Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(11):95-103
(http://derpharmachemica.com/archive.html)

Optimization of melassigenic ions removal operation from beet sugar syrups and mother liquorby Electrodialysis

Hajar Qabli*, Manal Rafik, Merieme Tahri, Majdouline Larif, Sarra Kitanou, Mohamed Taky and Azzedine Elmidaoui

Laboratory of Separation Processes, Department of Chemistry, University Ibn Tofail Faculty of Sciences, BP1246 Kenitra, Morocco

---

ABSTRACT

Electrodialysis technology was used to remove the melassigenic ions of mother liquor of beet sugar and beet sugar syrup, obtained from the Moroccan sugar industry. The operations were conducted using an electrodialysis pilot plant equipped with two ions exchange membrane with high temperature and organic resistance first on mother liquor diluted at 25% with water and juices and secondly on beet sugar syrup at two higher Brix (52 and 60 Bx). The performances of the electrodialysis operation were evaluated and the best operation conditions were determined. This study confirms the effectiveness and the efficiency of the ED process to reduce melassigenic ions for beet sugar solution.

Keywords: Electrodialysis, mother liquor of beet sugar, beet sugar syrup, melassigenic ions.

INTRODUCTION

The goal of any production process is to produce as large a quantity of product within the quality criteria. The sugar industry has long maintained an interest in the application of membrane filtration for both quality improvements and as a pre-treatment for processes to produce value-added products [1].

In the technological process of sugar production the main problem is the separation of alkali metal cations which were suspected of being highly melassigenic by holding sugar in molasses and preventing it from being recovered as crystalline sugar [2].Sugar processing is one of the most energy-intensive processes in the food industry, which is a challenge for membrane separation processes like microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO) [3].

The application of new methods in sugar beet factories have been investigated in: Purification of raw syrup method, Concentration of diluted syrup by reverse osmosis; Separation and extraction of color compounds. [4]

Cross-flow microfiltration (MF) membranes can be used to remove non-sucrose compounds, or to fractionate the retentate rich in colorants. Ultrafiltration (UF) membranes can be applied to concentrate the relevant juices in sugar industry and to remove non-sucrose compounds[10]. The purification of raw beet juice and of cane juices using Microfiltration and Ultrafiltration were investigated [4.5].

Decolorization of sugar can be achieved by Nanofiltration (NF) [6]. UF / MF process in cane sugar production acts as a pretreatment prior to other separation technologies by removing impurities from the raw juice, including starch, dextran, gums, waxes, proteins and polysaccharides. Concentration of raffinate from beet molasses can be achieved by chromatographic separators using Reverse Osmosis (RO) [6].

Reverse Osmosis (RO) can be used to recycle pulp press water [7], oralso to recover pectin from sugar beet pulp [8]. Forward osmosis is a viable membrane process for concentration of sucrose solutions (48◦Brix), increased temperature leads to an increase in the draw and feed solute diffusion coefficient and to a decrease in water viscosity [9].

ED can also be used for the removal of inorganic matter from clarified sugarcane juice [11,12]. Although some minerals such as phosphates, silica and magnesia are partially removed by clarification, potassium, sodium and low concentrations of sulfates are not completely removable.

In order to overcome the problems caused by melassigenic ions such as K^+, $Ca^{2+}$and Na^+, many methods have been employed to remove them, including membrane processes, synthetic adsorption, coagulation and ion exchange resins. Among these methods, ion exchange (used in the Quentin method) and electrodialysis are well-established technologies [13,14].

The purpose of this work is to follow the parameters of the demineralization for the mother liquor solution and in the beet sugar syrups using an electrodialysis pilot plant.

MATERIALS AND METHODS

The study was conducted using a pilot plant (TS-2-10) supplied by the EURODIA Co. The stack design characteristics of the pilot plant are given in table 1.
The treated volumes are of the order of 1.5L.

Table 1: Characteristics of the pilot plant TS-2-10

Generator	Stabilized power supply 60200-60V. 20A electronic P.FONTAINE.
Total area	2 dm^2
Active surface	200 cm^2
MEC	CMX (EURODIA)
MEA	AFN (EURODIA)
Cell number	10
Cell voltage	1.6 V maximum
Flow rate	0-500 L/h

The pilot plant was fitted with a conventional cation-exchange membrane CMX and animproved anion exchange membrane AFN. All these membranes were manufactured by Tokuyama Co. The plant was operated in batch mode. The tests of electrodialysis were realized on the mother liquorat 25 % dilutions with the water and with the juice.

Due to the high loss of the mother liquor trials, the tests could not be realized with concentrations at 80%.Beet sugar solutions were freshly collected at the output of each phase, undergoing no preliminary treatment, they are cooled to a temperature between 38°C and 42°C, and circulated (diluted with distilled water or the purified juice) into the diluted compartment with a flow rate of 200 (L/h). The brine compartment is filled with NaCl (M= 5g/L) solution with a flow rate of 200 (L/h). To avoid any electrochemical reaction caused with the electrodes we introduce a solution of Na_2SO_4 (M=20 g/L) into the electrode compartments with a flow rate of 200 (L/h).
The sugar crystallization process takes 3 jets:

The first jet: crystallized syrup of the highest possible purity 94-95% and will give in 2 at 3 hours: A trade white sugar of purity ≥ 99.9%, and water-mother or mother liquor (after separation of crystals by centrifugation) of purity 86-88%.

The second jet: Ensure the crystallization of the mother liquor of 1st jet in 3 to 4 hours. It will give a sugar of less quality that in the 1st jet, more colorful and have more ash. It is redesigned to be mixed with the syrup resulting from evaporation and will enter in crystallization of 1st jet to give the white sugar. The mother liquor obtained in 2nd jet of purity from 76 to 78 % will be crystallized in 3rd jet.

The 3rd jet: Charged with crystallizing a product at a very low purity (thus in speed of slow crystallization), the 3rd jet will be carried out in a way appreciably different from the first and 2nd jet. [15].

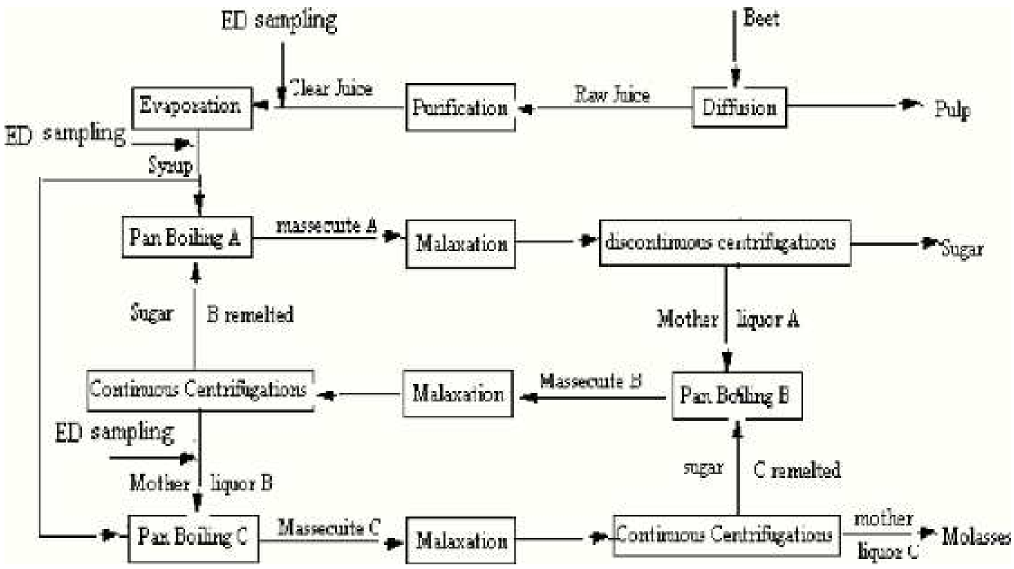

Fig.1: Principle of sugar process[15]

For The raw syrup the electrodialysis operations were conducted on the diluted syrup with water (60 Bx) and on the diluted syrup (52 Bx) with juice.The dilution was obligatory because the high viscosity of the syrup.

Table 2: Electrodialysis membranes characteristics

Grade	**CMX**	**AFN**
Type	Strongly acidic Cation exhange membrane	Strongly basic Anion exchange membrane
Characteristics	High mechanical Strenght (Na^+form)	High acid diffusion Coefficient (Cl^-form)
Electric Resistance ($\Omega.cm^{-1}$)	3.0	0.5
Burst Strenght(Kg.cm^{-2})	$\geq$0.40	$\geq$ 0.25
Thickness (mm)	0.17	0.16

Table 3: Characteristics of the mother liquor

	Mother liquor diluted at 25% with water	Mother liquor diluted at 25% with the juice
Parameters	58 Bx	62 Bx
Conductivity (µS/cm)	4.81	3.31
pH	8.83	8.3
Brix	58	62
Purity (%)	72.20	74.18
Ash Content (g % Bx)	10.28	7.31
Coloration (ICUMSA)	15280.69	13044.83
Na^+ (g/L)	6	6.8
K^+ (g/L)	12.7	13.8
Ca^{2+} (g/L)	9.5	9.15

The parameters followed during the ED operation are: Na^+, K^+ and Ca^{2+} contents, conductivity, temperature, pH,Brix, purity, coloration, ash content.

The amount of, Na^+, K^+ and Ca^{2+} was determined by flame photometer (PFP7, Jenway). The Brix (Bx) was measured with a refractometer (Abbe, type RL3) and expressed in weight percentage. The ash was determined by conductivity (conductivity meter type Orion Research 101) according to the Icumsa method [16].The coloration was measured with a spectronic (miltron Roy21D) according to the Icumsa method [6].The purity was measured by an expression: (Polarization/Bx)*100.

RESULTS AND DISCUSSION

The mother liquor B diluted to 25% with water and juice

ED cannot be led on the mother liquor crude due to the high viscosity. Sugar solutions at two Brix 58Bx and 62Bx were obtained by diluting the mother liquor to 25% with water and juice. The ED operation was carried out on the dilutemother liquor(Brix 58 and 62) and under the following conditions:

Voltage: 13V and 16V. The applied current density is 4.89 A for diluted mother liquor at 58 Bx and 3.90 A, at 62 Bx.

Temperature: 40 ° C
Flow rate 19.56 (L/ h).

The results obtained on the two diluted mother liquor were summarized on Table4 and Table 5. Assays show a good reproducibility.

The figures 2-4 show the variations of purity, coloration and ash content as a function of the electrodialysis time and for two Brix. Variation of sodium, potassium and calcium are given in figures 5-7.

The pH of the mother liquor remains almost unchanged for the two tested Brix,this can help minimize formation of inversion of saccharose. The rates of discoloration increase in time and reach 13.65 % for 58 Bx and 7.5 % for 62 Bx. The quality of the mother liquor was improved by the operation of electrodialysis.

A clear decrease of the content in ion sodium between 65.44 and 80 %, of the content in ion potassium between 78.62 and 90 %, and a decrease of the content in calcium between 21.21 and 34.85%.

The elimination of the melassigenic ions for the mother liquor of beet in the two Brix(58Bx and 62Bx) follows the order of $K^+ > Na^+ > Ca^{2+}$.

For a voltage (13V and 16V), the variation of purity and of coloration are practically decreased for 58 Bx, the same variation for 62 Bx are observed, but a small difference is observed in the content in Na^+ and K^+ for the two brix. This slight reduction can be attributed on one hand to the concentration polarizationand on the other hand to the presence of organic material which reduces the surface of the membrane.

Table 4: Conductivity, pH, purity and coloration of the treated mother liquor of beet by electrodialysis

Mother liquor of beet sugar		**Ash Content (g%Bx)**			**Na^+ (g/L)**			**K^+ (g/L)**			**Ca^{2+} (g/L)**		
		t_0	t_f	%	t_0	t_f	%	t_0	t_f	%	t_0	t_f	%
58 Bx	13V	7,18	1,73	75,90	5,9	1,35	77,11	10,3	1,05	89,81	6,79	3,51	48,30
	16V	10,28	2,46	76,07	6	1,2	80	12,7	1,25	90,15	9,50	6,19	34,85
62 Bx	13V	8,96	3,91	56,36	6,8	2,6	61,76	14,1	3,6	74,46	9,03	6,45	28,57
	16V	7,31	3,16	56,77	6,8	2,35	65,44	13,8	2,95	78,62	9,16	7,21	21,28

Table 5: **Ash content, sodium, potassium and calcium content of the treated mother liquor of beet by electrodialysis**

Mother liquor of beet sugar		**Conductivity(ms/cm)**			**pH**			**Purity (%)**			**Coloration (Icumsa)**		
		t_0	**t_f**	**%**	**t_0**	**t_f**	**%**	**t_0**	**t_f**	**Δ**	**t_0**	**t_f**	**%**
58 Bx	13V	5,92	1,11	81,25	8,17	7,5	8,2	72,31	82,73	10,42	15209,31	11976,35	21,25
	16V	4,81	0,95	80,24	8,86	8,45	4,6	72,21	81,79	9,58	15280,69	13193,36	13,65
62 Bx	13V	3,4	1,41	58,52	8,41	8,27	1,6	73,02	80,03	7,01	14344,14	13302,05	7,26
	16V	3,31	1,05	68,27	8,36	7,94	5,02	74,18	82,14	7,96	13044,83	12062,21	7,53

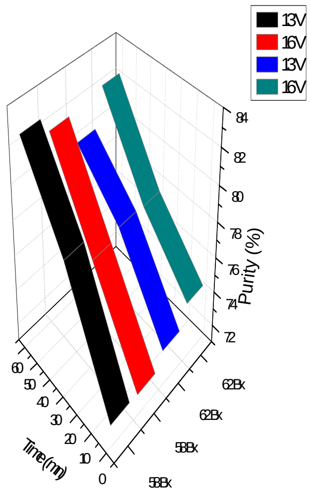

Fig.2: Time dependence of purity

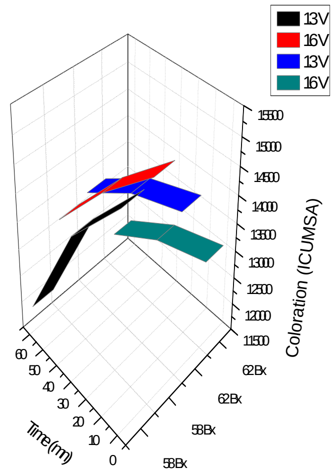

Fig.3: Time dependence of coloration

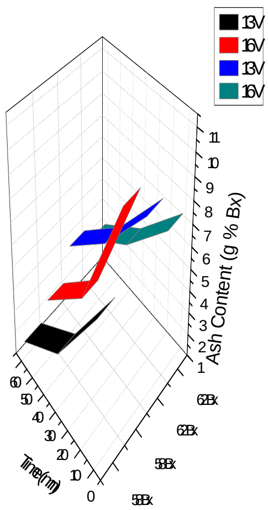

Fig.4: Time dependence of ash content.

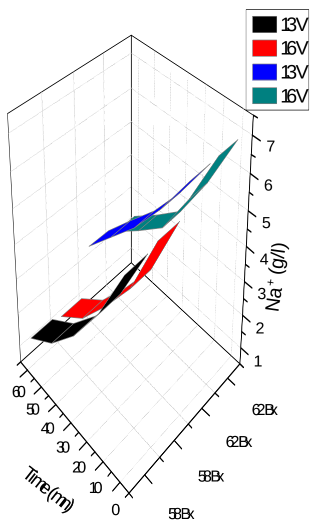

Fig.5: Time dependence of sodium content.

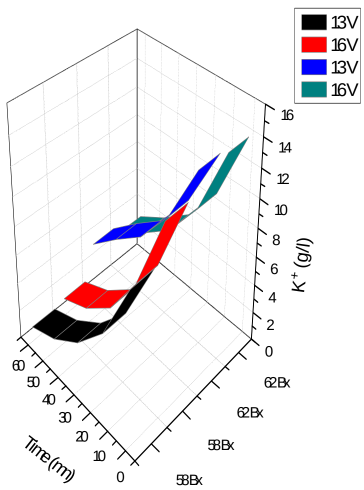

Fig.6: Time dependence of potassium content.

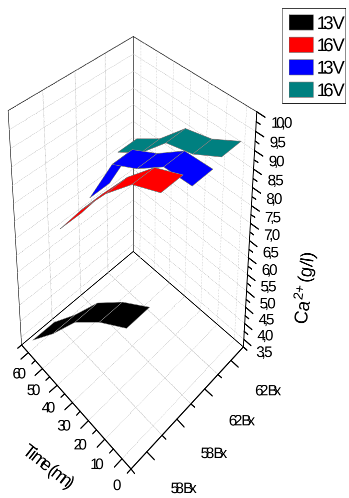

Fig.7: Time dependence of calcium content.

Between 13V and 16V there is a difference at removing of the melassigenic ions.

The removal rates of K^+ and Na^+ up to 90%, however the Ca^{2+}up to 50%.

The total rate of demineralization is more important for Bx 58 than in Bx 62, is upper to 90 %. The gain of purity reaches 9.58 for 58 Bx and 7.95 for 62 Bx. What shows that the dilution by the water is more effective than that by the juice.

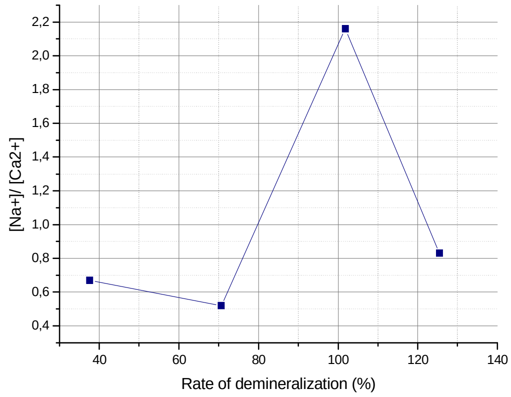

Fig.8: Reportof the concentration in sodium on the concentration in calcium during the demineralization

We notice that the report of the concentration in sodium on that in calcium decreases during the demineralization to aim towards its initial value, equal to 1.So the selectivity of the cations exchange membrane decreases during the demineralization.

The beet sugar syrup

The juice contains almost all of the present sugar in the beet, but also the other compounds which necessary need to be eliminated (mineral salts, organic compounds).The filtered juice contains approximately between 15 % and 85 % of water, from which a big part will be eliminated by evaporation. Brought to a boil in pipes in touch with the vapor, the juice crosses a series of the evaporators where the temperature and the pressure decrease gradually from one to the other one. Finely, the juice was transformed into containing syrup 65 in 70 % content of saccharose.

The syrup finishes its concentration in evaporators to be cooked working under vacuum to avoid the caramelization. A very fine crystals will be produced there which are going to form the syrup[17].

The electrodialysis operations were conducted on the diluted syrup with water (60 Bx) and on the diluted syrup (52 Bx) with juice under the following conditions:

Voltage: 13V and 16V. The applied current density is 2.93 A for diluted syrup at 60 Bx and 3.87A at52 Bx.

Temperature: 40 ° C.

Table 6: Characteristics of the syrup

	Syrup diluted at 10 % with water	**Syrup diluted at 10% with the juice**
Parameters	60 Bx	52 Bx
Conductivity (µS/cm)	1,72	2,81
pH	8,86	9,26
Brix	60,37	52,17
Purity (%)	89,6	88,43
Ash Content (g % Bx)	3,17	3,26
Coloration (ICUMSA)	4066,9	3602,4
Na^+ (g/L)	1,8	1,8
K^+ (g/L)	4	3,32
Ca^{2+} (g/L)	3,98	4,12

Tables 7 and 8 give the characteristics of the beet sugar syrup after electrodialysis operation. The variation with time of purity and coloration for the two Brix were shown in fig 9-10.

The syrup pH remains stable for the two tested Brix. At the end of the ED operation, the variation of pH did not exceed 25.8%. The discoloration rates increase with time and reach 38.57% for 60 Bx at 13V and 26.1% at 16V and

42.04% at 13V and 43.33% at 16V for 52 Bx. Such a difference in the color reduction was due to the removal of suspended solids and color components with molecular weights greater than the membranes. The syrup qualities were improved by the electrodialysis operation.

Table 7: Ash content, sodium, potassium and calcium contents of the treated beet syrup by electrodialysis

Syrup of beet sugar		Ash Content (g%Bx)			Na^+ (g/L)			K^+ (g/L)			Ca^{2+} (g/L)		
		t_0	t_f	%	t_0	t_f	%	t_0	t_f	%	t_0	t_f	%
60 Bx	13V	3,08	0,45	85,38	1,9	0,28	85,26	3,85	0,28	92,72	3,36	0,83	75,29
	16V	3,2	0,41	95,59	1,8	0,28	84,44	4	0,30	92,5	3,98	1,43	64.07
52 Bx	13V	3,8	0,53	86,05	1,77	0,05	97,17	4,25	0,05	98,82	3,91	0,31	92.07
	16V	3,2	0,52	83,75	1,8	0,07	96,11	3,32	0,06	98,19	4,12	0,46	88,83

Table 8: Conductivity, pH, purity and coloration of the treated beet syrup by electrodialysis

Syrup of beet sugar		Conductivity(ms/cm)			pH			Purity (%)			Coloration (Icumsa)		
		t_0	t_f	%	t_0	t_f	%	t_0	t_f	Δ	t_0	t_f	%
60 Bx	13V	2,26	0,29	87,16	8,81	7,66	13,05	90,5	96,01	5,51	3506,88	2154,06	38,57
	16V	1,72	0,32	81,39	8,86	6,57	25,84	89,6	96,28	6,68	4066,91	3005,41	26,1
52 Bx	13V	3,17	0,35	88,95	9,23	8,55	7,36	86,80	95,22	8,42	3545,39	2054,81	42,04
	16V	2,81	0,15	94,66	9,26	7,59	18,03	88,43	95,65	7,22	3602,44	2041,35	43,33

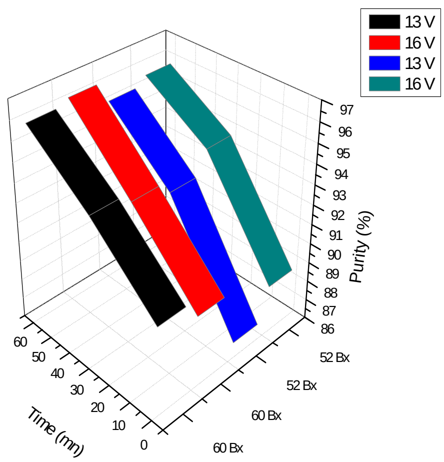

Fig.9: Time dependence of purity

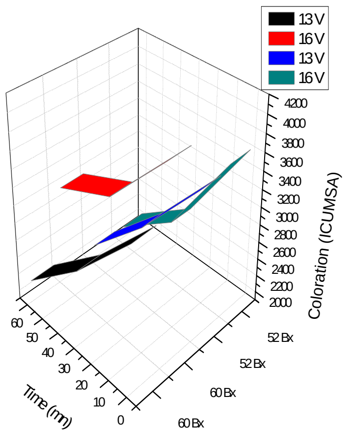

Fig.10: Time dependence of coloration

The time dependencies of the demineralization melassigenic ions were shown infig.11.The analysis concerns systematically the sodium, the calcium and the potassium which are the majority cations of beet sugar syrup and by which the content will be followed throughout the study.

The variation of ash content, further ED treatment of syrup during the first 30 min resulted in greater reduction of ash content, after 30 min the decrease becomes slower. Between 13V and 16V there is no difference at removing of the melassigenic ions.

The removal rates of K^+ and Na^+ decreased rapidly up to 30 min of electrodialysis operation and then decreased slowly, however the Ca^{2+} decreased rapidly for all the 60min.

The total rate of demineralization is more important for Bx 52 than in Bx 60, is upper to 90 %.The gain of purity reaches 6.68 for 60 Bx and 8.42 for 52 Bx. What shows that the dilution by the juice is more effective than that by the water.

The general look of curves calls back a decrease of exponential form. The Ionic composition would thus have an influence on the kinetics of demineralization.

The melassigenic ions rejection for syrup follows the order of $K^+ > Na^+ > Ca^{2+}$. These results can be attributed to the nature of the ion, the nature of membrane and to the ion content in the feed solution.

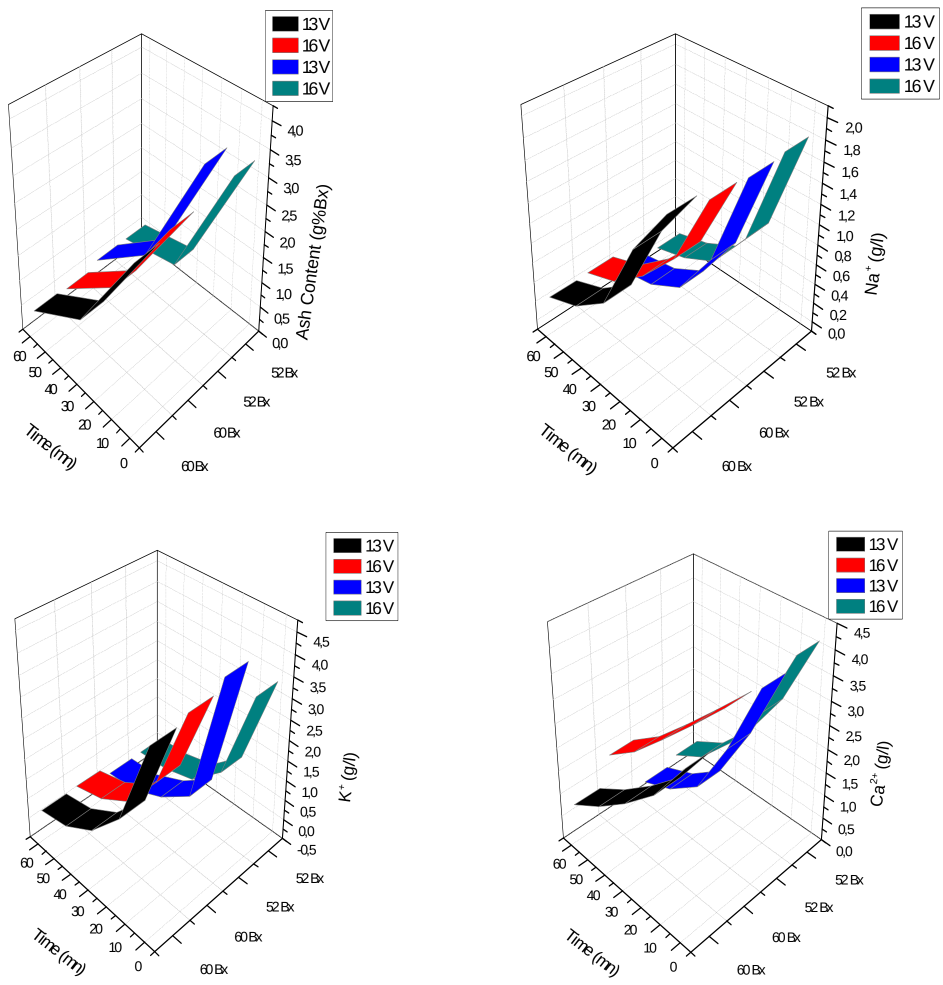

Fig11: Variation of removal rates for melassigenic ions and ash content as a function of time at different Brix

CONCLUSION

Based on experiments of ED of syrup and mother liquor of beet sugar, with dry matter content of 52 and 60 Bx for syrup and for mother liquor as 58 and 62 Bx, under a temperature of 40 °C, could be concluded the following:

- The total rate of demineralization for mother liquor is more important for Bx 58 than in Bx 62, is upper to 90 %, and for syrup is more important for Bx 52 than in Bx 60, is upper to 90 %.
- For mother liquor the gain of purity reaches 9.58 for 58 Bx and 7.95 for 62 Bx. What shows that the dilution by the water is more effective than that by the juice.
- For syrup the gain of purity reaches 6.68 for 60 Bx and 8.42 for 52 Bx.What shows that the dilution by the juice is more effective than that by the water.
- The melassigenic ions rejection for the two solution follows the order of $K^+ > Na^+ > Ca^{2+}$. These results can be attributed to the nature of the ion, the nature of membrane and to the ion content in the feed solution.

The application of Electrodialysis raised the quality of the mother liquor and of the syrup and show potential for improving the sugar yield.

REFERENCES

[1] R.J. Steindl and D.W. Rackemann. membrane filtration of clarified juice. **2010**.
[2] A.Elmidaoui, L. Chay, M. Tahaikt,M.A.Menkouchi Sahli, M. Taky, F. Tiyal, A. Khalidi, My R. Alaoui Hafidi. *Desalination*,**2006**,189, 209-214.
[3] A.Hinkova, Z. Bubnik, P. Kaldlec, V. Pour, H. Starhova. *Membrane filtration in the sugar industry*. (**19 May 2000**).
[4] M.Hamachi, B.B. Gupta, &R. Ben Aim, *Separation and Purification Technology*,**2003,**30, 229-239.

[5] T.Martoyo, M.Hino, H. Nagase, and A. Bachtiar, Pilot test on ultrafiltration of cane raw juice at the Indonesian plantation white Kedawoeng sugar factory. *Zuckerindustrie*, **2000**,125, 787-792.
[6] Anonymous, *Membrane Filtration Sugar, Starch, and Sweetener Industries*.**2002**.
[7] M.Bogliolo, A.Bottino, G.Capanelli, M.De Petro, A.Servida, G. Peyyi, &G.. Vallini, *Desalination*,**1996**,108, 261-271.
[8] D. Hatziantoniou, and J.A. Howell, *Desalination*, **2002**,148, 67-72.
[9]M.Esperanza,Garcia-Castello, R.Jeffrey, McCutcheon. And E. Menachem, *Journal of Membrane Science*, **2009**,338: 61–66.
[10] M.Anisa Anjum, K.Harleen, B.Anju, K.K.Raj, S. Khanand Shahnawaz Umer Khan. *ACommercialUtilization of Membranes in Food Industry*. **2013**.
[11] S.K. Thampy, P.K. Narayanan, G.S. Trivedi, D.K. Gohil V.R. Indusekhar, Demineralization of sugar cane juice by electrodialysis, Abstract, Proceeding of Twelfth Conference IMS, Bhavnagar, India, **1994**.
[12] F. Lutin, G. Guerif, G. Herz, Y. Tani, Ion exchange membranes: an industrial reality, *Proceeding of Euromembrane*, Bath UK, **1995**,2,75.
[13] S. Zhu, S. Yu, X. Fu, Xin-Sheng Chai, L. Zhu, X. Yang. *Desalination*,**2011**,268, 214–220.
[14] A. Elmidaou, F. Lutinb, L. Chay, M. Taky, M. Tahaikt, My R. Alaoui Hafidi. *Desalinatio*n ,**2002**,148 , 143-I 48.
[15] Burzawa, E., & Heitz, F. *Industries alimentaires et agricoles*, **1995**,112(7-8), 522-532.
[16] MO.ElKhattabi , My R.Alaoui Hafidi, El Amrani and A.Elmidaoui ,*Sug.J.Nov*.**1998**.
[17]Le sucre. Documentation pédagogique. Histoire du sucre. CEDUS. **1999** ; Du soleil au sucre. CEDUS. 2011 ;Mémo statistique. CEDUS. **2012**.