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Preparation of Polyelectrolyte Modified Membrane for Removal of Arsenic

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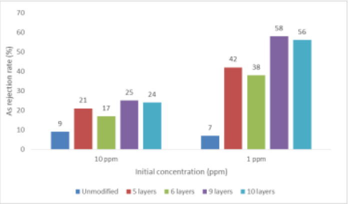
GRAPHICAL ABSTRACT



Trends in rejection rate for arsenic ion

ABSTRACT

Polyvinylidine fluoride was modified using polyelectrolyte (PE) multilayers, made of poly (allylamine hydrochloride) with poly (styrene sulfonate) to remove arsenic cations from aqueous solution. From the characterization of the naked and modified membrane using IR-ATR and water contact angle, it is shown that the polycation and polyanion has successfully been deposited on the surface of the membrane. The contact angle increased with the increasing layers of polycation while it decreased with increasing polyanion layers. Hence, the modification of the membrane was successful. It also has been shown that filtration through modified membrane is a process that can effectively remove metal ions from contaminated aqueous solutions. The efficiency of the filtration process as measured by the rejection rates of the modified membrane is around 20% to 60% for both 1 ppm and 10 ppm metal ions solutions and is greater than the naked membrane. As expected, the cross-flow velocity decreased as the number of deposited polyelectrolyte layers increases. The mechanism for the arsenic removal is electrostatic repulsion. Consequently, the use of layer by layer-modified membranes is a viable option for the removal of arsenic from wastewater.

Keywords: Polyvinylidine fluoride, poly(allylamine hydrochloride), poly(styrene sulfone), arsenic, layer by layer deposition

1. INTRODUCTION

Nowadays, water pollution is one of the major issues that have been argued in the global context. Heavy metals such as chromium, copper, lead, zinc, nickel, arsenic, etc may contain in several industrial wastewater stream. Furthermore, with the widely use of metals in industries, such as metallurgy, electroplating, machinery manufacturing or electronics, and other human activities such as agricultural practices or waste disposal, a large amount of wastewater containing toxic heavy metals are released into water bodies [1].

Heavy metals are natural elements of the Earth's crust. They cannot be degraded or destroyed. To a small extent they access into human body via food, drinking water and air. In order to preserve the metabolism of the human body, some heavy metals (e.g. copper, selenium, zinc) are vital as the trace elements. However, at higher concentrations of consumption they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via food chain. Heavy metals are perilous because they are likely to bio-accumulate [2]. Bio-accumulation in definition is an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment [3]. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Heavy metals can penetrate water system by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater [2].

Arsenic is a chemical element with the symbol As and atomic number 33. It is one of the heavy metals that belongs to the periodic table group 15 period 4. Arsenic is a naturally occurring element that is widely distributed in the Earth's crust [4]. Long-term exposure to arsenic from drinking-water and food can cause cancer and skin lesions. It has also been associated with cardiovascular disease and diabetes. In utero and early childhood exposure has been linked to negative impacts on cognitive development and increased deaths in young adults [5].

Toxic metals, probably existing in high concentrations, must be efficiently treated and removed from wastewaters [6]. A very high-risk effect will contribute to aquatic life if wastewaters were discharged directly into natural water resources, whilst the direct discharge into the sewerage system may affect negatively the subsequent biological wastewater treatment [7]. That is why the removal of heavy metals from discharged water becomes a world crucial issue and why environmental regulations nowadays compel industries to treat the wastewater in order to remove heavy metals [1].

In recent years, the removal of toxic heavy metal ions from sewage, industrial and mining waste effluents has been widely studied [7]. Chemical precipitation, ion-exchange, coagulation and flocculation, flotation, electrochemical treatment, membrane filtration and adsorption are examples of assorted technologies that have been working to abolish heavy metals from polluted waters [1]. The first two method require huge chemicals and either generate high volumetric sludge or release noxious chemical reagents into the environment during regeneration [8]. A very efficient method for removing arsenic from drinking water is a membrane process. Compared to methods used in the past, membrane processes offer a higher and more efficient removal rate. There are four types of membrane processes: reverse osmosis (RO), microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF). Each of these processes offer similar results but have different benefits in their uses [9]. Compared to other methods used to separate heavy metals, membrane microfiltration, ultrafiltration and nanofiltration are very promising since they present several advantages such as high separation efficiency, energy saving, easy operation, easy to scale up and low cost [1]. Membrane technology is superior to those as membrane itself does not accumulate arsenic or generate sludge which would cause disposal problems. Instead it prevents other dissolved impurities and harmful microorganisms to pass through the membrane [8].

In addition, several surface modification methods can also be used to produce membranes with even better separation performances including: UV-initiated membrane graft polymerization, plasma-induced graft polymerization, redox-initiated graft polymerization, dendrimer grafting, ion implantation or polyelectrolyte (PE) multilayers self-assembly using Layer by-Layer approach (LbL). LbL deposition is a thin film deposition technique. The films are formed by depositing alternating layers of oppositely charged materials with rinsing steps in between. This can be accomplished by using various techniques such as immersion, spin, spray, electromagnetism, or fluidics. This LbL method is currently the most widely used because it is cheap, rapid and provides good separation performances when other polymerization methods generally require highly costly equipment for large-scale membrane production.

Moreover, the LbL method, which consists in the alternate adsorption of oppositely charged polyelectrolytes, allows to obtain controllable and tunable layer properties such as thickness, porosity, hydrophilicity and surface charges. Thus, PE-modified membranes have recently been developed for application as fuel cell, gas separation, pervaporation separation, and anions or cations separation. The removal of heavy metal ions from aqueous solutions also seems to be a promising application for polyelectrolyte multilayer (PEM) films [1].

The aim of this work consists in the use of PEM film-modified membranes specifically polyvinylidine fluoride (PVDF) membrane to remove efficiently arsenic heavy metal from aqueous wastewater solutions.

2. EXPERIMENTAL

The experiment focussed on the modification of PVDF membrane for the removal of arsenic ion using polyelectrolytes polyallylamine hydrochloride and polystyrene sulfonate. The membrane was modified by LbL deposition with 5, 6, 9 and 10 layers of modification. After the modification, the membrane was characterized using Perkin Elmer Model 1600 IR-ATR and dataphysics water contact angle. Then, the modified membrane was used to filter arsenic solution with concentration of 10 ppm and 1 ppm. The permeate flux is then collected for AAS analysis.

2.1. Casting of membrane

This process was performed at AMTEC (Advanced Membrane Technology Research Centre). This process required the DOP solution (21% PVDF, 79% DMAC solvent), glass plate (30cm × 22.5cm), a glass rod and two basins of distilled water. The concentration of the DOP solution depending on the pore size of the membrane desired and in this case, the pore size desired is the size of ultrafiltration (0.1 to 0.01μm). Firstly, some DOP solution was poured into the glass plate. Then, using the glass rod, the solution was rolled until the end of the glass plate like a flat sheet of paper. The glass plate containing a layer of membrane was quickly rinsed onto a basin of distilled water. After 1 minute, the flat sheet of membrane was removed from the glass plate and rinsed in another basin of distilled water. After the process was finished, the membrane was stored in a closed container filled with distilled water and placed in a chiller.

2.2. Preparation of Polyelectrolytes

All solutions were prepared using deionized water. Solutions containing poly (allylaminehydrochloride) and sodium poly (styrene sulfonate) in 10^{-2} M NaCl were prepared at a concentration of 5 g L^{-1} without adjustment of their pH. PAH was positively charged since the pH of the PAH solution (=3.9) was strongly lower than the pKa of PAH (=8.8). Similarly, PSS was negatively charged since the pH of the PSS solution (=4.8) was higher than the pKa of PSS (=1.5)

2.3. Membrane Modification

The membranes were rinsed first in 10^{-2} M NaOH for 2 hours to extract the conservative (glycerine) and then rinsed with deionized water two times. Multilayer PE film preparation started with polycation (PAH) immersion of the membrane surface. PAH was first deposited with the negatively charged PVDF membranes due to electrostatic attraction. Twice for 1 min before immersion in the polyanion solution (PSS) the membranes were rinsed with deionized water, followed by two more rinses of 1 min each. Additional layers were deposited similarly to give the desired number of layers which were 5, 6, 9 and 10 layers. For both PEs, the time allowed for adsorption of PE was 30 min.

2.4 Membrane Characterization

Perkin Elmer Model 1600 Infrared-attenuated total reflection spectroscopy (IR-ATR) was used in order to demonstrate that the membranes were successfully modified by PE multilayer films using layer-by-layer technique. The IR-ATR spectrum of the naked PVDF membrane was performed and compared with the IR-ATR spectra of the PVDF membranes modified with 5, 6, 9 and 10 successive PE layers.

Contact angle OCA from dataphysics were used to monitor the evolution of the membrane's wettability during the growth of the PE multilayer film. The water contact angles of the membranes were measured using a Dropscan contact angle goniometer. This instrument was equipped with a CCD camera. A 5 μL drop of water was formed at the tip of a syringe needle and put in contact with the membrane surface by raising the membrane until contact occurred. After that, the contact angle was obtained by drawing the tangent close to the edge of the droplet. At least three drops were deposited in order to obtain reliable average water contact angle values.

2.5 Preparation of Arsenic Solutions

For 50 ppm of arsenic solution, 0.1041 g of $HAsNa_2O_4.7H_2O$ was used in 500mL of volumetric flask while for 10 ppm of arsenic solution, 0.0208g of $HAsNa_2O_4.7H_2O$ was used in 500mL volumetric flask and for 1 ppm of arsenic solution, 0.0021g of $HAsNa_2O_4.7H_2O$ was used in 500mL volumetric flask. All these arsenic solutions are made up with 2% HNO_3.

2.6 Membrane Filtration

Filtration experiments were performed using a crossflow separation unit in AMTEC. The membrane was housed in a planar module and the tangential filtrations were carried out at different crossflow velocity depending on the concentration of sample and membrane. A trans-membrane pressure (TMP) of 6 bars was applied. The feed tank was filled with a 500 mL to 1 L solution containing arsenic solution. The pH of these solutions was adjusted to pH 5 with HCl or NaOH 10^{-1} M. The permeate sample is collected for AAS analysis. Between each filtration, the membrane was cleaned by circulating deionized water for 10 min at a pressure of 6 bars several times until recovering the initial permeability of the membrane and also until the pH of permeate solution approached the deionized water pH.

3. RESULTS AND DISCUSSION

3.1. Characterization of membrane

The IR-ATR spectrum of naked and modified PVDF membrane was shown in Figure 1. From the spectrum, it is shown that the presence of CH_2 asymmetric at frequency of 3023 cm^{-1} followed by the presence of CH_2 symmetric at frequency of 2981 cm^{-1} and CF bond at frequency of 839 cm^{-1} for the naked membrane as shown in Table 1.

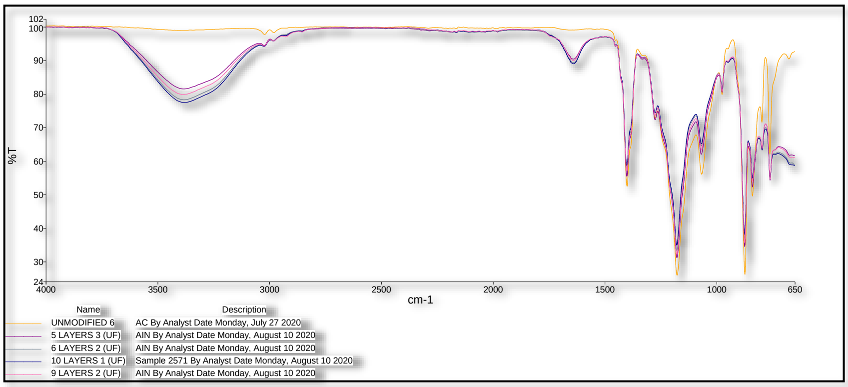


Figure 1. IR-ATR spectra of unmodified and modified membranes (after deposition of 5, 6, 9 and 10 layers of PAH and PSS).

Table 1. IR spectral data of naked PVDF

Assignment	Wavenumber(cm^{-1})
CH_2 (asymmetric)	3023
CH_2 (symmetric)	2981
C-F	839

Table 2. IR spectral data for modified membrane

Assignment	Wavenumber (cm^{-1})			
	5 layers	6 layers	9 layers	10 layers
N-H	3388	3388	3389	3390
C-N	1177	1177	1178	1177
C=C aromatic	1641	1642	1638	1638
	1401	1401	1401	1401
C-H aromatic	3023	3023	3029	3023
SO_3	1331	1334	1340	1337

IR-ATR spectrum of naked PVDF membrane was performed and compared with the IR-ATR spectra of the PVDF membrane modified with 5, 6, 9 and 10 consecutive PE layers (Figure 1). Comparing between the unmodified membrane and the modified membrane with 5 layers of modification, six new absorption peaks were observed at 3388 cm^{-1} which represent N-H bond and 1177 cm^{-1} which represent C-N bond. These two peaks proved that the deposition of PAH was successful. In addition, the other three spectrum which represent C=C aromatic (1641cm^{-1} & 1401 cm^{-1}), CH aromatic (3023 cm^{-1}) and SO_3 (1331 cm^{-1}) proved that the deposition of PSS was successful. As shown in Table 2, the modification of membrane with 5, 6, 9 and 10 layers of modification demonstrate the same vibration bands at very similar wavenumbers. For instance, for N-H bond, the frequency for both 5 and 6 layers of modification are 3388 cm^{-1}, 3389 cm^{-1} for 9 layers of modification and 3390 cm^{-1} for 10 layers of modification. The only difference between these four modifications is the intensity of the peak. For example, for unmodified membrane, there was no presence of N-H bond and C=C aromatic but when the deposition happen, there were presence of N-H bond and C=C aromatic and and the intensities of the peaks increased as number of polyelectrolyte increases. Consequently, the naked PVDF and modified membranes IR-ATR spectra are unambiguously different, suggesting that IR spectroscopy can be used to show that the PE multilayer film's modification of the PVDF membrane is effective.

Water contact angle measurements were also performed after each immersion of the PVDF membrane in a PE solution in order to monitor the evolution of the membrane's wettability during the growth of the PE multilayer film. The naked PVDF membrane was marked as layer 0 and had a contact angle of 68.15°. After 5 layers of adsorption of polycation (PAH) and PSS with the PAH as the final layer, the contact angle increased to more than 80°. On the contrary, the contact angle decreased to 73.25° after the 6th layer of adsorption of PE with final layer of polyanion. After that, each immersion of the membrane in the polycation solution led to an increase of the contact angle, and each immersion in the polyanion solution to a decrease, showing that the membrane's modification is effective. The modification progress of the membrane's surface after every immersion of PE is illustrated in Figure 2.

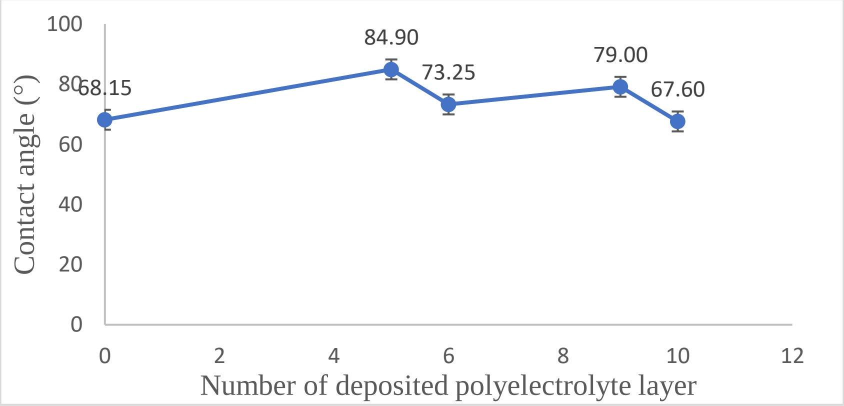


Figure 2. Evolution of the wettability of the membranes after their successive immersion in PE solutions of PAH and PSS

3.2. Filtration Performance

The filtrations of aqueous metallic ions solutions through the modified membrane were performed in order to determine its ability to remove metallic ions from contaminated solutions. The arsenic rejection rates were tested and calculated for different initial arsenic aqueous solution concentrations, which were 1 ppm and 10 ppm.

In the absence of chemical modification, the naked membranes were unable to retain the metal ions efficiently and have the retention rate lower than 10%. Consequently, with the modified membranes, the filtration process were able to reject metal ions efficiently and have rejection rates approximately 20% to 60% for both concentrations. The results of the filtration experiments are reported in Table 3. For 10 ppm arsenic aqueous solution, the naked membrane shows low rejection rate which is 9%. After the modification with 5, 6, 9 and 10 layers of PE, the rejection rates increase to 21%, 17%, 25% and 24% respectively. Similar to arsenic solution with lower concentration, which is 1 ppm, the rejection rates show the same trend after each layer of modification which is 42%, 38%, 58% and 56% respectively. So, the results obtained from these experiments demonstrate that the filtration through modified membrane is efficient, at different concentrations. It is clearly shown that, the efficiency of the process decreases with increasing concentration, but it still remains promising~~.~~

After 5 layers of adsorption of PE with polycation (PAH) as the fifth one, the rejection rates increased. On the contrary, the rejection rates decreased with 6 layers of adsorption of PE (polyanion PSS as the 6th layer). From the observation that we can made we can clearly identify that after each immersion of the membrane in the polycation solution, it led to an increase of rejection rates, while after each immersion in the polyanion solution it led to a decrease of rejection rates. Hence, when the surface of the membrane layer is covered with a polycation at the last layer, it will give high rejection rates while polyanion will give low rejection rates as illustrated in Figure 3.

Furthermore, from the comparison between the cross velocity of the naked and modified membrane, it is proved that the efficiency of the filtration was successful. This is because as the number of PE deposited increases, the cross flow velocity decreases (Figure 4). From Table 3, it is clearly observed that 10 ppm solution, the cross flow velocity for naked membrane was 5.2986×10^{-6} ms^{-1}. As the number of PE increases to 5, 6, 9 and 10 layers, the cross flow velocity decreases to 3.4328×10^{-6} ms^{-1}, 2.2489×10^{-6} ms^{-1}, 2.1726×10^{-6} ms^{-1} and 1.9694×10^{-6} ms^{-1} respectively. For 1 ppm arsenic concentration, it depicted the same trend as the naked membrane with a cross velocity of 4.6563×10^{-6} ms^{-1}, the modified membrane with 5, 6, 9 and 10 layers of modification showed decreasing cross velocity value which is 2.4053×10^{-6} ms^{-1}, 2.2877×10^{-6} ms^{-1}, 2.1218×10^{-6} ms^{-1} and $1.6411 \times 10^{-}6$ ms^{-1} respectively. Hence, it can be concluded that the efficiency of the filtration was successful as the rejection rate and cross flow velocity shows the expected trends.

Table 3. Filtration experiments for modern filtration system

Modification (layers)	**Initial Concentration, C_o (ppm)**	**Final concentration, C_p (ppm)**	**Cross flow velocity (ms^{-1})**	**Rejection rate (%)**
Unmodified	10	9.10	5.2986×10^{-6}	9
5	10	7.90	3.4328×10^{-6}	21
6	10	8.30	2.2489×10^{-6}	17
9	10	7.50	2.1726×10^{-6}	25
10	10	7.60	1.9694×10^{-6}	24
Unmodified	1	0.93	4.6563×10^{-6}	7
5	1	0.58	2.4053×10^{-6}	42
6	1	0.62	2.2877×10^{-6}	38
9	1	0.42	2.1218×10^{-6}	58
10	1	0.44	1.6411×10^{-6}	56

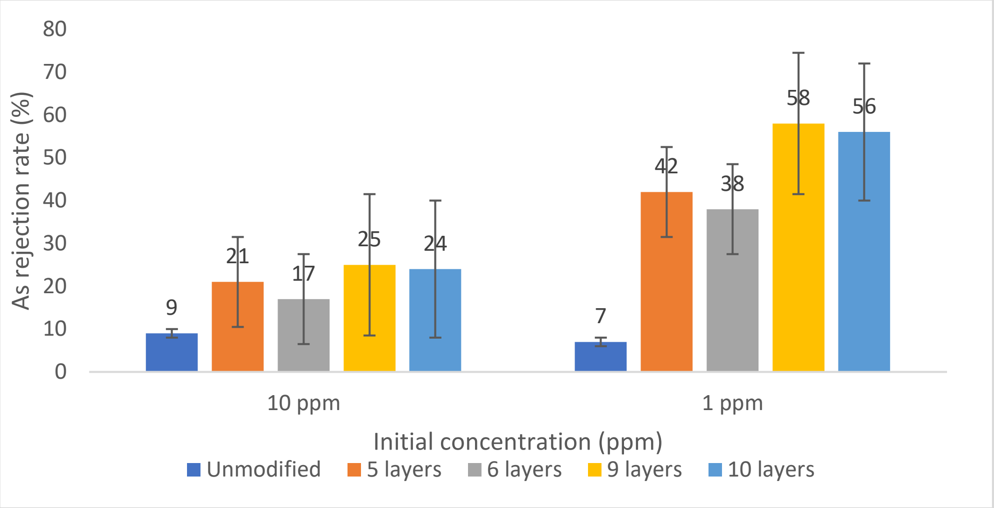


Figure 3. Trend in rejection rate for arsenic solution where it increased as number of polycation layers increase and decreased as number of polyanion layers increases

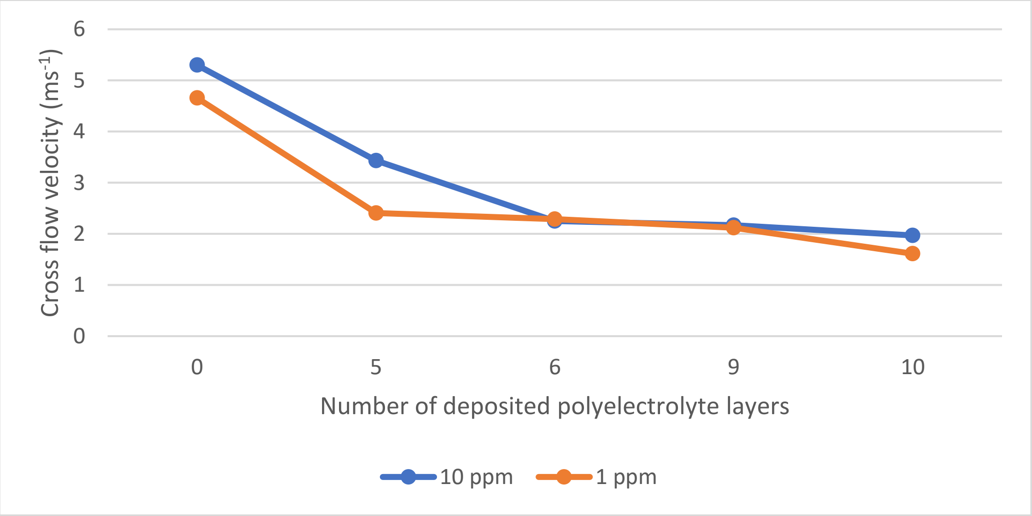


Figure 4. Trend in cross flow velocity for arsenic solution where it decreased as number of PE increases

From the previous discussion, it can be concluded that the mechanism for the removal of arsenic ion is electrostatic repulsion not adsorption. This is because after 5 layers of adsorption of PE with PAH as the fifth one, there is electrostatic repulsion occur as both charge of solution and membrane were positive (**Figure 5**). Hence it contribute to high rejection rates. On the contrary, the rejection rates decreased with 6 layers of adsorption of PE (polyanion PSS as the 6th layer) as they have opposite charge and attractive electrostatic occur. Hence, when the surface of the membrane layer is covered with a polycation at the last layer, it gave high rejection rates due to the electrostatic repulsion mechanism while polyanion gave low rejection rates due to less electrostatic repulsion. On the other hand, from the immersion of naked and modified membrane with 5 layers of modification (to study the adsorption mechanism), the concentration of arsenic solution after the immersion of membrane is higher than initial concentration (Table 4). This clearly show that no adsorption occur from the arsenic solution onto the membrane surface. Hence, it can be conclude that the mechanism for the arsenic removal is electrostatic repulsion.

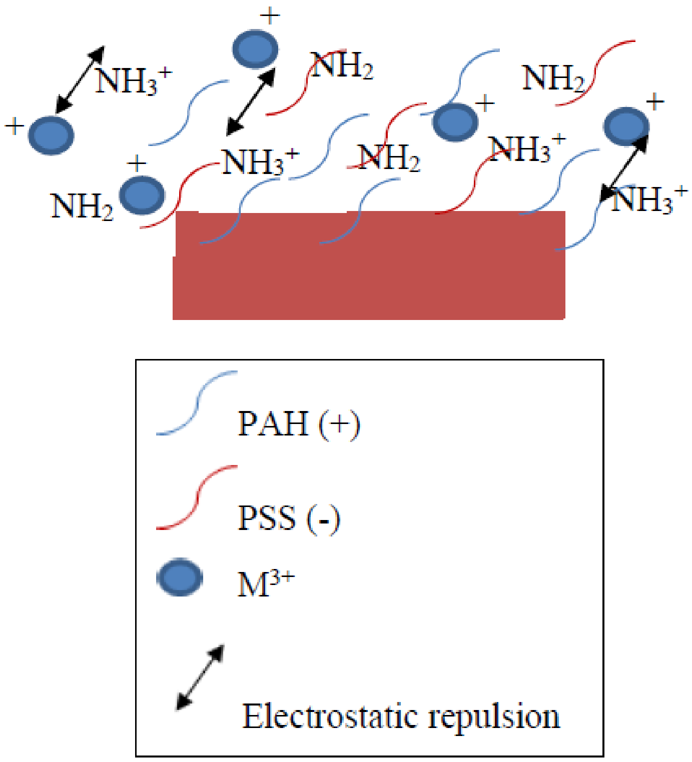


Figure 5. Chemical mechanism on the membrane adsorption of metal ion

Table 4. Result for As adsorption test on unmodified and five modified PE layers

Modification (layers)	Concentration (ppm)	Initial Concentration, C_o (ppm)	Final Concentration, C_p (ppm)
Unmodified	1	0.79	0.85
5	1	0.79	0.83

4. CONCLUSION

The modification of hydrophobic PVDF with PAH and PSS was performed in order to study the removal of As ion from wastewater. From the characterization of the naked and modified membrane using FTIR and contact angle, it is confirmed that the polycation and polyanion has successfully been deposited on the surface of the membrane. The contact angle increases the increasing polycation while it decreases with increasing polyanion. It also has been shown that filtration using modified PVDF membrane is a process that can improve the efficiency of As removal from contaminated aqueous solutions. The efficiency of the filtration process as measured by the rejection rates showed that the rejection rate of initial PVDF membrane increases from 9% to 20% to 60% for both 1 ppm and 10 ppm metal ions solutions. The efficiency of the process decreases with increasing concentration, but it still remains promising. In addition, the cross-flow velocity also decreases as expected as the number of deposited PE increases. The mechanism for the arsenic ion removal was electrostatic repulsion as from the immersion of PVDF membrane with arsenic solution, no adsorption was observed on the surface of membrane. In conclusion, the use of LbL-modified membranes in order to remove As ion from wastewater is a viable option.

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