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Cost-effective polyvinylchloride-based adsorbing membrane for cationic dye removal

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Abstract. The current study focused on the preparation of low-cost PVC-based adsorbing membrane. Metakaolin, as available adsorbent, was embedded into the PVC matrix via solution blending method. The as-prepared PVC/metakaolin mixed matrix membranes were characterized using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, atomic force microscopy (AFM), pure water permeability and contact angle measurements. The results confirmed the improvement of PWP and hydrophilicity due to the presence of metakaolin in the PVC matrix. Additionally the structure of PVC membrane was changed due to the incorporation of metakaolin in the polymer matrix. The static adsorption capacity of all samples was determined through dye removal. The effect of metakaolin dosage (0-7%) and pH (4, 8, 12) on dye adsorption capacity was investigated. The results depicted that the highest adsorption capacity was achieved at pH of 4 for all samples. Additionally, adsorption data were fitted on Langmuir, Freundlich, and Temkin models to determine the appropriate governing isotherm model. Finally, the dynamic adsorption capacity of the optimum PVC/metakaolin membrane was studied using dead-end filtration cell. The dye removal efficiency was determined for pure PVC and PVC/metakaolin membrane. The results demonstrated that PVC/metakaolin mixed matrix membrane had a high adsorption capacity for dye removal from aqueous solution.

Keywords: metakaolin; wastewater treatment; membrane adsorber; ultrafiltration; cationic dye

1. Introduction

Textile industry is one of the most significant sources of dye disposal into the receiving environment, causing some human illnesses. It is reported that about 18 to 88 grams of dye may be presented in wastewater to produce 1 kilogram of textile product (Toprak and Anis 2017). Regarding its toxic effect, the treatment of textile effluent is strongly required. Accordingly, different separation processes including physical-chemical flocculation (Buthelezi *et al*. 2012; Choy *et al*. 2001), ozonation (Aksu, 2005), membrane process (Chidambaram *et al*. 2015; Ong *et al*. 2014; Shao *et al*. 2013; Zhong *et al*. 2012; Ingole *et al*. 2016) and adsorption (Fu *et al*. 2015; Gupta *et al*. 2011; Rafatullah *et al*. 2010; Sadaf *et al*. 2014) have been proposed by researchers. Among these methods, adsorption and membrane separation process were gained more attention due to their satisfactory removal outcomes and cost-effective nature. Anyhow, the aforementioned methods have some inconveniency that can be resolved through the hybrid process.

Adsorption systems may operate either in the batch or semi-continuous mode. During any adsorption process, crucial problems may happen such as non-uniform particle suspension or packing bed, additional unit operation for adsorbent-solution separation, high pressure drop for fixed beds and so on (Suen 2015). To overcome the abovementioned disadvantages, incorporation of adsorbent particles (nano or micro-sized) as the fillers into the polymeric substrate was suggested by researchers. For this purpose, mixed matrix membranes with an asymmetric porous structure can be applied to provide the adsorptivity with target solutes (Suen 2015; El-Gendi *et al*. 2016). This kind of mixed matrix membrane is nominated as adsorbing membrane and can be applied as a newly introduced membrane-based technology for separation processes such as water and wastewater treatments. For an adsorbing membrane, the polymer matrix plays two key roles, including support of particles in its fixed matrix and providing specific pathways for solutes to easily reach the adsorption sites of filler (Lin 2014; Suen 2015). To provide the abovementioned pathway, UF membranes with micropores were proposed in most literature.

Up to now, polyvinyl chloride (PVC) has been introduced as one of the most attractive polymer materials in the field of membrane technology due to its availability, low-cost, appropriate stability (especially mechanical stability) and excellent solubility in the commercial solvent. These properties make PVC a flexible candidate for preparing UF membranes through the immersion-precipitation method (Behboudi *et al*. 2016; Marbelia *et al*. 2016; Aryanti *et al*. 2015). Although PVC has no individual adsorbing ability in contact with organic contaminants such as dyes, it can be used to prepare the base matrix of adsorbing membranes (Gholami *et al*. 2013). Organic

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and/or inorganic materials with superior adsorbing properties can be incorporated into PVC matrix as adsorbents. In the case of dye removal, various adsorbents such as activated carbon (Martins and Nunes 2015), clays (Ben Hassine *et al*. 2016), biosorbents (Rahman and Akter 2016), MOF (García *et al*. 2014), ZnO (Hassan *et al*. 2014) and etc. are applied. Among these, clays can be considered as appropriate adsorbent regarding their individual surface properties.

Kaolin with the chemical formula of $Al_2Si_2O_5(OH)_4$ is one of the most commercially available layered mineral clay, extensively used as the basic material of ceramic, coating, dye additives, catalyst and adsorbents (Adeyemo *et al*. 2017; Karaoˇglu *et al*. 2010). Metakaolin is the dehydroxylated form of kaolin with higher reactivity. Dehydroxylation of kaolin leads to increasing porosity and inter-basal spacing of layered structure (Monash and Pugazhenthi 2010). So, due to its specific structure, this mineral admixture can be applied as a low-cost alternative to the expensive adsorbents for contaminant removal from water.

There are some literature focused on the preparation and characterization of adsorbing MMMs for dye removal application. Lin *et al*. (2014) introduced a new PSf-based mixed matrix membrane by inserting plant waste as adsorbent into the polymer matrix. Banana peel, tea waste, and shaddock peel were used as fillers. Adsorption capacity of resultant membranes was studied through methylene blue and methyl violet 2B dyes removal from water. Their results showed that the performance of resultant membranes had retained after three adsorption-regeneration cycles. Adsorption performance of 4A-zeolite/polyvinyl alcohol (PVA) membrane was studied by Baheri *et al*. (2016) through the methylene blue removal from aqueous solution. They reported that the maximum removal efficiency of 87.41 % was obtained by incorporation of 20 wt% of 4A-zeolite into the PVA matrix. Cheong *et al*. (2017) investigated the adsorption and photocatalytic activity of GO@ZIF-67/PAN mixed-matrix membrane through methylene blue dye (MB) removal. They found that the presence of GO@ZIF-67 composite in PAN matrix enhanced removal efficiency of the resultant membrane when compared with pure PAN.

Since there is a worldwide tendency to design the separation process with a potentially economic feature, in this work, the preparation of low-cost adsorbing membrane for cationic dye removal was studied. Accordingly, low-cost and available metakaolin clay was incorporated into a mechanical stable PVC matrix at the different dosage of the adsorbent. The resultant membrane was characterized using, SEM, EDS, AFM, ATR-FTIR, zeta potential, and contact angle analysis. Furthermore, the isotherm and kinetic mechanism of adsorption for all samples were obtained. Additionally, the dynamic adsorption performance of the PVC/kaolin membrane was measured.

Normally, strong winds have been associated with two types of wind in typhoon prone region. The first one is the nature wind and the other one is the typhoon, or say severe tropical cyclone. Many investigations about the vibration and buckling (static stability) characteristics of frames of various types have been carried out. Cheng (2011) have studied the elastic critical loads for plane frames by using the transfer matrix method.Ageneral digital computer method has been described by Chengand Xu (2012).

2. Experimental

2.1. Materials

PVC (K68, Bandar Imam Petrochemicals, Iran) with an average bulk density of 580 g/L was used to prepare a polymeric matrix of membrane. Kaolin as the base material to prepare metakaolin was supplied by Rokh Sefid mine of Gonabad, Iran. The N-methyl-2-pyrrolidone (NMP) was provided from Merck Co. azo dye (acid Red 151, 459 Da) used in this work was obtained from Sigma Aldrich. Distilled water was used throughout the experiments.

2.2. Preparation of metakaolin particles

Kaolin mineral was powdered using a ball mill and sieved to prepare powder with the particle size less than 200 nm. Particle size distribution and results of XRF analysis for used kaolin were previously reported (Namvar-Mahboub *et al.*, 2017). Then a certain amount of powdered kaolin was heated in an oven at 600 ˚C for 5 h.

2.3 Preparation of PVC/metakaolin membrane

Mixed matrix adsorbing membranes was prepared via the solution blending method. Accordingly, a certain amount of metakaolin (0 – 7 wt.%) was dispersed in NMP via sonication for 1 h. Then PVC was gradually added into dispersed solution and stirred at 60 ºC for 24 h. After 6h, the resultant solution was cast on a glass plate with an adjusted casting knife at 300 μm and immersed in water bath. The resultant membranes were nominated regarding their filler dosage (Table 1)

2.4. Characterization of adsorbing membranes

The presence of metakaolin in the polymer matrix and its interaction with PVC chains was investigated through the ATR-FTIR technique. This analysis was conducted using Avatar 370 Nicolet Spectrometer equipped with Attenuated Total Reflectance device (Nexus 100) coupled to a ZnSe crystal at a 45° operating angle. ATR-FTIR spectra of pure and mixed matrix PVC membranes were obtained in the range of 4000 to 400 cm^{-1}. Scanning electron microscope (SEM, LEO1450VP, Zeiss, Germany) was performed at 20 kV to study the morphology of as-prepared membranes. The presence of adsorbent in polymer matrix was also probed using EDS detector. AFM analysis (full plus series 0101/A, Ara, Iran) was applied to determine surface roughness of mixed matrix membranes. The surface contact angle of membranes was measured as an index of hydrophilicity. Accordingly, contact angle measuring instrument (OCA15 plus, 196Data physics, Germany) was used to evaluate contact angle of DI water droplets on three different locations of each sample.

Table 1 Composition of as-prepared membranes

Membrane code	Metakaolin (wt.%)	NMP (wt.%)	PVC (wt.%)
PVC-K0	0	84	16
PVC-K3	3	84	13
PVC-K5	5	84	11
PVC-K7	7	84	9
PVC-9	0	89	9

2.5. Water permeability and Batch adsorption experiments

As it is expected, NF and smaller pore size UF membranes can effectively separate dye from water, and there is no need for adsorbents. However, adsorbing membranes are introduced to modify UF membrane performance for wastewater treatment. Thus, pure water flux of as-prepared membranes was determined to confirm the formation of UF adsorbing membranes. For this case, permeability was determined using dead-end filtration set up at 2 bar and 20 ˚C. Accordingly, the permeability of each membrane was calculated by Equation 1:

$$Permeability = \frac{Q}{A.p} \tag{1}$$

where Q is water flow rate (L/h), A (m^2) is the active surface area of membrane and p is transmembrane pressure (bar).

The batch mode was applied to investigate the adsorption behavior of PVC/metakaolin membranes at different dye concentrations (10, 20, 50 and 100 ppm), different pHs (4, 8, 12) and 20 ˚C. In each experiment, 0.3 g of adsorbing membrane was added into 100 cc of dye and the solution vessel was placed on a shaker for 48 h. During the adsorption process, sampling was carried out, and the dye concentration of each sample was determined using UV-spectrophotometer (Phonix). The adsorption capacity of mixed matrix membranes was calculated according to Equation 2:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where, C_0 and C_e are dye concentrations at initial and equilibrium conditions (mg/L), respectively. V (L) is the solution volume, and m is the gram of mixed matrix membrane.

2.6 Dynamic adsorption experiments

Dynamic adsorption experiments were conducted through dead-end filtration set up equipped with 4 cm disc module. In this case, the most efficient adsorbing membrane concerning its pure water flux and adsorption capacity was used. Dynamic experiments were carried out at optimal pH condition for 30 min intervals till maximum adsorptions were achieved (5h). Then regeneration process was performed using NaoH solution (0.4 M) and this trend continued for 5 cycles to inspect membrane durability and reusability.

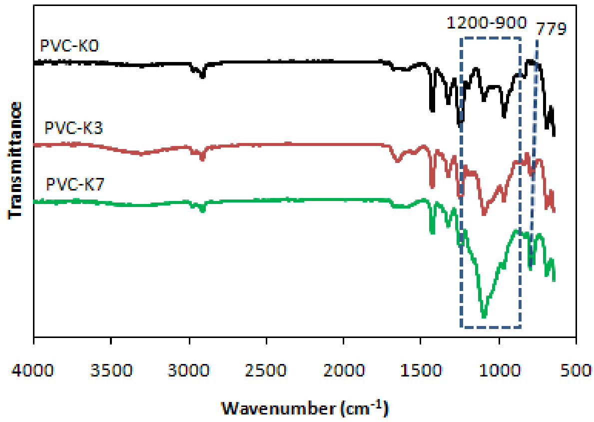

Fig. 1 ATR-FTIR spectra for PVC and PVC/metakaolin membranes

3. Result and discussion

3.1 ATR-FTIR analysis

To study the inorganic-organic interactions between PVC chain and metakaolin, ATR-FTIR analysis was performed. Fig. 1 presents ATR-FTIR spectra of PVC and PVC/metakaolin membranes.

As can be seen, characteristic bands of pure PVC was observed at 694, 968-1200, 1249-1438, 1679 cm^{-1} corresponding to the C-Cl stretching, C-C stretching, CH_2 deformation and C=C trans of PVC chain, respectively (Simak 1982). For mixed matrix membranes, a strong broad band could be observed in the wavenumber range of 900 to 1200 cm^{-1} which was related to the presence of Si–O–Si of kaolinite layers with characteristic band at 1095 cm^{-1}. Moreover, the band of Al-O bonds at 693 cm^{-1} overlapped with C-Cl stretching of PVC chains. Additionally, new characteristic band at 779 cm^{-1} was appeared which was corresponded to Si–O–Al and Al-O bonds of metakaolin, respectively. Also, a broad and low-intense band around 3330 cm^{-1} was attributed to inner and outer surface –OH stretching vibrations of the lattice (Parvinzadeh and Almasian 2012). It is evident from Fig. 1 that by increasing metakaolin dosage, intensity of its characteristic band increased in PVC matrix.

3.2 Membrane morphology, hydrophilicity and permeability

The impact of metakaolin on the structure of PVC membrane was probed via surface and cross-sectional SEM images of as-prepared membranes (Fig.2 and Fig. 3). As it is evident from Fig. 2, for all membranes, there was an asymmetric structure with finger-like pores which were elongated and expanded from up to down (across) the membrane. As stated elsewhere, this kind of structure is formed due to solvent-nonsolvent miscibility and exchange rate during phase inversion method. Anyhow, by the incorporation of metakaolin as adsorbent in polymer matrix, the form of finger-like pores changed to large tear-shape pores at the bottom of membranes. From cross-sectional view, one can conclude that more porous structure has been formed.

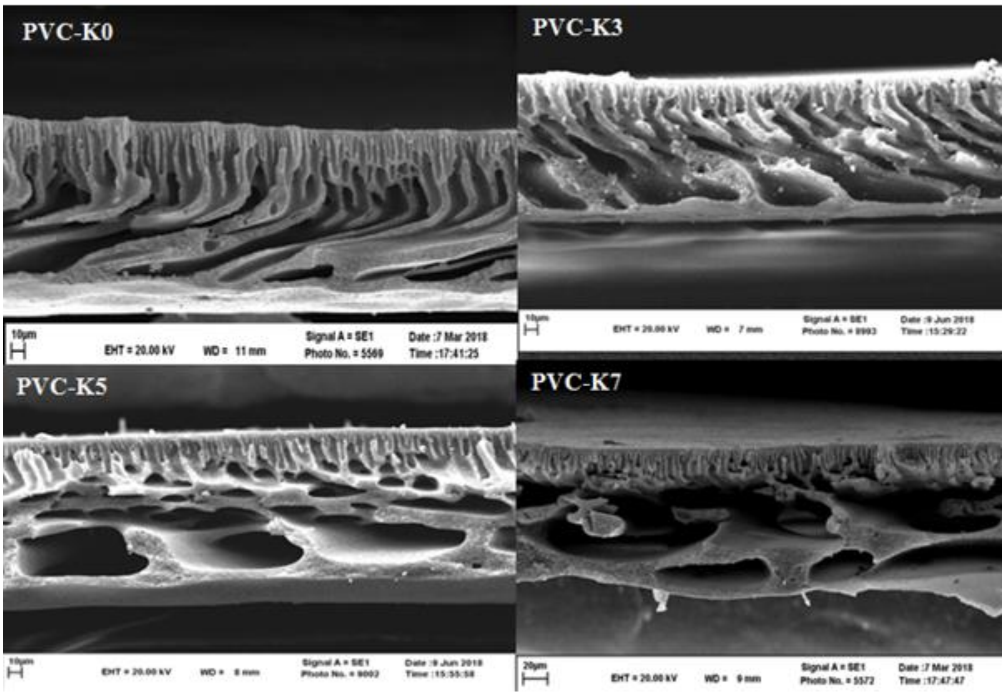

Fig. 2 Cross-sectional view of PVC and PVC/metakaolin membranes

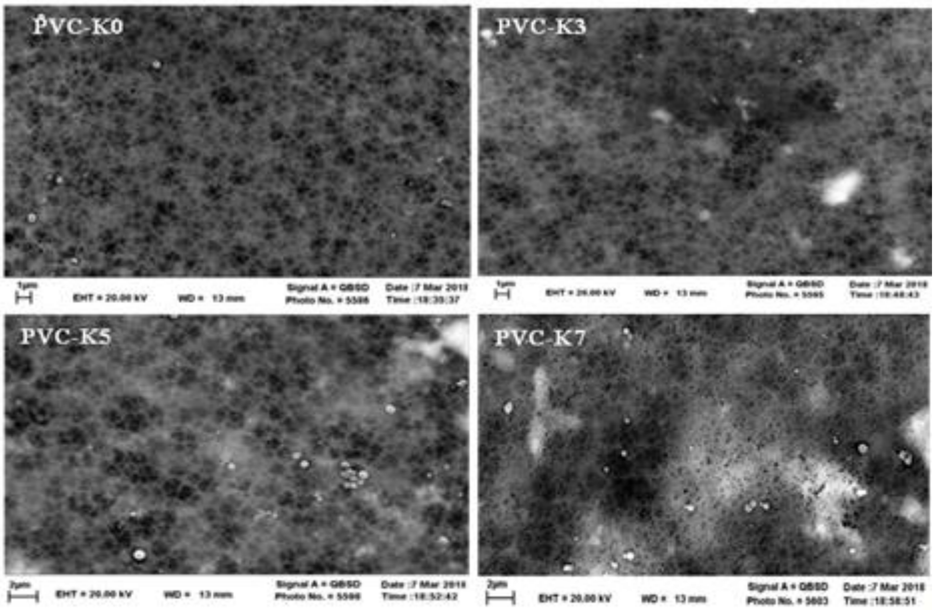

Fig. 3 Surface structure of PVC and PVC/metakaolin membranes

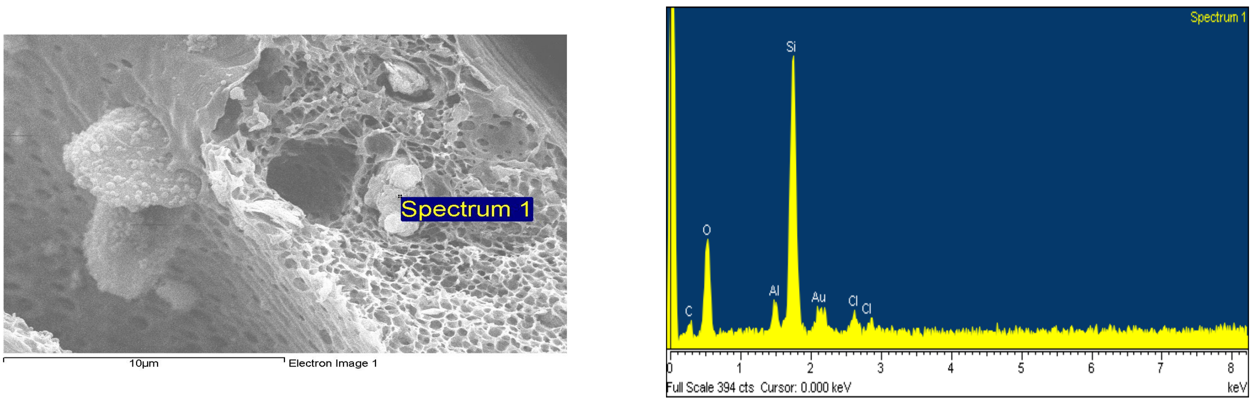

Fig. 4 EDX spectra of PVC/metakaolin membrane

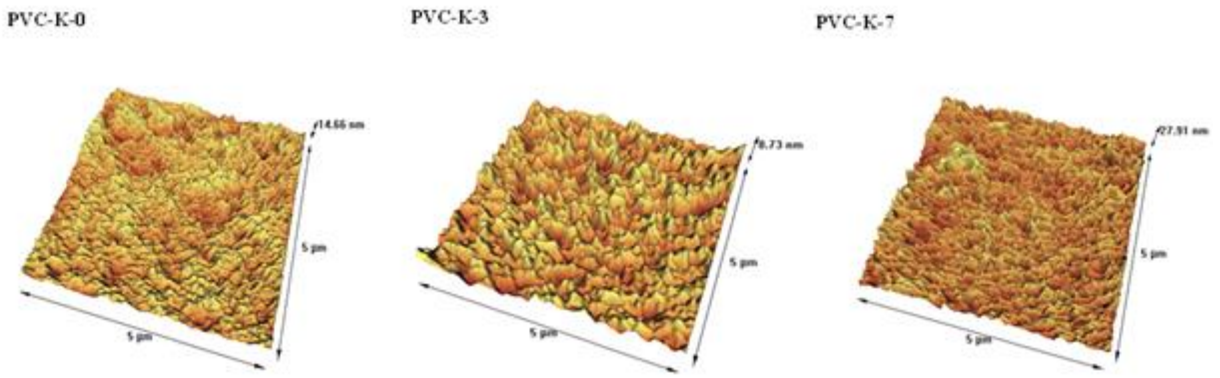

Fig. 5 AFM images of PVC and PVC/metakaolin membranes

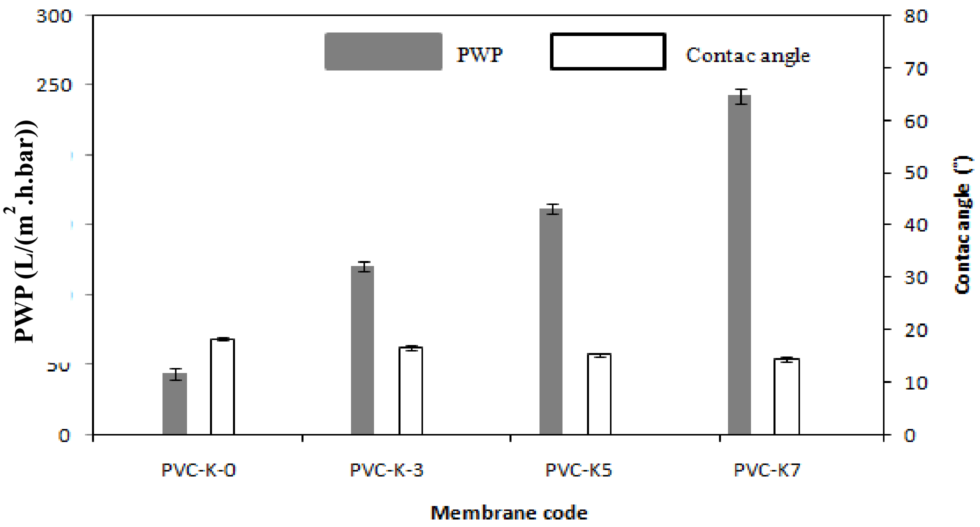

Fig. 6 The effect of metakaolin dosage on PWP and contact angle values of adsorbing membrane

In the case of surface images, it seems that by the incorporation of a low amount (3%) of metakaolin into polymer matrix no individual changes could be observed. However, increasing metakaolin dosage from 3 to 7 led to the formation of more porous surface. Additionally, adsorbent concentration increased at the surface of resultant membranes and tended to agglomerate in some places. The change of membrane morphology can be explained as follows. By the addition of adsorbent dosage, polymer amount decreases and accordingly total solid remains constant for all casting solutions. However, the viscosity of casting solution may be reduced due to presence of kaolin instead of some part of PVC. Additionally, mixed matrix membrane structure can be affected by hydrophilic nature of metakaolin through increasing of solvent-nonsolvent exchange rate which makes more porous structure (Manickam *et al*. 2014).

The presence of metakaolin on the surface of as-prepared membrane was also confirmed by EDX analysis and results are presented in Fig. 4. The presented EDX spectrum was related to high magnification SEM image of PVC/metakaolin membrane. As illustrated in this figure, characteristic peaks of C and Cl were attributed to PVC chains and characteristic peaks of Si, Al, and O were related to the elements of metakaolin.

Table 2 Surface roughness parameters

Code	R_a (nm)	R_q (nm)	R_P (nm)
PVC-K-0	2.26±0.76	2.89±0.98	13.18±3.35
PVC-K-3	2.96±0.88	3.63±1.04	11.44±2.58
PVC-K-7	5.43±1.01	7.6139±2.24	21.66±2.48

Fig. 5 illustrates AFM images of pure PVC and mixed matrix membranes. The surface roughness parameters of samples are also presented in Table 2. All parameters were measured for 10 µm×10 µm of each samples and the results were the average of three measurements.

It should be notified that R_a is average roughness, R_q is the root mean square of the Z data and R_P demonstrates maximum profile peak height. By considering Table 2, it can be stated that the effect of the low amount of metakaolin on surface roughness of resultant membrane can be ignored. While high amount of this clay can moderately increases surface roughness of PVC/metakaolin membrane.

Pure water permeability of as-prepared membranes was determined to investigate the effect of metakaolin on water

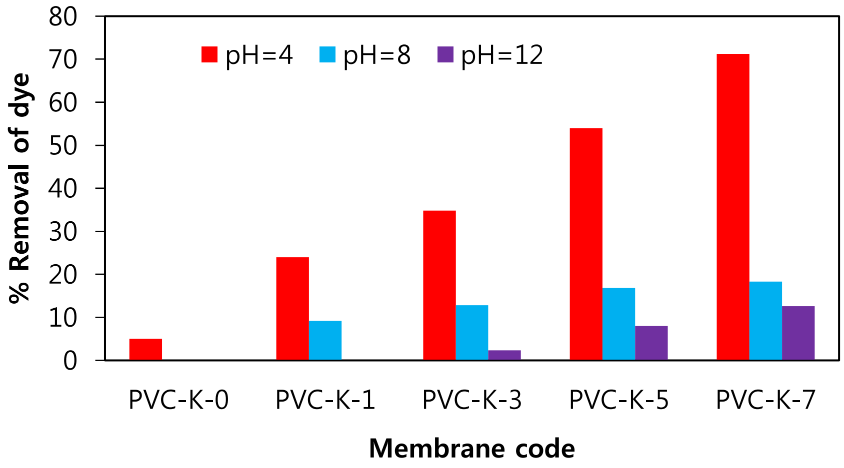

Fig. 7 Effect of pH and filler dosage on dye adsorption capacity of mixed matrix membranes (at 20 ppm of dye solution)

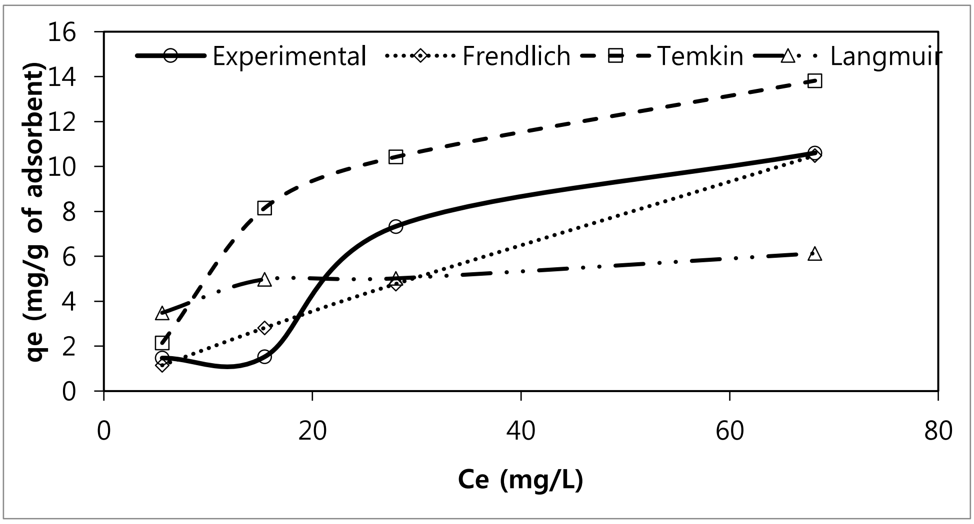

Fig. 8 Adsorption Capacity vs. equilibrium concentration for PVC-K-7, at 20 ˚C

transport rate through PVC-based membrane. Since surface hydrophilicity of membrane affects water flux, water contact angle of each membrane was measured. The PWP and contact angle values of pure PVC and PVC/metakaolin membrane is presented in Fig. 6.

As illustrated in this figure, by incrementing metakaolin dosage water contact angle decreased slightly and as a consequence, membrane hydrophilicity increased. In addition, metakaolin–embedded PVC displayed PWP enhancement when compared with pure PVC membrane. This can be explained by SEM and contact angle results. Metakaolin as hydrophilic material improves surface hydrophilicity of as-prepared membranes. On the other hand incorporation of this filler leads to formation of more open structure of membrane and accordingly higher water flux can be achieved.

3.3 Adsorption properties of membrane

Adsorption can be introduced as an innovative function of mixed matrix membranes which their fillers are adsorbents. Thus, here, the adsorption behavior of as-prepared PVC/metakaolin membrane was studied. Since solution pH has individual effect on adsorption capacity of ionic solutes, the adsorption capacity of all as-prepared membranes was determined at different pH (Fig. 7). As can be seen, the maximum adsorption capacity could be obtained at acidic media (pH of 4). This can be attributed to surface charge of dye as pollutant. It seems that at acidic media red dye tends to be positively charged. On the other hand, metakaolin as adsorbent of PVC adsorbing membrane has negative charge at pH of 4 and higher (Schroth and Sposito 1997). In this case, electrostatic forces between red dye and trapped adsorbent lead to enhancement of adsorption capacity.

By increment of solution pH, adsorption capacity decreased. This implied that basic solution was not suitable media for dye adsorption on resultant membranes. Form Fig. 7, it can be also found that the maximum adsorption was achieved at 7% dosage of metakaolin. Accordingly adsorption mechanism of PVC-K-7 membrane was studied via equilibrium adsorption capacity vs. equilibrium dye concentration data (Fig. 8).

The adsorption isotherm model for PVC-K7 was also investigated through data fitting on Langmuir, Frendlich and Temkin models (Ayawei *et al*. 2017). Linear form of

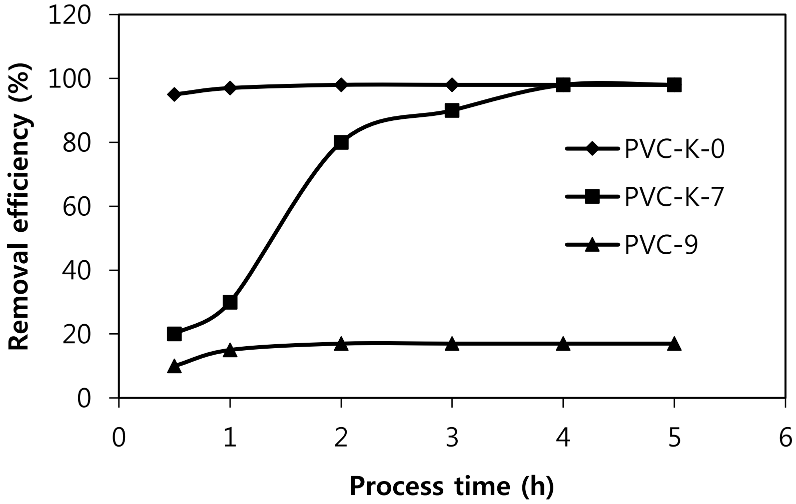

Fig. 9 Dye removal efficiency of pure PVC and PVC/metakaolin membrane during dynamic adsorption at 20 ˚C.

Langmuir model is presented in Equation 3:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

where C_e is dye concentration at equilibrium (mg/L), K_L is Langmuir constant (L/g), q_m and q_e are maximum and equilibrium adsorption capacity (mg/g), respectively.
Frendlich model in its linear form is written as follows:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (4)$$

where K_F and n are Frendlich constant and adsorption intensity constant, respectively.

In addition to common adsorption isotherms (Langmuir and Frendlich $_{\text{models}}$), adsorption data were fitted by Temkin isotherm model. This model considers the effect of indirect solute-adsorbent interactions. However, Temkin isotherm is verified for moderate range of ion concentrations (Ayawei *et al.* 2017). The linear form of the model is depicted in Equation 5:

$$q_e = \frac{RT}{b}\ln K_T + \frac{RT}{b}\ln C_e \quad (5)$$

where K_T is Temkin constant (L/g), b is Temkin constant related to the heat of adsorption (J/mol), R is gas constant (J/(mol.K)) and T is process temperature (K).

Table 3 demonstrates constant values of three mentioned models and $_{R2}$ value of each fitted model. According to the results, it may be stated that Langmuir isotherm had more ability for prediction of adsorption behavior of as-prepared PVC/metakaolin membrane. Anyhow, the obtained parameters were applied to predict adsorption capacity of PVC-K-7 for three studied isotherms. The predicted values are presented in Fig. 8. As can be seen, Temkin isotherm may predict adsorption trend better than other isotherms, while no one can predict adsorption capacity precisely. This may be due to adsorbing membrane structure which affects active sites of adsorption.

Table 3 Frendlich and Temkin Isotherm parameters derived from adsorption experiments

Frendlich			Temkin			Langmuir		
K_F (mg/g)	n	R^2	b (J/mol)	K_T (L/g)	R^2	K_L (L/mg)	q_m	R^2
0.25	1.13	0.81	628	0.55	0.842	0.201	6.578	0.87

3.4 Performance of adsorbing membrane via dynamic experiments

In order to investigate performance of as-prepared membranes, dynamic dye adsorption was carried out in a dead-end filtration module at operating pressure of 1 bar. For this purpose, PVC-K-7, which depicted higher adsorption capacity, was selected as membrane sample. The feed concentration and pH adjusted at 20 ppm and pH of 4, respectively. Moreover, the performance of pure PVC membrane with the same total dissolved solid (PVC-K-0) and the one with same polymer concentration (PVC-9) was determined. Figure 9 illustrates dye removal efficiency of each membrane as a function of spending time.
As can be seen, removal efficiency was more than 97% for both PVC-K-0 and PVC-K-7 membranes, while permeate flux of PVC-K-7 was 5.4 fold of PVC-K-0 (Fig. 6). It seems that, PVC-K-0 removed dye from aqueous solution by governing filtration. As illustrated in Fig. 7, adsorption capacity of pure PVC membrane (PVC-K-0) was less than 10 % for acidic media and zero for pH> 4. Accordingly, it can be stated that adsorption may have no individual effect on dye removal performance. in the case of PVC-9, removal efficiency was less than 20 %. This may be due to reduction of polymer content which leads to formation of more open structure. In this case, dyes molecules transport through membrane easily and as a consequence dye concentration on permeate side deceases. It should be mentioned that dye adsorption on PVC matrix is very low. Interestingly, for PVC/metakaolin membrane, dye removal efficiency increase to 97% after 5h. As can be seen in Fig. 9, by passing time, dye removal efficiency increases from 20 to

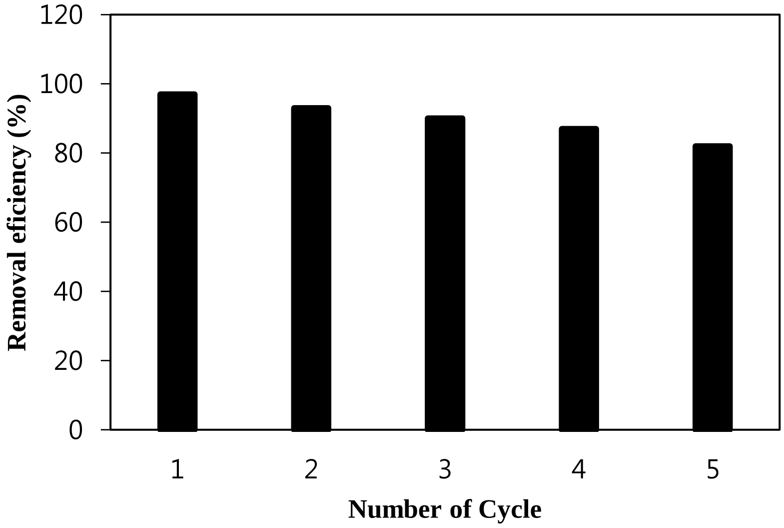

Fig. 10 Dye removal efficiency of PVC/metakaolin membrane for 5 cycles

97%. This trend can be explained by combining filtration and adsorption mechanism for dye removal. Indeed, by increase of operating time, more solute adsorbs on membrane and influences removal efficiency, incredibly. Comparing three membrane performances depicts that metakaolin had played a key role to enhance PVC membrane performance for dye removal through change of physical and chemical structure of as-prepared PVC-based membranes.

Fig. 10 illustrates adsorption capacity of PVC-K-7 for 5 cycles. As can be seen, adsorption efficiency decreases from 97 % for cycle 1 to 82% for cycle 5. It seems that, the as-prepared adsorbing membrane has appropriate adsorption efficiency after 4 cycles.

4. Conclusion

Low-cost PVC-based adsorbing membrane was prepared via solution blending method. Metakaolin as available adsorbent was embedded into PVC matrix at different dosages. The as-prepared PVC/metakaolin mixed matrix membranes were characterized and results showed that by incorporation of metakaolin in polymer matrix, membrane structure tended to be more open. Additionally, the PWP and hydrophilicity of as-prepared membranes improved significantly. The dye adsorption capacity of all samples was investigated via batch and dynamic experiments. The batch adsorption results implied that at low pH of 4 and metakaolin dosage of 7 % the maximum adsorption efficiency was obtained. Adsorption data fitting was also carried out and according to the findings, among three models of Langmuir, Frendlich and Temkin, Langmuir was appropriate for adsorption behavior prediction. Dynamic adsorption capacity of optimum PVC/metakaolin membrane was also studied and compared with pure PVC membrane. From corresponding results, one can conclude that metakaolin had superior effect on performance of PVC membrane in dye removal.

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