Al-Ti_2O_6 a mixed metal oxide based composite membrane: A unique membrane for removal of heavy metals

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$Al\text{-}Ti_2O_6$ a mixed metal oxide based composite membrane: A unique membrane for removal of heavy metals

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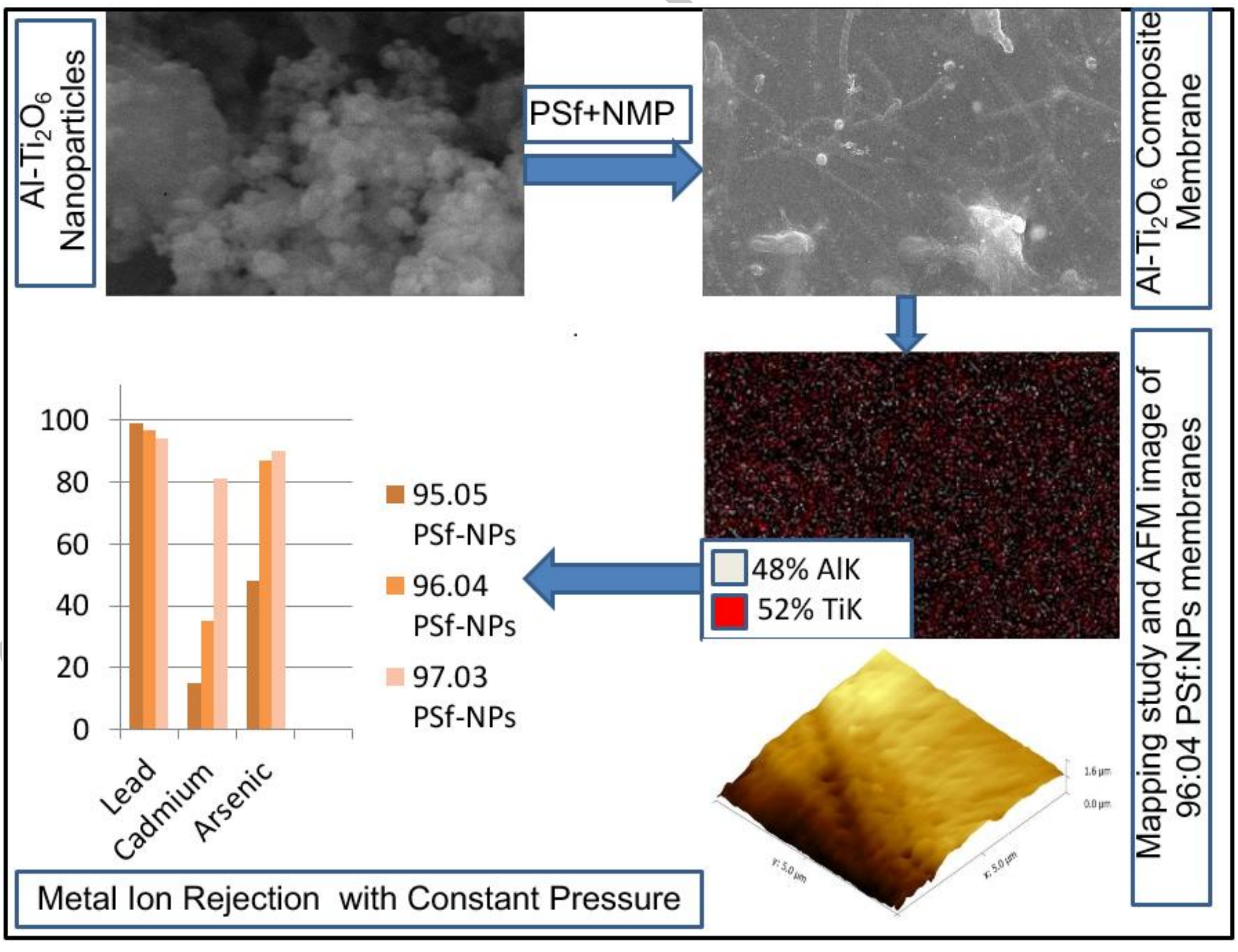
Graphical Abstract:



Abstract:

In the current study, a novel Al-Ti_2O_6 nanoparticles and polysulfone composite membranes were prepared and used for the removal of heavy metal ions. Al-Ti_2O_6 was prepared by precipitation method and the membranes were prepared by diffusion induced phase separation method with different compositions of Al-Ti_2O_6. The prepared Al-Ti_2O_6 nanoparticle was confirmed by XRD, and SEM analysis. However, FE-SEM was used to confirm the presence of nanoparticles in the membrane. EDX and elemental mapping were performed to confirm uniform distribution of nanoparticles in the membranes. The hydrophilicity of the membrane was measured by contact angle, water uptake and water flux study and it was increased with respect to increasing concentration of nanoparticles. Performance of the membrane was analyzed by rejection of heavy metals such as As, Cd, and Pb. The membrane was showed rejection percentage of about 96 % for As, 98% for Cd and 99% for Pb. The concentration of nanoparticles and filtration time was investigated in detail. The obtained results prove Al-Ti_2O_6 a mixed metal oxide composite membrane a potential candidate for the removal of As, Cd, and Pb.

Key Words: Mixed matrix membranes, surface roughness, hydrophilicity, heavy metal rejection.

1. Introduction

In recent times, membrane has become an engine for separation and purification processes [1-6]. The membrane market geared in an astounding way. A more number of membranes are required for fulfill the membrane market. Thin film composite membrane (TFC) [7], cellulose acetate [8], polysulfone (PSf) [9], Polyvinylidene fluoride (PVDF) [10], Polyethylenimine (PEI) [11] and chitosan [12] membranes are presently available in the market. Still, there is a vast requirement of materials for membrane in present market as the existing materials has their own drawbacks.

Recent year's water pollution has increasing due to urbanization and development of industries and less availability of ground water. The effect of water contamination is so serious it can't be recovered thorough existing membranes. Meanwhile, the concentration of these pollutants increased rapidly which is extremely unsafe to the earth. However, ground water is also full of hazard materials. The heavy metals emitting from the industry rich in concentration are arsenic, chromium, cadmium, lead, nickel, copper, and mercury. Overwhelming metal contamination is a genuine natural issue, which has an extraordinary damage to human well-being. The productive evacuation of overwhelming metal particles in water has been a hot research theme in the field of wastewater treatment. In this unique circumstance, a definite cautious evaluation of both environmental and economic issue sought to be considered [13-15]. The complete aquatic system is in trouble because of these heavy metals [16]. The concentration polarization [17], charge interaction between the ions, interference of ions, and less charge distributions are major drawbacks for the existing membranes [18]. Mixed matrix membranes (MMM) is one of the attractive options as compared to existing membrane materials [19]. Insertion of hydrophilic NPs to polymer matrix enhances the membrane properties in terms of both selectivity and productivity, which has vast range of literature. TiO_2 [20], MgO [21], TNT [22], Al_2O_3 [23], AgO [24], carbon nanotubes [25], graphene [26], Fe_2O_3 [27], zeolites [28] and CuO [29] have showed tremendous impact on performance of membranes. However, PSf is one of the best materials for the membrane applications. Several reports have showed vocabulary of the PSf in mixed matrix membranes, in the interest of unique property of long size monomer, which helps in well distribution of NPs inside membrane matrix. However, according to literature survey, the mixed metal ions are rarely used for membrane applications. Two metal ions in the same membranes are more effective because versatile properties of the membrane made to several applications [30]. The zeolite with two metal oxides Al and Si showed better impact in membrane separation [28]. However, such experiments were rarely done in literature. Hence, an attempt has been made using Al-Ti_2O_6 and PSf composite mixed matrix membrane.

In the current study, Al-Ti_2O_6 NPs was prepared in the laboratory and used with PSf for the preparation of nanocomposite membranes. As for literature knowledge Al-Ti_2O_6 NPs and PSf composite membranes was not yet reported. The membranes were prepared by diffusion induced phase separation method with different concentration of Al-Ti_2O_6 NPs. The prepared Al-Ti_2O_6 NPs subjected for characterization of XRD, ATR-IR and SEM analysis. FE-SEM, EDX and elemental mapping were performed for membranes to know uniform distribution of nanoparticles. The contact angle, water uptake and pure water flux study were performed to know hydrophilicity. Performance of the membrane was known by rejection of heavy metal ions such as As, Cd, and Pb. The concentration of NPs, trans-membrane pressure and filtration time was investigated in detail and discussed with literature and scientific support.

2. Experimental

2.1 Materials & Methods

Titanium tetra-iso-propoxide (TTIP), ethanol, aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$), and ammonium hydroxide (NH_4OH), was procured from Reachem, Russia. Potassium dichromate, 1-methyl-2-

pyrrolidone (NMP), lead acetate, sodium arsenate, cadmium nitrate was purchased from Sd. fine, India. Udel Polysulfone was purchased from Chain made.

2.2 Synthesis of $AlTi_2O_6$ mixed metal oxide nanoparticles (NPs) by precipitation method.

The 0.33 M of aluminum nitrate solution was prepared using de-ionized water followed by addition of ethanol to it. Further, (0.67 M) TTIP was added drop wise to the solution. After formation of homogeneous solution, ammonium hydroxide was added to the solution until the pH is attained to 12 and till the precipitate is formed. After the completion of the precipitation, the solution was undergone to centrifugation at 4,000 rpm for 30 minutes. The obtained precipitin is washed until the pH reach to 7. The final precipitin was dried in hot air oven at 40 ^{o}C for two hours. The obtained powder was further undergone calcination under furnace at 300 ^{o}C for 3 hours. After the heat treatment the obtained powder were further characterized using different techniques.

2.3 Preparation of Polysulfone-$AlTi_2O_6$ composite membrane.

The PSf-NPs membrane is prepared through phase inversion technique [31]. Initially, NPs were physically grinded for 1hour. Powdered NPs was sonnicated in NMP for 1 hr and followed by stirring for 2hr to avoid the agglomeration. Afterwards, PSf was added slowly and stirred for 24hrs to get viscous solution. The viscous solution was casted on glass plate using glass rod. Then, casted glass plate was dipped on coagulation bath containing distilled water. The membrane is pled out from glass plate by phase inversion process within few minutes. The prepared membrane was stored in distilled water for 24hr to achieve required mechanical strength.

Table 1: Membrane composition and code

Membrane code	Polysulfone`	NPs	NMP
neet PSf	20%	--	80%
97:03(PSf-NPs)	17%	3%	80%
96:04(PSf-NPs)	16%	4%	80%
95:05(PSf-NPs)	15%	5%	80%

2.4 Characterization

2.4.1 XRD

X-ray diffraction analysis was carried for membrane and NPs in order to determine the materials structural features. D8 Advance (Rikagu Ultima-4X-ray) diffractometer with Cu Kα radiation (λ = 1.5418 Å). The measurements were performed at room temperature at a speed of 2^o/min form 5^0 to 50^0. The mean dimension, d, of the oriented domains was obtained by elaborating the most intense X-ray peak by the Scherer's equation.

2.4.2 SEM

The membrane morphology was observed using Scanning electron microscope analysis (Vega Tescan and Hitachi S3400 and Jeol JSM-7100F FESEM). In order to make membrane conductive a thin layer of platinum was sputtered over the sample before observation. Also X-ray elemental mapping analysis of Aluminum and Titanium on the surface was performed to know the uniform distribution.

2.4.3 AFM

AFM was performed in APE Research model F 80 AFM with SPM data analysis software to provide information about surface roughness of membranes. Samples were taken 1×1cm^2 for an effective area of 5 µm at 5 different places. The scans were performed in air medium and the obtained average result is reported.

2.4.4 Water contact angle

The water contact angle (WCA) of the membranes was measured using a contact angle goniometer by the sessile drop technique at room temperature. At least 5 measurements were carried out on each substrate sample, and the average value was reported.

2.4.5 Water Uptake studies

Hydrophilicity of membranes was determined by water uptake experiments [32]. Initially, membranes were cut into 2×2 cm^2 and immersed in distilled water for about 24hrs and wet weight of the membrane was taken by removing excess of surface droplets using tissue paper. Further, membranes were dried in vacuum desiccators and dry weight of membranes was taken. The percentage of water uptake was calculated using equation [33].

$$\%\text{ water uptake} = \left(\frac{Wwet}{Wdry} - 1\right) \times 100$$

Where, W_{wet} and W_{dry} are the weight of wet and dried membrane respectively.

2.4.6 Pure water flux studies

The pure water flux of the membrane was determined using customized dead unit filtration unit having an effective membrane having diameter of 4 cm^2. The unit was equipped with nitrogen cylinder in order to provide required pressure. The membrane were cut circular shape with the help of a sharp blade and fixed into the static cell. The pure water flux of the membranes was calculated directly by measuring permeate stream in terms of liter per meter square per hour ($Lm^{-2}h^{-1}$).

2.4.7 Metal ion rejection study

The same filtration unit was used for rejection study. The feed solution consists of metal ions such as Pb^{+2}, Cd^{+2} and As^{+3} with concentration of 10ppm. The pressure was varied from 200kPa to 800kPa with step wise increase by 200kPa. A volume of 10mL permeate was collected at different pressure and the concentration of feed as well as permeate was analyzed by Atomic absorption spectroscopy (Agilent Technologies 55AA). The percentage of rejection was calculated using the below equation.

$$\%\ \text{rejection} = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

Where C_p is permeate concentration, C_f is feed concentration [34].

3. Result and discussion

3.1 Characterization of Nanoparticles

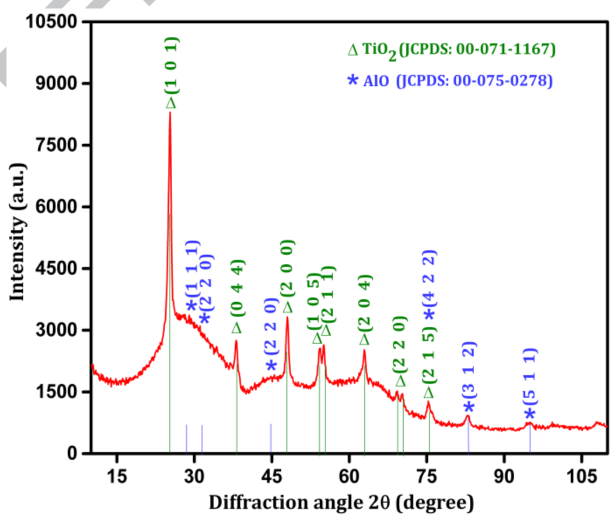


Fig.1. XRD analysis of NPs

The XRD pattern of the synthesized mixed metal oxide nanoparticles is shown in Fig. 1. The major peaks for the obtained mixed metal oxide nanoparticles are ~25 º (101), ~38 º (044), ~48 º (200), ~54 º (105), ~55 º (211), ~62 º (204), ~69 º (220), and ~75 º(215) which are found to be best matched with theTiO_2

phase JCPDS file no. 01-071-1167 which are tetragonal crystalline. However, the peaks obtained at ~27 º (111), ~32 º (200), ~45 º (220), ~75 º (422), ~83 º (312), and ~94º(511) correlates with the AlO phase JCPDS file no. 01-073-1702 which also shows that the obtained phase of mixed metal oxide nanoparticles are also cubic crystalline.

3.2 Morphology of the NPs

The co-precipitated technique provides white powder of Al-Ti_2O_6 NPs. When examine using SEM, it can be seen that the particles were uniform sphere like morphology. Fig. 2a and 2b shows the SEM images of NPs. The diameter of NPs was found in the range of ~43 to 57 nm.

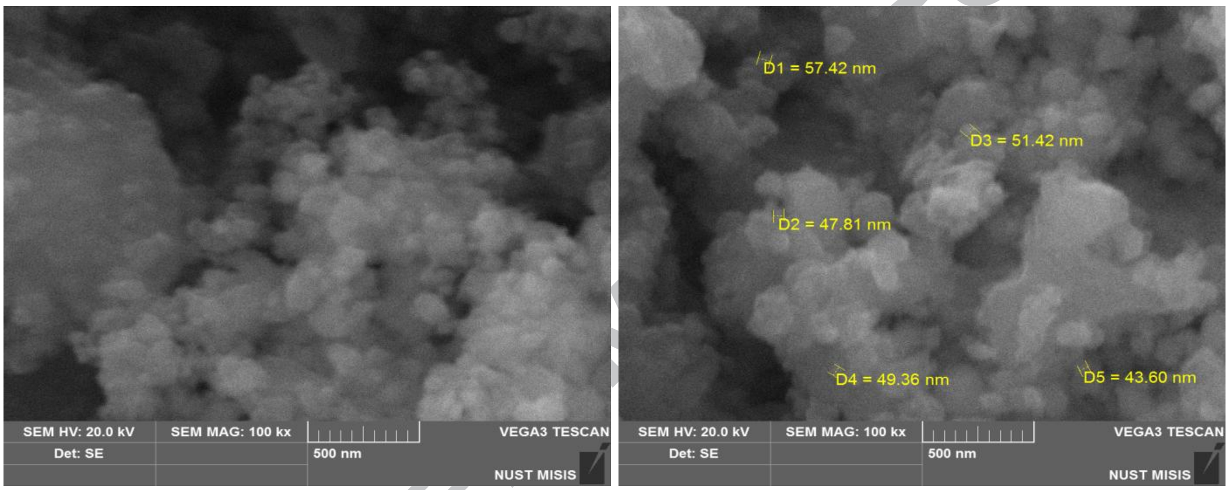


Fig.2 SEM images of a) & b) Al-Ti_2O_6 NPs

3.3 Characterization of membranes

According to literature survey, the inorganic additives mixed in the membrane have their own impact on the membrane morphology [35]. The structural morphology of MMMs was properly measured using SEM analysis. The well dispersion of NPs was observed on the surface image of membranes. However, the agglomeration was slightly seen in more concentrated NPs membranes. This type of agglomeration and dispersion was quite common in MMMs membranes [19].

Addition of the hydrophilic NPs into casting solution changes in kinetics and thermodynamics behavior during the phase inversion process and also it hinders the interaction between polymer chains, which leads to porous structure. Some reports pointed that the hydrogen bonding with solvent and hydrophilic pillars decreases outer flow of non-solvent which allows more water inside the membrane matrix. This creates more pores on membrane surface. Through these pores and nature of hydrophilicity, of the NPs bring them on the membrane surface. EDX analysis shows the presence of Ti and Al in the membrane surface.

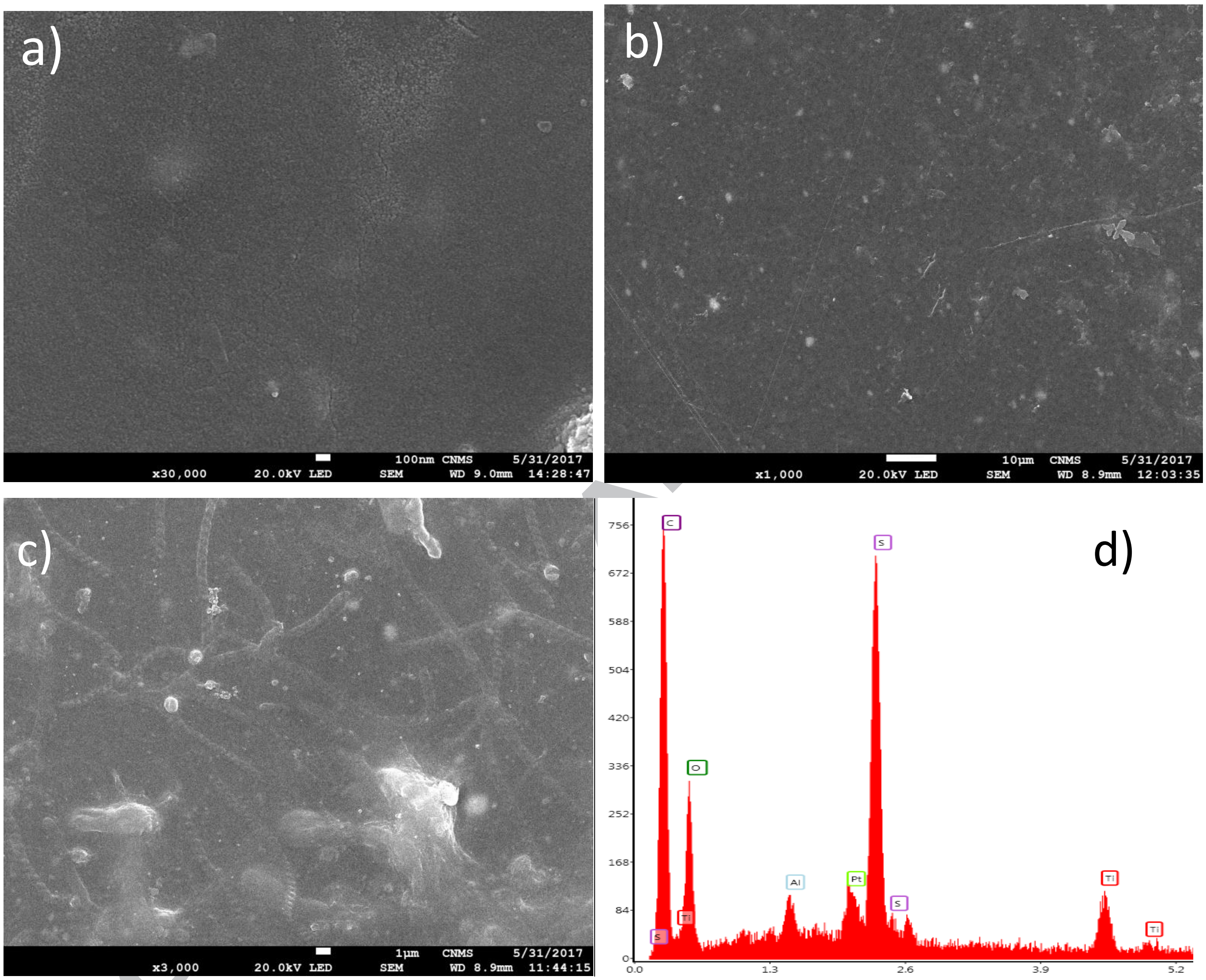


Fig. 3 FE-SEM analysis of a) 97:03(PSf-NPs) b) 96:04(PSf-NPs) c) 95:05(PSf-NPs) membranes d) EDX of the mixed matrix membrane

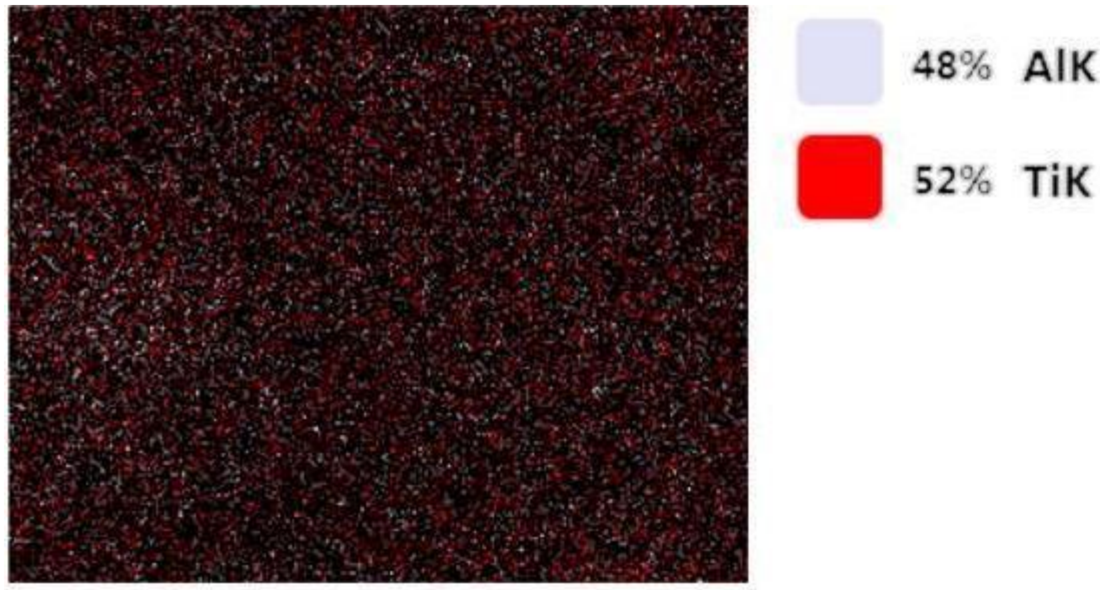


Fig. 4 Mapping study of 96:04 PSf:NPs membranes.

Elemental mapping study has been done to the membrane surface. The Figure 4 shows that the Ti and Al are staying together and uniformly distributed throughout the membrane surface. Both the metals staying together indicate that there is a strong interaction/bond between them.

3.4 Atomic Force Microscopy

The hydrophilic NPs enhance the membrane property by changing the surface morphology. The AFM analysis was done to know the surface roughness of the membrane. The image clearly shows that uppermost brightest area and dark valleys on the surface. The surface roughness was maximum in 96:04 PSf:NPs membranes. This is because hydrophilic NPs move towards outer surface by pulling of water in phase inversion. However, in highest concentration, membrane showed less Ra value because more concentration of NPs increases the viscosity of the casting solution. The thick casting solution forms smooth surface layer which decreases the surface roughness. However, V. Nayak et al. observed similar tendency with hydrophilic pillars [36].

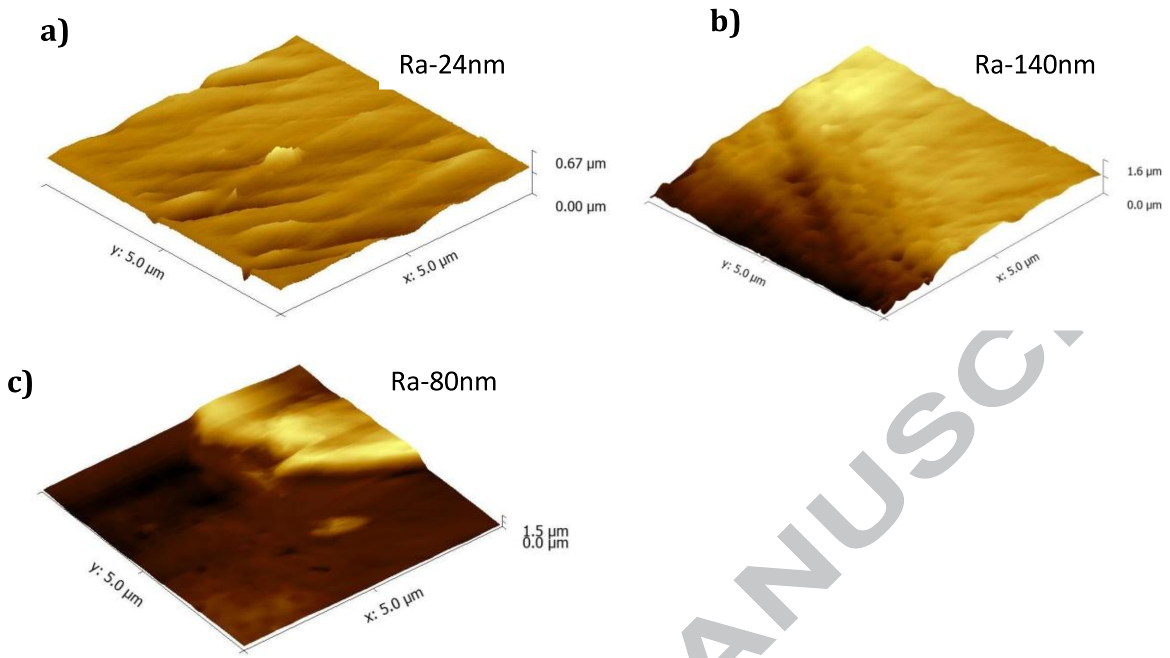


Fig. 5 AFM images of Polysulfone-$AlTi_2O_6$ composite membrane a) 97:03(PSf:NPs) b) 96:04(PSf:NPs) c) 95:05(PSf:NPs)

3.5 Water uptake& contact angle studies

Table 2 Contact angle and water uptake study of the membranes

Membrane code	**Water Uptake in %**	**WCA in °**
neat PSf	42±2	73±2
97:03(PSf-NPs)	98±4	67.2±2
96:04(PSf-NPs)	175±5	54±3
95:05(PSf-NPs)	198±4	51±1

Hydrophilicity of the membrane is one of the important requirements for water filtration membranes. Water uptake study and contact angle measurement are enough to prove the hydrophilicity of the membranes.

The water uptake is depends on number of hydrophilic sites present in the membrane. The membrane with 97:03(PSf:NPs) showed less water uptake and increase in concentration of NPs increases the water uptake because of more number of hydrophilic sites. The membrane with 97:05(PSf:NPs) showed 200 % of water uptake which is maximum in the mixed matrix membrane. The same tendency was observed in contact angle study of similar literature [37].

The WCA is decrease from 74^0 to 51^0 with increase in concentration of NPs. This result implies that hydrophilicity of the membrane surface improved by addition of NPs. This means the hydrophilic NPS migrates spontaneously towards the membrane surface to reduce the interface energy. This was also confirmed by SEM images. Hence, the presence of NPs increases the capacity of wet ability or water absorption by showing lower WCA. Moreover, NPs has more electronegative atom which has ability to make hydrogen bonding. Hence, membranes are showing more hydrophilicity as compared to the membranes containing single metal ion nanoparticles.

3.6 Pure water flux

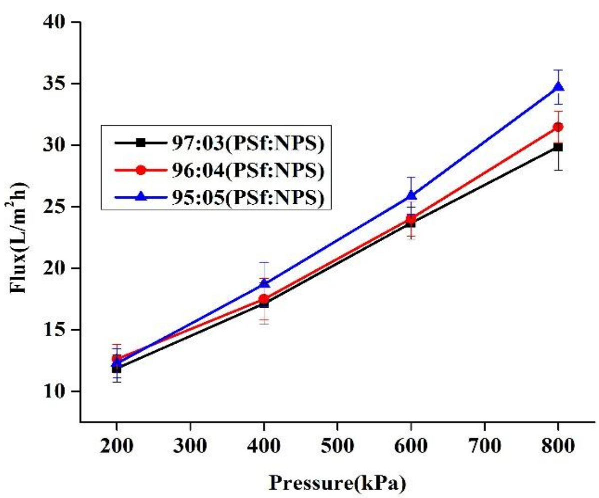


Fig. 6 Pure water flux of Polysulfone-$AlTi_2O_6$ composite membrane

The hydrophilicity of the membrane effectively support to the productivity of purification system. Hence, pure water fluxes (PWF) was studied at different applied pressure showed in Figure 6. The common observation was found that the PWF is increases with respect to applied pressure. However, composition concentration of NPs has also showed same tendency of the hydrophilicity. Literature also supports that higher the hydrophilicity, higher will be the PWF [30]. The PWF of 95:05, (PSf:NPs) membrane shows the highest of ~35L/m^{2}h and 95:03, (PSf:NPs) shows ~24L/m^{2}h at 800 kPa pressure. The same was explained by changes of membrane morphology, porosity and hydrophilicity of the membrane which was previously discussed.

3.7 Metal ion rejection with constant pressure

The prepared membranes were studied for Pb, Cd and As rejection performance. Fig.7 shows the Pb, Cd and As rejection respectively of all the prepared membranes. In order to study the effect of pore size on membranes the rejection studies were carried out at constant applied pressure 200kPa. As, Cd and Pb ions are present in an aqueous solution with the size of 205 pm, 158 pm and 202 pm, respectively.

The high rejection of the heavy metal ions with all the prepared membranes was affected by many factors. From the results, two observations were made; one being that the rejection of metal ion has decreased as the time increased from 20 min to 120 min and other being that the rejection of metal ion has been maximum when the concentration of NPs is 97:03 (PSf:NPs) in case As and Cd while in 97:05 (PSf:NPs), Pb rejection is maximum. This trend can be explained as follows, PSf is hydrophobic in nature, having insignificant interaction with metal ions, whereas NPs is hydrophilic which plays a major role in rejection of heavy metal ion. At a low concentration of NPs the negative charge on the surface of the membrane is less, but as the concentration of NPs increases, the negative charge increases. As a result, the repulsion between heavy metal cations and charge on the membrane will be more, which further helps in high rejection, however with the increase in time it is not only charge which rejects the heavy metal ions, however the size exclusively plays a vital role. Pb being larger in size in aqueous medium when compared with As and Cd can surround more number of water molecules around, which further supports in increasing the size of metal ions and helps in increasing the rejection performance. Hence, the 95:05(PSf:NPs) showed almost ~99% rejection for Pb.

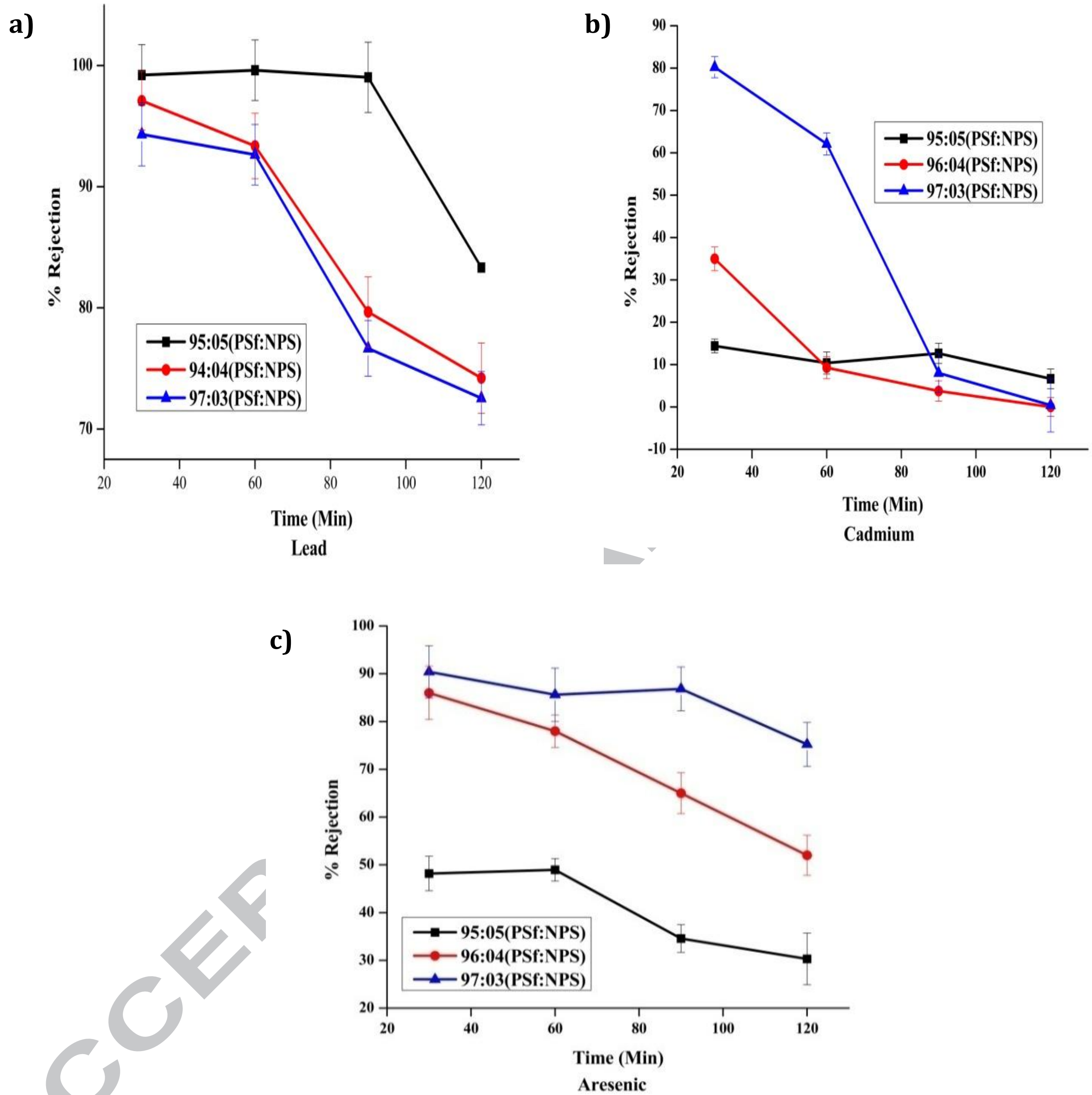


Fig.7 Rejection study of membrane

As the concentration of NPs increases although the charge on the surface of membrane increases but the amount of pores also increases which leads to the easy escaping of the small size heavy metal ions. Hence, membrane with 95:03(PSf:NPs) showed almost ~90% and ~80% rejection. As and Cd metal ions rejection which can be understood from the size of As and Cd in aqueous solution and the porosity concept. Similar results for heavy metals and other salts were reported for NF 270 membranes by Y. Sato et. al. and Al-Rashdi et.al [38, 39].

Conclusion

The proposed membrane showed effective impact on removal of heavy metal ions like As, Cd and Pb. This work involves a foremost, budgetary, simplistic technical method and most effective method to procure heavy metal ions present in aqueous solution. The well dispersed hydrophilic NPs additives were prepared by using simple co-precipitation technique. The presence and uniform distribution of the additive into the membrane matrix was confirmed by elemental mapping. The results revealed that, modified membranes displayed enhanced porosity, water uptake capacity, hydrophilicity as well as the heavy metal ion adsorption and all together played an important role in the high rejection of the heavy metal ions. Also the modified membrane exhibited superior pure water fluxes. Overall the NPs are an effective inorganic additive to improve the membrane performance and it can be employed as a potential candidate for the further studies.

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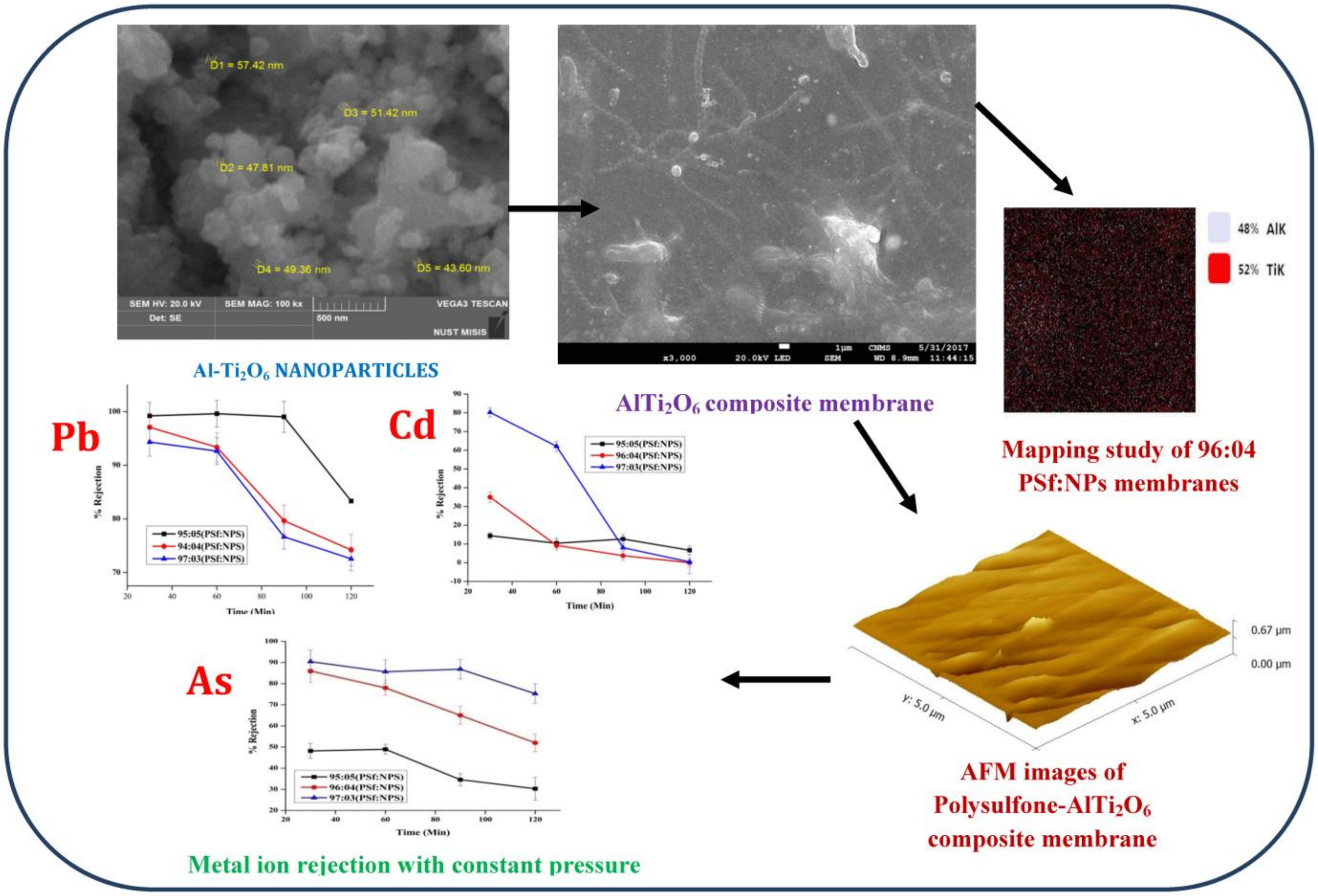
D1 = 57.42 nm
D3 = 51.42 nm
D2 = 47.81 nm
D4 = 49.36 nm
D5 = 43.60 nm
Al-Ti2O6 NANOPARTICLES
AlTi2O6 composite membrane
48% AlK
52% TiK
Mapping study of 96:04 PSf:NPs membranes
Pb
Cd
As
% Rejection
Time (Min)
95:05(PSf:NPS)
94:04(PSf:NPS)
96:04(PSf:NPS)
97:03(PSf:NPS)
0.67 µm
0.00 µm
y: 5.0 µm
x: 5.0 µm
AFM images of Polysulfone-AlTi2O6 composite membrane
Metal ion rejection with constant pressure

- Al-Ti_2O_6 a mixed metal oxide composite membranes
- About 96 % of Arsenic rejection
- Well dispersed NPs
- Results supported by characterization tool