



Preparation and Characterization of Polyvinyl Chloride/Polymethyl- Methacrylate/Graphite [PVC/PMMA/G] Membrane Used for the Purification of the Bioethanol Produced from the Hydrolysis and Fermentation of Rice waste



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Abstract

Rice waste as a starchy food waste that is discharged daily into the environment in huge amounts has been used as a valuable source for the production of bioethanol. The tested parameters investigated that phosphoric acid as a chemical representative combined with autoclaving as a physical representative are the most potent conditions for the liberation of glucose units from the starch molecules among other tested conditions. The optimization process revealed that the maximum production of simple sugars of 12.39 mg/ml from rice waste can be obtained through the pre-treatment of 5% rice waste with 20% H₃PO₄ and autoclaving followed by the amylase hydrolysis. These liberated glucose units have been successfully fermented into 5.2 mg/ml bioethanol using a yeast strain (*Pichia nakasei* with the accession number OK092294). The separation of the produced bioethanol from other media components was performed via amicon cell ultrafiltration system integrated with polymeric membrane. The membrane was prepared from Polyvinyl chloride/Polymethylmethacrylate/ Graphite [PVC/PMMA/G] with different thicknesses 400, 500 and 600 μm. For membrane characterization, Fourier transform infrared (FT-IR), scanning electron microscope (SEM), tensile strength, water contact angle, and water and ethanol uptakes have been used. Among the tested membranes thicknesses, the obtained results showed that the best membrane thickness is 500 μm which recorded 939.526 (mg/m².h) and 10.557 for flux of permeate and separation factor, respectively.

Keywords: Bioethanol, rice waste, amicon cell, PVC/PMMA/G membrane

1. Introduction

Alternative energy is an aspect that has been recently originating due to the upcoming depletion of

the petroleum products in addition to their increasing value. Bioethanol is one of the alternative energies that can be produced from renewable biomass and

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has recently received a considerable attention. It can be used as an alternative fuel or as a chemical feedstock [1]. The incorporation of bioethanol into fuel is expected to reduce both of the global warming and the environmental pollution [2]. Food wastes are environmental wastes that thrown daily in huge amounts all over the world. These wastes contain high concentrations of carbohydrates that can be easily hydrolyzed into simple sugars using specific enzymes [3]. These free sugars can be effectively fermented into bioethanol using microbes that can be used as an alternative energy after proper purification [4, 5]. Because a larger concentration of ethanol would suppress microorganisms for bioethanol fermentation, resulting in the fermentation process stopping, fermentation broths normally contain less than 10% ethanol by weight [6]. Distillation necessitates a lot of energy, which means significant startup costs [7], pervaporation, is a new membrane separation method and become the best technique in purification and separation of biofuels due to it have several benefits such as cost-effective, energy free and extremely efficient [8]. There are a wide range of membranes that used for pervaporation separation such as polyvinylidene fluoride (PVDF) as a porous membrane [9], Cellulose acetate (CA), in addition to ethanol permeability-selectivity pervaporation membranes classified into three categories polymeric, inorganic and mixed matrix membranes [6]. Polymeric membrane like hydrophobic membranes have been identified as the most adaptable and promising membrane materials in PV applications for ethanol separation from water, Polydimethylsiloxane (PDMS) [10, 11], Polymethylmethacrylate (PMMA) [12] and Polyvinyl butyral (PVB) [13]. Acrylonitrile (AN), Methyl acrylate (MA), and Methyl methacrylate (MMA) are examples of prepared membranes with hydrophobic properties such as Poly (Acrylonitrile-co-Methyl acrylate) [8] and ethylenediamine modifying Poly (Acrylonitrile-co-

Methyl acrylate) [14]. Inorganic membranes, such as those made of ceramics or zeolites, are frequently utilized for dehydrating organic molecules using PV nowadays [15]. Hybrid membranes are also known as mixed matrix membranes (MMMs). In most cases, MMMs are made by dispersing inorganic particles (also known as fillers) into continuous polymer matrices [16, 17]. To improve the PV performance of polymers for ethanol separation, a variety of nanofillers have been used in combination with them such as zeolitic imidazolate frameworks (ZIFs) [18], carbon nanotubes [19], carbon blacks [20], graphene-like fillers (graphene and graphene oxide derivatives) [21] and polyhedral oligomeric silsesquioxanes (POSSs) [11, 22]. Polyvinyl chloride (PVC) membranes were applied for different applications such as separation of organic mixture [23], water treatment [24], fuel cell [25] and biomedical applications [26]. The aim of this research was to valorize the using of the rice waste that is daily thrown in the environment in huge amounts through its exploitation in the formation of bioethanol as an alternative source of energy. The parameters used for the releasing of the highest amount of glucose from the rice waste that could be fermented into bioethanol by a yeast strain have been addressed. The work was also extended to the purification of the produced bioethanol from the fermentation broth through the preparation and characterization of Polyvinyl chloride/ Polymethyl methacrylate/Graphite [PVC/PMMA/G] polymeric membrane.

2. Experimental and materials.

2.1. Materials

Polyvinyl chloride (PVC) and Polymethylmethacrylate (PMMA) were obtained from Sigma-Aldrich, Germany. N, N-dimethylformamide (DMF) and graphite were gained from Fisher Scientific UK. The purity of all used chemicals is 99%.

2.1.1. Sample collection

The cooked rice samples were collected from different households and restaurants in New Borg Elarab city as a starchy waste that can be used as a raw material for the liberation of glucose units that would be fermented into bioethanol using yeast isolates.

2.4.2. Yeast strains and enzymes

Pichia nakasei with the accession number OK092294 that has been previously isolated and genetically identified by our group has been used for the fermentation of glucose units into bioethanol through the current work. The liquid form of the amylase enzyme with the concentration of 700 U/g was purchased from Sigma Aldrich (Germany).

2.1.3. Chemical and physical pre-hydrolysis of rice waste

Specific amounts of the collected rice waste were submitted for different combined chemical and physical treatments in order to obtain the optimum conditions that would result in the production of highest glucose units. The tested chemical methods include the pre-hydrolysis of the 5% rice waste in 50 ml of either distilled water or acids (20% HCl, 20% H₂SO₄, 20% H₃PO₄, and 100% CH₃COOH), or bases (5M NaOH or 5M KOH). Each one of the tubes treated with one of these chemical treatments has been separately submitted for one of the physical treatments according to the following conditions:

- Autoclaving at 121°C and 15 psi for 20 min.
- Microwaving at 750 W and 120°C for 5 min.
- Sonication at 20 kHz and 75°C for 20 min.
- Hot plating at 100°C for 20 min.

After each separated physical treatment, the total amount of the liberated glucose units in each treatment has been investigated using glucose spectrophotometric determination method.

2.1.4. Enzymatic hydrolysis

Amylase enzyme has been tested for its ability to liberate glucose units from the starch polymeric molecule under specified conditions. A total volume of 50 ml acetate buffer (pH 5.5) was amended with 2.5 g of the rice waste to have a final waste concentration of 5%. A 252 U of the amylase enzyme (700 U/g) was subsequently inoculated. The tubes were then incubated at 30°C and 150 rpm for 72 h. The glucose concentration was interval measured every 24 h.

2.1.5. Optimization of H₃PO₄ concentration

To investigate the optimum acid concentration, different concentrations of 5-40% H₃PO₄ have been individually used for the pre-hydrolysis of 5% rice waste in a 50 ml total volume. All the prepared containers were submitted for autoclaving at 121°C and 15 psi for 20 min. After autoclaving, the released glucose units were determined using glucose determination kit and the optimum acid concentration for the hydrolysis of rice waste was investigated.

2.1.6. Optimization of substrate concentration

The optimum amount of the rice waste that would result in the production of the highest sugar concentration was investigated. Multiple amounts of the waste (4-11%) were amended into 50 mL of 20% H₃PO₄ followed by autoclaving at 121°C and 15 psi for 20 min. The amount of released glucose units after the aforementioned treatments were spectrophotometrically analyzed and calculated.

2.1.7. Combined physical/chemical and enzymatic hydrolysis

To investigate if the combination among different pre-hydrolysis methods is able to increase the amount of the glucose units released from the breakdown of the rice waste; physical, chemical, and enzymatic treatments were gathered and followed. A total volume of 50 ml H₃PO₄ (20%) were amended with

5% rice waste and were autoclaved at 121°C and 15 psi for 20 min with subsequent adjustment of the final pH to 5.5 using 3N NaOH. The whole amount was dispensed into multiple tubes with 5 ml volume for each. Each tube was received another 5 ml acetate buffer (pH 5.5) followed by the addition of different amounts of the amylase enzyme (8.4-336 U). All the tubes were incubated at 50°C and 150 rpm for 72 h. The liberated glucose amounts were determined and the optimum enzymatic concentration was investigated.

2.1.8. Fermentation

A total volume of 250 µl of YPG overnight pre-culture of the yeast *Pichia nakasei* were inoculated into 50 ml hydrolyzed rice waste (pH 5.5) with a final glucose concentration 12.39 mg/ml. The flask was tightly covered with parafilm and was incubated at 30°C and 150 rpm for 72 h. After incubation, the produced bioethanol was determined using spectrophotometric method.

2.1.9. Spectrophotometric determination of glucose

The glucose units that have been liberated after each experiment were estimated using the glucose determination kit (Biosystem, Spain) according to the manual instructions [14].

2.1.10. Determination of bioethanol concentration

The concentration of the produced bioethanol after the fermentation of the glucose liberated from rice waste hydrolysis using *Pichia nakasei* strain was determined using spectrophotometric method according to [27] according to a previously prepared ethanol standard curve (1-100 mg/ml).

2.1.11. Membrane preparation

Two solutions from PVC and PMMA were prepared as follow, solution A of PVC (8%) and 10% PMMA (solution B). The certain amount 8:2 V/V solution A:

B and 0.1 g of graphite were sonicated for 1h at 60 °C in the presence of DMF solvent. After the solution had become homogenous then was casting using doctor blade with different thickness 400, 500 and 600 µm. The prepared membranes were dried for 48 hours in a hot air oven set to 60 °C under vacuum as shown in scheme 1.



Scheme 1: Preparation of PVC/PMMA/G membrane

2.2. Characterization

The chemical bonding and possible interactions within the produced polymeric membranes were investigated using Fourier transform infrared (FT-IR) spectra (Shimadzu FTIR-8400 S, Japan). SEM was used to analyze the membrane morphologies in cross section and on the top surface (JEOL JSM-6360LA, Japan), using the Universal Testing Machine, the tensile strength of polymer-based membranes was determined at room temperature (Shimadzu UTM, Japan). A goniometer was used to calculate the membrane's contact angle (VCA 2500 XE e). By injecting 5 µl of water in drops on five different locations of the membrane surface, the wettability (hydrophilicity) was determined. For the calculation of membrane hydrophilicity, the collected values were averaged and taken into account.

2.2.1. Purification process

The experiments were performed using an amicon stirred ultrafiltration cell (USA) with a [PVC/PMMA/G] membrane via different thicknesses of 400, 500, and 600 μm , which was subjected to several nitrogen pressures (20–70) psi for numerous time intervals, where the volume, concentration, flux of permeate and separation factor were determined for each pressure [14]. The separation factor was determined by the following equation:

$$\text{Separation factor } (\beta_i) = \frac{Y_i/(1 - Y_i)}{X_i/(1 - X_i)}$$

Where Y_i and X_i are the mass fractions of component i in permeate and feed side, respectively.

3. Results and discussion

3.1. Combined chemical/physical pre-hydrolysis of rice waste

The combination of chemical and physical conditions in order to increase the amount of the produced glucose units using rice waste has been tested. As shown in figure 1 and table 1, the amounts of the produced glucose units were largely depending on the type of the used chemical solvent and which physical technique has been followed. It has been detected that using of distilled water followed by hot plating resulted in the liberation of 2 mg/ml as the highest measured glucose concentration among the other tested physical techniques. However, the treatment of the rice waste with 20% HCl followed by sonication showed the highest liberated amount of glucose (4.9 mg/ml) compared with 4.2 mg/ml for both autoclaving and hot plating and 3.7 mg/ml for microwaving.

Similarly, testing of using chemical treatment of 20% H_2SO_4 followed by hot plating was the best combination compared with using other physical techniques. It showed the liberation of 2.6 mg/ml of glucose compared with 0.89, 0.35, and 0.32 mg/ml using microwaving, sonication, and autoclaving, respectively. Rice waste was also treated with 100%

CH_3COOH followed by the four physical techniques.

The obtained data showed that, using of microwaving was the optimum physical one that resulted in the measurement of 1.5 mg/ml of glucose as the highest measured glucose amount using the same acid followed by autoclaving, sonication, or hot plating.

On the other hand, using of alkaline treatments were not favored as a chemical treatment of rice waste. However, using of both NaOH and KOH followed by hot plating showed the highest liberation of glucose units of 0.3 and 0.77 mg/ml, respectively, compared with autoclaving, microwaving, and sonication. It worth mentioning that the highest ever measured glucose concentration was recorded as 5.3 mg/ml when the rice waste was treated with 20% H_3PO_4 followed by autoclaving. Our data are in agreement with [28] and [29] who mentioned that the diluted acids are preferred for the liberation of glucose units from wastes. However, the applied autoclaving technique would improve the pre-hydrolysis process as it can apply the combination of pressure and high temperature and hence is considered a potent physical treatment method [30].

Table 1

The concentration of the glucose units liberated after the pre-hydrolysis of rice waste using different chemical and physical treatments

Chemical/Physical treatments	Autoclaving	Microwaving	Sonication	Hot plating
	Glucose concentration (mg/ml)			
d. H_2O	1.6	0.66	1.2	2
20% HCl	4.2	3.77	4.9	4.2
20% H_2SO_4	0.32	0.89	0.35	2.6
20% H_3PO_4	5.3	2.5	2.9	4.8
100% CH_3COOH	0.44	1.5	0.56	0.9
5M NaOH	0.27	0.14	0.22	0.3
5M KOH	0.56	0.49	0.53	0.77

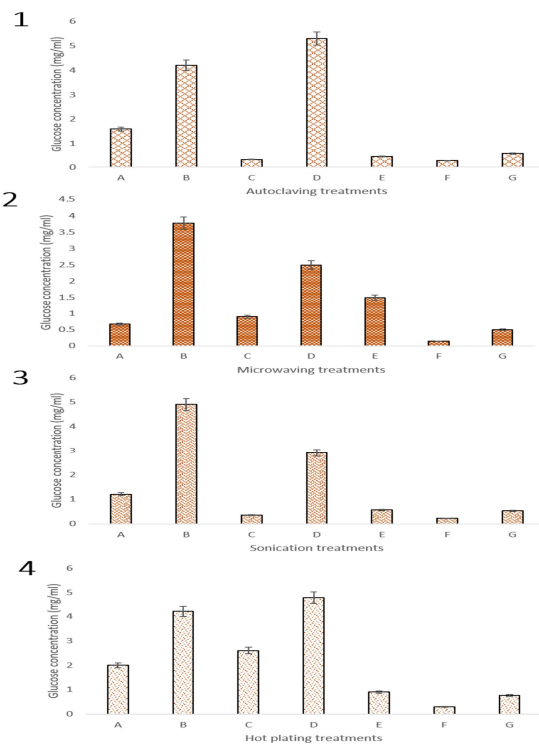


Figure 1: Effect of combined chemical and physical pre-hydrolysis of rice waste on the amount of the liberated glucose units. (1): Autoclaving treatments, (2): Microwaving treatments, (3): Sonication treatments, and (4): Hot plating treatments. While the letters of the x axis refer to: (A): distilled water treatment, (B): 20% HCl treatment, (C): 20% H₂SO₄ treatment, (D): 20% H₃PO₄ treatment, (E): 100% CH₃COOH treatment, (F): 5M NaOH treatment, and (G): 5M KOH treatment

Enzymatic hydrolysis

The application of amylase enzyme for the hydrolysis of rice starchy waste into simple fermentable sugars has been investigated. As shown in figure 2, there was a gradual increase in the measured glucose units with time increasing. The highest glucose concentration was detected after 72 h of incubation as 1.68 mg/ml compared with 1.46 and 1.56 mg/ml after 24 and 48 h, respectively. These data indicate that the sole application of amylase enzyme for the hydrolysis of rice waste into simple fermentable sugars is not the optimum condition. As mentioned formerly, the application of 20% phosphoric acid followed by autoclaving resulted in the production of 5.3 mg/ml glucose, which is approximately two-fold glucose measurement than the sole application of enzymatic hydrolysis. Accordingly, it could be better to combine both chemical/physical and enzymatic treatments in order to increase the overall final glucose concentration. Using of amylase enzyme for the hydrolysis of the starch of cereals and food waste for the production of bioethanol has been reported [31].

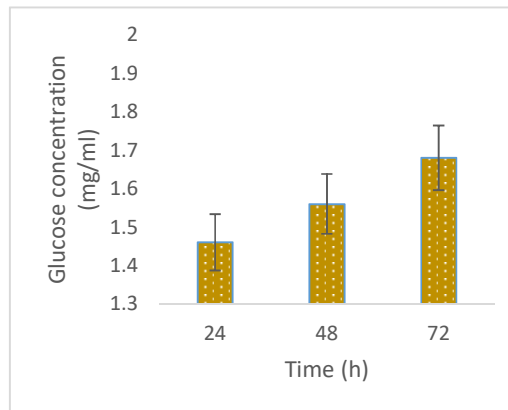


Figure 2: The concentrations of glucose units liberated after three successive days of the hydrolysis of rice waste using amylase enzyme

3.2. Optimization of acid concentration

Testing of different H₃PO₄ concentrations followed by autoclaving has been performed in order to investigate the optimum acid concentration for the pre-treatment of rice waste. As shown in figure 3, the amount of liberated glucose units has been proportionally increased with increasing the acid concentration to a certain limit where it started to drop. At the concentrations 5, 10, and 15%, the measured glucose concentrations were 2.5, 3.7, and 4 mg/ml, respectively. These concentrations have been elevated to 5.3 mg/ml when 20% of the acid followed by autoclaving were applied to the waste. This concentration (20%) resulted in the highest measured glucose value among all tested acid concentrations and hence was considered as the optimum one. From 25 to 40% H₃PO₄, the measured glucose concentrations were gradually decreased starting from 5.02 mg/ml of glucose using 20% acid till 4.4 mg/ml of glucose when 40% acid was applied. These results investigate that acids can be effectively used for the pre-hydrolysis of starchy wastes as has been reported for their effective hydrolysis of cellulosic wastes [29]. However, using of acids followed by autoclaving is preferred since it can apply both of pressure and high temperature [30]. Our results are

in agreement with [32] who reported that phosphoric acid can be used as a catalyst for the pretreatment of switchgrass and was able to release total sugars from 15 to 72 mg per gram of the biomass. In addition, [33] has also recorded the successful application of phosphoric acid for the hydrolysis of sugar cane bagasse into fermentable sugars.

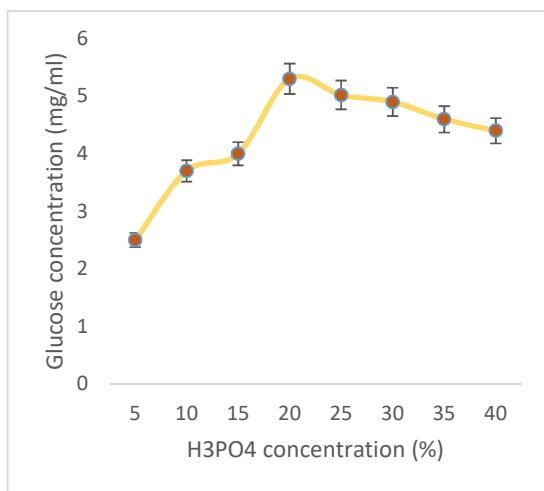


Figure 3: Effect of different concentrations of H₃PO₄ on the amount of the liberated glucose units liberated from rice waste when autoclaving was followed

3.3. Optimization of substrate concentration

As shown in figure 4, the amount of released glucose units was not significantly affected if the substrate concentration was changed from 5 to 11%. All the measured glucose concentrations were close to each other at these tested amounts of the rice waste. The glucose concentration was measured as 5.4-5.6 mg/ml for the seven tested concentrations (5-11%). However, lower glucose concentration of 4.5 mg/ml was recorded when the substrate concentration was reduced to 4%. These data indicate that the starting from 5% of the rice waste can be considered as an optimum substrate concentration, and the lower one (5%) will be selected as the optimum one as it can result in the production of high glucose units using lower amount of the substrate.

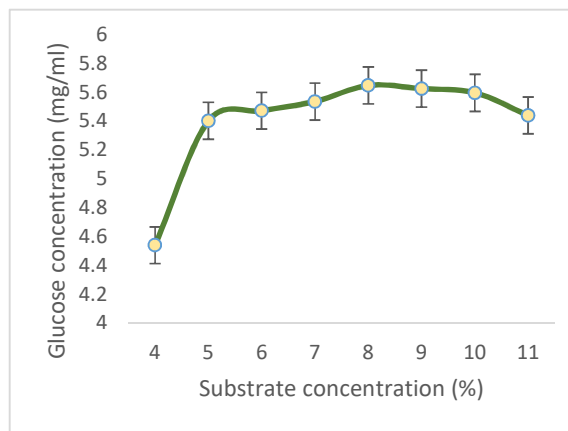


Figure 4: The effect of the rice waste concentration on the amount of the liberated glucose units after physical and chemical treatments using 20% H₃PO₄ and autoclaving

3.4. Combined physical/chemical and enzymatic hydrolysis

In order to increase the amount of glucose units that could be liberated from the rice waste; the combined physical, chemical, and enzymatic treatments were applied. As shown in figure 5, the addition of the amylase enzyme to the treated rice waste resulted in the elevation of the produced glucose concentration compared with untreated tubes as reported in figures 1-4. It has been observed that, the amount of liberated glucose units was gradually increased when the amount of amended amylase enzyme was increased up to 210 U. After that, the increasing in the amount of the amended enzyme was resulted in decreasing the liberated glucose concentrations. It could be concluded that the highest measured glucose concentration was recorded as 12.39 mg/ml when 210 U of amylase enzyme was applied and hence was considered as the optimum enzymatic concentration.

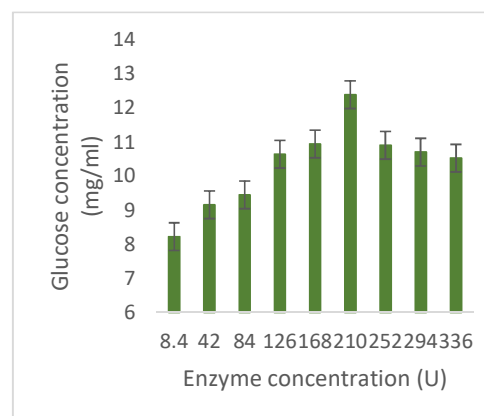


Figure 5: Effect of various volumes of the amylase enzyme on the amount of glucose units liberated after the treatment with 20% H₃PO₄ and autoclaving

3.5. Determination of bioethanol concentration

After three days of incubation of the yeast strain *Pichia nakasei* with the glucose units produced from the hydrolysis of rice waste using physical, chemical, and enzymatic treatments; the produced bioethanol was investigated. It has been shown that the yeast strain was able to ferment 12.39 mg/ml of glucose into 5.2 mg/ml of bioethanol indicating the successful fermentation of simple sugars into bioethanol using *Pichia nakasei* yeast strain. The data of the literature reported the ability of multiple yeast strains to convert sugars into bioethanol [34, 35]. However, the type of the organism and the concentration of the used glucose can largely affect the amount of the produced bioethanol. *Pichia nakasei* has been previously reported as a potent bioethanol producer that produced 2.9 mg/ml bioethanol from the glucose liberated from cardboard waste [14]. In addition, *Saccharomyces cerevisiae* TC-5 yeast strain was able to produce larger amount of bioethanol (20.13–21.64 g/L) at 35–40°C when different combined and separated conditions of saccharification and fermentation processes were applied [36].

3.6. FTIR Spectrum analysis

FTIR is a useful tool for studying structure of polymers, which differ depending on polymer composition and may reveal complexation and interaction between the constituents. FTIR spectra were in the transmittance mode. figure 6.a show the FTIR spectra for PVC and PMMA blanks, for PVC Spectrum shows band at 2951 cm^{-1} which related to (–CH) stretching asymmetric mode and the wagging of methylene groups in PVC is attributed at 1430 cm^{-1} . In addition, bands represent the deformation –CH₂, rocking C–H, C–C, and C–H trans wagging group of PVC appeared at 1329 cm^{-1} , 1249 cm^{-1} , 1065 cm^{-1} , and 959 cm^{-1} [37, 38].

The FTIR spectra of PVC/PMMA/G samples with different thickness (400,500 and 600 μm) before and after separation process are shown in Figure 6.b C–Cl stretching band appeared at 650 cm^{-1} which attributed to the change in frequency after blending with methacrylate due to interaction between the hydrogen of the methacrylate and the C–Cl dipole of PVC leads to a conclusion about the complexation between the two polymeric matrices. Additionally, the peaks of CH stretching, C=O bond which became intense following separation process, CH₃ and O–CH₃ stretching vibrations in PMMA, are respectively assigned at 2951, 1721, 1449 and 1159 cm^{-1} [39-41].

The assignments of IR spectrum of the prepared membranes after separation process have some changes in band intensities and band positions (shift) as compared to that of the blend before separation. The typical absorbance due to C–Cl in the base compound at 650 cm^{-1} undergoes a decrease in intensity and C=O stretching at 1721 cm^{-1} is shifted to 1735 cm^{-1} and became intense following separation process. While a peak of 2931 cm^{-1} becomes stronger after separation. This indicates a considerable change in the blends after separation process.

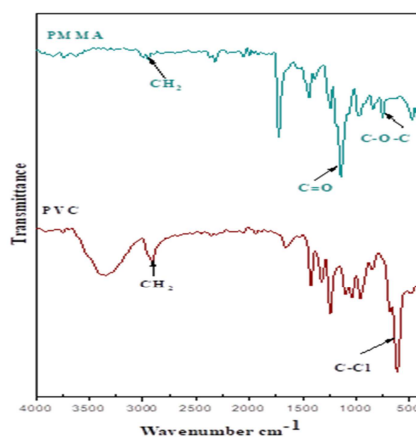


Figure 6.a: FTIR absorption spectra for PVC and PMMA blanks

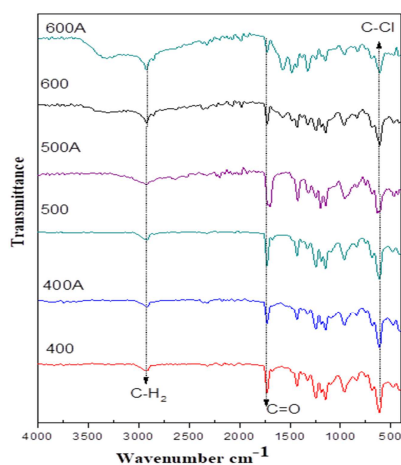


Figure 6.b: FTIR absorption spectra for PVC/PMMA/G membranes

3.7. Morphology of the Prepared membranes

SEM image can provide a primary indication for the saturation or homogeneity procedures of the samples prepared. To recognize the morphological phase and the impact of separation process on the PVC/PMMA/G membranes surface. Figure 7 (a & b) illustrates the SEM micrograph of the surface of prepared membranes with different thickness before and after separation process. As shown in figure 7a, the prepared films have a smooth surface without cracks which indicates that the phase separation did not occur due to the good miscibility between PVC and PMMA. In other words, prepared membranes tend to generate a more compact matrix of PVC film and leads to better development of the films. As a result, the separation process can be occurred quickly and easily with no blocking phase appeared. Also, the small white spots are dispersed on the surface of the blend with some agglomerations after separation process which indicates a close state of saturation. Additionally, figure 7b shows the SEM images of the cross-section of the polymer matrices with change in thickness after separation process. As can be seen from the images of blends, they show uniform

morphological features without any phase separation. This shows the miscibility of blends to a large extent [40, 42, 43].

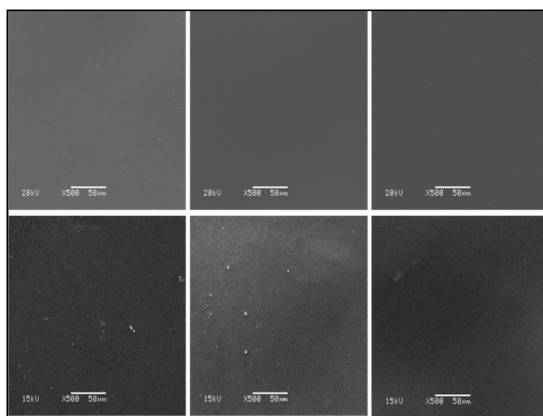


Figure 7.a: SEM images for the surface of the polymeric PVC/PMMA/G membranes

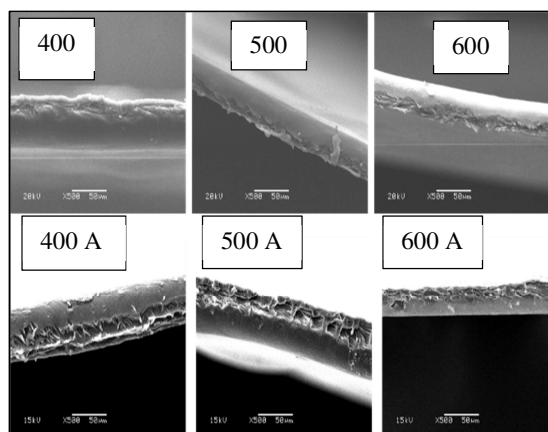


Figure 7.b: SEM images for the cross section of the polymeric PVC/PMMA/G membranes

3.8. Tensile properties of PVC/PMMA/G membranes

Illustrative tensile values of polymeric PVC/PMMA/G blends membranes are depicted in table 2. In all cases, the material's microscopic structure or internal molecular is being rearranged, with atoms being moved to new equilibrium positions. Table 2 summarizes the values of ultimate tensile strength and elongation at break. The values of PMMA/PVC/G blends tensile strength show that as the thickness of the blends increases up to 500 μm , the ultimate tensile strength increases. Because of its brittle nature, PMMA has a high strength. The

addition of PVC to PMMA reduces ultimate tensile strength, which further reduces blend stiffness, making the material useful for engineering purposes. By increasing the thickness of the PMMA/PVC/G blend, the tensile strain is obviously improved. According to table 2, PVC is a ductile polymer, the elongation at break and fracture energy of the PVC/PMMA/G blends are greater than those of the PVC polymer alone, indicating a high level of compatibility. The enhanced properties of these blends can be linked to specific interactions between molecules of the constituent polymers, such as H-bonding and dipole-dipole interactions. It has been proposed that the hydrogen of vinyl chloride can form a hydrogen bond by interacting with the ester carbonyl group (the acrylic polymer's H-bond acceptor). [44, 45].

Table 2

Mechanical properties of PVC/PMMA/G blends

membr:	Thickness (μm)	Max Force (N)	Elongation at break (%)
PVC	400	7.22 \pm 0.50	1.3 \pm 0.20
400	400	11.56 \pm 0.1	2.09 \pm 0.20
400A	418	10.22 \pm 0.50	1.66 \pm 0.60
500	500	28.12 \pm 0.10	3.68 \pm 0.20
500A	523	25.12 \pm 0.20	2.51 \pm 0.80
600	600	12.23 \pm 0.08	2.65 \pm 0.30
600A	628	10.01 \pm 0.09	2.42 \pm 0.20

3.8. Water contact angle

The hydrophobicity of the prepared membranes was measured using water contact angle before and after separation process, as shown in figure 8 the three thickness of the prepared polymeric PVC/PMMA/G

membranes 400, 500 and 600 μm are represent as 76.47 $^\circ$, 82.89 $^\circ$ and 83.16 $^\circ$ respectively before separation process. The water contact angle was increased after separation process for three tested prepared membranes and the best thickness is 500 μm its recorded 91.45 $^\circ$ which better than 400 and 600 μm , that's due to the nature of selected materials for the prepared membrane and the ethanol which absorbed by the membrane after separation process. The obtained results confirmed that the prepared polymeric PVC/PMMA/G membranes have hydrophobic characteristic and matched with Kozbial, Tokuda and Kathryn [46-48] which reported the hydrophobic properties for PVC, PMMA and graphite.

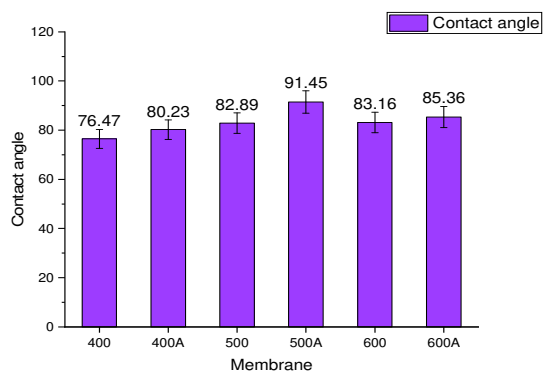


Figure 8: Water contact angle of the prepared polymeric PVC/PMMA/G membranes 400, 500 and 600 μm before separation process, 400A, 500A and 600A after separation process

3.9. Water and ethanol uptake

The obtained results of water and ethanol uptake were reported at table 3 based on the weight of membrane on the dry and wet state. The three thickness of the prepared polymeric PVC/PMMA/G membranes 400, 500 and 600 μm were reported low result percentage of water uptake 6.73, 18.26 and 42.85% compared with results percentage of ethanol uptake 150, 286.84 and 114.48% respectively. Figure 9 is describing the difference between the water and ethanol uptake and this gap confirmed the hydrophobicity characteristic of the prepared membrane as reported in water contact angle results. The thickness 500 μm represent the highest percentage of ethanol.

Table 3

Results percentage of water and ethanol uptake for the prepared polymeric PVC/PMMA/G membranes with thickness 400, 500 and 600 μm

Sample No	Water uptake W%	Ethanol uptake W%
400	6.73 %	150 %
500	18.26 %	286.84 %
600	42.85 %	114.48 %

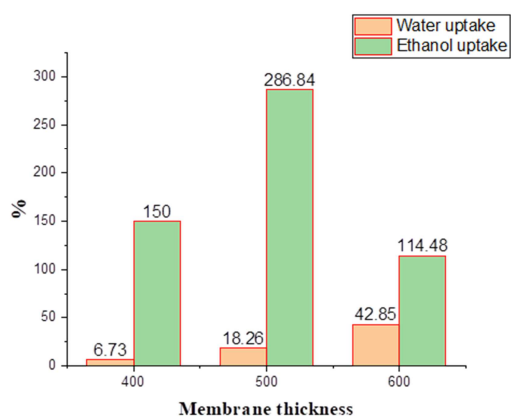


Figure 9: Water and ethanol uptake percentage of the prepared polymeric PVC/PMMA/G membranes with different thickness 400, 500 and 600 μm

3.10. Separation process via polymeric membrane

Various research reports that exhibited multiple separation approaches described the purification of ethanol from water. Pervaporation has been the favored process for separating technology for the past few years [49, 50]. The current work is based on a similar pervaporation mechanization via the prepared polymeric PVC/PMMA/G membranes with different thickness 400, 500 and 600 μm have been using during the separation process. The bioethanol produced during fermentation process was separated via the prepared polymeric membrane under varying nitrogen pressures through ultrafiltration system amicon cell. Tables 4 summarize the results of three thickness tests of the prepared polymeric membrane. Figure 10 represents the permeate volume and concentration data that obtained during the separation process for 400, 500 and 600 μm of the prepared polymeric membrane, its observed that for thickness 400 μm the highest volume permeate and

concentration were 0.7 ml and 2.360 mg/ml respectively under nitrogen pressure 50 psi. On the other hand, the best volume and concentration were recorded at 40 psi as 0.9 ml and 2.982 mg/ml respectively for thickness 500 μm of the prepared polymeric membrane, but the lowest results were obtained from 600 μm thickness as 0.3 ml and 1.579 mg/ml for the volume and concentration of permeate. The flux and separation factor results were showed in figure 11 that the greatest flux and separation factor were obtained from 500 μm thickness of the prepared polymeric membrane as 939.526 ($\text{mg}/\text{m}^2.\text{h}$) and 10.557 respectively. The lowermost flux and separation factor were recorded as 702.466 ($\text{mg}/\text{m}^2.\text{h}$) and 4.107 respectively for 600 μm thickness from between the three thickness of the prepared polymeric membrane that applied for the separation process. It worth mention that from the observed data the best thickness of the prepared membrane is 500 μm .

Table 4: Separation process of produced bioethanol under various nitrogen pressures

Memb rane thickl ness (μm)	Ti me (h)	Press ure (psi)	Perm eate volu me (ml)	Permeate concentr ation of ethanol (mg/ml)	Flux of perm eate ($\text{mg}/\text{m}^2.\text{h}$)	Separ ation factor
400	2	20	0.4	0.821	204.824	2.910
	2	30	0.4	1.662	711.305	4.443
	3	40	0.5	2.085	764.725	7.592
	4	50	0.7	2.360	806.517	8.326
	3	60	0.6	2.132	776.328	7.713
	2	70	-	-	-	-
500	1	20	0.3	0.842	220.991	3.344
	3	30	0.5	1.768	745.238	4.655
	3	40	0.9	2.982	939.5	10.557

					26	
	3	50	0.8	2.591	845.2	9.679
					30	
	2	60	0.6	2.204	788.5	7.835
					60	
	2	70	0.4	1.325	404.8	4.241
					91	
600	2	20	0.5	0.868	236.3	3.248
					20	
	3	30	0.3	1.579	702.4	4.107
					66	
	4	40	0.3	1.538	687.5	3.876
					12	
	3	50	0.2	1.491	679.9	3.838
					04	
	2	60	-	-	-	-
	2	70	-	-	-	-

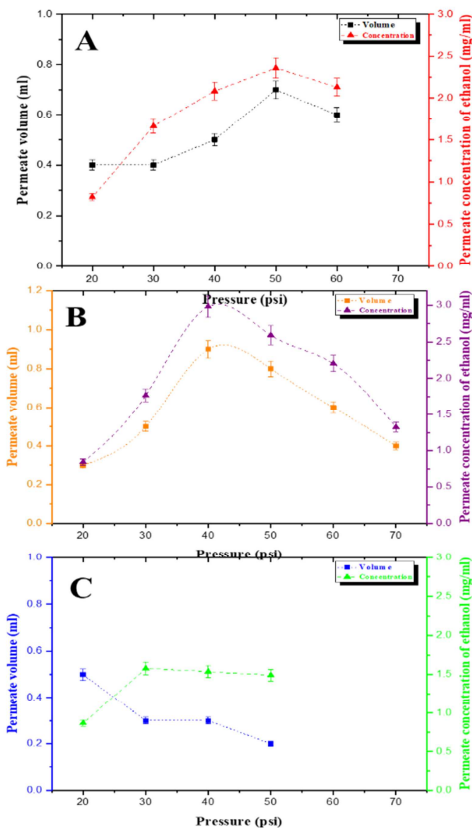


Figure 10: Separation process of produced bioethanol under various nitrogen pressures, A, B and C are the prepared polymeric PVC/PMMA/G membranes thickness 400, 500 and 600 μm

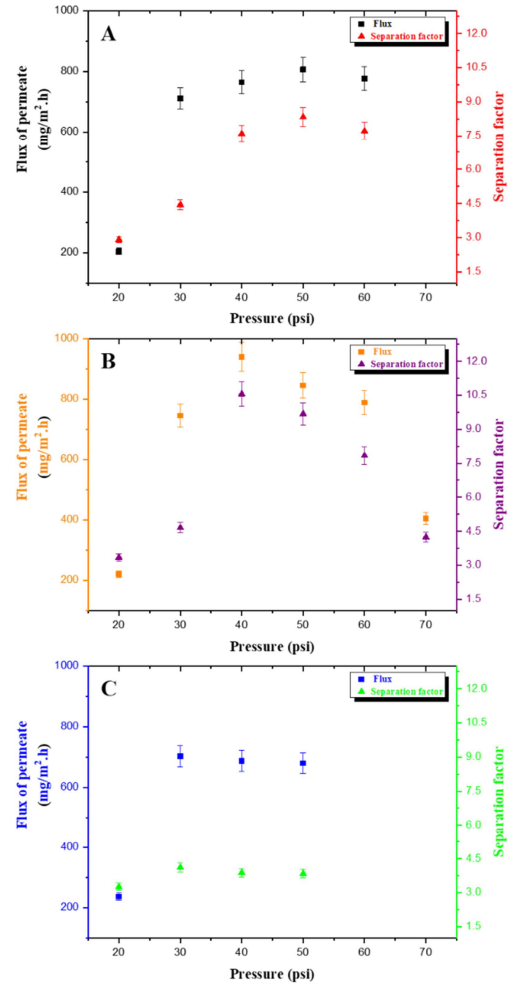


Figure 11: Flux and separation factor of produced bioethanol under various nitrogen pressures, A, B and C are the prepared polymeric PVC/PMMA/G membranes thickness 400, 500 and 600 μm

4. Conclusion

The current work succeeded to use the daily thrown rice waste as a raw material for the production of bioethanol using yeast strain. The optimum conditions for the production of glucose from the starch molecules were depending on the autoclaving of the waste in phosphoric acid followed by enzymatic treatment. The produced sugars were successfully fermented into bioethanol that has been effectively separated using PVC/PMMA/G polymeric membrane.

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Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Authors' contributions: All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by all of them, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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