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Polyacrylonitrile/starch semi-biodegradable blend membrane: preparation, morphology and performance

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ABSTRACT

In the present study, semi-biodegradable membrane of polyacrylonitrile was prepared by immersion precipitation technique, whereas starch, sorbitol, 1-methyl-2-pyrrolidone and water were used as natural biodegradable polymer, additive, solvent and non-solvent, respectively. Experiment design was done by response surface methodology. Effects of three parameters including starch and sorbitol concentration and coagulation bath temperature (CBT) were investigated on the membrane morphology, contact angle, biodegradability, pure water flux, as well as treatment ability. The results revealed that increasing CBT and concentration factors led to improvement in membrane porosity and thickness. Furthermore, membrane wettability and biodegradability were principally influenced by starch concentration. All three parameters were found to have direct effects on PWF and reverse effects on rejection of pollution indices of the raisin wastewater during the treatment process.

Keywords: Polyacrylonitrile; Membrane; Starch; Biodegradability; Response surface methodology

1. Introduction

Remediation of wastewater is known as a significant task for environmental processing. Among various techniques, membrane separation processes offer a number of advantages in terms of less energy requirements, environmental impacts and capital investments. The most significant part of a membrane separation process is the membrane itself. Also, polymeric membranes are the most commonly used elements in the membrane processes [1].

The majority of polymeric membranes with asymmetric structure have been prepared by phase inversion method [2]. In fact, all polymers can be used as barrier or membrane material but only a limited number of them are used in practice, since they show big differences in their chemical and physical properties. Generally, various polymers such as cellulose and its derivatives (like cellulose acetate), polysulfone, polyethersulfone, polyacrylonitrile (PAN), polyvinylidene difluoride, poly (vinyl chloride), polyetherimide and so on could be used to prepare membranes through phase inversion method [3].

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Over the past two decades, biodegradable polymers have been attracting more attention, primarily, for two major reasons: environmental concerns and the realization that our petroleum resources are finite. Thus, many efforts have been done to substitute petro-based polymers by biodegradable ones with similar properties in a low cost and effective manner [4]. According to the previous studies, applying biodegradable polymers in membrane preparation is mostly contributed to chitosan [5–9] and after that poly (lactic acid) [10–12]. Starch is a natural, popular and cheap biodegradable polymer produced in abundance from many renewable resources. Moreover, starch has good film-forming ability that makes it a suitable candidate for preparation of a degradable or semi-degradable film in different applications. However, in a limited number of studies, starch was used for the membrane fabrication [7,13]. These membranes were symmetric and their different properties were analyzed along with their permeabilities. Moreover, Yang and Tsai [14] studied preparation of green tubular membrane substrate by addition of starch to the ceramic membrane by the purpose of improving the final membrane porosity and permeability.

Apparently, no previous study considered the effects of blending starch as a biodegradable hydrophilic polymer with a conventional polymer of PAN for the preparation of an asymmetric membrane applicable in separation processes.

In the present study, starch was blended with PAN by different ratios in order to improve both the final membranes hydrophilicity and the degradability. Membranes were prepared using phase inversion method induced by immersion precipitation technique. The effect of coagulation bath temperature (CBT), starch concentration and sorbitol concentration was discussed in terms of different membranes characteristics including membrane morphology, contact angle (CA), biodegradability, pure water flux (PWF), as well as treatment ability. Response surface methodology (RSM) technique was applied to evaluate the effect of each parameter on the mentioned membranes characteristics.

2. Experimental

2.1. Materials

PAN with molecular weight of 150,000 g/mol was supplied by Sigma-Aldrich. Starch and 1-methyl-2-pyrrolidone (NMP) were prepared from Merck, Germany. Also, Sorbitol, the plasticizer, with an average molecular weight of 182.17 g/mol was obtained from Sigma–Aldrich. Raisin wastewater was sampled from a local raisin factory. The wastewater characteristics were as below:

Turbidity (NTU): 433.6, TDS (mg/l): 1.94 and COD (g/l): 6.54.

2.2. Preparation of membranes

Various PAN/starch/sorbitol/NMP solutions were prepared while combined concentration of PAN and starch was fixed (12 wt.%) for all solutions. The solutions had been stirred continuously to get a homogeneous mixture. Then, they were allowed to stand overnight before casting for degassing. The solutions were casted at room temperature on a glass plate by spreading with a film applicator. Afterwards, the glass plate was immersed in a coagulation bath to complete the phase separation. The coagulation medium was double distilled water. Finally, the membranes were dried and kept to be tested. The casting solutions compositions besides the applied CBT for preparation of the membranes are declared in Table 1.

2.3. Membrane characterization

2.3.1. Scanning electron microscopy

Cross-sectional images of the prepared membranes were inspected using a scanning electron microscope (Philips-XL30). Thus, all samples were soaked and frozen in liquid nitrogen and then fractured. After plated with gold, they were transferred into the microscope.

2.3.2. Contact angle

To measure CA, an instrument (G10, KRUSS, Germany) was used to evaluate the membranes hydrophilicity. Deionized water was also utilized as the probe liquid. To minimize the experimental error, CA was measured at three points of each sample and the average of three values was reported.

2.3.3. Degradation tests

Compost and soil burial tests were carried out to examine the biodegradability of the prepared membranes. The dried membrane samples were cut into 35 by 35 mm square. Then, they were weighed and placed into fresh compost containing 60 ± 2% moisture and also soil containing 30 ± 2% moisture in room temperature and in a controlled atmosphere. The samples were periodically taken out of the test environment and, carefully washed with distilled water and then dried in oven to achieve a constant weight.

Table 1
Preparation variables and characterization of prepared membranes

Synthesized membrane	Preparation variables			Prepared membranes characterization						
								Rejection (%)		
	CBT (˚C)	Starch (wt.%)	Additive (wt.%)	CA (˚)	Weight loss in compost (%)	Weight loss in soil (%)	PWF (l/m^2 h)	Turbidity	COD	TDS
M1	0	0	5	64.8	2.4	0.5	756	69.4	71.7	27.3
M2	40	0	5	62.3	2.1	0.8	1,152	63.1	60.2	5.7
M3	0	30	5	51.75	16.5	10.4	1,250	67.7	69.4	26.8
M4	40	30	5	50.6	17.6	10	1,400	58.5	49.5	1.03
M5	0	15	0	55.4	12.2	5.4	756	72.2	72.5	33.5
M6	40	15	0	53.08	12.5	5.1	1,296	63.6	62.2	6.2
M7	0	15	10	54	12.5	5.9	1,224	63.3	60.7	6.7
M8	40	15	10	51.8	12	5.4	1,400	56.3	43.1	1.03
M9	20	0	0	72.7	0	0	648	71.2	74.8	30.4
M10	20	30	0	52.5	16.7	11.1	1,152	67.9	68.3	24.7
M11	20	0	10	64.1	2.2	0.9	936	61.2	55.6	13.4
M12	20	30	10	51.85	22	12.5	1,620	58.2	50.8	8.2
M13	20	15	5	52	14.8	4.8	1,260	59.6	52.7	12.4
M14	20	15	5	52.3	15.4	4.6	1,150	58.9	52.6	11.8
M15	20	15	5	51.85	15	5	1,210	59.3	52.3	10.8

The membranes weight loss after three months were reported to evaluate the degradation extent.

2.3.4. Membrane performance evaluation

The prepared membranes performance was investigated based on measuring pure water permeability and wastewater treatment ability. For this purpose, a laboratory scale cross-flow filtration unit was used. The details of the experimental set-up are shown in Fig. 1. Each flat sheet membrane was first precompressed with pure water at transmembrane pressure (TMP) of 7 bar for 1 h. Then, the PWF was evaluated at TMP of 7 bar and room temperature. Applying raisin wastewater as feed solution, the membrane ability in reducing three different pollution indices of turbidity, chemical oxygen demand (COD) and total dissolved solids (TDS) was analyzed. All the experiments were carried out twice and the average results were reported.

2.4. Experimental design

RSM is a useful technique in designing experiments for evaluating the effects of several factors influencing responses by varying them simultaneously

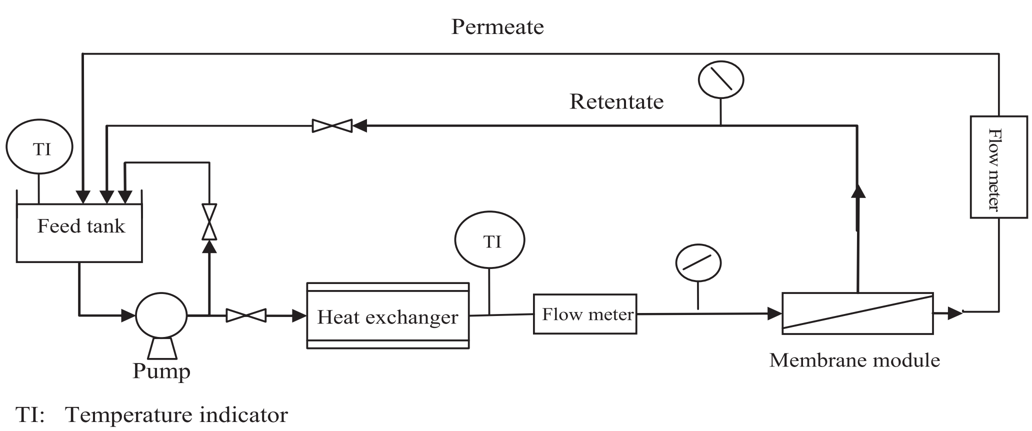

Fig. 1. Schematic diagram of the experimental set-up.

and carrying out a limited number of experiments with the objective to optimize the response as opposed to the conventional method of optimization that involves varying one parameter at a time while keeping the others constantly [15].

R^2-value is the percentage of total variation in the response that is explained by predictors or factors in the model. Higher R^2-value, closer to 1, represents the model that better fits data. The adjusted R^2-value is particularly useful when models with different numbers of terms are compared. Adjusted R^2-value is a modification of R^2-value that adjusts for the number of explanatory terms in a model. Unlike R^2-value, the adjusted R^2-value increases only if the new term improves the model more than what would be expected by chance. Its absolute value will always be less than or equal to R^2-value.

The response surface design development is based on Box–Behnken design. In this study, there were three factors of CBT, starch and additive concentration, each at three levels (low, medium and high) while three centre points were selected. The design involved 15 experiments (shown in Table 1) and the response variables are CA, biodegradability in compost and soil, PWF, besides the rejections of different pollution indices from raisin wastewater. Regression analysis performed in all results used Minitab software at a confidence interval of 95%.

3. Results and discussion

Through comparing different models, full quadratic model was found to be statistically significant for predicting CA, PWF and rejecting percentages results, while the linear + squares model was statistically significant for predicting the membrane biodegradation results. Accordingly, these two models were selected and used to represent the responses.

3.1. Membrane morphology

Scanning electron microscopy (SEM) cross-sectional images of the fabricated membranes are shown in Fig. 2, illustrating the effects of CBT, starch concentration and sorbitol concentration, respectively. Generally, the prepared membranes exhibit typical asymmetric structure comprising a dense thin top layer and a porous sub-layer filled up by macro pores. To have a more comprehensive understanding of the considered factors that affected the membranes morphology, two other membranes were prepared and analyzed. For both new membranes, the CBT and concentration of starch were fixed at 20°C and 15 wt.%, respectively. However, the sorbitol concentration was selected to be 10 and 0 wt.% for M16 and M17, respectively.

As shown in Fig. 2(a), increasing CBT 0-40°C obviously enhances the membrane porosity and membrane thickness. Raising CBT increases mutual diffusivities between solvent (NMP) and non-solvent (water) in the casting solution during solidification process which consequently increases the film precipitation rate. In fact, at higher CBTs, for constant polymer content, nucleuses of polymer-poor phase will grow rapidly and increase the formation of macrovoids in the membrane structure, thereupon more porous membrane will be obtained [1,16].

According to Fig. 2(b), along with increasing starch concentration 0-30 wt.%, membrane thickness is increased and macrovoids are more arranged in the membrane sub-layer. This observation may be attributed to improving affinity of the mixed polymers to water as previously discussed by other researchers [17,18]. Starch is a hydrophilic polymer; thus, its addition to the casting solution causes greater affinity of the PAN/starch blend to water as a coagulation medium. Accordingly, the time that is needed for NMP/water exchange during the membrane solidification is increased. The longer the solvent exchange through the skin formed when the casting solution is immersed in water, the more developed the processes of polymer-lean phase growth and coalescence, therefore, the larger the macropores. Generally, this structure is formed by rapid growth towards the depth of the polymeric film during the coagulation step. When the "setting" of the polymer rich phase matrix is longer, the pores can expand in depth towards the other face.

Furthermore, increasing sorbitol concentration 0-10 wt.% results in macrovoid growth and also improvement in membrane porosity and thickness (shown in Fig. 2(c)). It can be said that presence of sorbitol as a hydrophilic additive with non-solvent properties (additive that is similar to non-solvent) increases thermodynamic instability of the cast film which causes instantaneous demixing during the immersion process. As a result, membrane porosity and extension of macrovoids in membrane sublayer is increased [1,19].

3.2. Contact angle

Hydrophilicity is an important factor of the membrane that affects the membrane permeability. Results of CA for the prepared membranes are shown in Table 1. Response surface regression (RSM) for CA vs. starch and additive concentration besides the CBT is presented in Table 2.

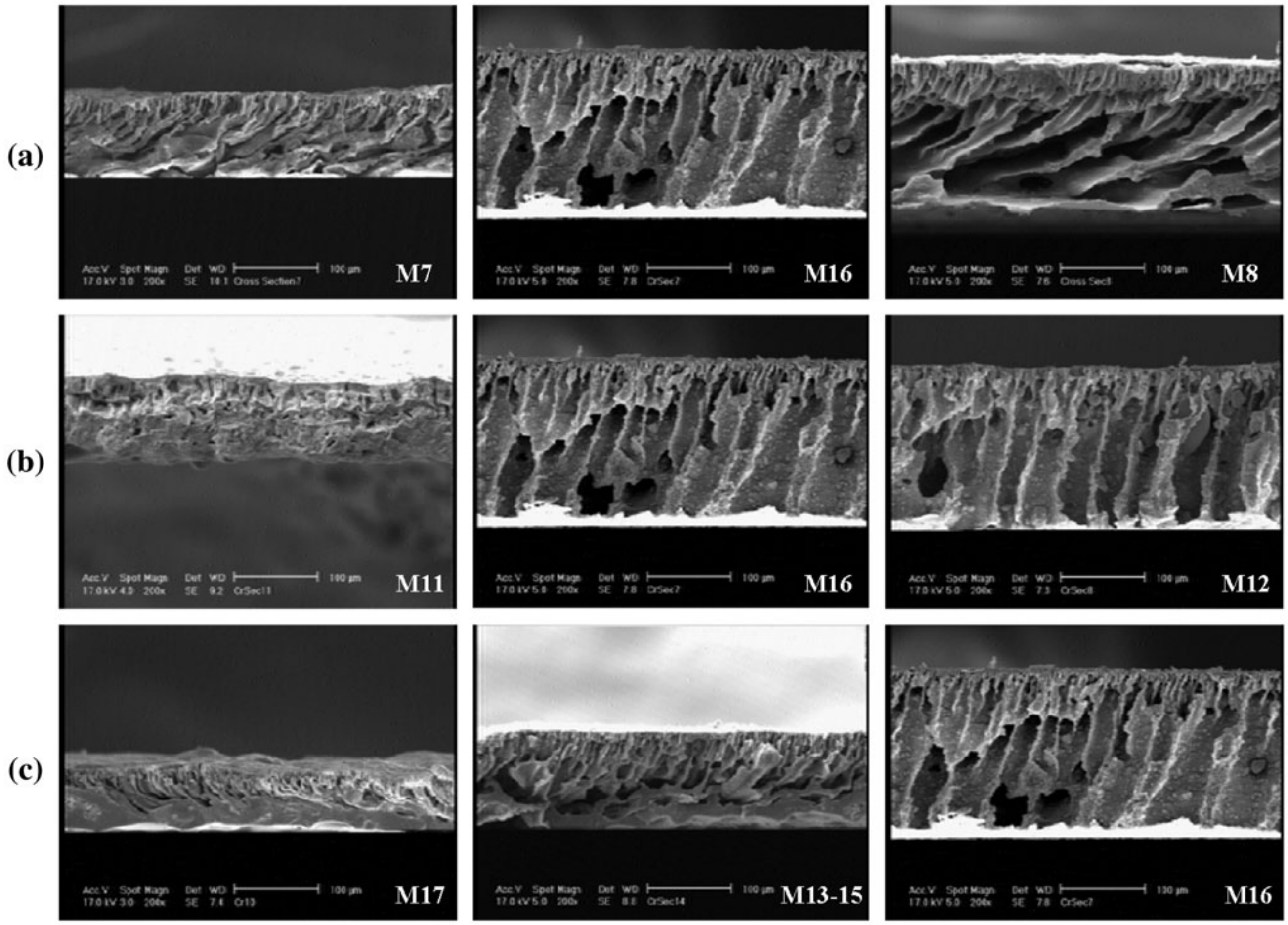

Fig. 2. Effect of CBT (a) starch concentration, (b) sorbitol concentration and (c) on morphology of the synthesized membranes.

The item "*p*" in Table 2 refers to each parameter effect on the response. Therefore, whenever *p*-value is less than 0.05, the related parameter has a significant effect on the CA. In fact, the larger magnitude of coef (coefficients) and correspondingly the smaller *p*-value will increase the significance of the related parameter. Removing insignificant parameters can be resulted in an improved model. Here, backward elimination procedure was performed to reduce the insignificant parameters. With respect to Table 2, starch is the most significant parameter associated with CA due to starch's high hydrophilicity. The calculated R^2-value is 0.975, reasonably close to 1, that is acceptable. It shows that about 97.5% of the variability in the data is explained by the model.

The three dimensional surface plots demonstrate the effect of different process variables on CA and are presented in Fig. 3. The effect of each two parameter is clearly seen while the third parameter was kept at the middle level. CA decreases obviously when the starch concentration changes 0-30 wt.%. Accordingly, the minimum CA is observed at starch concentration of 30 wt.%. However, changes in sorbitol concentration and CBT do not considerably affect the membrane hydrophilicity. Although sorbitol as a hydrophilic additive can help decreasing CA, its effect is negligible in comparison with the starch concentration effect. As expected, the highest CA is obtained for M9 which is prepared without addition of starch and sorbitol.

3.3. Degradation tests

Weight loss of the buried membranes in compost and soil is presented in Table 1. The adjusted test duration for all membranes was three months. Generally, observable changes during biodegradability process were started by colour changing due to micro-organism diffusion. Then, the membranes became brittle and gradually broke up. These steps are shown in Fig. 4 for M10.

Table 2
Estimated regression coefficients for membranes CA, biodegradability in compost and soil, PWF and turbidity rejection percentage

	Membranes CA		Biodegradability in compost		Biodegradability in soil		PWF at TMP = 7 bar		Turbidity rejection percentage	
Term	Coef	*P*	Coef	*P*	Coef	*P*	Coef	*P*	Coef	*P*
Constant	51.618	0.000	15.067	0.000	4.800	0.000	1,210.62	0.000	59.267	0.000
CBT	−1.021	0.070	0.075	0.887	−0.112	0.564	157.75	0.001	−3.887	0.000
Starch	−7.150	0.000	8.262	0.000	5.225	0.000	241.25	0.000	−1.575	0.000
Additive	−1.491	0.016	0.912	0.112	0.387	0.072	166.00	0.001	−4.487	0.000
CBT × CBT	–	–	−1.671	0.057	−0.025	0.930	−74.08	0.127	2.317	0.000
Starch × Starch	6.069	0.000	−3.746	0.001	0.650	0.046	−44.58	0.327	3.092	0.000
Additive × Additive	2.277	0.013	−1.096	0.183	0.675	0.040	−61.50	0.178	2.267	0.000
Starch × Additive	1.988	0.021	–	–	–	–	–	–	–	–
CBT × Starch	–	–	–	–	–	–	-91.00	0.065	-0.725	0.038
CBT × Additive	–	–	–	–	–	–	45.00	0.307	0.400	0.195
	R^2 = 97.5%		R^2 = 97.3%		R^2 = 99.0%		R^2 = 96.1%		R^2 = 99.5%	
	R^2 (adj) = 95.7%		R^2 (adj) = 95.4%		R^2 (adj) = 98.3%		R^2 (adj) = 91%		R^2 (adj) = 98.9%	

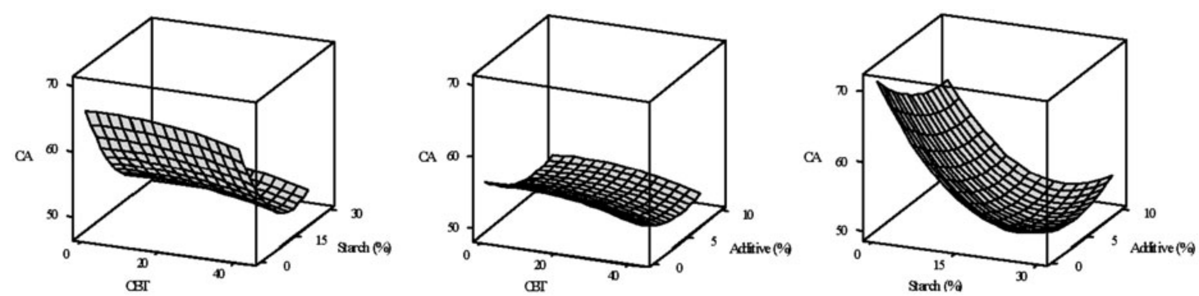

Fig. 3. Surface plots related to CA (left to right: sorbitol concentration = 5 wt.%, starch concentration = 15 wt.% and CBT = 20˚C).

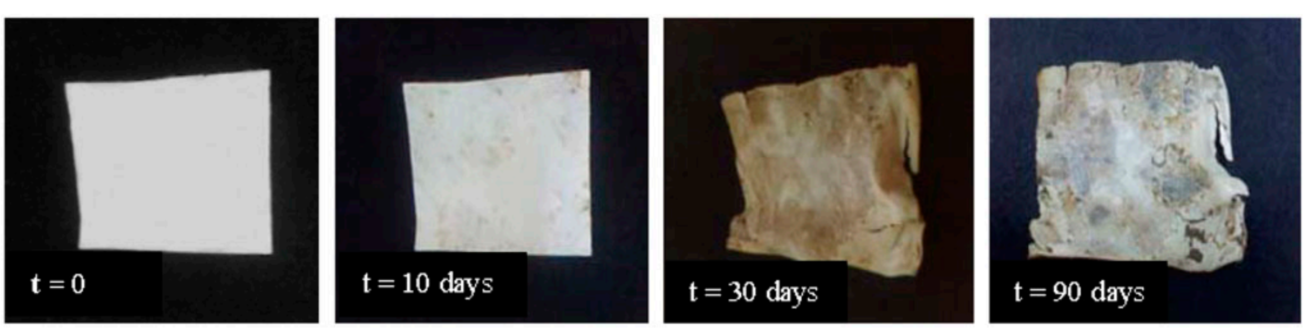

Fig. 4. M10 biodegradation in compost.

Response surface regression for biodegradability in compost and soil vs starch and additive concentration and also CBT is presented in Table 2. The linear +squares model was found to be statistically significant for the biodegradability tests as responses. According to Table 2, the main effect of starch is the most significant factor associated with biodegradability in both environments. The calculated R^2-values are reasonably close to 1 that is acceptable. It should be added that the starch presence was shown to considerably improve the membrane hydrophilicity and also porosity. Knowing as factors effecting polymer biodegradability [20], higher hydrophilicity and more open structure have positive influences on enhancing biodegradation rate of PAN/starch membrane in natural environment. Generally, the main enzymes involved in starch hydrolysis are amylases [21] which are widely distributed in bacteria and fungi [22]. For example, the two bacterial strains of *Bacillus amyloliquefaciens* and *Bacillus licheniformis* have been exploited on the industrial scale [23]. Moreover, studies on fungal amylase have concentrated mainly on *Rhizopus sp.* and *Aspergillus niger* [21].

The three dimensional surface plots that demonstrate the effect of different process variables on biodegradability in compost and soil are presented in Fig. 5. Obviously, biodegradability in compost and soil increases when the starch concentration changes 0-30 wt.%. Moreover, changes in sorbitol concentration and CBT do not show a considerable effect on increasing biodegradability.

3.4. Membrane performance

Permeation experiments were carried out to study permeability properties of the prepared PAN/starch/sorbitol membranes. Generally, it is known that PWF is obviously affected by the membrane hydrophilicity, porosity and accordingly preparation variables [1].

The obtained results for PWF through the prepared membranes are displayed in Table 1. Moreover, response surface regression for PWF at TMP = 7 bar vs. starch and additive concentration besides the CBT is presented in Table 2. The three dimensional surface plots which demonstrate the effect of different process variables on PWF are presented in Fig. 6.

To investigate the membrane performance in separation process, the raisin effluent was used as the treatment feed and each membrane permeate was analyzed for different pollution indices of turbidity, TDS and COD. In Table 2, performance of the prepared membranes is reported based on the rejection percentages of the mentioned indices. Furthermore, the variations of the pollutants rejection percentages for the prepared membranes are presented in Fig. 7. All pollutants indices follow the same trend. To evaluate the influence of the membrane preparation variables on

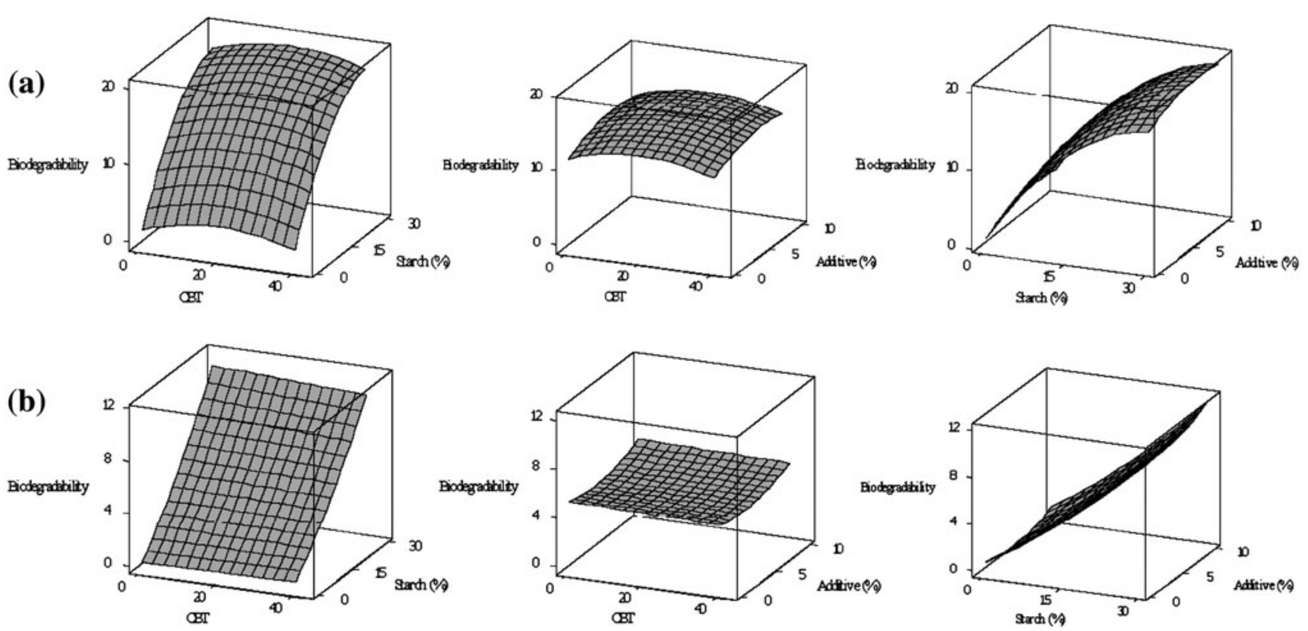

Fig. 5. Surface plots related to biodegradability in compost (a) and soil (b) (left to right: sorbitol concentration = 5 wt.%, starch concentration = 15 wt.% and CBT = 20˚C).

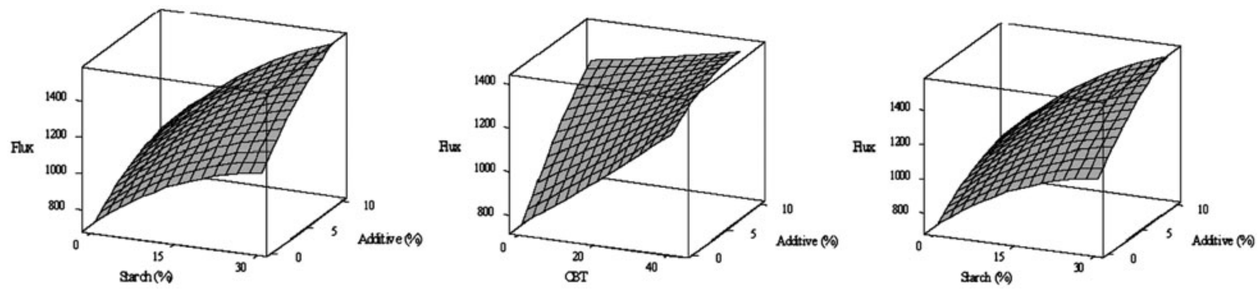

Fig. 6. Surface plots related to PWF at TMP of 7 bar (left to right: sorbitol concentration = 5 wt.%, starch concentration = 15 wt.% and CBT = 20˚C).

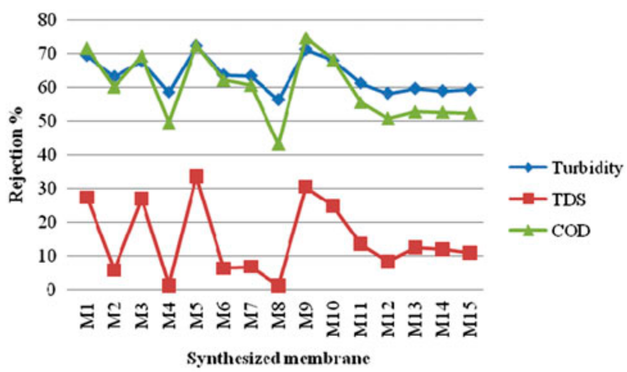

Fig. 7. Rejection percentages of the pollution indices vs. prepared membranes.

the permeate quality; turbidity rejection percentage of the prepared membranes was selected as the input data for further analysis by RSM for turbidity rejection percentage vs. starch and additive concentration and also CBT is presented in Table 2.

For both PWF and turbidity rejection results, the full quadratic model is found to be statistically significant. The analysis was done through coded unites. With respect to Table 2, the calculated R^2-values for PWF and turbidity rejection percentage are 0.961 and 0.995, respectively, reasonably close to 1. It shows that about 96.1 and 99.5% of the variability in the data are explained by the model.

The three dimensional surface plots for turbidity rejection are presented in Fig. 8. Results of PWF and different pollutants rejection percentages confirm the SEM images and hydrophilicity results. Increasing CBT, starch and sorbitol concentration led to increasing macrovoid formation and membrane porosity which reduces the main resistance against the water permeation. Thus at higher levels of these factors, higher PWFs were obtained. This improvement is intensified for membranes with higher concentration of starch due to the simultaneous effects of the membrane hydrophilicity and porosity. Therefore, the highest and lowest PWFs were obtained for M12 and M9, respectively.

Comparing the rejection results shows that increasing membranes porosity and thereupon permeability, the membranes selectivities were reduced. The negative effects of increasing CBT or additive concentration on the membrane selectivity are in agreement with other researchers' findings [24]. However, here, the

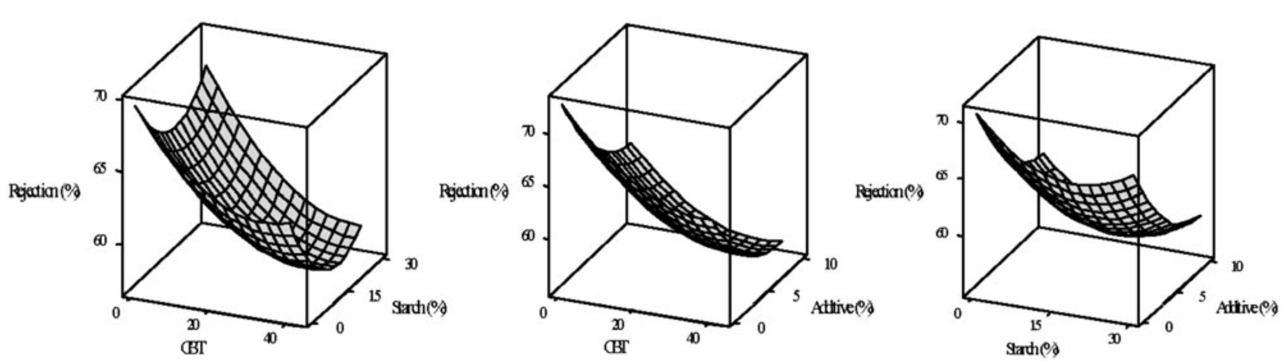

Fig. 8. Surface plots related to turbidity rejection percentage (left to right: sorbitol concentration = 5 wt.%, starch concentration = 15 wt.% and CBT = 20˚C).

decrease in rejections of the pollution indices is not always very crucial as it can be seen that selectivity of M3, M5 and M10 is very close to the pure PAN membrane (M9), while the PWFs of the mentioned membrane are much higher. Certainly, decrement of the rejections of pollution indices become really considerable for much more permeable membranes including M12, M8 and M4. With respect to results, selecting suitable levels for the considering factors (CBT and concentration factors) can effectively help on obtaining novel PAN/starch/sorbitol membrane with superior degradation properties as well as proper hydrophilicity, permeability and also selectivity.

4. Conclusions

Asymmetric membranes of PAN/starch/sorbitol were prepared using immersion precipitation technique. The effect of preparation conditions including solution casting composition and CBT was investigated on different membrane specifications, including morphology, hydrophilicity, biodegradability and PWF. Furthermore, performance of the prepared membranes was evaluated in treating raisin wastewater. Representing the membranes characteristics shows that:

- Increasing starch and sorbitol concentration besides CBT leads to increasing the membrane porosity as well as thickness.
- All the prepared membranes are hydrophile with CA below 90° and starch concentration is the most effective parameter to determine the membrane hydrophilicity.
- Starch concentration is the most effective parameter on membrane biodegradability. Other parameters do not affect this characteristic considerably.
- All mentioned parameters have significant effects on membrane performance. Actually, increasing starch and sorbitol concentration as well as increasing CBT reduce the main resistance against water and also pollutants passage through the membrane.

References

[1] E. Saljoughi, M. Sadrzadeh, T. Mohammadi, Effect of preparation variables on morphology and pure water permeation flux through asymmetric cellulose acetate membranes, J. Membr. Sci. 326 (2009) 627–634.

[2] S. Yang, Z. Liu, Preparation and characterization of polyacrilonitrile ultrafiltration membranes, J. Membr. Sci. 222 (2003) 87–98.

[3] J. Xu, Z.L. Xu, Poly(vinyl chloride) (PVC) hollow fiber ultrafiltration membranes prepared from PVC/additives/solvent, J. Membr. Sci. 208 (2002) 203–212.

[4] V.P. Cyras, L.B. Manfredi, M.T. Ton-That, A. Vazquez, Physical and mechanical properties of thermoplastic starch/montmorillonite nanocomposite films, Carbohydr. Polym. 73 (2008) 55–63.

[5] S.S. Shenvi, S.A. Rashid, A.F. Ismail, M.A. Kassim, A.M. Isloor, Preparation and characterization of PPEES/chitosan composite nanofiltration membrane, Desalination 315 (2013) 135–141.

[6] S. Jana, A. Saikia, M.K. Purkait, K. Mohanty, Chitosan based ceramic ultrafiltration membrane: Preparation, characterization and application to remove Hg(II) and As(III) using polymer enhanced ultrafiltration, Chem. Eng. J. 170 (2011) 209–219.

[7] F. Liu, B. Qin, L. He, R. Song, Novel starch/chitosan blending membrane: Antibacterial, permeable and mechanical properties, Carbohydr. Polym. 78 (2009) 146–150.

[8] M.S.P.D. Lima, M.S. Freire, J.L.C. Fonseca, M.R. Pereira, Chitosan membranes modified by contact with poly(acrylic acid), Carbohydr. Res. 344 (2009) 1709–1715.

[9] L.H. Li, J.C. Deng, H.R. Deng, Z.L. Liu, L. Xin, Synthesis and characterization of chitosan/ZnO nanoparticle composite membranes, Carbohydr. Res. 345 (2010) 994–998.

[10] A. Moriya, P. Shen, Y. Ohmukai, T. Maruyama, H. Matsuyama, Reduction of fouling on poly(lactic acid) hollow fiber membranes by blending with poly(lactic acid)–polyethylene glycol–poly(lactic acid) triblock copolymers, J. Membr. Sci. 415–416 (2012) 712–717.

[11] T. Komatsuka, A. Kusakabe, K. Nagai, Characterization and gas transport properties of poly(lactic acid) blend membranes, Desalination 234 (2008) 212–220.

[12] A. Moriya, T. Maruyama, Y. Ohmukai, T. Sotani, H. Matsuyama, Preparation of poly(lactic acid) hollow fiber membranes via phase separation methods, J. Membr. Sci. 342 (2009) 307–312.

[13] X. Ma, P.R. Chang, J. Yu, P. Lu, Characterizations of glycerol plasticized-starch (GPS)/carbon black (CB) membranes prepared by melt extrusion and microwave radiation, Carbohydr. Polym. 74 (2008) 895–900.

[14] G.C.C. Yang, C.-M. Tsai, Effects of starch addition on characteristics of tubular porous ceramic membrane substrates, Desalination 233 (2008) 129–136.

[15] M.M.D. Zulkali, A.L. Ahmad, C.J.C. Derek, Membrane application in proteomic studies: Preliminary studies on the effect of pH, ionic strength and pressure on protein fractionation, Desalination 179 (2005) 381–390.

[16] V. Ghaffarian, S.M. Mousavi, M. Bahreini, H.J. Jalaei, Polyethersulfone/poly (butylene succinate) membrane: Effect of preparation conditions on properties and performance, Ind. Eng. Chem. 20 (2014) 1359–1366.

[17] J.-F. Blanco, J. Sublet, Q.T. Nguyen, P. Schaetzal, Formation and morphology studies of different polysulfones-based membranes made by wet phase inversion process, J. Membr. Sci. 283 (2006) 27–37.

[18] A. Rahimpour, S.S. Madaeni, S. Mehdipour-Ataei, Synthesis of a novel poly(amide-imide) (PAI) and preparation and characterization of PAI blended polyethersulfone (PES) membranes, J. Membr. Sci. 311 (2008) 349–359.

[19] A. Idris, L.K. Yet, The effect of different molecular weight PEG additives on cellulose acetate asymmetric dialysis membrane performance, J. Membr. Sci. 280 (2006) 920–927.
[20] K. Cho, J. Lee, K. Kwon, Hydrolytic degradation crystalline behavior of poly(butylene succinate)s with different morphologies, J. Appl. Polym. Sci. 79 (2001) 1025–1033.
[21] A.M. Omemu, I. Akpan, M.O. Bankole, O.D. Teniola, Hydrolysis of raw tuber starches by amylase of *Aspergillus niger* AM07 isolated from the soil, Afr. J. Biotechnol. 4 (2005) 19–25.
[22] S. Mishra, N. Behera, Amylase activity of a starch degrading bacteria isolated from soil receiving kitchen wastes, Afr. J. Biotechnol. 7 (2008) 3326–3331.
[23] S.S. Alariya, S. Sethi, S. Gupta, B.L. Gupta, Amylase activity of a starch degrading bacteria isolated from soil, Arch. Appl. Sci. Res. 5 (2013) 15–24.
[24] E. Saljoughi, M. Amirilargani, T. Mohammadi, Effect of PEG additive and coagulation bath temperature on the morphology, permeability and thermal/chemical stability of asymmetric CA membranes, Desalination 262 (2010) 72–78.