







Use of Ultrasound to Prepare Permeable Crosslinked PVA Membranes

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Highlights

- Ultrasonication as a green alternative technique to enhance membrane permeability.
- Combined effect of nanofillers and ultrasonication.
- Effect of ultrasonication and nanofillers on crosslinked-PVA membranes.

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Abstract

The major topic covered in this paper is the application of ultrasound to crosslinked- poly(vinyl alcohol) (c-PVA) membranes as a *novel, simple, eco-friendly, green-method* to enhance the reduced permeabilities of c-PVA membranes due to crosslinking. The effect of sonication on the swelling and diffusion behaviors of c-PVA membranes was compared with that of the additive added crosslinked composite membranes, for which n-SiO₂ and n-Ag were used as nanofillers. Aqueous solutions of rhodamine-b (RB) and Fe³⁺ were used to determine the permeation characteristics of the membranes. By the study, it was determined that although the presence of n-Ag and also n-SiO₂ increased the hydrophilicity and the permeation capability of the c-PVA membranes, ultrasonication (US) was found to be more effective, eco-friendly method to promote the permeation characteristics of the membranes.

1. INTRODUCTION

PVA is a non-toxic, chemically stable, biocompatible polyhydroxy polymer and it has good film forming ability and high hydrophilicity [1, 2]. Although PVA membranes have been commonly preferred for their high affinity toward water, especially in dehydration and separation processes [3-8], they have poor physical stability in water. So, the preparation of hydrophilic, highly permeable, water-insoluble PVA membranes is an important challenge. Crosslinking process is commonly used to improve their physical stability in aqueous systems [4, 9-12]. However, crosslinking process reduces the hydrophilicity of PVA membranes as well as their permeability. Although several alternative modifications have been used to address the reduced hydrophilicity and permeability of c-PVA membranes, e.g., grafting [2, 5, 13, 14], blending [5, 8, 14] and filling with fine inorganic particles [1, 15-21], the use of efficient, eco-friendly green methods for the preparation of c-PVA membranes to minimize or eliminate undesired chemicals [22-27] is important, since in the last decade, increasing environmental awareness needs to use eco-friendly methods.

Sonochemistry is used in membrane technology as a new branch of chemistry because of it is defined as a green and effective method [28-29]. The attractive application of ultrasonication (US) in membrane technology is seen in the determination of fouling layer (cake layer) thickness [30], pore shape and pore size [31] as well as porosity [32]. Its general use is found in filtration processes to clean or protect membrane surfaces from cake layer formations [33-39]. The application of US to solid phase membranes to enhance

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their permeabilities is one of the most interesting usages of sonication. However, there are only limited numbers of studies to enhance the permeabilities of the membranes by using US [17, 40-43]. Asman et al. [17] studied the effect of sonication on the release of theophylline by using cellulose acetate (CA) and n-SiO₂/CA membranes. They determined that ultrasonic-treatment enhances the permeability of theophylline through the membranes and increases their water-sorption abilities. Masselin et al. [40], studied the effect of sonication on polyethersulfone (PES), polyvinylidene fluoride (PVDF) and polyacrylonitrile (PAN) membranes; by their study it is deduced that, PES film is mainly affected by the ultrasonic treatment over all its surface. Wang et al. [41] tried to synthesize T-type zeolite membranes by using ultrasonic-assisted pretreatment preceding the hydrothermal synthesis; as a result of their study the synthesis time of the membranes becomes shorter and greater separation factor as well as the flux was obtained. Julian and Zentner [42] examined the effect of ultrasonic-assisted permeation of hydrocortisone and benzoic acid and have concluded that the permeability of the films can be increased by ultrasonic irradiation. Kost et al. [43] examined ultrasound-induced drug release behaviors of implant matrix systems. They have concluded that ultrasound leads to the degradation of the polymers and increases the release rate of incorporated molecule of the system.

The present work deals with the effect of US on the permeation characteristics of the crosslinked PVA membranes. For this aim, US was applied for the first time to c-PVA membranes as a green membrane treatment method to improve permeabilities of the membranes. Additionally, the combined effect of nanofillers and US on the characteristic properties of c-PVA membranes was also investigated. Swelling studies and water-contact angle (CA) measurements were used to determine hydrophilicity and water sorption tendency of the membranes. Characterizations of the membranes was done by SEM, XPS (ESCA) and DSC analysis. Permeation studies were performed by simple diffusion method Rhodamine-b (RB) and Fe³⁺ were preferred as model compounds in the study.

2. EXPERIMENTAL

2.1. Materials

PVA (M_n , 72 000 g/mol), RB, analytical grades of Na₂SO₄, KOH and FeCl₃.6H₂O were purchased from Merck Chemicals Ltd., UK. Nanopowders of silica (10 nm) and silver (< 90 nm) were obtained from Aldrich.

2.2. Membrane Preparation

Membranes were prepared by casting method [44-46]. A predetermined amount of an aqueous solution of PVA (5 % (m/v)) was placed onto petri dishes and it was dried in an incubator at 40°C till to complete dryness was obtained. The dried membranes were immersed in aqueous KOH solution (75 g/L), which was saturated with Na₂SO₄ for crosslinking process [47] to prepare the c-PVA membranes.

Crosslinked composite PVA membranes (SiO₂/c-PVA and Ag/c-PVA) were prepared by using the technique used for the preparation of c-PVA membranes. In this case, n-SiO₂ and n-Ag was added to the aqueous PVA solution (5% (m/v)) at a percent composition of 10% ($m_{\text{filler}}/m_{\text{PVA}}$) respectively and homogeneous nanofiller/PVA solution was used as casting solution.

In order to prepare US-treated c-PVA, SiO₂/c-PVA and Ag/c-PVA membranes (called as US-c-PVA, US-SiO₂/c-PVA and US-Ag/c-PVA membranes, respectively) corresponding crosslinked membrane was subjected to ultrasonic waves in a sonicator (X-traH Elma, Germany), at a frequency of 35 kHz and an input power of 160 W. Sonication process was carried out in a thermostated water bath, for a constant period of 60 min. Membrane thicknesses (l) were determined using a micrometer (Aldrich, Germany) and at least ten point measurements was used to determine the average membrane thicknesses. The abbreviations of the different membranes are listed in Table 1.

Table 1. Definition of the membranes

Membrane	Definition
c-PVA	Crosslinked PVA membrane
US-c-PVA	US-treated c-PVA membrane
SiO ₂ /c-PVA	Crosslinked n-SiO ₂ /PVA composite membrane
US-SiO ₂ /c-PVA	US-treated SiO ₂ /c-PVA membrane
Ag/c-PVA	Crosslinked n-Ag/PVA composite membrane
US-Ag/c-PVA	US-treated Ag/c-PVA membrane

2.3. Membrane Characterization

The membrane hydrophilicities and water sorption tendencies were determined by swelling studies and water contact angle measurements. The swelling ratio (S_w) values of the membranes were calculated by Equation (1) [48], where, W_w and W_d are the wet and dry weights of the membranes respectively.

$$S_w = (W_w - W_d) / W_d \quad (1)$$

Contact angle micrometer (Surface Electro Optics PHX 150) was used to investigate the interaction of the membrane surface with water. The reflected CA values were the averages of the measured angles at both side of the drop.

Morphological and thermal analysis of the membrane samples were analyzed using SEM, X-ray photoelectron spectroscopy (XPS, ESCA) and DSC techniques. For the SEM images of the membranes, the samples were dried and sputtered with Au/Pd in vacuum, before viewing by SEM (Quanta-400 FE-SEM Analyzer (FES Company)). ESCA (XPS) analysis was done by using PHI-5000-VersaProbe ESCA (XPS).

DSC analysis was performed using Perkin Elmer system to determine the thermal behavior of the membranes. Typical sample weight was ~ 5 mg and the samples were analyzed at a heating rate of 5 °C/min under N₂ atmosphere.

2.4. Permeation Studies

Permeation studies for aqueous solutions of RB (50 ppm) and Fe³⁺ (0.01M) were performed against distilled water at constant temperature, using a two-compartment horizontal diffusion cell. Sampling of the acceptor solution was done at definite time intervals and the aliquots were replaced by an equal amount of distilled water. Analysis of the RB and Fe³⁺ samples was done spectrophotometrically at 553 nm and 238 nm, respectively.

3. RESULTS AND DISCUSSION

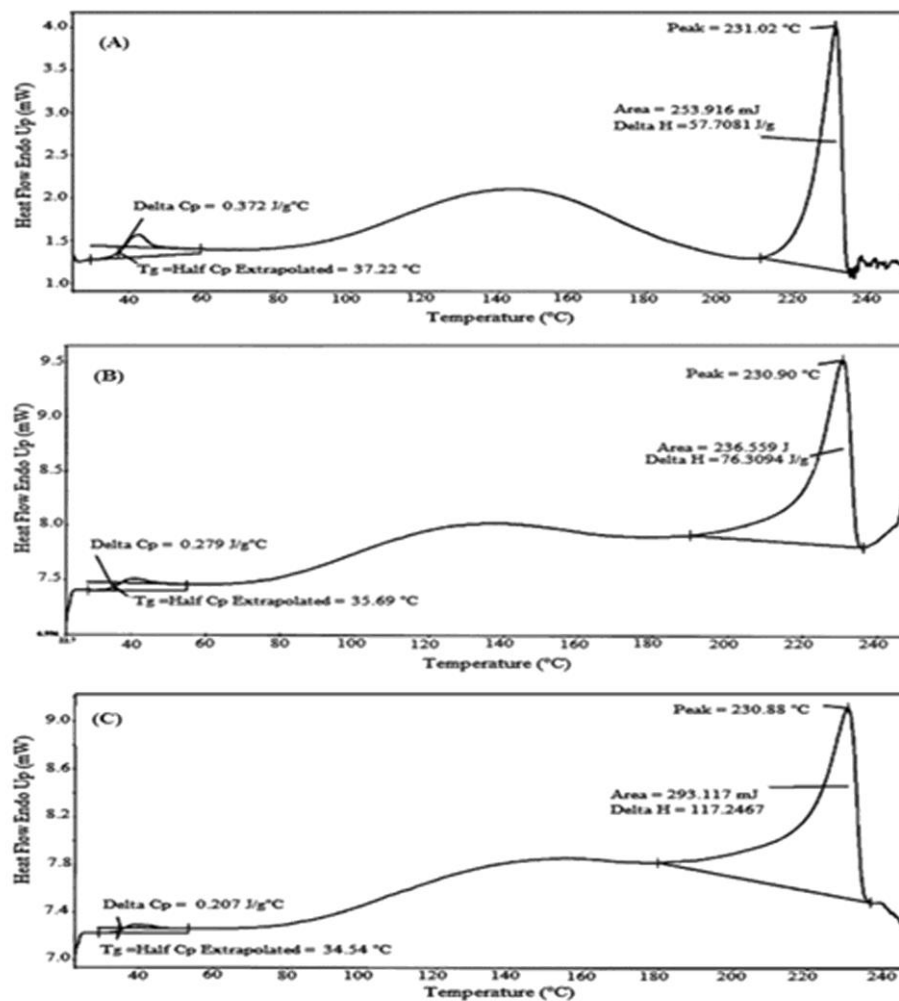
3.1. Effect of the Presence of n-SiO₂ and n-Ag on the Hydrophilicity of the c-PVA Membranes

c-PVA, Ag/c-PVA and SiO₂/c-PVA membranes were casted at a controlled thickness of 50±5 μm, 70±5 μm and 130±5 to investigate the effect of the presence of n-SiO₂ and n-Ag on the hydrophilic character of the crosslinked PVA membranes. For this aim, the swelling ratio values (S_w) of the membranes were computed by using Equation (1) and the results are shown in Table 2.

Table 2. Swelling behaviours of the membranes

l (μm)	S_w (m/m)		
	50 \pm 5	70 \pm 5	130 \pm 5
c-PVA	1.53	1.42	1.36
Ag/c-PVA	1.64	1.65	1.49
SiO ₂ /c-PVA	1.90	1.84	1.74
US-Ag/c-PVA	2.15	2.08	1.86
US-SiO ₂ /c-PVA	2.35	2.28	2.16

Table 2 shows that, Ag/c-PVA and SiO₂/c-PVA membranes have greater swelling values than c-PVA for each thickness. Increase in swelling by the presence of fillers suggests that both n-Ag and especially n-SiO₂ increases the water sorption tendency, i.e., hydrophilicity of the c-PVA membranes. Increase in the membrane hydrophilicity in the presence of SiO₂ most probably resulted from the high polar character of the Si-O bond of SiO₂, which attracts water molecules and makes membrane material more hydrophilic [49].

**Figure 1.** DSC thermogram of (A) c-PVA, (B) Ag/c-PVA and (C) SiO₂/c-PVA membranes

The enhancement in the hydrophilicity of the membranes is resulted from the interaction of Ag with water molecules via Ag-O interactions [50]. Bi et al. [51] investigated that SiO₂ containing nafion membranes showed good water uptake and retention characteristics. Meng and Sun [52] reported that the presence of

Ag in TiO₂ films decreases the water contact angle values of the films, indicating increase in the hydrophilic character of the films. Watanabe et al. [53] used nafion/SiO₂ doped membranes in their study. They have reported that nafion/SiO₂ membranes have greater hydrophilicity than hygroscopic oxides/nafion, such as TiO₂.

To determine the effect of n-SiO₂ and n-Ag on the thermal behaviors of the c-PVA membrane, DSC thermograms of c-PVA, Ag/c-PVA and SiO₂/c-PVA membranes were shown in Figure 1. From the thermograms, the observed glass transition temperature (T_g) of c-PVA, Ag/c-PVA and SiO₂/c-PVA membranes are seen as 37.22°C, 35.69°C and 34.54°C respectively. As it is seen that higher T_g value was obtained for c-PVA than that of both Ag/c-PVA and SiO₂/c-PVA membranes. Since polymers with lower T_g possess higher segmental mobility, decrease in T_g suggests an increase in the chain movement and free volume by the possible decrease in the intermolecular interactions. This brings greater availability to the water molecules for the permeation from the membrane material with a lower T_g . This results in a higher interaction with water molecules and greater S_w values for Ag/c-PVA and SiO₂/c-PVA than c-PVA membranes, which supports the S_w values given by Table 2.

3.2. Effect of Sonication on the Characteristics of Ag/c-PVA and SiO₂/c-PVA Membranes

In this part of the study Ag/c-PVA and SiO₂/c-PVA membranes at different thicknesses were supplied to US, as explained in part 2.2, to determine the effect of sonic treatment on the swelling behaviors of crosslinked-composite membranes. Sonication process was performed at room temperature. Table 2 also reflects the swelling behaviors of the US-treated composite membranes. From the results, it can be stated that the sonic-treated composite membranes have considerably greater S_w values than the untreated, i.e., Ag/c-PVA and SiO₂/c-PVA membranes. Such an additional increase in the swelling of the membranes indicates that the sonic treated membranes have more available free-volumes for the diffusion of water molecules than the untreated membranes.

In Figure 2, ESCA analyses of Ag/c-PVA and US-Ag/c-PVA membranes were reflected. From the figures, it is seen that there appears a distinct decrease in carbon peak intensity for US-Ag/c-PVA membranes. Similar decrease is also seen in Figure 3, which represents the ESCA analysis of SiO₂/c-PVA and US-SiO₂/c-PVA membranes, respectively. These results indicate that some of the the loosely held PVA chains which may not chemically bound in polymeric membrane material are likely to be removed by sonication. This could be due to two reasons: (a) PVA chains that are not involved in the crosslinking reactions may be removed from the polymer network by the effect of sonication, or (b) ultrasound may lead to depolymerization of some of the PVA chains with the cleavage of the weakest bonds [5, 17]. Grönroos et al. [28] applied ultrasound to PVA solutions and they have reported that an ultrasonic frequency of 23 kHz leads to the extensive depolymerization of PVA chains by the cleavage of the weakest bonds. Price et al. [54] applied a high intensity US to the suspensions of polyethylene, polypropylene, poly (vinyl chloride) and poly (methyl methacrylate); they have concluded that US results in a change in particle sizes and surface morphology of the materials and also removes some of the material from polyethylene film.

Figure 4 represents the SEM micrographs of US-treated and untreated crosslinked composite membranes. As clear from the micrographs, sonic treatment also affects the surface morphologies of the membranes and causes an increase in surface area of the membranes [55-57], which results in greater interactions of membrane material with the feed.

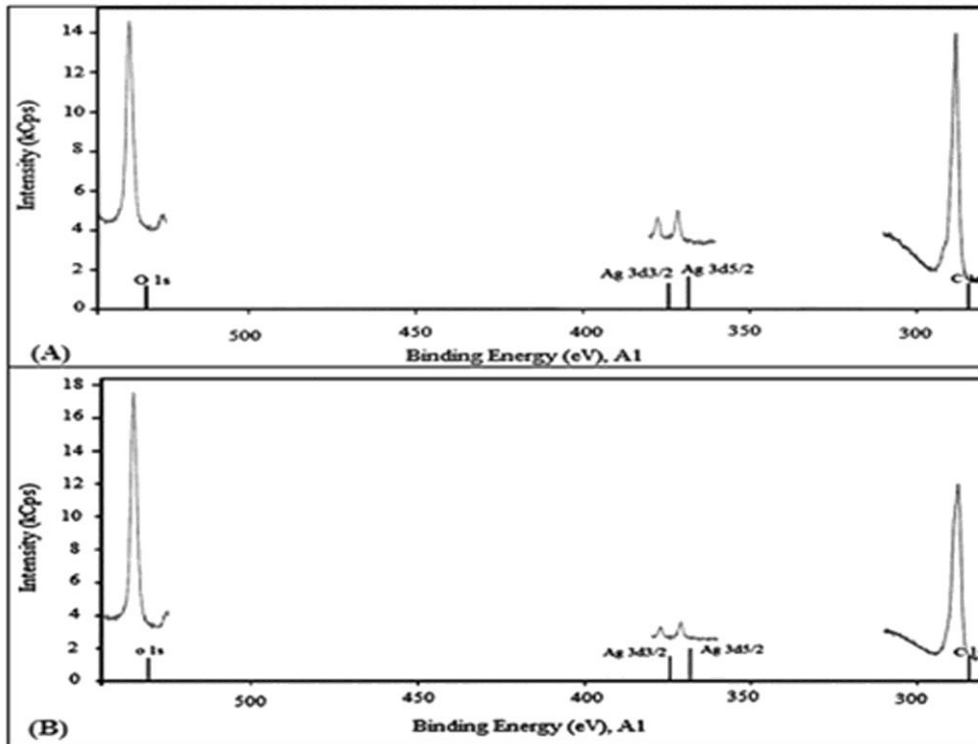


Figure 2. ESCA analysis of (A) Ag/c-PVA and (B) US-Ag/c-PVA membranes

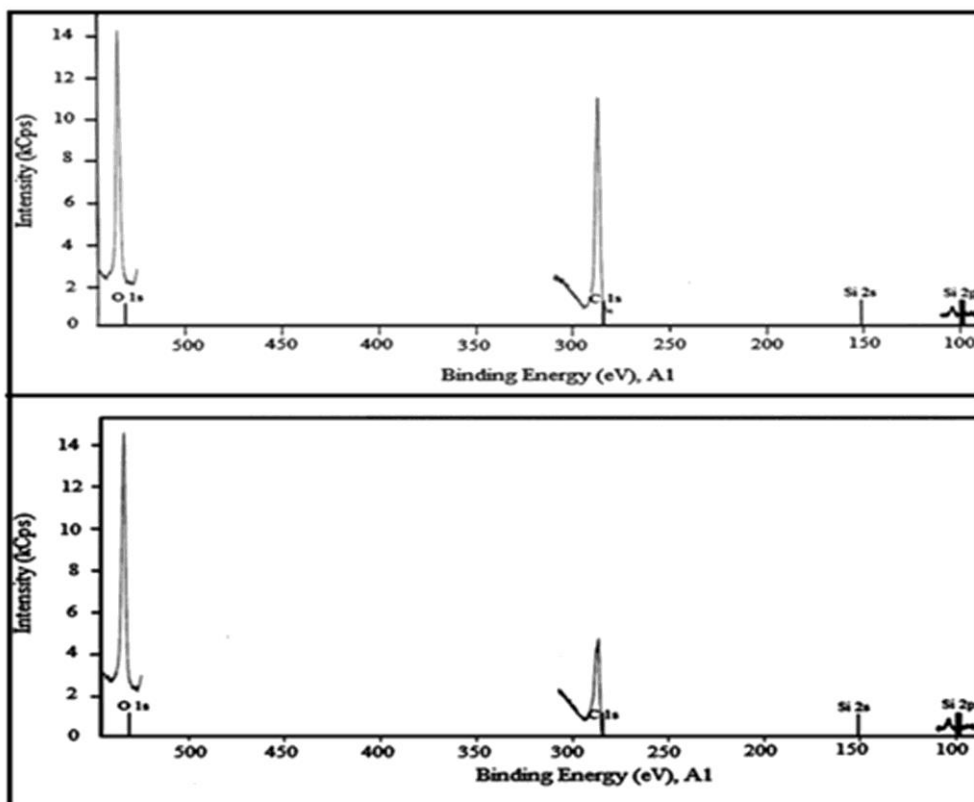


Figure 3. ESCA analysis of (A) SiO₂/c-PVA and (B) US-SiO₂/c-PVA membranes

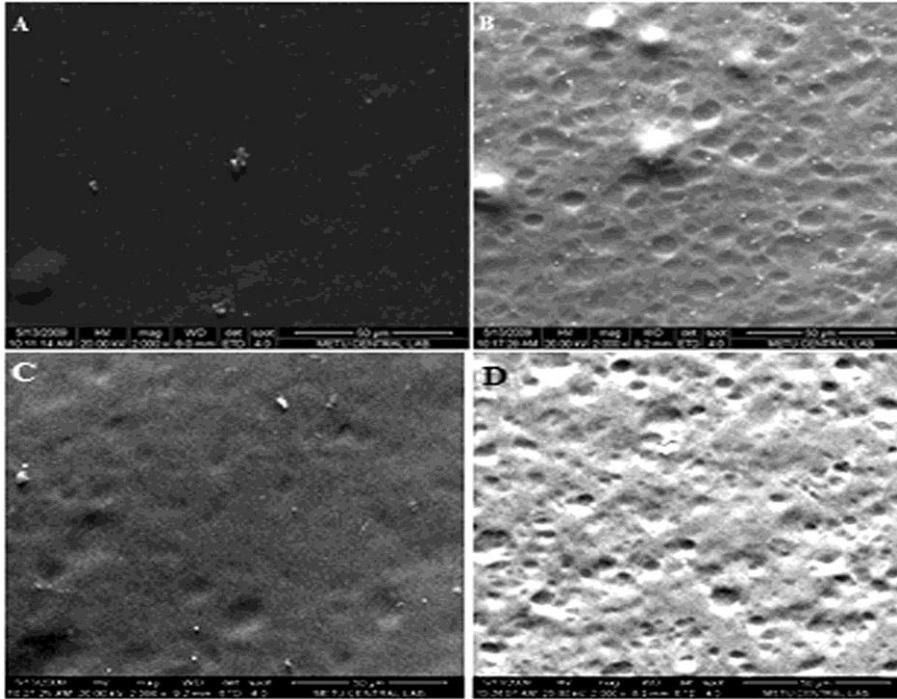


Figure 4. SEM image of (A) Ag/c-PVA (B) US-Ag/c-PVA (C) SiO₂/c-PVA (D) US-SiO₂/c-PVA membranes (x2000)

3.3. Permeation Capabilities of US-Treated and Untreated Membranes

To compare the permeation capabilities of the sonic treated and untreated membranes, they were placed in a horizontal diffusion cell and permeation studies were carried out by using aqueous solutions of RB (50 ppm) and Fe³⁺ (0.01M), as explained in part 2.4. The results were reflected in Figure 5 as permeant percentages of RB and Fe³⁺, by mass.

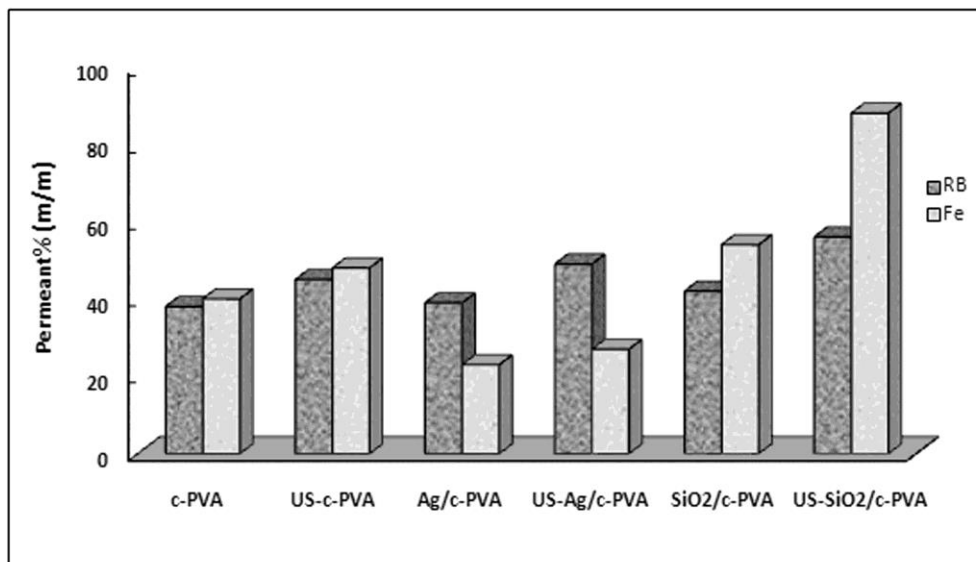


Figure 5. Comparison of the permeation performances of the US-treated and untreated membranes ($l = 50 \pm 5 \mu\text{m}$)

Figure 5 shows that, permeant percentages of RB and also Fe^{3+} is greater for both US-c-PVA and US-SiO₂/c-PVA membranes and an additional increase in permeation of RB and Fe^{3+} was obtained in the presence of silicone dioxide. Such a greater permeation is most probably resulted from the hygroscopic property of SiO₂.

Merkel et al. [58] have reported an increase in permeability and selectivity by adding nanostructured fumed silica, since silica particles contain polar -OH groups. They have also shown that physical dispersion of nonporous fumed silica particles in glassy amorphous poly (4-methyl-2-pentyne) surprisingly enhances both membrane permeability and selectivity for large organic molecules over small permanent gases. Rodgers et al. [21] prepared silicon dioxide containing nafion membranes to improve their transport properties by using well known hygroscopic properties of silicone dioxide particles.

Figure 5 also shows that, Ag/c-PVA and US-Ag/c-PVA membranes have almost the same permeation for RB and lower permeations for Fe^{3+} with respect to both c-PVA and US-c-PVA membranes. In order to clarify the unexpected behavior of Ag-including PVA membranes, interaction of water with the outer layer of the membrane surface was analyzed by contact angle measurements and the results were reflected in Table 3. As it is seen from the table, sonic treated membranes are all have lower contact angles than that of the untreated c-PVA membrane. This confirms the greater sorption tendency and also the greater permeation availability of the US-c-PVA, US-Ag/c-PVA and US-SiO₂/c-PVA than the parent c-PVA membranes since low water contact angle values represent high interactions between the membrane surface and water [59].

Table 3. Water-contact angle values of the membranes

Membrane	Contact angle (°)
c-PVA	46±2
US-c-PVA	38±1
US-Ag/c-PVA	35±3
US-SiO ₂ /c-PVA	28±3

In addition to the water-contact angle values of the membranes, free volume fractions (ϵ) of the membranes which serve as diffusion available fraction of the membranes were also computed by using Equation (2) [60], where W_1 and W_2 are the weight of the wet and dry membranes; D_w and D_p are the density of water and polymer respectively. $(W_1 - W_2)/D_w$ corresponds to the volume occupied by water molecules and W_2/D_p is simply the volume of the polymer chains present in the membrane specimen.

$$\epsilon = \frac{\frac{W_1 - W_2}{D_w}}{\frac{W_1 - W_2}{D_w} + \frac{W_2}{D_p}} \quad (2)$$

Table 4. Free volume fractions (ϵ) of the sonic treated and untreated membranes ($l = 50 \pm 5 \mu\text{m}$)

Untreated Membranes	$\epsilon \times 100$	US-treated membranes	$\epsilon \times 100$
c-PVA	46	US-c-PVA	63
Ag/c-PVA	50	US-Ag/c-PVA	65
SiO ₂ /c-PVA	68	US-SiO ₂ /c-PVA	73

The calculated free volume fractions of the sonic-treated and untreated membranes were reflected in Table 4. As it is evident from Table 4, the free volume fractions of US-c-PVA, US-Ag/c-PVA and US-SiO₂/c-PVA membranes are all greater than the untreated c-PVA, Ag/c-PVA and SiO₂/c-PVA membranes, respectively. So it can be stated that sonic treatment increases the permeation available free volumes of the membranes. Therefore, the lower permeation for the Ag/c-PVA composite membranes, particularly for the permeation of Fe³⁺, can only be explained by the possible electrostatic repulsive effect of Ag [7, 61].

4. CONCLUSIONS

Although the water sorption capacity of the c-PVA membranes can be enhanced by using n-Ag and especially n-SiO₂, this works has clearly shown that ultrasonic treatment is a more efficient method than the use of nanofillers to increase both the permeation capability and sorption tendency of the c-PVA membranes. It can be concluded that *ultrasonication is an efficient, environment-friendly, economical, solvent free green membrane modification method* to enhance the permeability of water insoluble, crosslinked PVA membranes.

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CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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