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Efficient Phosphate Ions Removal Using Multi-Layered Poly(allylamine hydrochloride)/ Poly(styrene sulfonate) Incorporated Electrospun Cellulose Membrane

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ABSTRACT

Phosphate ion removal in wastewater via nanofiltration is a major challenge in wastewater treatment. In this study, cellulose acetate (CA) incorporated with graphene oxide/ sodium dodecyl sulphate (GO/SDS) and poly(allylamine hydrochloride)/poly(styrene sulfonate) (PAH/PSS) were synthesized using the electrospinning method. The membranes were characterized using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), water contact angle, and field emission scanning electron microscope (FESEM). In addition, a multi-layered electrospun cellulose membrane was stacked using a layer-by-layer (LbL) technique to produce a functional ultra-filtration membrane for enhanced phosphate ions removal. The results showed that the modified membranes had better hydrophilicity and lower flux rates as compared to the unmodified membrane. The incorporation of compressed multi-layered for both unmodified and modified membranes also indicated increased phosphate ions removal efficiency up to 18.99 % and 43.08 %, respectively. In addition, post-filtration revealed that phosphate was adsorbed onto the three-layer modified membrane. PAH/PSS-modified CA/GO/SDS membrane is an innovative modification of the cellulose membrane for the phosphate-contaminated water system.

Keywords: Electrospun, cellulose membrane, poly-electrolyte, phosphate ions removal, multi-layer

1.0 INTRODUCTION

Excess of phosphate in water bodies is due to activities by industrial waste, and human activities that will lead to algae blooming, which depleting dissolved oxygen in the water bodies. This process will not only kill aquatic life but also disturb the natural food chain and degrade water quality. This excess of phosphate or eutrophication commonly happens in most rivers and mostly directly affects the water supply for humans since it goes into wastewater treatment plants. Eutrophication can result in a wide-ranging ecological catastrophe in the aquatic environment, including a loss of biological variety, landscape function loss, and a possible health risk to humans (Diaz & Rosenberg, 2008). Excessive phosphate should be removed, according to the

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World Health Organization (WHO), the maximum amount of phosphate in drinking water is 5.0 mg/L, while the RDA (Recommended Daily Allowance) should not exceed 800. Therefore, the removal of phosphate ions is crucial before discharging into water bodies to maintain the water quality and save the environment.

Phosphate ions from wastewater can be removed from such a system using several techniques such as adsorption, chemical precipitation, and reverse osmosis. These techniques are highly efficient in removing matrix or toxic material from wastewater (Amin *et al.*, 2021). However, these methods are generally costly and require the use of many chemicals. On the contrary, membrane filtration of phosphate ions can provide a greener approach while being more economical. Filtration processes in industries and homes such as microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) have been used widely. The characteristics, structural composition, permeability, and rejection rate of different types of filtration and membranes were all distinctive. In addition, NF is a press-driven membrane separation technology that combines the advantages of ultrafiltration and reverse osmosis (Zhao *et al.*, 2015). NF system also provides unique advantages for multivalent ions and has a relatively low energy consumption and a high permeate flux.

Cellulose acetate (CA), a derivative of cellulose, can be easily obtained from natural resources and recycled in the environment by biodegradation (Zhou *et al.*, 2011). It is widely used in biological separation, desalination, and treatment of different water bodies due to its advantages of good biocompatibility, non-toxicity, excellent hydrophilicity, high flux, and easy film-forming (De Guzman *et al.*, 2021). However, it has poor mechanical properties and low density for water treatment operations. To generate hydroxyl groups on the surface of CA nanofibers, the membrane must be coated with GO/SDS and produce CA/GO/SDS membrane (Amin *et al.*, 2021). Electrospinning is a versatile method used to create membranes. Larger-scale preparation uses this method because of its simplicity, minimum consumption of solution, controllable fiber diameter, convenience to process, cost-effectiveness, simplicity, and reproducibility in processing the fibers, and technical advances (Thenmozhi *et al.*, 2017). Thus, CA is used as a cellulose base due to its good water affinity contributed by the hydroxyl groups, high rigidity, biocompatible, and solvent resistance (Abedini *et al.*, 2011).

Graphene oxides (GO) have lots of interest due to the fact of their constrained dispersibility, as well as having lots of preferred reactive sites for special chemical modification. GO promotes an extremely high surface area that can help the material to have an excellent adsorption capacity. Moreover, the oxygen-containing functional groups and aromatic basal planes within the GO network help GO to actively attach to several organic and inorganic species via electrostatic interactions, hydrogen bonding, and π-π stacking interactions. Moreover, Sodium dodecyl sulfate (SDS) can be used as a surfactant in the production of graphene which can promote the ionic interactions between the sulfate, nitrate, fluoride, perchlorate, and lithium with graphite.

To generate more hydroxyl groups and make the filtration better, CA nanofiber must be incorporated with GO/SDS to produce CA/GO/SDS membrane (Amin *et al.*, 2021). Meanwhile, the structure of the CA/GO/SDS membrane is more compact and has a smaller size of pore than the CA membrane which makes it a potentially better filtration composite. Still, nano-sized molecules are able to permeate through the filtration system. Multiple layers of membrane are technically superior to a single-sheet membrane. In this study, the layer-by-layer (LbL) technique is introduced to coat several layers of CA/GO/SDS on the primary membrane and subsequently, with several layers of PAH/PSS. The effect of numbers or layers of polyelectrolyte multilayer film on the membrane properties is that the deposited number of layers on the substrate has a great influence on the permeation performance, where the higher the number of layers, the higher the resistance for mass transfer and flux decline, the higher the salt rejection due to the dense of polyelectrolyte multilayer films (Saqib & Aljundi, 2016). Therefore, PAH/PSS, negatively and positively charged compounds are suitable surface modifiers for the existing cellulose membrane. LbL is also utilized to accommodate several layers of PAH/PSS which can increase the salt rejection and flux decline on the membrane, and thus increase the efficiency of phosphate ion removal in wastewater via nanofiltration. Of all the LbL techniques, the self-assembly is the most costly and energy-efficient which involves alternating consecutive immersion (dipping) of a solid substrate into opposite charge solutions (Saqib & Aljundi, 2016).

Therefore, this work implements the use of cellulose acetate (CA) incorporated with graphene oxide/ sodium dodecyl sulphate (GO/SDS) using an electrospinning method and next, functionalized through immersion with poly(allylamine hydrochloride)/ poly(styrene sulfonate) (PAH/PSS) to produce a functional ultra-filtration membrane. Multiple layers of CA/GO/SDS membrane are compressed to create even layers. In addition, these membranes are stacked using an L-b-L technique to create a multi-layered PAH/PSS cellulose membrane for enhanced phosphate ions removal. Single-layered and multi-layered membranes were compared based on their characteristics and phosphate ion removal efficiency.

2.0 METHODS

2.1 Materials

The preparation of fiber CA/GO/SDS membrane for removal of phosphate ion was done by using cellulose acetate powder (CA), graphene oxide and sodium dodecyl sulphate (GO/SDS), N,N-dimethylacetamide (DMac), acetone, and distilled water. All analytical grade materials and solvents used in this experiment were commercially available and obtained from Sigma-Aldrich and Merck. In the layer-by-layer method, poly (allylamine hydrochloride) (PAH)/poly (styrene sulfonate) (PSS) were prepared in NaCl solutions. All the chemicals were used without further purification.

2.2 Preparation of CA/GO/SDS Membrane

Cellulose acetate solution was prepared by mixing 5.8 mL acetone and 2.9 mL dimethylacetamide into 1.3 g of CA (13% wt/wt) simultaneously. The solution was stirred by using a magnetic stirrer at 60°C to make sure all of the CA powder had been dissolved. After that, the preparation of GO/SDS solution was prepared by adding 5.8 mL acetone and 2.9 mL dimethylacetamide into the mixture of GO and SDS. Then, the GO/SDS solution prepared was added drop wisely into a CA solution while stirring using a magnetic stirrer when it was already at room temperature. Then, the CA/GO/SDS solution was loaded into a 10 mL syringe pump to be electrospun. A syringe pump was used to feed the polymeric solution at the speed of 2 mL/h through a stainless needle with a diameter of 18G. A distance of about 15 cm was set between the needle and the collector. Baking paper was wrapped to cover the drum and 18 kV voltage was applied to the system. Relative humidity and temperature in the system were controlled to achieve consistency in electrospinning. CA/GO/SDS membrane was modified by compressing one layer and three-layer membrane to increase the efficiency of filtration due to the decreasing size of the pore. The compression of one layer of the membrane started with peeling the membrane and cutting it to a 6.5 cm x 6.5 cm dimension. Then, the membrane was covered using aluminium foil to be compressed using a heat press machine under a pressure of 5 Pa at 60^{o}C for about 15 minutes. For the three-layer membranes, the compressed membranes were combined one by one to get a three-layer membrane.

2.3 Modification of CA/GO/SDS with Polyelectrolytes

Modification of the CA/GO/SDS membrane was done using multi-layered poly(allylamine hydrochloride)/ poly(styrene sulfonate) through functionalization of the membrane surface during the immersion process. The homogeneous compressed CA/GO/SDS electrospun membrane is dipped (immersed) in a dilute solution of poly (allylamine hydrochloride) (PAH), the positively charged and similar membrane is dipped next in polystyrene sulfonate (PSS), and the negatively charged polyelectrolyte solutions, which count as two layers or 1 bi-layer. This step is repeated until it reaches a 7-layered PAH/PSS deposited on the electrospun membrane which is named CA/GO/SDS/PAH/PSS.

2.4 Characterization of Composite and Modified Membrane

Single-layered and multi-layered CA/GO/SDS and CA/GO/SDS/PAH/PSS were characterized using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), water contact angle, and field emission scanning electron microscope (FESEM). Lastly, the phosphate concentration was determined before and after filtration by the absorbance or ortho-phosphate at λ max of 690 nm and test number 1-77 by using VIS II spectrophotometer nanocolor.

2.5 Removal Efficiency

Single-layered and multi-layered membranes were cut into a circular shape that fits in the membrane holder of the filtration system. The filtration system was rinsed with distilled water for 30 minutes. After the rinsing process, 500 mL of 10 ppm phosphate solution was pumped into the filtration cell by using a stainless-steel gear pump with a pressure of 0 bar. The experiment must be at room temperature and in total re-circulation with the permeate stream re-circulating back into the phosphate solution feed tank. Then, distilled water was used to clean the feed tank between each filtration with different concentrations of phosphate solution for 5 minutes at 0 bar pressure until it was completely clean. Lastly, the determination of the removal efficiency (%) was done by calculating the difference in of concentration phosphate solution before and after filtration. The experiment was repeated at 50 ppm and 100 ppm phosphate solutions.

3.0 RESULTS AND DISCUSSION

3.1 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

FTIR spectra of both membranes at different layers were compared. Figure 1 shows the spectra of the membranes. The unmodified electrospun membrane showed the presence of C=C aromatic at 1639 and 1431 and absorption peak of carbonyl, C=O peak at 1741 stretching vibrations. In addition, there was a presence of hydroxyl group at 3200 - 3500. There was also a C-H peak at 2944 corresponding to the C=C aromatic in GO/SDS. Different layers of electrospun CA/GO/SDS modified with PAH/PSS were also characterized to confirm their attachments. One-layer modified membrane gave an N-H peak at 3457 that is redundant with the O-H peak, which makes it show a medium broad peak in the spectrum, while a three-layer modified membrane gave N-H peaks at 3453 which also found and shown by, who found the presence of N-H peak at the 3453 after their mixed-matrix membrane was incorporated with an amino functional group. Both modified membranes also show there was the presence of a C-N peak at 1173 and 1171 at one-layer and three-layer modified membranes, respectively.

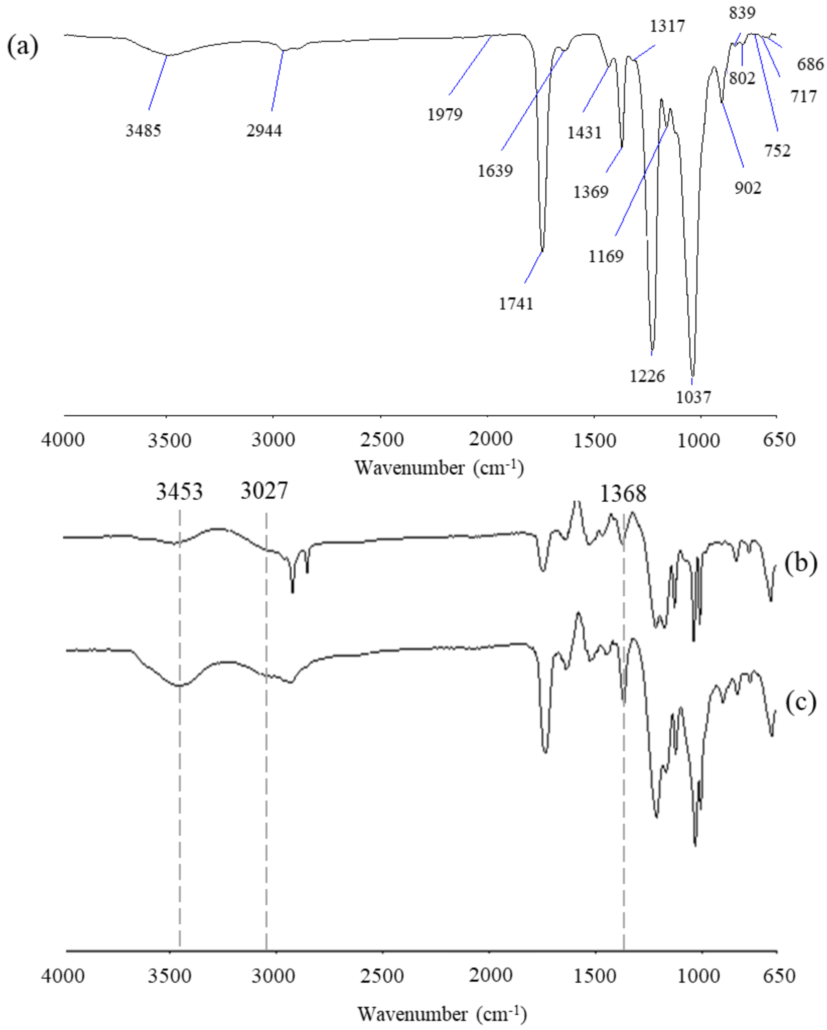

Figure 1 FTIR spectra of (a) unmodified single-layered CA/GO/SDS, (b) single-layered CA/GO/SDS/PAH/PSS, and (c) multi-layered CA/GO/SDS/PAH/PS

One layer of modified membrane gave a C=C aromatic peak at 1641 and 1462, and a C-H aromatic peak at 2955. The wavelength of the C-H aromatic peak was lower than the theoretical value due to delocalized electrons in the aromatic structure. It also showed a spectrum peak at 1368. On the other hand, the three-layer membrane gave a C=C aromatic peak at 3453, a C-H aromatic peak at 3027, and a peak at 1368. This finding can be confirmed and compared with the FTIR results obtained by Dong (Dong *et al.*, 2021) who showed the success of incorporation of SO3 functional group onto their membranes. The differences between one-layer and three-layer membranes are the intensity of each peak as the complexity of the membrane increases as the number of layers increases. This is also in line with the previous findings by other researchers like Gomes (Gomes *et al.*, 2012) which showed that the intensity of the FTIR peak increased with the increased number of layers of polymer deposited on the original support. The properties of the CA/GO/SDS membrane modified with PAH/PSS did not disrupt even though three-layer membranes were being compressed under 60°c and 4 kPa, as they exhibited a similar spectrum.

3.2 Water Contact Angle

Water contact angle was performed to determine the wettability of each unmodified membrane which were one layer (non-compressed), one layer (compressed), and three layers (compressed). The wettability of the unmodified membranes is tabulated in Table 1. In addition, modified membranes with PAH/PSS were characterized using the water contact angle at one layer and three layers as depicted in Table 2.

Table 1 Water contact angle of unmodified and modified CA/GO/SDS membrances at different layers

Layers	**Contact angle (°)**		
	Left	**Right**	**Average**
1 (non-compressed)	129.12	129.24	129.18
1 (compressed)	0	0	0
3 (compressed)	17.22	17.22	17.22

Table 2 Water contact angle value for modified membrane

Layers	**Contact Angle (°)**		
	Left	**Right**	**Average**
1	2.60	2.60	2.59
3	12.90	12.90	12.87

The one-layer (non-compressed) unmodified membrane showed 90° more hydrophobic at 129.18°. The water droplet on the membrane was retained and did not penetrate the membrane. As for one layer (compressed) membrane, it portrayed a lower angle than 90° at 0° indicating a highly hydrophilic membrane. The water droplet rapidly penetrated the membrane as soon as the water droplet was dispensed from the needle of the instrument. The three layers (compressed) also showed an angle lower than 90° at 17.22° which was also hydrophilic. Here, the water droplet penetrated the membrane at a slower rate as the water was dispensed from the needle and retained momentarily at the aforementioned angle for 1 minute before penetrating the membrane completely. These results showed that the compression process of membranes has altered the hydrophilicity of the membranes. This behavior was also recorded by Aldakheel (Aldakheel *et al.*, 2020) when they applied the compression technique to their gas diffusion layer membrane. It is stated that the compression activity onto the membranes will alter the surface roughness of the membrane, thus leading to the decrease of hydrophobicity.

It was observed that one layer (compressed) membrane was more hydrophilic than three layers (compressed). Thus, a layers (compressed) membrane is more suitable for filtration as fast penetration of water has to be avoided. On the contrary, one layer (non-compressed) membrane is probably not suitable for filtration due to its hydrophobic properties. Additionally, one layer (compressed) has a better wettability in contact angle measurement compared to three-layer (compressed) and one-layer (non-compressed) membranes. Water contact angle measurement was also performed after the layer-by-layer method on the membrane modified with PAH/PSS as shown in Table 2.

The hydrophilicity of the membrane was tested on one and three layers of electrospun membrane CA/GO/SDS/PAH/PSS. One layer of the modified membrane gives more hydrophilicity as it gives a lower contact angle, 2.59° as compared to three layers of electrospun membrane modified with PAH/PSS as it gave a contact angle, of 12.87°. The results of the contact angle measurements were the reasons for the flux rate of one layer of the electrospun membrane being higher than three layers of the electrospun membrane due to its higher hydrophilicity properties. The number of polyelectrolytes (PAH/PSS) deposited onto the membranes plays a vital role in the thickness of the membrane. The thickness will certainly influence the wettability of the membrane surface which was also discovered by Ciejka (Ciejka *et al.*, 2021) where the higher number of PAH deposited on the membrane as polycation will increase the contact angle values.

3.3 FESEM

The morphology of CA, CA/GO/SDS, and CA/GO/SDS/PAH/PSS surfaces was determined at 10 × magnification as can be referred to in Figure 2. A typical porous structure was observed for all samples. The difference in morphology between CA and CA/GO/SDS was due to the CA membrane which has a smooth and uniform fiber structure as depicted in Figure 2(a). Meanwhile, the CA/GO/SDS membrane in Figure 2(b) has rough fibers and a more compact arrangement. The CA membrane has a smaller diameter fiber than the CA/GO/SDS membrane due to the decreasing hydrophilicity of GO/SDS and the cohesion between the GO/SDS and CA.

Surface morphology of unmodified electrospun CA/GO/SDS yielded smooth and uniform fiber diameter ranging roughly from 200-350 nm, but after immersion process of the electrospun membrane with PAH/PSS, the morphology was observed as rough and varied pores diameter as shown in

Figure 2(c). The immersion process with polyelectrolyte was an instant method where the method would result in an uneven modification on the membrane surface, and it yielded an average of 200 nm pore size and several larger pores diameter. The fibrous fiber of the CA/GO/SDS/PAH/PSS membrane can be observed from the image; however, due to the membrane surface modification with PAH/PSS, the morphology of the fibers was concealed by the deposition of polyelectrolytes. These changes in surface appearances could be a good indicator of the increasing toughness of the modified membrane. This phenomena were also reported and consistent with previous studies by Chandra (Chandra *et al*., 2018) and Baig (Baig *et al*., 2021). Figure 2(d) shows the aerial view of the modified membrane which shows the whitish flat membrane sheet indicating a good membrane formation.

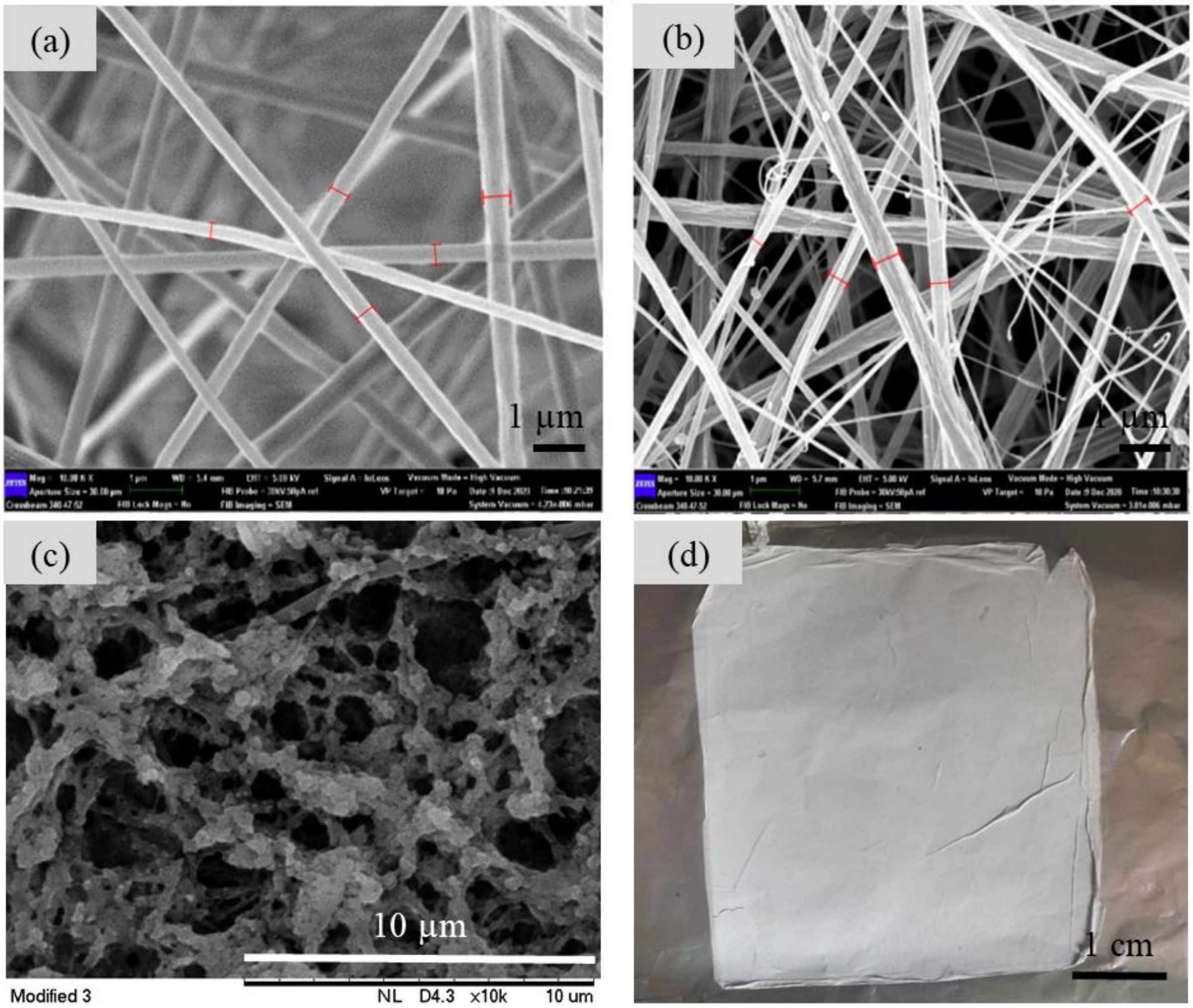

Figure 2 Surface morphologies of (a) CA, (b) CA/GO/SDS, (c) CA/GO/SDS modified with PAH/PSS, and (d) top-view of the modified membrane. The red marks indicate the width of the electrospun fibers

3.4 Phosphate Ions Removal Efficiency

The filtration of phosphate ions using compressed one layer and three layers of unmodified and modified membranes was performed using a filtration system developed by Advanced Membrane Technology Centre (AMTEC), Universiti Teknologi Malaysia. The capacity of the membranes to remove phosphate ions was determined using an aqueous phosphate solution. The removal of phosphate ions was conducted using three different concentrations of 10 ppm, 50 ppm, and 100 ppm. The initial and final phosphate concentrations were determined via a UV-visible spectrophotometer and nanocolor kit. Figure 3 indicates the phosphate colour reduction after filtration with unmodified and modified CA/GO/SDS membranes.

There is no removal for one layer membrane due to the high hydrophilicity of the membrane which also contributed to the higher flux rate of the filtration. Phosphate ions cannot be trapped by one layer of membrane. Thus, the efficiency for removing phosphate ions was 0%. One layer of compressed membrane might not be efficient for removing phosphate ions using filtration due to less the fibrous structure of the cellulose and a very thin layer of membrane. Adversely, the high flux rate was able to tear through the membrane making the membrane incapable of filtering the phosphate. A similar observation was also seen for compressed one-layer modified CA/GO/SDS membrane with PAH/PSS. No colour reduction was observed indicating 0% removal efficiency. From the results obtained, the modification of the electrospun membrane with PAH/PSS decreased the flux rate compared to the unmodified membrane at 191 ml/min, 164 ml/min, and 135 ml/min for 10 ppm, 50 ppm and 100 ppm phosphate solutions, respectively, while unmodified membranes with the flux rate of 200 ml/min, 205 ml/min, and 198 ml/min, for 10 ppm, 50 ppm and 100 ppm, respectively, as depicted in Table 3. Although the flux rate decreased, the efficiency did not increase. This was also an indicator that multi-layer membrane modification was required.

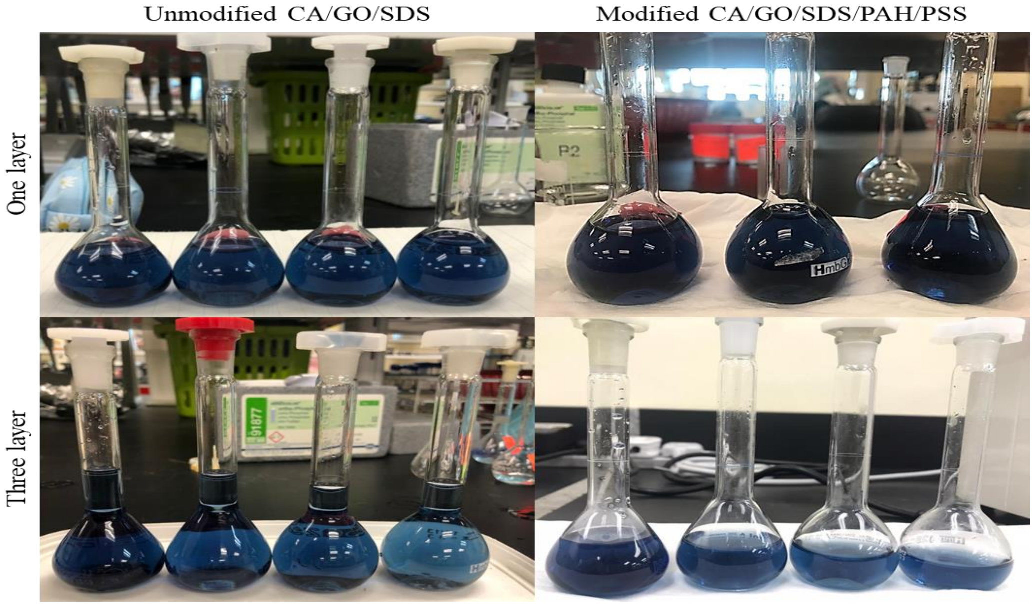

Figure 3 Colour reduction of phosphate ions using the unmodified and modified membranes at one and three layers. From left to right are the control colour, 100 ppm, 50 ppm, and 10 ppm

Next, the filtration process was done using three layers of both unmodified and modified compressed membranes. The filtration results for 10 ppm, 50 ppm, and 100 ppm phosphate solutions are shown in Table 3. Based on the result, the higher concentration of phosphate will give a better efficiency for removing phosphate ions using a three-layer membrane. After the PAH/PSS modification, the efficiency of phosphate removal was clearly significant as observed in Figure 4. The removal efficiency was increased as the concentration of phosphate solution increased since ion phosphate has higher competition in higher concentration to diffuse through the membrane pores. This is consistent with the adsorption study of phosphate ions at higher concentrations which have been demonstrated by Xu (Xu *et al.*, 2020) and Bhatti (Bhatti *et al.*, 2018). It was clearly stated by these researchers that the phosphate ions removal capacity was strongly dependent on the initial concentration of the phosphate solutions treated. Other than that, it can also be observed that the flux rate was also improved as the flux rate value decreased for a three-layer membrane compared to a one-layer membrane. Table 3 summarizes the phosphate removal efficiency using different modifications and layers of membranes.

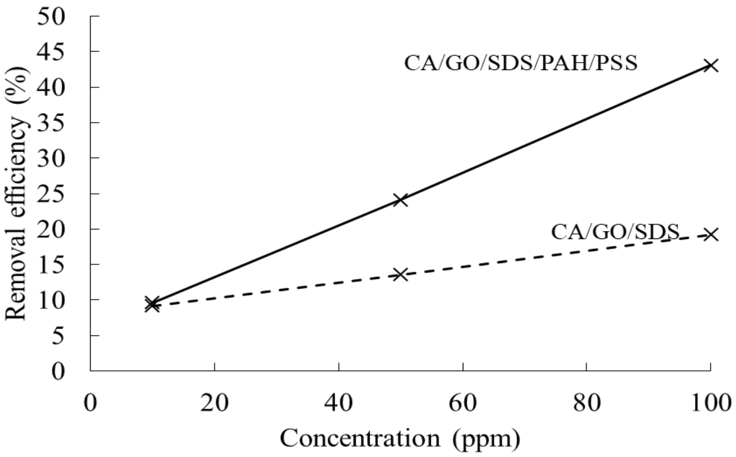

Figure 4 Phosphate ions removal efficiency at different phosphate concentrations for three layers of unmodified and modified membranes

Table 3 Phosphate ions removal efficiency of one layer and three layers of unmodified and modified membranes

Type of membrane	Concentration (in ppm)			Flux rate (mL/min)	Efficiency (%)
	Phosphate	Initial	Final		
Unmodified CA/GO/SDS one layer	10	8.13 ± 0	8.13 ± 0	200	0
	50	40.43 ± 0	40.43 ± 0	205	0
	100	81.25 ± 0	81.25 ± 0	198	0
Unmodified CA/GO/SDS three layers	10	8.13 ± 0	7.38 ± 0.45	60	9.23
	50	40.43 ± 0	34.9 ± 0.1	47.7	13.67
	100	81.25 ± 0	65.81 ± 0.65	44	18.99
Modified CA/GO/SDS/ with PAH/PSS one layer	10	8.13 ± 0	8.13 ± 0	191	0
	50	40.63 ± 0	40.63 ± 0	164	0
	100	81.25 ± 0	81.25 ± 0	135	0
Modified CA/GO/SDS/ with PAH/PSS three layer	10	8.00 ± 0	7.24 ± 0.05	60	9.625
	50	40.43 ± 0	30.86 ± 0.13	47.7	24.11
	100	81.25 ± 0	46.18 ± 0.18	44	43.08

3.5 Modified Membrane Analysis after Phosphate Filtration using FTIR

There was no change in the FTIR spectra before and after the filtration at the one-layer modified membrane. There was no change in the band intensity confirming zero phosphate removal. Interestingly, a slight difference was noticed at 3600 cm^{-1} where the -OH functional group seemed to appear slightly after filtration. This confirmed the hydrophilicity of the membrane post-filtration where some water molecules were adsorbed by the membrane. As expected, FTIR spectra of the three-layered membranes showed significant differences. They showed greater intensities at wavelengths ranging from 700 to 1800 cm^{-1}. The peak difference arose due to the trapping of phosphate ions in the membrane during filtration. Figure 5 demonstrates the difference in the FTIR band formation before and after the phosphate filtration using different layers of the modified membrane. This is consistent with the recent finding by Zhang (Zhang *et al*., 2021) who investigated the phosphate-loaded behavior of the lanthanum hydroxide adsorbents using the ATR-FTIR method in the frequency between 900 cm^{-1} to 1200 cm^{-1}.

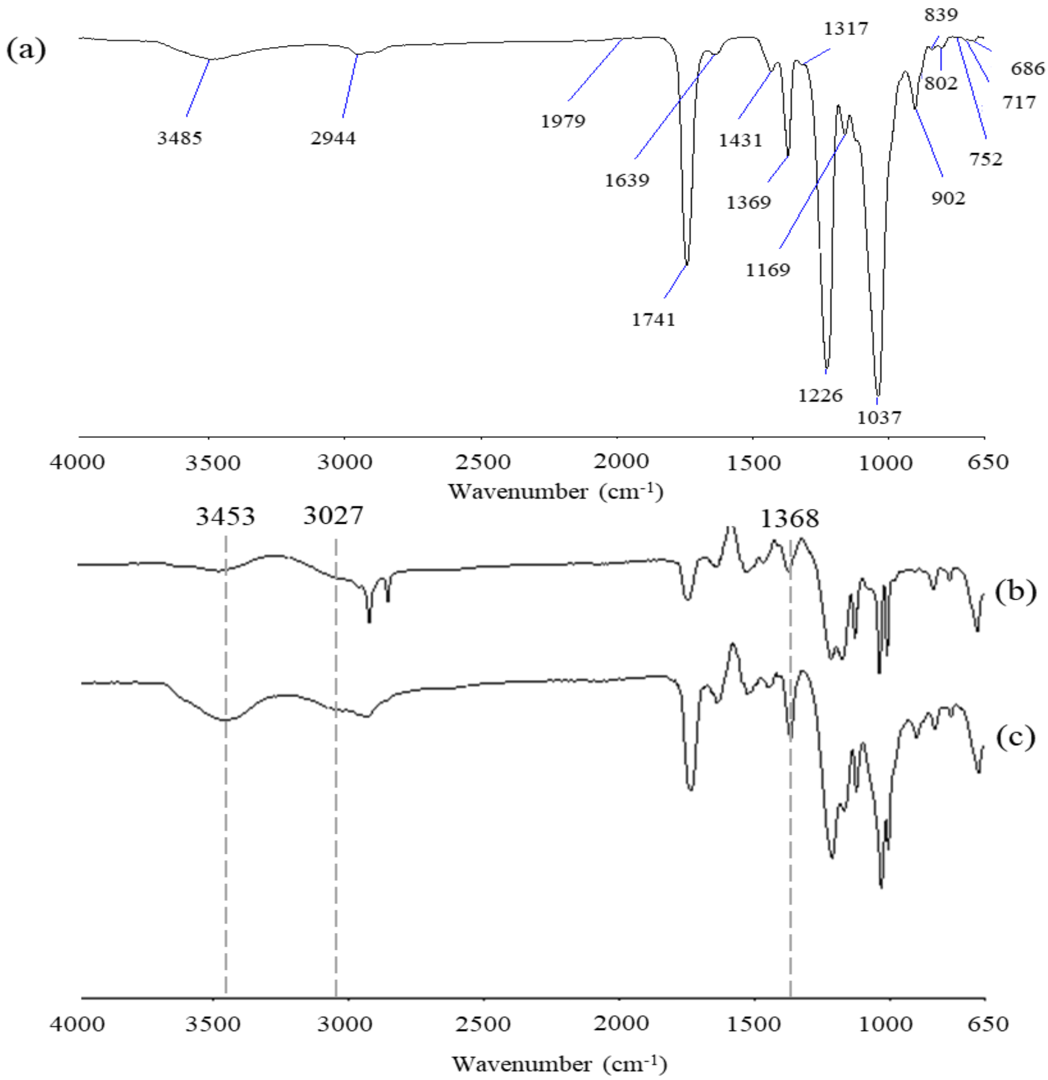

Figure 5 FTIR spectra of (a) one layer modified membrane and (b) three layer modified membrane, before and after the filtration of phosphate

4.0 CONCLUSION

Multi-layered electrospun cellulose modified and unmodified membranes had improved in their physicochemical properties such as decreased hydrophilicity as compared to single-layer membranes via water contact angle assessment. The modification of the CA/GO/SDS membrane with PAH/PSS was confirmed by the changes in the morphological structure and the formation of new FTIR peaks around 3450 cm^{-1} and 1171 cm^{-1} of the post-modified membrane. The high flux rate was also reduced due to the multiple layers implication of the cellulose membranes. Also, post-modification of CA/GO/SDS membrane with PAH/PSS showed an increase of more than 30% in the removal efficiency of phosphate at three-layered membranes. CA/GO/SDS/PAH/PSS multi-layered membrane has proven as a great filter for phosphate-contaminated water systems with low hydrophilicity and lower flux rate.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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