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# Adsorption of Methyl Orange from an Aqueous Solution onto a BPPO-Based Anion Exchange Membrane

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aqueous solution and molarity of NaCl. Adsorption isotherm study showed that adsorption of MO was fitted well to the Freundlich adsorption isotherm because the value of the correlation coefficient ( $R^2 = 0.974$ ) was close to unity. Adsorption kinetics study showed that adsorption of MO fitted well to the pseudo-second-order kinetic model. Adsorption thermodynamics evaluation represented that adsorption of MO was an endothermic ( $\Delta H^{\circ} = 18.72 \text{ kJ/mol}$ ) and spontaneous process. The AEM presented a maximum adsorption capacity of 18 mg/g. Moreover, the regeneration of the prepared membrane confirmed its ability to be utilized for three consecutive cycles. The developed BPPO-based AEM was an outstanding candidate for adsorption of MO from an aqueous solution.

# 1. INTRODUCTION

Nowadays, organic dye-based water pollution resulting from the textile and chemical industry has fascinated the world's interest because of the negative impacts on human health.<sup>1</sup> Usually, dyes are stable to heat, light, and oxidizing agents. Besides, dyes contain a synthetic origin and a complex aromatic molecular structure that makes biodegradation more sophisticated.<sup>2</sup> They contain chromosphere compounds with high molecular weight, accumulating in water bodies and thus reducing photosynthetic activity and luminosity. Likewise, most synthetic dyes impress the quantity of dissolved oxygen, accommodating eutrophication processes by enhancing the organic load. The colored wastewater becomes part of the ecosystem and causes disturbance to aquatic life.<sup>3</sup>

adsorption capacity of MO increased with the increase in contact

time, membrane dosage (adsorbent), temperature, and pH while

declined with the increase in initial concentration of MO in an

Dyes can be classified based on their charge, functional groups, and usefulness. On the basis of chemical structures, they can be classified into azo, anthraquinone, indigoid, nitro, triarylmethane, and so forth, and based on their use, they may be classified as cationic dyes, anionic dyes, and nonionic dyes.<sup>4,5</sup> The most significant aspect of these dyes is their charge, as it impresses the productiveness of the adsorption

process.<sup>6</sup> Methyl orange (MO) is a primarily employed dye from the azo group, which also has very low biodegradability and thus can persist in the environment for an extended period of time. Hence, it is crucial to subject the water sources containing MO to some process.

Cycle 2

Number of Cycles

Until now, several methods including electro-oxidation, advanced oxidation processes, coagulation and flocculation, ultrafiltration, nanofiltration, reverse osmosis, biological degradation and membranes processes, separation process, coagulation or flocculation combined with flotation and filtration, precipitation, electroflotation, electrodialysis, and adsorption have been utilized for the removal of dyes and wastewater treatment.<sup>7–17</sup> The frequent issues associated with these methods are high electrical consumption and the use of

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Figure 1. Bromination of PPO and the development of the BPPO-based AEM.

chemical reagents.<sup>10</sup> Adsorption is considered as an easy one for wastewater treatment because of its simplicity and cheapness.<sup>18–21</sup> It provides an outstanding substitute for the treatment of wastewater, especially when the adsorbent does not need excessive pretreatment stages before its application.<sup>22,23</sup> Moreover, it is an environmentally friendly alternative.<sup>19</sup>

Previously, researchers have used a variety of adsorbents including the ion exchange membrane (IEM),<sup>19</sup> MOF-199@ AFGO/CS,<sup>24</sup> porous Zn(II) metal-organic gel,<sup>25</sup> Cu<sub>2</sub>O@Cu composite,<sup>26</sup> -MoS<sub>2</sub> microspheres,<sup>27</sup> active carbon prepared from endemic Vitis vinifera L. grape seeds (AC-VVL),<sup>28</sup> citratecross-linked Zn-MOF/chitosan (ZnBDC/CSC) composite,<sup>29</sup> magnetic lignin-based carbon nanoparticles,<sup>30</sup> three-dimensional hierarchical PbS/ZnO heterojunction microspheres,<sup>31</sup> chitosan/polyvinyl alcohol/zeolite electrospun composite nanofibrous membrane,<sup>32</sup>  $Co_3O_4$  nanoparticle,<sup>33</sup> hierarchical porous zeolitic imidazole frameworks-67@layered double hydroxide (ZIF-67@LDH),<sup>34</sup> and so forth for the removal of MO from wastewater. Currently, all the adsorbents employed for the removal of dyes and heavy metal ions are based on the adsorbent's interaction with the functional groups of the adsorbents.<sup>35</sup> Therefore, several adsorption sites and a large surface area of the matrix are significant factors for adsorption efficiency of membranes for the removal of pollutants from wastewater.<sup>19,36</sup> Hence, the fabricated brominated poly(2,6dimethyl-1,4-phenylene oxide) (BPPO)-based anion exchange membrane (AEM) can be confessed as an excellent choice for the removal of dye from an aqueous solution because of its large surface area for adsorption. Two types of IEMs such as P81 and ICE450 were utilized for the removal of methyl violet 2B from an aqueous solution.<sup>23</sup> Moreover, Cibacron Blue 3GA was removed by employing the AEMs from an aqueous solution.<sup>23</sup>

Our previous work reported the applications of bioadsorbents,<sup>37</sup> commercial AEMs,<sup>20,38</sup> and fabricated AEMs<sup>19</sup> for the removal of anionic dyes from an aqueous solution at room temperature. Although the adsorption phenomenon remained the prime focus of research for the removal of contaminants and a comprehensive literature exists, yet due to the challenging situation by newly emerging pollutants, more efficient and novel materials are the utmost need of time. This research reported the development of a novel BPPO-based AEM by introducing the 3-(dimethylamino)-2,2-dimethyl-1propanol (DMADMP) moiety into the polymer matrix via the solution casting method. The fabrication of the BPPO-based AEM by incorporating DMADMP for MO adsorption has not been reported yet. The prepared AEMs exhibited a large surface area for adsorption of MO from an aqueous solution. Moreover, the prepared AEM contained the cationic head group, while MO contained the anionic head group, resulting in electrostatic force of interaction between the AEM and dye molecule. These properties of the prepared AEM made it an excellent adsorbent compared to the reported adsorbents in the literature. The prepared AEM was characterized physicochemically in detail. It was used for batch adsorption of MO from an aqueous solution. The effect of operating parameters such as the contact time, membrane dosage (adsorbent), initial concentration of MO in an aqueous solution, pH, ionic strength, and temperature on the removal of MO was explored. Adsorption isotherms, kinetics, and thermodynamic studies were also conducted. Moreover, the regeneration of the adsorbent was investigated.

# 2. EXPERIMENTAL SECTION

2.1. Materials. Chlorobenzene (MW: 112.55 g/mol and purity: 99+%), 2,2'-azo-bis-isobutyro nitrile (AIBN) (MW: 164.21 g/mol and purity: 98%), ethanol (MW: 46.06 g/mol and purity: 99%), chloroform (MW: 119.38 g/mol and purity: 99.4%), N-bromo-succinimide (NBS) (MW: 177.99 g/mol, purity: 98%, and grade: extra pure), sodium chloride (NaCl) (MW: 58.44 g/mol and purity: 99.8%), N-methyl-2pyrrolidone (NMP) (MW: 99.133 g/mol and purity: 99.90%), DMADMP (MW: 131.22 g/mol, 97%), sodium sulfate  $(Na_2SO_4)$  (MW: 142.04 g/mol and purity: 99+%), potassium chromate (K2CrO4) (MW: 194.19 g/mol and purity: 99.99%), silver nitrate (AgNO<sub>3</sub>) (MW: 169.87 g/mol and purity: 99.90%), and MO (MW: 337.33 g/mol and grade: indicator grade) were kindly supplied by Sinopharm Chemical Reagent Co. Ltd. China and employed as received. Sigma-Aldrich Chemicals kindly provided poly(2,6-dimethyl-1,4phenyleneoxide) (PPO) (MW: 122.16 g/mol, appearance form: white powder, and product category: polymer). Deionized water was employed throughout this work.

**2.2. Bromination of PPO.** It was performed as reported (see Section S1 in the Supporting Informationfor details).<sup>39,40</sup>

**2.3. Development of the BPPO-Based AEM.** Herein, the solution casting method was employed to develop the BPPO-based AEM as described in the literature.<sup>41-43</sup> First, 8% wt solution of BPPO was prepared by dissolving its measured amount (0.8 g) into 10 mL of NMP. The BPPO-based AEM was developed by introducing 0.40 g of DMADMP into the prepared casting solution. The reaction mixture was stirred at 40 °C vigorously to accelerate the reaction overnight and then casted onto a glass plate at 60 °C for 1 day. The prepared membrane was peeled off from the glass plate and cleaned with

deionized water. Figure 1 represents the chemical structure of the BPPO-based AEM.

**2.4. Characterizations.** 2.4.1. Instrumentation. The proton NMR (DMX 300 NMR) spectrometer operating at 300 MHz was employed to confirm the successful bromination of PPO. Fourier transform infrared (FTIR) spectroscopy was employed to confirm the successful development of the BPPO-based AEM by attenuated total reflectance with the FTIR spectrometer (Vector 22, Bruker) in the range of 4000–400 cm<sup>-1</sup>. Morphology of the prepared membrane was investigated by field emission scanning electron microscopy (FE-SEM, Sirion 200, FEI Company, Hillsboro, OR, USA). Thermal stability of the prepared BPPO-based AEM was studied using a Shimadzu TGA-50H analyzer with a heating rate of 10 °C/min within the temperature range of 25 to 800 °C under a nitrogen atmosphere.

2.4.2. Ion Exchange Capacity, Water Uptake, and Linear Expansion Ratio. Ion exchange capacity (IEC) of the BPPObased AEM was calculated using classical Mohr's method.<sup>44–49</sup> In this method, the dried AEM was immersed into 1.0 M NaCl solution for 48 h such that all the charge sites were changed into the Cl<sup>-</sup> form. To remove excessive NaCl, the AEM was washed with distilled water. In order to confirm the removal of excessive Cl<sup>-</sup>, the silver nitrate solution test of the distilled water used for washing was carried out. The absence of the cloud precipitate confirmed the removal of Cl<sup>-</sup> ions. The membrane was then immersed into 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution for 48 h. The quantity of Cl<sup>-</sup> ions released was determined by titration with 0.05 M AgNO<sub>3</sub> using K<sub>2</sub>CrO<sub>4</sub> as an indicator. It was measured using the below equation

$$IEC = \frac{C_{AgNO_3}V_{AgNO_3}}{m}$$
(1)

where m (mmol), V (mL), and C (g/mL) denote the dry mass of the AEM, titer volume during titration, and the concentration of AgNO<sub>3</sub> solution, respectively.

Water uptake  $(W_R)$  of the AEM was calculated by immersing its dried samples into deionized water at room temperature. The wet weight of the AEM was determined after removing surface water with a tissue paper. It was determined from the difference in mass before and after drying the membrane using the below relationship.<sup>50–52</sup>

$$W_{\rm R} = \frac{W_{\rm wet} - W_{\rm dry}}{W_{\rm dry}} \times 100\%$$
<sup>(2)</sup>

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  represent wet and dry masses of the AEM, respectively.

The linear expansion ratio (LER) of the BPPO-based AEM was also studied. For this purpose, the membrane was cut into  $5 \times 5$  cm<sup>2</sup> pieces. It was determined using the below equation<sup>53-56</sup>

$$LER = \frac{(L_{wet} - L_{dry})}{L_{dry}} \times 100\%$$
(3)

where  $L_{wet}$  and  $L_{dry}$  show wet and dry lengths of the membrane samples, respectively.

**2.5. Batch Adsorption Procedure.** Batch adsorption of MO from an aqueous solution onto the prepared BPPO-based AEM was performed as described (see Section S2 in the Supporting Informationfor details).<sup>19,23</sup>

**2.6. Adsorption Kinetics.** Kinetics study for adsorption of MO was carried out by employing several kinetic models (see Section S3 in the Supporting Information for details).

**2.7.** Adsorption lsotherms. Herein, adsorption of MO onto the BPPO-based AEM was studied by employing Langmuir, Freundlich, and Dubinin–Radushkevich (D-R) isotherms (see Section S4 in the Supporting Information for details).

**2.8. Thermodynamics Study.** The values of change in Gibb's free energy ( $\Delta G^{\circ}$ ), enthalpy ( $\Delta H^{\circ}$ ), and entropy ( $\Delta S^{\circ}$ ) for adsorption of MO were calculated to study adsorption thermodynamics as described<sup>19,20,57</sup> (see Section S5 in the Supporting Information for details).

#### 3. RESULTS AND DISCUSSION

**3.1. Preparation of the BPPO and AEM.** The proton NMR spectrum of BPPO is depicted in Figure 2. NBS was



Figure 2. <sup>1</sup>H NMR spectra of BPPO.

used as a brominating agent, and AIBN was used as an initiator during bromination of PPO. It can occur either at the benzylic position or at the aromatic ring based on reaction conditions and reagents.<sup>39,58</sup> In the current work, it occurred at its benzylic position by refluxing chlorobenzene solution at 135 °C. Proton NMR spectroscopy was employed to measure the degree of bromination of BPPO. The proton NMR spectrum of BPPO is shown in Figure 2. It showed that the characteristic benzyl bromide group was present at 4.3 ppm. The degree of bromination was 75% measured from the integral area ratio between the benzyl bromide group and unreacted benzyl signal at 2.1 ppm.

FTIR spectra of the prepared BPPO-based AEM and pure BPPO are shown in Figure 3. By comparing FTIR spectra of the prepared BPPO-based AEM with pure BPPO, it was noted that the prepared AEM represented a band at 1050 cm<sup>-1</sup> which was absent in the spectrum of the pure BPPO membrane. It was due to C–N stretching vibration which showed the successful fabrication of the BPPO-based AEM. Moreover, the disappearance of the signal at 750 cm<sup>-1</sup> for C–Br stretching in the bromobenzyl groups from the developed AEM<sup>19,42</sup> showed its successful fabrication.

**3.2. Morphology.** The structure of IEMs has a significant effect on their applications. Morphology of the prepared BPPO-based AEMs was investigated by employing FE-SEM (Sirion 200, FEI Company, Hillsboro, OR, USA). The morphological results of the surface and cross section of the



Figure 3. IR spectrum of the pristine BPPO and AEM.

fabricated BPPO-based AEM are shown Figure 4. Results showed that both the surface and cross section were free from



Figure 4. SEM micrographs of the surface and cross section of the developed BPPO-based AEM.

any holes or cracks, indicating homogeneous morphology. Moreover, there was small roughness on the surface and cross section of the prepared BPPO-based AEM. Hence, the prepared BPPO-based AEMs represented a homogeneous structure.

**3.3. Thermal Stability.** Thermal stability of the developed BPPO-based AEM was studied using thermogravimetric analysis (TGA) within the temperature range of 30 to 800 °C under a nitrogen atmosphere, and attained results are depicted in Figure 5. The weight loss of these membranes occurred in three steps.<sup>55,56</sup> Below 140 °C, the weight loss was associated to the loss of residual water and the solvent. The weight loss in the range of 190 to 250 °C was due to degradation of the quaternary ammonium group into the polymer matrix<sup>59,60</sup> which contributes to the second weight loss step. The weight loss around 450 °C was attributed to degradation of the polymer backbone<sup>42,61</sup> which is the final step. TGA results represented that the prepared BPPO-based AEM exhibited excellent thermal stability.

**3.4. IEC, Water Uptake, and Linear Swelling Ratio.** IEC is a significant property of IEMs. It has an important impact on the properties of IEMs such as the water uptake and swelling ratio. It was found to be 2.66 mmol/g for the prepared BPPO-based AEM. It has significant influence on adsorption performance of the prepared AEM. Similarly, water uptake  $(W_R)$  is an important factor of IEMs based on the quantity of



Figure 5. TGA curves of the prepared AEM.

ion exchange content into the membrane matrix.<sup>62</sup> It represents hydrophilicity and water with holding capacity of the prepared AEM. It was found to be 68% for the developed AEM at ambient temperature. It showed that the prepared AEM could be used for adsorption of dye from an aqueous solution. Moreover, the LER of the developed BPPO-based AEM was measured at ambient temperature. It was found to be 31% for it. Results showed that it exhibited good swelling resistance required for adsorption application.

**3.5. Effect of Operating Factors on Adsorption of MO onto the Developed BPPO-Based AEM.** The effect of contact time, membrane dosage (adsorbent), initial concentration of dye, temperature, pH, and ion strength on adsorption capacity of MO was investigated. The details are given below:

3.5.1. Effect of Contact Time. Figure 6a represents the effect of contact time on adsorption capacity of MO from an aqueous solution at room temperature. It was observed that adsorption capacity increased with enhancing contact time. Table 1 provides an interesting comparison of MO adsorption performance of the prepared BPPO-based AEM with different adsorbents reported in the literature. It was found to be increased from 7.30 to 17.85 mg/g with increasing contact time from 100 to 2880 min. Similar results were obtained in our previous research.<sup>23</sup> It was noted that the adsorption of MO was fast in the beginning due to the presence of several active empty sites onto the surface of the prepared AEM at room temperature. It then increased slowly until equilibrium was attained.<sup>23</sup> With the passage of time, adsorption of MO from an aqueous solution was found to be declined because of coverage of empty active sites onto the prepared AEM surface and equilibrium was attained after 2880 min, and this optimum time was used for further research work.

3.5.2. Effect of Membrane Dosage. It is significant to study the effect of mass of the adsorbent on adsorption of dye from an aqueous solution. The effect of membrane dosage (adsorbent) on the adsorption capacity of MO from an aqueous solution was investigated at room temperature, and attained results are shown in Figure 6b. From here, it was observed that adsorption capacity was decreased from 36.50 to 17.85 mg/g with increasing the membrane dosage from 0.01 to 0.05 g. It is similar to our previous work.<sup>20</sup> It is associated with the increase in the number of active sites by an increase in membrane dosage (mass of adsorbent).<sup>63</sup> Initially, the

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Figure 6. (a) Effect of contact time, (b) effect of membrane dosage (adsorbent), (c) effect of initial concentration of MO on adsorption capacity of MO using the developed BPPO-based AEM from an aqueous solution.

Table 1. Comparison of Adsorption Capacity of thePrepared Membrane for MO with Other ReportedAdsorbents

samples	adsorption capacity (mg/g)	references
BPPO-based AEM	17.85	this work
chitosan	15.75	75
cork powder	16.66	76
AEM BIII	19.85	77
AEM DF-120B	19.90	77
AEM BI	19.95	77

adsorption of MO from an aqueous solution was rapid with the increase in the mass of the adsorbent. However, no significant change in the removal of MO with a further increase in the membrane dosage was observed.<sup>64</sup>

3.5.3. Effect of Initial Concentration of MO in Aqueous Solution. Figure 6c shows the effect of initial concentration of MO in an aqueous solution on adsorption capacity of MO at room temperature. It was represented that adsorption capacity was found to be increased from 17.85 to 84.20 mg with the increase in initial concentration of MO from 50 to 400 mg/L in an aqueous solution. The initial dye concentration gave significant driving force to overcome the resistance of mass transfer from an aqueous phase to the solid phase.<sup>63</sup> It increased the interaction between the fabricated BPPO-based AEM and MO. Hence, adsorption capacity of MO onto the

prepared AEM was enhanced with initial concentration of dye in an aqueous solution.

3.5.4. Effect of Temperature. Figure 7a depicts the effect of temperature on adsorption capacity of MO from an aqueous solution. It was noted that the adsorption capacity of MO was enhanced from 17.85 to 19 mg/g with the increase in temperature from 298 to 333 K. It indicated that adsorption of MO onto the prepared AEM was an endothermic process. With the increase in temperature from 298 to 333 K, the increase in adsorption of MO may be either associated to the acceleration of some initially slow adsorption steps or to the formation of some active spaces onto the prepared AEM.<sup>65,66</sup>

3.5.5. Effect of pH. The pH of solution has a crucial effect on adsorption capacity of dyes. The change in the pH of a solution can modify the surface charge of the adsorbent and degree of ionization of the dye.<sup>67,68</sup> The effect of pH on the adsorption capacity was investigated by varying pH from 4 to 10. Figure 7b describes the influence of pH on the adsorption capacity of MO. Results depicted that adsorption capacity was increased by increasing pH. Initially, a slight increase was observed, but at higher pH, the adsorption trend was more pronounced, and the maximum adsorption capacity was obtained at pH 8. This phenomenon can probably be explained based on the fact that MO is an anionic dye, while the BPPO-based AEM possesses the cationic head group. In neutral or basic aqueous solution, MO dissociates into the anionic charged form. The higher adsorption capacity of MO at pH 8 was possibly due to electrostatic force on interactions



Figure 7. (a) Effect of temperature, (b) effect of pH, and (c) effect of ionic strength on adsorption capacity of MO using the developed BPPObased AEM from an aqueous solution.

between the anionic dye and cationic head group of the adsorbent (BPPO-based AEM). It can be further observed that only a slight difference in the adsorption capacity value at pH 7 and pH 8 appeared. As the aim was to study the potential of the membrane for water treatment, a compromise was made and pH 7 was selected for further studies.

3.5.6. Effect of Molarity. The effect of ionic strength on adsorption capacity of MO was also demonstrated by changing molarity of NaCl from 0.2 to 1.0, and attained results are shown in Figure 7c. Results showed that adsorption capacity of MO was found to be decreased from 17.85 to 12.0 mg/g with the increase in molarity of NaCl into aqueous solution of dye. It was associated to the competition between the MO anions and chloride ion (Cl<sup>-</sup>) for the active adsorption sites.<sup>63,69</sup>

The efficacy of the developed AEM was compared with the variety of adsorbents used in previous studies. However, a variety of biomasses have been evaluated for the removal of MO, but they possess some drawbacks such as their regeneration. Some of the adsorbents previously studied are waste-cellulose-based activated carbon,<sup>70</sup> modified graphene network,<sup>71</sup> shrimp-shell-based char,<sup>72</sup> biochar from lotus biomass,<sup>73</sup> and pomelo-peel-based activated biochar.<sup>74</sup> Therefore, the focus of current study was to design a membrane possessing ion exchange properties with facile adsorption and desorption capability. Table 1 presents a comparative study with some of the materials used for the MO's removal.

**3.6.** Adsorption lsotherms. Herein, adsorption isotherms including Langmuir, Freundlich, and D-R were used to

explain adsorption of MO onto the BPPO-based AEM. The Langmuir adsorption isotherm for adsorption of MO is represented in Figure 8a, and the values of its determined parameters are given in Table 2. For the Langmuir adsorption isotherm, the correlation coefficient  $(R^2)$  was 0.921, representing that the Langmuir adsorption isotherm is fitted to experimental data for adsorption of MO onto the developed BPPO-based AEM. Moreover, the value of  $R_L$  (0.12-0.51) denoted that adsorption of MO was a favorable process. Figure 8b depicts the Freundlich adsorption isotherm for adsorption of MO. Determined values of its factors (n and  $K_f$ ) are shown in Table 2. For it, the correlation coefficient  $(R^2)$  was 0.974, indicating that adsorption of MO fitted well to the Freundlich adsorption isotherm. The values of the Freundlich constant "n" range from 2 to 10, denoting good adsorption, 1-2, denoting moderate adsorption, and less than one, showing poor adsorption.<sup>66,78</sup> Moreover, the D-R adsorption isotherm for it is shown Figure 8c, and the measured values of its parameters are represented in Table 2. The determined value of mean adsorption energy (E) was 0.971 kJ/mol, exhibiting that adsorption of MO onto the prepared BPPO-based AEM was a physical adsorption process.<sup>3</sup>

**3.7. Adsorption Kinetics.** Kinetics study for adsorption of MO from an aqueous solution onto the prepared BPPO-based AEM was explored using several models including the pseudo-first-order model, pseudo-second-order model, Elovich model, liquid film diffusion model, modified Freundlich equation, and Bangham equation. Figure 9a represents the plot of the



Figure 8. (a) Langmuir, (b) Freundlich, and (c) D-R adsorption isotherms for adsorption of MO onto the developed BPPO-based AEM.

Table 2. Measured Values of Adsorption Isotherm Parameters for Adsorption of MO onto the Developed BPPO-Based  $AEM^a$ 

adsorption isotherm model	parameters	
Langmuir isotherm	Q <sub>m</sub>	102.25
	$K_{\rm L} \times 10^{-2}$	1.90
	$R^2$	0.921
	$R_{ m L}$	0.12-0.51
Freundlich isotherm	n	2.24
	$K_{ m f}$	7.80
	$R^2$	0.974
Dubinin-Radushkevich (D-R) isotherm	$Q_{\rm m}$	1613
	β	0.532
	$R^2$	0.660
	Ε	0.971
<sup><i>a</i></sup> $Q_m$ (mg/g), $K_L$ (L/mol), $K_f$ [(mg/g) (mol <sup>2</sup> /l <sup>2</sup> ), and $E$ (kI/mol).	$(L/mg)^{1/n}$ ], $C_{1}$	<sub>m</sub> (mol/g), $\beta$

pseudo-first-order model for adsorption of MO onto the prepared BPPO-based AEM. The measured values of parameters ( $k_1$  and  $q_{e(cal.)}$ ) are given in Table 3. It was noted that there was a large difference between the values of experimental adsorption capacity (17.86 mg/g) and calculate adsorption capacity (10.17 mg/g). Moreover, the value of the correlation coefficient ( $R^2 = 0.934$ ) was found to be lower than

unity. It showed that the pseudo-first-order model was not good to explain the rate process. Figure 9b depicts the plot of the pseudo-second-order model for adsorption of MO. From Table 3, it was noted that the values of calculated and experimental adsorption capacity were very close to each other. In addition, the value of the correlation coefficient ( $R^2$  = 0.997) was close to unity. It exhibited that adsorption of MO onto the developed BPPO-based AEM obeyed the pseudosecond-order model. The plot of the Elovich model for adsorption of MO is represented in Figure 9c, and the measured values of its parameters ( $\alpha$  and  $\beta$ ) are shown in Table 3. For the Elovich model, the value of the correlation coefficient  $(R^2 = 0.945)$  was lower than the pseudo-secondorder model. From here, it was concluded that the Elovich model is not good to discuss adsorption of MO onto the developed BPPO-based AEM. Moreover, the plot of the liquid film diffusion model is denoted in Figure 9d, and the calculated values of its parameters ( $k_{\rm fd}$  and  $C_{\rm fd}$ ) are given in Table 3. Again, the value of the correlation coefficient  $(R^2)$  for the liquid film diffusion model was lower than that of the pseudosecond-order model, representing that it is not suitable to explain adsorption of MO from an aqueous solution onto the developed BPPO-based AEM.

Figure 10a depicts the plot of the modified Freundlich equation for adsorption of MO onto the developed BPPObased AEM from an aqueous solution. The calculated values of



Figure 9. (a) Pseudo-first-order model, (b) pseudo-second-order model, (c) Elovich model, and (d) liquid film diffusion model for adsorption of MO onto the developed BPPO-based AEM.

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	kinetic models	parameters	
	pseudo-first-order model	$q_{\rm e(exp.)}$	17.86
		$q_{\rm e(cal.)}$	10.17
		$k_1 \times 10^{-4}$	4.09
		$R^2$	0.934
	pseudo-second-order model	9e	19.20
		$k_2 \times 10^{-4}$	2.12
		$R^2$	0.997
	Elovich model	α	0.26
		β	0.28
		$R^2$	0.945
	liquid film diffusion model	$k_{ m fd}$	7.12
		$C_{\rm fd}$	-0.63
		$R^2$	0.884
	modified Freundlich equation	т	3.28
		k	0.10
		$R^2$	0.919
	Bangham equation	$k_{o}$	0.76
		α	0.30
		$R^2$	0.919
7.1			/ /

Table 3. Measured Values of Kinetic Parameters forAdsorption of MO onto the Developed BPPO-Based AEMa

<sup>*ak*</sup><sub>1</sub>: (/min);  $q_e$ : mg/g;  $k_2$ : g/mg·min;  $\beta$ : g/mg;  $\alpha$ : mg/g·min; k: L/g·min;  $k_{fd}$ : (/min); and  $k_o$ : mL/g/L.

its parameters (*m* and *K*) are given in Table 3. The value of the correlation coefficient ( $R^2 = 0.919$ ) was found to be lower than that of the pseudo-second-order model. From this, it was

concluded that the modified Freundlich equation is not convenient to explain adsorption MO. In addition, the plot of the Bangham equation for adsorption of MO onto the developed BPPO-based AEM is shown in Figure 10b, and the determined values of its factors ( $\alpha$  and m) are shown in Table 3. For adsorption of MO onto the developed BPPObased AEM, the double logarithmic plot did not give a linear curve, exhibiting that the diffusion of the adsorbate (MO) into pores of the adsorbent (BPPO-based AEM) is not the only rate-controlling step.<sup>11,79</sup> It may be that both film diffusion and pore diffusion were crucial to different extents for adsorption of MO onto the developed BPPO-based AEM from an aqueous solution.

**3.8.** Adsorption Thermodynamics Study. Figure 10c represents the plot of 1/T versus ln  $K_c$  for adsorption of MO onto the developed BPPO-based AEM. The calculated values of Gibb's free energy ( $\Delta G^{\circ}$ ), enthalpy ( $\Delta H^{\circ}$ ), and entropy ( $\Delta S^{\circ}$ ) are given in Table 4. Based on the second law of thermodynamics, for a spontaneous process,  $\Delta G^{\circ} = \Delta H - T\Delta S$  should be less than zero. It was noted that the value of enthalpy ( $\Delta H^{\circ} = 18.72$  kJ/mol) was positive, indicating that adsorption of MO was an endothermic process. Moreover, the positive value of entropy ( $\Delta S = 80.10$  J/mol) represented the increase in randomness at the MO–AEM interface during adsorption of MO which is similar to that reported in our previous work.<sup>23</sup> On the other hand, it was observed from Table 4 that the value of Gibb's free energy ( $\Delta G^{\circ}$ ) at all



Figure 10. (a) Modified Freundlich equation, (b) Bangham model, and (c) plot of 1/T vs ln  $K_c$  for adsorption of MO onto the developed BPPObased AEM.

Table 4. Measured	Values of Thermodynamic Factors for
Adsorption of MO	onto the Developed BPPO-Based AEM

temperature (K)	$\Delta H^{\circ}$ (kJ/mol)	$\Delta S^{\circ}$ (J/mol)	$\Delta G^{\circ}$ (kJ/mol)
298	18.72	80.10	-23.85
313			-25.10
323			-25.85
333			-26.65

temperature studied was negative, representing that adsorption of MO was a spontaneous and feasible process.

**3.9. Regeneration Studies.** The ability of an adsorbent to be regenerated for successive removal cycles turns the method cost-effective and suitable for practical applications. Keeping in view this aspect, the membrane was treated with 0.5 mol/L sodium chloride salt solution. The membrane was studied for the removal of dye (MO) for three consecutive cycles, and no appreciable loss in its adsorption capacity was noted. This can be observed by the adsorption capacity value obtained after each cycle. Attained results are shown in Figure 11. The salt solution not only helps to displace the attached anions from the surface of the membrane but also disrupts dipole–dipole and ion–ion interactions between the analyte and the membrane's functional groups.

## 4. CONCLUSIONS

In this research, the development of the BPPO-based homogeneous AEM was carried out via the solution casting method. FTIR spectroscopy confirmed the successful



Figure 11. Regeneration of the BPPO-based AEM.

fabrication of the BPPO-based AEM. It showed higher homogeneous morphology and thermal stability. The prepared AEM showed a water uptake of 68%, an IEC of 2.66 mmol/g, and an LER of 31%. The adsorption capacity was increased from 7.30 to 17.85, 17.85 to 84.20, 17.85 to 19, and 9.30 to 18.10 mg/g with contact time, initial concentration of MO in an aqueous solution, temperature, and pH, respectively, while decreased from 36.50 to 17.85 and 17.85 to 12.0 mg/g with membrane dosage and molarity of NaCl, respectively, in an aqueous solution. Adsorption isotherm investigations exhibited that adsorption of MO onto the developed BPPO-based AEM was fitted well to the Freundlich adsorption isotherm. Adsorption kinetics study showed that adsorption of MO onto the developed BPPO-based AEM fitted to the pseudo-second-order model because the value of the correlation coefficient was close to unity ( $R^2 = 0.997$ ). Moreover, the adsorption thermodynamics result indicated that adsorption of MO was spontaneous and feasible. The positive value of enthalpy ( $\Delta H^{\circ} = 18.72 \text{ kJ/mol}$ ) showed that MO adsorption was an endothermic process. The membrane was regenerated with no significant decrease in adsorption capacity. It showed that the developed BPPO-based AEM was an extraordinary candidate for adsorption of MO from an aqueous solution at room temperature.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03148.

Bromination of PPO and batch adsorption procedure; adsorption kinetic and isotherm models applied to study MO adsorption onto the BPPO-based AEM; and adsorption thermodynamics details (PDF)

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## Notes

The authors declare no competing financial interest.

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#### NOMENCLATURE

AEM, anion exchange membrane BPPO, brominated poly 2,6-dimethyl-1,4-phenylene oxide MO, methyl orange

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