

Fabrication and Surface Modification of PVDF Membrane for Zinc and Cadmium ions Removal

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ABSTRACT

Rapid industrialization and urbanization in this era have leads to water pollution and worsen the water scarcity. In this study, a modified poly(vinylidene fluoride) (PVDF) membrane was used to remove zinc and cadmium ions from solutions with concentrations of 10 ppm and 50 ppm, respectively. The hydrophobic PVDF support membrane was modified by a Layer-by-Layer (LbL) deposition technique with polycation, chitosan, and polyanion, poly(styrene sulfonate) to increase its hydrophilicity and metal ions rejection percentage as well as decreasing membrane fouling. Chitosan's hydroxyl and amine groups created an electrostatic interaction with the sulfonate group of poly(styrene sulfonate). The polyelectrolyte-modified membranes were characterized by using infrared spectroscopy and water contact angle measurements. The membrane filtering experiments revealed that the 5, 6, 9, and 10 layers of polyelectrolytes deposited membranes retained zinc/ and cadmium ions well, demonstrating the practicality of polyelectrolytes deposition on organic membranes because all rejection percentages were greater than 25%. The robustness of modified membranes was also tested by repeating 10 consecutive filtrations with the same membrane, and it was demonstrated that the modified membrane still had a higher rejection percentage that was two times higher and was less likely to foul due to less decreasing trends in permeate flux when compared to the unmodified membrane. It is expected that electrostatic repulsion and attraction as well as the steric effect were the primary mechanisms by which the modified membrane removed metal ions from contaminated solution.

Keywords: Heavy metal removal, poly(vinylidene fluoride), chitosan, poly(styrene sulfonate), layer-by-layer

1.0 INTRODUCTION

Heavy metal pollution is one of the harmful threats towards the ecosystem due to their hazardous consequences, non-biodegradability and severe risk towards human health due to

bioaccumulation in the living organisms (Ibrahim *et al.*, 2020). According to the previous report, an approximate 80 % of polluted wastewater from several industry such as refining, metal plating, painting, and textile has been discharged into the

water system without a proper treatment (Alizadeh *et al.*, 2018). The most common heavy metal found in wastewater are arsenic, copper, lead, zinc, cadmium, chromium, iron and manganese (Shrestha *et al.*, 2021). These heavy metals can cause adverse effect towards human health when being inhaled, ingested or contacted dermally which consequently resulted in liver damage, respiratory and cardiovascular diseases (Bharti *et al.*, 2022; Malas *et al.*, 2020).

Therefore, the removal of heavy metal from the discharged water has become an important topic among the researchers in order to fulfil the environmental regulations. In fact, a variety of separation techniques, including ion exchange, adsorption, chemical precipitation, coagulation-flocculation, flotation, electrochemical methods, and membrane filtration, have been used to remove heavy metals. (Azimi *et al.*, 2017) (Upadhyaya *et al.*, 2018). Among these separation techniques, membrane filtration has received more attention due to its flexibility in separation, concentration and purification of huge diversity materials in many industries, simplicity as no phases change involve, mild operating condition and space saving. The porous structure and lower cost of polymeric membranes have made them an ideal choice for the production of different types of membrane such as ultrafiltration (UF) and nanofiltration (NF) in wastewater treatment (Efome *et al.*, 2019). A few types of polymeric materials have been used for the membrane preparation such as cellulose acetate (CA), polyvinylidene fluoride (PVDF), polyethersulfone (PES), polysulfone (PSU), and polypropylene (PP) (Changani, 2020) (Gohil and Choudhury, 2018). Among the materials, PVDF is widely applied in the UF application due to its high

mechanical strength, excellent chemical resistance and thermal stability, as well as high organic selectivity (Warsinger *et al.*, 2018). Nevertheless, the hydrophobic nature and fouling tendency has limited its application in wastewater treatment system. Thus, several modification methods such as chemical grafting (Shen *et al.*, 2018), redox-initiated graft polymerization (Straub *et al.*, 2020) and polyelectrolyte (PE) multilayers self-assembly using LbL approach (Maiti *et al.*, 2022) have been applied to improve the PVDF performance

In this study, PVDF membrane has been fabricated with PE using LbL modification method. The LbL method was consisted of alternate adsorption of cationic PE (chitosan) and anionic PE (polystyrenesulfonate), which allow to achieve controllable layer properties in term of hydrophobicity, surface charge and porosity. ATR-FTIR spectroscopy was used to prove the successively formation and growth of the PE multi films onto the surface of PVDF membrane while water contact angle (θ) was applied to examine the change of wettability of the PE-modified PVDF membrane from a hydrophobic PVDF pristine membrane. In this case, the hydrophilic layers deposited on the PVDF membrane surface are crucial to reduce the contact between membrane surface and the sources of pollutants thus diminishing fouling. Besides, the efficiency of separating performances of unmodified membrane and PE-modified membranes at different concentrations with different number of PE deposition layers were compared by evaluating their rejection percentage and permeate flux. Over and above that, the robustness between unmodified membrane and PE-modified membranes were also tested with both zinc and cadmium solutions

over 3.5 hours which represented ten successive filtrations.

2.0 EXPERIMENTAL

2.1 Preparation of Support Membrane and Polyelectrolyte

The PVDF membrane with 21 wt.% concentration was prepared by dissolving 21 g of PVDF in 71 g of dimethylacetamide (DMAc) organic solution under continuous stirring for 48 hours. The chitosan (CS) PE solution was obtained by dissolving 1.25 g of CS powder in 0.25 L of 0.1 M HCl and the pH was adjusted to 5.5 using 2.0 M NaOH. Simultaneously, the anionic PE, poly(styrene sulfonate) (PSS) solution was prepared by dissolving 1.25 g of PSS powder in 0.25 L of 0.02 M NaCl. Both mixtures were stirred until the polymers have completely dissolved in their solvent to obtain concentration of 5 g/L.

2.2 Modification of Membrane

In this study, LbL self-assembly approached was performed to modify the PVDF membrane. The modification of PVDF flat sheet membrane was started by immersing the sample in the form of round shape with 5.6 cm diameter into the CS solution. Then, the CS adhered membrane was rinsed with deionized water two times for one minute to remove any loosely bound PE before immersion into the next polyanion, PSS solution. The negatively charged PSS was adhered on the positively charged chitosan layer through electrostatic forces after the immersion. The time taken for each PE layer to be deposited on membrane was fixed to 30 minutes. A consecutive immersion and rinsing steps were repeated in order to get 5, 6, 9 and 10

layers of PE-modified membranes. The modified PVDF membranes were denoted as PVDF- x , where x is the number of polyelectrolyte layers deposited on the membrane.

2.3 Characterization of Membrane

Fourier transform infrared spectroscopy–attenuated total reflectance (FTIR–ATR) characterization was performed using Fourier Transform Infrared (FTIR) Spectrophotometer (IRTracer-100 Shimadzu, Japan). All spectra were recorded at room temperature within the range of 650 to 4000 cm^{-1} to determine the functionalized groups of the modified PVDF membrane. The water contact angles of the membranes were measured using a DropMeter A-100 contact angle system (Maist Vision Inspection & Measurement Co. Ltd.) to characterize the membrane wetting behaviour. A water droplet at 2 μL was deposited on the dry membrane using a micro syringe. Membrane was raised until it was in contact with the water droplet. A microscope with a long working distance 6.5 \times objectives was used to capture micrographs. The water contact angle (θ) was automatically measured by the computer which connected to contact angle meter. The water contact angle (θ) measurements of the modified membrane and the unmodified membrane were also compared.. Both of the membrane characterization methods were repeated for at least 4 times by detecting 4 random pieces of membrane under FTIR-ATR spectrometer and placing 4 water droplets on membrane in order to collect the average measurements thus minimize the experimental error.

2.4 Filtration Measurement

Filtration measurement was carried using a cross-flow separation unit

according to the literature (Mokhter *et al.*, 2017). The tangential filtration was performed by placing the membrane in a planar module crossflow filtration system in Advanced Membrane Technology Research Centre (AMTEC) as shown in Figure 1. Prior to the filtration, the feed tank was filled with 0.5 L of heavy metal ions sample solution. Different concentration (ppm) of sample solutions for zinc and cadmium were prepared artificially by mixing proper amount of their respective salt, ZnCl₂ and CdCl₂ into proper amount of deionized water to obtain the desired concentration (10 ppm and 50 ppm) as the feed. 0.2 M of HCl and NaOH were utilized to adjust the pH of these sample solutions to pH 5 as



Figure 1 AMTEC crossflow filtration system

2.5 Permeate Flux and Rejection Percentage Measurements

The permeate flux for metal solution (J_v) and pure water (J_w) in unit of ms^{-1} was obtained by weighing the stabilized permeate solution which was collected after 10 mins of pumping at 6 bars of TMP using Equation 1:

$$J_v(J_w) = \frac{m_p(g)}{\rho(g.m^{-3})S(m^2)t(s)} \quad (1)$$

where m_p (g), ρ (g.m^{-3}), t (s), and S (m^2) represents the permeate mass, density of solution, permeation time and effective area of membrane, respectively. The concentrations of cation in the permeate solution (C_p) and in the initial solution (C_0) were determined by atomic absorption spectrometry using a PinAAcle 900 Series AA Spectrometers (Perkin Almer). The metal ions rejection percentage, R , can be determined by using Equation 2:

$$R (\%) = 100 \times \left(1 - \frac{C_p}{C_0} \right) \quad (2)$$

3.0 RESULTS AND DISCUSSION

3.1 Physicochemical Properties

FTIR-ATR measurement was performed to identify the structural difference between the pristine and modified PVDF membrane. Figure 2 illustrates the FTIR-ATR spectra in the range of $4000\text{-}650 \text{ cm}^{-1}$. The pristine PVDF membrane exhibited several IR peaks at the bands corresponded to stretching and vibration bands of $-\text{CH}_2$ groups (3024 , 2982 and 1401 cm^{-1}), and the stretch of $-\text{C-F}$ group (1177 cm^{-1}) (Lu *et al.*, 2017). In particular, all modified PVDF membranes exhibited two sharp peaks at 3390 and 1639 cm^{-1} which corresponded to $-\text{NH}$ and $-\text{NH}$ group vibration bends together with the $-\text{C}=\text{C}$ bond, respectively (Sun *et al.*, 2018). A similar trend of IR peaks was observed in all the PE-modified PVDF, suggesting a successful PE modification.

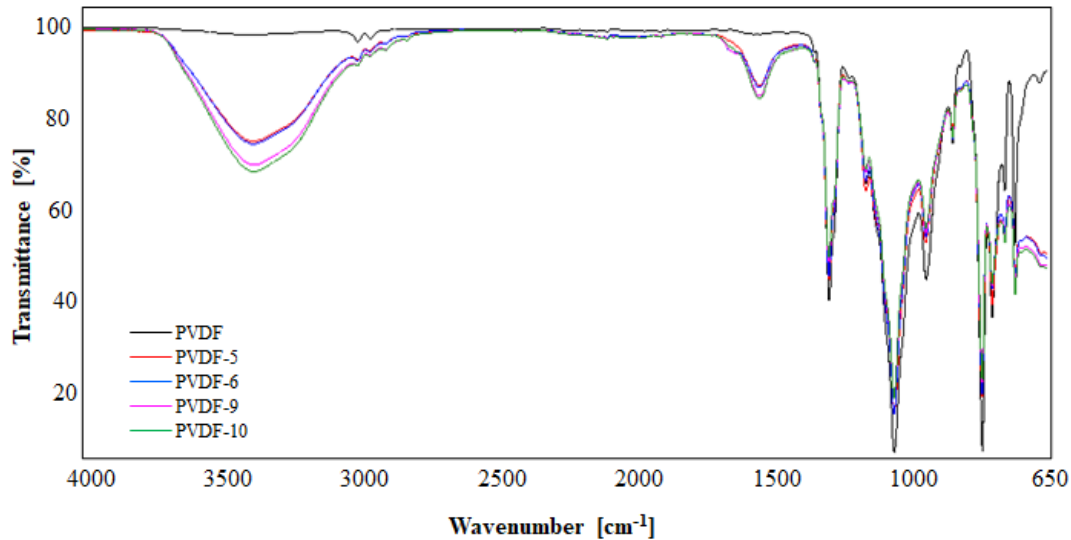


Figure 2 FTIR-ATR spectra of pristine and modified PVDF membranes

The water contact angles of the membranes are studied to evaluate the surface hydrophilicity of the pristine and PE-modified PVDF membranes and the results are presented Figure 3. The pristine PVDF exhibited a water contact angle of $82.9^{\circ} \pm 1.0^{\circ}$ and the value decreased to $68.0^{\circ} \pm 1.1^{\circ}$ and $66.1^{\circ} \pm 0.1^{\circ}$ after five and six PE layers deposition, respectively. This result was attributed to the hydrophilic character of chitosan structure which consisted of numerous hydroxyl groups and amine groups. Meanwhile, a slight increase was observed in nine layers PE deposition ($69.7^{\circ} \pm 1.1^{\circ}$) followed by smallest value of water contact angle for 10 layers PE deposition ($62.3^{\circ} \pm 2.1^{\circ}$). This result suggests that polyanion, PSS which contained sulfonate group has provided slightly more hydrophilicity properties to the PVDF membrane than the polycation, chitosan. The PSS polyelectrolyte is acidic and known as homogeneous phase and non-

conductive PE. It contains hydrophilic properties that can enhance the membrane performance for the heavy metals rejection due to the presence of sulfonic acid functional group. The amount of sulfonic acids added on the PVDF membrane surface is proportional to the hydrophilicity of the membrane (Zhang *et al.*, 2018). When the PVDF membrane is functionalized with PSS layer, the hydrophilicity of the PSS can be migrated spontaneously on the PVDF membranes as PSS added is acting as nanoadditive content that can help to improve membrane hydrophilicity property. It is also believed and confirmed by other research works that the functionalization of base membrane with PSS polyelectrolyte can increase the membrane porosity compared to the unmodified membranes. The hydrophilicity of PSS is also believed to have a capacity of enhancing the membrane flux (Mosadegh & Mahdavi, 2021).

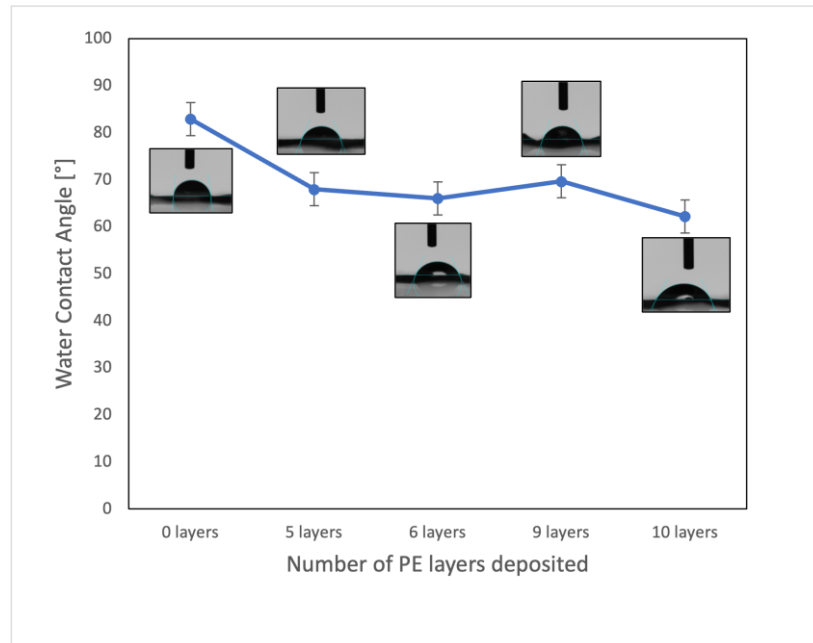


Figure 3 Wettability test of pristine and PE-modified PVDF membranes

3.2 Evaluation of Membrane Filtration Performance

The ability of the PE-modified membrane to remove metallic ions from contaminated solutions was tested by performing filtration test at different Zn^{2+} and Cd^{2+} ion concentrations. This results were also compared with the pristine PVDF membrane (before surface modification). Figure 4 illustrated the result obtained for the rejection percentage of the membranes when using 50 ppm of Zn^{2+} and Cd^{2+} ion concentrations. As expected, the pristine PVDF membranes were not capable enough to do the rejection of Zn^{2+} and Cd^{2+} ions from sample solution more than 20% due to the PVDF membrane pores size that are not small enough to retain heavy metal ions from passing the membrane pores and go directly into the permeate solution. To improve the rejection percentage of Zn^{2+} and Cd^{2+} ions, the strategy was to modify the pristine PVDF membranes surface using the functionalization of chitosan and PSS

polyelectrolytes. This procedure was done by immersion of the membrane into the PE solutions alternately which called Layer-by-Layer functionalization. From the functionalization of membranes for 5,6,9 and 10 layers, it was observed that the PVDF-5 gives two times higher value of rejection percentages of both Zn^{2+} and Cd^{2+} ion compared to the pristine PVDF membrane. This result showed that the membrane modification has significantly enhanced the removal efficiency of the divalent metal ions from their relative solution. The PVDF-6 showed the highest rejection percentage for both Zn^{2+} and Cd^{2+} . This results confirmed the properties of chitosan and PSS that have been functionalized on the PVDF membrane during modification process. The surface of the PVDF membrane now is covered with high density of amino and sulfonate functional groups charges coming from the CS and PSS polyelectrolytes, respectively. This contribute to the steric effect on the membrane surface especially few and different layers of

PE were deposited on the membrane. Besides, the fact that the membrane pores size been reduced after modification, it allows the rejection of heavy metal ions to take place better compared to the pristine membrane. Based on the study done previously, the repulsion and attraction electrostatic between the surface charges of PE-modified membrane and heavy metal ions charges may also occur during the filtration process. The proposed mechanism of heavy metals rejection is shown in the Figure 6. However, the rejection percentage value were decreasing for PVDF-9, followed by PVDF-10. This might be due to the high number of PE layers deposited on the membrane surface is not effective to improve the membrane performance. During immersion process in the PE solutions, the leachate of the previous deposited functional groups to the solution can also happen instead of new ones can be added on the membrane especially when the number of layers increase at certain numbers. In overall observation, the results showed that the PE-modified membrane had higher rejection percentage towards Cd^{2+} compared to Zn^{2+} ion. This can be explained that even though both dications Cd^{2+} and Zn^{2+} have the same number of charges, there are two different species that have different affinity towards the functional groups of the PE-modified membranes besides having different ionic radii in consequence of having different rejection percentage performance.

The performance results of the PVDF membranes in the rejection of 10 ppm and 50 ppm Cd^{2+} ion concentrations are displayed in Figure 5. It was notified that both of PVDF-5 and PVDF-10 showed higher rejection percentage in 10 ppm compared to the 50 ppm Cd^{2+} ion concentrations. Similar observation has reported by

previous study which showed that metal ions rejection percentage was decreasing with the increasing of metal ions concentration despite it still remained very promising (Mokhter *et al.*, 2017). However, the PVDF-6 and PVDF-9 showed a contradict result with higher rejection percentages of 50 ppm than 10 ppm for Cd^{2+} ion. This observation was also contradicted to the result reported by Magnenet *et al.*, which showed a constantly increasing trend of rejection percentage of copper ions using polyether sulfone (PES) ultrafiltration membranes when there was an increasing of PE layers deposit on membrane (Magnenet *et al.*, 2013). This contrary result was plausibly due to the present of more functional groups like amino and sulfonate groups on the PES membrane used there which acted as chelating agents of the metal ions (chelation effects) increasing of the membrane surface (stronger electrostatic force). Besides, the decreased in the membrane pores size rendering more difficult the passage of the metal ions through the membrane pores (steric effects). On that account, it can be assumed that the cadmium ions which is different from copper by comparison with the previous study had been collected inside the vials was degraded thus making the experimental results different from the expected results or it can be any experimental error from the sample preparation or instrumentation analysis. Despite of that, the removal of cadmium ions from both 10 ppm and 50 ppm of cadmium solutions by the PE-modified membrane were still considered practicable because the rejection percentage was promising not less than 25% and the R % values were much more improved compared to the pristine PVDF membrane (Figure 1 and Figure 2). Apart from that, the result also clearly presented that the permeate flux had decreased with the

increasing layers of PE on the membrane and this could be due to the decreasing of the membrane pores size (Table 1 and Table 2). Fast permeate flux needs to be avoided because it can

limit the rejection of heavy metals by the membranes and the tendency of the heavy metal ions to pass through the membrane into the permeate solutions are also high.

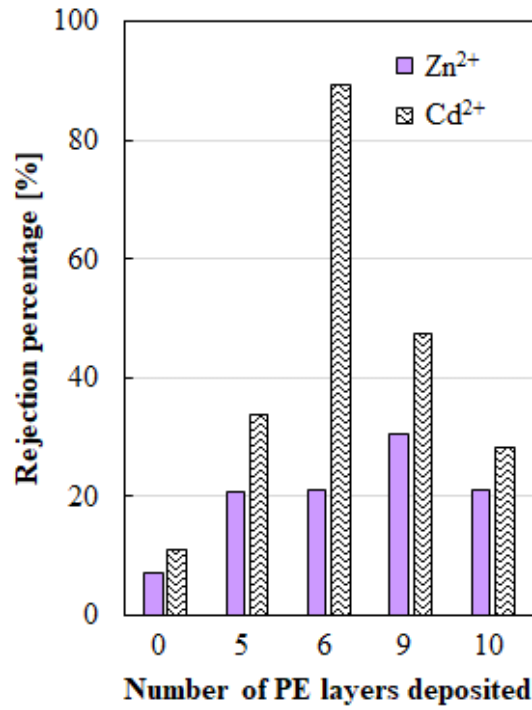


Figure 4 Rejection percentages of Zn²⁺ and Cd²⁺ over the pristine and PE-modified PVDF membranes

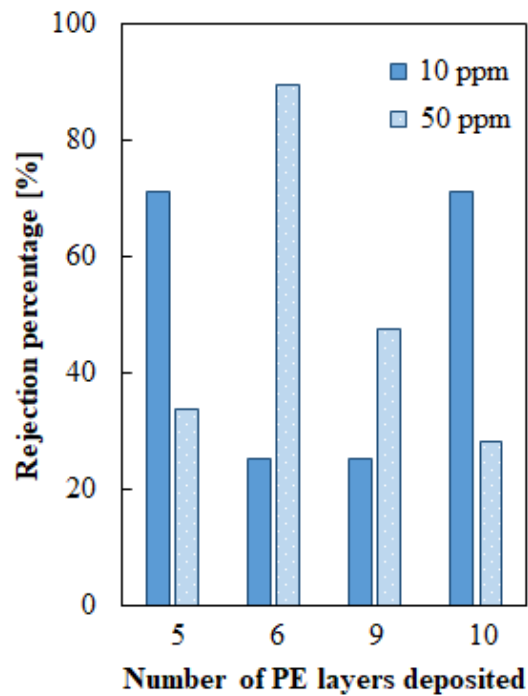


Figure 5 Rejection percentage of Cd²⁺ at 10ppm and 50 ppm concentrations of cadmium solutions over the PE-modified PVDF membranes

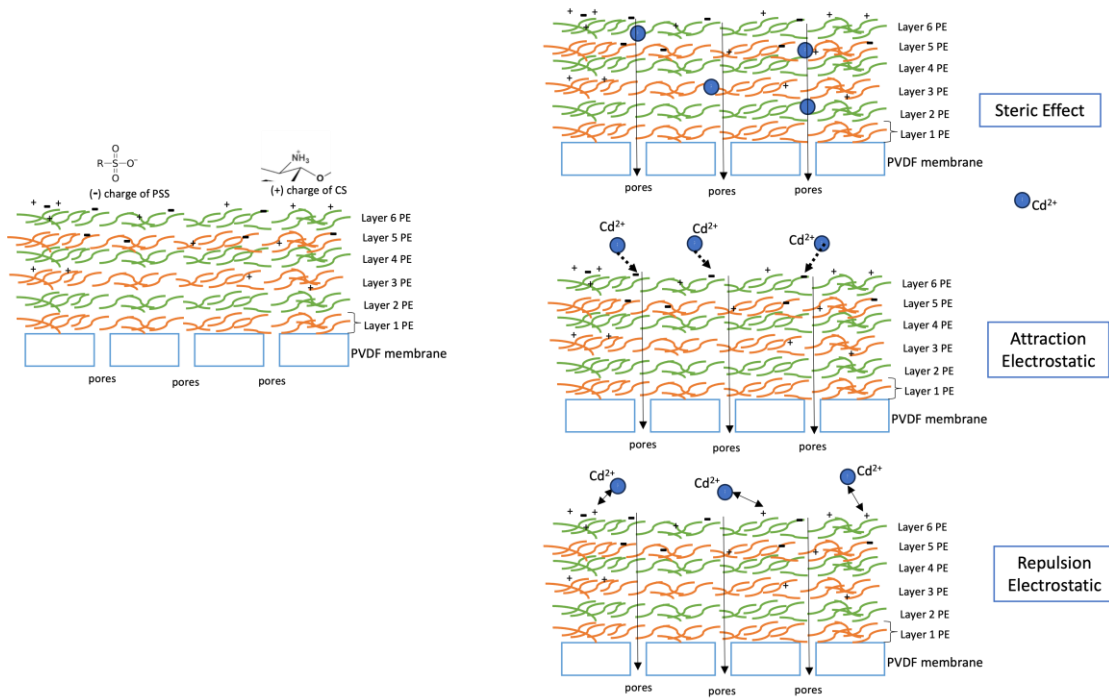


Figure 6 Proposed possible mechanism of heavy metal ions rejection by PE-modified PVDF membrane

Table 1 Feed concentration (C_o), residual concentration (C_p), rejection percentage and permeate flux of Zn^{2+} from 50 ppm of zinc solution

PE layers deposited	Concentration (ppm)	Zn^{2+}		Rejection Percentage (%)	Permeate flux ($\mu\text{m/s}$)
		C_o	C_p		
0	50	15.20	14.10	7.24	1.896
5	50	18.40	14.60	20.65	2.169
6	50	18.40	14.50	21.20	2.554
9	50	18.40	12.80	30.43	1.947
10	50	18.40	14.50	21.20	1.774

Table 2 Feed concentration (C_o), residual concentration (C_p), rejection percentage and permeate flux of Cd^{2+} from 10 ppm and 50 ppm of cadmium solution

PE layers deposited	Concentration (ppm)	Cd^{2+}		Rejection Percentage (%)	Permeate flux ($\mu\text{m/s}$)
		C_o	C_p		
0	50	43.10	35.70	17.17	1.604
5	10	7.43	2.14	71.15	2.763
	50	43.10	28.60	33.64	2.231
6	10	8.38	6.26	25.30	2.547
	50	42.21	4.50	89.34	2.725
9	10	8.38	6.26	25.30	2.397
	50	43.10	22.60	47.56	2.034
10	10	8.00	2.30	71.25	1.909
	50	43.10	30.90	28.31	1.929

After the modification has been made on the PVDF membrane, the

results obtained are quite significant to show the improvement even though the

rejection rate are quite low for certain PE-modified PVDF membranes especially for zinc ions. The results are still promising since after the modification has been made, we managed to get more than 25% of rejection percentage of heavy metal ions while less than 10% using pristine membranes which is similar to our previous work using PES membrane (Mokhter *et al.*, 2018). Besides that, Assaifan *et al.*, 2022 also showed similar trend using PVDF membrane to treat cadmium ions which they managed to get maximum 60% of rejection of cadmium. Ibrahim *et al.* in 2022 also discovered rejection percentage of cadmium from as low as 50% using PVDF-Tin Oxide ion exchange mixed matrix membrane and another study conducted by Abdulkarem *et al.*, 2021 recorded quite a similar trend for the rejection of zinc and cadmium using PVDF-Zirconium Phosphate membranes. The unmodified and modified PVDF membranes were recorded to reject from 12% up to 43% only for both zinc and cadmium ions.

3.3 Robustness of PE-Modified Membrane

The robustness of separation performances of the PE-modified membranes was evaluated by performing 10 successive filtration

experiments using the pristine PVDF and PVDF-9 membrane which were conducted during few days. The long-term performances were studied for zinc and cadmium solution using metal concentration of 50 ppm for each ion solution and the data obtained is tabulated in Table 3. The data obtained was used to calculate the permeate flux (J_y) initial and final filtration of zinc and cadmium solution together with their rejection percentage were calculated. A constant decreasing trend in the rejection percentages was observed for both zinc and cadmium ions. Noteworthy, the rejection percentage of PVDF-9 membrane was two times higher than the pristine PVDF membrane over 10 filtration tests for 50 ppm of cadmium ion, which indicated the feasibility of PE to enhance the long-term separating performance of pristine PVDF membrane. Furthermore, the permeate flux of both zinc and cadmium ions with PVDF-9 membrane shown a less decreasing trend from initial to final filtration when compared to the unmodified membrane. Since the permeate flux can be used to pinpoint the membrane fouling, a membrane is less likely to foul if its permeate flux is close to 1 (Fontananova *et al.*, 2015). Therefore, the ability of a PE-modified PVDF in resisting membrane fouling was successfully verified in this study.

Table 3 Evolution of 50 ppm Zn^{2+} and Cd^{2+} ions rejection percentages and their permeate flux of the unmodified and 9 deposited PE films membrane over 10 successive filtration tests

Metal ions	Layers of PE-deposited	Concentration (ppm)	Initial rejection (%)	Final rejection (%)	Initial flux ($\mu\text{m/s}$)	Final flux ($\mu\text{m/s}$)
Zn(II)	0 layers	50	7.24	4.61	1.896	1.652
	9 layers	50	9.21	4.61	2.034	1.913
Cd(II)	0 layers	50	17.17	10.90	1.604	0.896
	9 layers	50	47.56	24.13	1.968	1.838

4.0 CONCLUSION

In this study, PVDF membrane was successfully modified with chitosan and polystyrene via layer-by-layer functionalization method for removal of zinc and cadmium ions. It is clearly shown that the PE-modified PVDF membranes are able to improve the rejection percentage of Cd^{2+} and Zn^{2+} from below 20% initially up to 90% and 30%, respectively. Based on the comparison with previous studies and other researchers works, the rejection percentage of zinc and especially cadmium ions are promising and significant since most of the PE-modified PVDF membranes show better rejection performance compared to the unmodified membranes. Undeniably, PE like PSS which consisted of sulfonate functional group while the amines and hydroxyl functional group that contained by CS have greatly diminished the hydrophobicity of a PVDF membrane thus making aqueous solution easier to pass through the membrane along with the higher retention of metal ions. Furthermore, PE-modified PVDF membrane was also showing less decreasing of permeate flux when compared to the pristine PVDF membrane which demonstrated the capability of PE to suspend the phenomenon of membrane fouling. On this account, PE multilayers membrane might own attractive potential applicability to remove heavy metal ions in the wastewater treatment industry and remain its robustness over long term filtration at the same time. Moreover, the utilization of natural polymer like chitosan should be paying more attention as these materials are non-toxic, biodegradable and they can substitute the petroleum-based polymers with extensive applications but causing severe environmental and

health problems which require further investigations in the future work.

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