

PREPARATION AND CHARACTERISATION OF CELLULOSE ACETATE BUTYRATE (CAB) –ZnO BLEND MEMBRANE IN AQUEOUS AND ACIDIC MEDIA

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Abstract: *The present work describes the preparation of the composite ion exchange membrane. Membranes were prepared by solvent-vaporization method. CAB and ZnO were used as the polymeric material. Membrane characterizations were carried out on the basis of water content, thickness, porosity, SEM and pH studies. The morphology and hydrophilicity of the ZnO particles confined within Cellulose Acetate Butyrate membrane were analyzed by SEM. A structural model of the co-mixed membrane (CAB-ZnO) has been proposed.*

Keywords- *Water content, cellulose acetate butyrate, porosity.*

1. INTRODUCTION

Membranes play indispensable roles in various fields like membrane water treatment, membrane gas separation. Many of the researchers are also making attempt to find out the relationship between membrane fabrication, membrane morphology and membrane performances. During the last decades, using membrane separation processes for different applications like gas separation, protein concentration and water treatment has been quite remarkable [1]. A nowadays application of membranes has been spread over various industries such as pharmaceutical, biochemical and food as well as in low energy consumption which is one of the major postulates. In all kinds of membranes such as microfiltration or ultrafiltration, membrane porosity, pore size, pore size distribution and pore density are the important key factors for evaluation membrane performance and its separation [2]. Membrane preparation from mixture systems with two polymers with different properties has been considered. This is an easy way to get advantages of both polymers and especially reduce membrane's hydrophobicity by blending with a less hydrophobic one. Zhao et al recently studied the effect of ZnO particles on PES membrane, either, and reported about 110-220% increment in water permeation, and also observed reduction in irreversible resistance of the membrane [3]. In last few decades, organic-inorganic composite materials have gathered colossal attention among these various processes. Each component in the composite has its own property which enhances on combining. Inorganic-organic composite materials are increasingly important due to their extraordinary properties within a single molecular composite, which arise from the synergism between the properties, such as mechanical, thermal, electrical and magnetic compared to pure organic polymer and inorganic materials. In these materials, organic materials offer structure, flexibility, convenient processing, tuneable electronic properties and metallic behaviour.

The interplay of the active layer structure and the hydrophobicity/hydrophilicity of the polymer surface results in different polymer- water interactions and therefore in different selective permeation characteristics. Water in membrane pores is known to exist in the form of distinct structures: monomeric water, weakly and strongly H-bonded clusters. The characteristic of the water in the pores is determined by (i) the hydrophobicity of the surfaces, (ii) the time and conditions of exposure to water [4]. CAB is selected as the polymeric material, due to the excellent film-forming properties and capable of developing a defect-free layer of neat membrane. The CAB exhibits excellent film-forming properties due to the butyryl group in CAB can effectively improve and expand the capacity of material volume cellulose chain membrane through enlarging the free volume. CAB polymer possess several prominent characteristics including high impact resistance, well maintained weather resistance, notable chemical resistance with excellent film forming characteristics inherited from acetyl and butyryl groups.

Cellulose Acetate Butyrate (CAB) is a thermoplastic polymer which has good mechanical properties with biocompatible, semi-crystalline, thermoplastic, UV resistant polymer that can be used in different forms (film, membrane, fibers, microspheres) both alone and in combination with others substances. Due to the hydroxyl groups of CAB, it is expected to it provides hydrogen bond interactions. Also, the presence of acetyl and butyryl substituent allows to CAB to interact with hydrophobic moiety of solvents. It can be readily processed and is also susceptible to biodegradation. There are numerous reports in the literature associated with polymer blends based on cellulose derivatives. However, only few describe material based on CAB and their susceptibility to biodegradation. So far, no information about the effect of Zinc oxide incorporation into CAB matrix on the degradation of the material has previously been available [5]. CAB do not form gel in presence of water and they are widely used for preparing pH sensitive and semi-permeable microporous membrane.

In particular, Cellulose acetate butyrate (CAB) is a water insoluble polymer that has been employed to prepare directed compression matrices and has been used as a semi-permeable membrane for osmotic pumps. Also, this polymer has been used to obtain sustained release microparticles using the emulsion solvent evaporation method. The drug release from CAB microparticles has been shown to be affected mainly by the particle size, the molecular weight of the polymer and the drug to polymer ratio in the formulation.

In our study we used a novel hybrid material, obtained via solvent vaporization method which combines two components: organic polymer (CAB) and inorganic solid (ZnO particles). Hybrid materials, due to their unique properties are promising systems with potential application in coatings, membranes, biomaterial, sensors and Catalysis. CAB could be used in extended release due to its more hydrophobic nature. The

increase in the butyryl content in CAB decreases water permeability since the butyryl moiety is more hydrophobic than acetyl moiety. The CAB membranes are very hydrophobic and have a longer lateral group (four carbons), suggesting a potentially lower immobilisation yield. The CAB membranes are much more permeable, which offers resistance to the diffusion of both the substrates and products of the enzymatic reaction [6].

With the Cellulose Acetate Butyrate, one must consider (a): the increasing no. of alkyl groups and (b): the presence of two different types of substituent groups. An increase in the member of alkyl groups should decrease the diffusion coefficient and the water sorption capacity. There should also be an increase in contact angle value. However, the diffusion coefficient of CAB is higher than that of Cellulose Propionate. This is probably because there are two different substituent groups to increase the free volume within the membrane. Present studies addressed the easily feasibility and development of CAB based, low permeability membranes for application in osmotic drug delivery. CAB exhibited good solubility in organic solvents, while being more hydrophobic than CA. Therefore CAB blend membranes were investigated to achieve low permeability [7]. The CAB membrane matched the CA membrane in robustness but had superior drying properties, offering particular advantages for thermolabile formulations. The CAB membranes appeared to have stability comparable to the standard CA membrane [8]. CAB based membrane founds higher surface with its higher surface irregularities and porosity, which might be due to the difference size of the butyrate groups, having CAB membranes with more open structure at the end.

Zinc oxide (ZnO) is a material with a partly covalent and partly ionic character, which gives it many interesting properties. ZnO or ZnO based compounds are used in heterogenous catalysis to produce many chemical, e.g. in the formation of methanol from CO and H₂. The asymmetry of ZnO in the crystal structure allows anisotropic growth that can provide large surface to volume ratio. Materials with hydroxyl groups like cellulose can easily bind ZnO through possibly hydrogen bondings and do not require any type of surface treatments [9]. The applications of Zinc oxide powder in industry are numerous.

Ion transport and ion exclusion properties depend on the volume fraction of water in the polymer membrane, and the chemical nature of the polymer membrane, and the chemical nature of the polymer itself can influence fine-tuning of the transport properties to obtain membranes with other useful properties, such as chemical and dimensional stability [10].

In the present study CAB-ZnO co-mixed membrane is prepared and dried under controlled conditions and its dimensional characterization is carried out in dried as well as in wet conditions. ZnO has been incorporated in CAB texture with the object of the enhancement of its water retaining capacity. The membrane (CAB-ZnO co-mixed) is brought in contact of aqueous, acidic and basic solutions to investigate its sustainability with the surroundings. Adsorption capacity is also estimated. Water content at different immersion time is estimated along with rate constant of water uptake. Surface morphology of the prepared membrane has been investigated with the help of SEM analysis.

2. EXPERIMENTAL

2.1 Materials

Cellulose Acetate Butyrate (CAB, $M_w = 65,000$) was used as a membrane material. The substitution degree of acetyl and butyryl groups, were 2.04 and 0.71 respectively. Acetone was used as a solvent for membrane preparation via solvent- vaporization method. Throughout the experiment, distilled water was used. The used polymer of the chemical structure is given below.

Polymer	Chemical Structure
Cellulose Acetate Butyrate	<p>R = H or CH_3CO or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}$</p>

The non-polar character of cellulose acetate butyrate arises out of the hydrocarbon group in the ester part of the molecule and that this non-polar character of this polymer is stronger than that of cellulose acetate [11]. Consequently, the cellulose acetate butyrate polymer material may be expected to attract esters depending upon their non-polarity.

Considering the tendency of solute separation and its molecular weight, it seems simpler that molecular size plays a major role in solute separation in the case of CAB membranes than steric parameters in cellulose acetate membranes.

2.2 Preparation of the Composite Ion- exchange membranes

The heterogeneous ion- exchange membranes were prepared by the solvent- vaporization method. The preparation proceed by using in a desired quantity of CAB and ZnO was dispersed in 20% solution of dissolving solvent acetone by constant stirring for 3-4 hrs until a thick slurry was obtained. It was spread on a clean, dried glass plate. The glass plate was kept in an electric oven at 80-90°C for about half an hour to remove the solvent. The plate was then immersed in distilled water to detach the membrane in a proper way. Now the prepared membranes were cut in three pieces of equal size. It is dried in incubator at, 60°C, regularly to get constant dry weight. Thicknesses of these membranes are measured with the help of screw gauge having least count 1×10^{-3} cm.

2.3 Characterisation of the membrane

The pre-requisite criterion for understanding the performance of an ion- exchange is its complete physico-chemical characterization, which involves the determination of all such parameters that affect its electrochemical properties. These parameters include membrane water content, porosity, thickness and swelling etc.

2.3.1 Thickness

The membrane thickness value was averaged from nine measurements at different locations on the effective surface region of the membrane by using the screw gauge. The measurements were taken at different sides of the membrane.

2.3.2 Determination of water content

Water content is a physical scaling of membrane property that indicates the degree of hydrophilicity and hydrophobicity of a membrane. Moreover, it is related to the porosity of a membrane. The water uptake of the membranes has a great influence on the proton conductivity, because of proton conduction. However too much water result in the excess swelling of the membrane and the further loss its mechanical property. So the suitable water molecules around the functional groups are necessary.

The water content was measured as the weight difference between the dried state and swollen state of the membranes. The wet membrane was weighed and then dried in an oven at 60°C until the constant weight was obtained. The following equation can be used to calculate the water content.

$$Q_w = [\text{Wet weight} - \text{dry weight}] / \text{dry weight} \quad (1)$$

The samples used for water content studies were in a beaker of 25 mL and conditioned as required. The initial weight and dimensions of samples were first determined and kept immersed in distilled water at room temperature and conditions. The samples were removed at appropriate time intervals, gently blotted with filter paper to remove excess water on the surface, and weighed again. This process was repeated until equilibrium swelling was reached as indicated by constant weight (about 300 min). The data collected were used for further calculations and analysis.

2.3.3 Porosity

Porosity was determined as the volume of water incorporation in the cavities per unit membrane volume from the water content data. The membrane porosity was determined by the mass loss of wet membrane after drying. The membrane sample was mopped with water on the surface and weighed under wet status. Then, the membrane sample was dried until a constant mass.

Table: 1 Time-dependence of Porosity and Compactness of the composite membrane.

Time(min)	Porosity	Compactness
60	0.7293	0.2707
120	0.5932	0.4068
180	0.4643	0.5357
240	0.3418	0.6582
300	0.2258	0.7742

The porosity decreases with the alternate time; this is due to the incorporation of ZnO within the polymer structure leading to the decrease in the occupied volume. Additionally, the void fraction of the Cellulose Acetate Butyrate was decreased with addition of ZnO. These results are consistent with the decrease in water content. The decrease in void volume led to a decreased amount of uptake of water into the structure, causing the water content to decrease in the membrane.

2.3.4 SEM Analysis

It is convenient method which enables to determine the membrane properties such as dimension, shape and the number of pores in a special area of a membrane can be inspected by image processing analysis. Obtained images from the SEM can be used for microscopy structure observation as well as digital image analysing. Prior to SEM imaging (Philips XL30-ESEM), all the samples were cut into small sizes (stubs 12.7mm diameter) and were sputter coated (EMscope Biorad SC500) with a gold and platinum mixture in a vacuum. SEM images were taken at different magnifications: high (scale bar =10µm), medium (scale bar =25 and 50µm), and low (scale bar =100µm) for all samples.

To attain high performance membranes for specific applications, it is essential to manipulate the morphological structures of the membranes; therefore, the morphological studies of various sections of control and surface modified membranes were made by Scanning electron microscope. SEM was used to provide primary characterisation of the prepared membrane morphology [12]. The membranes with a CAB matrix are, on the contrary dense. As can be clearly seen, individual particles are surrounded by the polymer matrix and their interconnections are limited. SEM microphotographs were taken in a high vacuum, hence the particles are dry and contracted and also the cavities between the matrix and the particles may be formed.

The SEM surface image of parchment supported membrane is presented below in diagram. It can be seen that the membrane is heterogeneous in nature as well as dense with visible cracks. SEM image of Cellulose Acetate Butyrate with Zinc Oxide appears to be composed of dense and loose aggregation of small particles and formed pores probably with non-linear channel but not fully inter connected. Particles are irregularly condensed and adopt a heterogeneous structure composed of masses of various sizes.

SEM Photograph of CAB with ZnO	SEM Photograph of CAB
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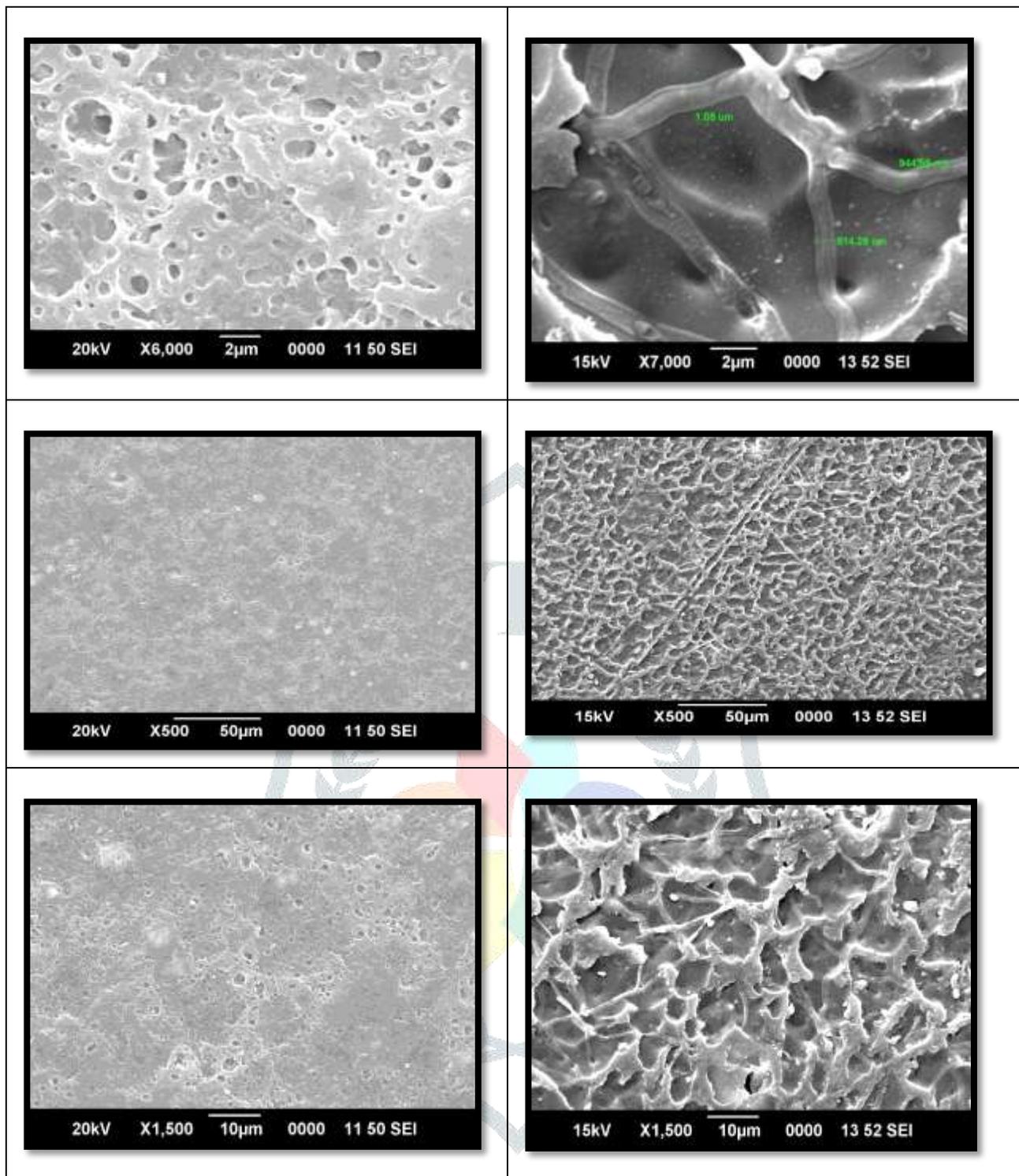


Fig: 1 SEM Photograph of membrane

2.3.5 pH Studies on the Membrane Performance :

Change in pH can increase or decrease membrane surface charge. Even at a certain point membrane surface can be neutral which is nominated as isoelectric point [IEP]. The effect of pH on the solute separation becomes more important. The membrane surface has negative charge, therefore if in this pH range solute appeared negative, high rejection would expect due to electrostatic repulsion between solute and membrane [13].

3. Result and Discussion:

Fig.2 illustrates the water uptake of the membrane; the composite membranes showed a decreasing with the introduction of ZnO. With the increasing of time, the results were collected by the membrane, water uptake decreased with the lost of hydrophilic groups.

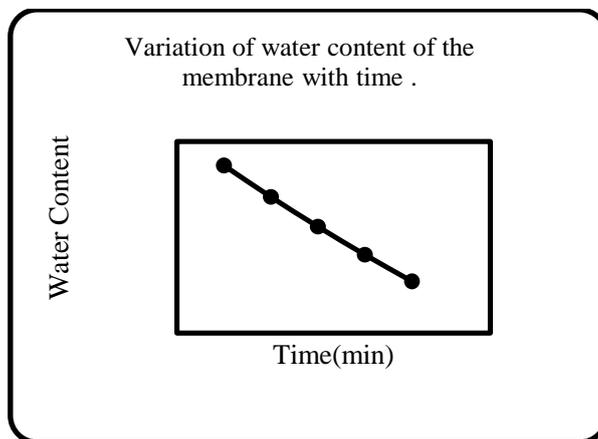


Fig: 2

Several versions of membranes are available that differ by membrane thickness, density of functional groups and the capping groups on the ends of polymer chains. We anticipate that the permeation of water with correlate the volume fraction and inversely with the membrane thickness. The result shows that water content decrease with the time and volume fraction of water in the membrane.

Water uptake of the membranes was rationalized by measuring the change in mass of the membranes before and after the hydration. The presence of water affects the ionic properties as well as the chemical and mechanical stability of the membrane [14].

Table: 2 Time dependence of Water Content of the composite membrane.

Time(in min)	Water Content	Equilibrium Water Content
60	0.39363	0.2824
120	0.31974	0.2422
180	0.25019	0.2001
240	0.1842	0.1555
300	0.12165	0.1079

Equilibrium Water Content, however, decreased significantly with increasing time. The decrease in equilibrium water content confirmed the change of porosity in the support layer after each interval of time, because the surface pores as well as cavities inside the support layer as responsible for accommodating water in the membranes.

The results of water content capacity and equilibrium water content of CAB based ZnO composite membrane are summarized in Table 2. The water content of a membrane depends on the vapour pressure of the surroundings. In case of most of the transport measurements only the membrane water content at saturation is needed, and that too mostly as a function of solute concentration. Thus low order of water content and porosity with thickness of membrane suggests that interstices are negligible and diffusion across the membrane would occur mainly through exchange sites.

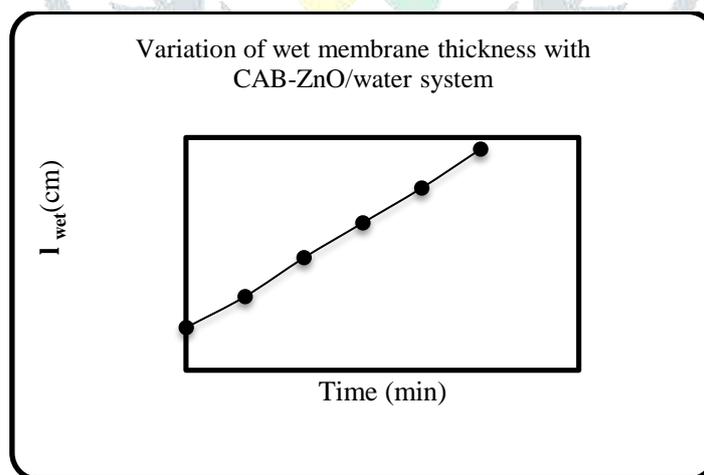


Fig: 3

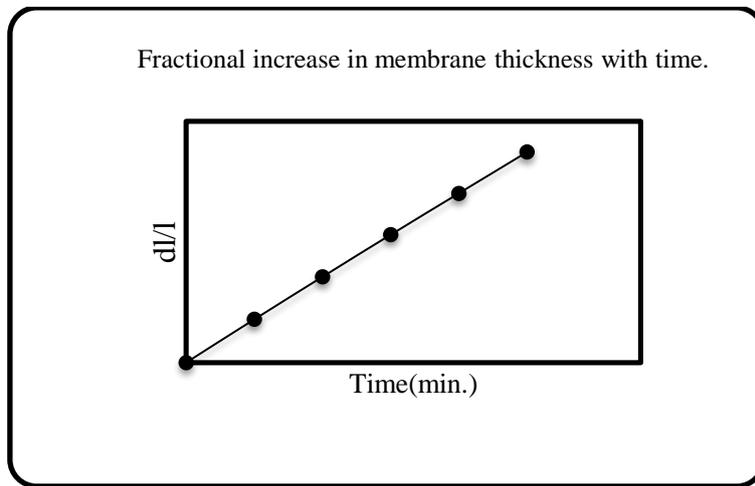


Fig: 4

I_{wet} indicates variation of membrane thickness with time increases means number of layer as a hydration layer increases and resulting in increased membrane thickness.

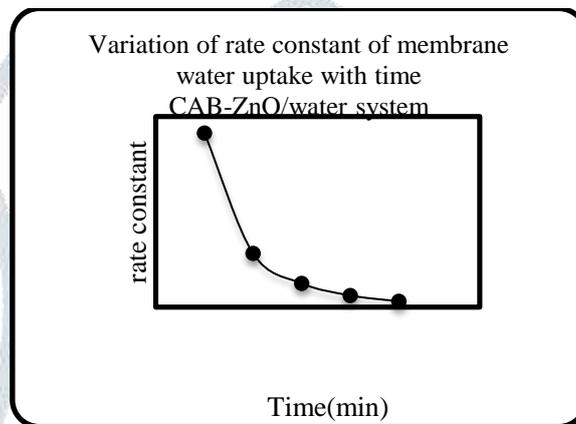


Fig: 5

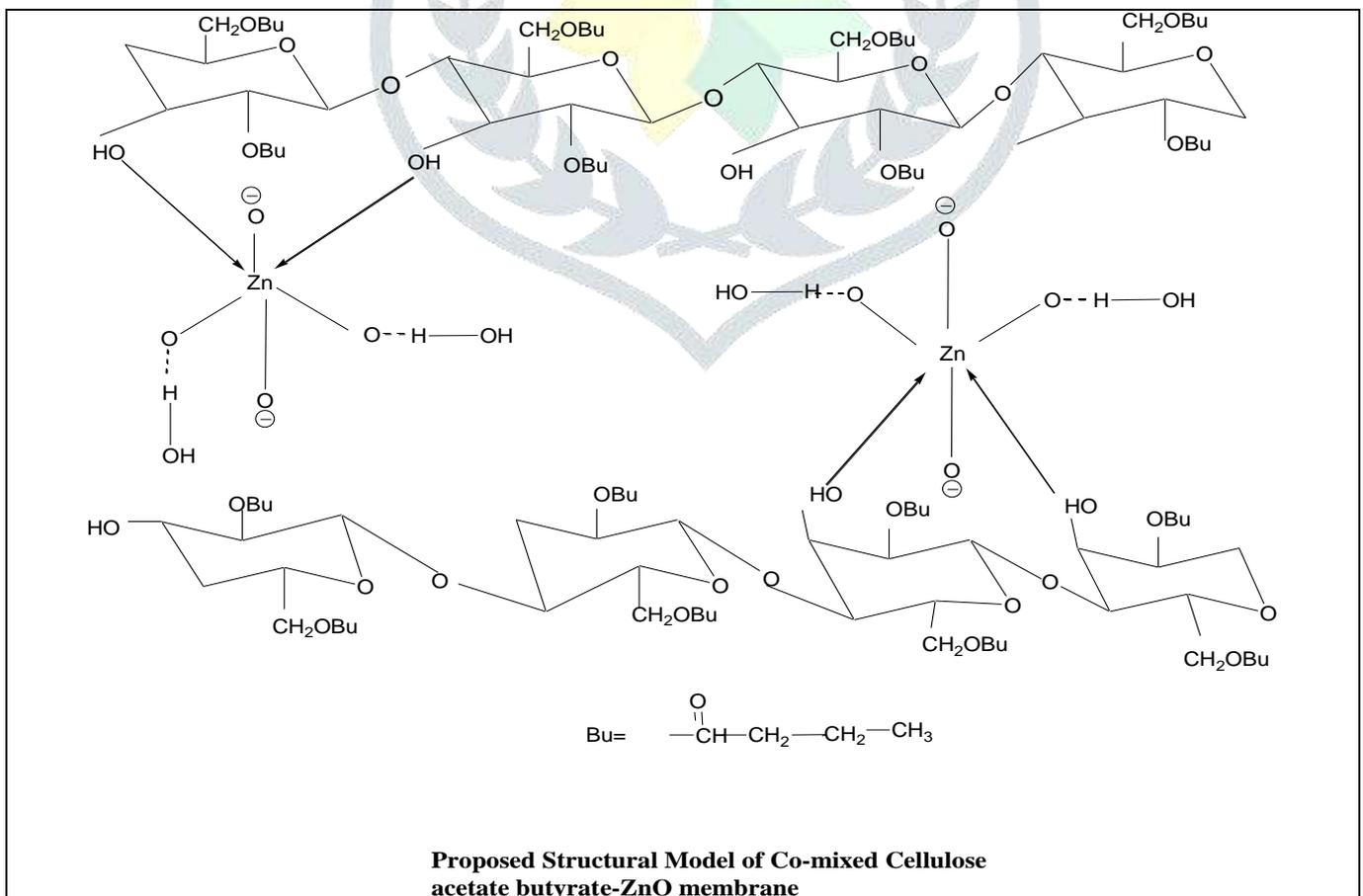


Fig.6

In Figure, when ZnO co-mixed with cellulose acetate butyrate it form composite membrane. The hydroxyl group present on third position of CAB membrane donates its lone pair of electron to vacant d-orbital of Zn atom of ZnO. It form Zn-O co-ordinate bond. Due to formation of co-ordinate bond, the electron density of Zn increased and resulting negatively charged matrix of the composite CAB/ZnO membrane. The composite membrane is expected to be more complicated than CAB without ZnO membrane. The water molecules attached CAB and ZnO membrane with the help of H-bonding. The presence of butyryl, larger and more hydrophobic than acetate, has a strong influence on the permeation performance. ZnO may play the role of a water “binder”, decreasing strongly the amount of free water around the cellulose acetate butyrate.

The adsorption process also depends on the physicochemical characteristics of the aqueous solutions, such as pH.

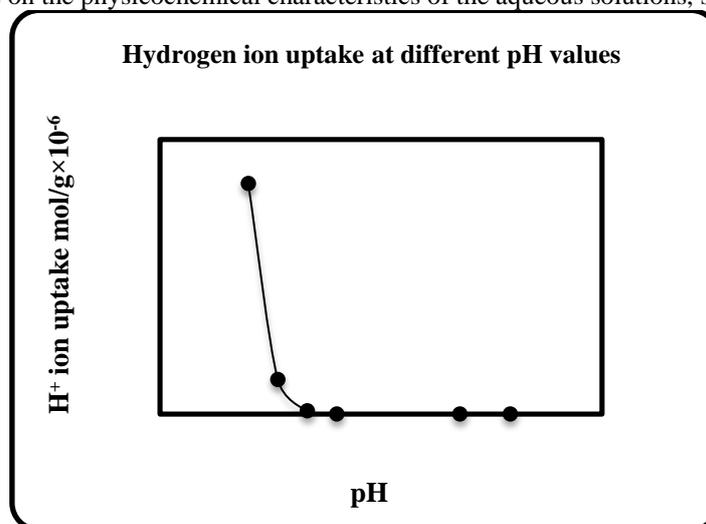


Fig: 7

The cause of the increase in the pH during the experiments without pH-control can be by a rupture of internal hydrogen bonds caused by a swelling of the membrane, followed by the protonation of butyryl groups with water as proton donor. However, as the adsorption process progresses the pH of the solution increases. Since in basic medium less H⁺ ion present in solution therefore the proton binding capacity decreases with increase of pH value. The results reveal that there is an inverse relation between the H⁺ adsorption capacity and the pH of the solution, i.e. the H⁺ ion uptake adsorption capacity decreases when the pH of the solution increases.

Effect of pH on the Membrane Performance:

A very important requirement is that the membranes should be chemically stable when in salt solutions of various pH. The membrane may exhibit an isoelectric point at a specific pH where membrane bears zero charge.

The stability and practical applicability of CAB-ZnO membrane were investigated under different pH conditions. The pH of the solution altered from 3 to 7. The data shows that the H⁺ ion uptake is decreased as the pH increases. It is concluded that the adsorption of H⁺ ion increases at pH 6.1. It denotes that isoelectric point (IEP) of the membrane is 6.1 and at this point, H⁺ ion is not interacted by the membrane.

Table 3: [H⁺] ion uptake at different pH values

(pH) _{initial}	(pH) _{final}	[H ⁺] ion uptake (mol/g)
3.0	3.45	209.75 × 10 ⁻⁶
4.0	5.42	31.27 × 10 ⁻⁶
5.0	5.98	2.91 × 10 ⁻⁶
6.0	6.42	0.02 × 10 ⁻⁶
10.7	10.21	70.641 × 10 ⁻¹¹

Due to the ionic nature of membrane matrix, HCl was dependent of dissolution medium pH. To study the influence of pH on the ion adsorption capacity of the membrane matrix, experiments were conducted at different initial pH values. The study showed that the solution pH strongly affects the adsorption capacity of membrane. Under the conditions examined (pH 3 and 7), hydrogen ion concentration is decreased when the pH increases. The adsorption capacity depends strongly on pH and on the species of ions in the external solution. The optimum pH value for the ion adsorption was found in between 3 and 7.

4. Conclusion

A CAB-ZnO mixed matrix membrane with particles fabricated by the combination of solution blending and solvent-vaporization method. The changes of physicochemical properties of obtained hydrophobic surfaces were determined by measuring the water content, thickness etc. From the results, it was revealed that CAB-ZnO particles constructed a membrane having more hydrophobic, smooth and tightly packed surface.

5. Acknowledgement

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