

ORIGINAL RESEARCH PAPER

## Novel Adsorptive Mixed Matrix Membrane by Incorporating Modified Nanoclay with Amino Acid for Removal of Arsenic from Water

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### ABSTRACT

In this work, polysulfone (PSf) mixed matrix membranes were prepared by incorporating modified montmorillonite with lysine amino acid (MMT-Lys) for arsenic removal from water. Different tests including XRD, zeta potential, FE-SEM, contact angle, and pure water flux (PWF) were carried out to characterize modified MMT and fabricated mixed matrix membranes. XRD analysis showed that MMT was successfully modified with Lys and its zeta potentials transferred from negative to positive after modification. Positive charge of MMT-Lys made it proper for anionic arsenic removal from water. The obtained results showed that pure water flux and surface hydrophilicity of the membranes improved as MMT-Lys contents increased from 0 to 1.5 wt.%. The batch adsorption of fabricated membranes as a function of arsenic initial concentration and solution pH was investigated. The removal efficiency was increased with increasing the arsenic initial concentration; however it was decreased with increasing pH of solution. The results also revealed that the arsenic adsorption was most favorable in the neutral pH. Moreover, membrane reusability of the PSf/MMT-Lys (1.5 wt.%) membrane was assessed by conducting five cycles of adsorption-desorption experiments in dead-end filtration. The obtained results showed the applicability of the prepared membrane for multiple cycles.

**KEYWORDS:** Amino Acid, Arsenic, Mixed Matrix Membrane, Montmorillonite, Water

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## INTRODUCTION

Arsenic contamination of drinking water is one of the most serious concerns in the world. Arsenic can be found in water in inorganic form as oxyanions of arsenite, As(III), or arsenate, As(V) [1]. The major health concern of arsenic exposure through drinking water is the risk of skin, lung, liver and lymphatic cancer. Due to these health hazards associated with arsenic contaminated water, the World Health Organization (WHO) has set 10 ppb as the maximum contaminant level (MCL) of arsenic in drinking water [2]. Various treatment technologies including precipitation [3],

coagulation [4-6], ion exchange, adsorption [7-10] and membrane filtration through nanofiltration (NF) [7, 11-14] have been extensively used for arsenic removal. Among these methods, membrane processes have got much attention and demonstrated to be effective. However, NF membranes require high operational pressure and costly membrane. Consequently, researchers have focused on the development of new membrane based processes for arsenic removal from water. In this practice, adsorptive mixed matrix membrane was introduced for an efficient removal of small pollutants from water at low pressure [15-20].

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Table 1. Casting solution composition of neat and adsorptive mixed matrix PSf membranes.

Membrane	PSf (wt. %)	PEG (wt. %)	NMP (wt. %)	MMT-Lys (wt. %)
PSf	15	10	75	-
PSf/MMT-Lys (0.5 wt.%)	14.925	10	75	0.075
PSf/MMT-Lys (1.0 wt.%)	14.85	10	75	0.15
PSf/MMT-Lys (1.5 wt.%)	14.775	10	75	0.225

Adsorptive mixed matrix membranes are a kind of MF/UF membranes developed by embedding the inorganic materials into porous polymeric matrix [20, 21]. The adsorptive membranes combine the selectivity of adsorption method with the flow behavior of MF/UF membranes [22]. In terms of adsorptive membranes, reversible interaction is very important to have reusable membranes. Since electrostatic interaction is reversible, positive charged inorganic materials possess wider practical in anionic pollutant removal [23]. To prepare highly efficient adsorptive membranes for arsenic removal, investigators have used several adsorbents incorporating in polymer matrix. One of the most common ligand in positive charged adsorbents is amine group. The amino acids with amine and carboxylic groups are zwitterionic compounds that contain both positively and negatively charged chemical groups [24, 25]. Depending on the pH of their environment, amino acids may carry a net positive charge, a net negative charge, or no charge [26]. By taking this point into consideration, Lys as positively charged amino acid was used to modify MMT by a simple cation exchange method. Modified MMT with Lys was embedded in porous polymeric matrix. As for the polymer matrix, polysulfone (PSf) has been widely used in MF/UF membranes due to its outstanding properties such as low cost, availability, high mechanical strength, thermal and chemical stabilities, resistance over wide range of pH, as well as easy processability and variety of active functional groups [27-31]. In this study, modification of MMT and fabrication of PSf/MMT-Lys membranes were done successfully. The key membrane properties, such as hydrophilicity, PWF and morphology were evaluated. The adsorption isotherms of all membranes, dynamic adsorption and regeneration of membrane with high adsorption capacity were investigated and discussed.

## MATERIALS AND METHODS

### Materials

Commercial grade of polysulfone ( $\rho = 1250 \text{ kg/m}^3$ ,  $T_g = 190^\circ\text{C}$ ) purchased from Slovay and

used as polymer. Natural montmorillonite as nanoclay with cation exchange capacity (CEC) of 92.6 meq/100 g was obtained from Southern Clay Products Inc., Texas, USA. N-Methyl-2-Pyrrolidone (NMP) ( $\rho = 1030 \text{ kg/m}^3$ ) as solvent and polyethylene glycol (PEG) ( $M_w = 20000 \text{ (g/g mol)}$ ) as pore former were provided from Merck and used to fabricate membrane. Disodium hydrogen arsenate heptahydrate  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  to prepare arsenic solutions, lysine as surfactant and finally, NaOH and HCl were purchased from Merck, respectively.

### Synthesis and Characterization of MMT-Lys

The modified MMT with Lys was prepared by displacement of the sodium cations of MMT with the protonated Lys. Typically, 0.2 g of the MMT was dispersed in 25 ml of distilled water and suspension was continuously stirred for 24 h to swell the layered silicates. The Lys solution prepared separately by dissolving 0.1 g in 25 ml deionized water at  $30^\circ\text{C}$  following by incorporating of HCl while pH of solution adjusted to 3. Then solution added slowly to clay and mixture was subjected to mechanical stirring for 12 h in water bath at  $70^\circ\text{C}$ . After precipitation, the final modified MMT was separated by centrifugation and washed with water. Finally, the modified Mt was dried at  $60^\circ\text{C}$  for 12 h. X-ray diffraction (XRD) patterns of the resulting clays were obtained on (D500 Siemens, Germany) diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ) under a voltage of 35 kV and a current of 30 mA between  $2\theta$  of 2-50°.

The zeta potentials of unmodified and modified MMT were measured on a Nano ZS (red badge) ZEN 3600. The pH dependences of zeta potentials for MMT and MMT-Lys were measured in the aqueous solutions at different pH values, adjusted by NaOH and HCl.

### Preparation of Membranes

All membranes were prepared using non solvent induced phase separation method. Modified MMT in various weight percentage (0.5, 1.0 and 1.5) was dispersed into 40 g NMP using sonication by probe

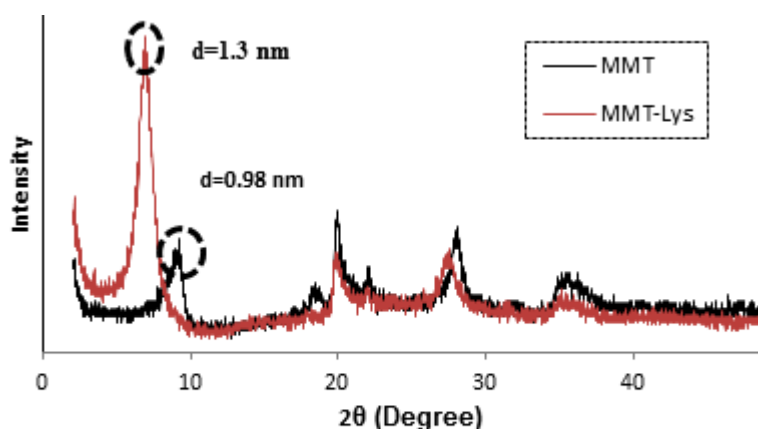


Fig. 1. XRD patterns of MMT and MMT-Lys.

system (Sonopuls HD 3200, Bandelin) for 30 min. Then, 7.8 g PSf and 2.6 g PEG were added to particles solution and mixture was stirred at 60 °C for 8h. After that, resulted homogenous solution sonicated for 15 min and then enough time was given for bubbles to be completely released. At least a portion of the achieved solution was poured onto flat plate glass and spread out using an automatic casting knife at the speed of 10 mm/sec. The thickness of all membranes was kept constant at 150 micrometers. Immediately after casting, the film was immersed in a water bath to initiate phase inversion. The obtained membranes were thoroughly rinsed with deionized water and dried at 70 °C to remove the residual solvent. The composition of each casting solution is given in Table 1.

#### Membrane Characterization

The morphology of the membranes was characterized by FE-SEM (MIRA3 FEG-SEM, Tescan). Cross-section samples were prepared by fracturing the membranes in liquid nitrogen. All samples were coated with gold by sputtering before observation to make them conductive.

The hydrophilicity of membranes was evaluated by measuring contact angle between membrane surface and water droplet using a contact angle goniometer (PGX, Thwing-Albert Instrument Co.). The average of 3 measurements was reported.

Pure water flux of membranes was determined using an in-house fabricated dead-end filtration system having 5cm<sup>2</sup> of membrane area. To minimize compaction effects, the pre-wetted membranes were compacted for 30 min at 2 bar. Then the pressure was reduced to 1.5.

#### Adsorption Capacity of Membrane Adsorbers

The adsorption capacity of membrane adsorbers in arsenic removal were investigated in batch adsorption. All adsorption isotherm experiments were performed in a series of sealed volumetric flasks containing 0.1g of membranes and 100 ml of As(V) solutions in the appropriate concentrations (5-15 ppm). The flasks were continuously shaken for 24 h at 25 °C while pH of the solution was adjusted to 7 at 200 rpm. The equilibrium adsorption amount and removal efficiency of As(V) by the membranes were calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{M_m} \quad (1)$$

$$\text{As (V) removal efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (2)$$

where  $C_0$  (mg/L),  $C_e$  (mg/L) and  $C_t$  (mg/L) are concentrations at the initial, equilibrium and time  $t$  in the solution, respectively,  $V$  is the total volume (L) of the arsenic solution and  $M_m$  is the mass (g) of dry membrane used in the adsorption study. The equilibrium concentrations of arsenic in the solutions were analyzed by atomic absorption Varian 220-Graphite Furnace spectroscopy.

In order to understand the adsorption in more detail, Langmuir and Freundlich isotherms as two common models were used. The Langmuir isotherm equation which characterizes homogeneous system with single layer adsorption is given by Eq. (3):

$$\frac{1}{q} = \frac{1}{(K_L * C_e * q_{max})} + \frac{1}{q_{mi}} \quad (3)$$

where  $q$  is defined before,  $q_{max}$  is the maximum

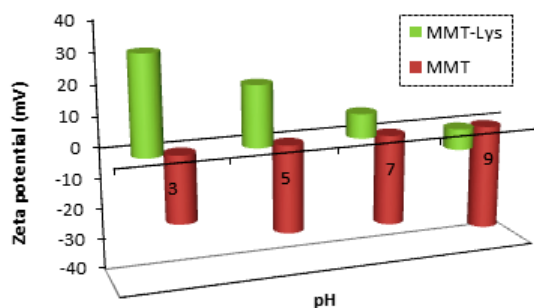


Fig. 2. Zeta potentials of MMT and MMT-Lys at different pH

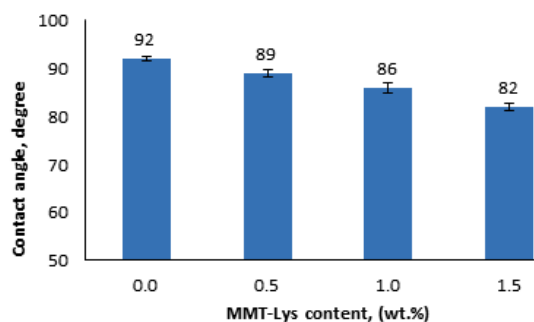


Fig. 3. Variation of contact angle of neat and adsorptive mixed matrix PSf membranes in different MMT-Lys contents

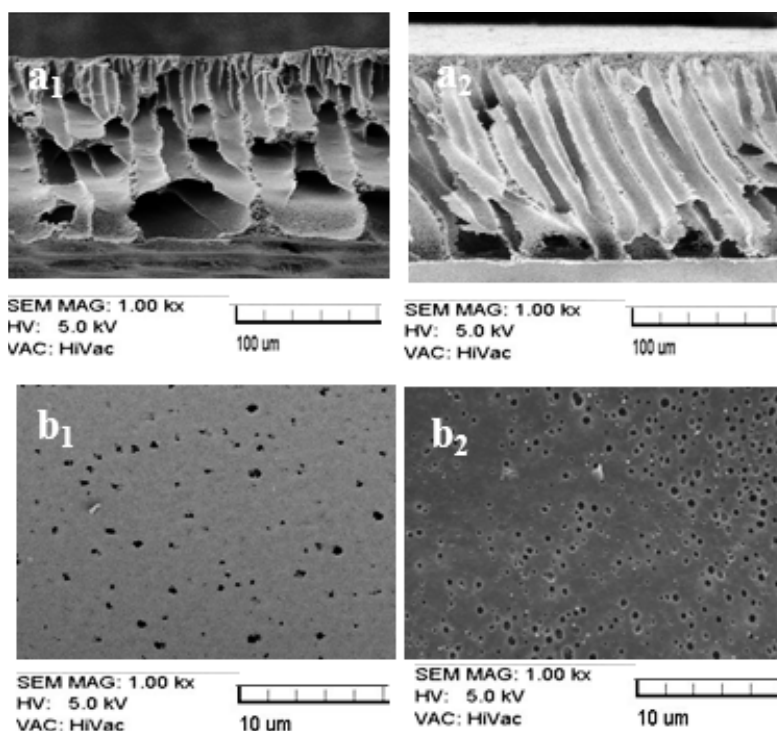


Fig. 4. FE-SEM images of cross-section (1) and top surface (2) of prepared membranes, (a) neat PSf and (b) PSf/MMT-Lys

adsorption capacity (mg/g),  $K_L$  is the Langmuir adsorption capacity (L/mg),  $C_e$  is the arsenic equilibrium concentration in solution (mg/L).

The Freundlich isotherm assumes that different sites with several adsorption energies are involved on a heterogeneous surface. The Freundlich isotherm equation is given by the following equation:

$$\ln(q) = \ln(K_F) + \left(\frac{1}{n}\right) \ln(c_{eq}) \quad (4)$$

where,  $K_F$  is the Freundlich constant and  $n$  is the

heterogeneity factor.

#### Dynamic Adsorption and Regeneration Studies

Filtration experiments were carried out in a dead-end filtration setup filled with 100 ppb As(V) solution. The system consisted of a cup connected to a pressure balloon and the filtration experiments were conducted at trans-membrane pressure of 1 bar and feed volume was 300 ml. Each cycle filtration followed by a regeneration step where 50 ml water with pH=9 filtered through the membrane. After regeneration, the second cycle of

Table 2. Langmuir and Freundlich isotherm parameters for As(V) removal using adsorptive mixed matrix membranes with different MMT-Lys contents at pH= 7.

Membrane	Langmuir model			Freundlich model		
	$K_L$ (L/mg)	$q_{max}$ (mg/g)	$R^2$	$K_L$ (mg/g)	1/n	$R^2$
PSf/MMT-Lys (0.5 wt.%)	0.27	8.59	0.999	2.21	0.469	0.980
PSf/MMT-Lys (1.0 wt.%)	0.49	11.17	0.999	3.38	0.445	0.984
PSf/MMT-Lys (1.5 wt.%)	0.53	14.12	0.999	4.81	0.501	0.988

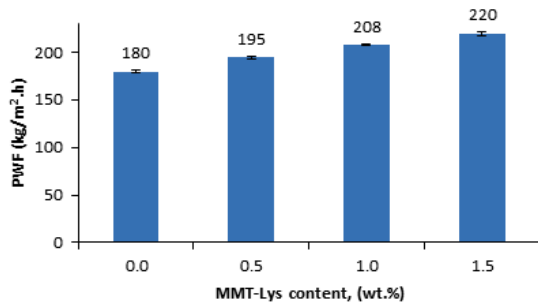
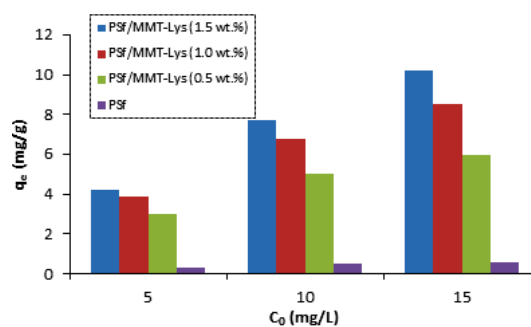


Fig. 5. Variation of pure water flux of neat and adsorptive mixed matrix PSf membranes in different MMT-Lys contents

Fig. 6. Equilibrium adsorption curves of As(V) onto the neat and adsorptive mixed matrix membranes, Conditions:  $m = 1.0$  g/L,  $T = 25$  °C,  $pH = 7$ 

experiments was initiated and this trend continued until 5 cycles.

## RESULTS AND DISCUSSION

### Characteristics of MMT-Lys

The X-ray diffraction patterns of MMT and MMT-Lys were depicted in Fig. 1. The basal spacing of the MMT is 0.98 nm which is calculated from the peak position at  $2\theta = 8.84^\circ$  using Bragg's equation. Diffraction peak of the MMT-Lys after the ion exchange shifted to a lower angle ( $2\theta = 6.95$ ,  $d = 1.3$  nm) compared to unmodified MMT. The increase in basal spacing of modified clays confirmed successful modification of MMT with Lys.

Zeta potentials of MMT and MMT-Lys in different pH were shown in Fig. 2. For MMT-Lys, the zeta potential was positive in wide range of pH while it was negative for unmodified MMT. Positive zeta potential means positive surface charge which increases the electrostatic attraction between adsorbent surface and the arsenic anions. This provided another evidence to demonstrate that Lys has been intercalated between MMT.

### Characterization of Membranes

The surface hydrophilicity is one of the significant properties of membranes and has significantly effect on the water flux of membranes. Fig. 3 shows the surface contact angles of the

membrane adsorbers as a function of MMT-Lys contents. As can be seen, water contact angle of PSf membrane was about  $92^\circ$  and incorporating of MMT-Lys resulted in reduction of water contact angle to  $82^\circ$  for PSf/MMT-Lys (1.5 wt.%). It can be seen that hydrophilicity of the membrane has been relatively improved. The increasing of membrane hydrophilicity is most due to the hydrophilic polar amine functional groups of modified clay.

FE-SEM images of the top surface and cross-section of PSf and PSf/MMT-Lys (1.5 wt.%) are shown in Fig. 4. As can be seen from Fig. 4(a) images, the membranes exhibit typical asymmetric structure consists of finger-like pores and macrovoids. Some differences can be seen between the PSf and the mixed matrix membrane. The cross sectional images of PSf membrane reveal the presence of macrovoids. It is also observed that macrovoids tend to decrease in size and become narrower, however finger-like pores become longer by incorporating MMT-Lys. Incorporating of MMT-Lys made the dope solution thermodynamically less stable and brought rapid nucleation from the polymer lean phase and promoted macrovoid formation.

The top surface images of membranes (Fig. 4(b)) show that the number of pores increases by incorporating MMT-Lys.

Results of pure water flux of PSf and membrane

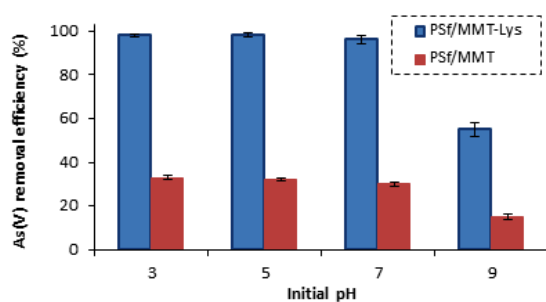


Fig. 7. Effect of pH on the adsorption of As(V) on the PSf/MMT-Lys (1.5 wt.%), Conditions: As(V) concentration= 100 ppb,  $m = 1.0$  g/L,  $T = 25$  °C

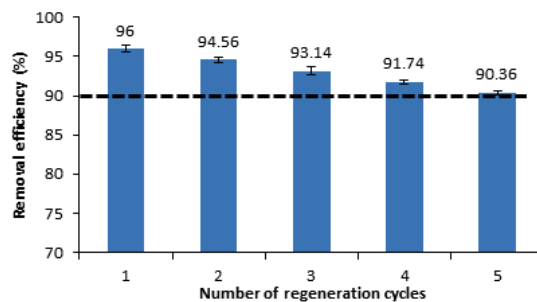


Fig. 8. As(V) removal efficiency in 5 consecutive cycles in dead-end filtration setup using PSf/MMT-Lys (1.5 wt.%)

Table 3. Equilibrium As(V) adsorption capacities and number of regeneration cycles of different mixed matrix membranes.

Adsorptive particles	Polymer	$C_0$ of arsenate (ppm)	$q_e$ (mg/g)	Number of regeneration cycles	Reference
Zirconia	PVDF	100	20	2	[34]
TiO <sub>2</sub>	PES	200	125	1	[17]
Laterite	Polyacrylonitrile	100	2.5	4	[35]
MMT-Lys	PSf	20	10.2	5	This study

adsorbers were shown in Fig. 5. According to the effect of MMT-Lys on pure water flux of membranes, it is obvious that addition of MMT-Lys in the casting solution increased pure water flux of membranes. However, higher content of MMT-Lys, i.e. 2 wt. %, resulted in decrease in water flux which has not shown in results. Consequently, 1.5 wt.% loading of MMT-Lys was selected as maximum amount for incorporation into PSf matrix. The main reason to justify the increase in the PWF of the membrane could be attributed to the bigger pore size as well as the extended macrovoids of the mixed matrix membrane[32].

#### Equilibrium Study

The relationships of the equilibrium adsorption capacities with the initial concentrations of the arsenic are shown in Fig. 6. Fabricated membrane adsorbers demonstrated increasing trend in adsorption capacity with increasing initial concentrations of arsenic, due to the increasing chance of adsorption interaction between arsenic and MMT-Lys in solution with higher As(V) concentrations. Comparison between adsorption capacities of mixed matrix membranes showed that the adsorption capacity increased by increasing the MMT-Lys content. The maximum adsorption capacity was seen in PSf/MMT-Lys (1.5 wt.%) membrane and it was used for filtration studies. The constants for the Langmuir and Freundlich

isotherms were calculated by linear regression of the linear forms of the isotherms and the obtained results were shown in Table 2. From  $R^2$  values, it was found that all mixed matrix membranes favor the Langmuir adsorption isotherm and the adsorption processes were monolayer adsorption.

#### Effect of Solution pH

The pH is an important parameter that controls the adsorption of arsenic. The removal efficiency of arsenic at different pH is studied in batch experiments and the obtained results are shown in Fig. 7. At initial pH ranging from 3 to 7, 90% of arsenic can be removed successfully. At pH lower than isoelectric point of MMT-Lys the surface of modified MMT in the membrane is in protonation state and causes to increase the positively charged sites. Consequently, the adsorption of arsenic increases through electrostatic attraction between arsenic anions and positive amino chain of MMT-Lys. However, in high pH, the removal efficiency of PSf/MMT-Lys (1.5 wt.%) declined to 50%. The main reason for decreasing the arsenic adsorption at high pH is repulsion between the negatively charged surface sites and arsenic anions.

#### Dynamic Adsorption Studies

For filtration study, PSf/MMT-Lys (1.5 wt.%) with high batch adsorption capacity was placed in a dead-end filtration cell. As(V) removal efficiency

throughout five consecutive cycles was examined at As(V) concentration of 100 ppb. In each cycle 300 ml of As(V) solution was filtered and followed by regeneration step where 50 ml of water with pH=9 was filtered through the membrane. As shown in Fig. 8, removal efficiency was 96% at the first step and decreased with increasing the regeneration cycles. Based on removal efficiency of cycles, it could be concluded that PSf/MMT-Lys (1.5 wt.%) was capable of As(V) removal for 5 cycles with simple regeneration method. This indicates that the adsorptive membrane can be used for multiple cycles.

In Table 3, equilibrium adsorption capacity and the number of regeneration cycles of prepared mixed matrix membrane were compared with other membranes reported in the literature for arsenic removal. The results reported in Table 3 confirm the acceptable adsorption capacity of developed PSf/MMT-Lys in comparison with other mixed matrix membranes with regard to their high As(V) initial concentration. Furthermore, incorporating MMT-Lys into membrane matrix can overcome the drawback of Laterite/polyacrylonitrile membrane which exhibits lower adsorption capacity. The main advantage of developed PSf/MMT-Lys membrane is its high regeneration capability due to the electrostatic interaction between arsenate oxyanions and positive groups of MMT-Lys in neutral pH. However, the adsorption of oxyanions on metal oxides has been regarded as a typical ligand-exchange process which always involves a highly specific chemisorption [33].

## CONCLUSION

The modified montmorillonite with lysine amino acid (MMT-Lys) incorporated polysulfone (PSf) membranes were prepared by non-solvent induced phase separation method. The performance of PSf/MMT-Lys adsorptive mixed matrix membranes for arsenic removal from water was investigated. The fabricated membranes exhibited higher pure water flux and hydrophilicity in compare of neat PSf membrane. The FE-SEM studies demonstrated that incorporating MMT-Lys leads to an increase in surface porosity and extended figure like voids. The batch adsorption studies exhibited that the arsenic adsorption was most favorable in the neutral pH. In addition, the obtained results revealed that PSf/MMT-Lys (1.5 wt.%) exposed high adsorption capacity and it was used for filtration studies. The dynamic adsorption experiment showed that

fabricated mixed matrix membrane can be used successfully for 5 multiple adsorption-desorption cycles.

## CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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