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by Rico Ramadhan

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

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Abstract. A new material of thin film sorbent based on self assembly polyelectrolyte multilayers (PEM) has been successfully developed. Several of important coating parameters including pH of coating solution, salt addition in coating solution, dipping time, and number of layers were optimized for drug extractor by using thin film microextraction (TFME) technique. The optimum conditions were evaluted by the highest extraction performance for tricyclic antidepressant drugs (TCAs). Cellulose acetate membrane was chosen as supporting material. While polyelectrolyte materials namely poly(allyl amine hydrochloric/PAAH) and poly(styrene sulfonic acid) (PSS) were choosen as coating materials. PAAH and PSS were deposited on the surface of supporting material, repeatedly. The results showed that the optimum coating conditions were the pH of PAAH 2 and PSS 2, no addition of salt in coating solution, the dipping time of each layer 5 minutes, and the number of layers 5. The optimized material was characterized by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), field emission-scanning electron microscopy (FESEM), and thermal gravimetry analyzer (TGA).

Keywords: Cellulose acetate, Polyelectrolyte Multilayers, Thin Film Extraction, Tricyclic Antidepressant, Sorbent

INTRODUCTION

Sample preparation technique based on microextraction has gained attention in line with the green chemistry concept. Microextraction technique has a basic principle to extract analyte into microliters of organic solvent or adsorb on small amount (mg) of adsorbent. As compared to LLE and SPE, microextraction techniques have the advantages not only in terms of solvent less until solvent free, but also provide improved signal enhancement, rapid, simple, and easily coupled with gas chromatography or liquid chromatography [1]

One of the most well-developed microextraction techniques is solid phase microextraction (SPME). The principle of this method based on the partitioning of analyte between the matrix sample and organic phase coated on a fused silica fiber. In the end of extraction process, the extraction phase is directly injection into GC or HPLC to quantitative analysis. The sensitivity of SPME can be increased by creating the temperature gap between the sample solutions and coating material during extraction process, therefore volatile compounds are appropriate to deal with this method. SPME has successfully redressed the weaknesses inherent in conventional LLE and SPE methods, but there are several problems commonly encountered SPME method. The major drawbacks involves the fiber which is fragile and easily broken, limited lifetime, expensive, longer equilibrium time due to the thickness of sorbent, higher possibility of carry over, and requires modification of injection port for the appropriate device and instrument [2]. Therefore, development of sorbent for SPME become interesting and important to improve the extraction performance and overcome the limitation inherent in SPME. Thin film microextraction (TFME) is one of the techniques derived from SPME with the geometry of sorbent in the form of thin sheet of polymeric membrane.

Recently, TFME has become a popular microextraction method due to its easy operation, low cost, and less time consuming. This method also successfully overcome the drawback from SPME by employing thin sheet extraction phase with several geometric shapes such as cotter pin [3], copper mesh holder [4] and 96-blade format thin film [5]. At the end of extraction process, this technique is combined with solvent desorption with the aid of ultrasonication, vortex, or centrifuge thus avoiding the thermal desorption units. The use of suitable material for extraction is very important in TFME. Thus far, poly(dimethyl siloxane) has been the most widely used material either in single or in mixed material. However, materials for efficient extraction of polar and semipolar compound are scarce due to the fact that the analytes are relatively difficult extracted from aquatic environment due to their high solubility in water. Therefore, a new material is needed to overcome these limitations. In this work, cellulose acetate coated polyelectrolyte multilayer (CA-PEM) was proposed as an extraction phase in TFME for tricyclic antidepressant drugs (TCAs). CA is natural polymer with low strength of phisical properties. Thus, modification CA with thin layer polymer will increase 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 the chemical structure, namely tertiary amines and secondary amine [6]. The presence of amine groups in TCAS will increase the hydrophylicity and also polarity. Thus, this material might be suitable for the adsorption of polar or semipolar compounds.

Polyelectrolyte is a polymer-based on electrolyte compound (polyanionic and polycationic) which has the ability to ionize in aqueous solution and conduct electricity. In the aqueous solution, anionic compounds exist as negatively charged species while cationic compounds stay as positively charged species. The anionic compounds and cationic compounds can aggregate through electrostatic interaction[7]. Polycationic and polyanionic have an ability to attract one another by electrostatic interaction and they also have the possibility to interact by hydrogen bonding and hydrophobic interaction depending on the kinds of polymer compounds (Borges and Mano, 2014). The interactions between polycationic and polyanionic create a new supramolecular architecture of polyelectrolyte multilayers that are useful for sorbent. The prepared material was charaterized using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), field emission-scanning electron microscopy (FESEM), and thermal gravimetry analyzer (TGA).

Methods

1. 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 homogen. The dope solution was degassed to remove some of the bubbles. An appropriate 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.

2. Deposistion 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.
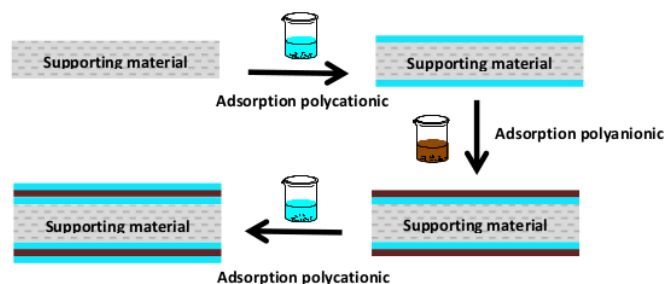

Figure 1: Self-assembly polyelectrolyte multilayers[8]

3. **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 a previous study [9].

a. **Optimization of combination pH of polycationic and polyanionic**

The combination pH 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.

b. **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.

c. **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.

d. **Optimization of the number of layers**

The assembly of layers is counted by the frequency of dipping a 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.

4. **Characterizations**

a. **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.

b. **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 crosssection 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.

c. **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

1. **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. The results were compared 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 (Figure 2). This condition might be due to the interactions of between analytes and CA-PEM during thin film microextraction. 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 a 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 [10]. In this study, the possible interactions between analytes and sorbent (CA-PEM) can occur by hydrogen bonding and π-π interaction.
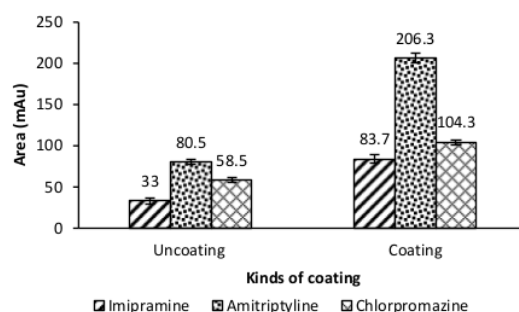

Figure 2: Extraction performance of CA and CA-PEM. Extraction conditions: 10 mL of donor, 100 μL acceptor phase (methanol), 840 rpm stirring rate, 30 min of extraction time, 10 min desorption time, without pH adjustment in sample solution, and without salt addition in sample solution

2. Optimization Parameter of Self Assembly Polyelectrolyte Multilayers
a. 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 [11,12]. 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 are shown in Figure3.
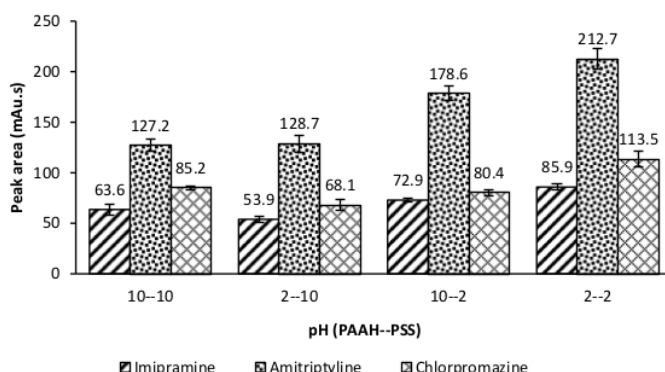

Figure 3: Optimization the pH of PAAH--PAA in LBL self-assembly CA-PEM. Extraction conditions: 10 mL of donor, 100 μL acceptor phase (methanol), 840 rpm stirring rate, 30 min of extraction time, 10 min desorption time, without pH adjustment and without salt addition.

The results clearly showed that the combination of pH 2 for PAAH and pH 2 for PSS achieved the best thickness for the adsorption of TCAs. PAAH is a weak polyelectrolyte containing ammonium groups (NH_3^+) with the pKa 7-10, while PSS contains sulfate groups (SO_3^-) with the pKa 0.5-1.5 [13] . 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 sulfonat [11,14]. Therefore, it can be described that at pH 2 (under the pKa), amine groups on PAAH are strongly ionized into positively-charged ammonium ions and also in pH 2 (above the pKa) 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 pKa of each polyelectrolyte solution, so

that at pH values far above or below the pKa it stay in partially ionized or almost in not-ionized state [15]. 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.

b. 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 are shown in Figure 4.

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 [16].
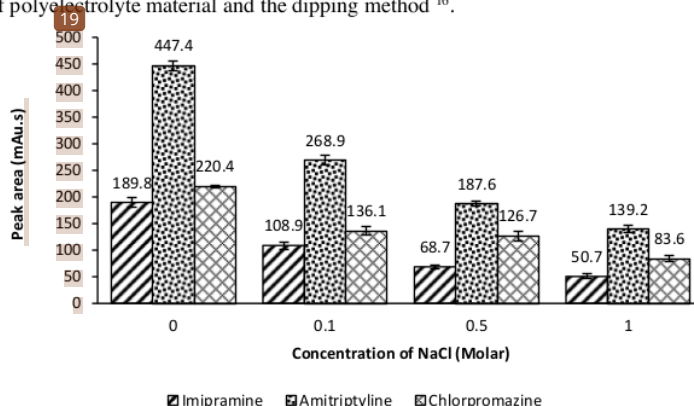

Figure 4: Effect of salt addition on CA-PEM extraction of TCAs. Extraction conditions: 10 mL of donor, 100 μL acceptor phase (methanol), 840 rpm stirring rate, 30 min of extraction time, 10 min desorption time, without pH adjustment in sample solution, and without salt addition in sample solution.

c. 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 [13]. In this work, four different dipping times (2, 5, 10, and 15 min) were chosen to investigate the optimum dipping time during PEM assembly in order to obtain the optimum layer condition.

The results (Figure 5) showed that the optimum dipping time was in the range of 5-10 min. Meanwhile, on increasing the dipping time from 10 min to 15 min resulted in reduced efficiency of PEM to extract TCAs. Nevertheless, as the efficiency for 5 min 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 [13].
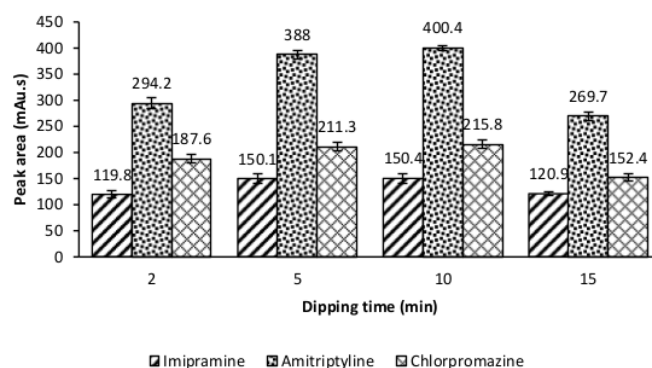
Figure 5: Effect of dipping time in LBL self-assembly CA-PEM. Extraction condition: 10 mL of donor, 100 μL acceptor phase (methanol), 840 rpm stirring rate, 30 min of extraction time, 10 min desorption time, without pH adjustment in sample solution, and without salt addition in sample solution.

d. 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 1 layer, 5 layers and 10 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 6.
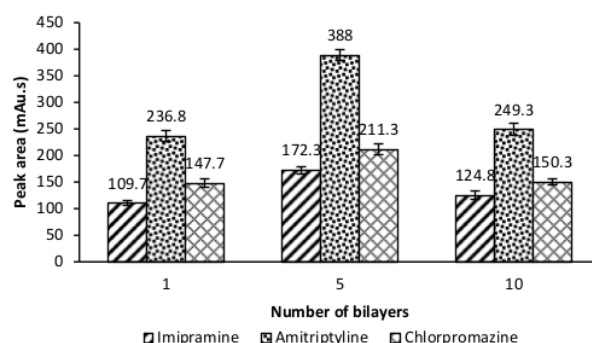

Figure 6: Effect of the numbers of layer in LBL self-assembly CA-PEM in the extraction of TCAs. Extraction condition: 10 mL of donor phase, 100 μL acceptor phase (methanol), 840 rpm stirring rate, 30 min of extraction time, 10 min desorption time, without pH adjustment in sample solution, and without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

Very thin coating layer can trigger uncompleted 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. It was reported elsewhere that to fully establish the layers assembly and eliminate the influence of the CA membrane, it takes about three layers [12]. 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 [12]. 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.

3. Characterizations

a. 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 7.

The presence of strong carbonyl (C=O) stretching in 1736 cm^{-1} exhibited as ester groups from CA (Figure 7a) [12]. After the deposition of polyelectrolyte multilayers, the presence of the functional groups of polyelectrolyte was evident. 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 1033cm^{-1} and the C-H bending aromatic (benzyl ring) at 1006 cm^{-1} [17].
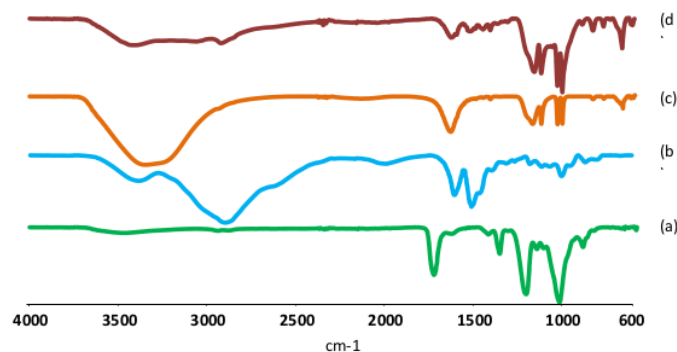

Figure 7: ATR-FTIR spectra of (a) CA (b) PAAH (c) PSS (d) CA-PEM

b. 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 8 shows that the SEM images for CA and CA-PEM under 2000 magnification. The SEM of CA (Figure 8) shows that the CA membrane has a lot of pores dispersed on the surface, and on the contrary the surface of CA-PEM shows bodies that probably represents granular polymers and subsequently, the surface of CA-PEM appears rougher than the surface of unmodified CA. Figure 8b also shows an evidence of underlying membrane (CA-PEM) observed. This phenomenon is also supported by Figure 9 which shows the crosssection 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.
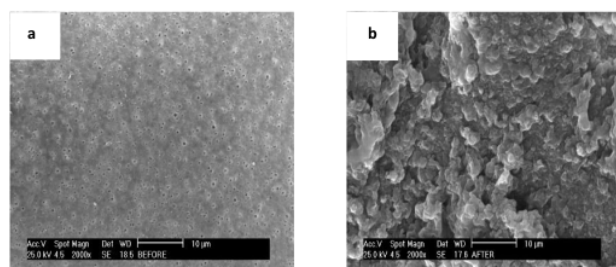

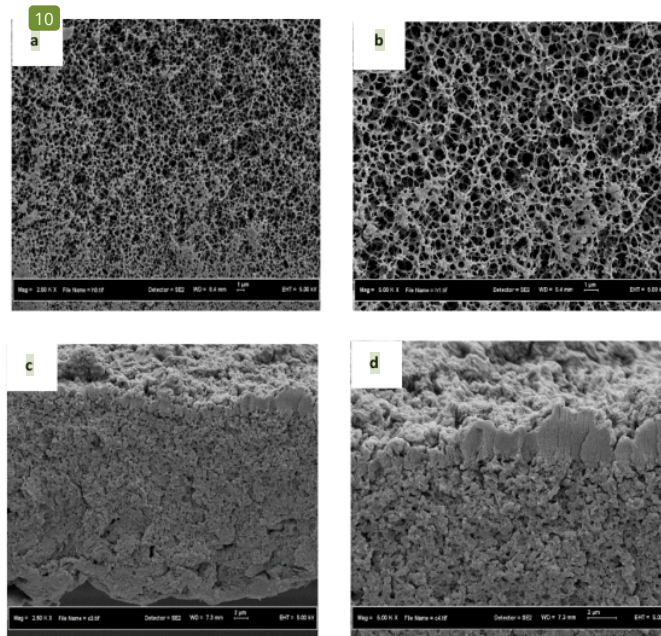**Figure 8:** SEM images (surface) of (a) CA (b) CA-PEM

Figure 9: FESEM images (cross section) of (a,b) CA (c,d) CA-PEM

4. Thermal gravimetric analysis (TGA)

Thermogravimetric analysis (TGA) 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 that correspond to two thermal degradations. The first degradation occurs in the range of 50-100 °C which shows a loss of weight for 1.527 % due to the water evaporation. A rapid degradation observed in the temperature 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 4.23. The significant weight decrease in the region 250-300 °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.
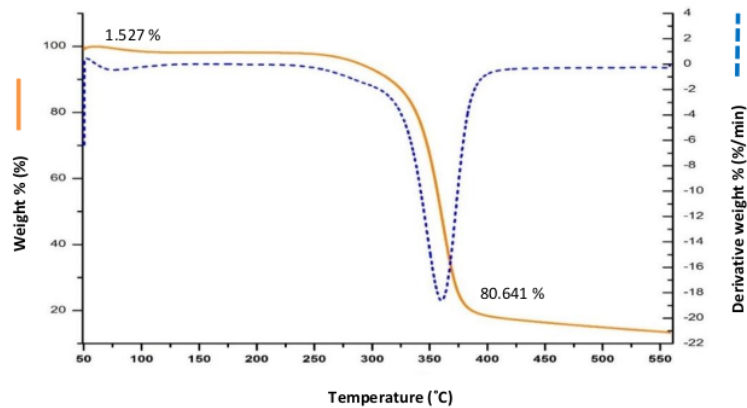
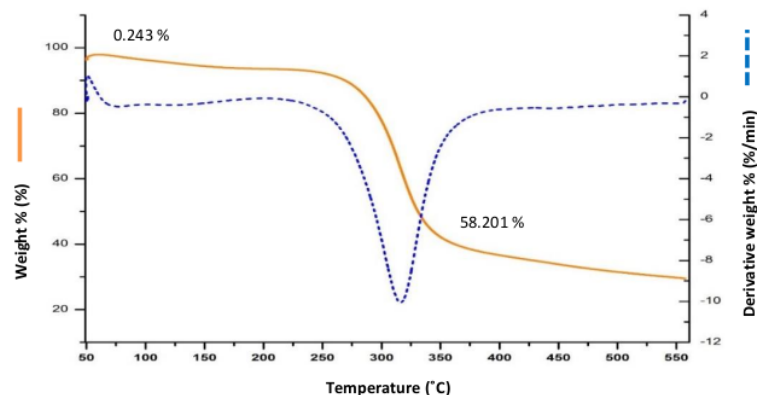

Figure 10: TGA Thermogram of CA

Figure 11: TGA 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 via layer-by-layer self-assembly method (LBL self-assembly). In the application of CA-PEM to the extraction of TCAs, the coating parameters for CA-PEM were optimized to enhance the extraction efficiency. The optimum coating conditions were achieved at pHs of 2-2 for dipping solution (PAAH-PSS), respectively, without salt addition in polyelectrolyte solution, dipping time for 10 min, and five pairs of layers.

ACKNOWLEDGMENT

REFERENCES

1. Bruheim, I., Liu, X. & Pawliszyn, J. Thin-Film Microextraction. **75**, 1002–1010 (2003).
2. Kataoka, H. Recent developments and applications of microextraction techniques in drug analysis. 339–364 (2010)
3. Kermani, F. R. Optimization of solid Pahse Microextracton for Determination of Desinfection by-Products in Water. (University of Waterloo, 2012).
4. Qin, Z., Bragg, L., Ouyang, G., Niri, V. H. & Pawliszyn, J. Solid-phase microextraction under controlled agitation conditions for rapid on-site sampling of organic pollutants in water. **1216**, 6979–6985 (2009).
5. Mirnaghi, F. S., Monton, M. R. N. & Pawliszyn, J. Thin-film octadecyl-silica glass coating for automated 96-blade solid-phase microextraction coupled with liquid chromatography – tandem mass spectrometry for analysis of benzodiazepines. *J. Chromatogr. A* **1246**, 2–8 (2012).
6. Rudorfer, M. V & Potter, W. Z. Metabolism of Tricyclic Antidepressants. **19**, (1999).
7. Decher, G. Layer-by-Layer Assembly (Putting Molecules to Work). 1–22 (2012).
8. Jewell, C. M. & Lynn, D. M. Multilayered polyelectrolyte assemblies as platforms for the delivery of DNA and other nucleic acid-based therapeutics ☆. **60**, 979–999 (2008).
9. Sanagi, M. M. *et al*. Analytical Methods Two-phase electrodriven membrane extraction combined with liquid chromatography for the determination of tricyclic antidepressants in aqueous matrices †. *Anal. Methods* **6**, 8802–8809 (2014).
10. Jiang, R. & Pawliszyn, J. Thin-film microextraction offers another geometry for solid-phase microextraction. *Trends Anal. Chem.* **39**, 245–253 (2012).
11. Krasemann, L., Toutianoush, A. & Tieke, B. Self-assembled polyelectrolyte multilayer membranes with highly improved pervaporation separation of ethanol / water mixtures. **181**, 221–228 (2001).

12. Ding, B., Fujimoto, K. & Shiratori, S. Preparation and characterization of self-assembled polyelectrolyte multilayered films on electrospun nanofibers. **491**, 23–28 (2005).
13. Ali, S. W., Rajendran, S. & Joshi, M. Effect of Process Parameters on Layer-by-layer Self-assembly of Polyelectrolytes on Cotton Substrate. **18**, 237–250 (2010).
14. Fadhillah, F. *et al*. Development of polyelectrolyte multilayer thin fi lm composite membrane for water desalination application. *DES* **318**, 19–24 (2013).
15. Crouzier, T., Boudou, T. & Picart, C. Current Opinion in Colloid & Interface Science Polysaccharide-based polyelectrolyte multilayers. *Curr. Opin. Colloid Interface Sci.* **15**, 417–426 (2010).
16. Ahmadiannamini, P. *et al*. Multilayered polyelectrolyte complex based solvent resistant nanofiltration membranes prepared from weak polyacids. *J. Memb. Sci.* **394–395**, 98–106 (2012).
17. Liakos, A. I. L. *et al*. SC. *Colloids Surfaces B Biointerfaces* (2018).

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