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Removal of boron from industrial wastewater using PVP/PVDF blend membrane and GO/PVP/PVDF hybrid membrane by pervaporation

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Abstract−Removal of boron from water is a significant issue worldwide. Boron levels in waters containing high concentrations should be kept under control. Boron removal from the industrial wastewater released from Eti Mine Boron plants was investigated by using blend and hybrid membranes in a laboratory-scale pervaporation system. Polyvinylpyrrolidone/Polyvinylidene fluoride blend membrane and Graphene oxide/Polyvinylpyrrolidone/Polyvinylidene fluoride hybrid membranes were synthesized for this process. The membranes were characterized by using scanning electron microscopy, Fourier transform infrared, X-ray diffraction and contact angle measurements. Separation performance was evaluated in terms of flux, removal ratio of boron, and boron concentration in permeate within the membrane. Membranes showed higher separation performance in industrial wastewater. The highest boron removal was obtained as 99.86% with a flux of 0.755 kg/m^2h when the 8 wt% graphene oxide loaded hybrid membrane was used. This study indicates that the Polyvinylpyrrolidone and Graphene oxide addition improved the membrane features and separation performances of the pervaporation process with improved hydrophilic membrane features can be preferred as an innovative water treatment method for the removal of boron from industrial wastewater. The obtained results show that pervaporation can be readily adapted to the removal of boron species by appropriate membrane selection.

Keywords: Boron, Industrial Wastewater, Membrane, Pervaporation

INTRODUCTION

Wastewater, which is generated during the production of refined boron products, includes high amounts of boron. The boron contamination in water causes pollution of both ground and surface water. The wastewater containing boron mixes with surface and groundwater to form many complexes with heavy metals such as Pb, Cd, Cu and Ni, and these chemical structures create much more harmful effects than the heavy metals that form them [1].

Boron acts as a significant micronutrient for plants, animals and humans, and also is an essential element for the normal growth of them. However, there is a restricted interval between its toxicity and deficiency; boron is beneficial for plants only in small amounts and excessive quantity is harmful and even lethal. Moreover, long term exposure to boron can poison the organism and damage the nervous, cardiovascular and digestive systems of humans and animals [2,3]. The criteria of the amount of boron in drinking water and seawater have changed by each state. According to the criteria for Turkish environmental legislation, the amount of boron in the water to be discharged into the sea should not exceed 500 mg/L [4].

Boron-containing wastewater is generated in the production of boron compounds such as boric acid in Bandırma Eti Mine. This water is collected in the wastewater pool and treated with caustic lime. After coagulation, synthetic colemanite is obtained and utilized as a raw material in boric acid. Therefore, wastewater containing high amounts of boron is treated and reduced to less than 500 ppm in order to be discharged into the sea. When all these are taken into consideration, boron levels in waters containing high concentrations should be kept under control. Removal of boron from water is a significant issue worldwide, which has been investigated recently [5,6]. The conventional separation processes and membrane separation processes are used for removal of boron from water.

Membrane process is a separation process in which characteristic properties of membrane such as porosity, selectivity, electrical charge are utilized to separate the components from gas or liquid mixture. In membrane processes, the feed stream is separated in two parts: permeate and retentate. The permeate passes through the membrane and the retentate includes components that are not transported across the membrane. Due to its multidisciplinary property, the membrane process is utilized in many industries such as water treatment for domestic water supply, pharmaceutical, chemical, food, metallurgy and other separation processes. Membrane technology has broad industrial and environmental applications due to the advantages of membrane separation such as energy saving process, clean technology, applicable with hybrid process and ability to replace traditional process. However, these processes have some drawbacks, such as membrane fouling, low flux and selectivity, short membrane lifetime [7-9].

There are membrane processes such as reverse osmosis, ultrafiltration, membrane distillation and conventional separation processes such as ion exchange, adsorption, electrocoagulation, precipitation that are utilized for the removal of boron from water [10-25]. However, some of them have disadvantages during separation process. Flocculants and coagulants are utilized to remove boron

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from wastewater. In this method, sedimentation is applied to separate them. Even though high efficiency has been achieved, the reagent is highly expensive [10]. In precipitation method using metal hydroxide is not an effective and environmentally process because of low boron removal and the large quantity of nonrecyclable wastes [26]. Membrane processes such as reverse osmosis, membrane distillation have been also applied for the removal of boron. However, the pH of the wastewater must be adjusted before the process and treatment of wastewater using methods such as ion exchange before discharging creates an additional unit. Moreover, utilizing porous membranes can result in clogging of pores and requires regular maintenance, which will increase the operating cost of the process [10,11,27]. Decreasing performance with time and high energy consumption are the disadvantages of the membrane distillation process [28]. However, the important advantage of membrane distillation is the high rejection ratio of the ions, molecules and colloids [29]. The advantages and drawbacks of boron removal processes from waste water are summarized in Table 1.

Pervaporation is an important alternative process to these conventional separation processes. Recently, many studies have investigated the treatment of wastewater and seawater by utilizing the pervaporation process to obtain drinking and municipal water [33,34]. Pervaporation membranes are also used for chemical, environmental and biotechnological processes due to their excellent separation efficiency, low energy usage, low cost, moderate operation conditions, prevention of additional chemical usage and being environmentally friendly. High product purity and quality is obtained and mixtures can be separated easily and economically without the usage of entrained agents. It is an eco-friendly technology due to the no waste and no emission production features. It can be performed under mild operating conditions such as low temperature, low energy. Pervaporation is a simple, compact, flexible and modular process [35-38]. Before the boron removal in the pervaporation process, there is no need to adjust the pH of the wastewater such as reverse osmosis process and no waste generated after water treatment like precipitation method. Moreover, clogging does not occur in the membrane due to the dense construction. In this membrane separation, water purification can be explained by the solution-diffusion mechanism. This mechanism is based on the interaction of the water on the surface of the membrane, dissolution on the membrane and desorption from the downstream of the membrane. The transition of the water molecules occurs among the molecular space of the membrane. In pervaporation process, a chemical potential gradient occurs across the membrane which could be created by utilizing a vacuum pump on the permeate side of the membrane. Therefore, pervaporation is considered economical, energy savings and environmentally friendly [39,40].

Polyvinylpyrrolidone (PVP) and Polyvinylidene fluoride (PVDF) were chosen as the membrane matrix. PVP is a hydrophilic membrane material, which could blend with organic and inorganic compounds. Its amide and carbonyl groups encourage the formation of hydrogen bonds between the water and membrane. The addition of PVP decreases the crystallinity of the polymer mixture and increases the free volume of the membrane. This situation leads to an increase in the swelling degree of the membrane and thus affects the separation performance [41]. In literature, many studies which used PVP have been investigated in the field of pervaporation for dehydration of organic solvent, separation of azeotropic mixture and desalination process [42-45]. However mechanical and chemical stability of the PVP membrane should be developed with compatible polymers due to its fragile structure. PVDF has been comprehensively utilized for the pervaporation process because of its

Table 1. Advantages and disadvantages of boron removal method

Method	Advantages	Disadvantages
Reverse Osmosis [10-12]	- It can be effectively utilized with more than 99% rejection for boron removal - Reject nearly all contaminants ions [1-3]	- Adjustment of the pH of wastewater should be required before the process - Additional unit is necessary to reduce boron levels, which increase the cost - High power cost
Membrane distillation [25,28,29]	- Lower operating pressure than RO - Highly the rejection ratio of the ions.	- High energy consumption
Precipitation [24,30]	- Precipitation is a simple and easily automated process.	- Ineffective process because of low removal rate - Large amount of metal hydroxide is required - Large amount of nonrecycable wastes is generated.
Ion exchange method [18,19]	- High boron removal efficiency - Solution pH is stable - Sorption rate is fast	- Expensive process - Regeneration of resin is required after process
Adsorption [20,31]	- Fast sorption rate (naturel adsorbents) - Low initial cost (Fly ash, waste sepiolite)	- Large consumption of adsorbent - Regeneration is difficult - Easy influence pH
Electrocoagulation [22,23]	- High boron removal efficiency	- High energy consumption
Ultrafiltration [32]	- Well established process - Low energy consumption and high productivity	- Significant fouling tendency - Clogging of pores

good chemical stability, mechanical properties, thermal resistance and membrane forming properties. PVDF has been used to improve the purification properties of the water as well as to increase the mechanical properties and chemical resistance of the membrane [46]. Recently, graphene based materials have been investigated for water purification [47-49]. Graphene oxide (GO) is two-dimensional structure that includes a large number of oxygen groups. Because of the presence of carbon-oxygen groups in the structure, graphene oxide makes a membrane hydrophilic surface and thus contributes to high water permeation. Additionally, graphene oxide gives the polymer good mechanical and thermal stability. Because of its properties, graphene oxide has emerged as an intensive interest in membrane application [49].

This study presents a new solution in removal of boron from wastewater by pervaporation process. PVP/PVDF incorporated graphene oxide membranes were fabricated for boron removal from wastewater. No study is available in the literature on the pervaporative removal of boron by the usage of PVP/PVDF and GO/PVP/PVDF membranes. The membranes showed excellent separation performance in wastewater treatment. According to the author's knowledge, this study is the first study on pervaporative separation that deals with the usage of pervaporation process on removal of boron.

MATERIALS AND METHODS

1. Materials

Polyvinylidene fluoride (PVDF) (polydispersity index range: 2.1-2.6; MW range: 300,000-360,000 Da) was purchased from Solvay. Polyvinylpyrrolidone (PVP) (360,000 MW) and boric acid were supplied by Sigma Aldrich Chemicals. Graphene oxide (GO) in an aqueous solution was supplied from Hazerfen Kimya A.S (Kocaeli, Turkey). Dimethylformamide (DMF) (99.9%) was purchased from Fisher Scientific. The wastewater including boron was supplied from Eti Mine, Balıkesir, Turkey. The chemical analysis of wastewater was determined with ICP-OES (inductively coupled plasma optical emission spectroscopy) given in Table 2. The synthetic solution containing 960 ppm boron was prepared by using boric acid.

Table 2. Chemical analysis of wastewater

Components (mg/L)					
B	Ca	Mg	Si	Fe	Na
2,900	317.95	325	6.25	0.06	0.08

2. Membrane Preparation

5 wt% of PVDF was first dissolved in DMF and stirred at room temperature to obtain a homogeneous polymer solution. PVP/PVDF blend membranes were prepared by mixing the PVP with PVDF solutions in different mass ratio (the PVP/PVDF ratios were 0.1, 0.2, 0.3 and 0.4). After optimum PVP/PVDF ratio was determined as 0.2, 4 wt%, 6 wt% and 8 wt% of GO according to the weight of PVDF polymer was added to the PVP/PVDF membrane solution. GO/PVP/PVDF membrane solution was mixed for at least three hours. The resulting polymer solutions were poured onto the glass surface and allowed to dry at 120 °C for 5 hours. The thickness of the membranes was about 190-200 μm. The properties of prepared membranes are given in Table 3.

The samples were labeled according to PVP/PVDF ratio and GO content, because PVDF amount is constant. For example, "4GO-0.2PVP/PVDF" represents the 0.2 PVP/PVDF ratio and 4 wt% GO.

3. Membrane Characterization

Morphological features of membranes were characterized by using scanning electron microscopy (SEM) (ZEISS) operated at 20 kV accelerating voltage. The cross section morphological structure of membranes was investigated by fracturing in liquid nitrogen. Before analyzing, membranes were covered by gold under a vacuum.

The FTIR analysis of the prepared membranes used Perkin Elmer FTIR spectroscopy in the band range of 4,000-450 cm^{-1} with a scanning resolution of 4 cm^{-1} and 4 scans per sample. The spectra were measured in transmission mode.

The wettability of the membranes was determined by utilizing an Attension/Theta lite contact angle instrument by dropping an average 4 μl of distilled water on the sample. Contact angle measurement was performed by using the sessile drop method. A piece of the membrane was cut from the membrane films and analyzed by placing it in a sample chamber at room temperature. All contact angle measurements were repeated three times and the mean value was taken.

XRD patterns of membranes were recorded in Bruker AXS/Discovery D8 XRD equipment. Analysis was performed by using CuKa radiation at rate of 0.02° over the 2θ range of 20-80°.

4. Sorption Degree Experiments

The sorption degree was carried out under room temperature to investigate the interaction of water with the membrane. All membranes were cut into small pieces and weighed on a precision scale

Table 3. Properties of prepared membranes

Membrane	PVDF content (wt%)	PVP/PVDF ratio (wt%/wt%)	GO content (wt%)
0.1-PVP/PVDF	5	0.1	-
0.2-PVP/PVDF	5	0.2	-
0.3-PVP/PVDF	5	0.3	-
0.4-PVP/PVDF	5	0.4	
4GO-0.2PVP/PVDF	5	0.2	4
6GO-0.2PVP/PVDF	5	0.2	6
8GO-0.2PVP/PVDF	5	0.2	8

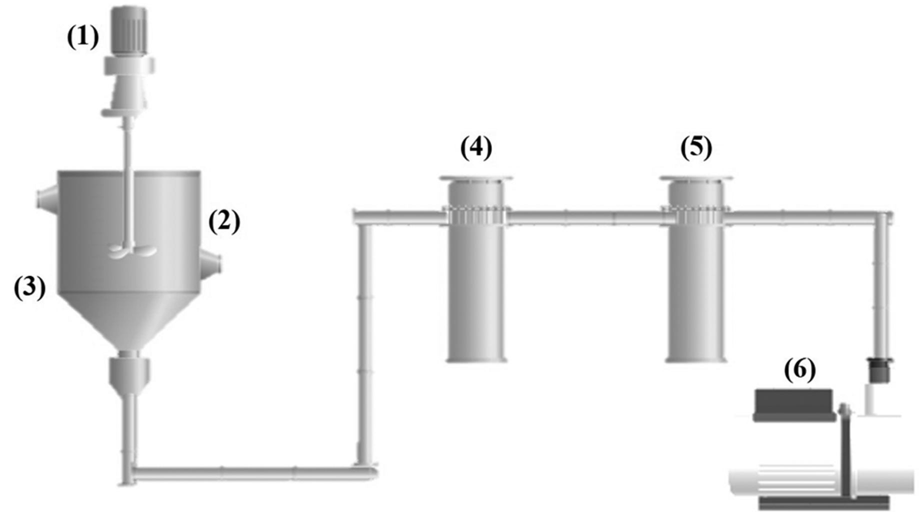


Fig. 1. Schema of pervaporation: (1) Mechanical mixer, (2) membrane chamber, (3) membrane, (4,5) cold traps, (6) vacuum pump.

to determine dry weight. The membranes were placed on petri dishes containing water. At certain time intervals, the membranes were lightly dried with filter paper and reweighed in precision scales. This process was continued until the weight of the membranes was stabilized. The sorption degree (SD) of the membranes was estimated by utilizing Eq. (1).

$$SD=\frac{M_s-M_d}{M_d} \tag{1}$$

M_s and M_d refer to the mass of swollen and dried membrane, respectively.

5. Pervaporation Experiment

The prepared membranes were tested for pervaporation on an experimental setup given in Fig. 1.

A specially designed cell made of stainless steel was utilized in pervaporation experiments. The effective membrane surface area was approximately 9.6 cm^2. The prepared membranes were cut according to the size of the cell and placed into the cell consisting of two parts. Experiments were carried out by using 30 ml of wastewater and synthetic solution. The wastewater was fed to the membrane cell. Experiments were performed at room temperature and realized for five hours. During the experiments, the feed side of the membrane cell was under atmospheric pressure and 10 mbar vacuum pressure was applied on the permeate side. Permeate was collected as a vapor phase in glass cold traps filled with liquid nitrogen. It was then heated to room temperature and the weight of the collected permeate was utilized for the determination of the flux and removal of boron. The compositions of the samples were analyzed in ICP-OES. The flux and removal ratio of boron (R) (%) was calculated by using Eq. (2) and Eq. (3), respectively.

$$J=\frac{m}{S\cdot t} \tag{2}$$

$$R=\frac{C_f-C_p}{C_f} \tag{3}$$

where m refers to the weight of the permeate (kg). S is the effective membrane area (m^2) and t is the permeation time (h). C_f (mg/L) is the concentration of boron in the feed side and C_p (mg/L) is the boron concentration in the permeate side.

Experimental studies were replicated three times and flux and removal ratio of boron were determined. Also, analyses were replicated three times for every experiment, so every sample was examined three times for the determination of flux and removal ratio of boron values. All values were close to each other in replicate experiments such as reusability experiments (It can be seen in Section 3.4. Reusability of Membrane). The flux and removal ratio of boron values were calculated for each of replicate and mean value was determined. The values in the figures are the mean values.

RESULTS AND DISCUSSION

1. Membrane Characterization

1-1. SEM

The cross section images of pristine PVDF, PVP/PVDF and GO/PVP/PVDF membranes are shown in Fig. 2. While Fig. 2(a), (b) shows the images of pristine PVDF and PVP/PVDF blend membrane, Fig. 2(c), (d) show different magnification of GO/PVP/PVDF membranes.

The pristine PVDF membrane exhibited dense construction in Fig. 2(a). The addition of PVP had changed the structure of the PVDF membrane. PVDF and PVP polymers showed good harmony and compatibility within the membrane. There is no observed phase separation. The homogeneous and compatible PVP/PVDF membrane had been achieved. The viscosity of membrane solution also increased importantly with PVP addition. This state made the mixing of membrane solution difficult [50]. Pore formation had not been observed. This is related to the membrane preparation technique. Membranes were synthesized by solution casting and solvent evaporation. The synthesis of the nonporous membrane was aimed at this study.

The presence of GO in the GO/PVP/PVDF membrane is seen clearly in Fig. 2(c), (d). Some GO particles are marked by the circle in the Figure. GO distributed homogeneously in the membrane. A

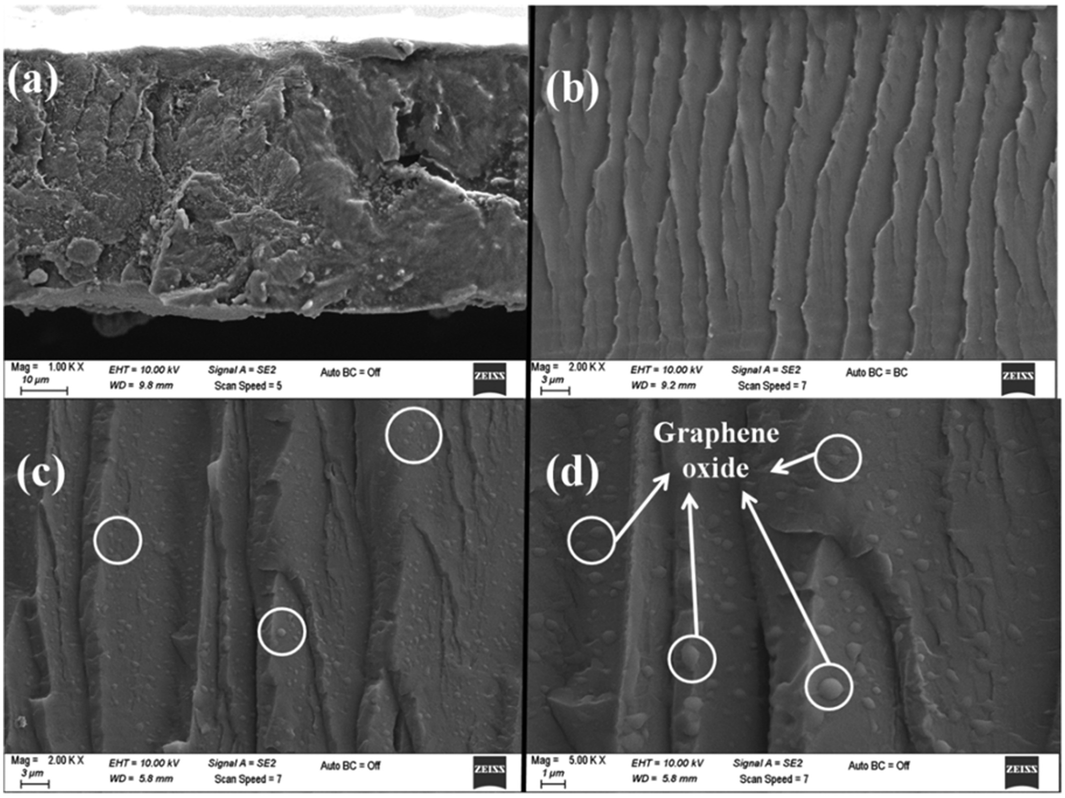


Fig. 2. The cross section images of membranes (a) pristine PVDF, (b) PVP/PVDF membrane, (c) 2000x magnification GO/PVP/PVDF membrane, (d) 5000x magnification GO/PVP/PVDF membrane.

good adhesion between the GO and PVP/PVDF membrane was provided. There are no voids between the GO and polymer matrix. That situation is related to the intense interaction between the GO and the PVP/PVDF membrane. The interaction was related to the formation of strong hydrogen bonding between oxygen-containing functional groups of GO and fluorine groups of PVDF. Besides, GO can be combined with PVP by hydrogen-bonding interactions. Particle agglomeration was not observed in the membrane. Fig. 2(d) shows the GO particle in the membrane more closely. The homogeneous GO distribution in the PVDF membrane can be seen obviously from Fig. 2(d) [51-53].

1-2. FTIR

The chemical bond structured of membranes was obtained by FTIR analysis. Fig. 3 shows the FTIR spectrum of pristine, blend, hybrid membranes and used membrane.

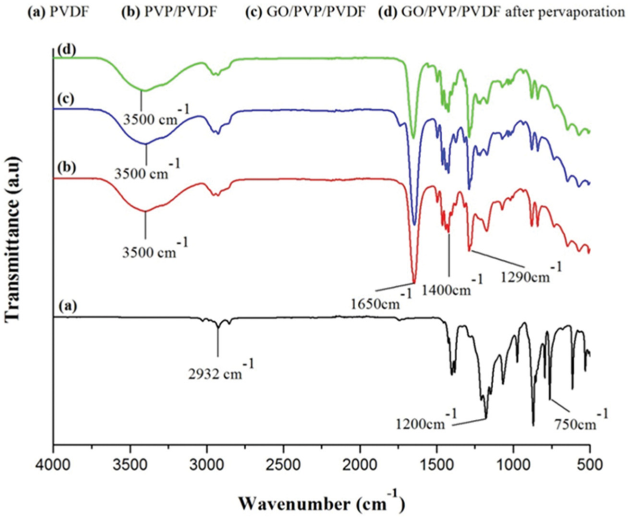
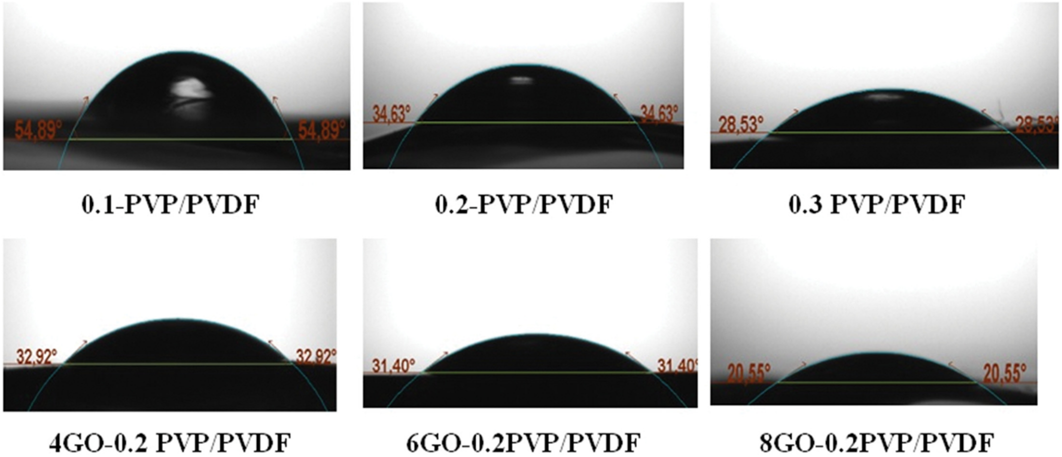


Fig. 3. FTIR spectra of (a) PVDF, (b) 0.2 PVP/PVDF, (c) 8GO-0.2 PVP/PVDF (d)8GO-0.2 PVP/PVDF membranes after pervaporation.

In PVDF, the bands located around 3,000 and 2,900 cm^{-1} corresponded to the CH_2 asymmetric and symmetric oscillation. The CH_2 functional group absorption band of PVDF at ~3,000 cm^{-1} shifts to lower frequency with the addition of PVP. This is related to the hydrogen bonding formation between the carbonyl group of PVP and the CH_2 group of PVDF. The formation of hydrogen bond resulted in weakened the interaction of carbon and hydrogen of CH_2 in the PVDF [54]. The characteristic C-C band reveals at 1,200 cm^{-1}. The peaks between 750 and 850 cm^{-1} are related to C-C-C stretching oscillation and CF and CF_2 stretching oscillation of PVDF [55]. Peaks around 1,650 cm^{-1} are imputed to the carbonyl stretching in membranes. The intensity of CF- and CF_2-based peaks decreased due to the PVP addition. The peak at 3,500 cm^{-1} is ascribed to the presence of -OH group for GO and PVP [56,57]. The peaks at 1,290 cm^{-1} and 1,350 cm^{-1} belong to C-OH stretching vibration and O-H deformation, respectively. The C-OH stretching vibration and O-H deformation is proven by the peak of 1,290 cm^{-1} and 1,350 cm^{-1}. As shown in Fig. 3, the characteristic peaks of the PVP oc-



0.1-PVP/PVDF 0.2-PVP/PVDF 0.3 PVP/PVDF

4GO-0.2 PVP/PVDF 6GO-0.2PVP/PVDF 8GO-0.2PVP/PVDF

Fig. 4. Results of contact angle.

curred at 1,400 cm^{-1}, 1,650 cm^{-1} and 1,550 cm^{-1}, which are assigned to stretching oscillation of C-N, C=O and CH_2 bonds, respectively. It could be observed that there was a band at 1,726 cm^{-1} in the spectra of GO/PVP/PVDF due to the oxygen-containing groups on the structure of the GO. Nevertheless, the peak disappeared in the GO/PVP/PVDF membrane spectra after pervaporation, indicating that some oxygen-containing groups on the GO surface were removed [58]. The FTIR spectrum of the membrane used in the pervaporation experiment is given in Fig. 3(d). All membranes show the same FTIR vibrational frequency. Thus, there was no observed significant difference in the structure of the membrane used in the experiment.

1-3. Contact Angle Results

The contact angle measurement is utilized to indicate the hydrophilicity or hydrophobicity of a membrane. Fig. 4 shows the contact angle between the surface of the membrane and water.

PVP membranes are generally hydrophilic. An increasing amount of PVP makes the membrane more hydrophilic. The lowest contact angle was found to be 28.06° on the 8 wt% GO loaded membrane. There is a large number of oxygen containing functional groups on the surface of GO/PVP/PVDF membrane due to the graphene oxide, and these functional groups can easily form hydrogen bonds with water. As a result, a low contact angle is observed of the membrane surface. This indicates that the GO doped membranes are relatively more hydrophilic. These results confirm the improvement of the surface hydrophilicity of the hybrid membrane compared to the PVP/PVDF membrane [59-61].

1-4. XRD Results

The crystallinity and amorphous phase of the membrane samples were characterized by XRD. Fig. 5 represents the XRD patterns of PVDF, 0.2-PVP/PVDF and 8GO-0.2 PVP/PVDF membranes.

The XRD profile of PVDF membrane shows intensive sharp peaks which indicate the crystalline nature. PVDF membrane exhibits two main diffraction peaks at $2\theta=25.1°$ and 39.7°, which indicates the characteristic peaks of PVDF crystals. These peaks are found to be absent in the PVP/PVDF and GO/PVP/PVDF membranes, indicating the amorphous nature of PVP and GO in the PVDF matrix. PVP/PVDF and GO/PVP/PVDF membranes were observed at 2θ region of 40-50°, which can be attributed to the amorphous nature of the blend and hybrid. The characteristic peaks of GO exhibited no additional diffraction peaks, indicating the uniform distribution over PVP/PVDF membrane [62].

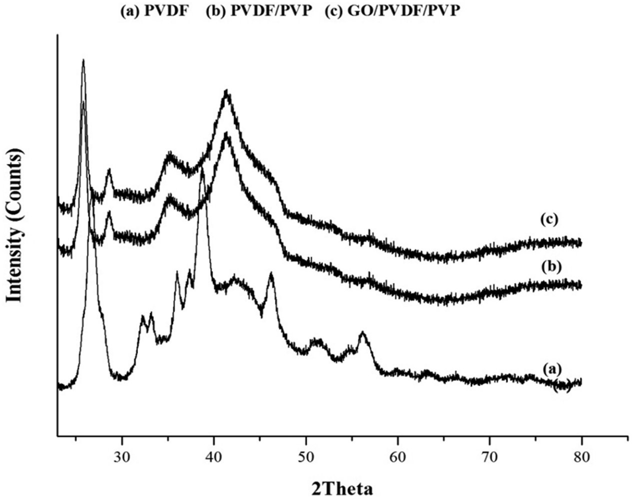


Fig. 5. XRD patterns of membranes.

1-5. Sorption Test

The sorption performance of the membranes in deionized water is given in Fig. 6.

The sorption characteristic of the membrane is based on the composition and structure of the polymer membrane. The PVP content was enlarged the sorption degree due to its hydrophilic property. The sorption degree of the membranes increased with increased GO content. The hydrophilicity of GO can be an important factor that affects the swelling. Furthermore, GO has carboxyl and hydroxyl groups which allow a higher percentage of sorption. When the amount of the GO increased from 4 wt% to 8 wt%, the sorption degree of the membrane increased from 80% to 95%. It is possible to observe that the membrane including GO exhibited a higher sorption degree than the PVP/PVDF membrane. It was observed that the degree of sorption of the membranes did not change

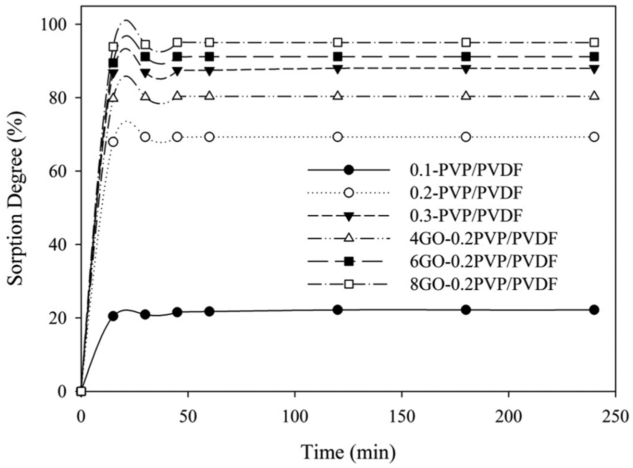


Fig. 6. Sorption test results.

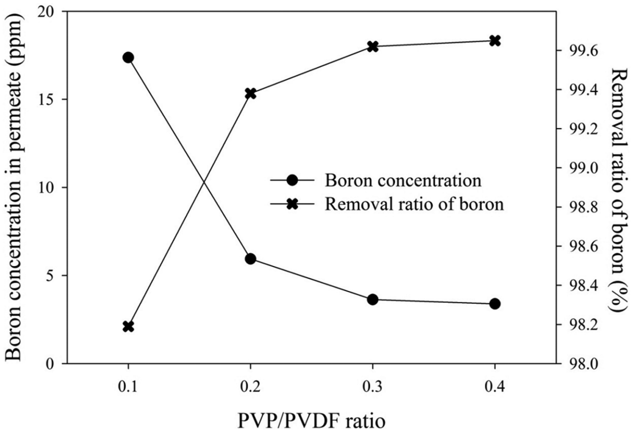


Fig. 8. Effect of PVP/PVDF ratio on boron removal.

after 30 minutes.

2. Results of Pervaporation of Synthetic Water

2-1. Effect of PVP/PVDF Ratio on Separation Performance of the Membrane

PVDF membrane is hydrophobic while PVP has a hydrophilic structure. It is expected that the addition of PVP to the PVDF membrane will increase the hydrophilic character of the membrane and so there will be a rise in the flux of water. To investigate the effect of PVP/PVDF ratio on separation performance of the membrane, the PVP/PVDF ratio was investigated in a range of 0.1-0.4. The obtained flux, removal ratio of boron and boron concentration in the permeate stream are given in Fig. 7 and Fig. 8. While the ratio of PVP/PVDF was 0.1, the membrane has 0.207 kg/m^{2}h of flux value. The usage of 0.2 as PVP/PVDF ratio increased the flux value to 0.623 kg/m^{2}h. Similarly, boron concentration in the permeate stream was decreased from 960 ppm to 17.37 and 960 ppm to 5.94, respectively. The removal ratio of boron was obtained as 98.19% and 99.38%. Due to the hydrophilic structure of PVP, the PVP/PVDF blend membrane exhibited a greater affinity towards water. The hydroxyl groups of PVP in the PVP/PVDF blend membrane form hydrogen bonding with water. At higher PVP ratio, there are more interactions between hydroxyl groups and water. With the addition of PVP into PVDF membranes, the crystallinity of the membrane declines and the amorphous region in the membrane increases. The addition of PVP disordered the polymeric structure of the PVDF membrane and increased the diffusion channels in the membrane matrix. As the PVP amount was increased, the PVP/PVDF membrane displayed more hydrophilic features and a high flux, removal ratio and low boron concentration on the permeate side were obtained [63-67].

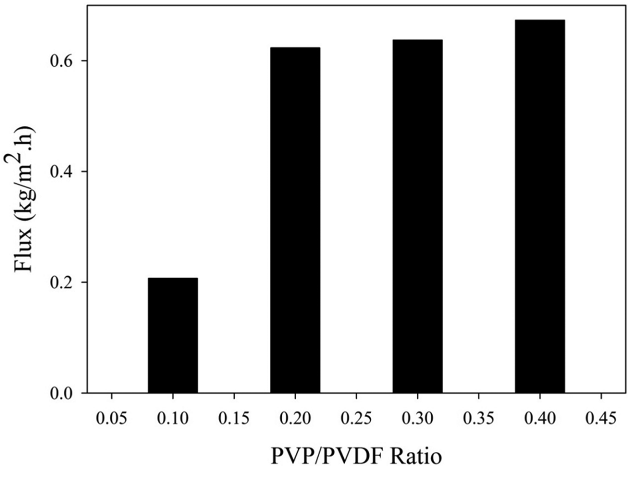


Fig. 7. Effect of PVP/PVDF ratio on flux.

Besides, after a more than 0.2 of ratio, separation performance was not exhibiting certain variation in flux, removal ratio and boron concentration in permeate stream. Flux value increased only 2.2% proportion with 0.3 of ratio according to the 0.2 of PVP/PVDF ratio. While flux value was 0.623 kg/m^2·h for 0.2 of PVP/PVDF ratio membrane, this value rose to 0.637 kg/m^2·h for 0.3 of PVP/PVDF ratio membrane. For 0.4 of PVP/PVDF ratio membrane, the removal ratio increased from 99.62 to 99.65, boron concentration exhibited a rather slight change. This situation can be explained by the contact angle given in Fig. 4. The contact angles of the prepared membranes at the ratios of 0.1, 0.2 and 0.3 PVP/PVDF are 54.89°, 34.63°, and 28.53°, respectively. The difference between 0.1 of ratio and 0.2 of ratio is considerably higher than the difference between 0.2 of ratio and 0.3 of ratio, so it is observed that there is no significant change in the contact angle after 0.2 of ratio. Additionally, in 0.2 of PVP/PVDF ratio membrane, membrane reaches dissolution saturation. After more than 0.2 of PVP/PVDF ratio, the transport is considered to depend only on the diffusion controlled of the water. It is not dependent on solubility on the membrane surface. Also, the high PVP loading ratio, polymeric membrane solution makes it viscous and difficult to mix. The homogeneous solution obtainment becomes difficult. Besides that, the usage of minimum amount PVP is also important in terms of economics, because low membrane and process cost is of capital importance in terms of process economics. The optimum PVP/PVDF ratio was determined as 0.2 in the membrane for all reasons above.

2-2. Effect of GO amount in PVP/PVDF Membrane on Separation Performance of the Membrane

The effect of GO amount in PVP/PVDF membrane on separa-

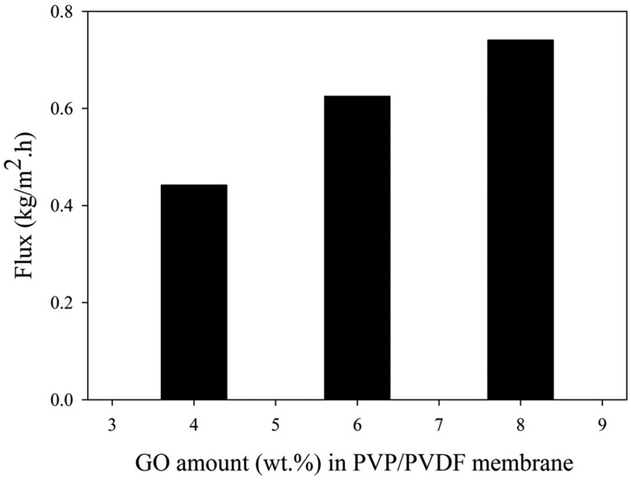


Fig. 9. Effect of GO amount on flux (The used membrane: 0.2-PVP/PVDF membrane).

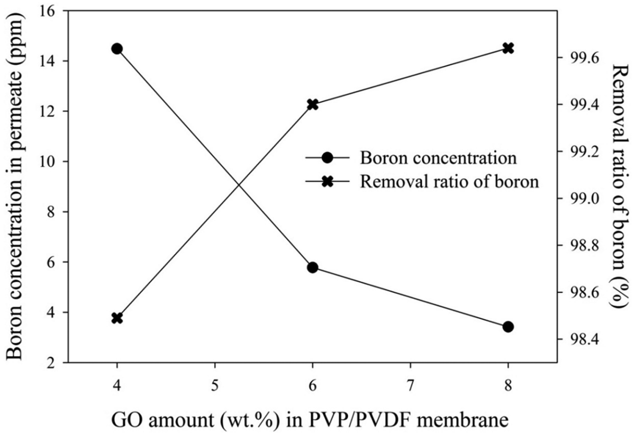


Fig. 10. Effect of GO amount on boron removal (The used membrane: 0.2-PVP/PVDF membrane).

tion performance of the membrane is given in Fig. 9 and Fig. 10 as flux and boron removal.

The addition of GO into the PVP/PVDF polymer membrane results in a more hydrophilic membrane. The low amount of GO loading in the PVP/PVDF membrane causes no change prominently the hydrophilic structure of the membrane. The obtainment of similar results has been also seen achieved in some studies [68]. The high ratio GO loaded PVP/PVDF membrane was increased the hydrophilicity of the PVP/PVDF membrane, because GO has hydrophilic oxygen-containing functional groups [69]. The increase in hydrophilic surface facilitates the diffusion of water molecules, and flux increases [70,71]. Usage of greater amount of hydrophilic additives prevents the boron accumulation on the membrane surface, a large amount of water provides transportation [72]. It can also be explained by the fact that as the hydrophilicity increases, the diffusion of the boron across the membrane is slower than the water. While the flux value of 4 wt% GO loaded PVP/PVDF membrane was 0.442 kg/m^2·h, 6 wt% and 8 wt% GO loaded PVP/PVDF membranes have 0.625 kg/m^2·h and 0.742 kg/m^2·h of flux values, respectively. These values are rather close to the PVP/PVDF blend membrane. The higher flux increment was achieved by using 8 wt% GO loaded PVP/PVDF membrane.

GO/PVP/PVDF membrane has higher permeate flux than the PVP/PVDF membrane. GO/PVP/PVDF membrane has less adsorption ability to boron due to the greater electrostatic repulsion. GO structure contains four different functional groups: the carbonyl, carboxylic, hydroxyl and epoxy groups. The GO surface has been loaded with negative charge due to these oxygen-containing functional groups. Also, PVP has oxygen and nitrogen which are responsible for the negative charge on the membrane surface. These effects reduce the adsorption of boron due to the electrostatic repulsion [52]. Therefore, 8 wt% GO loaded PVP/PVDF membrane has the lowest boron concentration in the permeate as 3.42 ppm. The lower amount of GO loaded membrane is 4 wt% GO loaded PVP/PVDF membrane. The electrostatic repulsion is less in this membrane. Therefore, the boron concentration value in permeate is higher and was obtained in 14.48 ppm. 8 wt% GO loaded PVP/PVDF membrane exhibited the best separation performance both of flux and removal ratio of boron.

The GO amount was loaded as a maximum 8 wt% on the membrane. It was observed that there were no certain differences on flux and boron removal values between 6 wt% GO loaded PVP/PVDF membrane and 8 wt% GO loaded PVP/PVDF membrane. Therefore, the more loading ratio from 8 wt% was not tried in the experiment.

3. Results of Pervaporation of Industrial Wastewater

The membrane which had the best separation performance was determined using synthetic water containing boron. 0.2 of PVP/PVDF ratio membrane and GO loaded PVP/PVDF membranes were investigated in the separation of industrial wastewater. Table 4 shows the acquired experimental results with industrial wastewater content.

The flux value of membranes is given in Fig. 11. As seen in Table 4 and Fig. 11, pervaporative separation is rather effective in the removal of boron from industrial wastewater.

Pervaporation was not only effective to separate boron, it also

Table 4. Comparison of the experimental results of permeate water with industrial wastewater

Analysis (mg/L)	B	Ca	Mg	Si	Fe	Na	R_B (%)	R_{Ca} (%)
Industrial wastewater	2,900	317.95	325	6.25	0.06	0.08	-	-
0.2PVP/PVDF permeate water	6.95	0.96	-	-	-	-	99.76	99.70
4GO-0.2PVP/PVDF permeate water	6.76	0.9	-	-	-	-	99.77	99.72
6GO-0.2PVP/PVDF permeate water	5.6	0.80	-	-	-	-	99.81	99.75
8GO-0.2PVP/PVDF permeate water	4.2	0.81	-	-	-	-	99.86	99.75

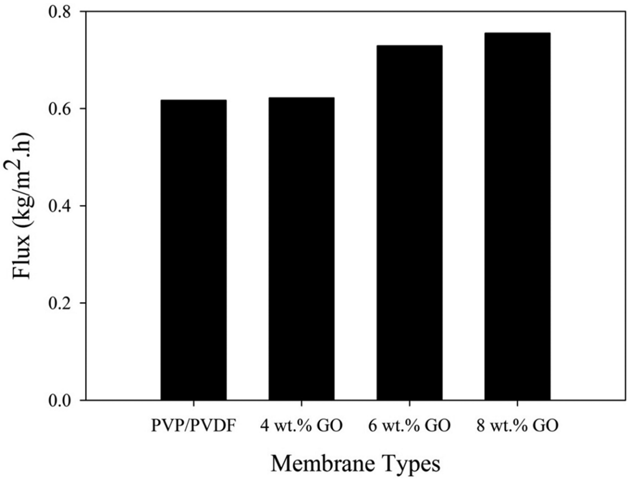


Fig. 11. Effect of membrane types on flux values for industrial wastewater (The used membranes: 0.2-PVP/PVDF membrane, 4GO-0.2PVP/PVDF, 6GO-0.2PVP/PVDF, 8GO-0.2PVP/PVDF).

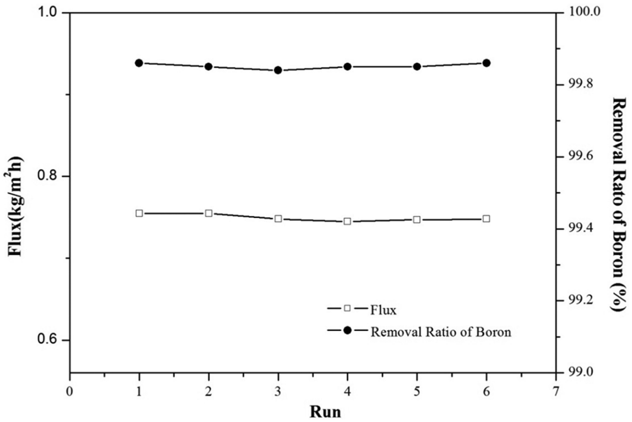


Fig. 12. 8GO-0.2PVP/PVDF membrane reusability in the pervaporation experiment.

gave excellent results for other ions from the industrial wastewater. The other ions were also separated successfully. The Mg, Si, Fe, Na ions in industrial wastewater were removed completely. The initial boron concentration is 2,900 ppm in industrial wastewater. When the PVP/PVDF blend membrane was used in the process, the boron and calcium concentration decreased from 2.900 to 6.95 and 317.95 to 0.96 ppm, respectively. The flux value was obtained as 0.617 kg/m^2·h with the same membrane. Compared to the PVP/PVDF blend membrane, GO loaded membrane had better separation performance. As the hydrophilicity of membrane increased, boron concentration in the permeate stream had been decreased. The boron concentration value had been obtained in 4.2 ppm by 8 wt% GO loaded PVP/PVDF membrane. The removal ratio of the boron was 99.86%. The calcium concentration in the permeate stream decreased from 317.95 to 0.81 ppm with the same membrane. The flux value was obtained as 0.755 kg/m^{2}h. While the GO loaded ratio changed from 4 to 6 wt%, the flux increased from 0.622 kg/m^{2}h to 0.729 kg/m^{2}h, boron concentration decreased from 2,900 to 6.76 and 2,900 to 5.6 ppm. The presence of boron on the permeate side is due to the concentration difference. As the concentration difference increases, the amount of boron passing to the permeate side increases. The same result was observed in reverse osmosis membrane, which is a dense membrane like pervaporation [10-13].

If the flux values of wastewater and synthetic water are compared, it has been observed that there is no significant difference between wastewater (0.755 kg/m^{2}h) and synthetic water (0.729 kg/m^{2}h) in terms of flux when utilizing 8 wt% GO loaded PVP/PVDF membrane. The membrane has close flux values for both of the water.

The obtained values compensate the criteria for Turkish environmental legislation which the amount of boron in the water to be discharged into the sea should not exceed 500 mg/L.

4. Reusability of Membrane

The effect of reusability on the separation performance of the membrane was investigated by utilizing 8 wt% GO loaded PVP/PVDF membrane. Industrial wastewater was used for reusability test. The flux and boron removal values obtained in the repeated experiments is given in Fig. 12.

The membrane was reused six times at the same experiment conditions. In each reusability experiment, the membrane was taken out from the membrane cell and washed with distilled water and

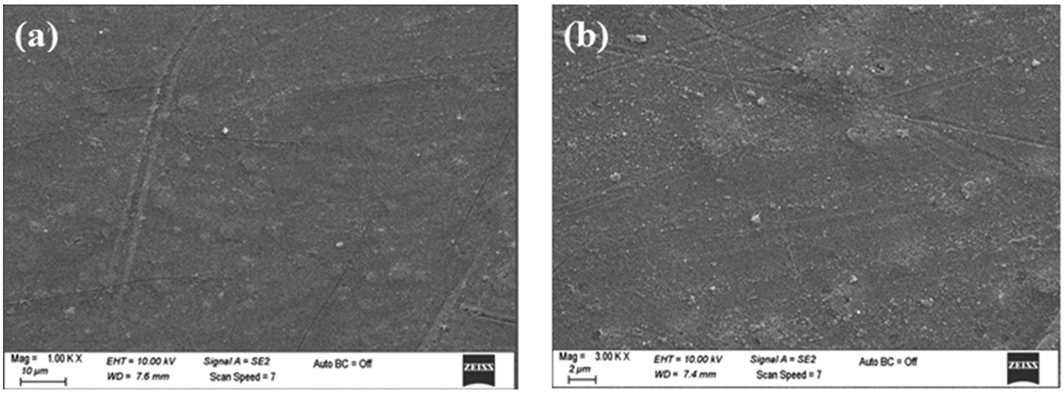


Fig. 13. SEM images of the used 8GO-0.2PVP/PVDF membrane (a) 1000x magnification (b) 3000x magnification.

put on drying and then reused. According to the results, similar flux and boron removal were observed from first to sixth usage. As seen in Fig. 12, whereas removal of boron and water flux was obtained as 99.89% and 0.775 kg/m^{2}h after the first use, 99.86% of removal of boron and 0.748 kg/m^{2}h was obtained after the sixth use. It can be seen in the figure that all values were close to each other. After six runs, 8GO-0.2PVP/PVDF membrane exhibits good chemical and mechanical stability.

The membrane was also tested with SEM analysis after being used six times. During reusability experiments, structural deformation was not observed. Fig. 13 indicates the surface images of the membrane after the sixth usage in pervaporation experiment. No surface degradation or membrane damage was detected for 8GO-0.2PVP/PVDF membrane. Additionally, no phase separation was observed in the membrane. This shows that prepared membrane is suitable for reusability and has strong mechanical and chemical resistance.

CONCLUSION

PVP/PVDF blend membrane and GO/PVP/PVDF hybrid membranes were developed for the removal of boron from industrial wastewater. The synthesized membranes displayed superior separation performance with the removal of boron >99.76% from industrial wastewater. The optimum PVP/PVDF ratio in the blend membrane was determined as 0.2 and the optimum GO amount in GO/PVP/PVDF hybrid membrane was specified as 8 wt%. Boron removal was obtained as 99.86% with a flux of 0.755 kg/m^{2}h when the 8 wt% GO loaded hybrid membrane was used. The membranes also gave excellent results for other ions from the industrial wastewater. The calcium concentration decreased from 317.95 to 0.96 ppm by 8 wt% GO loaded hybrid membrane. This study indicates that the PVP and GO addition improved the membrane features, and separation performance of the pervaporation process with improved hydrophilic membrane features can be preferred as an innovative water treatment method for the removal of boron from industrial wastewater. In this study, boron concentration was obtained as <7 ppm.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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