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Preparation and Characterization of Thin Film Sorbent Based on Self Assembly Polyelectrolyte Multilayers for Drugs Extractor

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Abstract. New materials based on self-assembled polyelectrolyte multilayers (PEM) thin film sorbents have been successfully developed. Several important coating parameters include the pH of the coating solution, the addition of salt to the coating solution, the dipping time, and the number of bilayers were optimized for drug extractors using the thin film micro extraction (TFME) technique. Optimum conditions were evaluated by the highest extraction performance for tricyclic antidepressant drugs (TCAs). Cellulose acetate membrane was chosen as the support material. Meanwhile, polyelectrolyte materials, namely poly (allyl amine hydrochloride) (PAAH) and poly(styrene sulfonic acid) (PSS) were chosen as coating materials. PAAH and PSS are deposited on the surface of the supporting material repeatedly. The results showed that the optimum coating conditions were pH PAAH 2 and PSS 2, no salt was added to the coating solution, the immersion time for each layer was 5 minutes, and the number of bilayers was 5. The optimized material was characterized by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), field emission-scanning electron microscopy (FESEM), and thermogravimetric-differential thermal analyzer (TG-DTA). The addition of PEM to the CA membrane also increased the thermal stability of CA-PEM. The results are inspiring and indicate that this sorbent has a great potential for thin film extraction sorbent and also suitable for thermal desorption application.

INTRODUCTION

Hospital and pharmaceutical company are the two main sources of pharmaceutical waste in the environment. In addition, some household activities such as consuming drugs without unclear prescription and lack of knowledge about the how to dispose of drugs after use have also led to an increase in the concentration of pharmaceutical waste in the environment. In hospital and pharmaceutical company, the waste usually treated prior to discharge in environment. However, controls are needed ensure that the process is in good condition to prevent the release of pharmaceutical residues in surface water [1,2]. The pharmaceutical residue present in surface water will be recycled and reused for household activities through tap water. This is very dangerous, because it can trigger drug resistance. However, control pharmaceutical residue is very challenging due to their low concentration and presence in complex matrices.

Sample preparation technique based on micro extraction has gained attention in line with the green chemistry concept. The micro extraction technique has the basic principle of extracting the analyte into microliters of organic solvent or adsorbing the analyte in a small amount (mg) of adsorbent. Compared to liquid-liquid extraction (LLE) and solid phase extraction (SPE), the micro extraction technique has advantages not only in terms of solvent less to solvent

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free, but also provides better signal enhancement, rapid, simple, and easy to combine with gas chromatography or liquid chromatography [3].

One of the most developed micro extraction techniques is solid phase micro extraction (SPME). The principle of this method based on the partition of the analyte between the matrix sample and the organic phase coated on the fused silica fiber. At the end of extraction process, the extraction phase is directly injected into GC or HPLC for quantitative analysis. The sensitivity of SPME can be increased by creating the temperature gap between the sample solutions and the coating material during extraction process, therefore volatile compounds are appropriate to deal by this method. SPME has successfully overcome the inherent weaknesses of the conventional LLE and SPE methods, but there are some problems commonly encountered with the SPME method. The main drawbacks involve fibers that are fragile and break easily, limited lifetime, expensive, longer equilibrium time due to sorbent thickness, higher carry over probability, and require modification of injection ports for suitable devices and instruments [4]. Therefore, the development of sorbent for SPME become interesting and important for improving extraction performance and overcoming the inherent limitations of SPME. Thin film micro extraction (TFME) is technique derived from SPME with sorbent geometry in the form of thin sheet of polymer membranes [5].

Recently, TFME has become a popular micro extraction method due to its easy operation, low cost, and less time consuming. This method also successfully overcomes the drawback from SPME by employing thin sheet extraction phase with several geometric shapes such as cotter pin [6], copper mesh holder [7] and 96-blade format thin film [4]. At the end of extraction process, this technique is combined with solvent desorption with the aid of ultrasonication, vortex, or centrifuge so as to avoid thermal desorption units. The use of suitable material for extraction is very important in TFME. So far, poly(dimethyl siloxane) is the most widely used material, either in single or in mixed form. However, materials for efficient extraction of polar and semi polar compound are still scarce due to the fact that the analytes are relatively difficult to extract from aquatic environment due to their high solubility in water. Therefore, new materials are needed to overcome these limitations. In this work, cellulose acetate coated polyelectrolyte multilayer (CA-PEM) is proposed as the extraction phase in TFME for tricyclic antidepressant drugs (TCAs). CA is natural polymer with low strength of physical properties. Thus, modification CA with a thin layer polymer will improve the mechanical properties and still support green chemistry. TCAs contain hydrophilic groups (amine group) and hydrophobic group (aromatic rings, heterocyclic rings, and halogen atoms). TCAs are divided into two subdivision based on their chemical structure, namely tertiary amines and secondary amine [8]. The presence of amine groups in TCAs will increase the hydrophylicity and also polarity. Thus, these materials may be suitable for the adsorption of polar or semi polar compounds.

Polyelectrolytes are polymer-based electrolyte compounds (polyanionic and polycationic) which have the ability to ionize in aqueous solution and conduct electricity. In aqueous solution, anionic compounds exist as negatively charged species whereas cationic compounds remain as positively charged species. Anionic compounds and cationic compounds can aggregate through electrostatic interaction [9]. Polycationic and polyanionic have the ability to attract each another by electrostatic interaction and they also have the possibility to interact by hydrogen bonds and hydrophobic interaction depending on the type of polymer compounds [10]. The interaction between polycationic and polyanionic create a new supramolecular architecture of polyelectrolyte multilayers which is useful for sorbent. The prepared materials were characterized using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), field emission-scanning electron microscopy (FESEM), and thermogravimetric-differential thermal analyzer (TG-DTA).

METHODS

Preparation of Cellulose Acetate Membrane

Cellulose acetate membrane was prepared by a Loeb-Sourirajan (L-S) phase inversion. 0.08% w/v of CA was dissolved in acetone and stirred for 30 min until homogeneous. The dope solution was degassed to remove some of the bubbles. A suitable amount of the dope solution was dispersed uniformly on a glass plate and casted. After casting, the glass plate was immersed into coagulation water bath at room temperature. The phase inversion immediately started and the films were peeled off from the glass plate after complete coagulation. The membrane was further washed to remove the additive.

Deposition Polyelectrolyte Solution on the Cellulose Actetate Membrane by Layer-by-Layer Self Assembly

The activation of the surface area of cellulose was carried out using 0.5 M sodium hydroxide solution. The membrane was removed from the solution and dried by hanging at room temperature. The membrane was then immersed into 0.02 M PAAH solution (polycationic) was dried. After the immersion process is completed, the membrane was rinsed with deionized water. Next, the membrane was dipped in the 0.2 M PSS solution (polyanionic) followed by drying. The washing step described above was repeated and the membrane was then further dipped in polycationic solution followed by polyanionic solution. These steps were repeated to assemble the desired number of layers. The schematic of polyelectrolyte assembly can be showed in Figure 1.

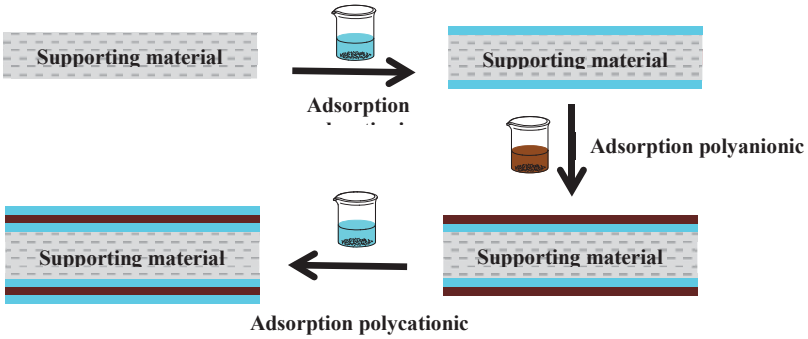

Figure 1. Self-assembly polyelectrolyte multilayers [9].

Optimization Parameter of Self Assembly Polyelectrolyte Multilayers

The optimization of coating parameters in the synthesis of polyelectrolyte multilayers is important in order to obtain the optimum coating condition. Several critical coating parameter were investigated including pH of polycationic and polyanionic solution, effect of salt addition in polyelectrolyte solution, dipping time, and number of layers were investigated by applying the coated membrane in the extraction and desorption of TCAs (IMI, AMI, and CHLO) using TFME method. The quantitative analysis was determined by HPLC-UV. HPLC conditions for the determination of TCAs were adopted from the previous study [11].

Optimization of combination pH of polycationic and polyanionic

The pH combination between polycationic and polyanionic is a parameter that influences the formation of polyelectrolyte multilayers. In this research, different combination pH of PAAH-PSS (2-2; 2-10; 10-2 and 10-10) were investigated during the optimization process. The pH was adjusted by adding HCL 0.1 M and NaOH 0.1 M.

Optimization of salt addition

Salt addition was prepared by diluting NaCl in deionized water to produce salt solutions with different concentrations. The solution was then used to dissolve the polyelectrolyte compound. Several of PAAH and PSS solution solutions with different salt concentrations (0; 0.1; 0.5 and 1 M) were investigated.

Optimization of dipping time

Dipping time has a closely relation with the equilibrium time to build the thin film. In this step, each of the membrane was dipped into polycationic and polyanionic solutions for 1; 3; 5 and 10 min, respectively to construct a PAAH and PSS layer.

Optimization of the number of layers

The assembly of layers is counted by the frequency of dipping in polycationic and polyanionic solution, repeatedly. A layer is constructed by depositing PAAH and PSS. The number of layers in the coating assembly affect to the thickness of material sorbent. Thus, the extraction efficiency from different number of layers were evaluated. In this research, different number of layers were used including uncoated membrane; 2 layers; 5 layers; and 10 layers.

Charaterization

Attenuated total reflectance Fourier transform infra-red spectroscopy (ATR-FTIR)

The optimum of polyelectrolyte coated membrane (CA-PEM) adsorbent was characterized using an attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) (Perkin Elmer Nicolet Avatar 370DTGS spectrometer, Ueberlingen, Germany) within the range of 600-4000 cm^{-1}. This characterization was used to determine the surface chemistry and components of the CA-PEM.

Scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM)

Characterization using SEM was carried out to investigate the surface morphology of CA-uncoated and CA-PEM. A Hitachi FESEM (Hitachi S-4800, Tokyo, Japan) was used to investigate the cross-section morphology of CA-uncoated CA-PEM. The aim of these characterizations is to determine the correlation between components in the CA-uncoated and CA-PEM.

Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis characterization was carried out to investigate the thermal stability of CA-uncoated and CA-PEM. This study was carried out under set temperature of 50 °C (hold for 1 min), then continuously heated from 50 °C to 560 °C at a rate of 10 °C min^{-1} and hold for 1 min at 560 °C. The results were used to compare the thermal stability between CA-uncoated and CA-PEM.

RESULTS AND DISCUSSION

Comparison performance between cellulose acetate uncoated and CA-PEM for extraction TCAs

The adsorption performances of CA uncoated membrane and CA-PEM to uptake TCAs were investigated by TFME method. TCAs were chosen as target model analyte because they have the possibility to form neutral and positive charge (basic drugs) in solution. Therefore, it can be assessed how the interaction of TFME on neutral or charged analytes provide the best extraction performance. The possible interactions between analytes and sorbent (CA-PEM) can occur by hydrogen bonding, electrostatic interaction and π-π interaction. The possible interactions between analyte and sorbent can be illustrated in Figure 2.

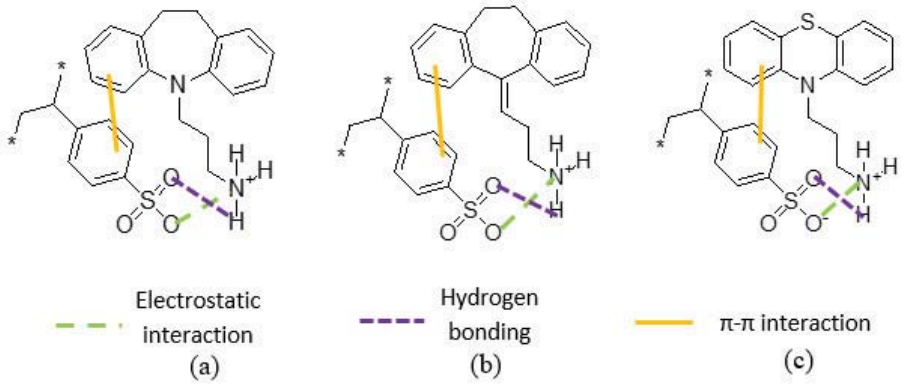

Figure 2. Possible interaction between CA-PEM and (a) imipramine, (b) amitriptyline, (c) chlorpromazine

The extraction performance of CA and CA-PEM were evaluated in order to know the differences of adsorption performance of CA membrane before and after coating. The results showed that CA-PEM has a higher extraction efficiency than the original CA membrane in three extraction replications, respectively (Figure 3). This condition might be due to the interactions of between analytes and CA-PEM during thin film micro extraction. Migration of analytes from sample solution (donor phase) to the extraction phase occurs by diffusion process with the aid of stirring. The diffusion process commonly takes place in the boundary layer of sample matrix and extraction phase with the aims to reach an equilibrium condition between two phases. During the diffusion process, the analytes have possibility to adhere on the surface of extraction phase by several interactions such as electrostatic interaction, Van der Waals forces, hydrophobic interaction, and hydrogen bonding [5]. The main interactions between analytes and sorbent (CA-PEM) can occur through hydrogen bonding and π-π interaction. While electrostatic interactions that occur are minor because after the last dipping process, the thin film is dried and washed to remove the unreacted polyanionic residue.

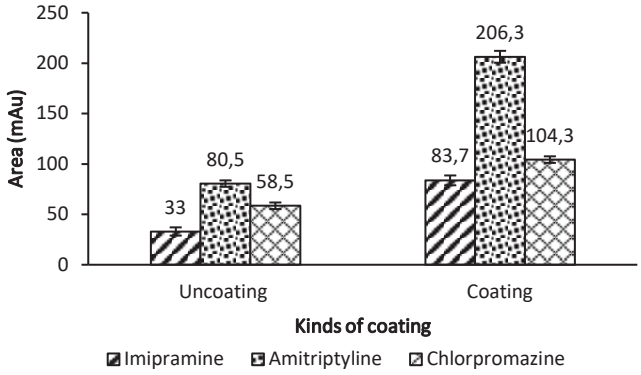

Figure 3. Extraction performance of CA and CA-PEM. Extraction conditions: 10 mL of donor, 100 µL acceptor phase (methanol), 840 rpm stirring rate, 30 min of extraction time, 10 min desorption time, without pH adjustment in sample solution, and without salt addition in sample solution

Optimization Parameter of Self Assembly Polyelectrolyte Multilayers

Optimization of combination pH of polycationic and polyanionic

One of the most important parameters during PEM assembly is the pH of the individual dipping polyelectrolyte solution due to its role to control the charge density of polyelectrolyte solution. PAAH and PSS are included in weak polyelectrolyte groups, so that the pH of polyelectrolyte solutions plays an important role to control the degree of ionization of the polar group during adsorption process [12,13]. In this study, four different combinations of pH for

PAAH and PSS, such as PAAH2-PSS2; PAAH2-PSS10; PAAH10-PSS2; and PAAH10-PSS10 were investigated to obtain the optimum pH for dipping solution. The results for optimization of pH of dipping solution in three extraction replications are shown in Figure 4.

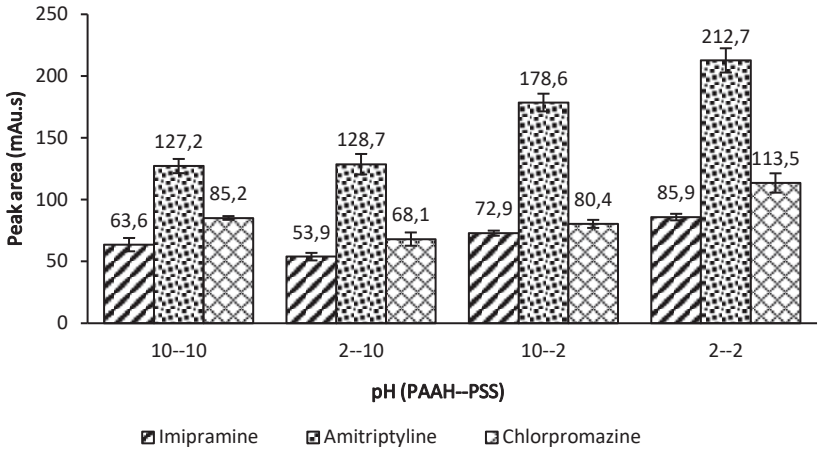

Figure 4. Optimization the pH of PAAH--PAA in LBL self-assembly CA-PEM. Extraction conditions: 10 mL of donor, 100 µL acceptor phase (methanol), 840 rpm stirring rate, 30 min of extraction time, 10 min desorption time, without pH adjustment and without salt addition.

The results clearly showed that the combination of pH 2 for PAAH and pH 2 for PSS achieved the best thickness and showed best performance for the adsorption of TCAs. PAAH is a weak polyelectrolyte containing ammonium groups (NH_3^+) with the p*K*a 7-10, while PSS contains sulfate groups (SO_3^-) with the p*K*a 0.5-1.5 [12]. Based on the pKa of the polycation and polyanionic, pH 2 and pH 10 were selected to evaluate the formation of the polyelectrolyte layer. At very low pHs, the amine groups of PAAH are protonated into positively charged ammonium ions while most of the sulfonate groups of PSS are in the non-charged state as sulfonic acid units. On the other hand, at high pHs, the ammonium ion are deprotonated into amine groups and the sulfonic acid units are strongly ionized into sulfonate [14], [15]. Therefore, it can be described that at pH 2 (under the p*K*a), amine groups on PAAH are strongly ionized into positively-charged ammonium ions and also in pH 2 (above the p*K*a) sulfonic acid groups are ionized into negatively-charged sulfonate ions. As general rule, the thickness of PEM increases when the pH is close to the p*K*a of each polyelectrolyte solution, so that at pH values far above or below the p*K*a it stay in partially ionized or almost in not-ionized state [16]. In this condition, the thickness of PEM will decrease and the most important interference occurred on the top of layer. Therefore, the combination of pH 2 for PAAH and pH 2 for PSS was then chosen as polycation and polyanion pHs and applied in the subsequently experiments.

Optimization of salt addition

The addition of salt in individual polyelectrolyte solution is very important as it can influence the layer thickness. In this study, four different concentrations of salt namely without salt addition; 0.1; 0.5; and 1 M were added in polyelectrolyte solutions, respectively. The PEM assemblies were then applied to the extraction of IMI, AMI, and CHLO. The results in three extraction replications are shown in Figure 5.

The results clearly showed that the extraction efficiencies (indicated by peak areas) decreased with the increasing salt concentration in the polyelectrolyte solution. The addition of salt might be blocked the PAAH and PSS interaction due to the ionic competition between polyelectrolyte and NaCl. it was also found that the increasing salt concentration in the polyelectrolyte solution did not have linear correlation with the thickness of polyelectrolyte film assembly. The polyelectrolyte building is not only affected by salt addition, but also depended on the selection of polyelectrolyte material and the dipping method [17].

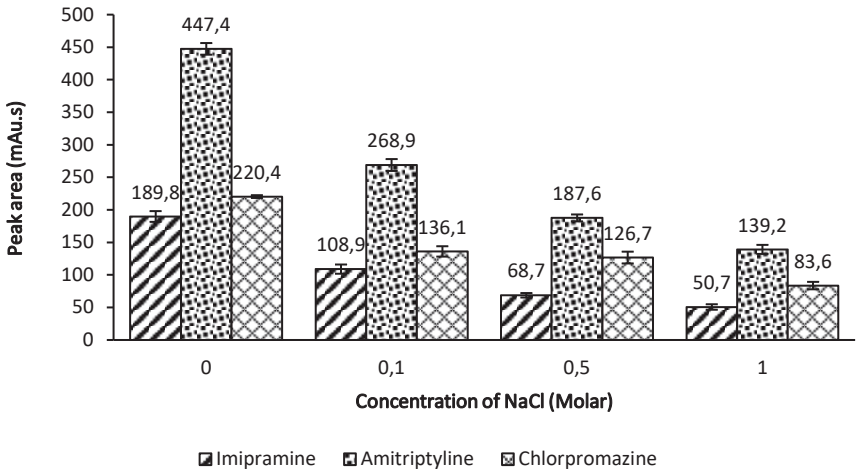

Figure 5: Effect of salt addition on CA-PEM extraction of TCAs. Extraction conditions: 10 mL of donor, 100 µL acceptor phase (methanol), 840 rpm stirring rate, 30 min of extraction time, 10 min desorption time, without pH adjustment in sample solution, and without salt addition in sample solution.

Optimization of dipping time

The build-up of PEM has a correlation with the dipping time due to the influence of molecular weight distribution, concentration, and the diffusion rate of polyelectrolyte material during adsorption process [12]. In this work, four different dipping times (2, 5, 10, and 15 minutes) were chosen to investigate the optimum dipping time during PEM assembly in order to obtain the optimum layer condition.

Figure 6 shows that the optimum dipping time in three extraction replications are in the range of 5-10 min. Meanwhile, on increasing the dipping time from 10 minutes to 15 minutes resulted in reduced efficiency of PEM to extract TCAs. Nevertheless, as the efficiency for 5 minutes dipping time was no significantly less than the efficiency of the 10 min. Thus, 5 min was adopted as the optimum dipping time and was used for further deposition treatment of polyelectrolyte. Furthermore, this provided a faster deposition process. Polyelectrolyte deposition efficiency is not only depending on dipping time during construction process, but also depending on the surface charge of previously layer, type and molecular weight of polyelectrolyte material which are affecting on the diffusion rate during deposition process [12].

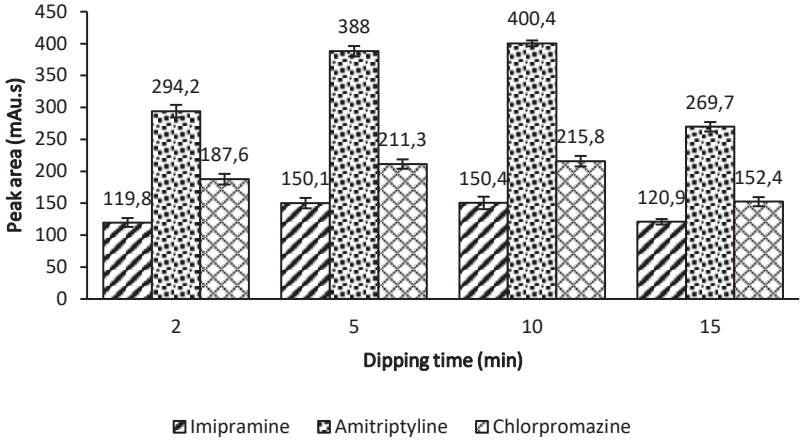

Figure 6. Effect of dipping time in LBL self-assembly CA-PEM. Extraction condition: 10 mL of donor, 100 µL acceptor phase (methanol), 840 rpm stirring rate, 30 min of extraction time, 10 min desorption time, without pH adjustment in sample solution, and without salt addition in sample solution.

Optimization of the number of layers

The thickness of coated material is dependent on the number of deposited layers. In order to determine an optimum thickness of PEM film for the extraction of TCAs from aqueous matrices, three variants number of layers were investigated namely one layer, five layers and ten layers. During the dipping process, the layers were deposited on both sides of the supporting membrane (CA). The results of the study on the influence of number of layers was shown in Figure 7.

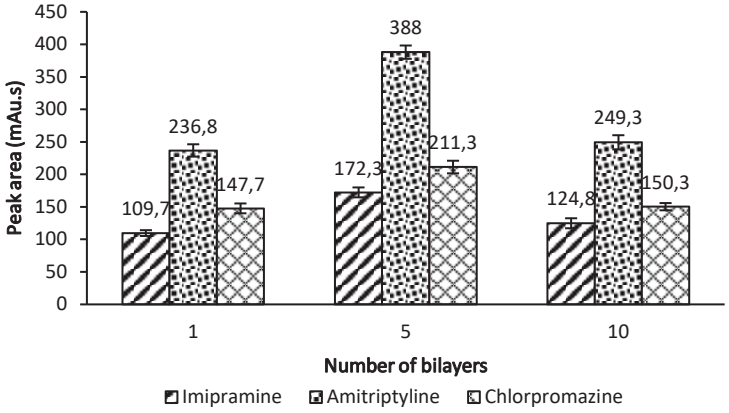

Figure 7. Effect of the numbers of layer in LBL self-assembly CA-PEM in the extraction of TCAs. Extraction condition: 10 mL of donor phase, 100 µL acceptor phase (methanol), 840 rpm stirring rate, 30 min of extraction time, 10 min desorption time, without pH adjustment in sample solution, and without salt addition in sample solution.

A very thin coating layer can trigger incomplete coating on the surface of CA membrane due to the possibility of the first layer to fulfill in the porous of CA membrane in order to build a foundation of multilayers. Very thin layer or single layer cannot fully cover the surface of CA membrane and this can affect the decreasing of extraction performance of TCAs. In previous study it was found that in order to fully construct the layer assembly and remove the influence of the CA membrane, approximately three layers were required [18]. Measurement of the extraction performance of TCAs as a function of film thickness indicated that most of the TCAs were adsorbed in the outermost surface layer, while the diffusion in the deeper of layer is limited. Thus, the adsorbed of anayte in the outermost of the layers was found to be somewhat independent of the total number of layers [18]. Higher number of layers has a higher possibility of absorption into deeper layer. Therefore, it can increase the possibility of carry-over during desorption process in the end of extraction. Thus, combination 5 bilayer showed an optimum coating condition to extract TCAs.

Characterizations

Attenuated total reflectance Fourier transform infra-red spectroscopy (ATR-FTIR)

The analysis was carried out by putting the punched of CA and CA-PEM on the ATR-FTIR spectra machine followed by ATR-FTIR detection analysis. The modified membrane was then compared with the raw material of CA, PAAH, and PSS. The ATR-FTIR spectra are shown in Fig 8. The presence of strong carbonyl (C=O) stretching in 1736 cm^{-1} exhibited as ester groups from CA (Figure 8a) [18]. After deposition of polyelectrolyte multilayers, the presence of polyelectrolyte functional groups is proven. The carbonyl (C=O) absorption peak of CA totally disappeared after the CA was coated with PAAH and PSS layers. This condition exhibited that the deposition of PAAH-PSS successfully encapsulated the CA membrane totally. With PSS as the top layer, the absorption peaks of the sulfonyl groups were observed at 1000-1200 cm^{-1} with the corresponding of SO_3^- symmetric stretching at 1033 cm^{-1} and the C-H bending aromatic (benzyl ring) at 1006 cm^{-1} [19].

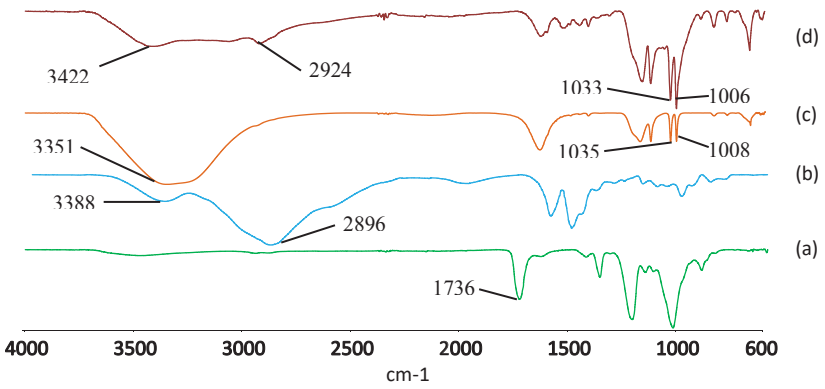

Figure 8. ATR-FTIR spectra of (a) CA (b) PAAH (c) PSS (d) CA-PEM

Scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM)

Characterization using scanning electron microscopy has a purpose to visualize the morphology (surface) of the materials by scanning with a high-energy beam of electrons. In this work, SEM was used to identify the surface area of membrane before (CA) and after coating (CA-PEM). The image of CA-PEM membrane was carried out under optimized condition of coating parameters. Figure 9 shows that the SEM images for CA and CA-PEM under 2000 magnification. The SEM of CA (Figure 9) shows that the CA membrane has a lot of pores dispersed on the surface, and on the contrary the CA-PEM surface showing bodies that may represents granular polymers and subsequently, the surface of CA-PEM appears rougher than the unmodified CA surface. The average diameter of the CA and CA-PEM pore size are about 1 µm of CA. Figure 9b also shows an evidence of underlying membrane (CA-PEM) observed. This phenomenon is also supported by Figure 10 which shows the cross-section of CA (a) and CA-PEM (b) where the encapsulation of polyelectrolyte completely covered the surface of CA membrane including the inside. This condition corresponds very well with the previous characterization using ATR-FTIR where the CA membrane was totally encapsulated with the polyelectrolyte. The average pore size of CA and CA-PEM diameters were analyzed using imageJ application. The data obtained are CA diameter of 5.579 µm and CA-PEM 0.515 µm, respectively.

Thermo gravimetric-differential thermal analysis (TG-DTA)

Thermo gravimetric differential thermal analysis (TG-DTA) was used to observe the decreasing of weight of a material that occur as a function of temperature or time while the sample is subjected to a controlled temperature program in a controlled atmosphere. In this study, the temperature was controlled in the range of 50-560 °C. The TGA thermogram of the raw material of CA (Figure 10) shows two weight losses corresponding to two thermal degradations. The first degradation occurs in the range of 50-100 °C which shows a loss of weight for 1.527 % for CA and 0.243% for CA-PEM due to the water evaporation. A rapid degradation observed in the temperature glass transition (Tg) at about 330 °C with 80.641 % of weight loss is attributed to a major degradation of CA chains. Similar degradation was observed in Figure 12. The significant weight decreased in the temperature glass transition (Tg) of 300 °C is likely due to the decomposition of CA chain. Nevertheless, the weight loss of CA-PEM (58.201 %) is obviously less than CA (80.641%) in the similar region. This condition represents that the interaction between CA and polyelectrolyte multilayers significantly enhance the thermal stability.

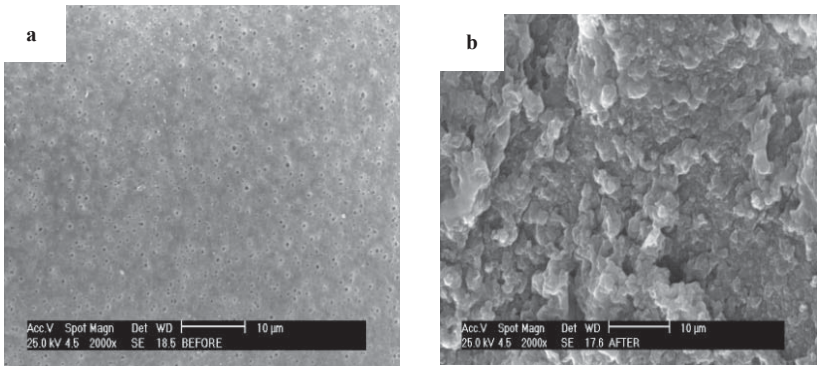

Figure 9: SEM images (surface) of (a) CA (b) CA-PEM

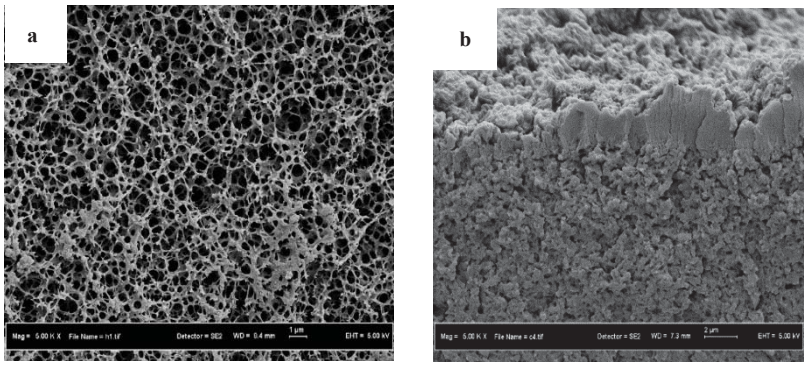

Figure 10. FESEM images (cross section) of (a,b) CA (c,d) CA-PEM

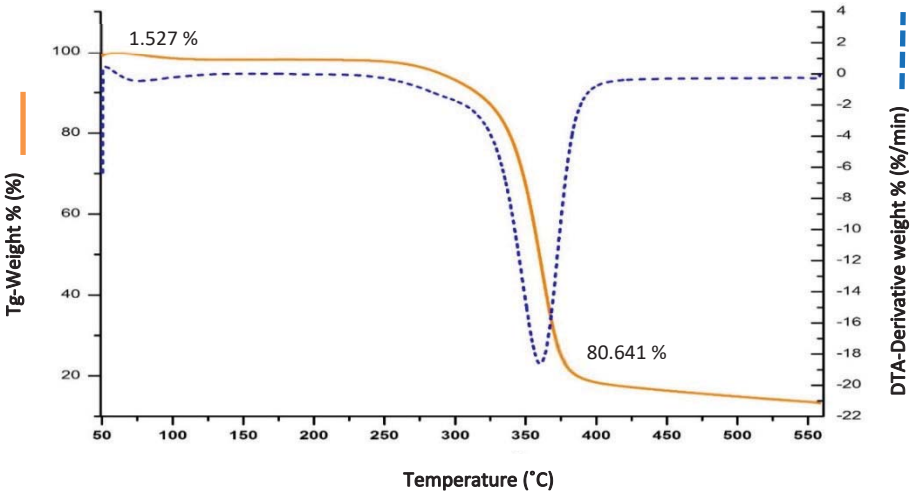

Figure 11. TG-DTA Thermogram of CA

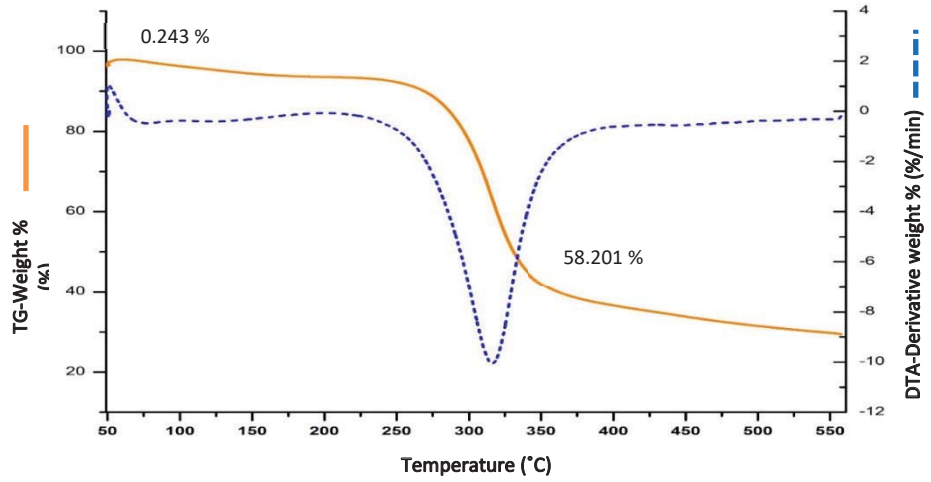

Figure 12. TGA-DTA Thermogram of CA-PEM

CONCLUSIONS

Polyelectrolyte multilayers poly(allyl amine hydrochloride) and poly(styrene sulfonic acid) coated cellulose acetate membrane (CA-PEM) was successfully synthesized by layer-by-layer self-assembly method (LBL self-assembly). In applying CA-PEM to the extraction of TCAs, the coating parameters for CA-PEM were optimized to improve extraction efficiency. Optimum coating conditions were achieved at pHs of 2-2 for immersion solution (PAAH-PSS), respectively, without the salt addition in the polyelectrolyte solution, dipping time of 10 min, and five pairs of layers. The characterization results show that CA-PEM is multiparous material with a smaller diameter than CA and also contains of OH-, NH-, and $-SO_3^-$ groups. The addition of PEM to the CA membrane also increased the thermal stability of CA-PEM. The results are inspiring and indicate that this sorbent has a great potential for thin film extraction sorbent and also suitable for thermal desorption application.

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