same behavior).



**Figure 2.7** The graph between the amounts of adsorbate ( $x$ ) adsorbed on the surface of adsorbent ( $m$ ) and pressure at constant temperature.

From figure 2.6 the molecules decreases and adsorption increases with and pressures ( $P$ ) increases. After saturated pressure ( $P_s$ ) the adsorption does not change because vacancies on the surface of adsorbent are limited, at saturated pressures ( $P_s$ ) vacancies is completely occupied and although increases pressure more than  $P_s$ , the adsorption does not change. The adsorption isotherm have many type depend on shape which are Type I, Type II, Type III, Type IV and Type V with difference theory use to explain that are Langmuir, Freundlich, Temkin and BET. The most theory use in adsorption isotherm which are Langmuir and Freundlich isotherm.



**Figure 2.8** Adsorption isotherm with difference experimental

### 2.1.6 Kinetic adsorption

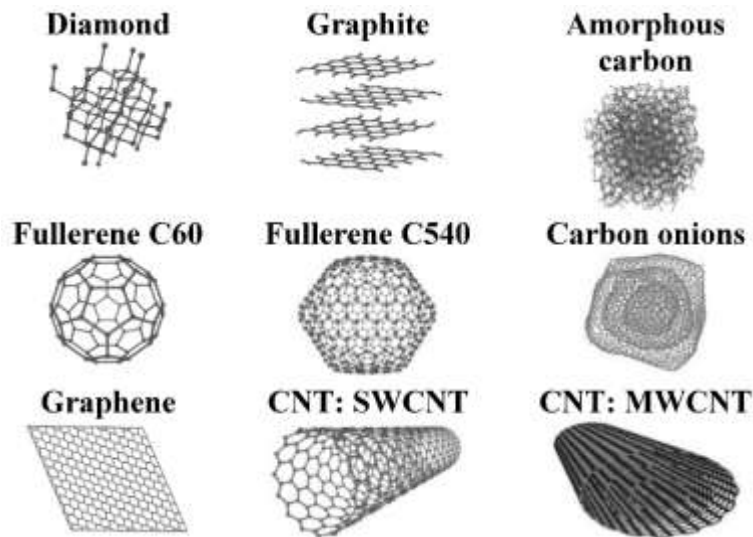
The adsorption reaction models developed to describe the kinetics of adsorption and this can operate the efficiency of adsorbent. The kinetic adsorption is studied the rate change per time i.e. number of molecules per time and concentration change per time. The result was fitting with the different model to obtain the real adsorption reaction. The model normally use in kinetic adsorption are first-order kinetic, second-order kinetic adsorption model and intra-particle model is a minor model to support the porous material.

## **2.2 Adsorbent for adsorption process**

Absorbent are conveniently divided into three class which are carbon based material, inorganic material and polymers (CUSSLER, 1997)

### 2.2.1 Carbon based material

The nonpolar surface, hydrophobic properties, lightly versatile material render the carbon-based material is famous for materials science development. In adsorption process, the nonpolar surface of carbon-based that normally use the adsorbed nonpolar molecule, especially hydrocarbon (CUSSLER, 1997). Example of carbon-based material was used in adsorption process are activated carbon and graphite.



**Figure 2.9** The examples of carbon based material (Săndulescu et al., 2015)

### 2.2.2 Inorganic material

Inorganic materials are material with polar surface, hydrophilic and consider with oxygen molecule. The example of inorganic material are clay and activated alumina.

### 2.2.3 Polymers

The adsorbent based on synthesis polymer is a polymer or resin with fixed the negative charge or positive charge on the surface for ion exchange based on adsorption process (CUSSLER, 1997)

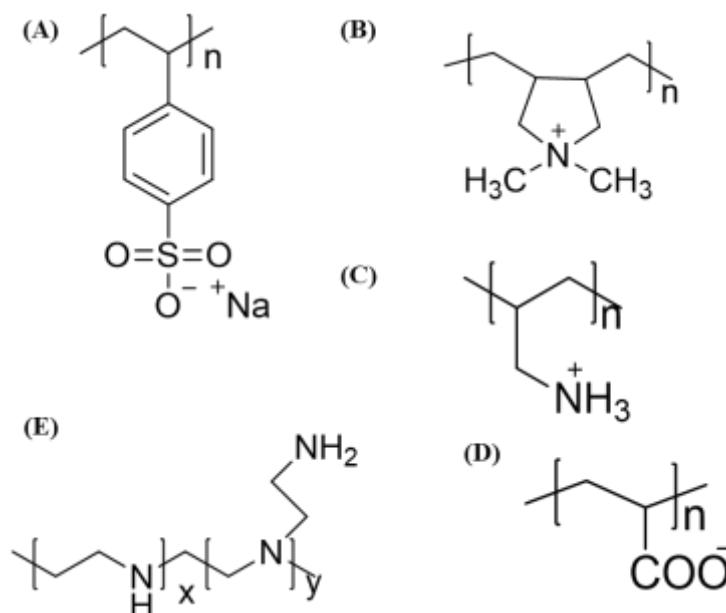
The polymeric adsorbent have many advantage such as high selectivity, large adsorption capacity, physical-chemical stability, easy to regeneration and low cost render polymeric adsorbent are interesting in industry. The polymeric adsorbent consists of synthesis resin (Amberlite IRA-401S, Vinit AT-1, and Purolite), polyamide, ion exchange cellulose (DEAE, AE, and ECTEOLA) and functionalized polymer. Recently, the higher interesting about the production of polymeric based adsorbent such as toxic potential, toxic residue, easy to produce and price (A. Mendez-Vilas, 2016)

## 2.3 Polyelectrolytes

Polyelectrolytes are polymers with an electrolyte group in repeating units. Polycations and polyanions are polyelectrolytes. These groups dissociate in aqueous solutions (water), occurred the polymers charged. Polyelectrolyte properties are similar with both electrolytes (salts) and polymers (high molecular weight compounds) and sometimes called polysalts.

The type of polyelectrolyte in term of charge can classify into two types are strong charge and weak charge polyelectrolyte. The difference between two types will be shows when dissolve in solvent, the strong charge polyelectrolyte are completely dissociate but the weak charge polyelectrolyte are not.

The example of strong charge Polyelectrolyte are sodium polystyrene sulfonate, NaPSS and Poly (diallyldimethylammonium chloride), PDADMAC. The weak charge such as Polyethyleneimine, PEI , Poly (allylamine hydrochloride), PAH and Poly(acrylic acid), PAA.

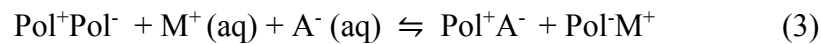


**Figure 2.10** The structure of polyelectrolyte (A) PSS, (B) PDADMAC, (C) PAH, (D) PAA and (E) PEI.

## 2.4 Stoichiometric and nonstoichiometric polyelectrolyte complex

Polyelectrolyte complex is the association of oppositely charge polyelectrolyte by solution mixing, the dense polymer are separated from the supernatant that is polyelectrolyte complex (PECs) in figure 2.10 and 2.11.

The interaction between positive charge and negative charge of polyelectrolytes occurred without heat (athermal) (Rmaile, 2007). From the interaction were liberated the small molecule which is salt counter ion and water molecule are surround (Albert Sommerauer, 1967) and stay inside the complex (Hariri, Lehaf, & Schlenoff, 2012). The electrostatic interaction are randomly occurred in the complex.

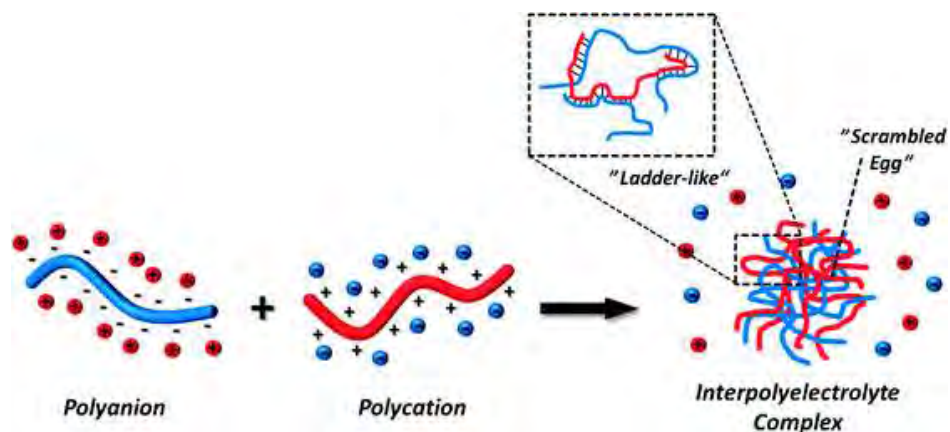


When  $\text{Pol}^+\text{Pol}^-$  is the polyelectrolyte complex

$\text{M}^+$  and  $\text{A}^-$  are cation and anion of salt in the solution

$\text{Pol}^+\text{A}^-$  and  $\text{Pol}^-\text{M}^+$  are polyelectrolyte with cation or anion

The complexation of polyelectrolyte following with Coulomb's law, a law of physics it describes the force interacting between static electrically charged particles in the scalar form. The added salt for controlling the composition of complexes such as size, length between the charged particle. After added salt the interaction between  $\text{Pol}^-\text{Pol}^+$  interactions become broken, this process called “Doping” process. (Wang & Schlenoff, 2014)

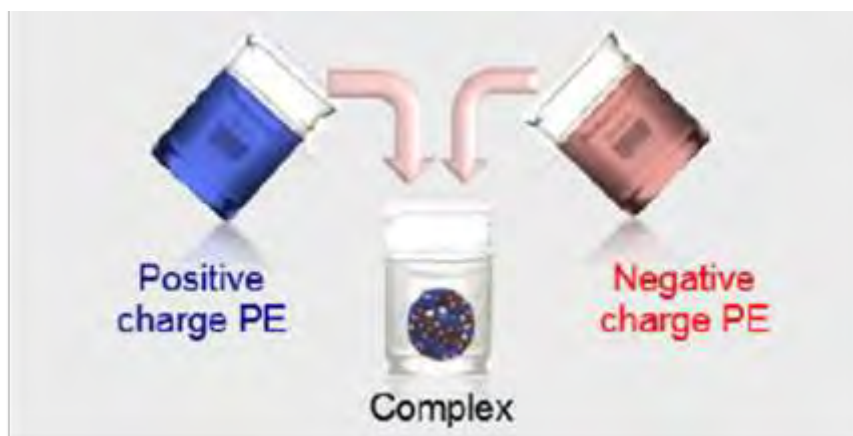




**Figure 2.11** The schematic of polyelectrolyte complex formation (Pergushov et al., 2012)

The formation of PECs depend on many parameter such as chemical composition, the concentration of polyanion solutions, rate and order of mixing, pH, temperature and Mw of interacting polyelectrolyte(Hariri & Schlenoff, 2010)

The concentration of salt were main affect with PECs formation because the increasing of salt doping, the physical crosslink of the complex decreased(Hariri & Schlenoff, 2010). Moreover, the increasing of salt were obtain the location of water molecule which are the water molecule go inside the complex when the concentration of salt increased (Fu, Fares, & Schlenoff, 2017; Hariri & Schlenoff, 2010; Wang & Schlenoff, 2014).



**Figure 2.12** The solution mixing method to prepare polyelectrolyte complex (Michaels, 1960)

After association of polyelectrolyte, the electrostatic interaction will occur. The compensation in PECs can categories into three types (Hariri et al., 2012; Porcel & Schlenoff, 2009; Shamoun, Reisch, & Schlenoff, 2012) in figure 2.12.

#### *A Intrinsic sites*

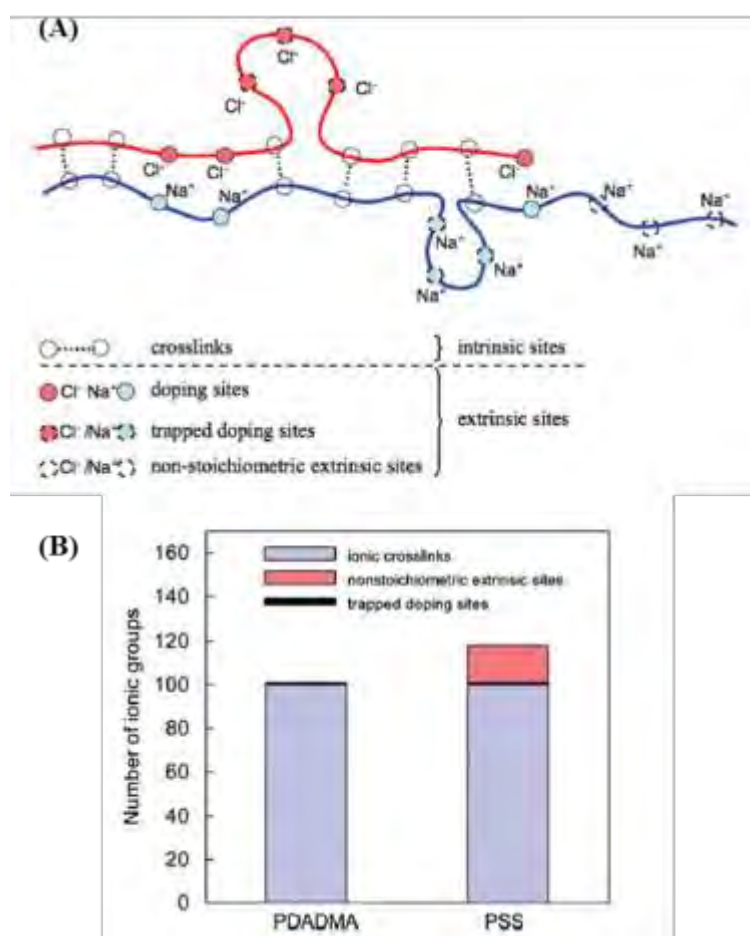
Intrinsic site is the interaction between polymer and polymer or crosslinking. It's become fully crosslink while without salt.

### B Extrinsic sites

The salt counter ions binding with polyelectrolyte, this site occurred from the doping effect.

### C Non-stoichiometric extrinsic sites

The non-stoichiometric extrinsic sites is Na counter ion binding with excess PSS that occurred from non-1:1 stoichiometric



**Figure 2.13** (A) the schematic of compensation in PECs and (B) the number of ionic group were occurred in 1:1 stoichiometric PECs (Porcel *et al.*, 2009).

PECs are applied in many applications such as battery separator and fuel cell membrane, electrical conductive coating, medical application, contact lenses, enzyme mimics, ultrafiltration and membrane.

#### 2.4.1 Stoichiometric and Non-stoichiometric polyelectrolyte complexes

The stoichiometric and non-stoichiometric are the conditions for controlling the complex aggregation (Dautzenberg, 1997). Different surface charges would be obtained with different conditions.

The differences between two conditions:

##### *2.4.1.1 Stoichiometric polyelectrolyte complexes*

The polyelectrolyte complexes formed by using stoichiometric (1:1 ratio) conditions result in a non-charged surface.

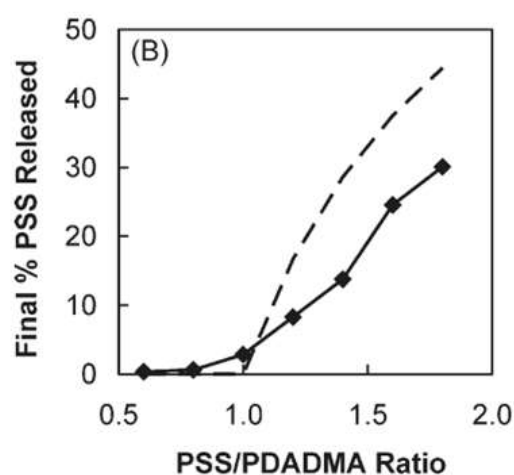
In fact, the real stoichiometric is unnecessary to be 1:1 ratio because of strong differences in molecular weight between polyelectrolytes (Porcel & Schlenoff, 2009).

The study about the effect of salt concentration with stoichiometric polyelectrolyte complexes. From the results, the preparation of 1:1 PSS/PDADMAC complex with 2.5 M NaCl and the complex were annealed in water for 48 hours. The elemental analysis was used to find the weight percentage in PECs and the annealed solution. The elemental analysis results represented the amount of sulfur and nitrogen to be 9.84 and 3.7 wt% (excess PSS chain in PECs) and it can detect a small amount of chloride ion in the annealed solution (PDADMAC occurred in the annealed solution). From the results, they calculated the real ratio when prepared 1:1 PSS/PDADMAC complexation that are 1.17:1 PSS/PDADMAC (Porcel & Schlenoff, 2009).

#### 2.4.1.2 Non-stoichiometric polyelectrolyte complexes

This condition is forming polyelectrolyte complex in excess of polycation or polyanion, the different surface charges are obtained.

The formation of the PECs with 1:1 PMETAC/PSS, 1:2 PMETAC /PSS and 2:1 PMETAC /PSS were different. In nonstoichiometric PECs (1:2 and 2:1) shows the large complex particle were formed. Light scattering were used to detect the hydrodynamic size of the PECs aggregation. From the results, the hydrodynamic size of PECs decreases in order of 1:2 > 1:1  $\approx$  2:1, the concentration don't dependent with the hydrodynamic size. The uncharged PECs were close to cationic because of larger cationic polyelectrolyte and PSS presented in 1:1 (uncharged) and 2:1 (cationic) PECs. Moreover, maximum PSS occurred in 1:2 (anionic) PECs (away on backbond and excess) that cause 1:2 PECs had higher hydrodynamic size(Shovsky, Varga, Makuška, & Claesson, 2009). The excess PSS can stay in two different position which are nonstoichiometric extrinsic site(Porcel & Schlenoff, 2009) and free PSS between entanglements of PECs (occurred in both stoichiometric and nonstoichiometric PECs). The releases of PSS were detect by chopped 1:1 PECs in to small piece and soak in water (change water every hour). The solution after soak PECs chopped were detect the excess polyelectrolyte by UV-visible spectroscopy in figure 2.12(Hariri & Schlenoff, 2010)

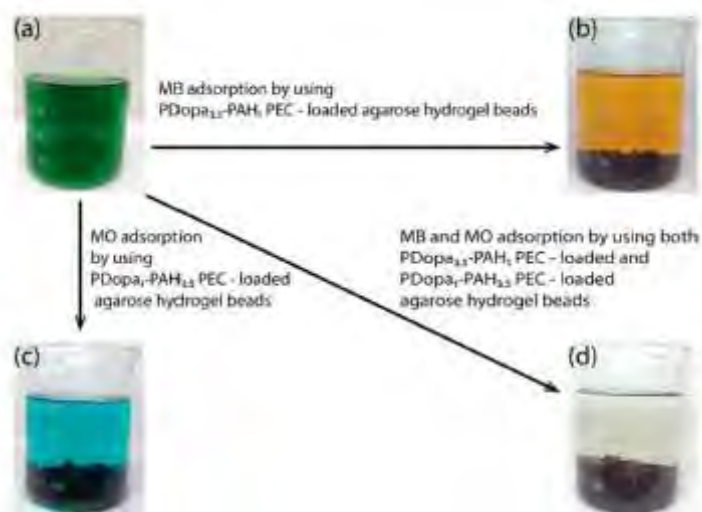


**Figure 2.14** Total release of PSS after 9 days of rinsing and the dot line represented the trend of PSS excess released (Hariri *et al.*, 2010).

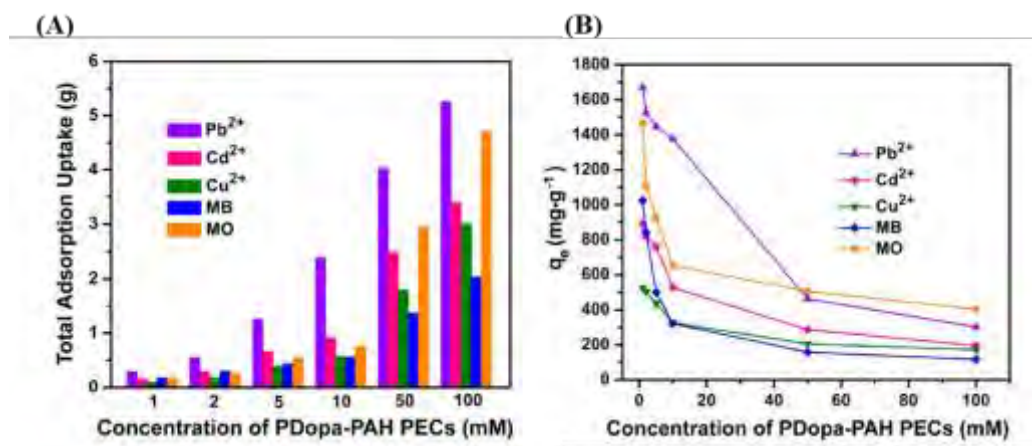
## 2.5 Polyelectrolyte complexes with wastewater adsorption application

The PECs membrane are one type of polymeric adsorbent were used to adsorption process because of nontoxic (water based), easy to fabrication and high adsorption efficiency that PECs membrane become famous in wastewater treatment technology.

The lignosulfonates and chitosan polyelectrolyte complexes with different ratio was prepared for Methylene Blue (cationic) and Congo red (anionic) dyes adsorption. In the result, lignosulfonate and chitosan polyelectrolyte complexes with stoichiometric complex get the maximum sorption for cationic and anionic pollutants. Moreover, the high adsorption efficiency of lignosulfonate and chitosan PECs was from the required functional properties(Palamarchuk et al., 2015). The PECs membrane can be operated in heavy metal adsorption. The PECs prepared by positively charged poly(allylamine hydrochloride) (PAH) and negatively charged poly(L-3,4-dihydroxyphenylalanine) (PDopa) with difference ratio which are 3.5:1 and 1:3.5 of PAH-PDopa. The PECs of PAH-PDopa were loaded in hydrogel bead. The various ionic pollutant which are heavy metal and ionic organic dye were used to study the adsorption efficiency of PAH-PDopa hydrogel bead. The result shows high efficiency of removal with both heavy metal and ionic organic dye that was the quantitatively of functional group from PAH-PDopa in difference molar ratio in figure 2.13 and 2.14 (Yu, Liu, Yuan, Brown, & Wang, 2015).



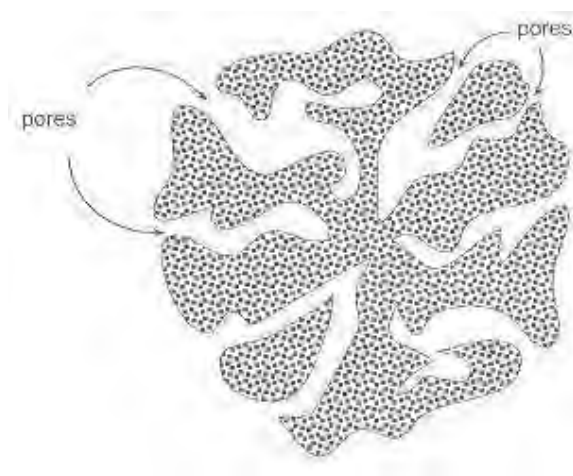
**Figure 2.15** Photographs of MB/MO mixture solution before (a) and after the selective removal of MB by using PDopa3.5-PAH PEC-loaded agarose hydrogel beads (b) and MO by PDopa-PAH3.5 PEC-loaded agarose hydrogel beads (c) and the complete removal of both MB and MO by using both composite hydrogel beads (d) (Yu *et al.*, 2015).



**Figure 2.16** (A) the total adsorption uptake of PAH-PDopa PECs with difference initial dye concentration and (B) the adsorption capacity of PAH-PDopa PECs with difference initial dye concentration (Yu *et al.*, 2015).

## 2.6 Activated carbon

Activated carbon is a carbon based adsorbent can produced by carbonization process to get the carbon-rich. The activated carbon has a high specifically internal surface (between 500 - 1500 m<sup>2</sup>/g) and pore structure operated(Y. C. Sharma, Uma, & Upadhyay, 2011). This large internal surface render the active carbon have high adsorption efficiency.



**Figure 2.17** A normal carbon particle has manifold pores that provide a large surface area for water treatment (Lemley et al., 1995)

The adsorption of contaminants onto the surface of activated carbon is activated carbon filtration, it is commonly used technology for particle adsorption.

The activated carbon can from various byproducts such as petroleum coke, bituminous coal, lignite, wood products, coconut coir, sugar cane, and rice husk. Rise husk is basic material for synthesis activated carbon, the commercial low cost activated carbon were observed from this material and the thermal activation is the normal method to prepared low-cost activated carbon. The rice husk activated carbon (RHAC) were used to study the removal of the selected dye, malachite green. The SEM image shows the large distribution of pore size and low surface area (around 152.95 m<sup>2</sup>/g) of RHAC. The result for dye removal was shown the high percentage of removal up to 94.91 and 93.75% at 40 minutes from 60 -100 mg/l of initial dye concentration(Y. C. Sharma et al., 2011). The activated carbon from coconut coir was developed by the thermal activation process were studied in the removal of

methylene blue (cationic dye). From the result, the removal of dye were increased from 74.20% to 93.58% while decreased dye concentration from 100 to 60 mg/l (Yogesh C. Sharma, Uma, & Upadhyay, 2009). It showed high adsorption efficiency although, it is low-cost material.

Many research tried to increase some properties of activated carbon which increase the surface area, decreases pore size (macropore to micropore) and applied the surface charge. So, the development of the method to prepare activated carbon was observed.

The palm shell activated carbon was prepared by the physiochemical activated process to provide the high surface of 476.8 m<sup>2</sup>/g. The removal of rhodamine B (cationic dye) was studied. The result showed 95% dye removal with 62.6 μmol/L at temperature 50°C (Mohammadi, Hassani, Mohamed, & Najafpour, 2010). The chemical activation of hydrothermally carbonized (HTC) was observed to produce the activated carbon for increased the surface area. The specific surface areas of activated carbons from this process were ~1000 m<sup>2</sup>/g, when compared with commercially activated carbons and pore size about 4 nm. The methylene blue was used to study the adsorption efficiency, the result shows the adsorption capacity was 341 mg/g with maximum initial dye concentration (Hao, Björkman, Lilliestråle, & Hedin, 2014). The modified activated carbon by loading copper inside for dye adsorption application. The differences between ordinary activated carbon and modified activated carbon are compared. The maximum adsorption capacity is increased after using the modified activated carbon (Shu et al., 2017).

The comparison between commercial activated carbon with activated carbon from oil palm shell and coconut shell which varies concentration of metal ion solution so from result the commercial activated carbon has very high adsorption capacity to removing oxyanions is Cr(VI) but the prepared activated carbons have higher adsorption capacity in removing heavy metal cations such as Ni(II) and Pb(II). The problem of commercial activated carbon its cannot adsorb metal ion at low concentration but the prepared activated carbons can adsorb because activated carbon from oil palm shell and coconut shell are acid activated carbon so it's more active with heavy metal cations much more commercial activated carbon (Rahman *et al.*, 2014). The ability of activated carbon to remove nickel (Ni) in wastewater treatment

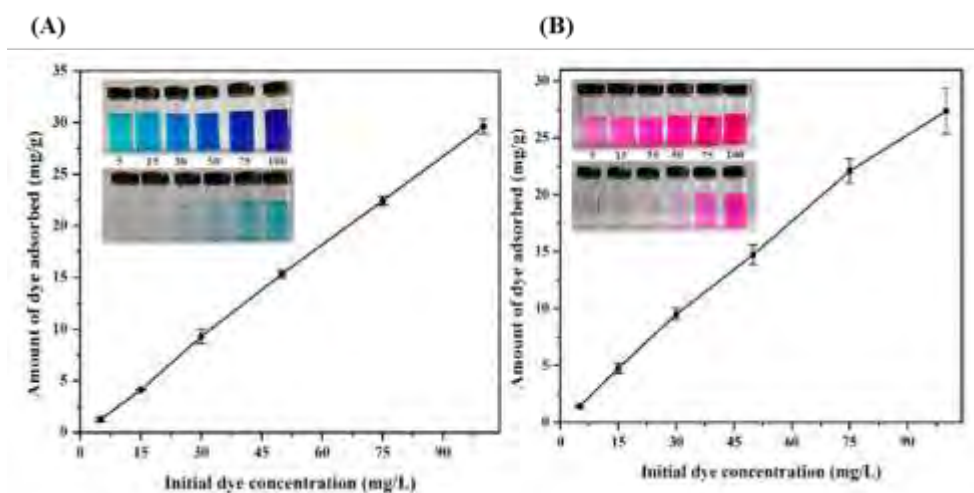


application. From the result, the activated carbon showed the greatest remove of nickel with 90 % percentage (Karnib, Kabbani, Holail, & Olama, 2014)

## 2.7 The hybrid or composite of PECs with fillers for wastewater adsorption application

Pure polyelectrolyte complexes have many application such as membrane for separation, drug delivery etc. The researchers tried to improve the properties of PECs in many way which one is filler addition. Many types of filler can be incorporated into PEC to get different properties and used in various applications.

Humic acid was immobilized on a polypropylene supported sodium alginate/hydroxyethyl cellulose blend membrane cross-linked with glu-taraldehyde (GA) for the dye removal application which is methylene blue (MB) and rhodamine B (RhB). The cationic dye was reacted with the anionic membrane that contained COOH groups from humic acid. Membranes removed more than 98% from initial dye concentration. The membrane was easily regenerated by simple acid treatment and its efficiency remained to maintain with four adsorption cycles in figure 2.16 (Shenvi, Isloor, Ismail, Shilton, & Al Ahmed, 2015).



**Figure 2.18** The adsorption capacity of PECs with difference initial dye concentration (A) methylene blue and (B) rhodamine B (Shenvi *et al.*, 2015).

## CHAPTER III EXPERIMENTAL

### 3.1 Materials and Equipment

#### 3.1.1 Materials and Chemicals

- Poly(diallyldimethylammonium chloride) (PDADMAC; Sigma-Aldrich; average Mw 200,000-350,000)
- Poly(sodium-p-styrenesulfonate) (PSS; Acros Organics; average Mw ~ 70,000)
- Activated carbon (Ningxia Yinjian Kaben Activated Charcoal)
- Copper sulfate salt ( $\text{CuSO}_3 \cdot \text{H}_2\text{O}$ ) (Sigma-Aldrich)
- Cd metal +  $\text{HNO}_3$  1000 ppm (TraceCERT<sup>®</sup>)
- $\text{Li}_2\text{CO}_3$  +  $\text{HNO}_3$  1000 ppm (TraceCERT<sup>®</sup>)
- $\text{Pb}(\text{NO}_3)_2$  +  $\text{HNO}_3$  1000 ppm (TraceCERT<sup>®</sup>)
- $\text{Cr}(\text{NO}_3)_3$  +  $\text{HNO}_3$  1000 ppm (TraceCERT<sup>®</sup>)
- Zn metal +  $\text{HNO}_3$  1000 ppm (TraceCERT<sup>®</sup>)
- Sodium chloride (NaCl; Lobal Chemie)
- Methylene Blue (MB; Carlo Erba Reagents)
- Methyl Orange (MO; Carlo Erba Reagents)
- Methyl Violet (MO; Carlo Erba Reagents)
- 

#### 3.1.2 Equipment

- Field Emission Scanning Electron Microscope (FE-SEM), Hitachi S-4800 for characterized the morphology of PEC sorbents

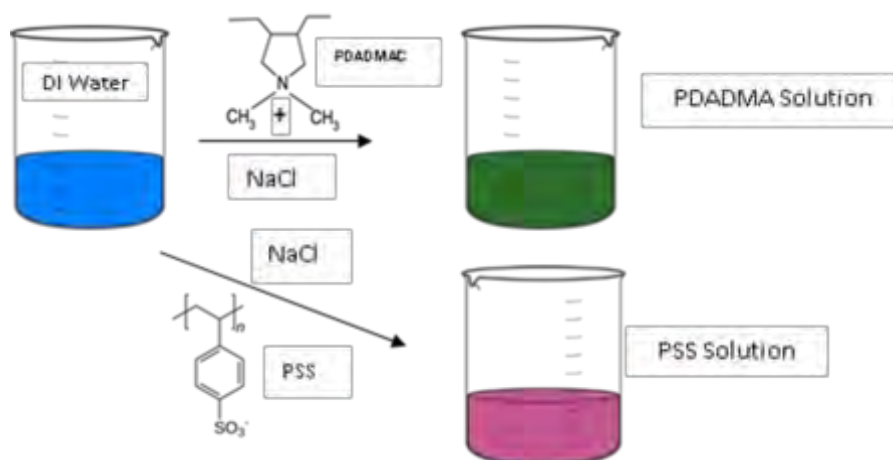
- Fourier Transform Infrared spectroscopy (FT-IR), Thermo Scientific, Nicolet iS5 ATR-FTIR spectrometer was used to detect functional groups in PEC sorbents.
- CHNS Elemental analyzer, Leco CNH2000 for characterized the elemental analysis of PEC sorbents.
- UV-Vis spectrophotometry, Avantes, AvaSpec-2048.
- Atomic absorption spectrophotometer (AAS) Varian, SpectrAA 300

## 3.2 Adsorbent preparation

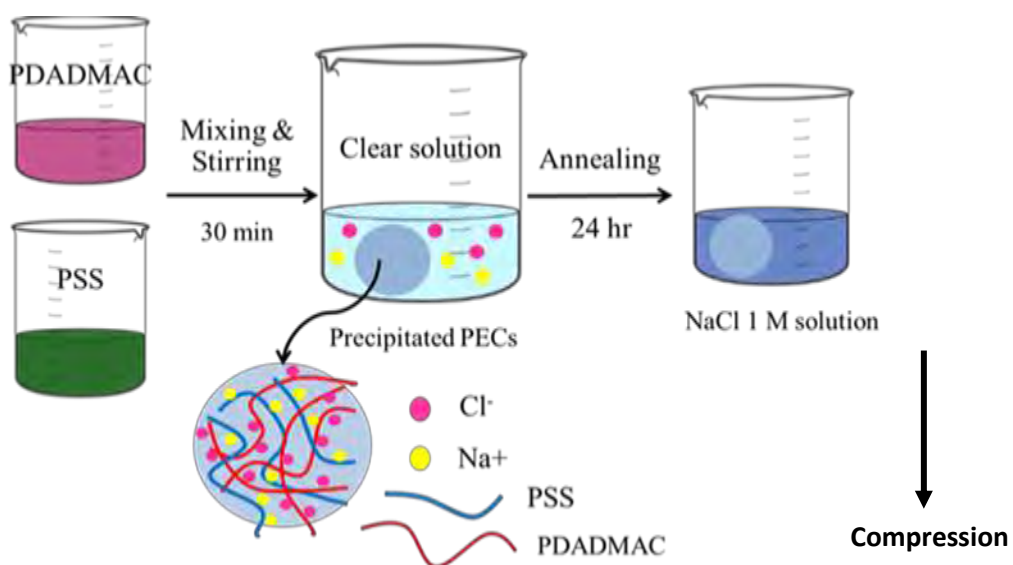
### 3.2.1 Polyelectrolyte complexes (PECs) adsorbent preparation

#### *3.2.1.1 Preparation of stoichiometric and non-stoichiometric polyelectrolyte complexes sorbent for adsorption experiments.*

Polyelectrolyte complexes (PECs) sorbents were produced by mixing between PDADMAC (polycation) and PSS (polyanion) together. For the stoichiometric (1:1 PDADMAC/PSS) and non-stoichiometric 1:2 (PDADMAC/PSS) PECs with 2 M NaCl. After obtaining PECs, compression molding was used to compress PECs into films. The preparation steps of PECs represent in figure 3.1 and 3.2



**Figure 3.1** Stoichiometric and non-stoichiometric PEC solution preparation



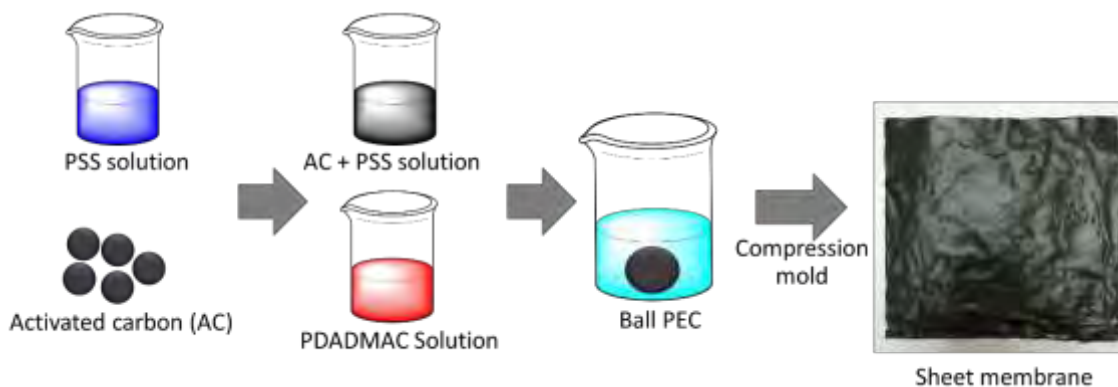
**Figure 3.2** Stoichiometric and non-stoichiometric PEC film preparation

*3.2.1.2 Preparation of stoichiometric and non-stoichiometric PECs/activated carbon hybrid membrane as adsorbent for adsorption experiments.*

The %weight of activated carbon used in 1:1 PDADMAC/PSS PECs/activated carbon membrane are 0, 5, 10, 15, 25, 35, 45 and 55%. In 1:2 PDADMAC/PSS PECs/activated carbon membrane are 0, 5, 25 and 55%. The preparation shows in figure 3.3.

**Table 3.1** Technical specification of activated carbons (Ningxia Yinjian Kaben Activated Charcoal)

Properties	Value
Apparent Density (g/l)	420 - 560
Diameter (mm)	1.5 -2.0
Moisture Content (%)	$\leq 3.0$
Hardness (%)	$\geq 95.0$
PH Value	7.0-9.0
Methylene Blue Number (mg/g)	$\geq 180$
Iodine Value (mg/g)	$\geq 1000$
Ash Content (%)	$\leq 8.0$
Size (Mesh)	325



**Figure 3.3** Preparation PECs/activated carbon hybrid membrane as adsorbent for adsorption experiments.

### 3.2.2 Polyelectrolyte complexes (PECs) for formation behavior studies

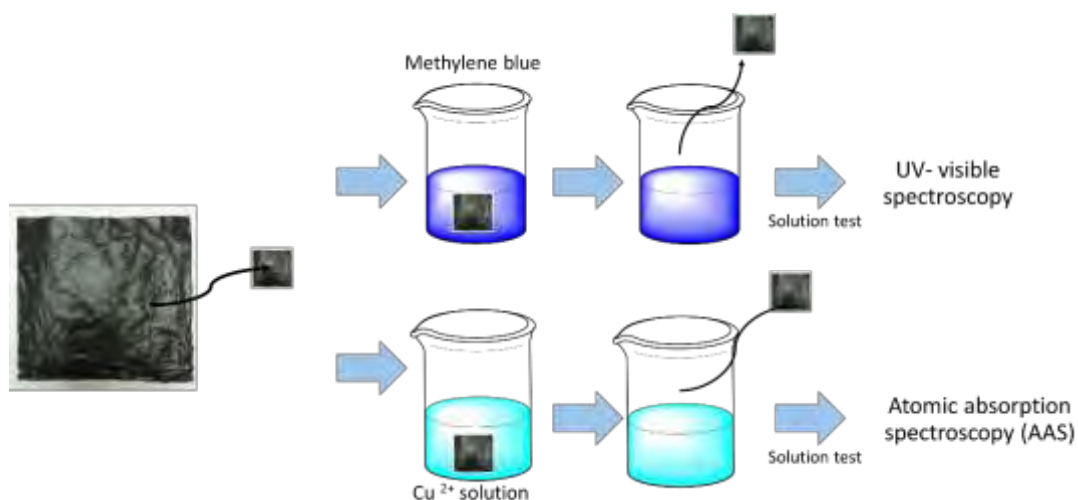
#### *3.2.2(1) PECs with different polyelectrolyte concentration*

The concentration of PDADMAC and PSS are used to studies are 300 mM, 250 mM, 200 mM, 150 mM and 100 mM with ratio 3:1, 2.5:1, 2:1, 1.5:1, 1:1, 1:1.5, 1:2, 1:2.5 and 1:3 of PDADMAC/PSS 2M NaCl. The preparation following with figure 5.1 and 5.2.

#### *3.2.2(2) PECs with different NaCl concentration*

The concentration of NaCl are used to studies are 0.0, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 and 5.5 with 1:1 PDADMAC/PSS. The preparation following with figure 3.1 and 3.2.

### 3.3 The sorption experiments



**Figure 3.4** Batch adsorption studies of methylene blue and Cu ion adsorption

#### 3.3.1 Dye adsorption

Dye concentration during the adsorption experiment was determined via UV- Vis spectrophotometry, calibration curve of dye was built by using standard solutions of known concentration.

##### *3.3.1(1) Single-Solute system kinetic adsorption study*

In this study, PEC sorbents were cut into 1x1 cm and weighed. These sorbents were added to 10 mL of 10 mg l<sup>-1</sup> methylene blue solution. After the sorbents were removed, the concentration of dye solutions before and after the adsorption experiment was determined by using UV- Vis spectrometer on time set for kinetic study based on calibration curve as show on figure 3.3. The adsorption capacity ( $q_e$ ) of dye on PEC sorbents were calculated as equation 3.1

$$q_e = V \cdot (C_0 - C_e) / m \quad 3.1$$

Where  $C_0$  is the initial concentration (ppm),  $C_e$  is the equilibrium concentration (ppm),  $V$  is the volume of the solution (L), and  $m$  is the amount of PEC sorbents (g) (Mouzdahir et al., 2010).

### *3.3.1(2) mixer dye adsorption study*

The 30 mL mixed dye solution of MO/MB/MV was prepared by mixing between 10 mL of 30 mg l<sup>-1</sup> MO solution, 12 mL of 30 mg l<sup>-1</sup> MB solution and 8 mL of 15 mg l<sup>-1</sup> of MV solution. This experiment was carried out in the same method as single-solute system. The concentration of MO, MV and MB in mixed dye solution before and after adsorption experiment were determined by using UV-Vis spectrophotometer base on calibration curve at a wavelength corresponding to the maximum absorbance, 464, 594 and 663 nm. The adsorption capacity of MO and MB on PEC sorbents were calculated as equation 3.1.

### *3.3.1(3) The adsorption isotherm study*

The variation of initial concentration for adsorption studies. The initial concentration of MB used are 2, 5, 10, 20 and 50 mg l<sup>-1</sup>. The adsorption process are followed with figure 5.4 after that the concentration of MB before and after will detect by UV-spectrometer. The adsorption capacity calculate as equation 3.1.

## 3.3.2 Heavy metals sorption

### *3.3.2(1) Single-Metal ions with kinetic sorption studies*

Copper sulfate (CuSO<sub>4</sub>) was used in the heavy metals (Cu<sup>+</sup>) sorption experimental. To prepare CuSO<sub>4</sub> solution, CuSO<sub>4</sub> powder was dissolved in DI water. These sorbents (2.5 x 2.5 cm) were added to 50 mL of 50 mg l<sup>-1</sup> CuSO<sub>4</sub>



solution. After the sorbents were removed, the concentration of  $\text{CuSO}_4$  before and after the sorption experiment was determined by using atomic absorption spectroscopy (AAS) on time set for kinetic study. The process follow with figure 3.3. The variation of initial concentration for adsorption studies.

### 3.3.2(2) *The selectivity of metal ions on PEC membrane*

#### (A). *The mixier of divalet heavy metal ions.*

The 50 mL mixed heavy metal ions solution of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  was prepared by mixing between 10 mL of  $25 \text{ mg l}^{-1}$  of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions solution, respectively and DI water 10 ml. This experiment was carried out in the same method as single metal experiment The concentration of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  in mixer metals solution before and after sorption experiment were determined by using AAS at  $\text{mg l}^{-1}$  unit the process follow with figure 3.3. The adsorption capacity of heavy metal ions on PEC sorbents were calculated as equation 3.1.

#### (B). *The mixier of difference ions valet heavy metal*

The 30 mL mixed heavy metal ions solution of  $\text{Li}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$ . was prepared by mixing between 6 mL of  $25 \text{ mg l}^{-1}$  of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions solution respectively and DI water 12 ml. This experiment was carried out in the same method as single metal experiment The concentration of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  in mixer metals solution before and after sorption experiment were determined by using AAS at  $\text{mg l}^{-1}$  unit the process follow with figure 3.3. The adsorption capacity of heavy metal ions on PEC sorbents were calculated as equation 3.1.

### 3.3.1(3) *The sorption isotherm study*

The variation of initial concentration for adsorption studies. The initial concentration of  $\text{Cu}^{2+}$  ion used are 2, 5, 10, 20 and 50  $\text{mg l}^{-1}$ . The adsorption process are followed with figure 3.4 after that the concentration of  $\text{Cu}^{2+}$  ions before and after will detect by AAS. The adsorption capacity calculate as equation 3.1.

### 3.4 Characterization.

To measure water uptake of PEC sorbents, PEC sorbents were cut into small size ( $1 \times 1 \text{ cm}^2$ ) and then weighed. PEC sorbents were soaked in deionized water. After time set, PEC sorbents were removed from the water and carefully wiped with paper towel and then quickly weighted. The process was repeated until the PEC sorbents had constant weight. Degree of swelling (%) was calculate by using equation 3.2.

$$\text{Degree of swelling (\%)} = \left( \frac{m_s - m_d}{m_d} \right) \times 100 \quad 3.2$$

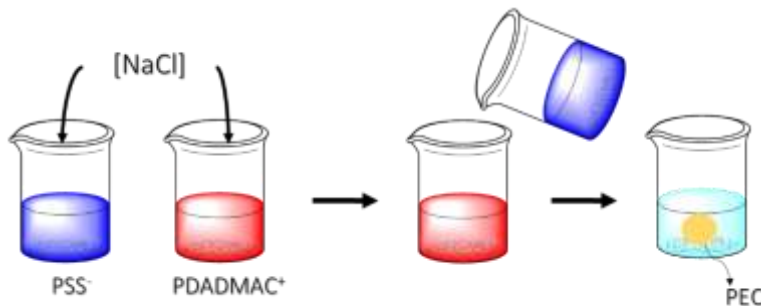
Where  $M_s$  is mass of the swollen PEC sorbent in g.

$M_d$  is mass of the dry polymer in g (Smitha et al., 2004).

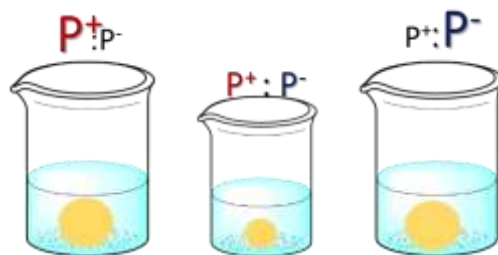


**CHAPTURE IV**  
**RESULT AND DISSCUSION**

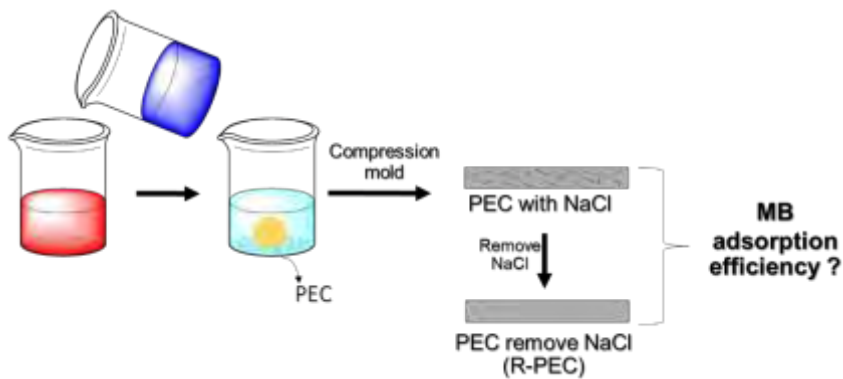
**4.0 The schematic explain the series of discussion part in this chapter**



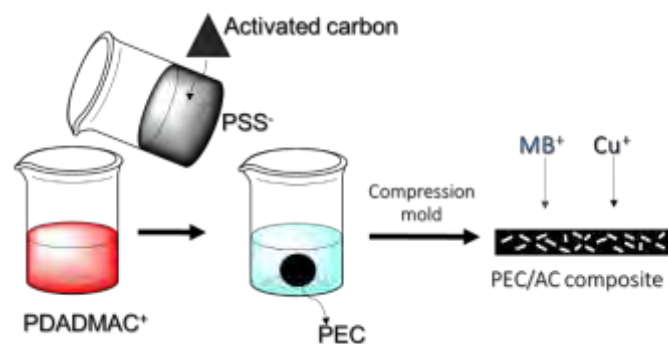
Fabrication of PEC as function of [NaCl]



Effect of P<sup>+</sup>/P<sup>-</sup> ratio



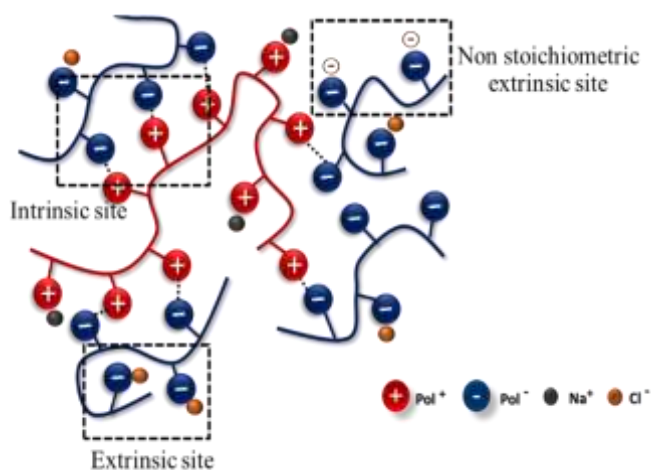
Effect of NaCl removal on adsorption capacity



Effect of PEC/AC composite removal on sorption capacity of cationic dye and heavy metal

#### 4.1 Polyelectrolyte complex, Polyelectrolyte complex/Activated carbon hybrid membrane preparation, characterization and physical properties.

Polyelectrolyte complex (PECs) is the physical crosslink hydrogel (electrostatic interactions) between opposite charge polyelectrolyte (Rafatullah et al., 2010). Scheme 4.1 illustrates the concept of electrostatic interaction on PEC formations which are the intrinsic compensation is interaction between polyelectrolytes as well as extrinsic compensation is bond between free site on polyelectrolyte and salt ions (Shovsky et al., 2009).



**Scheme 4.1** Type of charge compensation in polyelectrolyte complexes

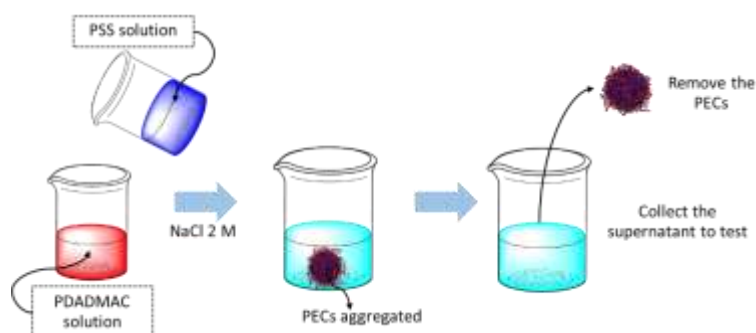
##### 4.1.1 The preparation of PEC from solution mixing process

Poly(styrene sulfonate), PSS and Poly(diallyldimethylammonium chloride), PDADMAC use as polycation and polyanion in this research. The colloidal particle of PEC observed after mixed the solution PSS and PDADMAC. The ionic strength was controlled by salt concentration. The salt concentration was studied to observe the great concentration in this research.

*4.1.1 (1) The PEC conformation studied with salt doping effect based on salt concentration.*

Salt ions is important parameter that have more effect with PEC formation. It can control the ionic strength of the complex including the contribution of the ionic bond. Salt concentration were operated to study the ionic strength contribution in difference salt concentration and the effect of ionic strength with PEC conformation.

In this study, sodium chloride (NaCl) was used and prepared in difference concentration consist of 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5 and 5.5 M respectively in PEC 1:1 ratio and scheme 4.2 represented the preparation of polyelectrolyte complex.

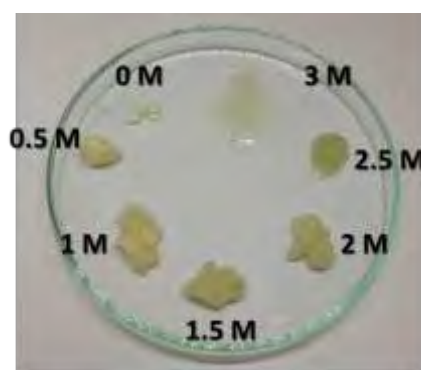


**Scheme 4.2** The preparation of polyelectrolyte complex by solution mixing process



**Figure 4.1** The appearance in solution of 1:1 PDADMAC/PSS in different NaCl concentration

Figure 4.1 represent the complex formation when concentration of NaCl increased. The complex formation were transform from solid (undoped) to soft solid (solid doped), rubbery form (coacervate) and solution when NaCl increased because salt ion can break the ion pair between complex(Wang & Schlenoff, 2014) resulted in the density of physical crosslink from electrostatic interaction.



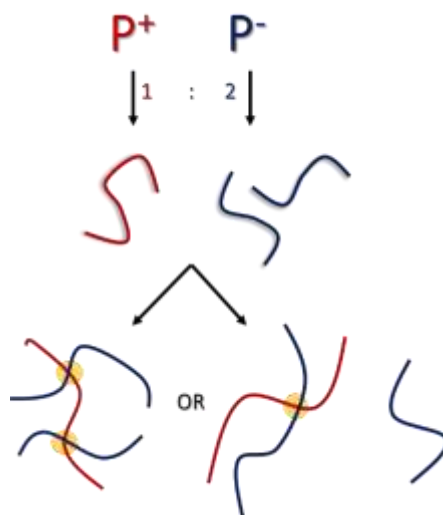
**Figure 4.2** The formation appearance of polyelectrolyte complexes in 0 – 3.0 M NaCl

Figure 4.2 shows the complex texture were change with salt concentration as a result of ionic screening and water molecule can go inside the complexes at the same time(Wang & Schlenoff, 2014). Above 2.5 M NaCl, the complex become small unit and all electrostatic link between polyelectrolyte are broken, the complex become solution.

From all result, 2M of NaCl shows highest ionic strength contribution and not loss of polyelectrolyte stock as show on tableA4 and 1:1 2M NaCl. The advantage of PEC with good ionic strength contribution is high incorporated of filler.

#### 4.1.1 (2) *The PEC conformation studied with effect of stoichiometric and non-stoichiometric.*

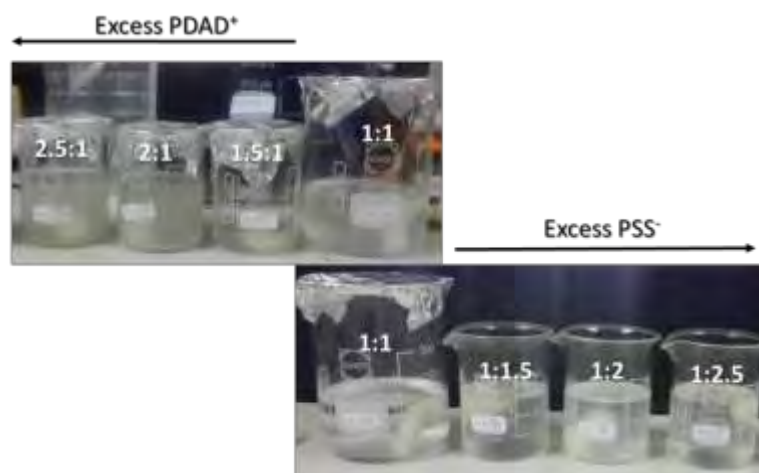
We can prepare PEC with equal molar ratio of  $P^+$  and  $P^-$ . But we can also prepare non-stoichiometric PEC by adding excess  $P^+$  or  $P^-$ . What would happen if we prepare non-stoichiometric. We expect maybe excess charge within the PEC.(schematic 4.3)



**Scheme 4.3** The schematic illustrate the structure of non-stoichiometric that have chance to occur.

Poly (diallyldimethylammonium chloride), PDADMAC and Poly(styrene sulfonate), PSS were prepared with different concentrations (0.1M, 0.15M, 0.2M, 0.25M and 0.3M) with 2.0 M NaCl. Figure 4.3 represents aggregated polyelectrolyte complexes after mixed

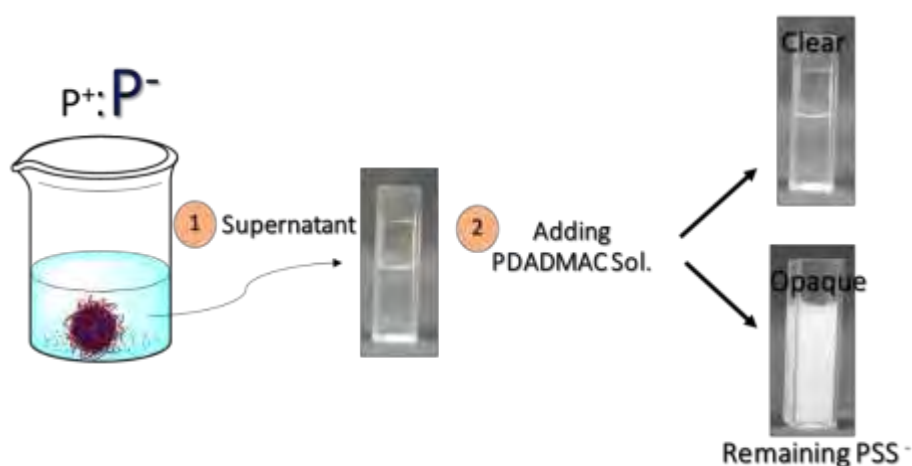




**Figure 4.3** Polyelectrolyte complex formations in different concentration of polyelectrolyte.

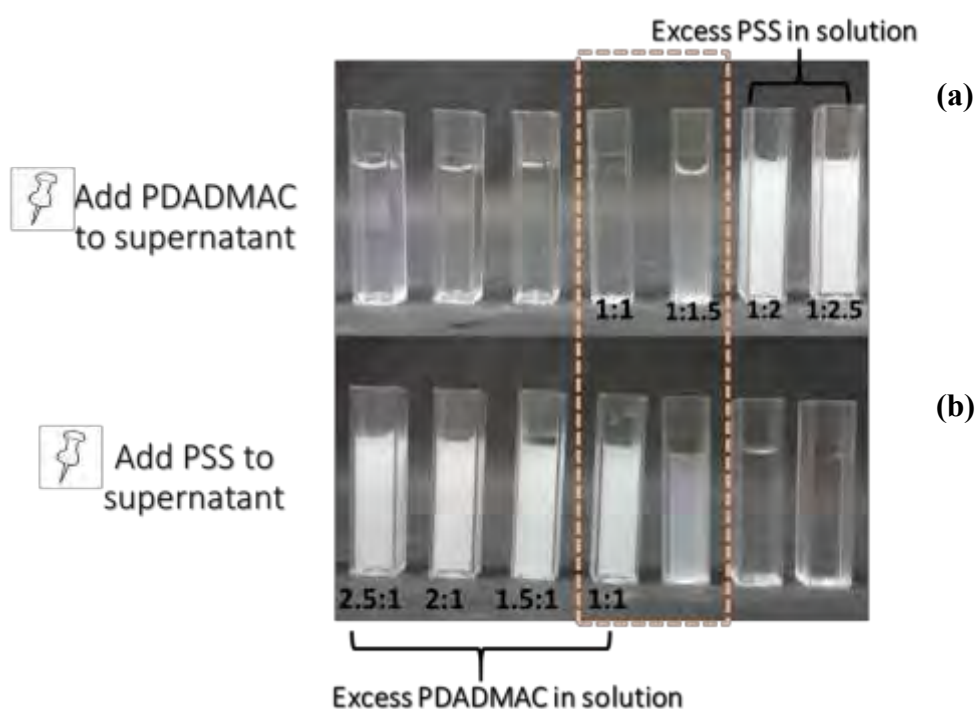
The figure 4.3 represents the PEC formation in different concentration of polyelectrolyte. The size of ball complex a little bit different which are in non-stoichiometric PEC are bigger than stoichiometric PEC.

When we prepare non-stoichiometric PEC observe any excess  $P^+/P^-$  remain in solution or all excess is found in PEC, it equal to yield. We expect that some unbounded  $P^+/P^-$  remain in solution.



**Scheme 4.4** The schematic explained the analyze the polyelectrolyte remaining in the supernatant.

Scheme 4.4 depicts the step to analyze the remaining polyelectrolyte by mixing with oppositely charged polyelectrolyte stock ( $P^+/P^-$ ) in the supernatant. The solution after added can explain the type of polyelectrolyte in the supernatant.

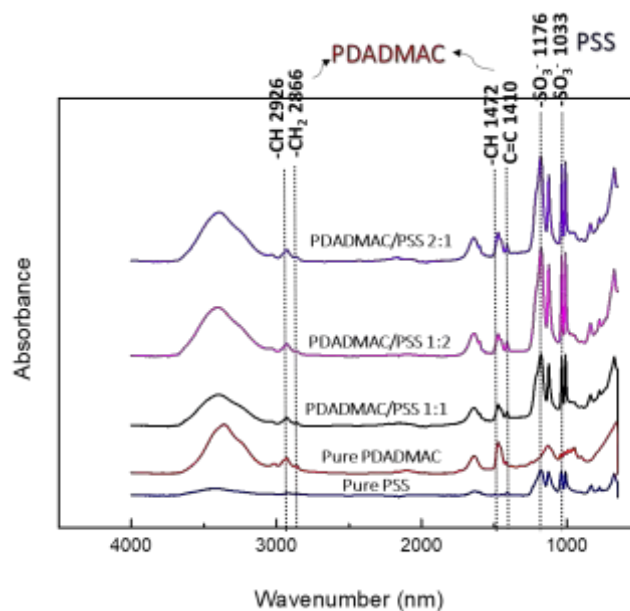


**Figure 4.4** (a) The supernatant after adding stock PDADMAC solution; (b) The supernatant after adding stock PDADMAC solution.

After adding pure PDADMAC solution, the supernatant solutions that contain excess PSS, it changed from clear to opaque (figure 4.4 (a)). However, the supernatant solutions that do not have excess PSS do not become opaque. For excess PDADMAC, it shows similar results as PSS (figure 4.4(b)).

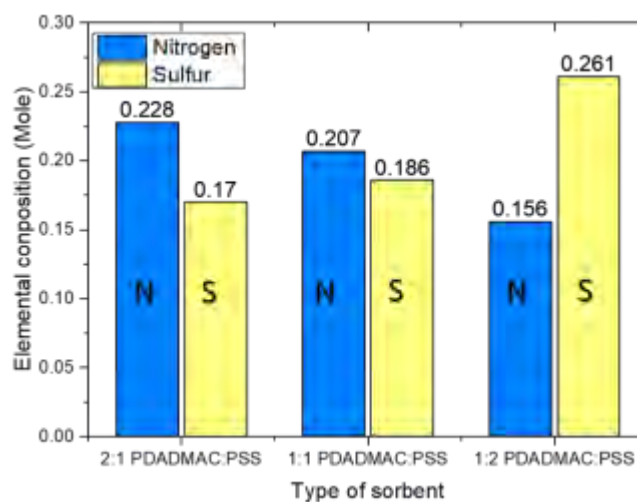
The stoichiometric polyelectrolyte complex (1:1) is not a real stoichiometric mixture because it has excess PDADMAC in solution. It might come from the fact that the higher average molecular weight of PDADMAC than PSS, or the charge in monomer size (Porcel & Schlenoff, 2009) and in 1:1.5 PDADMAC:PSS, the appearances of supernatant after adding PSS or PDADMAC solution, the supernatant remained transparent. We can conclude that the 1:1 PDADMAC:PSS is not real.

stoichiometric and the real stoichiometric for complex should be occur between 1:1.5 PDADMAC: PSS and 1:2 PDADMAC: PSS.



**Figure 4.5** FTIR spectra of pure polyelectrolyte and polyelectrolyte complex of stoichiometric and non-stoichiometric.

The FTIR spectra display the characteristic peaks of PSS and PDADMAC in both stoichiometric and non-stoichiometric polyelectrolyte complexes as shows on figure 4.5.



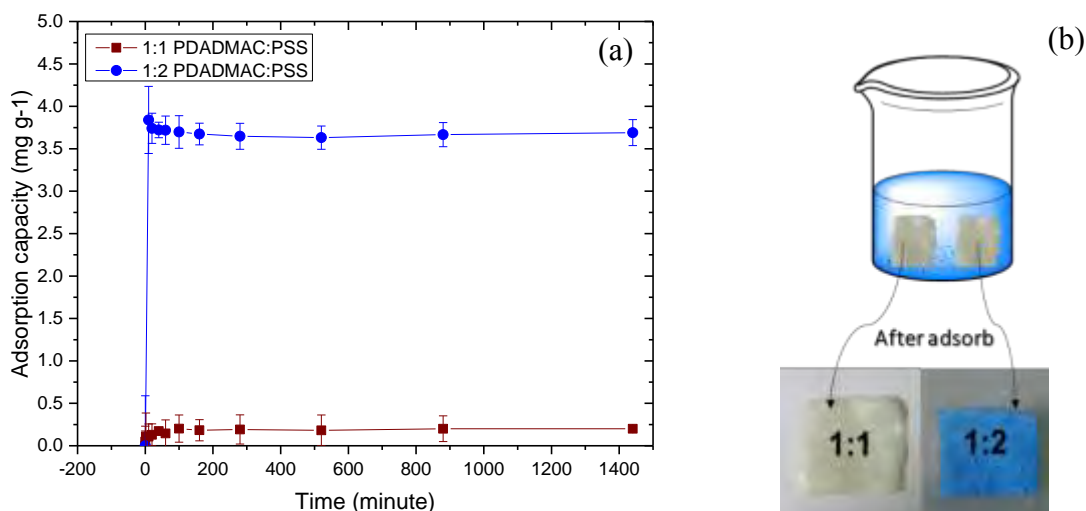
**Figure 4.6** Elemental composition polyelectrolyte complex of stoichiometric and non-stoichiometric calculated into mole

On figure 4.6 illustrate elemental composition polyelectrolyte complex of stoichiometric and non-stoichiometric. The two characterization confirm the excess polyelectrolyte when change mole ratio. The non-stoichiometric are second parameter influence with the properties of PEC and after prepare, it will have unpaired from excess polyelectrolytes residual in the system(Shovsky et al., 2009) although occur excess charge on membrane surface also.

#### 4.1.2 The confirming of excess charge on the non-stoichiometric PEC by Methylene blue adsorption.

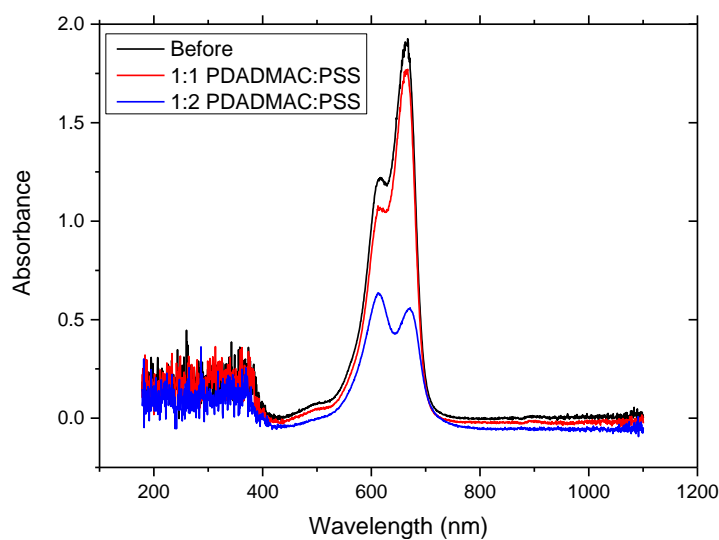
In this work are interesting the excess anion on the surface use for remove the cationic dye and heavy metal. The methylene blue dye used to examine the negative surface charge of excess PSS in 1:2 PDADMAC:PSS mole ratio and compare with stoichiometric PEC which is 1:1 PDADMAC: PSS mole ratio. If there is excess PSS PEC, the cationic dye should adsorb.

The cationic dye, methylene blue, prepared in  $10 \text{ mg l}^{-1}$  with 10 ml of solution after that the small membrane immersed in this solution with 1 days. The UV spectrometer was used to detect the residue concentration in different time.



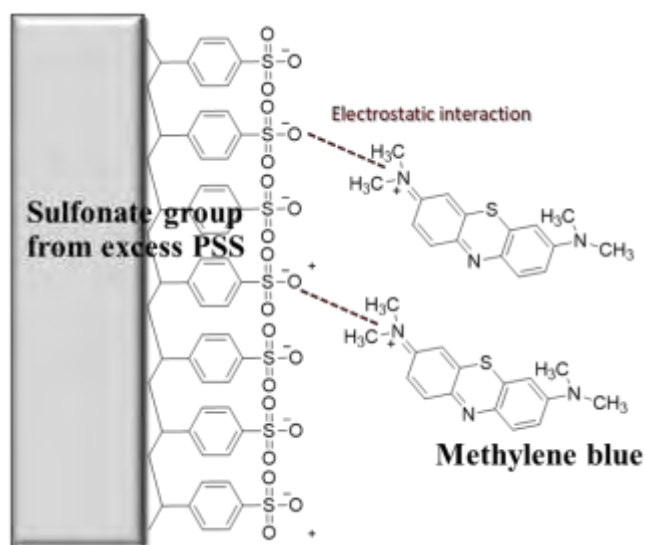
**Figure 4.7** (a) Adsorption capacity of 1:1 PDADMAC: PSS and 1:2 PDADMAC: PSS with time, (b) 1:1 PDADMAC: PSS and 1:2 PDADMAC: PSS membrane after dye adsorption experiment (white; 1:1 and blue; 1:2)

Figure 4.7 illustrates the adsorption capacity of 1:1 PDADMAC:PSS and 1:2 PDADMAC:PSS. From result, 1:2 PDADMAC:PSS rapidly adsorbed in methylene blue after adding in the solution whereas 1:1 PDADMAC:PSS didn't show any adsorption



**Figure 4.8** Absorbance spectra of dye solutions after dye adsorption experiments by using PDADMAC: PSS 1:1 and 1:2 as absorbent (at 7200 minutes).

The UV-spectra were confirmed (figure 4.8). This is because the 1:2 PDADMAC:PSS contain excess charge to bind with methylene blue via electrostatic interaction (Yu et al., 2015).



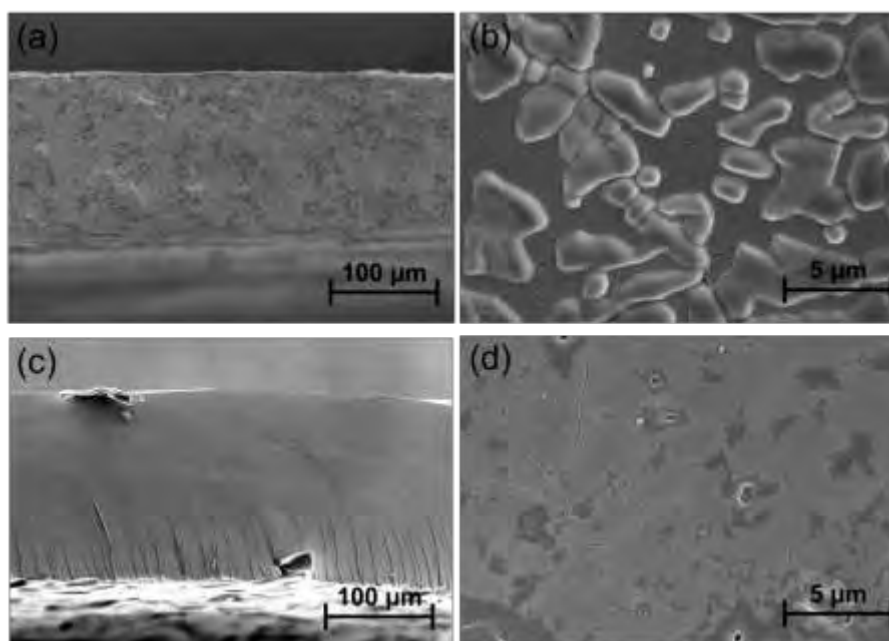
**Scheme 4.5** Schematic illustration of nonstoichiometric polyelectrolyte complex with methylene blue via electrostatic interaction.

The electrostatic interaction occurred between excess sulfonate in PSS and amine group in methylene blue (scheme 4.5), therefore PDADMAC: PSS 1:2 can adsorb more than 1:1 PDADMAC:PSS.

The adsorption of 1:2 PDADMAC:PSS increased with time. At initial (1 minute), the adsorption capacity value close to equilibrium capacity and become equilibrium after 10 minutes. Normally, the 1:2 PDADMAC:PSS should be have higher adsorption capacity more than this value (on figure 4.7(a)) because it have a lot of excess PSS in non-stoichiometric PEC as show on mole ratio plot in figure 4.6. So, it may have another parameter that effect with sorption capacity of PEC.

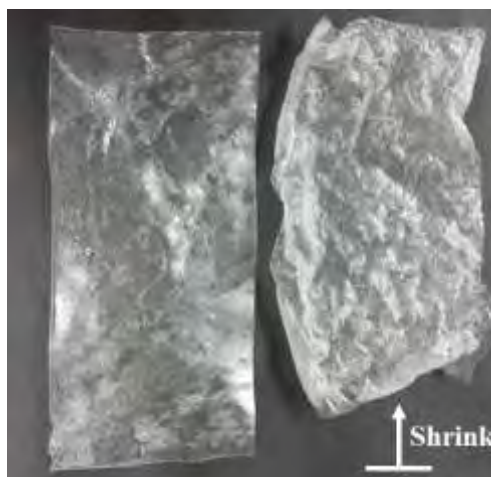
#### 4.1.3 The salt removal process for improve adsorption efficiency of PEC membrane

From the result of MB adsorption in title 4.1.2, the figure 4.7 (a) represented the kinetic adsorption of 1:2 PDADMAC:PSS mole ratio. The kinetic result shows the rapidly adsorption process with saturated MB adsorption after 10 minute. From the reference of PEC membrane, the salt release have chance to occur in aqueous environment and it affect with adsorption efficiency. The table C1 are confirming the release of  $\text{Na}^+$  in adsorption system by atomic absorption spectrometer (AAS) and Figure 4.9 shows the SEM image of in PEC membrane with NaCl crystal, (a) as crossection and (b) on surface , from that reason, washing salts is necessary.



**Figure 4.9** SEM images of 1:2 PDADMAC:PSS mole ratio with 2M of NaCl (a.) is crossection for 100  $\mu\text{m}$  ;(b.) is surface for 5  $\mu\text{m}$  and salt removal of 1:2 PDADMAC:PSS mole ratio (R-1:2 PDADMAC:PSS) (c.) is crossection for 100  $\mu\text{m}$  ;(d.) is surface for 5  $\mu\text{m}$

Salt removal PECs was prepared by soaking PDADMAC: PSS membrane in pure water 5 hour and change water every hour. The PDADMAC: PSS membrane was sonicated two time, 10 minute each and then dried under room temperature. The PEC membrane after salt removal process confirm by SEM image.

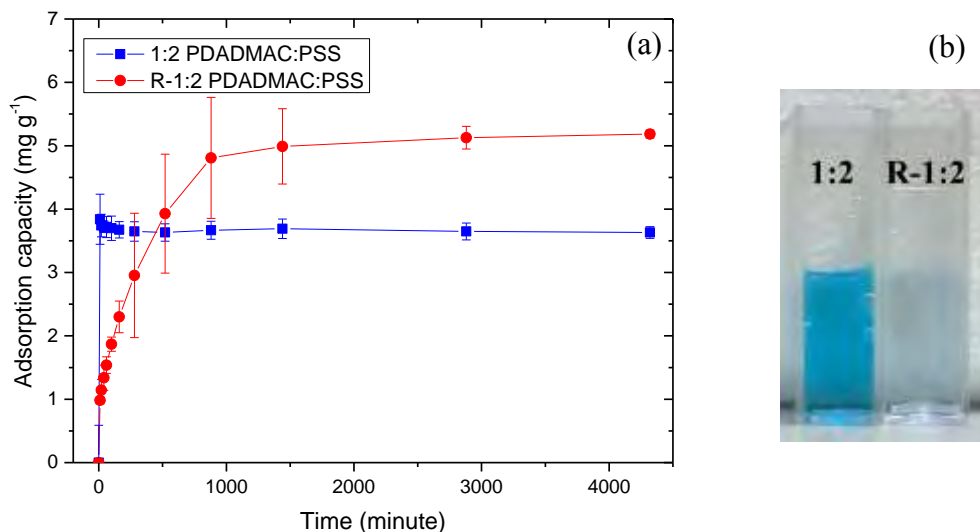


**Figure 4.10** 1:2 PDADMAC:PSS membrane before remove salt (left) and after remove salt (right).

The membrane appearance represented on figure 4.10. The membrane after remove salt, it shrinks because the intra-chain, inter-chain bond and entanglement in PECs were intact together and membrane become stiffness. The strong intra-chain bond reduce the stretching ability of PECs(Sun et al., 2015) so it needs to control the rate of salt removal to get the lowest salt content and even tough membrane.

After that, the R-1:2 PDADMAC:PSS was adsorbed with MB adsorption for demonstrate the improving of adsorption capacity. The 10 mg l<sup>-1</sup> of MB solution with 10 ml were used. After that the R-1:2 PDADMAC:PSS was cut to small size and immersed in the solution for 3 days.





**Figure 4.11** (a) The adsorption capacity with time of R-1:2 PDADMAC:PSS compare with 1:2 PDADMAC:PSS membrane ; (b) solution of MB after adsorption process.

Figure 4.11 (a) represents the relationship between adsorption capacities of 1:2 PDADMAC:PSS and R-1:2 PDADMAC:PSS with time and figure 4.11(b) shows the MB solution of both adsorbent after adsorption process. From result, R-1:2 PDADMAC:PSS membrane demonstrate higher adsorption capacity at equilibrium more than 1:2 PDADMAC:PSS so, the salt removal can decrease the amount of  $\text{Na}^+$  ions release, it render adsorption capacity of R-1:2 PDADMAC:PSS increased. Because it occur the screening effect on the surface of the membrane render the excess negative charge of 1:2 PDADMAC:PSS was neutralize by  $\text{Na}^+$  ions ( $\text{Na}^+$  release from PEC membrane) (Han, Wang, et al., 2007; Han, Zou, et al., 2007)

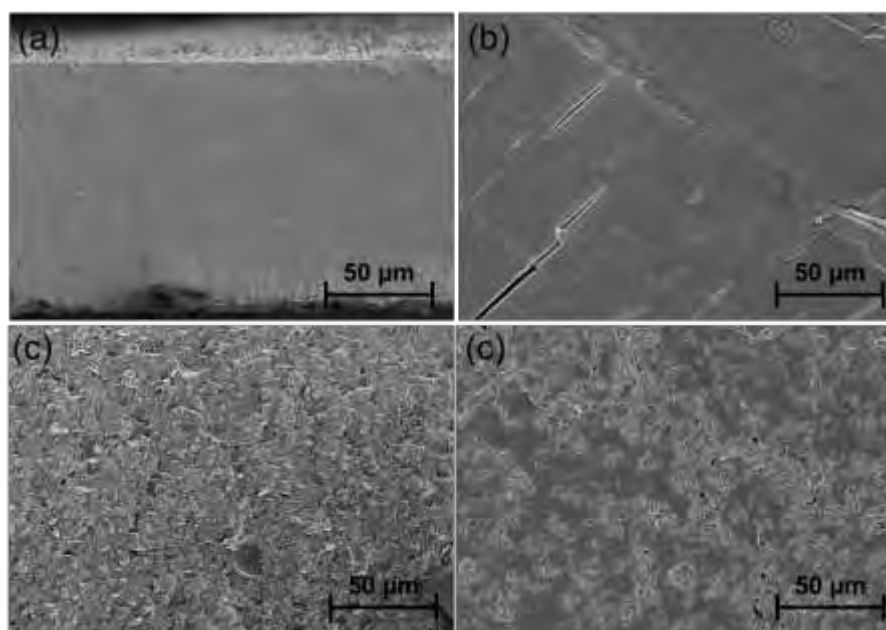
## 4.2 Hybrid PEC/AC hybrid membrane for cation dye adsorption application.

### 4.2.1 Preparation of PEC/AC membrane

Activated carbon (AC) is commonly used as adsorbent in wastewater treatment. Because of its high adsorption efficiency although, activated carbon

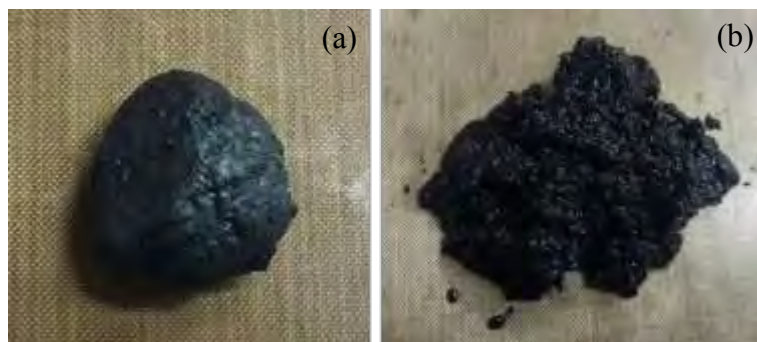
present many advantage. But it also have several drawbacks. The hardening separation from wet environment fetch the AC go to second pollutant in the treatment system. In this research was incorporated AC in PEC membrane for improve the disadvantage of AC and used AC to improve adsorption capacity in PEC membrane.

The AC was incorporated into 1:1 PDADMAC:PSS and 1:2 PDADMAC:PSS with difference w/w% which were 0, 5, 10, 15, 25, 35, 45 and 55% in 1:1 PDADMAC:PSS as well as 0, 5, 25 and 55 % in 1:2 PDADMAC:PSS.



**Figure 4.12** SEM image of PECs with and without activated carbon (A) cross section of 1:1 0%AC, (B) surface of 1:1 0%AC, (C) cross section of 1:1 55%AC and (D) surface of 1:1 55%AC for 50.0  $\mu\text{m}$ .

Figure 4.12 represents the SEM images of membranes before and after loaded activated carbon. The membrane after loading activated carbon shows high roughness of both crosssection and surface, it confirmed the loading of activated carbon in PEC matrix.

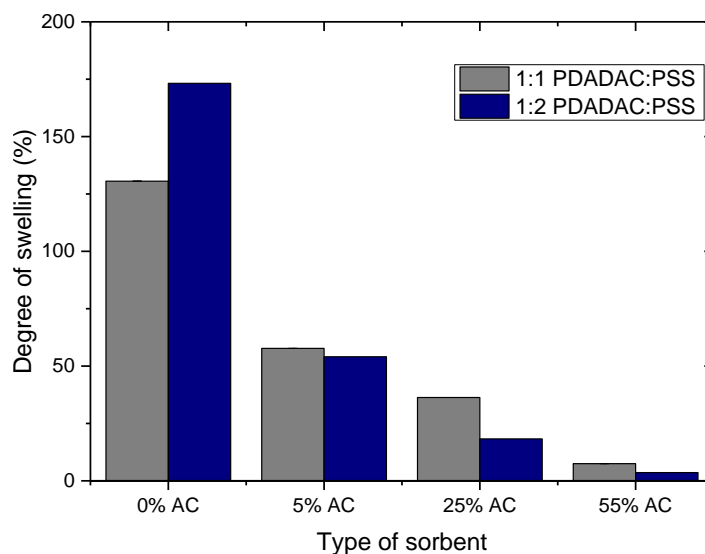


**Figure 4.13** The flocculation of PECs with 10% activated carbon (a) and 55% activated carbon (b) in 1:1 PDADMAC:PSS mole ratio.

While amount of fillers increased up to 45% weight and 55% weight, hybrid membranes flocculation were occurred because the filler change a role from fillers to become matrix (figure 4.13). Generally, in polymer composites, filler were as reinforcement materials or additives that dispersed in polymer matrixes. However, the shape of filler particles and volume fraction can change the fillers from reinforcement materials or additives to become matrixes.

In high amount of fillers loading, the maximum packing were generated and the macroscopic such as the homogenous fluid paste change to dry and the discontinuous composition were occurred (Ishida, 1997). The difference morphologies shows different properties of hybrid membrane. The morphologies of composite depends on filler type, filler particles and fillers size. In this case, PEC/AC hybrid membrane showed two morphologies: ideal morphology and particle pore blockage as it was also reported elsewhere (Aroon, Ismail, Matsuura, & Montazer-Rahmati, 2010).

The ideal morphology is polymer/filler particle interaction. Which the permeability for liquid or gas depend on polymer matrix and particle volume fraction. The increasing of fillers volume fraction showed different morphology such as particle pore blockage (with extremely loaded). Particle pore blockage can occurred in porous filler adding, it results in reduction of permeability (Aroon et al., 2010) so in this morphology, the aqueous solution (like methylene blue) hard to diffuses through the membranes.

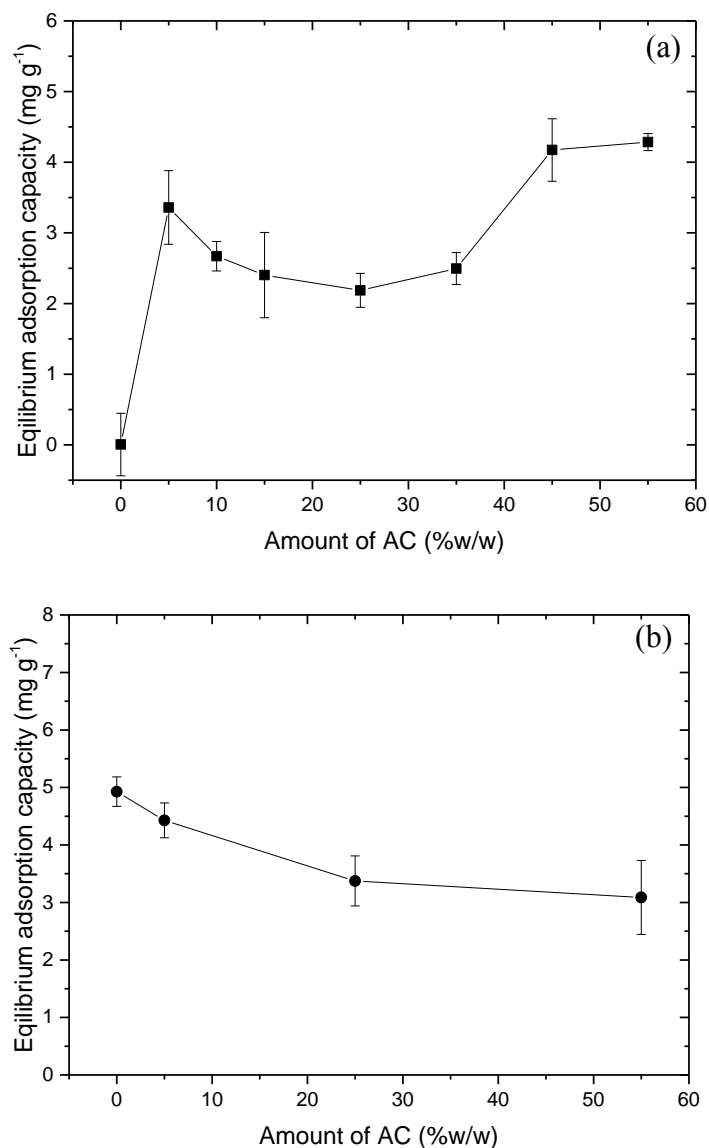


**Figure 4.14** The degree of swelling ; ■ 1:1 PDADMAC:PSS with and without AC and ■ 1:2 PDADMAC:PSS with and without AC.

The figure 4.14 shows the degree of swelling of PEC with and without AC, this result can confirm high packing of AC, which are the degree of swelling shows the opposite trend with %AC because high packing of AC block water past thought membrane.

#### 4.2.2 Effect of activated carbon in PEC with MB adsorption efficiency

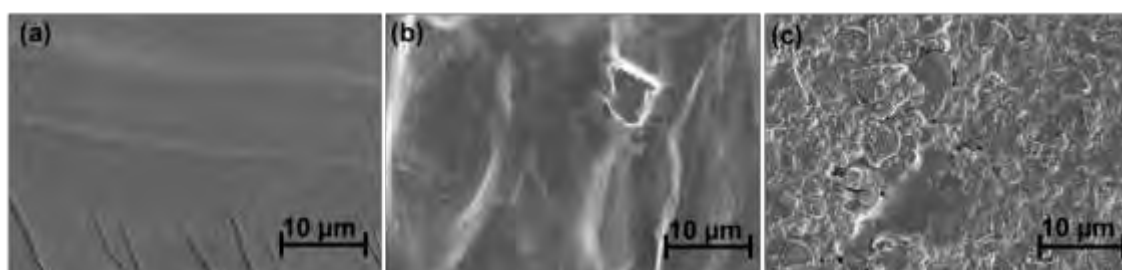
The activated carbon (AC) incorporated in 1:1 and 1:2 PDADMAC:PSS with difference %w/w. After compressed by compression molding to get the sheet membrane, it go to the removal process to get R-PEC after that it cut to small size and soak in  $10 \text{ mg l}^{-1}$  of MB solution about 10 days. The differentiation of MB concentration before and after immersed were detect UV spectrometer.



**Figure 4.15** The relationship between amount of AC and equilibrium adsorption capacity (a) 1:1 R-1:1 PDADMAC:PSS ;(b) R-1:2 PDADMAC:PSS with 10 mg l<sup>-1</sup> of MB and 10 days test.

Figure 4.15 represents the relationship between amount of fillers and adsorption capacity. In figure 4.15(a) the adsorption capacity of R-1:1 increased with increased amount of fillers but after 10% weight activated carbon, the adsorption capacity strongly decreased because of excess AC particles blocked. The increasing of filler operated high compact of the membrane (Sodhani & Reese, 2014)

and excess filler particles filled between entanglements of hybrid membrane. In case of 15% -35% are over loaded of fillers in matrix that cause affect with molecule diffusion the decreased of adsorption capacity in 15% - 35% activated carbon operate. In contrast, the adsorption capacity increased again after 45% because filler high enough for change the domain properties of the dense membrane to likely pure fillers furthermore the surface roughness of membrane (figure 4.16) are increasing render the adsorption capacity increased and get maximum adsorption capacity in 1:1 PECs mole ratio. Against, in figure 4.15 (a).



**Figure 4.16** SEM surface image of R-1:1 PECs (a) R-1:1 0%AC, (b) R-1:1 25%AC, (c) 1:1 55%AC for 10.0 µm.

Figure 4.15 (b) represents the adsorption capacity of R-1:2 PDADMAC:PSS mole ratio with and without activated carbon, 1:2 0%AC shows high adsorption capacity than R-1:2 with AC because the same reason with 1:1 PDADMAC:PSS mole ratio so this result can be conclude that are the R-1:2 0%AC have adsorption efficiency than R-1:2 with AC and it get highest adsorption capacity.

#### 4.2.3 The adsorption behavior of MB on PEC/AC hybrid membrane by kinetic adsorption study

The kinetic adsorption use to study the behavior of adsorption, it depending on type of adsorbent. It operated by soak the small size R-PEC in 10 mg l<sup>-1</sup> as initial concentration and sampling the solution in difference time. After that used the UV spectrometer to detect the residue MB concentration.

After that, the kinetic adsorption were fitted with pseudo-first-order and pseudo-second-order equation for studied the rate of sorption process. (Followed with equation 4.1, 4.2)

Pseudo-first-order equation; 
$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4.1)$$

Where  $q_e$  is the amount of dye adsorbed at equilibrium time ( $\text{mg g}^{-1}$ )

$q_t$  is the amount of dye adsorbed at time ( $\text{mg g}^{-1}$ )

$k_1$  is the first order rate constant ( $\text{min}^{-1}$ )

$t$  is time (min)

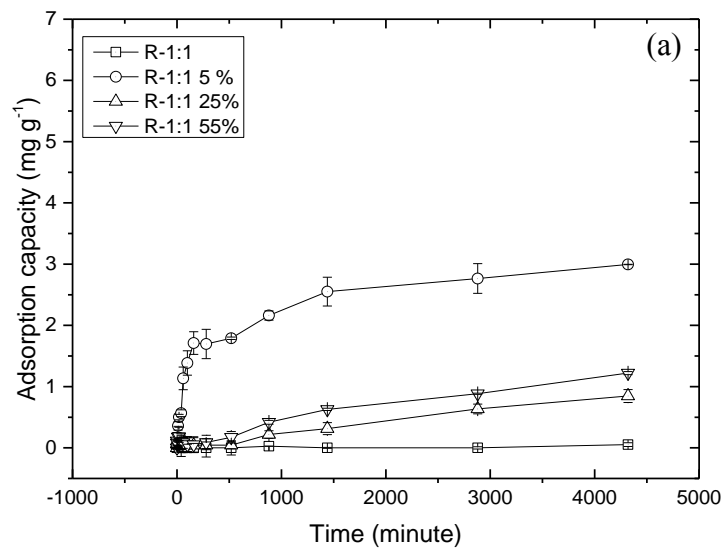
Pseudo-second-order equation; 
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4.2)$$

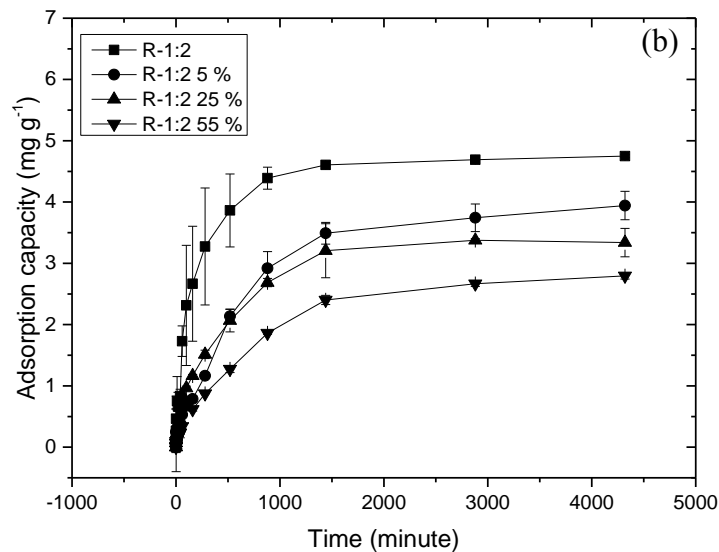
Where  $q_e$  is the amount of dye adsorbed at equilibrium time ( $\text{mg g}^{-1}$ )

$q_t$  is the amount of dye adsorbed at time ( $\text{mg g}^{-1}$ )

$k_2$  is the first order rate constant ( $\text{min}^{-1}$ )

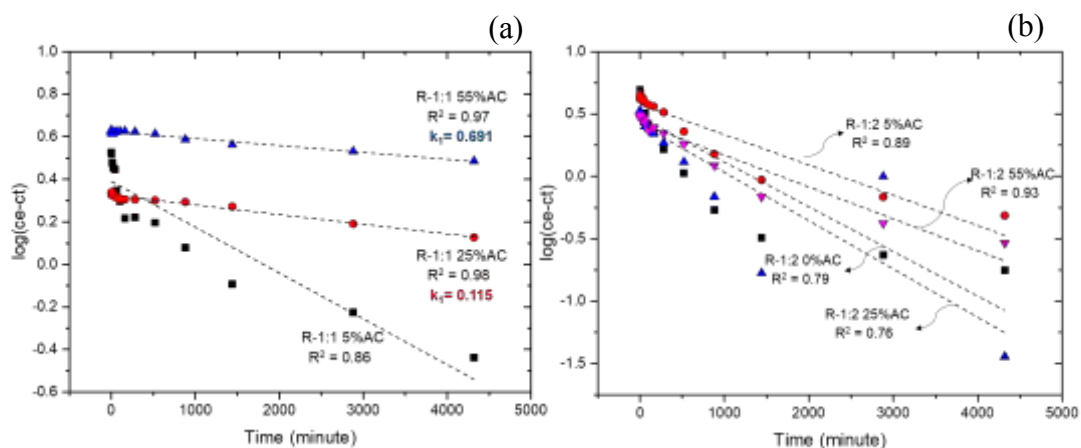
$t$  is time (min)



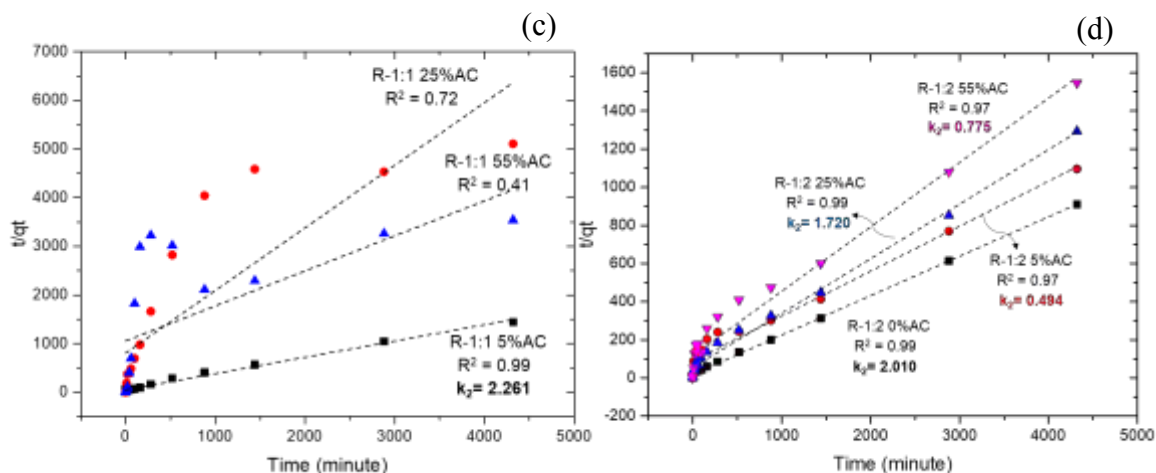


**Figure 4.17** The kinetic adsorption PEC/AC hybrid membrane (a)R-1:1 0%AC, R-1:1 5%AC , R-1:1 25%AC and R-1:1 55%AC; (b) R-1:2 0%AC, R-1:2 5%AC , R-1:2 25%AC and R-1:2 55%AC with 3 days

Figure 4.17 shows the kinetic adsorption behavior of PEC/AC hybrid membrane. In figure 6.17 (a) represents the adsorption behavior of R-1:1 0%AC, R-1:1 5%AC, R-1:1 25%AC and R-1:1 55%AC have a clearly slower rate of adsorption because when add AC in PEC, it increase the hydrophobic property to PEC render the solution cannot diffuses pass though the membrane. Moreover, the R-1:2 with AC (figure 4.16 (b)) shows higher adsorption rate than R-1:1 with AC because R-1:2 have excess PSS on the surface







**Figure 4.19** The kinetic adsorption model fitting of PEC/AC hybrid membrane (a) and (b) is pseudo-first order equation.; (c) and (d) is pseudo-second order equation  
 \* $k_1$  is first order kinetic rate ( $\times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ ),  
 \*\* $k_2$  is second order kinetic rate ( $\times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ )

The fitting of the R-1:1 with AC and R-1:2 with AC data with kinetic model shows on figure 4.19 where 4.19 (a),(b) are pseudo-first order fitting and 4.19 (c),(d) pseudo-second order fitting. For R-1:1 0%AC is not fit because it not adsorb. In R-1:1 with AC, only R-1:1 5%AC can fitting with pseudo-second order and others consist of the R-1:1 25%AC , R-1:1 55%AC can fitting with pseudo-first order. So, in R-1:1 with AC use  $k_1$  for R-1:1 25%AC , R-1:1 55%AC and  $k_2$  for R-1:1 5%AC for explain the rate of adsorption. The R-1:1 5%AC shows higher adsorption rate than R-1:1 25%AC , R-1:1 55%AC because in 5%AC, MB can penetrate pass though the surface of the membrane render AC inside the membrane show its performance. In contrast, R-1:1 25%AC , R-1:1 55%AC have slow adsorption rate because the surface block by excess AC render the MB hard to penetrate pass the membrane surface.

For R-1:2 with AC, the kinetic adsorption data of R-1:2 with AC can fit with pseudo-second order more than pseudo-first order. The adsorption rate ( $k_2$ ) of R-1:2 0%AC shows faster rate than R-1:2 with AC because of excess PSS and not have AC particle blocking. Furthermore, the R-1:2 0%AC show highest adsorption capacity on both calculation and experimental as show on table B8.

#### 4.2.4 The adsorption isotherm of MB on PEC/AC hybrid membrane

The adsorption isotherm is the theory their study with equilibrium adsorption in term of quantitative. Many model are used to study depend on type of sorption method. The two parameter model used to study in this research which are Langmuir , Freundlich, Dubinin-Radushkevich and Temkin isotherm model. The experiment were set by vary the concentration of MB with 5 difference concentration which are 2, 5, 10, 20 and 50 mg l<sup>-1</sup> subsequently, immersed the PEC/AC membrane in solution with 15 days (21600 minutes) and used UV spectrometer to detect MB absorbance before and after adsorption. The adsorbent were used in adsorption isotherm which are R-1:1 with and without AC, R-1:2 with and without AC.

Langmuir model equation; 
$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \quad (4.3)$$

Where;  $C_e$  is equilibrium concentration (mg l<sup>-1</sup>)

$q_e$  is equilibrium adsorption capacity (mg g<sup>-1</sup>)

$K_L$  is Langmuir coefficient (l mg<sup>-1</sup>)

$Q_0$  is maximum monolayer coverage capacity (mg g<sup>-1</sup>)

Freundlich model equation; 
$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4.4)$$

Where;  $C_e$  is equilibrium concentration (mg l<sup>-1</sup>)

$q_e$  is equilibrium adsorption capacity (mg g<sup>-1</sup>)

$n$  is Freundlich coefficient

$K_f$  is an approximate indicator of adsorption capacity (mg g<sup>-1</sup>)

Dubinin-Radushkevich model equation; 
$$\ln q_e = \ln q_s - K_{ad} \varepsilon^2 \quad (4.5)$$

Where;  $q_e$  is equilibrium adsorption capacity (mg g<sup>-1</sup>)

$q_s$  is theoretical isotherm saturation capacity (mg g<sup>-1</sup>)

$K_{ad}$  is Dubinin-Radushkevich isotherm constant ( $\text{mol}^2 \text{kJ}^{-2}$ )

$\varepsilon$  is Dubinin-Radushkevich isotherm constant (calculate from equation 4.6)

$$\varepsilon = RT \ln \left[ 1 + \frac{1}{C_e} \right] \quad (4.6)$$

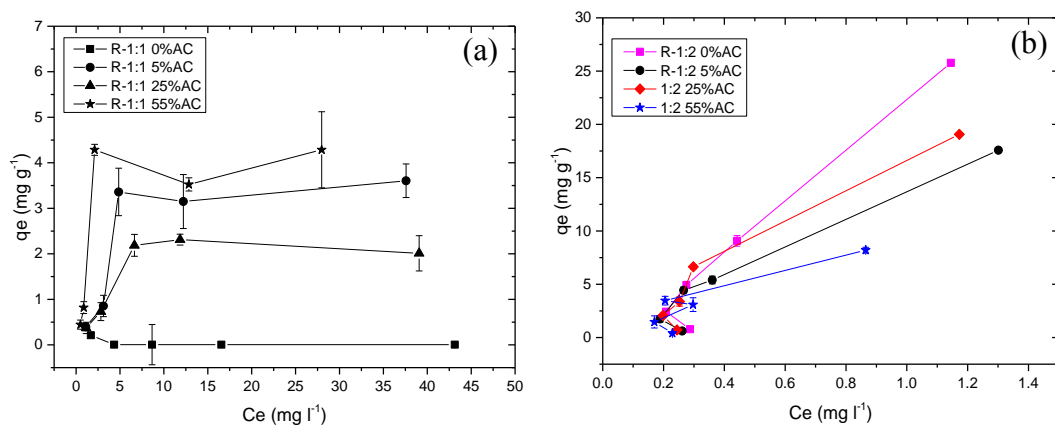
Temkin model equation;  $q_e = B \ln A_T + B \ln C_e$  (4.7)

Where;  $q_e$  is equilibrium adsorption capacity ( $\text{mg g}^{-1}$ )

$B$  is constant related to heat of sorption ( $\text{J mol}^{-1}$ )

$A_T$  is Temkin isotherm equilibrium binding constant ( $\text{L g}^{-1}$ )

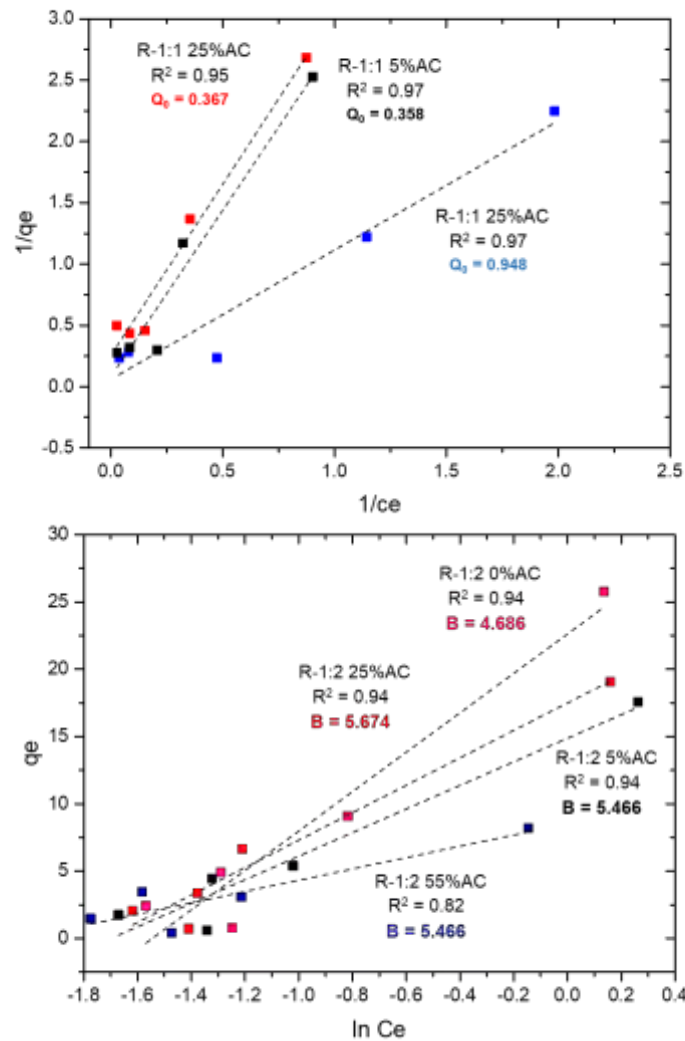
$C_e$  is equilibrium concentration ( $\text{mg l}^{-1}$ )



**Figure 4.20** Adsorption isotherm of MB on PEC/AC membrane (a) R-1:1 PDADMAC:PSS/AC hybrid membrane ; (b) R-1:2 PDADMAC:PSS/AC hybrid

The figure 4.20 represents the relationship between equilibrium adsorption capacity ( $q_e$ ) and equilibrium concentration ( $C_e$ ). The result of R-1:1 0%AC and R-1:1 with AC (figure 4.20 (a)) and R-1:2 0%AC and R-1:2 with AC (figure 4.20 (b)) shows the same trend which is  $q_e$  the increased with  $C_e$  because of the driving force effect. The higher concentration lead to faster and more binding molecule when compare with lower concentration (Baral, Das, Roy Chaudhury, & Das, 2009). Besides, the increasing of dye concentration observe a driving force to

overcome the mass transfer resistance of methylene blue between liquid phase to solid phase, the higher adsorption capacity overcome (Shenvi et al., 2015).

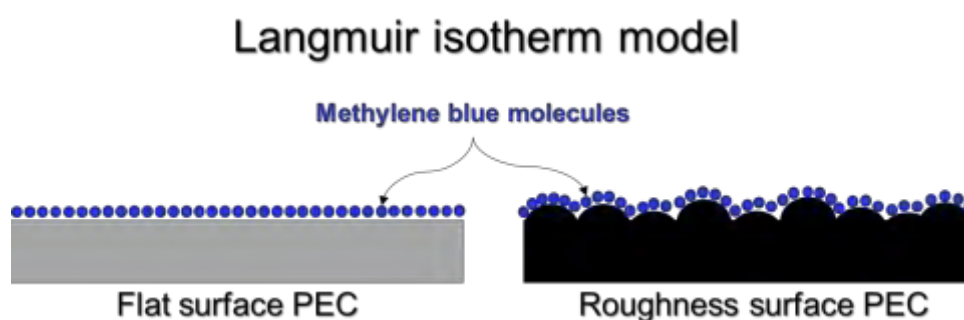


**Figure 4.21** Adsorption isotherm fitting of MB on PEC/AC membrane (a) R-1:1 5%AC, 25%AC and 55%AC with Langmuir adsorption isotherm ; (b) R-1:2 0%AC, 5%AC, 25%AC and 55%AC with Temkin adsorption isotherm

Where  $Q_0$  parameter is maximum monolayer coverage capacity ( $\text{mg g}^{-1}$ ) of Langmuir isotherm model

$B$  parameter is constant related to heat of adsorption ( $\text{J mol}^{-1}$ )

Furthermore, R-1:1 0%AC and R-1:1 with AC, most of R-1:1 indicate the graph behavior equal to Langmuir graph model when fit the data with Langmuir equation, the  $R^2$  of R-1:1 with AC get highest (figure 4.21 (a)). The result fit with Langmuir model display the physical adsorption mechanism and all surface sites have the same energy or equal affinity for the adsorbate (monolayer of adsorption). Other than, in the  $Q_0$  parameter indicate the maximum monolayer of MB on sorbent surface, the R-1:1 55%AC shows highest  $Q_0$  because high roughness surface (schematic 4.6).



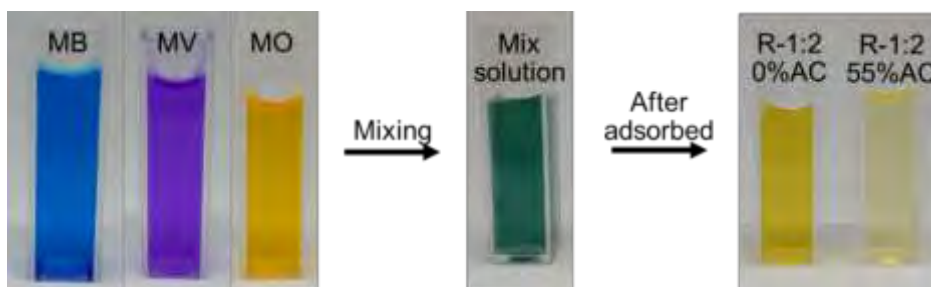
**Schematic 4.6** The combining of MB on the flat surface (left) and roughness surface (right)

In contrast, R-1:2 show the difference behavior of adsorption isotherm, it can fit with Temkin isotherm model with  $R^2$  close to one, the Temkin isotherm describe about heat of adsorption from figure 4.21 (b) show B parameter, is an indication of the heat of adsorption. In this result, B parameter indicate a physical adsorption process (A.O, Olalekan, Olatunya, & Dada, 2012). The all of result, R-1:2 0%AC still operate highest adsorption capacity although initial concentration increased and higher than R-1:2 with AC.

#### 4.2.5 Mixer dye adsorption study on PEC/AC hybrid membrane

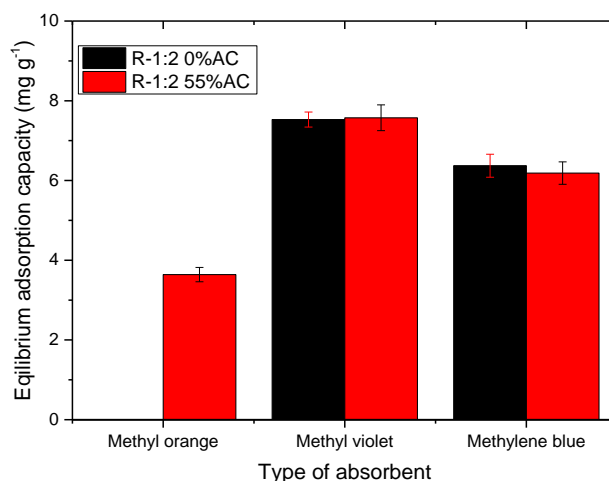
The selectivity part operated for study the effect from difference type of cationic dye and anionic dye with adsorption efficiency. The experiment were

prepare mixing solution between two cationic dye consist of Methylene blue (MB) and Methyl violet (MV) and one anionic dye which is Methyl orange (MO). The small membrane immersed in 10 ml of mixer solution with concentration  $10 \text{ mg l}^{-1}$  per one dye type. The adsorption process operated 15 days for this experimental and the concentration detected by UV-spectrometer. The sample used in this experiment are R-1:2 0%AC and R-1:2 55%AC. The R-1:2 55%AC still used to study the selective although it have low adsorption capacity because the behavior of AC are non-selectivity so it should be adsorb MO, anionic dye.



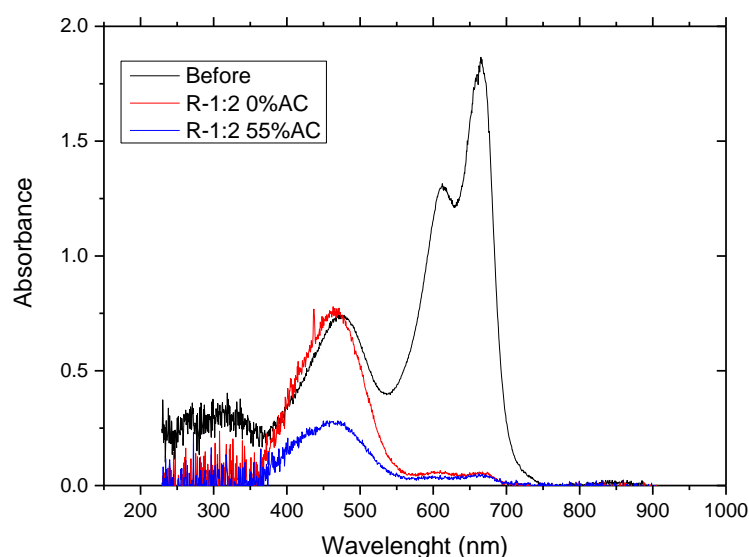
**Figure 4.22** The mixer solution before and after adsorption process by R-1:2 0%AC and R-1:2 55%AC

Figure 4.22 represents the mixer solution before and after adsorbed by R-1:2 0%AC and R-1:2 55%AC. The solution of R-1:2 0%AC after adsorption shows full concentration of MO but in R-1:2 55%AC can adsorb all dye type including MO also.



**Figure 4.23** Equilibrium adsorption capacity of dye mixer on PEC/AC hybrid membrane ■ R-1:2 0%AC ; ■ R-1:2 55%AC.

The figure 4.23 represents the equilibrium adsorption capacity of mixer dye on PEC/AC hybrid membrane. The result show high selectivity of MB and MV on R-1:2 0%AC because excess PSS on surface and R-1:2 55%AC show the same trend with R-1:2 0%AC but it can adsorb anionic dye (MO) also because of AC are non-selective adsorbent



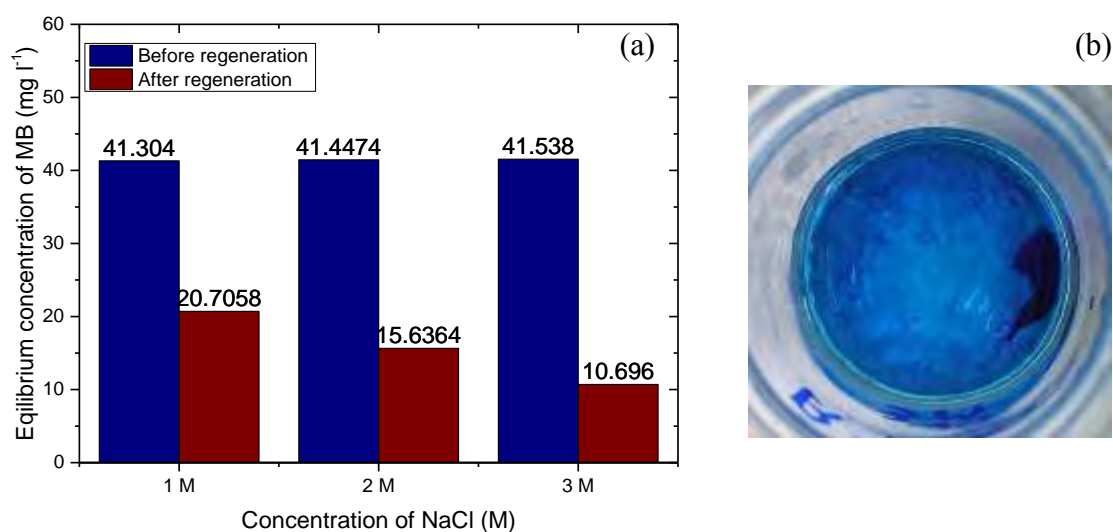
**Figure 4.24** UV spectra of mixer solution before and after adsorption process by R-1:2 0%AC and R-1:2 55%AC

The figure 4.24 shows UV spectra of the mixer solution before and after adsorption process, confirmed the adsorption mechanism occur in R-1:2 0%AC and R-1:2 55%AC.

#### 4.2.6 The studied of regeneration of MB from PEC membrane

The regeneration experiment operated in MB adsorption because from part 4.2.4, the MB adsorption mechanism on R-1:2 0%AC can fit with Temkin

isotherm model, it indicated the physical adsorption mechanism of MB on PEC membrane so it able to regenerate MB from PEC membrane. The regeneration is normally cheaper method than replacement. There have been many method propose to regenerate the membrane consist of physical regeneration and chemical regeneration(Lu, Lin, Yu, & Chern, 2011). In this research are using NaCl solution to regenerate PEC because PEC structure have high effective with salt, it can categories in the physical regeneration type because of water based method and medium pH. The membrane sample were used in this experiment which is R-1:2 0%AC after saturate adsorbed  $50 \text{ mg l}^{-1}$  of MB. The three sample of saturated R-1:2 0%AC has equilibrium adsorption concentration are 41.305, 41.447 and 41.538  $\text{mg l}^{-1}$ , respectively. And the NaCl concentration were used to regenerate which are 1M, 2M and 3M of NaCl, respectively. The experiment operated 5 days.



**Figure 4.25** (a) The equilibrium concentration of MB inside R-1:2 0%AC; ■ before regeneration and ■ after regeneration ; (b) The structure of R-1:2 0%AC was destroy from higher NaCl solution.

The figure 4.25 (a) shows the equilibrium concentration ( $C_e$ ) of R-1:2 0%AC after saturated adsorb in adsorption process on title 4.2.4, from the result after regenerated by immerse in NaCl solution, the  $C_e$  in R-1:2 0%AC are decreasing with NaCl concentration increased because the NaCl extend the PEC structure(Yu et al.,



2015) render the MB come out from PEC membrane and 3M of NaCl provide maximum regeneration. Although, 3M NaCl is providing maximum regeneration but it destroy structure of PEC as shows on figure 4.25(b). So, the best NaCl concentration get great MB regeneration which is 2 M NaCl.

### 4.3 Metal ion adsorption of PEC/activated carbon hybrid membrane

The adsorption and ion exchange are categories of sorption. It can be perform in solid-gas and solid-liquid. Both of them can use the same model to studies behavior like Langmuir and Freundlich isotherm as well as the kinetic adsorption theory, it is depend on process.

Ion exchange consist of the inter change of ions between two phase, the one phase can soluble (solution) and in another phase insoluble (on sorbent), when the solution phase contact with sorbent interface (that have ion with the same charge), the ion exchange occurred(Alexandratos, 2009).

In adsorption process are different with ion exchange which are due to the unbalance residual force at the surface of solid phase (sorbent), the unbalance start to attract with the molecule species that have opposite charge. The example of adsorption mechanism is electrostatic interaction(M.Douglas LeVan, 1999).

In this result, the sorption process occur two mechanism which are adsorption and ion exchange to obtain  $\text{Cu}^{2+}$  ions removal of PEC and PEC/AC hybrid membrane.

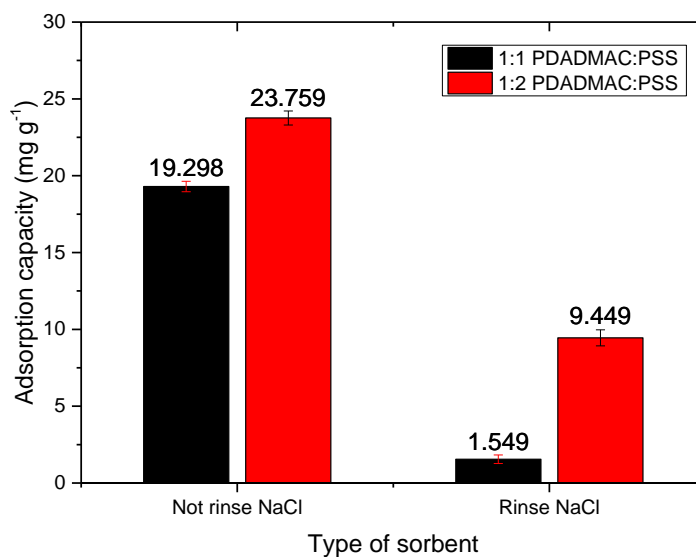
**Table 4.1** The comparison of  $\text{Cu}^{2+}$  ions adsorption capacity with general adsorbent.

Type of adsorbent	Name of adsorbent	$\text{Cu}^{2+}$ adsorption capacity	Initial concentration	Ref.
Activated carbon (AC)	1.Powder AC	10 mg g <sup>-1</sup>	25 mg l <sup>-1</sup>	(Macías-García, Gómez Corzo, Alfaro Domínguez, Alexandre Franco,
	2.Granular AC	4.448 mg g <sup>-1</sup>	63.546 mg l <sup>-1</sup>	

				& Martínez Naharro, 2017) (An, Park, & Kim, 2001)
<b>Ion exchange</b>	1.Cation exchange	74.984 mg g <sup>-1</sup>	63.546 mg l <sup>-1</sup>	(An et al., 2001)
<b>Polyelectrolyte resin</b>	1.Polystyrene sulfonate (PSS) 2.Chitosan	15 mg g <sup>-1</sup> 158.865 mg g <sup>-1</sup>	50 mg l <sup>-1</sup> ultrafiltration 9.97x10 <sup>5</sup> mg l <sup>-1</sup>	(Chen, Shafer-Peltier, Randtke, & Peltier, 2018)  (Z A C A R I A R E D D A D & Y V E S A N D R E S 2002)

#### 4.3.1 Effect of NaCl with adsorption efficiency of PEC membrane without activated carbon

The PEC membrane not rinse are 1:1 0%AC, 1:2 0%AC and PEC with NaCl rinsed are R-1:1 0%AC, R1:2 0%AC used to study the effect of NaCl inside the membrane that occurred ion exchange with Cu<sup>2+</sup> ions and the membrane was immersed with 10 days (14400 minutes) in 50 mg l<sup>-1</sup> of Cu<sup>2+</sup> ions solution.



**Figure 4.26** The adsorption capacity of ■; 1:1 0%AC and R-1:1 0%AC  
 ■; 1:2 0%AC and R-1: 0%AC

The figure 4.26 on black column show completely clear result about ion exchange effect on 1:1 0%AC and R-1:1 0%AC because 1:1 0%AC is stoichiometric PEC, it should be not adsorb  $\text{Cu}^{2+}$  ion with natural behavior of stoichiometric. Whereas, the 1:1 0%AC, it shows high adsorption capacity more than R-1:1 0%AC. That is confirm the occurring of ion exchange between  $\text{Na}^+$  ions inside the membrane and  $\text{Cu}^{2+}$  ions in the solution The figure 4.26 on red column show the sorption efficiency of the 1:2 0%AC. From the result when compare the adsorption capacity between 1:2 0%AC and R-1:2 0%AC, 1:2 0%AC show higher capacity than R-1:2 1:2 0%AC and in table 4.2 show the capacity of  $\text{Cu}^{2+}$  ions sorption ( $q_e$ ) compare with capacity of  $2\text{Na}^+$  release ( $q_{2\text{Na}^+}$ ) that can confirm the ion exchange mechanism affect with sorption capacity of  $\text{Cu}^{2+}$  ions.

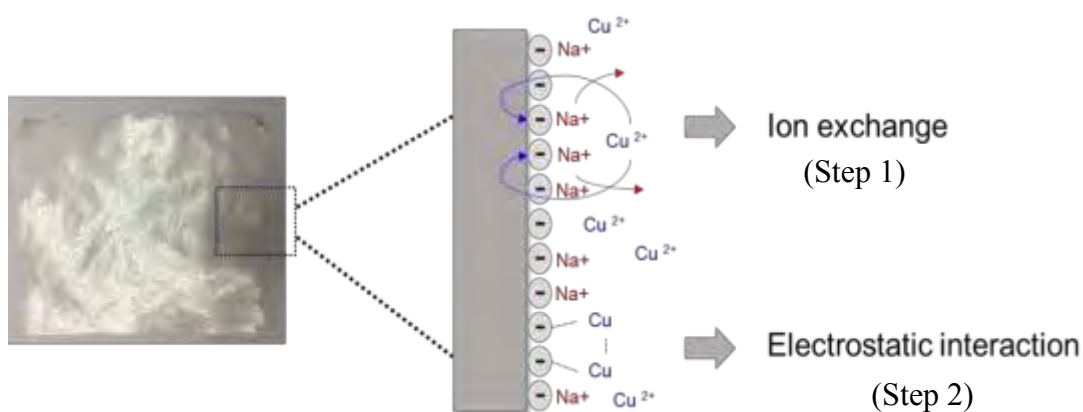
**Table 4.2** The effect of  $\text{Cu}^{2+}$  ions adsorption on  $2\text{Na}^+$  ions release from PEC membrane calculate follow with Zacaria R. et al (2002)(Z A C A R I A R E D D A D & Y V E S A N D R E S 2002).

Type of	$q_e$ of $\text{Cu}^{2+}$	$q_{2\text{Na}^+}$ release	Ratio $q_e/$	Possibility of
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sorbent	ions (mg g <sup>-1</sup> )	(mg g <sup>-1</sup> )	PSS excess*	adsorption mechanism
1:1 0%AC	19.297	19.056	0.74	98.75% ions exchange+ 1.25% electrostatic interaction
1:2 0%AC	23.759	22.113	0.69	93.07% ions exchange+ 6.9% electrostatic interaction

\*PSS excess value on table C2

Table 4.5 explain the possibility of sorption mechanism on 1:1 0%AC, which calculate follow with Zacaria R. et al, it occur 100% ion exchange mechanism. Furthermore, 1:2 0%AC have another mechanism to adsorb Cu<sup>2+</sup> ions which is electrostatic interaction because R-1:2 0%AC also adsorb Cu<sup>2+</sup> ions albeit not have Na<sup>+</sup> ions in the system and in table 3.3.2 show the possibility of sorption mechanism can occur in 1:2 0%AC which are 93% of ion exchange and 7 % of electrostatic interaction.



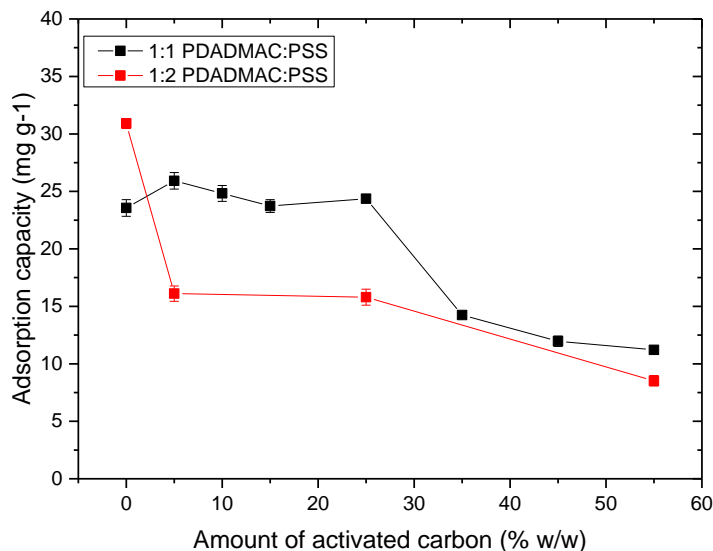
**Schematic 4.7** The mechanism of ion exchange and electrostatic interaction that occur on 1:2 0%AC

The schematic 4.6 illustrate the mechanism that can occur on the 1:2 0%AC membrane consist of ion exchange and electrostatic interaction. In ion exchange mechanism, the ion exchange between  $\text{Na}^+$  on PSS and  $\text{Cu}^{2+}$  in solution after that the electrostatic interaction operate, it binding with exchanged  $\text{Cu}^{2+}$ . So, we can conclude the mechanism that occur in  $\text{Cu}^{2+}$  sorption on PEC membrane have 2 step of mechanism.

#### 4.3.2 Effect of activated carbon in PEC with adsorption efficiency

The powder activated carbon is famous material in heavy metal adsorption process because of high porosity and high adsorption capacity. Whereas, the powder activated carbon after adsorption process are become secondary waste in aqueous system because it occur precipitate powder and hard to separate. The granular activated carbon (GAC) are observe in the market to solve that problem but the GAC get the low adsorption capacity because the decreasing of surface area and high packing render GAC to get the slow rate of adsorption. Many research incorporated the powder AC in high performance resin to improve the secondary waste problem (in powder form) although the slow rate and low adsorption capacity of GAC form (Pack powder AC).

The activated carbon (AC) incorporated in 1:1 and 1:2 PDADMAC:PSS PECs with difference %w/w. After compressed by compression molding to get the sheet membrane, it were cut to small size and soak in  $50 \text{ mg l}^{-1}$  of  $\text{Cu}^{2+}$  ion solution about 15 days (21600 minute). The  $\text{Cu}^{2+}$  ions solution before and after immersed were detect the concentration by atomic absorption spectrophotometer (AAS) and calculated from concentration to adsorption capacity with equation 5.1 in chapter V.



**Figure 4.27** The relationship between adsorption capacity of  $\text{Cu}^{2+}$  ions with amount of filler (%w/w) of 1:1 PDADMAC:PSS and 1:2 PDADMAC:PSS

From the result, after incorporate activated carbon in PEC, the adsorption capacity become decrease in both 1:1 and 1:2 PEC. While, 1:2 PEC are having the excess PSS on the surface, the adsorption capacity still get low adsorption capacity (Figure 4.27).

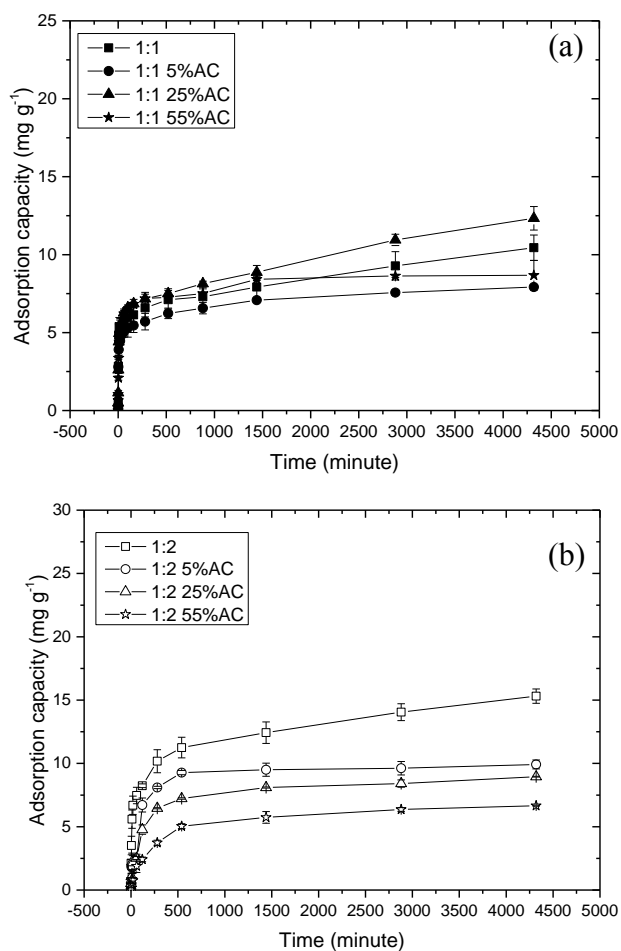
The adsorption capacity of 1:1 with AC are decreased when add AC more that 25% w/w because high packing of AC particle in PEC render the solution hard to diffuse from the surface pass though the membrane, the result of degree of swelling can confirm this hypothesis. In 1:2 with AC 1show the same trend with 1:1 with AC.

#### 4.3.3 The adsorption behavior of $\text{Cu}^{2+}$ ions on PEC/AC membrane by kinetic adsorption study

The kinetic adsorption use to study the behavior of adsorption operated by soak the small size membrane in  $50 \text{ mg l}^{-1}$  as initial concentration and sampling the solution in difference time. After that used the AAS to detect the

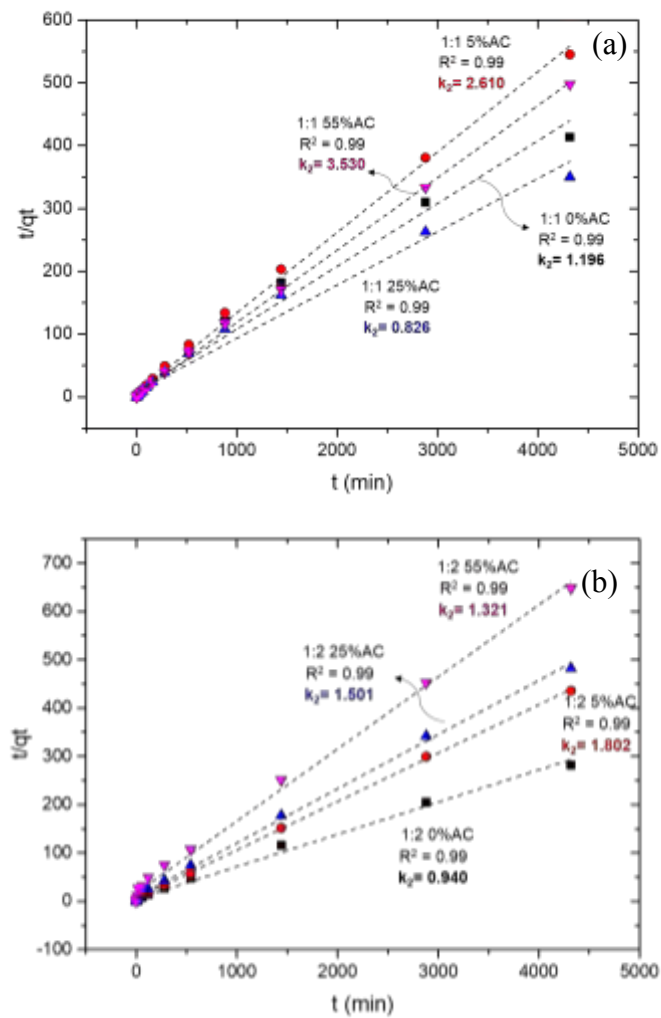
residue  $\text{Cu}^{2+}$  ions and calculated from concentration to adsorption capacity by equation 3.1.

Furthermore, the kinetic adsorption were fitted with pseudo-first-order and pseudo-second-order equation for studied the rate of sorption process



**Figure 4.28** The relationship between adsorption capacity of  $\text{Cu}^{2+}$  ions with time (a) 1:1 0%AC, 1:1 5%AC, 1:1 25%AC and 1:1 55%AC ; (b) 1:2 0%AC, 1:2 5%AC, 1:2 25%AC and 1:2 55%AC

Figure 4.28 represents the kinetic adsorption behavior of  $\text{Cu}^{2+}$  ions on PEC membrane. The behavior of 1:1 0%AC and with AC, 1:2 0%AC and with AC shows the same behavior.



**Figure 4.29** The kinetic adsorption model fitting of PEC/AC hybrid membrane (a) 1:1 0%AC, 1:1 5%AC, 1:1 25%AC and 1:1 55%AC ; (b) 1:2 0%AC, 1:2 5%AC, 1:2 25%AC and 1:2 55%AC with pseudo-second order kinetic model  
 $*k_2$  is second order kinetic rate ( $\times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ )



**Table 4.3** Kinetic parameters for  $\text{Cu}^{2+}$  ions sorption onto commercial activated carbon

Adsorbent	Pseudo-first order		Pseudo-second order		ref
	$k_1$ ( $\times 10^{-4} \text{ min}^{-1}$ )	$R^2$	$k_2$ ( $\times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ )	$R^2$	
<b>Powder activated carbon</b>	9.7	0.912	70.7	0.999	(Macías-García et al., 2017)

Normally, many research are reported the majority of adsorption model occur in pseudo-first-order rate mechanism. However in this result can fit with pseudo-second-order equation, this equation agree with chemisorption as a rate to control mechanism. The parameter fitted with pseudo-second-order equation show on figure 4.25 and commercial activated carbon show on table 4.3. From the result of  $k_2$  that can categories the adsorption behavior of PEC/AC hybrid membrane to two categories which are ion exchange and porous material adsorption behavior.

The porous material adsorption behavior demonstrate in 1:1 5%AC, and 1:1 55%AC, it show high rate of adsorption when compare with other PEC/AC membrane. Because of AC are have high surface area and when add in PEC, PEC surface change from flat to high roughness surface (in 1:1 55%AC), it render adsorption interface of the membrane increased and in 1:1 5%AC, show high rate of adsorption because it have performance of ion exchange and AC together ( $\text{Cu}^{2+}$  ion can pass through the membrane surface not like 1:1 55%AC). Whereas, the adsorption capacity of 1:1 5%AC, and 1:1 55%AC show opposite trend with rate of adsorption.

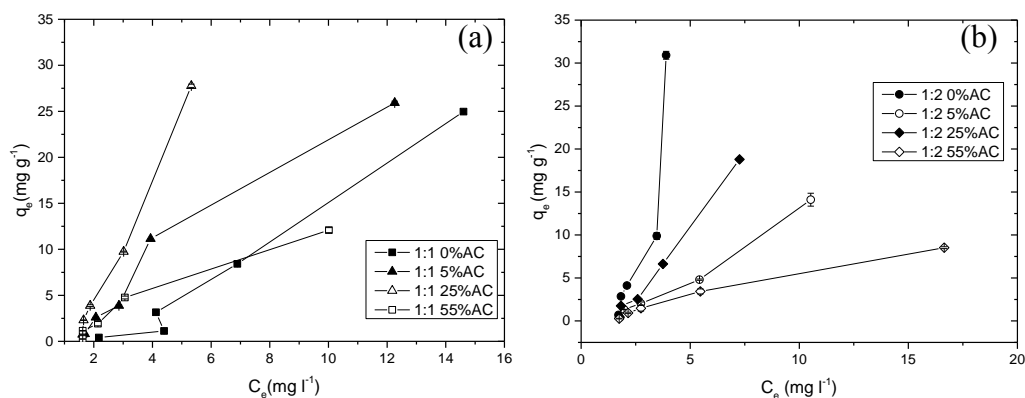
The second categories is ion exchange consist of 1:1 0%AC, 1:1 25%AC and all of 1:2 mole ratio. This categories show low rate of adsorption ( $k_2$ ) because  $\text{Cu}^{2+}$  ions need time to penetrate through the interface of the membrane by ion exchange with  $\text{Na}^+$  ions after  $\text{Cu}^{2+}$  ion pass through the membrane. Furthermore,

1:2 0%AC are show highest adsorption capacity when compare with 1:2 5%AC, 1:2 25%AC, 1:2 55%AC and 1:1 PECs (with and without AC). The excess PSS comes with high amount of charge compensator (NaCl) because  $\text{Na}^+$  like to stay with PSS render the 1:2 0%AC occur high rate of ion exchange. Mo From that render the 1:2 0%AC get highest adsorption capacity.

#### 4.3.4 The adsorption isotherm of $\text{Cu}^{2+}$ ions on PEC/AC hybrid membrane

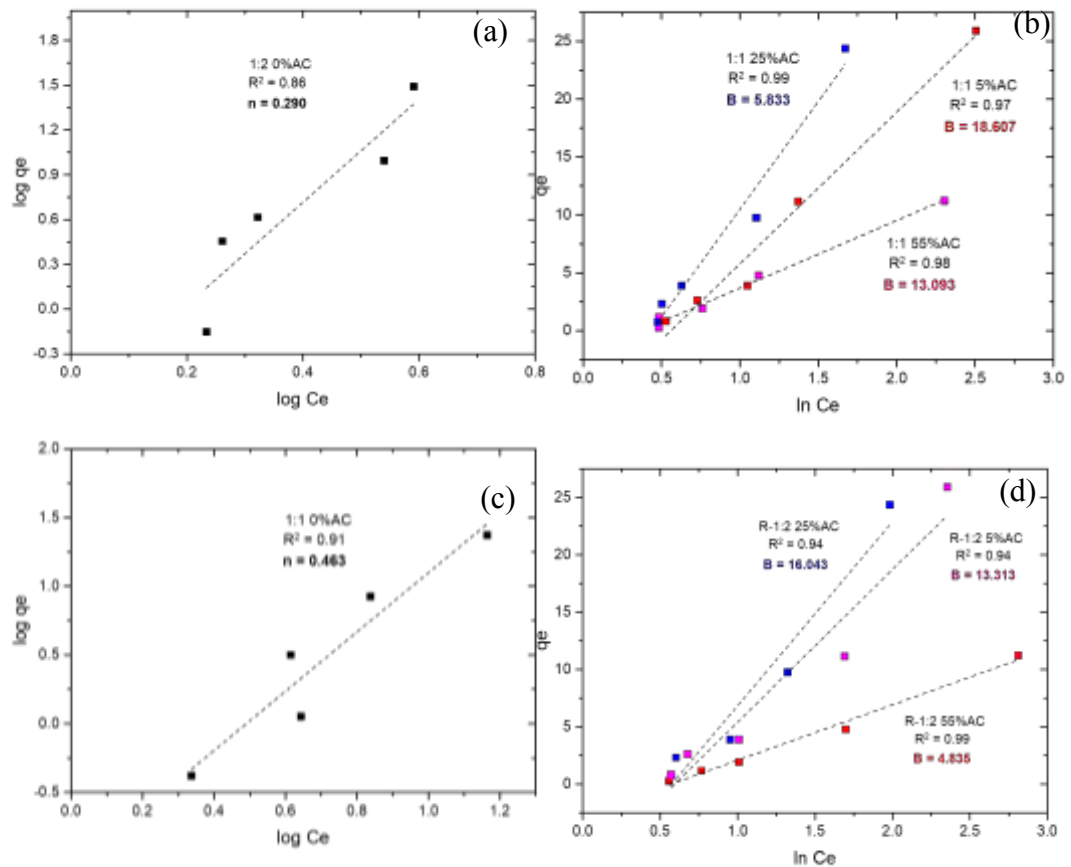
The adsorption isotherm is the theory their study with equilibrium sorption in term of quantitative. This research concern about the quantity of adsorption/ion exchange of  $\text{Cu}^{2+}$  ions per unit mass of sorbent [38]. Many model are used to study depend on type of sorption method. Normally, the isotherm model of adsorption is different with ion exchange because of process but in this research are using batch sorption process in both mechanism so, it can be use the same model to study.

The two parameter model used to study in this research. The experiment were set by vary the concentration of  $\text{Cu}^{2+}$  ions in 5 difference concentration which are 2, 5, 10, 20 and 50  $\text{mg l}^{-1}$  after that immersed the PEC/AC membrane in solution with 15 days (21600 minutes) and used AAS to detect  $\text{Cu}^{2+}$  ions before and after sorption.



**Figure 4.30** Sorption isotherm of  $\text{Cu}^{2+}$  ions on PEC/AC membrane (a) 1:1 PDADMAC:PSS/AC hybrid membrane ; (b) 1:2 PDADMAC:PSS/AC hybrid

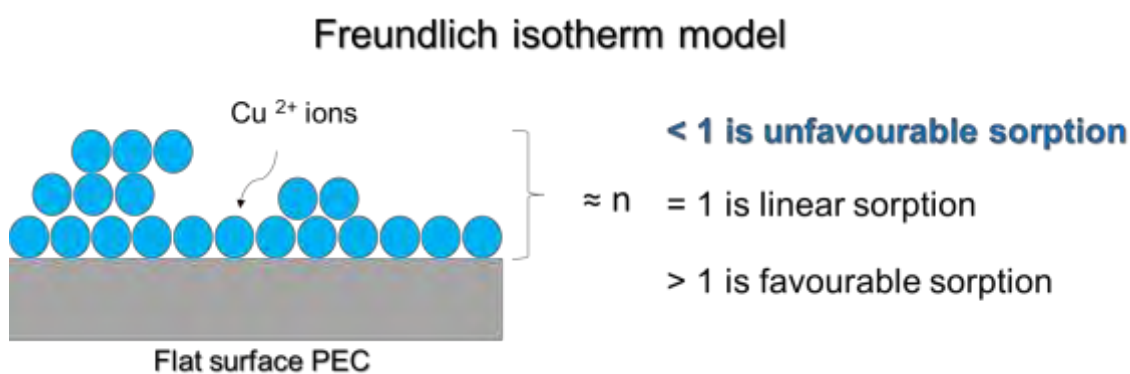
Figure 4.30 (a, b) shows the sorption isotherm between equilibrium adsorption capacity ( $q_e$ ) and equilibrium concentration ( $c_e$ ) of 1:1 PECs and 1:2 PECs. From the result, the equilibrium adsorption relate to adsorption capacity and the increasing of initial concentration render the adsorption capacity increased because the increasing of  $\text{Cu}^{2+}$  ions concentration lead to faster and more binding adsorbate molecule (Baral et al., 2009) and more  $\text{Cu}^{2+}$  ions observe a driving force to overcome the mass transfer resistance of  $\text{Cu}^{2+}$  ion between liquid phase to solid phase (Shenvi et al., 2015).



**Figure 4.31** Sorption isotherm of  $\text{Cu}^{2+}$  ions on PEC/AC membrane (a) 1:1 PDADMAC:PSS/AC hybrid membrane ; (b) 1:2 PDADMAC:PSS/AC hybrid

The adsorption isotherm uses to study about how the adsorbate molecules distribute itself between the liquids phase to the solid phase that has many ways to occur depend on sorbent material. The sorption that can occur consist of physical, ion exchange and chemical adsorption (Z A C A R I A R E D D A D & Y V E S A N D R E S 2002)

The fitting of the data with isotherm model as show on figure 4.31 show the graph fitting of Freundlich and Temkin isotherm. The 1:1 0%AC and 1:2 0%AC membrane can fit with Freundlich models are show the binary adsorption behavior and surface of that membrane are heterogonous surface or surface supporting sites of varied affinities(Vijayaraghavan, Padmesh, Palanivelu, & Velan, 2006). The  $n$  value in Freundlich models is parameter characteristics of sorbate-sorbent system when linear adsorption isotherm operate,  $n$  equal to one but in this case  $n$  values less than 1, it mean the sorption of  $\text{Cu}^{2+}$  ions on PEC/AC membrane is unfavourable sorption processes(A.O et al., 2012) it can estimate the adsorption process type of PEC/AC membrane is chemical sorption(A.O et al., 2012) as show on schematic 4.8



**Schematic 4.8** The combining of  $\text{Cu}^{2+}$  ions on the flat surface

Furthermore, 1:1 with AC and 1:2 with AC can fit with Temkin isotherm equation, it descript about heat of adsorption from figure 4.31 (b,d) show B parameter, is an indication of the heat of adsorption. In this result, B parameter indicate a physical adsorption process (A.O et al., 2012)

#### 4.3.5 The selective of heavy metal ions on PEC/AC hybrid membrane

The selective sorption part are operate in this research for simulate the real nature situation of heavy metal that always coexist in aqueous environment [47].The heavy metal most observe in natural and high toxic with human body consist of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Li}^{+}$ ,

$\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Cu}^{2+}$  (Zhang et al., 2008) and this heavy metal were used to study the selective sorption of PEC membrane.

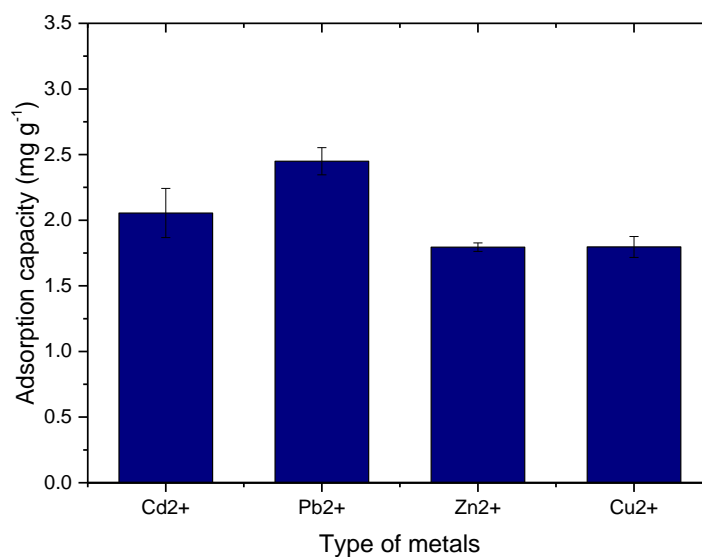
The selective sorption efficiency of heavy metal are separate into two part which are the selective of four divalent(Z A C A R I A R E D D A D & Y V E S A N D R E S 2002) heavy metal and the selective of metal with difference valent metal consist of monovalent, divalent and trivalent. In this experiment were use 1:2 0%AC to study this behavior.

**Table 4.3** The metal ions radii(r)(Chemist, 2018)

Type of metal ions	r (pm)
<b>Li<sup>+</sup></b>	76
<b>Na<sup>+</sup></b>	102
<b>Cu<sup>2+</sup></b>	73
<b>Zn<sup>2+</sup></b>	74
<b>Cd<sup>2+</sup></b>	95
<b>Pb<sup>2+</sup></b>	109
<b>Cr<sup>3+</sup></b>	62

#### 4.3.5 (1) *The sorption efficiency of 1:2 0%AC with difference divalent metal ions*

The divalent metal were use in this experiment consist of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ . The mixing solution concentration after mixed were operated  $5 \text{ mg l}^{-1}$  per one type of metal after that soak the small size membrane in 20 ml of mixer solution with 5 days. And then, the AAS were used to detect the concentration of metal ions before and after sorption.

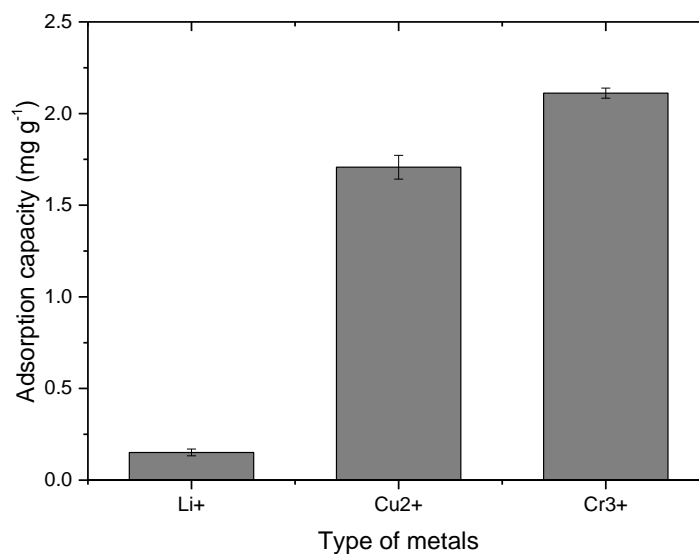


**Figure 4.32** Adsorption capacity of 1:2 0%AC with difference divalent metal ions

In figure 4.32 indicate the adsorption capacity of 1:2 0%AC with difference divalent metal ions. From the result, the efficiency of removal for each divalent metal are  $Pb^{2+} > Cd^{2+} > Zn^{2+}, Cu^{2+}$ . The  $Pb^{2+}$  ions are become more adsorbed when compare with other ions because size ions of  $Pb^{2+}$  close to  $Na^+$  (on table 6.3.5) so, the ion exchange between  $Pb^{2+}$  and  $Na^+$  easy to occur more than other ions or can called  $Pb^{2+}$  is strong affinity with  $Na^+$  (Zhang et al., 2008).

#### 4.3.5 (2) *The sorption efficiency of 1:2 0%AC with monovalent, divalent and trivalent metal ions*

The difference ions valent metal were use in the method are  $Li^+$ ,  $Cu^{2+}$  and  $Cr^{3+}$ . The mixing solution concentration after mixed operated  $5 \text{ mg l}^{-1}$  per one type of metal after that immersed the small size membrane in 20 ml of mixed solution with 5 days. The AAS were used to detect the concentration of metal ions before and after sorption.



**Figure 4.33** Adsorption capacity of 1:2 0%AC with difference metal ions

The figure 4.33 shows the adsorption capacity of 1:2 0%AC with different ions valent. From the result, Cr<sup>3+</sup> ions adsorbed more than Cu<sup>2+</sup> ions and Li<sup>+</sup> ions respectively. Normally, the adsorption stability increase with ion valent increased because the trivalent ions are more stable adsorption configurations than divalent and monovalent(Wu, Zhang, Liu, & Qu, 2018). From that reason, when Na<sup>+</sup> come out in ion exchange system, Cr<sup>3+</sup> can attack with free site (that site when Na<sup>+</sup> come out) faster than other ions.

## CHAPTER V

### CONCLUSIONS AND RECOMMENDATION

#### 5.1 Conclusion

The polyelectrolyte complex and PEC/AC hybrid membrane were fabricated by solution mixing method. The PEC were used to cationic dye and heavy metal ions sorption application by used excess negative charge on the membrane surface (excess PSS). The mole ration were used to study consist of 1:1 PDADMAC:PSS and 1:2 PDADAC:PSS mole ratio.

In cationic dye sorption (MB), the mechanism operated in this part is adsorption mechanism via electrostatic interaction. The 1:2 PDADMAC:PSS show higher adsorption capacity than 1:1 PDADMAC:PSS because of excess PSS in 1:2 PEC. The salt removal method in PEC (R-PEC) use to decrease the screening effect from salt ions and improve adsorption capacity in 1:2 PEC. The R-1:2 without AC got highest MB adsorption capacity for single-solute adsorption method. After fitting the R-1:2 data with kinetic model and adsorption isotherm, the data can fit with pseudo-second order kinetic model and Temkin isotherm model operates the physical adsorption mechanism. In the multi-solute adsorption system, R-1:2 PDADMAC:PSS can adsorb both MB, MV (cationic dye) but less adsorb anionic dye (anionic dye). The final part in cationic dye, the regeneration, 2M NaCl can regenerate about half of the MB in a saturated membrane with 5 days.

In contrast, the ion exchange mechanism operated in heavy metal ions adsorption. The 1:2 PDADMAC:PSS mole ration without salt removal and activated carbon shows highest  $\text{Cu}^{2+}$  ions sorption capacity. When fitting the 1:2 data with kinetic model and adsorption isotherm, the data can fit with pseudo-second order and Freundlich isotherm model operates the chemical sorption mechanism (ion exchange is in categories). The selectivity part, in the same ions valent (divalent),  $\text{Pb}^{2+}$  shows higher sorption capacity than other divalent and in the difference ions valent ( $\text{Li}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ ), the  $\text{Cr}^{3+}$  shows higher sorption capacity that other ions valent.



## 5.2 Recommendations

Especially, the activated carbon (AC) can improve the sorption efficiency but need to control amount of AC for protect excess packing. In my opinion , in rang 1-4 %, it may provide the improving of sorption efficiency because from my result, AC about 5% show acceptable sorption capacity because solution can pass the membrane. So, the AC still provide high sorption capacity if not excess packing.

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## APPENDICES

### Appendix A Polyelectrolyte complex, Polyelectrolyte complex/Activated carbon hybrid membrane preparation, characterization and physical properties

**Table A1** Raw data of PEC chemicals composition from CHN and CHN-S analyzer

PEC mole ratio	Chemical composition (%)				Weight of sample to test (g)
	C	H	N	S	
<b>2:1 PDADMAC:PSS</b>	42.17	8.80	3.13	5.44	0.10190
<b>1.5:1 PDADMAC:PSS</b>	42.35	8.81	2.98	5.77	0.10535
<b>1:1 PDADMAC:PSS</b>	42.32	8.52	2.81	5.98	0.10303
<b>1:1.5 PDADMAC:PSS</b>	41.22	8.42	2.45	6.75	0.10536
<b>1:2 PDADMAC:PSS</b>	39.26	7.96	2.05	8.58	0.10635

**Table A2** The degree of swelling of 1:1 PDADMAC:PSS with, without AC and 1:2 PDADMAC:PSS with and without AC

	<b>1-1 PDADMAC:PSS</b>	<b>1-2 PDADMAC:PSS</b>
0% AC	130.586 ±0.012	173.210 ±0.015
5% AC	57.723 ±0.008	54.039 ±0.005
25% AC	36.328 ±0.001	18.248 ±0.005
55% AC	7.500 ±0.000	3.621 ±0.006

**Table A3** Adsorption capacity of 1:1 PDADMAC: PSS and 1:2 PDADMAC: PSS with time

<b>time (min)</b>	<b>1:1</b>	<b>1:1 5%</b>	<b>1:1 25%</b>	<b>1:1 55%</b>
<b>0</b>	0.000 ±0.174	0.000 ±0.029	0.000 ±0.182	0.000 ±0.152
<b>0.3</b>	0.048 ±0.181	0.085 ±0.180	0.000 ±0.091	0.000 ±0.044
<b>1</b>	0.133 ±0.077	0.117 ±0.008	0.000 ±0.125	0.034 ±0.072
<b>10</b>	0.369 ±0.149	0.440 ±0.150	0.227 ±0.182	0.039 ±0.029
<b>20</b>	0.144 ±0.129	0.213 ±0.185	0.124 ±0.159	0.042 ±0.180
<b>40</b>	0.127 ±0.002	0.191 ±0.199	0.124 ±0.149	0.224 ±0.177
<b>60</b>	0.110 ±0.159	0.142 ±0.119	0.052 ±0.129	0.252 ±0.150
<b>100</b>	0.129 ±0.160	0.092 ±0.145	0.022 ±0.002	0.312 ±0.185
<b>160</b>	0.037 ±0.125	0.082 ±0.057	0.077 ±0.159	0.448 ±0.199
<b>280</b>	0.126 ±0.172	0.164 ±0.092	0.286 ±0.160	0.685 ±0.185
<b>520</b>	0.128 ±0.182	0.123 ±0.091	0.415 ±0.125	1.047 ±0.182
<b>880</b>	0.130 ±0.152	0.313 ±0.144	0.417 ±0.272	1.275 ±0.191
<b>1440</b>	0.193 ±0.029	0.249 ±0.159	0.469 ±0.182	1.623 ±0.199
<b>2880</b>	0.155 ±0.180	0.562 ±0.160	0.823 ±0.145	1.980 ±0.152
<b>4320</b>	0.213 ±0.077	0.715 ±0.125	1.157 ±0.257	2.502 ±0.144
<b>5760</b>	0.225 ±0.150	0.836 ±0.066	1.691 ±0.091	3.023 ±0.125
<b>7200</b>	0.268 ±0.185	0.930 ±0.182	1.735 ±0.144	3.102 ±0.047
<b>8640</b>	0.225 ±0.199	1.030 ±0.152	1.974 ±0.159	3.220 ±0.182
<b>10080</b>	0.268 ±0.149	1.330 ±0.277	2.174 ±0.106	3.322 ±0.145
<b>11520</b>	0.369 ±0.129	1.620 ±0.150	2.274 ±0.182	3.454 ±0.199
<b>14400</b>	0.369 ±0.125	1.924 ±0.172	2.474 ±0.182	3.702 ±0.026

**Table A4** Chemicals composition of PEC from CHN and CHN-S analyzer

## Elemental composition (%)

- 2:1 PDADMAC:PSS 2M NaCl ; 42.17% C, 8.79% H, 3.13% N and 5.44% S
- 1:1 PDADMAC:PSS 2M NaCl ; 42.32% C, 8.52% H, 2.81% N and 5.97% S
- 1:2 PDADMAC:PSS 2M NaCl ; 39.26% C, 7.96% H, 2.05% N and 8.58% S
- 1:1 PDADMAC:PSS 0.5M NaCl ; 42.87% C, 8.24% H, 2.82% N and 6.39% S

## Elemental composition (mg/g of adsorbent)

- 2:1 PDADMAC:PSS ; 31.332 of N and 52.022 of S
- 1:1 PDADMAC:PSS ; 28.086 of N and 59.624 of S
- 1:2 PDADMAC:PSS ; 20.503 of N and 80.092 of S

Calculation of excess PSS bind with Na<sup>+</sup> ion in system

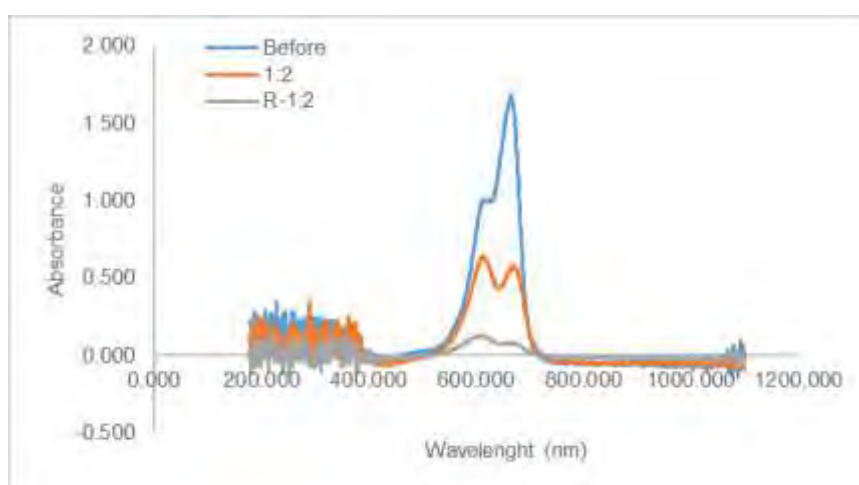
- 2:1 PDADMAC:PSS ; 20.690 of excess PSS (Assume all site neutral with Na<sup>+</sup>)
- 1:1 PDADMAC:PSS ; 27.582 of excess PSS (Assume all site neutral with Na<sup>+</sup>)
- 1:2 PDADMAC:PSS ; 59.589 of excess PSS (Not all of PSS was neutral with Na<sup>+</sup>)



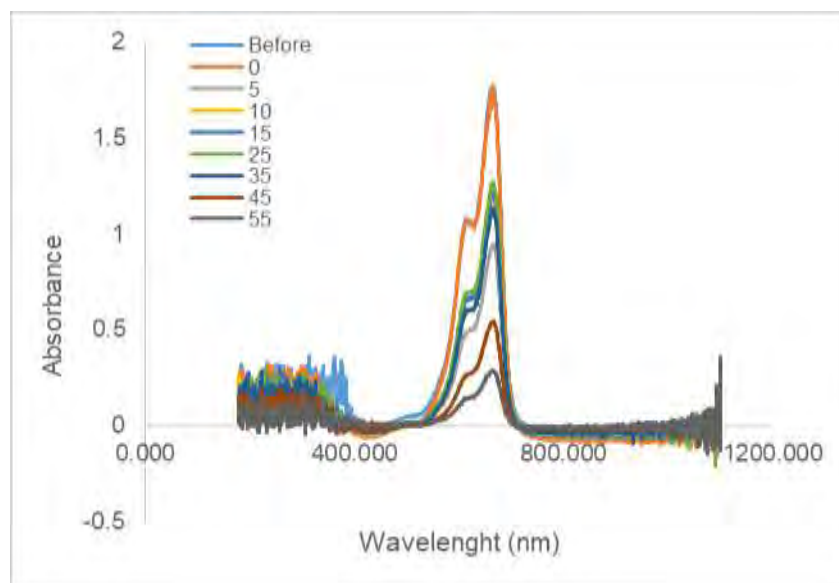
## Appendix B Hybrid PEC/AC hybrid membrane for cation dye adsorption application

**Table B1** Adsorption capacity of 1:2 PDADMAC: PSS and R-1:2 PDADMAC: PSS with time

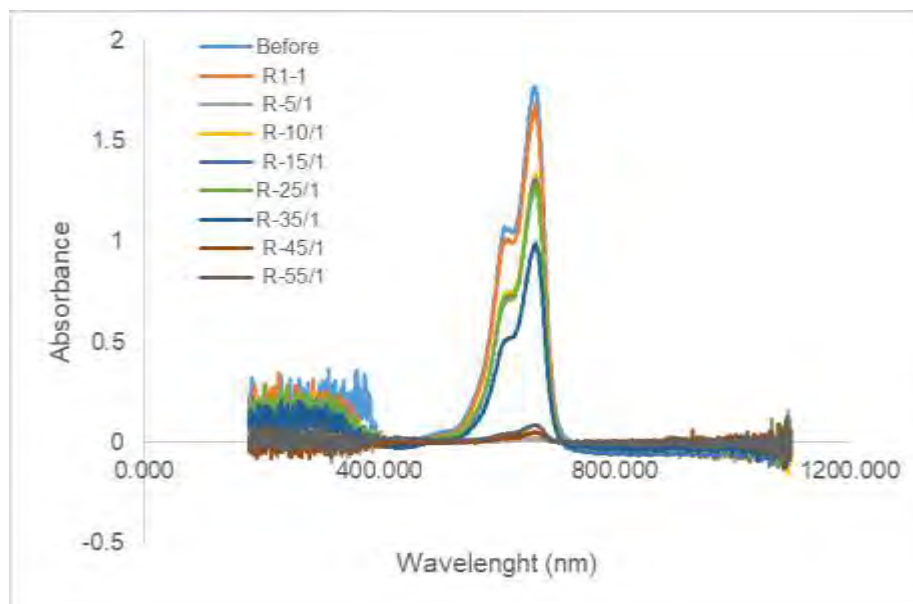
Time	1:2 0%AC	R-1:2 0%AC
0	0.000 ±0.000	0.000 ±0.000
0.3	0.711 ±0.589	0.266 ±0.012
1	4.403 ±0.395	0.464 ±0.354
10	3.930 ±0.178	0.752 ±0.370
20	3.947 ±0.092	0.665 ±0.399
40	3.901 ±0.167	0.833 ±0.230
60	3.840 ±0.192	1.730 ±0.112
100	3.741 ±0.128	2.314 ±0.250
160	3.721 ±0.153	2.667 ±0.981
280	3.719 ±0.137	3.275 ±0.938
520	3.698 ±0.142	3.863 ±0.954
880	3.674 ±0.153	4.389 ±0.595
1440	3.648 ±0.133	4.605 ±0.179
2880	3.631 ±0.092	4.692 ±0.063
4320	3.666 ±0.167	4.750 ±0.018
5760	3.690 ±0.192	4.815 ±0.026
7200	3.758 ±0.153	4.646 ±0.014
8640	3.851 ±0.137	4.824 ±0.253
10080	3.911 ±0.142	4.839 ±0.031
11520	3.930 ±0.395	4.715 ±0.024
14400	3.951 ±0.062	4.927 ±0.320



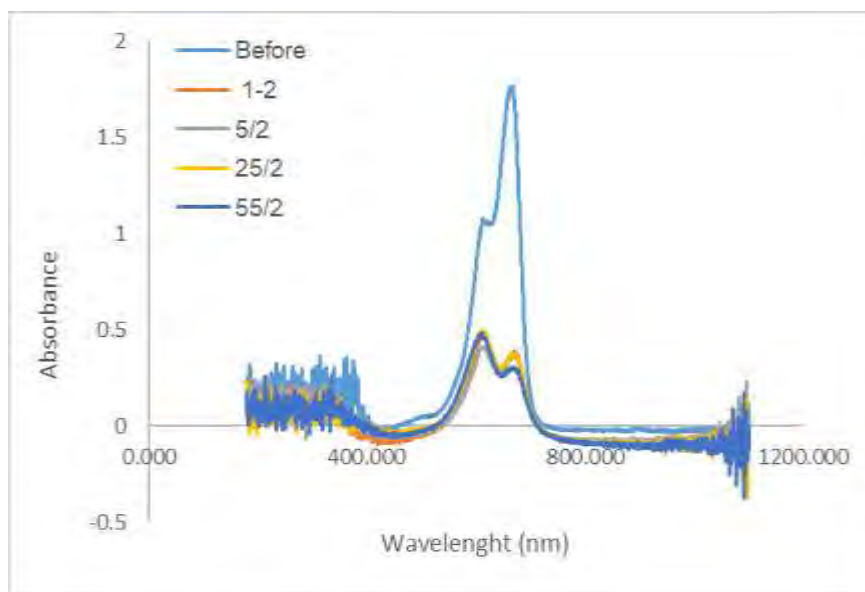
**Figure B1** UV spectra of 1:2 and R-1:2 PDADMAC:PSS after adsorption process



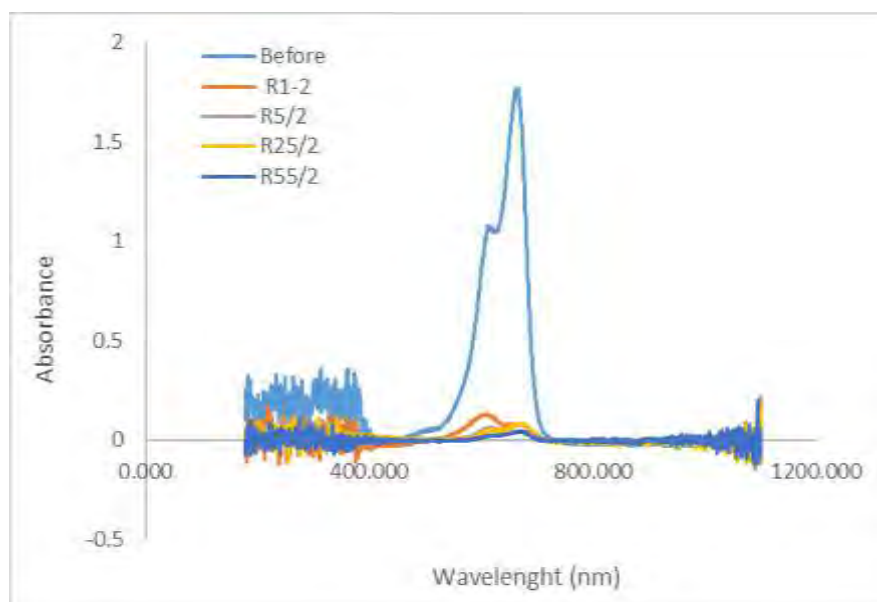
**Figure B2** UV spectra of 1:1 PDADMAC:PSS mole ratio with different %w/w of AC after adsorption of MB with  $10 \text{ mg l}^{-1}$  as initial concentration



**Figure B3** UV spectra of R-1:1 PDADMAC:PSS mole ratio with different %w/w of AC after adsorption of MB with  $10 \text{ mg l}^{-1}$  as initial concentration



**Figure B4** UV spectra of 1:2 PDADMAC:PSS mole ratio with different %w/w of AC after adsorption of MB with 10 mg l<sup>-1</sup> as initial concentration



**Figure B5** UV spectra of R-1:2 PDADMAC:PSS mole ratio with different %w/w of AC after adsorption of MB with 10 mg l<sup>-1</sup> as initial concentration

**Table B2** Adsorption capacity of 1:1 PEC with and without AC with time

<b>Time (min)</b>	<b>1:1</b>	<b>1:1 5%</b>	<b>1:1 25%</b>	<b>1:1 55%</b>
<b>0</b>	0.000 ±0.174	0.000 ±0.029	0.000 ±0.182	0.000 ±0.152
<b>0.3</b>	0.048 ±0.181	0.085 ±0.180	0.000 ±0.091	0.000 ±0.044
<b>1</b>	0.133 ±0.277	0.117 ±0.277	0.000 ±0.125	0.034 ±0.072
<b>10</b>	0.369 ±0.149	0.440 ±0.150	0.227 ±0.182	0.039 ±0.029
<b>20</b>	0.144 ±0.129	0.213 ±0.185	0.124 ±0.159	0.042 ±0.180
<b>40</b>	0.127 ±0.002	0.191 ±0.199	0.124 ±0.149	0.224 ±0.177
<b>60</b>	0.110 ±0.159	0.142 ±0.119	0.052 ±0.129	0.252 ±0.150
<b>100</b>	0.129 ±0.160	0.092 ±0.145	0.022 ±0.002	0.312 ±0.185
<b>160</b>	0.037 ±0.125	0.082 ±0.057	0.077 ±0.159	0.448 ±0.199
<b>280</b>	0.126 ±0.172	0.164 ±0.092	0.286 ±0.160	0.685 ±0.185
<b>520</b>	0.128 ±0.182	0.123 ±0.091	0.415 ±0.125	1.047 ±0.182
<b>880</b>	0.130 ±0.152	0.313 ±0.144	0.417 ±0.272	1.275 ±0.191
<b>1440</b>	0.193 ±0.029	0.249 ±0.159	0.469 ±0.182	1.623 ±0.199
<b>2880</b>	0.155 ±0.180	0.562 ±0.160	0.823 ±0.145	1.980 ±0.152
<b>4320</b>	0.213 ±0.277	0.715 ±0.125	1.157 ±0.257	2.502 ±0.144
<b>5760</b>	0.225 ±0.150	0.836 ±0.272	1.691 ±0.091	3.023 ±0.125
<b>7200</b>	0.268 ±0.185	0.930 ±0.182	1.735 ±0.144	3.102 ±0.272
<b>8640</b>	0.225 ±0.199	1.030 ±0.152	1.974 ±0.159	3.220 ±0.182
<b>10080</b>	0.268 ±0.149	1.330 ±0.277	2.174 ±0.106	3.322 ±0.145
<b>11520</b>	0.369 ±0.129	1.620 ±0.150	2.274 ±0.182	3.454 ±0.199
<b>14400</b>	0.369 ±0.125	1.924 ±0.272	2.474 ±0.182	3.702 ±0.252

**Table B3** Adsorption capacity of R-1:1 PEC with and without AC with time

<b>Time (min)</b>	<b>R-1:1</b>	<b>R-1:1 5%</b>	<b>R-1:1 25%</b>	<b>R-1:1 55%</b>
<b>0</b>	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000
<b>0.3</b>	0.001 ±0.002	0.061 ±0.055	0.067 ±0.075	0.114 ±0.136
<b>1</b>	0.003 ±0.006	0.018 ±0.026	0.059 ±0.051	0.082 ±0.045
<b>10</b>	0.008 ±0.013	0.359 ±0.069	0.054 ±0.045	0.179 ±0.172
<b>20</b>	0.033 ±0.057	0.502 ±0.045	0.044 ±0.076	0.184 ±0.152
<b>40</b>	0.033 ±0.173	0.566 ±0.056	0.044 ±0.121	0.099 ±0.129
<b>60</b>	0.000 ±0.000	1.135 ±0.185	0.044 ±0.121	0.086 ±0.094
<b>100</b>	0.000 ±0.060	1.386 ±0.200	0.044 ±0.121	0.055 ±0.131
<b>160</b>	0.000 ±0.072	1.711 ±0.185	0.044 ±0.121	0.054 ±0.127
<b>280</b>	0.000 ±0.149	1.696 ±0.240	0.044 ±0.053	0.087 ±0.117
<b>520</b>	0.000 ±0.117	1.789 ±0.020	0.044 ±0.057	0.173 ±0.090
<b>880</b>	0.027 ±0.000	2.161 ±0.076	0.218 ±0.062	0.418 ±0.031
<b>1440</b>	0.000 ±0.008	2.552 ±0.235	0.314 ±0.097	0.628 ±0.019
<b>2880</b>	0.000 ±0.019	2.765 ±0.243	0.636 ±0.080	0.883 ±0.010
<b>4320</b>	0.053 ±0.030	2.994 ±0.003	0.846 ±0.106	1.221 ±0.026
<b>5760</b>	0.030 ±0.057	3.024 ±0.025	1.061 ±0.105	1.603 ±0.000
<b>7200</b>	0.030 ±0.095	3.167 ±0.040	1.170 ±0.152	2.426 ±0.014
<b>8640</b>	0.000 ±0.075	3.131 ±0.136	1.526 ±0.185	3.256 ±0.121
<b>10040</b>	0.000 ±0.051	3.246 ±0.045	1.833 ±0.240	3.758 ±0.053
<b>11520</b>	0.001 ±0.045	3.296 ±0.172	2.020 ±0.020	4.158 ±0.057
<b>14440</b>	0.005 ±0.076	3.360 ±0.152	2.186 ±0.031	4.286 ±0.019

**Table B4** Adsorption capacity of 1:2 PEC with and without AC with time

<b>Time</b>	<b>1:2 0%AC</b>	<b>1:2 5%AC</b>	<b>1:2 25%AC</b>	<b>1:2 55%AC</b>
<b>0</b>	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000
<b>0.3</b>	0.711 ±0.589	0.075 ±0.212	0.173 ±0.834	0.086 ±0.136
<b>1</b>	4.403 ±0.395	3.866 ±0.162	2.939 ±0.449	0.458 ±0.155
<b>10</b>	3.930 ±0.178	3.974 ±0.254	2.884 ±0.566	1.703 ±0.172
<b>20</b>	3.947 ±0.092	3.885 ±0.565	2.762 ±0.485	1.729 ±0.158
<b>40</b>	3.901 ±0.167	3.817 ±0.594	2.686 ±0.075	1.686 ±0.151
<b>60</b>	3.840 ±0.192	3.757 ±0.128	2.629 ±0.193	1.626 ±0.115
<b>160</b>	3.741 ±0.128	3.697 ±0.142	2.599 ±0.173	1.570 ±0.113
<b>280</b>	3.721 ±0.153	3.712 ±0.181	2.547 ±0.183	1.543 ±0.132
<b>520</b>	3.719 ±0.137	3.695 ±0.153	2.518 ±0.189	1.528 ±0.156
<b>880</b>	3.698 ±0.142	3.644 ±0.162	2.494 ±0.180	1.503 ±0.149
<b>1440</b>	3.674 ±0.153	3.640 ±0.128	2.508 ±0.183	1.499 ±0.137
<b>2880</b>	3.648 ±0.133	3.689 ±0.131	2.572 ±0.248	1.495 ±0.137
<b>4320</b>	3.631 ±0.092	3.743 ±0.165	2.805 ±0.185	1.628 ±0.158
<b>5760</b>	3.666 ±0.167	3.817 ±0.194	2.706 ±0.075	1.553 ±0.151
<b>7200</b>	3.690 ±0.192	3.912 ±0.128	2.803 ±0.193	1.586 ±0.115
<b>8640</b>	3.758 ±0.153	3.915 ±0.181	2.942 ±0.183	1.682 ±0.132
<b>10080</b>	3.851 ±0.137	3.931 ±0.153	3.132 ±0.189	1.759 ±0.156
<b>11520</b>	3.911 ±0.142	3.982 ±0.162	3.242 ±0.180	1.797 ±0.149
<b>14400</b>	3.951 ±0.395	3.982 ±0.162	3.351 ±0.449	1.836 ±0.155

**Table B5** Adsorption capacity of R-1:2 PEC with and without AC with time

<b>Time</b>	<b>R-1:2 0%AC</b>	<b>R-1:2 5%AC</b>	<b>R-1:2 25%AC</b>	<b>R-1:2 55%AC</b>
<b>0</b>	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000
<b>0.3</b>	0.266 ±0.354	0.248 ±0.282	0.067 ±0.116	0.066 ±0.048
<b>1</b>	0.464 ±0.370	0.114 ±0.513	0.128 ±0.166	0.093 ±0.005
<b>10</b>	0.752 ±0.399	0.115 ±0.066	0.230 ±0.002	0.195 ±0.028
<b>20</b>	0.665 ±0.230	0.235 ±0.068	0.393 ±0.188	0.157 ±0.185
<b>40</b>	0.833 ±0.112	0.279 ±0.054	0.446 ±0.184	0.232 ±0.079
<b>60</b>	1.730 ±0.250	0.530 ±0.008	0.855 ±0.005	0.338 ±0.042
<b>100</b>	2.314 ±0.981	0.675 ±0.016	0.964 ±0.031	0.738 ±0.063
<b>160</b>	2.667 ±0.938	0.787 ±0.051	1.166 ±0.020	0.617 ±0.029
<b>280</b>	3.275 ±0.954	1.166 ±0.044	1.514 ±0.068	0.874 ±0.003
<b>520</b>	3.863 ±0.595	2.137 ±0.113	2.067 ±0.186	1.273 ±0.056
<b>880</b>	4.389 ±0.179	2.919 ±0.273	2.686 ±0.068	1.862 ±0.021
<b>1440</b>	4.605 ±0.063	3.491 ±0.178	3.206 ±0.441	2.402 ±0.075
<b>2880</b>	4.692 ±0.018	3.743 ±0.226	3.376 ±0.026	2.667 ±0.045
<b>4320</b>	4.750 ±0.026	3.943 ±0.232	3.338 ±0.232	2.795 ±0.051
<b>5760</b>	4.815 ±0.014	4.079 ±0.285	3.275 ±0.069	2.888 ±0.054
<b>7200</b>	4.646 ±0.253	4.104 ±0.307	3.305 ±0.429	2.946 ±0.050
<b>8640</b>	4.824 ±0.031	4.298 ±0.825	3.329 ±0.158	2.983 ±0.059
<b>10080</b>	4.839 ±0.024	4.315 ±0.816	3.333 ±0.166	3.009 ±0.056
<b>11520</b>	4.715 ±0.320	4.362 ±0.825	3.331 ±0.441	3.054 ±0.014
<b>14400</b>	4.927 ±0.012	4.428 ±0.796	3.374 ±0.169	3.087 ±0.013

**Table B6** adsorption kinetic model parameter of R-1:1 and R-1:2 with AC

Type of membrane	Pseudo-first order		Pseudo-second order		$q_e$ ( $\text{mg g}^{-1}$ )	
	$k_1^*$ ( $\times 10^{-3}$ $\text{min}^{-1}$ )	$R^2$	$k_2^{**}$ ( $\times 10^{-3}$ g $\text{mg}^{-1}$ $\text{min}^{-1}$ )	$R^2$	Calculated	Experimental
<b>R-1:1 5%AC</b>	4.606	0.86	2.261	0.99	2.989	3.359
<b>R-1:1 25%AC</b>	0.115	0.98	2.415	0.72	2.114	2.186
<b>R-1:1 55%AC</b>	0.691	0.97	4.917	0.41	4.203	4.285
<b>R-1:2 0%AC</b>	0.203	0.46	2.010	0.99	4.866	4.927
<b>R-1:2 5%AC</b>	0.230	0.68	0.494	0.99	4.504	4.428
<b>R-1:2 25%AC</b>	0.230	0.50	1.720	0.99	3.400	3.374
<b>R-1:2 55%AC</b>	0.230	0.63	0.775	0.97	3.142	3.087

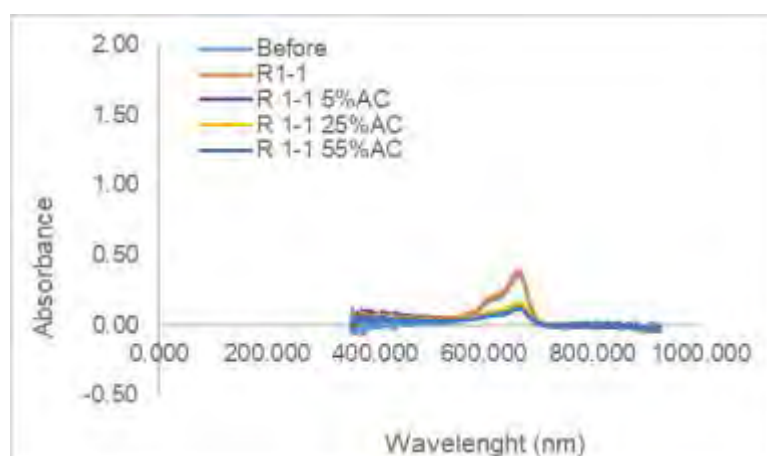
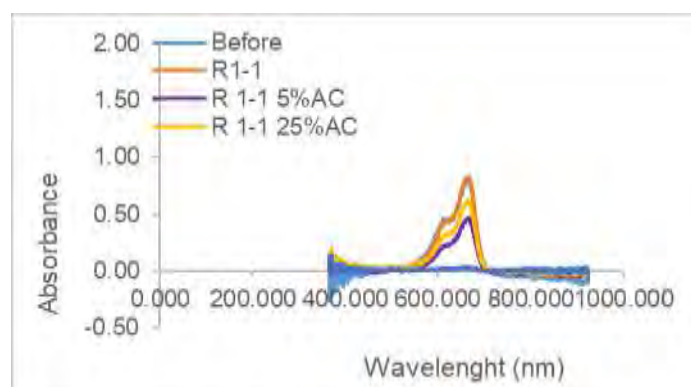
**Table B7** Isotherm adsorption capacity ( $\text{mg l}^{-1}$ ) of R-1:1 PEC with and without AC

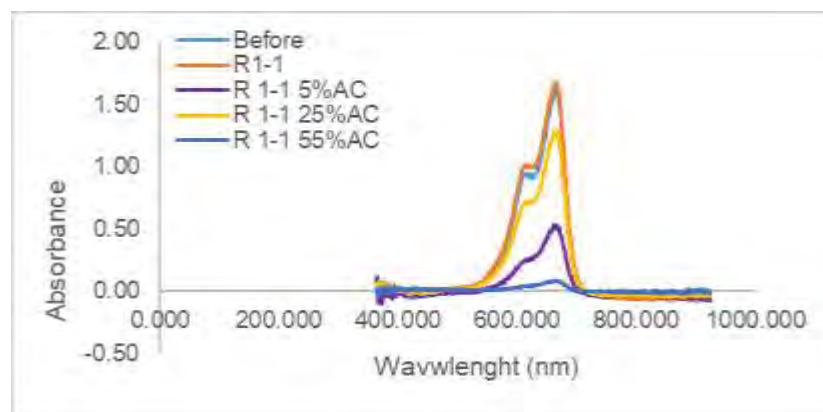
Initial Conc. ( $\text{mg l}^{-1}$ )	R1-1	R 1-1 5%AC	R 1-1 25%AC	R 1-1 55%AC
<b>2</b>	0.211 $\pm$ 0.000	0.396 $\pm$ 0.083	0.372 $\pm$ 0.124	0.445 $\pm$ 0.099
<b>5</b>	0.005 $\pm$ 0.000	0.854 $\pm$ 0.234	0.731 $\pm$ 0.197	0.819 $\pm$ 0.131
<b>10</b>	0.005 $\pm$ 0.442	3.360 $\pm$ 0.522	2.186 $\pm$ 0.241	4.286 $\pm$ 0.121
<b>20</b>	0.005 $\pm$ 0.029	3.150 $\pm$ 0.593	2.312 $\pm$ 0.120	3.524 $\pm$ 0.145
<b>50</b>	0.005 $\pm$ 0.032	3.606 $\pm$ 0.368	2.011 $\pm$ 0.387	4.286 $\pm$ 0.835



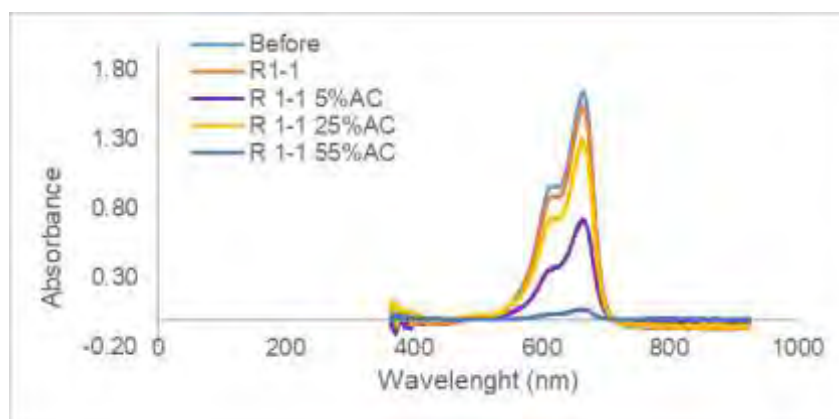
**Table B8** Isotherm adsorption capacity ( $\text{mg l}^{-1}$ ) of R-1:2 PEC with and without AC

Initial Conc. ( $\text{mg l}^{-1}$ )	R1-2	R 1-2 5%AC	R 1-2 25%AC	R 1-2 55%AC
2	0.778 $\pm$ 0.113	0.614 $\pm$ 0.088	0.718 $\pm$ 0.034	0.410 $\pm$ 0.038
5	2.423 $\pm$ 0.194	1.745 $\pm$ 0.311	2.064 $\pm$ 0.235	1.462 $\pm$ 0.570
10	4.927 $\pm$ 0.257	4.428 $\pm$ 0.304	3.374 $\pm$ 0.436	3.087 $\pm$ 0.644
20	9.072 $\pm$ 0.503	5.397 $\pm$ 0.366	6.641 $\pm$ 0.206	3.462 $\pm$ 0.406
50	25.774 $\pm$ 0.193	17.578 $\pm$ 0.186	19.071 $\pm$ 0.092	8.202 $\pm$ 0.268

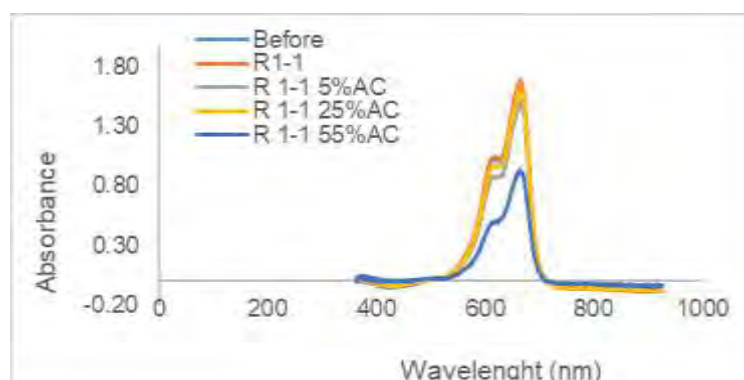
**Figure B6** UV Spectra of Rinse 1-1 with and without AC in 2 mg/l as initial concentration**Figure B7** UV Spectra of Rinse 1-1 with and without AC in 5 mg/l as initial concentration



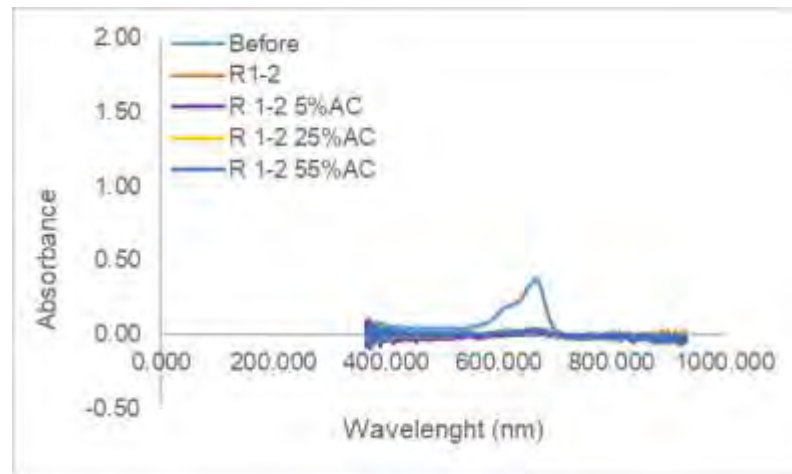
**Figure B8** UV Spectra of Rinse 1-1 with and without AC in 10 mg/l as initial concentration



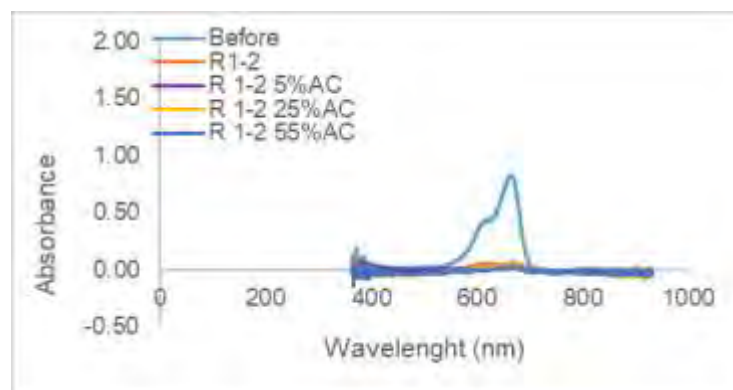
**Figure B9** UV Spectra of Rinse 1-1 with and without AC in 20 mg/l as initial concentration (dilute to 10 mg l<sup>-1</sup>)



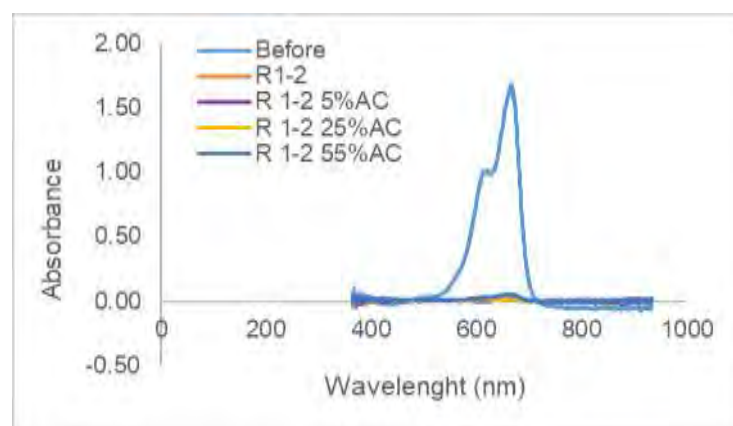
**Figure B10** UV Spectra of Rinse 1-1 with and without AC in 50 mg/l as initial concentration (dilute to 10 mg l<sup>-1</sup>)



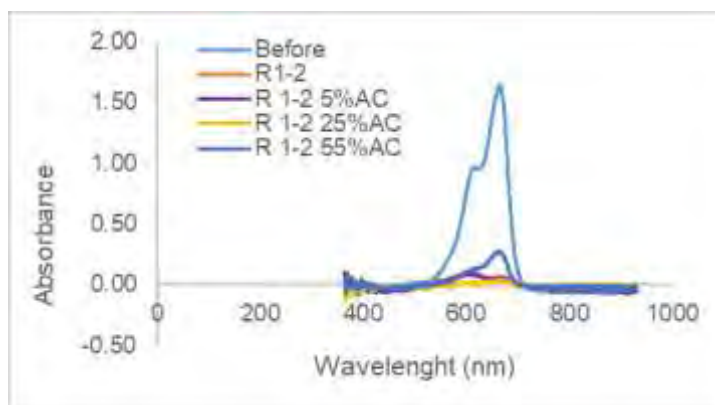
**Figure B11** UV Spectra of Rinse 1-2 with and without AC in 2 mg/l as initial concentration



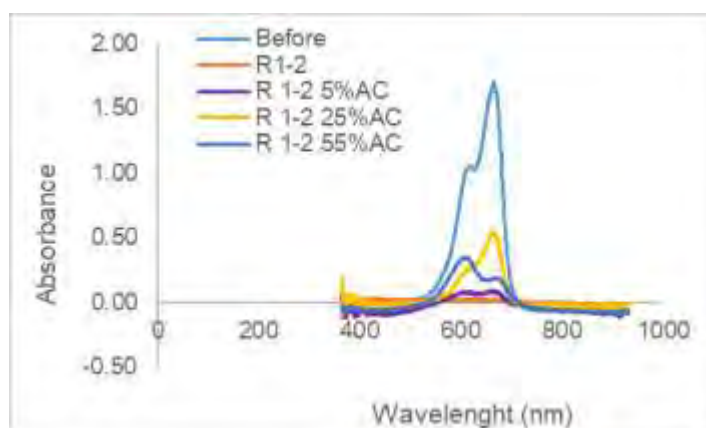
**Figure B12** UV Spectra of Rinse 1-2 with and without AC in 5 mg/l as initial concentration



**Figure B13** UV Spectra of Rinse 1-2 with and without AC in 10 mg/l as initial concentration



**Figure B14** UV Spectra of Rinse 1-2 with and without AC in 20 mg/l as initial concentration (dilute to 10 mg l<sup>-1</sup>)



**Figure B15** UV Spectra of Rinse 1-2 with and without AC in 50 mg/l as initial concentration (dilute to 10 mg l<sup>-1</sup>)

**Table B9** The Isotherm constant of two-parameter models for MB adsorption on PEC/AC membrane

		Type of sorbent							
		R-1:1 0%AC	R-1:1 5%AC	R-1:1 25%AC	R-1:1 55%AC	R-1:2 0%AC	R-1:2 5%AC	R-1:2 25%AC	R-1:2 55%AC
<b>Langmuir</b>	Q <sub>0</sub>	-0.003	0.367	0.358	0.948	6.835	5.893	6.064	6.027
	K <sub>L</sub>	-0.667	0.031	0.092	0.057	0.208	0.142	0.579	0.718
	R <sub>L</sub>	-0.032	0.282	0.151	0.205	0.081	0.110	0.032	0.027
	R <sup>2</sup>	0.85	0.95	0.97	0.95	0.18	0.20	0.23	0.09
<b>Temkin</b>	B	0.050	1.765	2.501	6.403	4.686	5.466	5.674	7.620
	A <sub>t</sub>	0.861	0.860	0.860	0.861	0.860	0.861	0.861	0.861
	R <sup>2</sup>	0.55	0.72	0.68	0.650	0.94	0.94	0.96	0.82

**Appendix C Hybrid PEC/AC hybrid membrane for cation dye adsorption application**

**Table C1** Adsorption capacity and concentration of Na<sup>+</sup> ions release detect by AAS

<b>Type of sorbent</b>	<b>Na<sup>+</sup> ions release concentration (mg l<sup>-1</sup>)</b>	<b>Na<sup>+</sup> ions release capacity (mg g<sup>-1</sup>)</b>
<b>1:1 0%AC</b>	78.086 ±0.044	38.112 ±0.031
<b>1:1 5%AC</b>	73.492 ±0.102	35.628 ±0.036
<b>1:1 25%AC</b>	65.742 ±0.090	31.950 ±0.087
<b>1:1 55%AC</b>	65.001 ±0.045	35.741 ±0.107
<b>1:2 0%AC</b>	90.600 ±0.061	44.226 ±0.057
<b>1:2 5%AC</b>	87.933 ±0.024	42.629 ±0.064
<b>1:2 25%AC</b>	73.567 ±0.090	35.753 ±0.015
<b>1:2 55%AC</b>	80.367 ±0.075	44.186 ±0.081

**Table C2** Adsorption capacity of 1:1 PEC with and without AC with time

<b>Time</b>	<b>1:1 0%AC</b>	<b>1:1 5%AC</b>	<b>1:1 25%AC</b>	<b>1:1 55%AC</b>
<b>0</b>	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000
<b>0.3</b>	0.000 ±0.000	0.000 ±0.000	0.495 ±0.000	1.046 ±0.000
<b>1</b>	0.495 ±0.857	0.270 ±0.382	1.137 ±0.156	0.643 ±1.479
<b>2</b>	2.847 ±0.336	2.799 ±0.589	2.612 ±0.671	2.086 ±0.936
<b>6</b>	4.844 ±0.687	3.902 ±0.348	4.412 ±0.327	3.365 ±0.984
<b>10</b>	5.381 ±0.704	4.399 ±0.420	4.957 ±0.514	4.412 ±0.198
<b>20</b>	5.308 ±0.586	4.460 ±0.107	5.209 ±0.599	4.693 ±0.490
<b>40</b>	5.485 ±0.588	4.874 ±0.037	5.691 ±0.255	5.264 ±0.121
<b>60</b>	5.556 ±0.516	5.067 ±0.359	6.273 ±0.243	6.216 ±0.197
<b>100</b>	5.950 ±0.511	5.284 ±0.576	6.596 ±0.181	6.505 ±0.198
<b>160</b>	6.141 ±0.529	5.456 ±0.448	6.857 ±0.271	6.824 ±0.020
<b>280</b>	6.588 ±0.458	5.702 ±0.527	7.168 ±0.416	7.182 ±0.280
<b>520</b>	7.106 ±0.580	6.235 ±0.339	7.501 ±0.310	7.269 ±0.062
<b>880</b>	7.302 ±0.589	6.568 ±0.364	8.140 ±0.156	7.509 ±0.299
<b>1440</b>	7.921 ±0.607	7.080 ±0.049	8.873 ±0.434	8.420 ±0.078
<b>2880</b>	9.282 ±0.692	7.564 ±0.149	10.948 ±0.360	8.635 ±0.098
<b>4320</b>	10.445 ±0.909	7.924 ±0.113	12.334 ±0.757	8.680 ±0.952
<b>5760</b>	11.461 ±0.815	9.204 ±0.205	14.463 ±0.591	8.910 ±0.759
<b>7200</b>	13.259 ±0.440	10.029 ±0.647	15.782 ±0.700	9.046 ±0.781
<b>8640</b>	14.287 ±0.283	11.290 ±0.389	16.818 ±0.329	9.178 ±0.737
<b>10080</b>	16.456 ±0.756	14.473 ±0.665	17.305 ±0.415	9.523 ±0.365
<b>11520</b>	17.249 ±0.955	16.194 ±0.199	19.065 ±0.308	10.255 ±0.159
<b>12960</b>	18.287 ±0.259	18.083 ±0.291	19.957 ±0.272	10.558 ±0.179
<b>14400</b>	19.298 ±0.343	19.600 ±0.480	20.919 ±0.374	10.820 ±0.026

**Table C3** Adsorption capacity of 1:2 PEC with and without AC with time

<b>Time</b>	<b>1:2 0%AC</b>	<b>1:2 5%AC</b>	<b>1:2 25%AC</b>	<b>1:2 55%AC</b>
<b>0</b>	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000
<b>0.3</b>	0.365 ±0.102	0.243 ±0.200	0.049 ±0.069	0.141 ±0.000
<b>1</b>	2.120 ±0.295	0.520 ±0.662	0.521 ±0.096	0.428 ±0.196
<b>4</b>	3.518 ±0.730	1.816 ±0.212	1.066 ±0.270	0.827 ±0.483
<b>10</b>	5.595 ±0.723	1.793 ±0.494	2.220 ±0.697	0.851 ±0.147
<b>20</b>	6.694 ±0.723	1.808 ±0.473	2.157 ±0.559	0.754 ±0.200
<b>60</b>	7.468 ±0.649	2.426 ±0.401	2.520 ±0.129	1.890 ±0.507
<b>120</b>	8.238 ±0.148	6.714 ±0.553	4.775 ±0.370	2.418 ±0.184
<b>280</b>	10.176 ±0.909	8.101 ±0.092	6.458 ±0.046	3.736 ±0.197
<b>540</b>	11.249 ±0.814	9.273 ±0.170	7.230 ±0.054	5.043 ±0.197
<b>1440</b>	12.428 ±0.850	9.502 ±0.518	8.099 ±0.045	5.739 ±0.463
<b>2880</b>	14.047 ±0.663	9.619 ±0.530	8.409 ±0.289	6.366 ±0.150
<b>4320</b>	15.311 ±0.566	9.917 ±0.352	8.954 ±0.034	6.663 ±0.038
<b>5760</b>	16.038 ±0.463	11.697 ±0.494	9.234 ±0.167	7.265 ±0.549
<b>7200</b>	17.116 ±0.612	12.275 ±0.162	9.368 ±0.601	7.420 ±0.219
<b>8640</b>	18.149 ±0.643	12.571 ±0.007	9.271 ±0.431	8.270 ±0.179
<b>10080</b>	19.553 ±0.774	12.717 ±0.005	10.225 ±0.384	9.020 ±0.294
<b>11520</b>	20.969 ±0.285	12.879 ±0.141	10.822 ±0.017	10.177 ±0.641
<b>12960</b>	22.530 ±0.613	13.223 ±0.205	10.924 ±0.649	11.255 ±0.519
<b>14400</b>	23.760 ±0.456	14.033 ±0.546	11.698 ±0.218	12.394 ±0.678



**Table C4** Kinetic parameters for Cu<sup>2+</sup> ions sorption onto PEC/AC hybrid membrane

Type of membrane	Pseudo-first order		Pseudo-second order				
	k <sub>1</sub> *	R <sup>2</sup>	k <sub>2</sub> **	t <sub>½</sub>	R <sup>2</sup>	q <sub>e</sub> (mg g <sup>-1</sup> )	
	(x10 <sup>-4</sup> min <sup>-1</sup> )		(x 10 <sup>-3</sup> g mg <sup>-1</sup> min <sup>-1</sup> )			Calculated	Experimental al (3days)
<b>1:1 0%AC</b>	1.621	0.9292	1.196	0.084	0.99	10.010	10.445
<b>1:1 5%AC</b>	1.381	0.8459	2.610	0.049	0.99	7.825	7.924
<b>1:1 25%AC</b>	1.889	0.9535	0.826	0.103	0.98	11.792	12.333
<b>1:1 55%AC</b>	2.072	0.8265	3.530	0.033	0.99	8.688	8.680
<b>1:2 0%AC</b>	1.612	0.9214	0.940	0.071	0.99	14.97	15.310
<b>1:2 5%AC</b>	2.072	0.9012	1.802	0.056	0.99	9.960	9.917
<b>1:2 25%AC</b>	1.842	0.8800	1.501	0.075	0.99	8.905	8.954
<b>1:2 55%AC</b>	1.381	0.9119	1.321	0.113	0.99	6.702	6.663

**Table C5** Adsorption capacity of 1:1 PEC with and without AC for isotherm studies with static test 15 days

Initial concentration (mg l <sup>-1</sup> )	1:1 0%AC	1:1 5%AC	1:1 25%AC	1:1 55%AC
<b>2</b>	0.417±0.088	0.806±0.010	0.740±0.018	0.252±0.021
<b>5</b>	1.127±0.036	2.602±0.031	2.300±0.027	1.146±0.028
<b>10</b>	3.161±0.101	3.883±0.074	3.875±0.101	1.919±0.234
<b>20</b>	8.418±0.050	11.139±0.012	9.751±0.051	4.763±0.150
<b>50</b>	24.965±0.207	25.918±0.180	27.771±0.180	12.086±0.275

**Table C6** Adsorption capacity of 1:2 PEC with and without AC for isotherm studies with static test 15 days

<b>Initial concentration (mg l<sup>-1</sup>)</b>	<b>1:2 0%AC</b>	<b>1:2 5%AC</b>	<b>1:2 25%AC</b>	<b>1:2 55%AC</b>
<b>2</b>	0.703±0.027	0.373±0.024	0.443±0.048	0.266±0.037
<b>5</b>	2.849±0.031	1.337±0.021	1.753±0.018	0.932±0.085
<b>10</b>	4.115±0.072	2.022±0.178	2.532±0.000	1.472±0.331
<b>20</b>	9.879±0.401	4.801±0.072	6.631±0.110	3.433±0.291
<b>50</b>	30.908±0.453	14.108±0.749	18.793±0.104	8.523±0.104

**Table C7** The Isotherm constant of two-parameter models for Cu<sup>2+</sup> ions sorption on PEC/AC membrane

		Type of sorbent							
		1:1 0%AC	1:1 5%AC	1:1 25%AC	1:1 55%AC	1:2 0%AC	1:2 5%AC	1:2 25%AC	1:2 55%AC
<b>Langmuir</b>	Q <sub>0</sub>	0.160	0.480	0.503	0.170	0.359	0.242	0.277	0.170
	K <sub>L</sub>	0.108	0.1590	0.236	0.127	0.276	0.140	0.191	0.127
	R <sub>L</sub>	0.134	0.101	0.072	0.120	0.063	0.111	0.086	0.120
	R <sup>2</sup>	0.89	0.71	0.5	0.67	0.54	0.62	0.54	0.67
<b>Freundlich</b>	n	0.463	0.627	0.414	0.861	0.290	0.579	0.445	0.746
	K <sub>f</sub>	11.402	1.517	1.912	2.681	4.600	3.788	3.822	3.897
	R <sup>2</sup>	0.91	0.86	0.85	0.72	0.86	0.91	0.88	0.87

**Table C8** Adsorption capacity of 1:2 PEC in the selectivity of divalent metal experiment

Type of metals	Adsorption capacity
<b>Cd<sup>2+</sup></b>	2.055±0.187
<b>Pb<sup>2+</sup></b>	2.449±0.103
<b>Zn<sup>2+</sup></b>	1.794±0.032
<b>Cu<sup>2+</sup></b>	1.797±0.080

**Table C9** Adsorption capacity of 1:2 PEC in the selectivity of ions valent metal experiment

Type of metals	Adsorption capacity
<b>Li<sup>+</sup></b>	0.151±0.019
<b>Cu<sup>2+</sup></b>	1.707±0.065
<b>Cr<sup>3+</sup></b>	2.111±0.028



## CURRICULUM VITAE

### Personal information

**Name:** Wanwanut Chueasupcharoen  
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### Educations

- The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand (2016-2018)**  
 Master of Science (Polymer Science) with 70% of scholarship support (GPA: 3.13)  
Research topic: The development of Polyelectrolyte Complex/Activated Carbon Hybrid membrane for Dye and Heavy Metal adsorption application.
- Maejo University, ChiangMai, Thailand (2012 – 2015)**  
 Bachelor of Science (Rubber and Polymer Technology (GPA: 3.19)  
Research topic: Jatropha Oil as Replacement of petroleum Oil in Rubber Vulcanized
- Sankampheang school, ChiangMai, Thailand (2008 – 2012)**  
 High school education in Science-Math Program.

### Research interests

- Rubber processing and their application
- Physical properties of rubber and polymer
- Polyelectrolyte complexes producing for wastewater treatment.
- Rubber compound development for tire wheel and other application.

### Expertise

- Rubber processing
- Filler types and filler effects in rubber compound and rubber product properties
- Oil types and oil effects in rubber compound and rubber product properties
- Polyelectrolyte complex and hybrid polyelectrolyte complex membrane preparation and behaviour of their membrane
- Experience machine used with rubber and polymer processing (Two-roll mill, internal mixture, compression moulding) and rubber test ( e.g. Moving Die Rheometer (MDR), tensile, elongation at break, hardness, rebound resilience, DIN abrasion and compression set)
- Characterizations that were used in research (Atomic absorption spectrometer, Fourier-transform infrared spectroscopy, UV visible spectroscopy, Brunauer-Emmett-Teller (BET) Surface Area Analysis and CHN, CHN-S Analyser).

### Honors, awards and certifications

- The best poster presentation award in surfactant, separation and environment section at 24<sup>th</sup> PPC symposium on Petroleum, Petrochemical and Polymer and The 9<sup>th</sup> research symposium on Petrochemical and Material Technology on 5<sup>th</sup> June 2018
- The best presentation bronze award in PPC seminar for polymer science, PPC, Chulalongkorn university.

- The poster presentation in 23-25<sup>th</sup> CU-Japan Southeast Asia Collaboration Hub of Bio-plastic Study, Chulalongkorn University.
- Student under 70% of scholarship support in Master degree of Polymer Science, The Petroleum and Petrochemical College, Chulalongkorn University.
- Research scholarship on master degree from The Center of Excellence on Petrochemicals and Materials Technology.

### **Research experiences**

- **May 2015-July 2015 (Mini-research project and internship in CS Rubber industry, Chonburi, Thailand )**
  - Mini-research topic 1: The study of clay type were used in rubber industry affect with rubber compound and rubber vulcanized properties.
  - Mini-research topic 2: The study of clay type were used in rubber industry affect with surface rubber extrude.
  - Line production internship.
- **September 2015- March 2016 (Undergraduate research project submitted for the degree of Bachelor of Rubber and polymer technology, Maejo University)**  
Research project: Jatropha Oil as Replacement of petroleum Oil in Rubber Vulcanized
- **May 2017- May 2018 (Graduate research project submitted for the degree of Master of Polymer science, Chulalongkorn university)**  
Research project: The development of Polyelectrolyte Complex/Activated Carbon Hybrid membrane for Dye and Heavy Metal adsorption application.

### **Other activities**

- Exchange student with Experience in Learning for MJU Students in the ASEAN Economic Community Project at UniversitasGadjahMada, The Republic of Indonesia from 1<sup>st</sup>-16<sup>th</sup> May 2013.
- MC of New Student Orientation and Cheer Activity of Maejo University
- Exchange student host
- Thai musical instruments player: Recorder flute, Thai flute (Klui Lip) and Thai mandolin (Sueng).

### **English proficiency tests**

- TOEFL score: 490 (the test year of 2018)
- CU-TEP score: 40 (the test year of 2017)

### **Reference**

- Asst. Prof. Stephan Theierry Dubas (Master degree advisor): The Petroleum and Petrochemical College, Chulalongkorn University.
- Asst. Prof. Thitinun Rattanaprom Faculty of Engineering and Agoindustry, Maejo University.