

Silica/ Charcoal Addition to the Composite Polyvinyl Fluoride Membranes for Water /Organic Vapor Separation

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Abstract

In the present work, Supported polyvinyl fluoride (PVF)/S/Ch membrane were prepared by wet/dry inversion method where PVF powder was dissolved in a required suitable solvent at dissolving percent 30% vol PVF/DMF at 50°C for 15 min and 500 cycle /min stirring velocity then different mixing weight ratio of organic and inorganic ceramic material (nano charcoal and SiO₂) are added (0.5,0.75, 1.0,1.25, and1.5)w/w to this solution with continuous stirring until reach homogeneity then a suitable membrane were molded in thickness (1 mm) and thinner then curing this membranes at 170°C for 24 hrs afterward chemical and physical properties are measured.

The results of (apparent density, porosity, and chemical absorption under moisture and acidic solution) proved that good chemical and physical properties were shown for samples supported by organic fillers (charcoal) than inorganic one of silica, and best samples have high chemical absorption and high permeability of membranes is PVF m/Ch A₅ and PVF m/SiO₂ A₃ for both organic and inorganic one.

Keywords: PVF/Charcoal- Silica membrane. Physical and chemical properties.

أضافة السليكا / جاركول الى متراكب البوليفينيل فلورايد لتصنيع غشاء فاصل للبخرة العضوية والرطوبة

الخلاصة

في العمل الحالي تم تحضير غشاء بوليمري من الاساس العضوي البوليفينيل فلورايد والمدعم بالمواد العضوية الجاركول وغير العضوية السليكا وذلك اعتمادا على الطريقة الرطبة والجافة في التحضير للمادة البوليمرية اولا وذلك باذابة المسحوق البوليمري بولي فاينيل فلورايد في كمية مناسبة من المذيب المناسب " داي ميثيل امين " وعند نسبة اذابة 30% نسبة حجمية عند درجة حرارة 50°م و سرعة تحريك 500 دورة / دقيقة لمدة 15 دقيقة ، ومع التحريك المستمر يتم اضافة نسب مختلفة من المضافات العضوية الجاركول وغير العضوية السليكا وينسب اضافة وزنية " 0.5 ، 0.75 ، 1.0 ، 1.25 ، و 1.5 " نسبة وزنية الى المزيج وصولا الى التجانس التام بعدها يتم صب المزيج المتجانس باسمك دقيقة للحصول على الغشاء البوليمري المدعم ، ثم انضاجة عند درجة حرارة 170 °م لمدة 24 ساعة بعدها يتم قياس الخصائص الفيزيائية والكيميائية .

ان نتائج هذه الفحوصات للغشاء البوليمري المحضر الكثافة الظاهرية، المسامية، الامتصاصية والفعالية الكيميائية تحت وسائط مختلفة رطبة وحمضية اثبت:

الحصول على افضل الخصائص الكيميائية والفيزيائية لكل النماذج المدعمة بالمضاف العضوي الجاركول مقارنة بالمضاف غير العضوي السليكا ، حيث يمتلك النموذج المثالي امتصاصية وفعالية كيميائية عالية اضافة الى نفاذية عالية وهو بولي فاينيل فلورايد/جاركول / النموذج 5 و البوليفينيل فلورايد/ السليكا النموذج 3 لكلا المضافيين.

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Introduction

The polymeric waterproofing membrane according to the modern studies have an improved biaxial elongation compared with conventional polymeric waterproofing membranes and comprise a composite of first layer, a second layer and a barrier layer between the first and second layers. The barrier layer comprises at least one organic polymeric material ; the first layer and the second layer better mechanical characteristics in comparison to the organic polymeric material used in the barrier layer, the first and the second layer comprise the same or different materials [1].

The polymeric water proofing membrane may include an adhesive promoter between the first layer and the barrier layer, as well as an adhesion promoter between the second layer and the barrier layer, where in the adhesion promoter between the first layer and barrier layer is selected independently from the adhesion promoter between the second layer and the barrier layer. The adhesion promoter includes adhesive polyolefin's such as maleic anhydride , vinyl acetate resin , the organic polymeric material of the barrier layer include polyamides, poly vinyl fluoride, poly vinylidene chloride and ethylene vinyl alcohol ; the organic polymeric material of the first layer and the second layer includes polyurethanes , propylene, propylene copolymer[2].

Many applications are found for supported polyvinyl fluoride membranes as sealing covering, coating and isolation of deposits and landfill which serve for reception of liquid and solid wastes, for the protection of water and underground

water as well as ground and soils, and for the protection of building and construction which are in contact with contaminated mediums [3-7].

Several researchers are studied the application of improved PVF/ membrane in different fields according to its better properties such as good resistance to atmospheric corrosion as well as good and simple workability especially heat sealing , as well as a good chemical, biological resistance against organic vapors.

Zhanliang w.etal applied PVDF-HFP, ethylene carbonate (EC), dimethyl carbonate (DMC) in improving of chemical absorbing of LiBF_4 salts [8]. Man W. etal studied a carbon-filled PET/PVDF blend to improve the electrical and mechanical properties of fuel cell at 2500% and 320% respectively [9]. Zhihong X.etal investigated the modification of PVDF ultra filtration membranes in further purification of Ginkgobiloba extraction (GBE) then purified from 21.3 wt% to 34.8 wt% in the GBE crude product [10]. Weiline X. prepared a new proton exchange membranes based of vinyl compounds by use of silica material then check optimum weight ratio that gave high permeability at PVF/PWF/ SiO_2 0.40:0.40:0.20 wt [11, 12]. Recently Le Gendre N. applied improved polyvinylidene fluoride membrane for protein biochemical analysis [13].

The present work aimed to prepare:

1. Water-proofing membrane, having a diffusion and permeability of organic material (aromatic and halogenated hydrocarbons such as dichlorobenzene to separate it from gas and water

that may be contaminated by the use of simple new methods.

2. Optimize the mixing weight ratio and type of improving permeability additive organic and inorganic material (charcoal, and silica) that gave good chemical – physical separation properties.
3. Optimization of this membrane by studying the comparison of these properties among standard of zero additive, organic additive PVF/Ch/An and inorganic additive PVF/ SiO₂/ An membranes.

Experimental: Materials:

1. Poly vinyl fluoride (PVF) : thermoplastic non-reactive pure fluoro polymer of low melting point 177°C , and low density (1.78) of KYNAR 500 PVF and TG at about (-35°C) and is typically (50-60%) crystalline.
2. Dimethyl amine fluoride (DMF) solvent of 99.9% BDH purity for this resin.
3. Charcoal of high purity 99.9% and fine oily black powder by BDH Company London.
4. Silica of high purity 99.9% and > 150 μm and >50 μm grain size fine white, porous powder supplied by Ar- Dema in Al- Romady town.

2.2. Procedures:

1. Preparation of base barrier layer:

A process for the preparation of the polymeric barrier layer membranes consisting of:

- Weigh fixed amount of polyvinyl fluoride resin powder of "3 g" for each run.
- Dissolved this fixed amount of a desired fixed volume of specified solvent (DMF) 60 ml with continuous stirring at 500 cycle /min for homogeneity.

2. Preparation of supported PVF\filler membranes a process for the preparation at the PVF \Ch\S membranes consisting of:

- Weigh different amount of organic (charcoal) and inorganic (silica) fillers as weight ratio from PVF/ filler additive w/w (0.5, 0.75, 1.0, 1.25, and 1.5) g\g respectively.
- Added each weight gradually with stirring to a prepared barrier solution (PVF resin) until finishing each sample powder.
- Follows the step of stirring for 15 min to distribute small nano particles of additive fillers (charcoal and silica) in the gaps of barrier layer particles.
- Clean and dry the porcelain molder (25ml) at 50°C for 24 hr., then grease it with Vaseline oil in order to simplify the finishing of dry molder.
- Molding the preparing solution at constant velocity 1 ml/min in clean and grease molder with a thin thickness maximum reach 3 mm max.

- Curing the final prepared solution in an oven at 170°C for 24 hr and leave it for 24 hr without heating for stability.
- Finishing the membranes PVF supported samples and checked its characteristic physical and chemical properties [14, 15].

Testing the prepared PVF \Ch, S\A membranes:

1. Physical properties:

- Apparent density g/ml:

This test is carried out by measuring three dimensions of prepared membrane samples PVF\Ch. S\A (diameter of desks cm, and height cm) also check and measure weight for each sample membrane and apply the specified law of apparent density in g/ml.

- Porosity (%):

This test is measured by checking weight of prepared membranes and exposing it to heat at 120°C for 24 hr in an oven then check its weight after heating afterward applied the following law to calculate porosity [16].

$$(\%) \text{ Porosity} = \frac{A-B}{A} * 100$$

A= weight of sample at 25°C

B= weight of sample at 120 °C for 24 hr

2. Chemical properties:

- Chemical absorption membrane under moisture medium:

This test is achieved by immersing the prepared PVF/Ch,S\A membranes in a specified volume of distilled water 250 ml of each container for both charcoal and silica membranes at 50°C

for 120 hr respectively, where the change in weight is checked each 24 hrs and continuous over 5 day [11].

- Chemical absorption membrane under acidic (10% H₂SO₄) medium:

This test is achieved by immersing prepared membrane samples in prepared sulfuric acid solution of 10% wt. concentration at 50°C for 5 days then check its weight every 24 hrs in order to calculate the chemical absorption activity of these membranes under different acidity medium [15].

Results and Discussion:

1. Preparation PVF/Ch,S\A n membrane

- Gradual curing and drying of molded membranes from 30°C to 170°C at heating rate of 10°C/min in order to avoid any distortion and bubbles in prepared membrane.
- The using of porcelain molder in order to keep heat simplifies finishing of prepared membranes.

2. Characteristic properties of prepared membranes

Physical properties:

Density of prepared membranes:

Figure (1) shows the effect of organic and inorganic fillers on the density of prepared membranes PVF/Ch,S\A. The apparent density of membranes is decreased with continuous increasing an additive weight until reach optimum additive ratio "1.0 g/g" for charcoals samples and "0.75 g/g" for

silica one according to high compatibility between organic particles of charcoal filler with barrier base resin PVF than inorganic particles of silica with addition of high specific gravity of silica reached (3.95) than low specific gravity of charcoal of (2.2) respectively [16].

- **Porosity of prepared membranes:**

Figure (2) shows the effect of both type and concentration of additive fillers (organic / charcoal, and inorganic/silica) on the permeability property of improved PVF\Ch,S\An membrane.

The values of porosity is increased with continuous increasing of weight ratio filler additive until reach optimum ratio of "1.5 g/g" for charcoal and "1.0 g/g" for silica due to high compatibility between organic additive filler charcoal and organic barrier material PVF than inorganic one of silica. In addition to high adsorptive properties of active carbon charcoal due it's porous and high surface area properties [16].

Chemical properties:

- **Under moisture medium:**

Figures (3, 4) show the effect additive concentration of organic (charcoal) and inorganic (silica) filler on the chemical absorption of membrane under moisture medium. The chemical absorption is increased with increasing time and weight of

additive filler until reach optimum addition PVFm/SiO₂A₄, and PVFm/ChA₃ for both prepared membranes according to high adsorptive properties of charcoal under moisture medium than silica one [16]. And figure (5) shows the comparison between standard and improved PVF membrane under moisture medium, high values of absorption appeared for improved membranes especially for organic additive filler of charcoal than inorganic of silica according to both compatibility and adsorptive properties of charcoal than silica one [16].

- **Under acidic medium (10% H₂SO₄):**

Figures (6, 7) show the effect of additive concentration of both organic (charcoal) and inorganic (silica) fillers on the chemical adsorption of membrane under acidic solution media. High adsorption properties appeared with high additive of organic charcoal until reach maximum adsorption at PVFm/ChA₅ than standard one also for silica additive that reach optimum additive of high adsorptive properties of PVFm/SiO₂A₃ of 1.5 g/250 ml according to inert structure of silica particles against sulfuric solution and high amount of charcoal required to equilibrium the acidity and give adsorptive optimum properties at PVFm/ChA₅ [15, 16].

Figure (8) shows the comparison of chemical adsorption between standard and improved PVF membrane under acidic solution (10% H₂SO₄) both improved PVF membranes have high adsorptive properties than standard PVF especially for charcoal additive organic filler than silica additive according to its compatibility and porous properties than silica one according to good physical and nature of chemical structure of charcoal of low specific gravity and high surface area than silica one [15, 16].

Also table 1 indicates the comparative physical and chemical properties between standard and optimum improved PVF membranes.

Conclusions:

1. Good physical and chemical properties achieved for improved PVFm\Ch A₀₅ and PVFm\SA₀₃ membranes especially for charcoal of high compatibility and low apparent density than silica membranes.
2. High porosity of charcoal membranes reached 19% than other standard of 9.5%.
3. High chemical absorption properties in g\250 ml of charcoal membrane reached 2.8 under moisture and sulphuric acid solution 10% media.
4. High characteristic properties (permeability +50%, density +88.5%, chemical +46.4% under moisture, and +82.1%

under acidic solution media) than standard PVFm.

5. Inert effect of silica membrane under acidic solution according to inert properties of silica particles.

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Table (1) the comparative properties between standard and improved PVF m\Ch, S/An.

Type of membrane	Apparent density g/ml	Porosity%	Moisture media ads. g\250 ml	Acidic media ads. g\250 ml
Standard PVF m	0.22	9.5	1.2	0.5
PVDF m\Ch A ₀₅	0.53	19.0	2.8	2.8
PVDF m\S A ₀₃	1.75	11.0	1.8	1.5

Table (2) shows the comparison percent increasing or decreasing in physical and chemical properties of PVF m\Ch, S\An.

Type of membrane	Apparent density g\ml	Porosity %	Under moisture media.	Under acidic media
Standard PVF m	0%	0	0	0
PVDF m\Ch A ₀	+ 58.5	+50	+46.4	+82.1
PVDF m\S A ₀	+87.4	+13.6	+33.3	+66.6

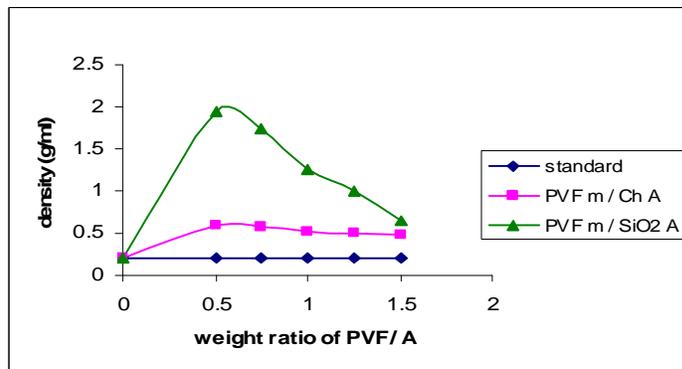


Figure (1) the effect of porous materials "charcoal, silica" on apparent density of prepared membrane.

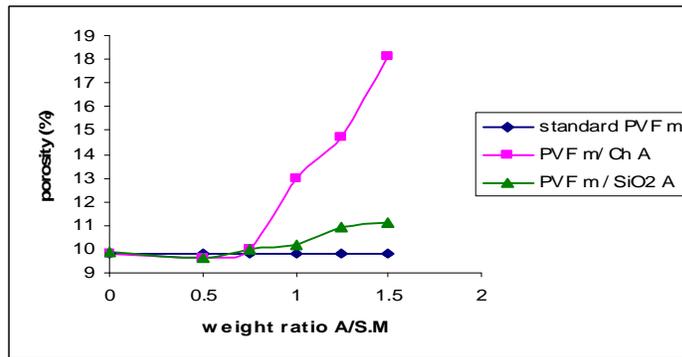


Figure (2) the effect of porous materials "charcoal, silica" on porosity of prepared membrane.

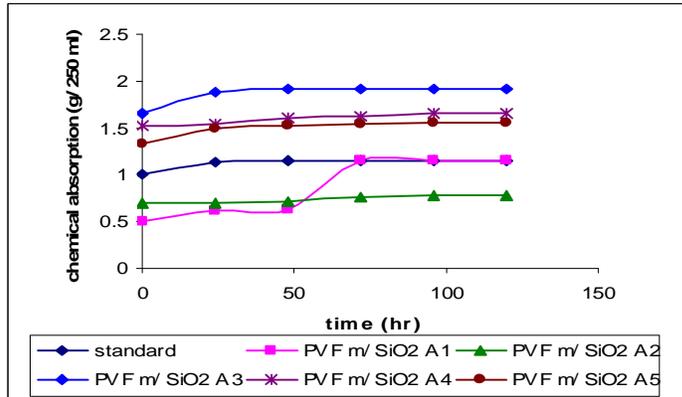


Figure (3) the effect of additive porous materials "silica" on chemical absorption of PVF m improved membrane under moisture media.

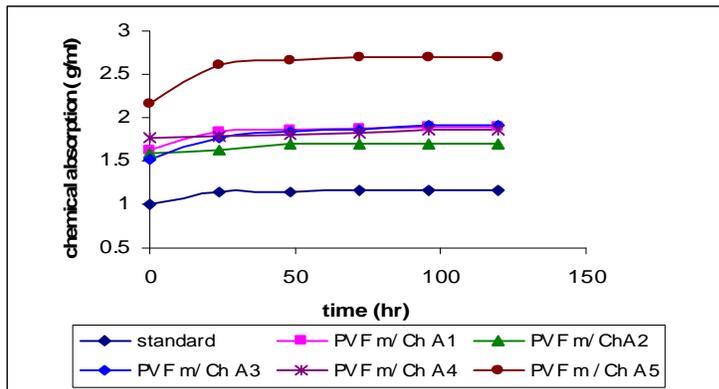


Figure (4) the effect of additive porous material "charcoal" on chemical absorption of improved PVF membrane.

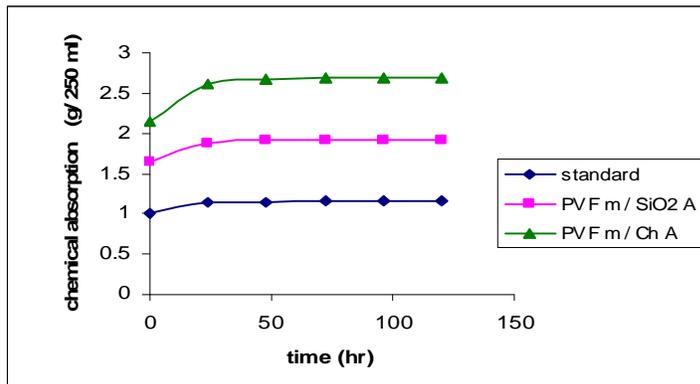


Figure (5) comparisons between standard and improved PVF membrane under moisture media.

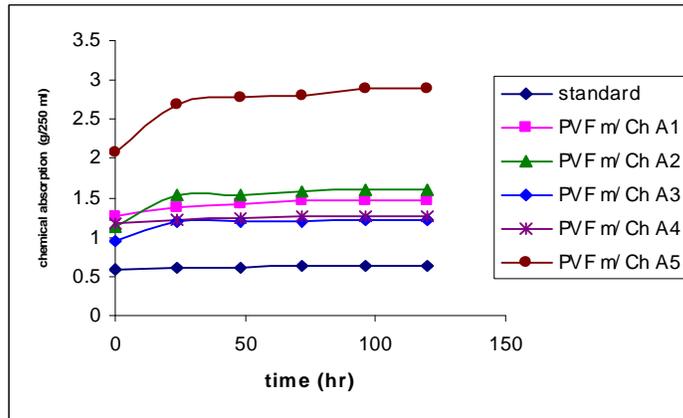


Figure (6) the effect of weight ratio porous material on acidic absorption of PVFm / A membrane.

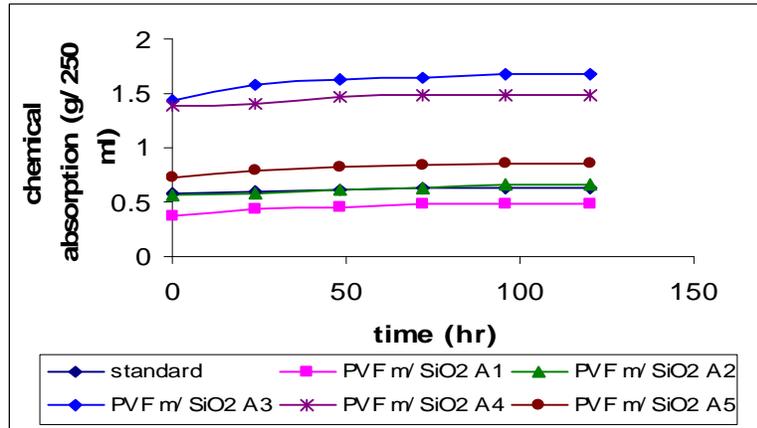


Figure (7) the effect of porous material additive "SiO₂" on chemical absorption of PVF improved membrane in acidic solution "10% H₂SO₄".

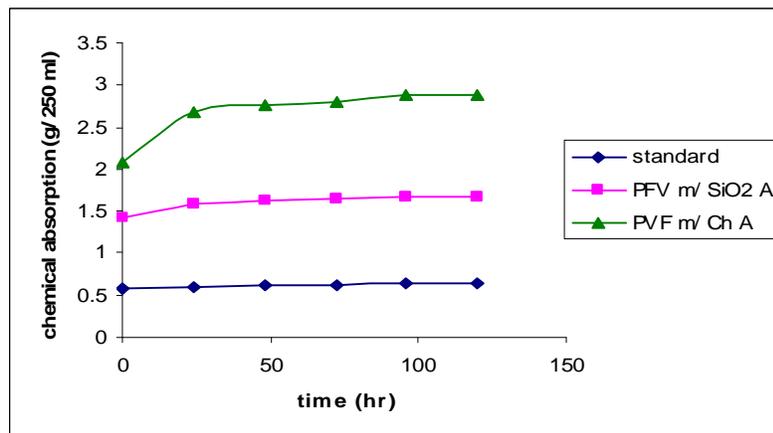


Figure (8) a comparison of chemical absorption between standard and improved PVF membrane under acidic solution "10% H₂SO₄".