GELATIN-ALGINATE COATED CELLULOSE ACETATE MEMBRANE FOR THE EXTRACTION OF HEAVY METAL IONS FROM WATER SAMPLES

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Abstract. Heavy metal ions are a common water pollutant from industrialized areas and extraction is one of the most popular methods to remove the target analytes. However, extraction and determination of metal ions in water are often very difficult to perform due to their solubility in water. In order to resolve some of the issues in the extraction of trace metal ions from aqueous samples, this study explores newly prepared polyelectrolyte films coated on cellulose acetate membrane as extracting phase. Optimization coating materials showed that gelatin-alginate coated cellulose acetate membrane have the best performance to adsorb metal ions from water. The results open a possibility of the method to be successfully applied as extracting phase to adsorb and enrich heavy metal ions from aqueous matrices.

Keywords: Gelatin; alginate; cellulose acetate; extracting phase

1.0 INTRODUCTION

Heavy metal ions are a common water pollutant with density more than 5 g cm^{-3} and identified as carcinogenic compound [1,2]. They usually come from industrialized areas like metal plating, mining, and electronic industries [3]. Their solubility in water is very high due to their capability to ionize, but their concentration is in trace amounts, therefore it is very difficult to remove and determine. Extraction and preconcentration method with high hidrophilicity of extracting phase are needed to achieve the desire detection limits.

Solid phase extraction is one of the most popular methods to preconcentrate trace metal ions from aqueous samples. Nevertheless SPE has several drawbacks such as higher consumption of sample volume and organic solvent, time consuming, and possibility of carryover of analytes. Therefore, several miniaturized extraction techniques were derived from SPE have been developed. Dispersive solid phase extraction (DSPE) is a technique derived from SPE that offers several advantages of DSPE is rapid, requires small volume of desorption solvent, and it can be combined with ultrasonicator or vortex to desorb analytes from adsorbent. Although DSPE is an established technique, an appropriate solid sorbent is a key to its success.

The use of membrane based sorbent is currently receiving attention to develop. Thin film microextraction in first time has been developed by Pawliszyn and co-worker in 2003 [4] and applied in solid phase microextraction technique. Other researchers have developed thin film as extracting phase combined with different kinds of polymer and porous material like silica, zeolite, and carbon nanotube [5,6,7]. The membrane can be easily prepared by utilizing inversion phase method and also easily to modify on the surface by coating or dispersed in the bulk polymeric material. In recent years, coated materials on the surface of membrane have become a popular method to improve their selectivity and adsorption capacity by increasing the volume of extracting phase. However, the thickness of the coating material plays an important role due to the long equilibrium time and desorption time that might increase possibility of carryover of analytes [8]. In order to overcome this problem, thin film coated membrane will be developed to produce thin and wide membrane as an extracting phase.

Cellulose is the most abundant and renewable biopolymer in nature and it can be utilized for preparation various functional material [9]. It was usually applied as filter in desalination field due to their capability to reject or remove different kinds of water pollutant. Cellulose rich of hydroxyl groups bonded at C2, C3, C6 and equatorial OH in C1 and C4 use for binding with other monomer by 1, 4-β-glycosidic linkaged [10,11]. Whereas cellulose acetate is derived from cellulose by substituting the hydroxyl groups in C6 with acetyl groups and it can increase the physical properties of cellulose. Hydroxyl groups in cellulose acetate are very easy to ionize, in order the possibility to substitute by another functional groups in their ionized state. This condition makes cellulose appropriate for extracting phase [5].

In this research, polyelectrolyte thin film was deposited on the surface of cellulose acetate membrane layer-by-layer by dip coating technique. Synthetic and natural polyelectrolyte namely poly (allyl amine hydrochloride), poly (4-styrene sulfonic acid), gelatin, and sodium alginate were chosen as coating materials. The application of polyelectrolyte coated membrane for the extraction of cadmium ions from water prior to flame atomic absorption spectrometer (F-AAS) determination was investigated. Coating parameters such as different kinds and pH of polyelectrolyte solution and salt addition in polyelectrolyte assemblies were also studied.

2.0 EXPERIMENTAL

2.1 Materials

Cellulose acetate was purchased from R&M chemicals (Edmonton, Canada). Acetone was obatained from Q-rëc (Selangor, Malaysia). Coating materials poly(allylamine hydrochloride) (MW=900,000), poly(4-styrenesulfonic acid) (MW=75,000) were purchased from Sigma Aldrich (St. Louis, Missouri, USA). Therefore sodium alginate was obtained from Q-rëc (Selangor, Malaysia) and fish skin gelatin was obtained from from Fluka Chemica (Buchs, Switzerland). Deionized water was produced by 18.2 MΩ Milli Q water purification system, Millipore, Germany. Standard heavy metal ion $Cd(NO_3)_2$ solution (1000 µg mL^{-1} in 0.5 M nitric acid) was purchased from Merck (Darmstadt, Germany). Salt strength in polyelectrolyte solution was adjusted by sodium chloride which was purchased from Fluka Chemica (Buchs, Switzerland). Hydrogen chloride 98% and sodium hydroxide pellets used for pH adjustment were purchased from from Fluka Chemica (Buchs, Switzerland). Nitric acid 65% as desorption solvent was purchased from Q-rëc (Selangor, Malaysia).

2.2 Apparatus

Erlenmeyer flask (25 mL) and flat glasses were used to prepare cellulose acetate membrane. A Favorit hot plate magnetic stirrer (Perak, Malaysia) and magnetic stirring bar (3 cm × 0.5 cm) were used to prepare cellulose acetate dope solution and stirring sample solution during DSPE process. Perkin Elmer, PinAAcle 900T atomic absorption spectrometer (AAS) (Waltham, Massachusetts, U.S) was used for quantitative analysis.

2.3 Research Procedure

2.3.1 Preparation of cellulose acetate membrane

Cellulose acetate (CA) membrane was prepared by desolving 2% of CA powder in 2:1 (acetone:formamide) and stirred until a homogenous solution was obtained. Then, the solution was poured on the glass plate and casted by a casting knife or glass tube. After casting, the CA membrane was immersed for 2 h in deionized water for coagulation at room temperature and the inversion phase was immediately started. After 15 min the membrane was peeled from the glass and followed by washing with deionized water to remove the additives.

2.3.2 Deposition polyelectrolyte solution in membrane by layer-by-layer self-assembly

In the first step, the prepared CA membrane was dipped for 2 min in 0.5 M sodium hydroxide. The membrane was then dried for 2 min and then dipped in cationic polyelectrolyte (i.e poly(allyl amine hydrohloride) or gelatin) for 5 min. Then the membrane was dipped in anionic polyelectrolyte (i.e poly(4-styrene sulfonic acid) or sodium alginate) for 5 min and this procedure was repeated to obtain five pairs of polycationic and polyanionic thin film coatings. The polyelectrolyte coated membrane was cut into circular discs (5 mm diameter) with a puncher. The coated membrane obtained was characterized by using a Perkin Elmer Spectrum ™ 400 attenuated total reflectance fourier transform infra red spectroscopy (ATR-FTIR) (Waltham, Massachusetts, U.S).

2.3.3 Aplication of polyelectrolyte coated cellulose acetate membrane in dispersive solid phase extraction

Water sample (100 mL) containing 0.1 ppm cadmium was transferred into a 250-mL glass beaker. 10 pieces of polyelectrolyte coated membrane discs (5 mm diameter) were conditioned in 0.5 M sodium hydroxide for 2 min before use. The treated membrane discs were dried at room terperature for 1 min and introduced into the sample solution. The sample solution was stirred at 700 rpm using a magnetic stirrer for 15 min. After the extraction , the coated membrane discs were removed and air dried for 1 min and put into a conical tube. The analyte was desorbed form the membrane discs by adding 2 mL of 0.5 M nitric acid, the solution was vortexed for 2 min at 500 rpm. The coated membrane discs were removed and the extraction solution was injected into F-AAS to determine the cadmium ions.

3.0 RESULTS AND DISCUSSION

3.1 Deposition Polyelectrolyte Materials on the Surface of Cellulose Acetate Membranes

Cellulose is a biopolymer that contains a lot of hydroxyl groups in its backbone. The backbone of cellulose can be easily modified with functionalize groups to improve its mechanical properties. Cellulose acetate is a derivative of cellulose obtained by changing one or more hydroxyl groups with acetyl groups that usually occur in C6. Insertion of acetyl group makes cellulose acetate that has higher stability and mechanical strength due to the improvement of intermolecular hydrogen bonding produced by acetyl groups. Cellulose acetate is insoluble in water, although their hydrophilicity is high due to the existence of a lot of hydroxyl groups; so it is also suitable to contact with water.

Polyelectrolytes are polymeric material which could be dissociated in aqueous solution making the polymer charged and electrical conducting. In water with an appropriate pH, polyelectrolytes can be partially and/or totally ionized depend on the weak or strong polyelectrolytes. Deposition polyelectrolytes material on the surface of cellulose acetate membrane utilizes the differences of charge between one layer and other layers. The deposition of polyelectrolyte on the surface of CA membrane is illustrated in Figure 1. Cellulose acetate being rich in hydroxyl (-OH) groups, can protonated easily by using basic solution into -O⁻. Negatively charged cellulose acetate's backbone was then immersed into polycationic solution such as poly (allyl amine hydrochloride) or gelatin (step a). Ionic interaction and hydrogen bonding occurred between CA membrane and polycationic layer. The surface of dipped membrane was immediately blocked by positive charges, and the coating process was continued by dipping the treated membrane into polyanionic solution (step b). This procedure was repeated (step c) until the desired number of layers was obtained with appropriate charge in the top layer. Because the dissociation of cadmium in water brings positive charge (cation), the top of layer were constructed into negative charge (polyanionic).

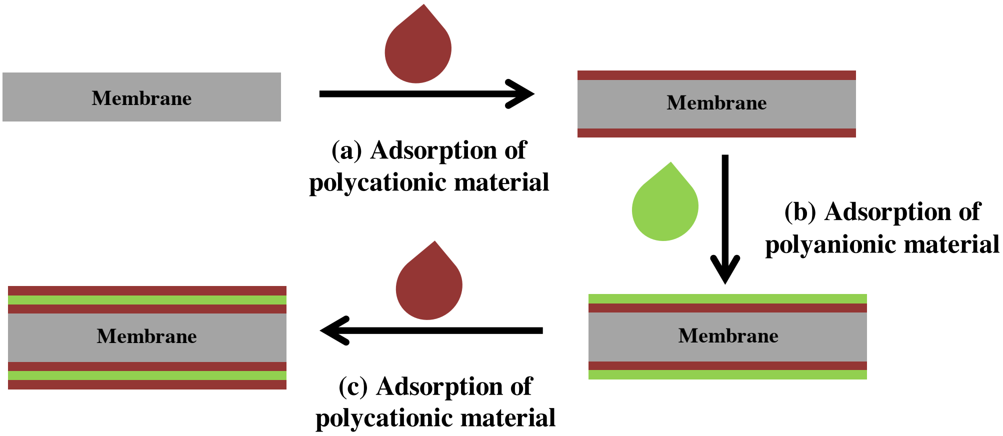

Figure 1: Deposition of polyelectrolyte on the surface of CA membrane

3.2 Characterization the Coated Membrane using ATR-FTIR

Deposition polyelectrolyte materials on the surface of CA membrane were investigated by ATR-FTIR to ensure the successfully depositing (Figure 2). CA uncoated membrane has a broad peak in 3456 cm^{-1} which indicated the presence of –OH groups and strong peak in 1736 cm^{-1} identified as carbonyl from acetyl group. Intensity of peak in 3369 cm^{-1} in CA-Gelatin-NaAlginate and 3403 cm^{-1} in CA-PAAH-PSS increased and it was identified as OH stretching. The strong bands at 1743 cm^{-1} and 1641 cm^{-1} in CA-Gelatin-NaAlginate were attributed to carbonyl (-CO stretching) and bending vibration of –NH [12]. In CA-PAAH-PSS, peak in 1733 cm^{-1} and 1636 cm^{-1} were identified as –CO stretching and –NH vibration. Sulfonyl group can be identified by wave number 1000-1200 cm^{-1} [13]. The shoulder at 1164 cm^{-1} is escribed as –CN from amine. Gelatin and NaAlginate was used as polycationic and polyanionic in this research with CA as a membrane holder.

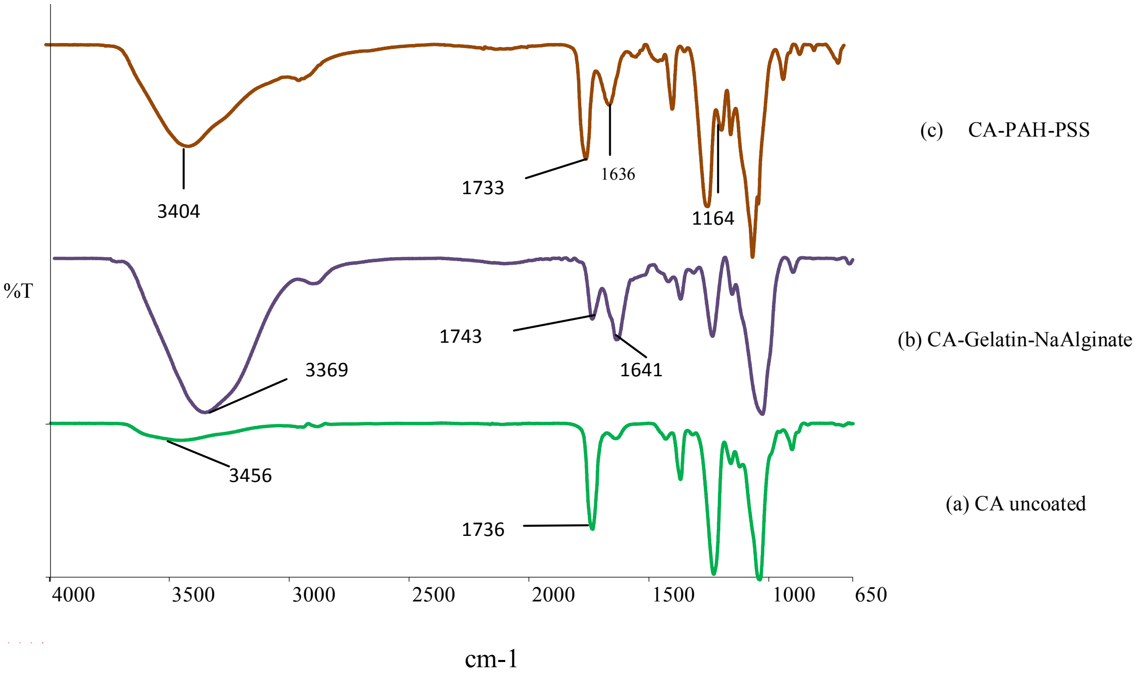

Figure 2: ATR-FTIR spectra of uncoated and coated CA membrane

3.3 Modification of Coating Materials

Four different combination of coating materials namely PAAH-PSS, PAAH-NaAlginate, gelatin-PSS, and gelatin-NaAlginate were compared with CA uncoated membrane by evaluating their performance in the extraction of cadmium ions from aqueous solution by DSPE method. The results showed that among synthetic-synthetic, synthetic natural, and natural-natural polyelectrolyte coated CA membranes, the natural-natural coated membrane showed the best performance than the others. This suggested that the combination natural-natural polycationic and polyanionic polymers have good absorption performance for Cd^{2+} and possibility open the possibility to apply to other selected metal ions. Regarding the chemical structure of the material, gelatin and sodium alginate have a lot of carboxylic groups and amino groups, not only in the branch but also in the main chain. On the contrary, synthetic-synthetic polyelectrolyte (PAAH-PSS) has the main chain dominated with –C-C- binding; so absorption performance largely depends on the amine and sulfonic group as a branch, and therefore the polarity and adsorption capacity is lower than natural coating material.

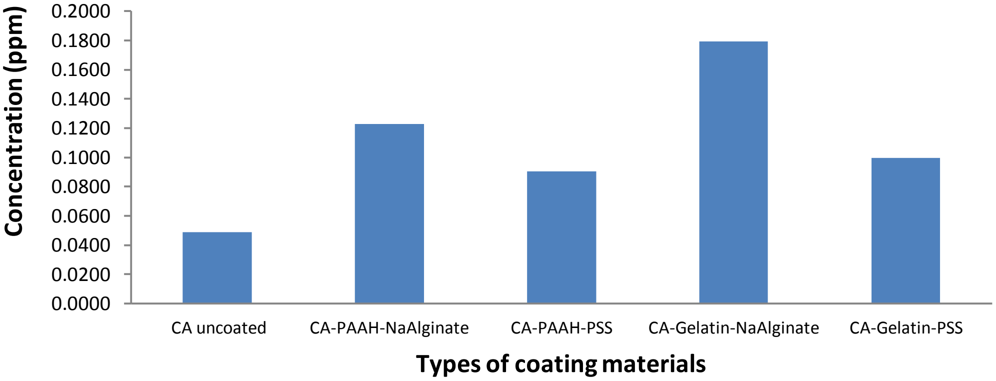

Figure3: Effect of coating materials

3.4 Effect pH of Polyelectrolyte Solution during Coating Process

pH has an influence in key role of polyelectrolytes assemblies. Under appropriate pH conditions, polyelectrolyte could be strong or less ionized that depends on pKa and pI (pH isoelectric) for polypeptide. Combination of gelatin at pH 10 and sodium alginate at pH 2.5 showed the best extraction performance. Gelatin has pI of about 8.5 and it is positively charged at low pH due to the protonation of amine to form ammonium ion [12]. On the other side, sodium alginate is strongly ionized at high pH due to its pKa (3.4-4.4) and at low pH it is aggregated as a colloid particle [14]. The number of anionic charges on sodium alginate will increase while net positive charge on gelatin was decreased and this condition can be occurred while sodium alginate dipped into gelatin solution with high pH. Thus high number of molecules of sodium alginate were adsorbed and deposited onto the gelatin layer. When gelatin was adsorbed and deposited at pH

10, all the –ONa groups in sodium alginate were in strong ionization condition and in turn, at pH 2.5 (sodium alginate solution) the previously layer adsorbed gelatin mostly rich of ammonium ion than carboxylic ion, therefore the thick films were obtained. The opposite of pH condition as solution and deposition time bring an influence effect to the film thickness [15].

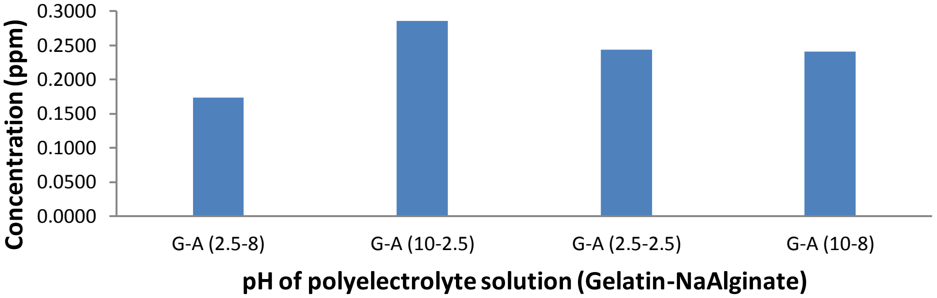

Figure 4: Effect of pH in films assemblies

4.0 CONCLUSION

In this work, polyelectrolyte-coated cellulose acetate membrane prepared by layer-by-layer assembly was introduced as a novel and inexpensive extracting phase for the determination of heavy metal ions. Among the different coating material, combination of gelatin-sodium alginate showed the best performance to extract metal ions from water. The pH of polyelectrolyte solution was also very important to affect the thickness of layers assembled. Gelatin at pH 10 and sodium alginate at pH 2.5 showed the best results of the film thickness.

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