SEPARATION OF SOYBEAN OIL FROM ORGANIC SOLVENTS USING POLYMERIC AND CERAMIC MEMBRANES

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Abstract. Membrane processes could enhance performance of oil-extracting plants, combined to conventional separation techniques, decreasing energy consumption. Also, when pressurized fluids are considered for oil extraction, membrane separation could be advantageously used for minimizing the need of solvent recompression. Thus, the aim of this work was to select and explore the application of polymeric and ceramic membranes for the separation of soybean oil from a mixture of this oil in n-hexane and in n-butane. After permeation membranes were characterized by different techniques to assess for membrane modification and fouling caused by the permeation process. The results showed that the tested membranes do not undergo any kind of degradation during permeation. Oil rejections up to 100%, total permeate fluxes of 65.3 kg/m² h were obtained. Oil rejections were higher in the separation of n-butane miscellas, when compared to oil/n-hexane mixtures. There was no change in process performance when an actual industrial miscella was used in place of synthetic miscellas. Fouling on the membrane is also an important issue in such separations, since the characterizations of the membranes showed that traces of oil can be found on the membrane surface, even after several washings with solvent. The present results indicate a possible applicability of membrane technology in vegetable oils processing and biodiesel industries during the solvent recovery step.

Keywords : Ceramic and polymeric membranes, solvent recovery, separation, n-hexane, n-butane.

1. Introduction

Brazil stands out as one of the world's largest producers of food. It features a technologically advanced agriculture, featuring vast extensions of agricultural land, which give rise to a good position in grain production, especially oilseeds. This context makes grain researchers and industries to invest in research, especially with regard to genetic improvement of seeds, in order to oil yield and grain quality obtained, and the development of technology to improve or develop new processes, obtaining products with high quality and high added value.

Soybean is an oil seed originating from northern and central China [1]. Brazil and the United States of America are the major producers of soybeans in the world, but the introduction of this oilseed in these countries was recent (eighteenth and nineteenth centuries). Soybean is primarily a seed grown for industrial extraction of oil and protein [2,3].

In conventional extraction plants of vegetable oil, distillation units, vacuum-operated and other auxiliary equipment using steam or some other form of heat are employed in the processing of oilseeds. A possible thermal degradation of the oil and an incomplete elimination of n-hexane are the major drawbacks of this technology, compared to technology that uses pressurized fluids as solvents in addition to the large amount of energy used in these processing steps [4].

The n-hexane is a relatively inexpensive solvent and is great for extracting nonpolar lipids. However, it has a high volatility and is considered to be toxic to animals and humans in low concentrations. Vapors of n-hexane should be monitored during industrial operation of extraction, since it can cause explosions due to its high flammability. Additionally, if the oil and defatted meal are used in foods, complete removal of the solvent is required [5]

The extraction of oilseeds with high added value by using compressed gas has many advantages. The advantages of using this technology can be summarized in three main aspects: 1) maximum preservation of quality oil due to low temperature used, and therefore it is more suitable for extraction of oil or high-value crops with modified lipid composition, 2) maximum preservation of the quality of brans, with high protein and 3) reduction of the total investment and cost-utility [6].

The membrane separation processes often have advantages over conventional separation procedures, which include energy savings in processing, the selectivity of the compounds obtained, the possibility of separation of thermolabile compounds, simplicity of operation of the system and easily scale a prototype at laboratory scale to industrial scale [7]. The basic parameters for a successful implementation of this technology in oils and fats industry requires special attention to the characteristics of feeding the oil / solvent aging / degradation of the membrane, pre-treatment (conditioning), and providing the process conditions, design sanitary, cleaning and disinfection of the membrane [8]. The energy savings in the application of membrane processes can occur at different stages of the process. The use of steam can be minimized, since the operating temperatures for processing membranes are less than those required in conventional separations. The greatest potential for reducing power consumption in the oil industry, through the use of membrane technology, is the complete or partial replacement of traditional degumming, refining and bleaching. Bleaching and degumming can be combined in a single step which is efficient in terms of energy expenditure. Reducing the loss of oil and solvents used in the bleaching are other advantages of applying the processing membrane in the manufacture of edible oils. A membrane ideal for solvent recovery should combine specific properties such as high oil retention and permeate streams suitable for industrial scale, as well as heat resistance, mechanical and chemically compatible with the process [9].

Nowadays, companies extracting vegetable oil and biodiesel are seeking to maximize energy efficiency in its plants, as well as alternative processes to obtain with higher quality oils. Thus, considering these factors is essential in the development of technology for this industry sector. When pressurized fluids are considered for oil extraction, membrane separation could be advantageously used for minimizing the need of solvent recompression. One of the major limitations for implementation of this technology in the vegetable oil processing is to find membranes that are stable to oil and organic solvents, with high oil retention, high permeate flux and low tendency to fouling.

In this context, the objective of this study was to investigate the separation of soybean oil/n-butane and soybean oil/n-hexane miscellas using ceramic and hollow fiber ultrafiltration membranes, testing the effect of pre-treatment on membrane permeability to n-hexane. This study is part of two researches about new technologies for extraction of essential and vegetable oils using pressurized and liquid fluids [10-12], and the use of the membrane separation process for recovery of solvents used in these processes [13-17]. The final purpose of these works is directed at the application of this technology to aid solvent recovery in the oil extraction plants.

2. Material and Methods

2.1 Experimental apparatus for soybean oil/n-hexane separations

Figure 1 shows the schematic diagram of the experimental apparatus developed for the assays using synthetic and industrial soybean oil/n-hexane miscellas. The membranes and solvents investigated in the conditioning step are presented in Tables 1 and 2, respectively. Transmembrane pressures between 3 to 5 bar and soybean oil/n-hexane mass ratios miscellas of 1:1 e 1:3 (w/w) were studied. The soybean oil was purchased in the local market and a biodiesel producer in the region of Erechim/RS, Brazil, supplied the industrial miscella.

2.2 Experimental apparatus for soybean oil/ n-butane separations

Figure 2 presents the schematic diagram of the experimental apparatus designed for the assays. The system was operated in continuous mode, where the currents of soybean oil and n-butane were mixed at the

entrance of the module with a static mixer (Valco), and the samples were collected at intervals of 10 minutes. Coriolis mass flow meters (Quantum –Brooks Instrument, model QMBM) together with its digital display (Brooks Instrument, model 0254AA1B11A) were installed in the permeate and retentate outlets for the quantification of these two currents.



Figure 1. Schematic diagram of the experimental apparatus used in separations soybean oil/n-hexane. A - Feed bottle containing the miscella (300 mL), B - Gear pump (Micropump, ColeParmer, Model 72211-15), C – Membrane module, D - Manometer (Salvi, 0-16 bar), E - Micrometric valve (NuPro, model SS-4BK), F -Rotameter (Conaut, model 440), G - Thermostatic bath (Marconi), H - Temperature sensor (PT-100).

Table 1. Membrane specifications	s of the manufacturer Pall Co.
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 Class ^a	Membrane material	Trade name	MWCO ^b	Permeation area (m ²)	pH range (25 °C)
UF	Zircon	S700-01446	5 kDa	0.0055	0-14
 UF	Zircon	S700-01447	10 kDa	0.0055	0-14

^a UF: ultrafiltration.

^b MWCO: molecular weight cut-off.

Table 2. Solvent information.			
Solvent ^a	Supplier		
n-hexane	Cinética Ltda		
ethyl alcohol	Vetec Química Fina		
	Ltda.		
n-propyl alcohol	Nuclear Ltda.		
n-butyl alcohol	Nuclear Ltda.		
^a All solvents were analytical grade			

2.3 Membrane conditioning

Preliminary assays have shown the need for a conditioning step of ceramic membranes prior to use, since no permeate flux was obtained using n-hexane when compared to the water at the feed. This behavior was attributed to the hydrophilic character of membranes. Thus, pre-treatments have been investigated for the conditioning before separations oil/solvents.

The experimental procedure for conditioning was initiated by the permeation of a homologous series of alcohols of different chain lengths (ethyl, n-propyl and n-butyl alcohols). The conditioning was started letting the membrane in contact with the respective alcohol for 24 hours. The alcohol flux was measured at transmembrane pressures from 2 to 6 bar. The alcohol was then exchanged for n-hexane and after 24 h the hexane flux was measured.



Figure 2. Schematic diagram of the experimental apparatus used in separations soybean oil/n-butane: A – thermostat bath, B - n-butane cylinder, C - syringe pump, D - liquid pump, E – sample flask, F – micrometric valve needle, G – check valve, H - ball valve, I – analogue pressure indicators, J - static mixer, K – micrometric needle valves, L - flow meters; M - glass collectors and N – membrane separation module.

2.4 Assays for separation of miscellas soybean oil/n-hexane

After membrane conditioning, the assays of separation of industrial miscella and synthetic miscellas of refined soybean oil/n-hexane were carried out in mass ratios oil/n-hexane 1:3 and 1:1 (w/w) and the transmembrane pressures (TMP) of 3, 4 and 5 bar. The pressurization was performed restricting the valve E of the system (Fig. 1). The feed flow rate was 120 kg/h. The flow rate was measured with a flow meter placed at the exit of retentate and converted to mass flux using the density of the miscella measured at the operating temperature in a digital densimeter (Anton Paar, model DMA 4500). All separation tests were performed in duplicate and at 25 °C. Variations in the results were below 10%.

The permeate samples were periodically collected in test tubes. During sample collection, the tube was immersed in an ice bath and immediately after sampling the tube was stoppered to avoid evaporation of n-hexane. The samples were then weighed on an analytical balance (Shimadzu, model AY220). The permeate flux was calculated by dividing the mass of permeate by the sampling time and the area of the membrane.

The concentrations of the feed and permeate streams were estimated by measuring the density of the miscella in a digital densimeter at 25 °C using a calibration curve. The rejection coefficient (retention) was calculated dividing the difference between the feed and permeate concentration by the feed concentration, then multiplying by 100.

2.5 Assays for separation of miscellas soybean oil/n-butane

The experimental procedure of this step is described in a previous work of the group [14]. Table 3 presents the experimental conditions used in these the separations.

Soybean oil/n-butane ratio (w/w)	Pressure (bar)	TMP (bar)
1:3	5, 7 e 10	2, 4 e 5
1:1	5, 7 e 10	2, 4 e 5

Table 3. Experimental conditions used in the separations of soybean oil/n-butane miscellas.

3. Results and Discussion

3.1 Membrane conditioning

Figure 3 presents the permeate fluxes of alcohols investigated in the conditioning of ceramic membranes. Fluxes obtained for ethyl alcohol varied between 9.5 and 25.6 kg/m² h; for n-propyl alcohol between 3.2 and 14.8 kg/m² h and for n-butyl alcohol between 3.8 and 14.2 kg/m² h, using a 5 kDa ceramic membrane with TMP's of 2, 4 and 6 bar.



Figure 3. Alcohol fluxes after the conditioning of the ceramic membrane (5 kDa).

The fluxes of n-hexane obtained after the conditioning of 5 kDa membrane in alcohols with different chain lengths are shown in Figure 4.



Figure 4. Fluxes of n-hexane after the conditioning of the ceramic membrane (5 kDa) with the different alcohols.

There was no expressive difference in the fluxes results of n-hexane permeated after conditioning of the ceramic membrane (5 kDa) in ethyl alcohol and n-butyl alcohol, and those yielded the highest n-hexane fluxes. Thus, due to availability and lower cost, ethyl alcohol was used in the conditioning. For the ceramic membrane of 10 kDa the same behavior of fluxes was observed (data not shown).

3.2 Separations of synthetic miscellas soybean oil/n-hexane

Figures 5 and 6 present the soybean oil rejection and total fluxes (oil + n-hexane) for the ceramic membranes (5 and 10 kDa) at the feed mass ratios of 1:3 and 1:1 (w/w).

In practically all pressures investigated, for both membranes and mass ratios, a different behavior to that observed in the literature was obtained, i.e., a decrease in rejection and an increase in the total flux with the permeation time.

Soybean oil rejections ranging between 26.8 and 40.0% (1:3 w/w) and 8.0 to 22.5% (1:1 w/w) with a total flux between 4.3 and 4.6 kg/m² h (1:3 w/w) and 0.7 to 2.8 kg/m² h (1:1 w/w) were obtained with the 5 kDa membrane.



Figure 5. Soybean oil rejections (left) and total permeated fluxes (right) for 5 kDa membrane.

For 10 kDa membrane, oil rejections ranging from 23.6 to 32.6% for the mass ratio 1:3 (w/w) and 9.3 to 11.8% (1:1 w/w) with total permeated fluxes from 5.4 to 8.1 kg/m² h (1:3 w/w) and 1.4 to 3.1 kg/m² h (1:1 w/w) were obtained.



Figure 6. Soybean oil rejections (left) and total permeate fluxes (right) for 10 kDa membrane.

Basso et al. [18] also showed an increase in the permeate flux with time, using a commercial alumina ceramic membrane with 0.01 mm (Selb, permeation area 0.2 m^2 and 19 channels) in degumming miscellas of soybean oil/n-hexane. These authors state that this behavior can be attributed to residual incrustation, which was not detected by the flux of pure n-hexane measurements, after the cleaning procedure. They also explain that the initial permeate flux was low probably due to the electrostatic interactions between the triacylglycerols, phospholipids and minor components of soybean oil with the surface of the membrane, which had hydrophilic character. As for the deposition of material on the membrane surface, a decrease of polar interactions with the components in the feed is noted, thereby resulting in an increase on the permeate flux.

In our study, it is believed that the increase of permeate flux with time may have occurred for the same reasons explained by Basso et al. [18], despite the structural differences of the membranes. Kong et al. [19], Ribeiro et al. [20], Tres et al. [14] and White and Nitsch [21] reported that an increase in rejection is often observed in the separation of vegetable oils containing organic solvents, due to the increase in the polarization

layer and fouling of the membrane, which increases the resistance to permeation [22]. In this study the phenomena of concentration polarization can be smaller than the incrustation as described previously [15].

The increase in the feed concentration for most of the experimental conditions decreased the total permeates flux due to the largest effect of concentration polarization and fouling. The increase in the feed pressure in the more diluted mass ratio (1:3 w/w) led to an increase in the total permeates flux in the conditions investigated in this study. Similar behaviors with the rejection occur, i.e., a reduction of rejection where the pressure increase was observed in most of the studied conditions.

As expected, the rejection of oil for the 5 kDa membrane was higher than those obtained with the 10 kDa membrane, the opposite effect was observed for the permeate flux, for the larger pores of the latter.

3.3 Separations of industrial miscellas of soybean oil/n-hexane

The industrial miscella is defined as the miscella rich in solvent with all constituents of the soybean oil (waxes, gums, phospholipids), removed in the first stage of extraction of oil from soybeans comprising 21% of oil and 79% of n-hexane measured with a digital density meter.

Figures 7 and 8 show the oil rejections and the total permeate flux of the ceramic membranes 5 and 10 kDa, respectively, fed with industrial miscella. Rejections of the mixture containing the vegetable oil and its minor compounds (waxes, gums, phospholipids) ranged from 7.7 to 16.9% while the total permeate flux ranged from 3.2 to 4.5 kg/m^2 h using the 10 kDa membrane.



Figure 7. Rejections (left) and total permeate flux (right) obtained with the 10 kDa membrane and the industrial miscella in the feed.

For the 5 kDa membrane, rejections from 18.0 to 25.4% with total permeated fluxes from 2.2 to 5.4 kg/m² h were obtained (Figure 8).



Figure 8. Rejections (left) and total permeate flux (right) obtained with the 5 kDa membrane and the industrial miscella in the feed.

A decrease in the rejection over the time is observed. This may be due to the presence of phospholipids, which act as surfactants, increasing the permeability of the oil through the hydrophilic membrane. An increase in the total permeates flux and in the rejection with an increase in the pressure is observed for the most assays.

Comparing the performance of the ceramic membranes in the desolventization of synthetic miscellas with the industrial miscella, similar results were obtained for rejection and for total permeate fluxes, showing the potential of use membrane processes in the desolventization step.

3.4 Separations of synthetic miscellas of soybean oil/n-butane

Figures 9 and 10 present the results of rejection and total flux for the 5 kDa membrane with different feed concentrations. Oil rejections between 98.1 and 100.0% (1:3 w/w) and 96.4 and 99.7 (1:1 w/w) with an oil flux ranging from 0.02 to 0.2 kg/m² h (1:3 w/w) and 0.03 to 0.3 kg/m² h (1:1 w/w) were observed for this membrane.



Figure 9. Rejection (left) and soybean oil flux (right) for the permeation of a soybean oil/n-butane mixture in mass ratio 1:3 (w/w) through a 5 kDa ceramic membrane.



Figure 10. Rejection (left) and soybean oil flux (right) for the permeation of a soybean oil/n-butane mixture in mass ratio 1:1 (w/w) through a 5 kDa ceramic membrane.

Figure 11 and 12 present the results of rejection and total flux for the 10 kDa membrane with different feed concentrations.

For the 10 kDa ceramic membrane, high rejection values were also obtained, but these were lower than those obtained with the 5 kDa membrane, as expected. Oil rejections between 84.1 and 97.0% (1:3 w/w) and 89.9 to 100.0% (1:1 w/w) with oil permeate flux ranging from 0.3 to 1.4 kg/m² h (1:3 w/w) and 0.01 to 1.0 kg/m²h (1:1 w/w) were observed for this membrane.

The literature presents no studies about separation of vegetable oils and pressurized n-butane, but the previously published by the group, involving flat sheet polymeric membranes [14]. Only studies dealing with systems where the CO_2 was used as solvent can be found. Rodriguez et al. [23] carried out the ultrafiltration of the lubricating oil used in engines with or without pressurized CO_2 using ceramic membranes with pore diameters between 50 and 300 kDa. The results indicated that an increase in operating pressure and TMP increased the oil flux permeate (100 bar, 60 °C, TMP 1 bar). The authors found that the fouling observed in the membranes only occurs when they worked below the CO_2 critical pressure (74 bar), assuming that the separation takes place in the pores of the membrane by reducing the pressure and shear stress. The CO_2 gas bubbles grow into the pores of the membrane, thus blocking them. This kind of fouling is irreversible, even if supercritical conditions of operation are used. The results for oil fluxes obtained in this study are comparable to those reported for commercial nano and ultrafiltration flat sheet and inorganic membranes [20,24].



Figure 11. Rejection (left) and soybean oil flux (right) for the permeation of a soybean oil/n-butane mixture in mass ratio 1:3 (w/w) through a 10 kDa ceramic membrane.



Figure 12. Rejection (left) and soybean oil flux (right) for the permeation of a soybean oil/n-butane mixture in mass ratio 1:1 (w/w) through a 10 kDa ceramic membrane.

Although a direct comparison of the performance of polymeric membranes and ceramic membranes at a concentration of vegetable oil solutions in organic solvents is complicated, due to the great difference in the properties of the material forming the membrane, it is interesting to draw a comparison with previous results of the group. In a previous work, Tres et al. [14], using six flat sheet commercial ultrafiltration membranes for the separation of refined soybean oil/n-butane miscellas, obtained similar results. The best oil rejection was obtained with a 4 kDa polymeric membrane (99.1%) with a oil permeate flux ranging from 0.03 to 0.2 kg/m² h at 20 bar of feed pressure and TMP of 10 bar. The membrane of 5 kDa showed the highest soybean oil flux (1.0 to 2.7 kg/m² h), with feed pressure of 25 bar and TMP of 1 bar, while the oil rejection was lower (66.9%, 1:3 w/w). With the mass ratio oil/n-butane of 1:1 (w/w), the 4 kDa membrane showed the highest oil rejection (91.8%) at 25 bar and TMP of 1 bar. Under these conditions, the flux of oil ranged from 0.31 to 0.06 kg/m² h.

For a 5 kDa membrane the highest rejection obtained was 80.7% with 10 bar and TMP of 1 bar, with an oil permeate flux from 0.7 to 0.2 kg/m² h.

3.5 Comparison between calculated rejections for mass and concentration

Assessment of the n-butane fluxes using a rotameter for measuring the gas flow rate is very inaccurate because of the lack of precision and large solubility of the n-butane in the oil at atmospheric pressure. Due to the solubility of the n-butane in the oil, part of the solvent was still in the liquid phase after expansion in the sampling vial, and thus not measured in the rotameter.

This problem has been solved by installing two mass flowmeters, in the outlet of the retentate and the permeate outlet, before the depressurization valve. Thus, the flowmeter indicated the flux of the mixture before expansion. Moreover, with this measurement, the concentration could be used to calculate the oil rejection, rather than the mass of oil collected.

Tables 4 and 5 present the total, oil and n-butane fluxes, and the experimental error when comparing these parameters calculated by oil mass and by oil concentration, for the 5 and 10 kDa membranes, respectively.

 Table 4. Total, oil and n-butane fluxes and experimental error when comparing these parameters calculated by mass and concentration for the 5 kDa membrane.

5 kDa (1:3 w/w)						
P	ressure and TMP	J _p Total	J _p oil	J _p n-butane (kg/m ² h)	Error (%)	
		$(kg/m^2 h)$	$(kg/m^2 h)$			
5	5 bar TMP 2 bar	9.59	0.03	9.56	11.98	
5	5 bar TMP 4 bar	10.88	0.01	10.87	14.67	
1	0 bar TMP 2 bar	5.44	0.04	5.40	5.55	
	5 kDa (1:1 w/w)					
P	ressure and TMP	J _p Total	J _p oil	J _p n-butane (kg/m ² h)	Error (%)	
		$(kg/m^2 h)$	$(kg/m^2 h)$	-		
5	5 bar TMP 2 bar	5.21	0.01	5.20	14.97	
5	5 bar TMP 4 bar	6.16	0.04	6.12	15.00	
5 1	5 bar TMP 4 bar 0 bar TMP 2 bar	6.16 5.27	0.04 0.03	6.12 5.24	15.00 14.36	

 Table 5. Total, oil and n-butane fluxes and experimental error when comparing these parameters calculated by mass and concentration for the 10 kDa membrane.

10 kDa (1:3 w/w)					
Pressure and TMP	J _p Total	J _p oil	J_p n-butane (kg/m ² h)	Error (%)	
	$(kg/m^2 h)$	$(kg/m^2 h)$	1		
5 bar TMP 2 bar	42.97	0.57	42.40	5.20	
5 bar TMP 4 bar	25.78	1.39	24.39	12.05	
10 bar TMP 2 bar	15.76	0.50	15.26	13.35	
10 kDa (1:1 m/m)					
Pressure and TMP	J _p Total	J _p oil	J _p n-butane (kg/m ² h)	Error (%)	
	$(kg/m^2 h)$	$(kg/m^2 h)$	•		
5 bar TMP 2 bar	15.76	1.15	14.61	10.44	
5 bar TMP 4 bar	17.19	1.14	16.05	15.14	
10 bar TMP 2 bar	17.05	1.05	16.00	14.66	

As it can be seen in Tables 4 and 5, differences in the mass balance in the system oil/n-butane less than 16% were obtained for both membranes in the experimental conditions investigated. Total fluxes between 5.21 and 18.48 kg/m² h with oil fluxes from 0.01 to 1.40 kg/m² h and n-butane fluxes between 5.20 to 42.40 kg/m² h were observed for both membranes and mass ratios investigated.

Comparing the results with previous works of the group [14,16,17], the system oil/n-butane has always resulted in higher oil rejections compared to the system oil/n-hexane. This behavior may be related to the coexistence equilibrium curve of the oil/n-butane phase equilibrium [25]. Depending on feed pressure and on overall composition of the system, the system can be operating with a mixture in the vicinity of the line of coexistence of phases. Thus, the inherently higher compressibility displayed by mixing in such condition, and the possible expansion due to the increased volume of the system by the presence of pores, can cause the vaporization of more volatiles and fluid, then leading the system into the biphasic region, causing the partitioning of phases, reducing with a result of these two effects the solubility of the oil in the solvent and hence the drag of the transmembrane solute.

4. Conclusions

In this work soybean oil rejections between 8.0 to 100% (5 kDa) and 9.3 to 100% (10 kDa) with an oil flux between 0.01 to 4.6 kg/m² h (5 kDa) and 0.01 kg/m² h to 8.1 kg/m² h (10 kDa) were observed for the miscellas investigated.

n-Butane fluxes varied from 5.2 to 42.4 kg/m² h for both membranes and experimental conditions investigated. Differences in the mass balance of the system oil/n-butane smaller than 16% were obtained for both membranes in the experimental conditions investigated.

As previously mentioned, the literature provides only few studies of separation of vegetable oil from nbutane by membrane separation processes. Thus, we highlight the pioneer nature of this work and importance of this to the literature.

Acknowledgements

The authors thank CNPq, FAPERGS, Intecnial S.A. and URI - Campus Erechim for financial support and scholarships.

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