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Membrane technology for the oriented process relating to the facilitated extraction and recovery of Sucrose, Glucose and Fructose from the sugar industry releases.

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Abstract

Our objective is to develop a new grafted polymer membrane (GPM) for recovering Glucose, Fructose, and Sucrose. The membrane have been developed with amphiphilic molecule extractive agent (Gluconic acid) and characterized. The membrane was adopted to study the oriented process for the selective and facilitated extraction each of these three sugars, as well as the influence of temperature factor on the performance of the studied process through used membrane.

The obtained results were used to determine the values of, macroscopic parameters permeability ***P*** and initial flux J_0, and microscopic parameters, association constant K_{ass} and apparent diffusion coefficient ***D****, related to this oriented process of the facilitated extraction of these substrates through the prepared membrane type (GPM). Similarly, the values of activation parameters (***Ea***, $\Delta H^{\#}$ ***et*** $\Delta S^{\#}$) on the transition state of the step association / dissociation of the substrate **S** with extractive agent **T** to form an unstable

pseudo entity [**ST**], required for the migration of the substrate across the membrane organic phase, were determined and used to explain the results and confirm the mechanism relating to this oriented process.

1) Introduction:

In the sugar industry, various researches are conducted, including research to improve process for the selective elimination of non-sugary substances. At our laboratory, experiments are performed in order to find solutions to the problems of improving and treatment in the sugar industry. These studies are based on membrane processes, which are part of new technologies that can play an important industrial role. The methods allow the extraction, purification, recovery, and recycling of industrial solutions, to accelerate economic development without harming the environment. These works are also carried out to reduce energy and water consumption needed for this important food industry.

Sugar, or sucrose, is an organic molecule composed of carbon (C), hydrogen (H) and oxygen (O). This compound consists of a fructose molecule and a glucose molecule, linked by a glycosidic bridge and these three molecules are naturally present in the chemical composition of the sugar. Sometimes, during the treatment of industrial solutions, the sucrose solution is hydrolyzed by the action of HCl acid, and gives a mixture of the three sugars sucrose, fructose and glucose, which requires the disposal of contaminated syrup. In this context, and in order to purify and enhance this syrup and molasses (a byproduct of crystallization) which contains between 40% and 69% sucrose compound.

2) Experimental and theoretical models:

2-1) Experimental:

a) Preparation and characterization of the membrane:

All chemicals reagents and solvents used were pure commercial products of analytical grade (Aldrich, Fluka, Redel-Dehaene).

The polymer membrane is produced from an initially stable and homogeneous mixture, to which a so-called “phase inversion” is applied.

b) Observation by SEM:

Image taken during the observation by SEM of the PSU membrane with and without carrier, show that the grafting of the AG carrier agent on the PSU changes the structure of the membrane. Indeed, the surface become porous, with relatively uniform pores. Section images show the presence of cavities of different sizes. The addition of the carrier allows the creation of pores within the membrane structure.

c) Characterized by FT-IR:

The membrane was characterized by FT-IR, the specter of PSU /GA membrane shows that all the characteristic absorption bands of the PSU are present with lower absorption intensities. The spectrum also shows the presence of a new band at 1720 cm^{-1} due to the vibration of elongation of the C=O of the carboxylic acid which shows that the extractive agent AG has been integrated into the polymer matrix of the developed membrane.

d) Transport cell:

Experiments of transport phenomenon were performed in cell represented by the diagram in Figure 1. This cell consists of two same volume compartments, separated by membrane (M). The cell is immersed in a water bath (TB), and a multi-agitator can stir at same speed solutions in both compartments.

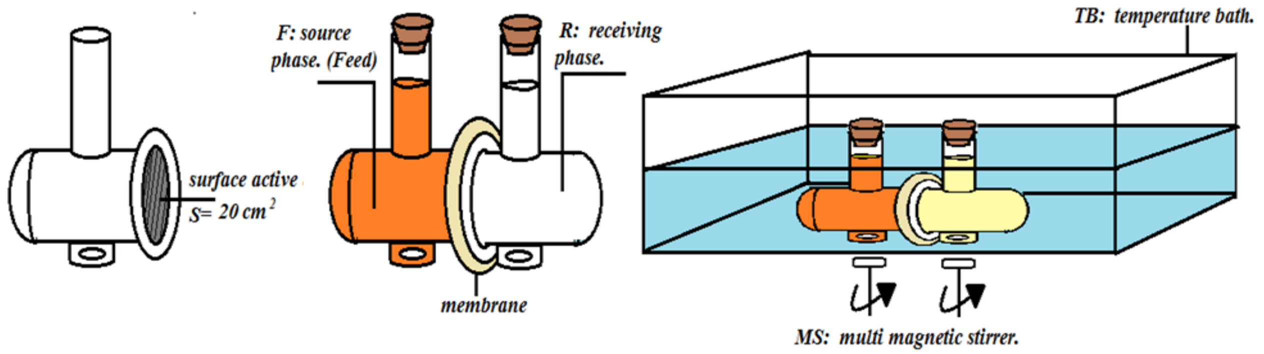


Figure1: Schema of transport cell.

2-2) modeling and theoretical calculations:

The facilitated transport of substrate S depends on the formation and dissociation of the substrate-carrier complex (TS) at the membrane-solution interfaces. The evolution of the term - $\ln(C_0 - 2C_r)$ versus time was studied, with C_r concentrations of substrate in the receiving phase.

a) Calculation of the macroscopic parameters: permeability P and flux J:

The slope (a) of the line – ln (C0 - 2Cr) = f (t), gives the permeability P according to equation: $\mathbf{P = a \times V \times l / 2S}$. **(1)**

With S the membrane surface in contact with the source phase solution, V the receiving phase volume.

The initial flux J_0 can be calculated from the permeability coefficient P by the following equation: $\mathbf{J_0 = P \times C_0 / l}$. **(2)**

l is the membrane thickness.

b) Calculation of the microscopic parameters D* and K_{ass}:

During the migration of complex (TS) through the membrane (rate determining step), the flux J is determined by equation: **$J = (D^*/ l) \times [TS]$. (3),** derived from Fick's first law. In order to determine the microscopic parameters D* and K_{ass}, we use the Lineweaver-Burk method to linearize the expression of equation:

$J_0 = (D^*/ l) \times [[T]_0 \times K_{ass} \times C0 / (1 + K_{ass} \times C_0)]$. (4)

According to equation: **$1/ J0 = (l /D^*) \times [(1 / [T]_0 \times K_{ass}) \times (1 / C0) + (1 / [T]_0)]$. (5)**

And draw the linear representation $1/ J_0 = f (1 / C_0)$.

With: K_{ass} = intercept (OO) / slope (p) and $D^* = (l / OO) * (1 / [T]_0)$.

Determination of activation parameters:

The initial flux is related to temperature factor by Arrhenius law, according to the following equation: **$J_0 (T) = A_j \exp(-E_a/RT)$. (6)**

R is the gas constant (8.314 $J.mol^{-1}.K^{-1}$). Aj a constant (preexponential factor), and E_a is the transition state activation energy on the formation-dissociation reaction of complex (T-S) at the membrane interface.

After linearization we get equation: **$\ln J_0= (-E_a/R)*(1/T) + \ln A_j$. (7)**

Thus the terms of activation energy (E_a) and pre-exponential factor (A_j) are determined from the slope and intercept for the linear function $Ln(J_0)$ versus f(1/T). According to the activated complex theory (Eyring theory), we can calculate the activation parameters, enthalpy ∆H# and entropy ∆S#, according to the expressions in the equation:

$\Delta H\# = E_a – 2500$ ($J. mol^{-1}$) and $\Delta S\# = R (LnA_j -30, 46)$ ($J.K^{-1}.mol^{-1}$) at 298 °. (8)

3**) Results and discussion:**

3-1) Influence of substrate concentration on the facilitated transport of Glucose, Fructose, and sucrose:

a) Determination of the macroscopic parameters: permeability P and flux J:

In this section, we will examine the effect of the initial concentration of substrates on the evolution of macroscopic parameters P and J0. In order to conduct a comparative study, we have realized studies under the same experimental conditions and we have change the initial concentration of substrate from 0.1 to 0.8M.(……) We have found the calculation model is verified and we were able to determine the values of macroscopic parameters P and J0. Figure: 2&3. (…..)

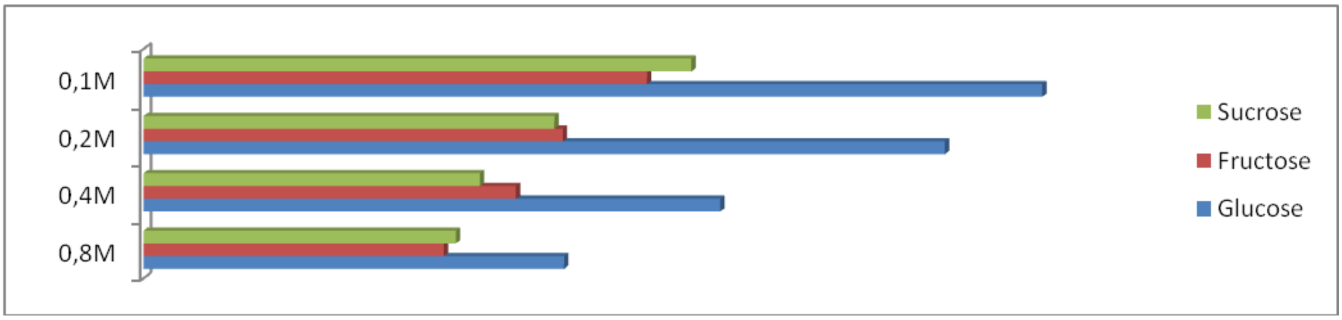


Figure 2: Evolution of permeability P with the initial substrate concentration relating to facilitated transport of Glucose, Fructose, and sucrose.

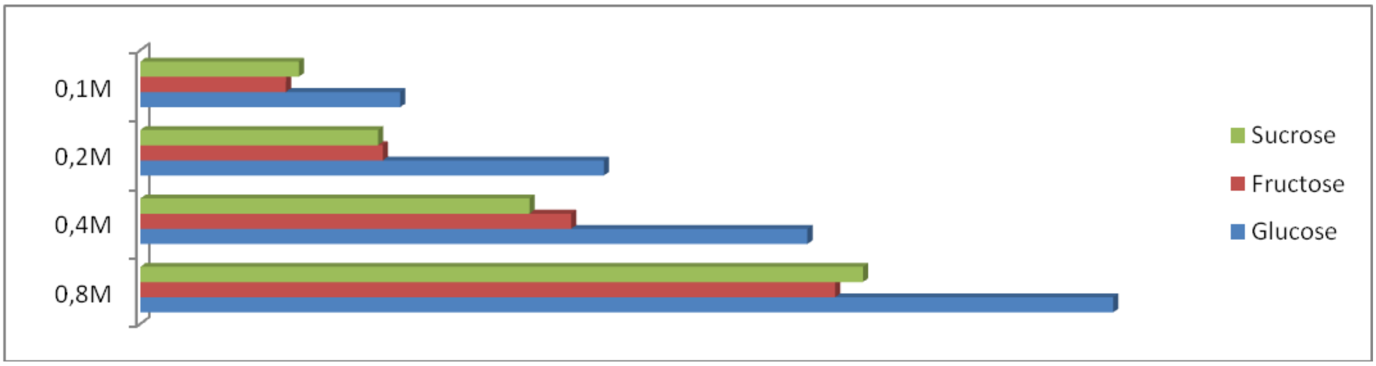


Figure 3: Evolution of initial flux J_0 with the initial substrate concentration relating to facilitated transport of Glucose, Fructose, and sucrose.

b) Determination of the microscopic parameters: apparent diffusion coefficient (D*) and the association constant K_{ass}:

To identify microscopic parameters (coefficients D * and constants Kass), we plotted Lineweaver-Burk lines $1/J_0 = f(1/C_0)$ provided by equation (5), the results obtained are represented by the graph of Figure: 4&5 for the three temperatures studied. (……)

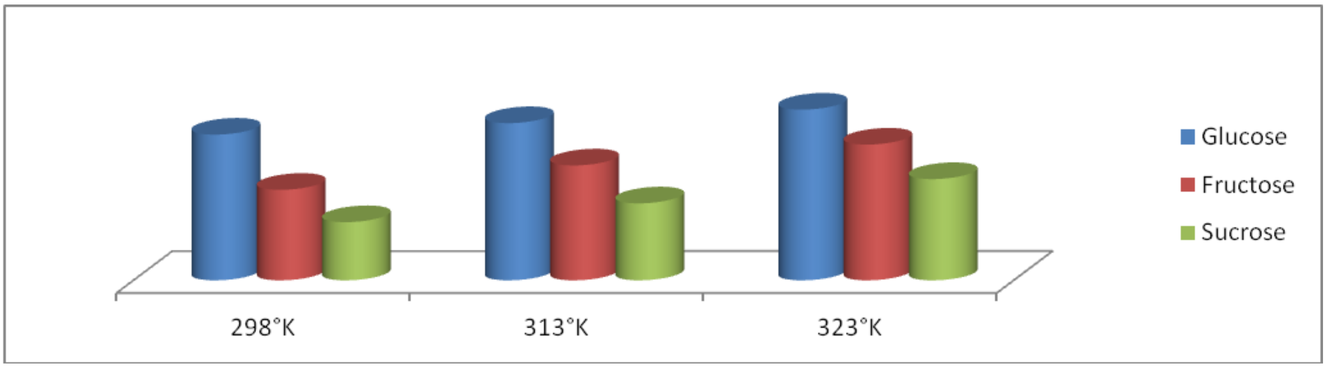
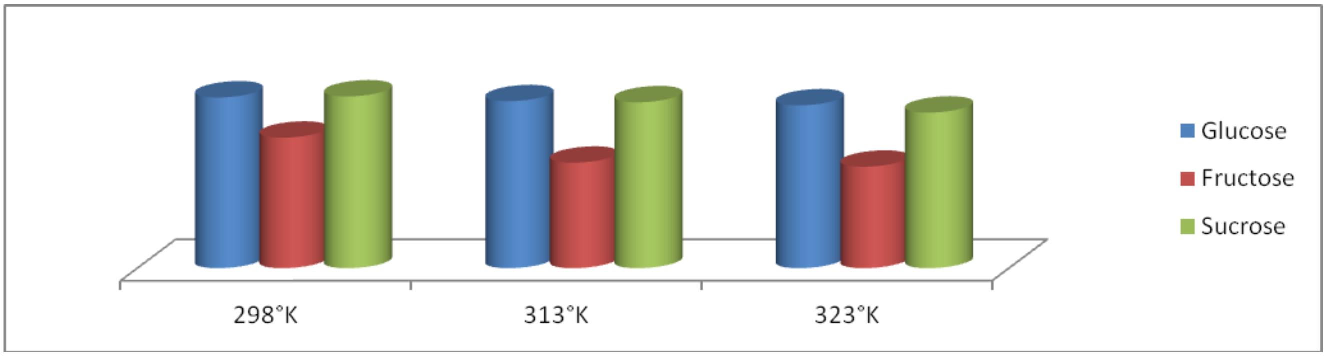


Figure 4: Evolution of apparent diffusion coefficient (D*) relating to facilitated transport of Glucose, Fructose, and sucrose.

The values of coefficients D* provides information on the distribution of free substrate S or as S-T entity through the GPM, so information on movement of substrates during its diffusion through the membrane phase.

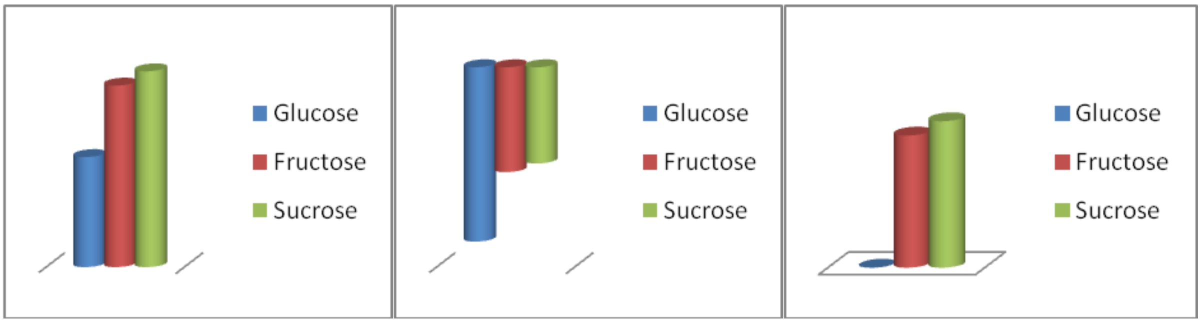


. Figure 5: Evolution of the association constant K_{ass} relating to facilitated transport of Glucose, Fructose, and sucrose.

The association constants K_{ass} provide information about the stability of pseudo-entities formed (S-T) between the substrates and carriers agents used, It means information about the strength and nature of interactions established to form these pseudo-entities S-T.

3-2) Effect of temperature on the facilitated transport of Glucose, *Fructose, and sucrose:*

This extraction process for these sugars with this type of membrane, we remark that transition state of which corresponds to diffusion of these substrates through the membrane requires an average energy (Ea and ΔH≠). Therefore, it has a variable and negative value of activation entropy parameter (ΔS≠) which indicates the transition state is early and depends on the nature of substrates.



Ea (j/ mol) **$\Delta S^{\#}$ $J.mol^{-1}.K^{-1}$** **$\Delta H^{\#}$ $J\ mol^{-1}$**

Figure: 6 the activation parameters for the extraction facilitated of Glucose, Fructose, and Sucrose by the GMP membrane Gluconic acid.

Conclusion:

The results conform well the proposed kinetic model, which allowed us to determine the macroscopic parameters (permeability P and initial flux J_0) for substrates studied. We found that GA carrier forms a stable complex with the Glucose relative to other sugars.

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