# Improvement in heavy metal removal from aqueous solution using polyetherimide nanofiltration membrane modified by coating approach

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GRAPHICAL ABSTRACT
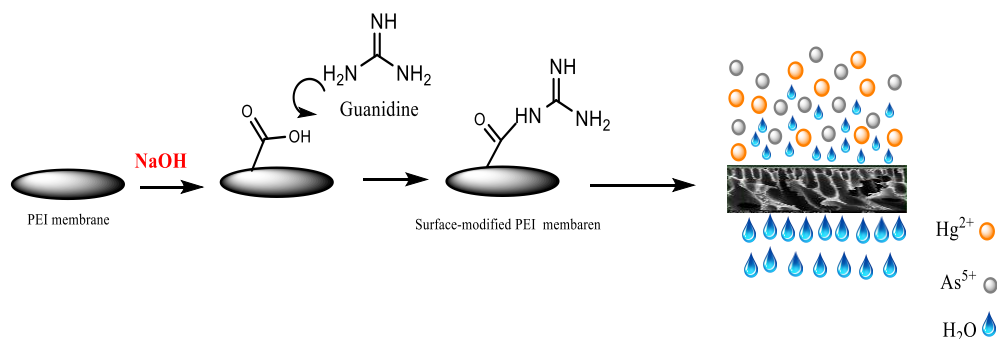
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ABSTRACT

This research focused on improving the antifouling properties and rejection performance of polyetherimide (PEI) nanofiltration membrane by chemical surface modification (surface coating). The hydrophilicity of the PEI nanofiltration membrane's surface was enhanced by anchoring guanidine on its surface which the used dosage of guanidine was considered as a variable (0.5, 1, and 1.5 g/L of guanidine concentration). ATR-FTIR, SEM, AFM, and water contact angle were used to characterize the surface-modified membranes. Also, dry milk powder solution was considered as an organic foulant to assess antifouling features of the fabricated membranes. According to the obtained results, the surface-modified membrane with 0.5 g/L of guanidine concentration was the optimal surface-modified membrane with pure water flux (PWF) and flux recovery ratio (FRR) of 11.6 kg/m^2.h and 88.8%, respectively. Moreover, the capabilities of the optimal surface-modified membrane and the pristine membrane for rejecting AS^{5+} and Hg^{2+} in aqueous solution with concentrations of 20 ppm and 50 mg/L were compared. Based on the obtained results, the optimal surface-modified membrane rejected more than 98.5 % of AS^{5+} and Hg^{2+} solutions with 20 and 50 mg/L of metal ion concentrations.

1. Introduction

Nanofiltration of polluted water is one of the most popular strategies for providing safe drinking water specially when contaminated water contains heavy metal ions. Heavy metal ions are prone to accumulate in human body which in turn different complications will be expected (Nayak et al. 2017). As a fact, the ordinary function of cells is influenced by the aggregation of heavy metals in different organs. Arsenic and mercury are two common heavy metals in water sources, causing various diseases in human body like kidney, liver, lungs and skin (Farzin et al. 2022). Therefore, heavy metal rejection has been considering as a priority for supplying drinking water (Eisapour Chanani et al. 2015). Nanofiltration is a moderate driven-pressure process which is efficient to reject multivalent ions(Ye et al. 2019). However, fouling phenomena could hinder the filtration process, consequently different strategies have been explored to improve antifouling properties (Oulad et al. 2019).

Mixed matrix and surface modification procedures were investigated extensively by researchers to boost membranes' antifouling features(Pandey et al. 2020; Peng et al. 2019). Surface modification such as grafting, interfacial polymerization, plasma treatment, surface coating. In surface modification bulk polymer has been intact, so mechanical and chemical

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resistances and morphology of bulk polymer have been maintained. Therefore, surface modification has been engrossed researchers' attention (Zaidi et al. 2019). Across different surface modification methods, surface coating is a simple and effective methodology to ameliorate surface properties like hydrophilicity and smoothness (Upadhyaya et al. 2018).

Different polymers have been dedicated to fabricate nanofiltration polymeric membranes for heavy metal rejection e.g. polysulfone (PES) (Zinadini and Gholami. 2016), polyether sulfone (PES)(Asadi et al. 2022), poly vinylidene fluoride (PVDF) (Zeng et al. 2016), polyvinyl alcohol (PVA) (Ullah et al. 2020), poly acrylonitrile (PAN) (Deng et al., 2019), polyetherimide (PEI) (Hebbar et al. 2014), polyvinyl chloride (PVC) (Hezarjaribi et al. 2021) and etc. PEI polymer with ether and imide groups displays an excellent resistance forward to chemical and mechanical tenses(Bakeri et al. 2010).

From the literature, glycidyl-POSS functionalized graphene oxide nanoplates was embedded in PEI based nanofiltration membranes to reject Na_2SO_4, $Pb(NO_3)_2$, $CrSO_4$ and $Cu(NO_3)_2$ from water. Based on the reported results, the ranges of $CrSO_4$, $Cu(NO_3)_2$ and $Pb(NO_3)_2$ rejections were (63–80 %), (51–55 %) and (53–78 %), respectively, for the amended membrane with flux recovery ratio (FRR) of 92 % (Bandehali et al. 2020).

Namvar-Mahboub and co-workers used both mixed matrix and surface modification to tailor PEI membrane to reject organic solvent. Amino-functionalized silica was embedded in PEI mixed matrix and then the obtained modified membrane was considered as a support layer to perform interfacial polymerization which the oil rejection of 94.72 % and permeate flux of 10.4 L/m². h were reported (Namvar-Mahboub and Pakizeh. 2013).

In a report, a PEI nanofiltration membrane modified with tetrakis (hydroxymethyl) phosphonium chloride as an ionic liquid to attain the better performance in rejecting heavy metal ions. From the achieved data, around 95% of Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+} and about 90% of Pb^{2+} were rejected (Zhang et al. 2022). In another study, polydopamine modified halloysite nanotube (HNT) was incorporated in PEI nanofiltration membrane which a membrane with 3wt% of HNT as additive showed 74.5 % of FRR and a superior potential for Pb^{2+} and Cd^{2+} removal (Hebbar et al. 2016). Also, Bowen and his group published the experimental data obtained from the fabrication of membranes with polyetherimide (PEI) and sulfonated poly (ether ether ketone) (SPEEK) to reject NaCl. With the increase of SPEEK from 3% to 6% in the casting solution, water permeability increased from $24.0 \pm 2.1 \times 10^{-11}$ to $36.6 \pm 3.0 \times 10^{-11}$ m³/sN, rejection of NaCl increased from 39% to 59% (Bowen et al. 2005).

In the present study, the surface of PEI membrane has been amended by guanidine in three levels of guanidine concentrations (0.5, 1, and 1.5 g/L). Guanidine with hydrophilic groups of NH and NH_2 was integrated on the PEI membrane's surface to improve its hydrophilicity and antifouling resistance. The successful integration of guanidine on the PEI membranes' surfaces was verified by ATR-FTIR test. Also, SEM, AFM, and water contact angle (WCA) tests were accomplished to analyze the surface-modified membranes' surface. Antifouling features of the fabricated membranes were examined by using dry milk powder solution. Finally, the optimal membrane and the pristine NF membrane were applied to reject As^{5+} and Hg^{2+} from aqueous solution with 20 and 50 mg/L of metal ion concentrations.

2. Materials and Methods
2.1. Materials

In order to fabricate the pristine membranes, polyetherimide, polyvinylpyrrolidone (PVP, MW = 25000 g/mol), N-Methyl Pyrrolidone (NMP) were purchased from Merk. To apply surface modification, guanidine and sodium hydroxide were delivered by Sigma-Aldrich. Also, to determine the antifouling properties of the PEI nanofiltration membranes, a commercial supply of milk powder (GUIGOZ Growt.h 3 Formula) was purchased.

2.2. Membrane fabrication

To fabricate PEI pristine membranes, the non-solvent induced phase inversion technique was applied. In this mean, 16 wt.% of PEI and 4 wt.% of PVP (to provide porosity) were dissolved in 80 wt.% of N-methyl pyrolidone (NMP). It should be mentioned that after trying different weight percentages of PEI and PVP, it was found that 16 % and 4 wt. % of PEI and PVP were the appropriate to obtain rationale permeate flux. At higher weight percentage of PEI and lower weight percentage of PVP, the obtained casting solution was very viscose and the obtained membrane was tight so that permeate flux was trivial. To test the performance of nanofiltration membrane the rejection of direct red and NaCl have been investigated which nearly 100 % of direct red and 70% NaCl were rejected. Therefore, the aforesaid weight percentages of PES and PVP were considered to fabricate the bare PEI membrane. The mixture was agitated for one day and then a casting knife with thickness of 150 μm was used to fabricate the PEI membranes. The obtained homogeneous mixed solution was casted on a clean glass surface and then immersed in a distilled water bath (as anti-solvent) immediately. After soaking the attained membrane in water bath for a night, it was placed between two sheets of filter paper for a day to get a dried membrane.

2.3. Surface modification

To apply surface modification, guanidine solutions with different concentrations of 0.5, 1, and 1.5 g/L were provided. Firstly, three sheets of the bare membrane were immersed in NaOH solution of 3 M for 1 h. Then, they were rinsed by distilled water to get neutral pH. Finally, the mentioned membranes were soaked in guanidine solutions with designated concentration for 2h and then rinsed by distilled water.

Table 1. The casting solution composition for membrane preparation.

Membrane type	PEI, wt.%	PVP, wt. %	DMF, wt.%	Guanidine concentration, g/L
M1	16	4	80	0
M2	16	4	80	0.5
M3	16	4	80	1
M4	16	4	80	1.5

2.4. Membrane characterization

Attenuated total reflectance (ATR), scanning electron microscopes (SEM), atomic force microscopy (AFM) and water contact angle techniques were applied to investigate the physicochemical features of the pristine and the surface-modified membranes. The surface morphologies and surface roughness of the fabricated membranes were analyzed by Philips-X130 and AFM USING Nanosurfs Mobile scanning probe-optical microscope (Switzer- land) equipped with Nanosurfs Mobile software (version1.8), respectively. To verify the attachment of guanidine on the membranes' surface ATR method was used on a Bruker TENSOR27 spectrometer in the range of 650–4000 cm⁻¹. Also, to evaluate the membranes' hydrophilicity, water contact angles of the pristine and surface-modified membranes were determined by a contact angle goniometer (G10, KRUSS, Germany).

2.5. Fouling evaluation

To assess antifouling properties of the surface-modified membranes, a dead-end setup has been applied as shown in Fig.1. Dry milk powder solution with concentration of 1000 ppm used as an organic foulant. A three-step filtration was performed for each membrane to determine main fouling parameters. At the first step, distilled water was passed through the mentioned setup under 4 bar of operating pressure which pure water flux ($J_{w,1}$) was calculated based on the following equation:

$$J_{w.1} = \frac{M}{A\Delta t} \tag{1}$$

where, M is the weight of permeate (kg), A is the membrane surface area and Δt is the filtration time. After that, permeate flux was measured over filtering dry milk powder solution for 90 min (J_p) and then the membrane was rinsed by pure water and soaked in distilled water for 20 min. Finally, pure water flux was measured again for 1h of filtering ($J_{w,2}$). According to the equations of 2-5, four main fouling parameters including flux recovery ratio (FRR), total fouling ratio (Rt), reversible fouling ratio (R_r), and irreversible fouling ratio (R_{ir}) have been calculated.

$$\text{FRR} = \left(\frac{J_{w.2}}{J_{w.1}}\right) \times 100 \tag{2}$$

$$R_t(\%) = \left(1 - \frac{J_p}{J_{w.1}}\right) \times 100 \tag{3}$$

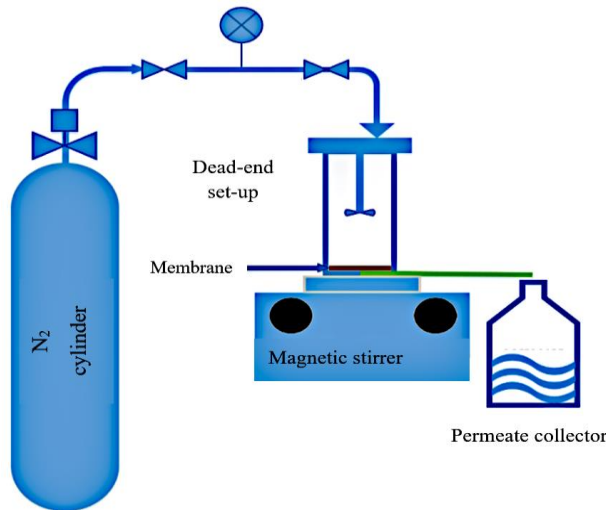$$R_r(\%) = \left(\frac{J_{w.2} - J_p}{J_{w.1}}\right) \times 100 \tag{4}$$

Fig.1. Schematic of the dead-end set-up.

3. Results and Discussion
3.1. Membrane surface analysis

To substantiate the successful integration of guanidine on the PEI membrane surface, ATR-FTIR spectra of the pristine PEI (M1) and also M2 with the lowest dosage of guanidine (0.5 g/L) are presented in Fig. 2. From the spectra shown in the figure, meaningful differences between the appeared peaks of M1 and M2 could be found as a result of anchoring guanidine on the PEI membrane surface. The peaks appeared at 1075 cm⁻¹ and 1237 cm⁻¹ are related to the C-O stretching vibration, and the peak of 1273 cm⁻¹ is attributed to the C-N stretching vibration. Also, symmetric and asymmetric starching vibration of C=O is responsible for the peaks observed at 1723 and 1777 cm⁻¹, respectively. All of the aforesaid peaks describe PEI structure which appeared in both M1 and M2 spectra, verifying that surface modification was implemented without detrimental impact on the original structure of the PEI membrane. While, some new peaks emerged in M2 spectrum including the peak of 1232 cm⁻¹ which is related to the amine C-N stretching vibration, and the peaks shown in 1553 and 1655 cm⁻¹ referred to the stretching and bending vibrations of amine N-H. Therefore, it could be concluded that amine group of guanidine is responsible for the observed new peaks in M2.

3.2. Membrane surface morphology

To portray the effect of surface modification on the membranes' surface, the cross-section SEM images of the pristine and surface-modified membranes were illustrated in Figs. 3a-d. From the figures, an asymmetric structure could be observed for all of the membranes includes the upper layer with tight pores which guarantee the quality of the permeate and the downer layer with loose pores which plays the main role in membrane's strength. Besides, a layer on the surfaces of M2, M3, and M4 could be found in SEM images, verifying a successful surface modification. It is worth noting that with increasing the guanidine dosage from 0.5 to 1.5 g/l, the thickness of surface layer has been increased so that M4 showed the thickest layer on the surface compared to the others. Besides, it could be seen that the pores of the upper layer in M4 was not as clear as the other membranes, corroborating that some pores were filled with guanidine molecules. It should be mentioned that the finger like structure of the fabricated membranes was not influenced by surface modification, verifying that guanidine was anchored on the membrane surface without altering the main matrix structure.
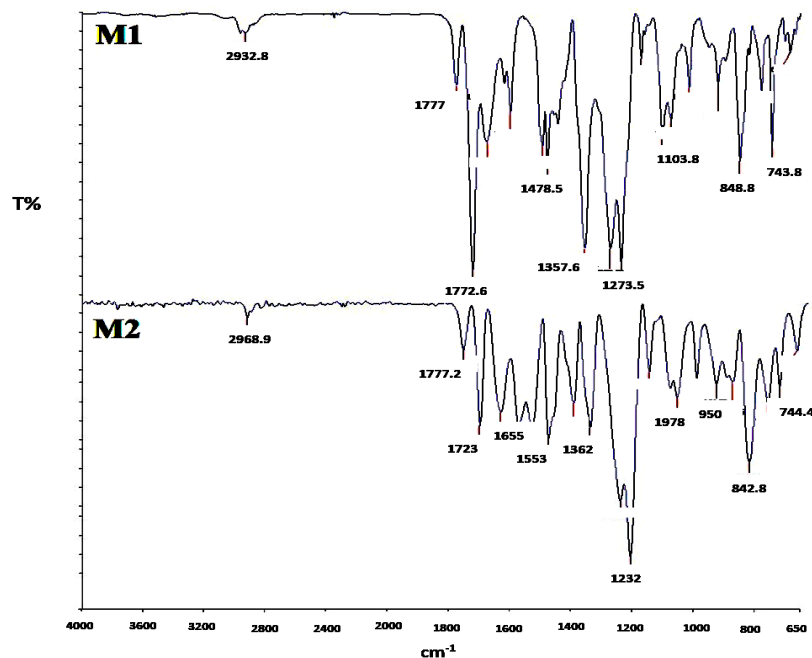

Fig. 2. ATR-IR spectra for M1 and M2.

filling up the valleys on the surface. The lower surface roughness, the lower fouling rate will be attained. As the difference between picks and valleys decreased, the possibility of trapping foulant agents will be decreased meaningfully, therefore antifouling properties of the pristine PEI membrane enhanced with inserting guanidine on the surface. While, a further increase in guanidine concentration from 1 to 1.5 g/l, Sa increased from 0.19 to 0.24 nm resulted in a thicker layer of guanidine and agglomerating guanidine on the surface of M4 (as can be seen in Fig. 3d).

3.3. Membrane hydrophilicity and PWF

The hydrophilicity of the fabricated membranes was assessed by measuring water contact angle (WCA). WCA of the pristine and surface-modified membranes are illustrated in Fig.5. The applied surface modification resulted in WCA of the pristine membrane to reduce so that WCA of the pristine membrane alleviated from 65.5º to 53.3º for M3. As a fact, the presence of guanidine on the membrane surface increased the membrane's hydrophilicity owing to its hydrophilic functional groups like NH and NH_2. It should be mentioned that an increase in guanidine loading from 1 to 1.5 g/l led to an increase in WCA to 60º which could be attributed to agglomerate guanidine on the membrane surface, causing a reduction in hydrophilic groups.

PWF is considered as an important parameter to introduce a new fabricated membrane, thus PWF is reported for all the prepared membranes in Fig. 5. In general, it could be found from the comparison of the membranes' PWF which surface modification had a negative impact on PWF. The pristine membrane's PWF was nearly halved by inserting guanidine layer with concentration of 1.5 g/l. A descending trend in PWF by increasing guanidine dosage from 0.5 to 1.5 g/L could be observed in the Fig., as a result of creating a thick guanidine layer on the membrane's surface which acts as a barrier to pass water molecules from the membrane.
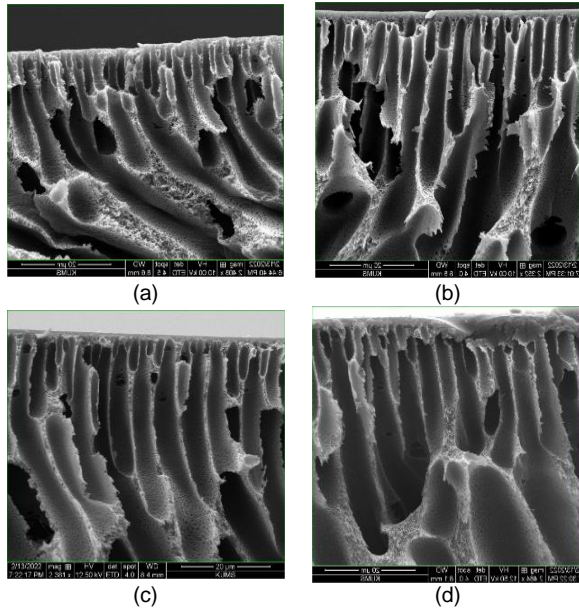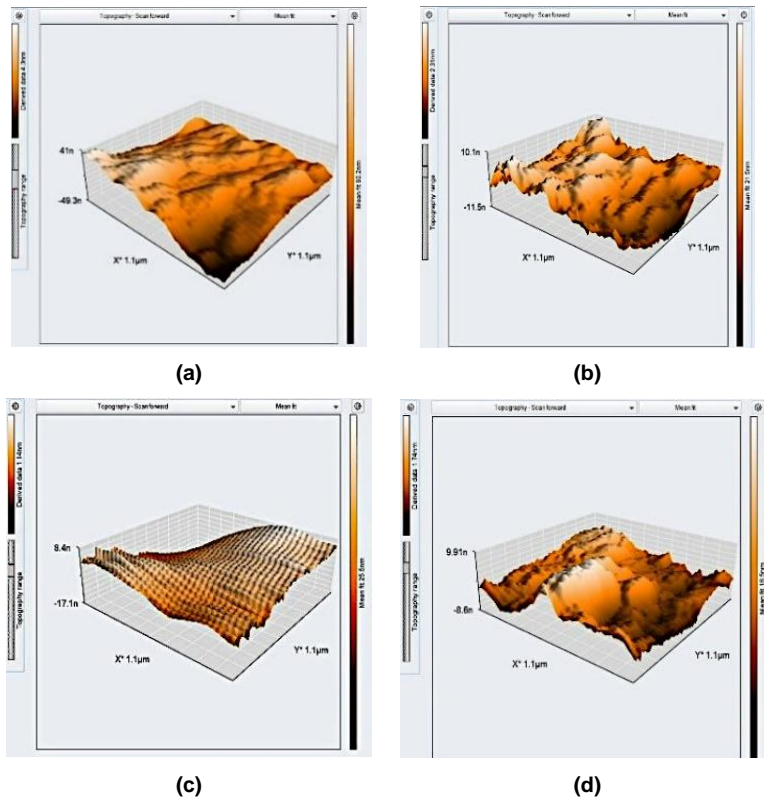
Fig. 3. SEM images of a) the pristine (M1), and surface-modified membranes with different guanidine concentration of b) M2, c) M3, d) M4

The surface roughness of the fabricated membranes was assessed by AFM technique which AFM images and roughness parameters presented in Figs. 4a-d and Table 2. From the images and roughness parameters, the pristine surface's roughness diminished by applying surface modification so that Sa value of the pristine membrane was reduced from 2.45 to 0.19 nm for M3. As a fact, the smoother surface was achieved by integrating guanidine on the bare membrane's surface due to

(a)   **(b)**

(c)   **(d)**

Fig. 4. AFM images of (a) the pristine (M1), and surface-modified membranes with different guanidine concentration of (b) M2, (c) M3, (d) M4

Table 2. Surface roughness parameters of the prepared membranes.

Membrane type	S_a, nm	S_q, nm	S_y, nm
M1	2.45	2.58	3.2
M2	0.32	0.42	5.35
M3	0.19	0.24	1.73
M4	0.24	0.33	3.27

It's worth noting that it's expected to get a rise in PWF as hydrophilicity is increased, however; in the present research the obtained PWF revealed a reduction with increasing hydrophilicity (decreasing WCA). This result could be explained by a barrier role of guanidine layer on the surface which impede water molecules' passage.
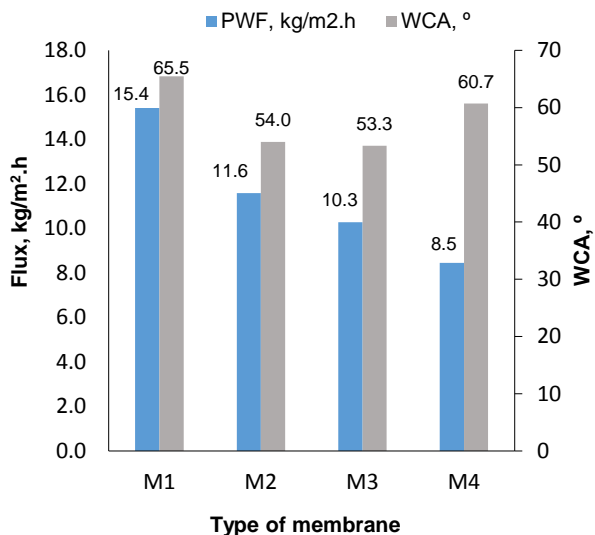

Fig. 5. Pure water flux and water contact angles of all the fabricated membranes

3.4. Antifouling properties

A three-step filtration has been applied to compare antifouling features of the surface-modified membranes and the obtained data are shown in Fig.6a. As could be seen from the figure, PWF of M1 in the first stage of pure water filtration was upper rather than the others, whereas, its permeate flux alleviated significantly during filtering dry milk solution and also the second stage of filtering pure water. In contrast to M1, the surface-modified membranes exhibited a moderate reduction in permeate flux over filtering dry milk solution and second pure water. This finding corroborates more hydrophilic surfaces of the surface-modified membranes caused by hydrophilic groups of guanidine which generate a hydration layer near the surface to hinder the formation of cake layer and pore blocking on the amended membranes' surfaces.

To present deeper insight into fouling behavior of the surface-modified membranes, FRR, R_r, and R_{ir} were calculated and reported in Fig. 6b. As it is obvious, the boost in FRR values of the surface-modified membranes is recognizable compared to the pristine one (M1), resulting from the presence of guanidine on their surfaces. The FRR of M1 was increased nearly 58% by applying guanidine solution with concentration of 0.5 g/l for surface modification (M2). Nonetheless, a descending trend in FRR could be seen with an increase in guanidine concentration from 0.5 to 1.5 g/L (M2 compared to M3 and M4). This outcome is in line with PWF data as discussed earlier. Likewise, the surface-modified membranes presented upper values of R_r and lower values of R_{ir} in comparison with the bare membrane (M1). Thus, it can be deduced that the surface-modified membranes are more reliable to perform in long-term application benefiting

from providing approximately constant permeate flux and also easy recovery compared to the bare PEI nanofiltration membrane. This assumption has been investigated and the obtained data is displayed in Fig.6c. In this mean, M1 (the pristine membrane) and M2 (as the optimal membrane) were operated for filtering dry milk solution (1000 ppm) over five cycles (800 min). It should be mentioned that M2 was considered as the optimal surface-modified membrane by noticing the data of PWF, FRR and R_{ir}. As expected, PWF of M2 was recovered almost completely during five cycles, nevertheless, PWF of M1 diminished over the operating cycles.
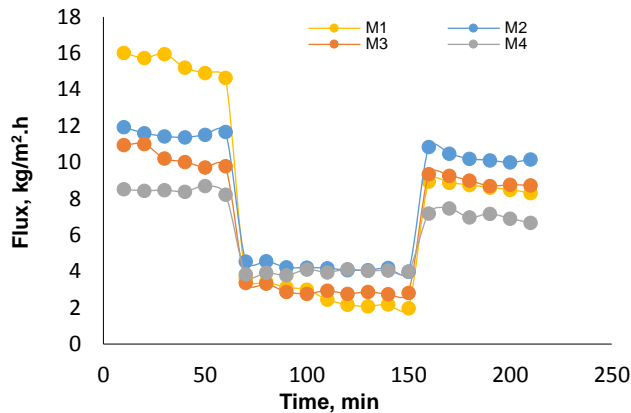
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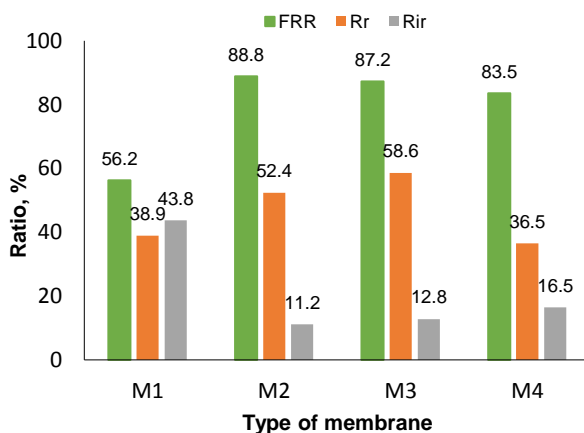
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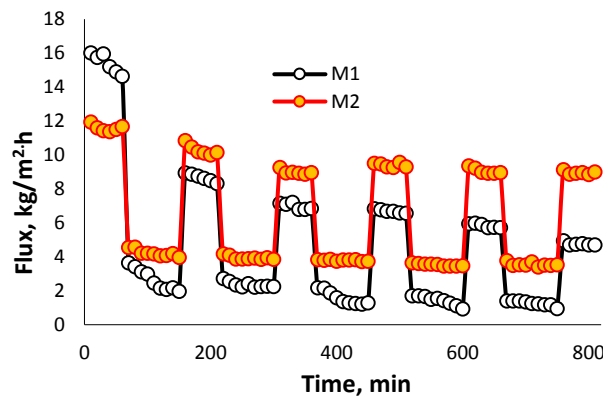
(c)

Fig. 6. (a) Three-step filtration performance, (b) antifouling parameters, (c) and long-term filtration for the pristine membrane, and (d) the optimal membrane.

3.5. Heavy metals rejection

To explore the performance of PEI nanofiltration membranes, the potential of M1 and M2 to reject two main heavy metal ions including Hg^{2+} and As^{5+} has been compared. As influent metal ion concentration acts as a key variable for rejection efficiency, two different influent heavy metal ion concentrations (20 ppm and 50 ppm) were examined. Figs. 7 a and b illustrate the effluent concentration of As^{5+} and Hg^{2+} for both the membranes (M1 and M2) at two levels of influent concentrations. At both the influent concentrations, M2 (the optimal membrane) showed an upper rejection efficiency for As^{5+}

and Hg^{2+} rather than M1 (the pristine membrane). However, the discrepancy between the effluent concentration of M1 and M2 is more significant at 20 ppm of heavy metals solutions. Despite, the smaller hydration radius of As^{5+} (0.35 nm) compared to Hg^{2+} (0.422 nm), M2 showed lower effluent concentrations for As^{5+} which could be related to the higher charge density of As^{5+} leading to more attraction on negative charged surface of M2(Gholami et al., 2022b). These results confirm that hydrophilic functional groups of guanidine play a main role in enhancing antifouling properties and metal ions rejection.
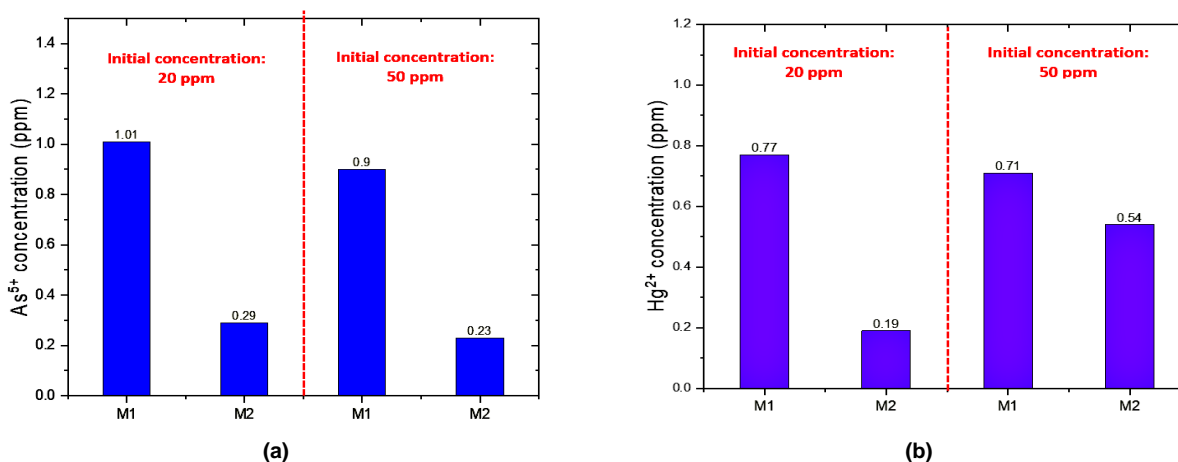

Fig. 7. The effluent concentrations of (a) AS^{5+} and (b) Hg^{2+} after passing through M1 and M2 at different influent concentrations.

Table 3. The heavy metals rejection data of some nanofiltration membranes.

Membrane	Technique	Heavy metal	Rejection, %	Ref.
TFN-mBTO-E	SM	As	97	(Pu et al. 2021)
PA-CSBF	SM	As	98	(Zeeshan et al. 2020)
PAA-PVDF 700	SM	Hg	97	(Islam et al. 2020)
GO-PES	SM	Hg	80.3	(Chen et al. 2019)
PMIA	MMM	As	90	(Zhao et al. 2012)
PPSU/MWCNTs	MMM	Hg	76	(Chandrashekhar et al. 2019)
NF30	Commercial	As	78	(Figoli et al. 2010)
NF90		As	94	
PSf/H-KIT-6	MMM	As	99.85	(Gholami et al. 2022a)
		Hg	99.27	
PEI/Guanidine	SM	As	≥ 98.5	This study
		Hg		

Surface modification (SM), Mixed matrix membrane (MMM), Cellulose nanocrystals (CNCs), Polyethersulfone (PES), Polarized ferroelectric membrane (mBTO-E), Core shell biofunctionalized (CSBF), Polyacrylic acid (PAA), Polyvinylidene fluoride (PVDF), Graphene oxide (GO), Poly (m-phenylene isophthalamide) (PMIA).

3.6. Comparative study

Some relevant researches have been tabulated in Table 3. From the obtained data, guanidine-integrated membrane shows an outstanding performance in rejecting As^{5+} and Hg^{2+} in comparison with other studies. As a fact, the optimal membrane of this work showed an upper rejection (more than 98.5%) relative to the other reported membrane modified with different surface and mixed matrix methods. It should be mentioned that the guanidine-integrated membrane is proficient to remove heavy metals as much as the reported PSF membrane embedded with H-KIT-6.

4. Conclusions

Polyetherimide nanofiltration membrane was modified by integrating guanidine molecules through covalent bonds on its surface. The surface modification was implemented at three levels of guanidine concentration including 0.5, 1, and 1.5 g/L. The hydrophilicity of the surface-modified membranes was

enhanced so that water contact angle of the bare PEI nanofiltration membrane was diminished from 65.5⁰ to 54⁰. FRR of the surface-modified membrane with 0.5 g/l of guanidine concentration (as the optimum surface-modified membrane) was 88.8%, while, it was 56.2% for the pristine membrane. Moreover, the performance of the optimum surface-modified membrane displayed a superior performance for rejecting As^{5+} and Hg^{2+} (more than 98.5%) rather than the pristine one.

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