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Modification of the organoleptic properties of beverages

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ABSTRACT

The quality of agricultural products used for the manufacture of beverages varies from year to year depending on weather conditions and at the same time according to their areas of origin. The aim of the beverage industry, however, is a product with the same properties in all seasons and in different years. Our aim was to verify the possibility of modification of the organoleptic properties of beverages, particularly the proportion of sweet and sour taste. We examined the possibility of adjusting the pH up or down of wine, wine must and apple cider by electrodialysis with bipolar membranes. This was followed by sensory evaluation of original and modified samples. The process and operating properties were also evaluated. For our samples the most suitable value to move the pH up was showed, the change of 0.5 units. At pH shift down, we observed fouling with precipitated calcium hydroxide in some samples. Therefore, in this respect is not yet possible with industrial application without further research.

Keywords: pH adjustment; EDBM (electrodialysis processes with bipolar membranes); Bipolar membrane; Beverages; Wine; Cider; Wine must; Apple juice; Acidification; Deacidification

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1. Introduction

For the purpose of flavour improvement and extension of shelf-life, number of chemical additives are added into beverages—flavour enhancers, acidity regulators, sweetening agents and preservatives. According to current legislation, all additives must be declared on product packaging. At the same time, consumers put more often than ever emphasis on natural character of beverages and the least content of additives. Using membrane processes it is possible to replace number of these additives.

Taste of beverages like wine, cider, apple juice, wine must, etc. is significantly affected by variability of natural ingredients due to climatic differences, year of harvest and fruit origin differences. This variability affects the most sugar/acid ratio, which changes in fruit during ripening process.

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Nowadays, problem of high pH is solved by cider uniting (mixing of sweet and sour ciders), sweetening or by acidification (addition of citric, ascorbic or tartaric acid). Addition of tartaric acid into wine is monitored and limited in EU. This addition also decreases tartrate stability of wine, which must be addressed afterwards. Calcium sulphate ($CaSO_4$) and calcium phosphate ($Ca_3(PO_4)_2$) are added into wine in some countries, however this is not permitted in Czech Republic. Flavour enhancement of other beverages is less complicated as it is not so strictly regulated by legislation. The only requirement is to declare the additives on product packaging.

2. Theoretical part

The sugar/acid ratio can be, to a certain extent, adjusted by electrodialysis with bipolar membranes (EDBM) [1].

Bipolar membrane consists of anion and cation layers. On interface of these two layers is an electric bilayer, which thickness (approx. 10 nm) depends on input voltage and ion concentration. Selective layers prevent ions from passing through membrane but water can pass freely. Molecule of water dissociates on boundary layer into H^+ and OH^- ions, which migrate through corresponding layer towards electrodes [2].

Significant advantage of this technology for beverage industry application is direct acidification or deacidification without addition of chemicals. The EDBM process was successfully used in beverage industry for fruit juice deacidification [3] or pH adjustment of wine. Advantage of this technology in beverage industry is its precise pH regulation. Too big change of pH during process of food and beverage manufacturing may cause array of undesirable changes in product characteristics (e.g. change of colour of wine due to acid–base reaction of anthocyanins at higher pH value, or increase in activity of tyrosinase due to pH increase accelerating oxidation of polyphenols which causes browning of apple juice [4]).

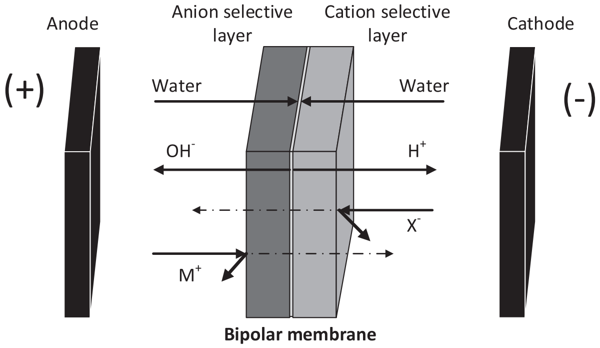

Fig. 1. Principle of bipolar membrane process.

EDBM technology enables pH adjustment as accurate as 0.05 of pH value and therefore to standardize sweet/sour taste ratio. This happens through ion replacement by H^+ or OH^- ion, depending on the target pH value we want to achieve. H^+ and OH^- ions are generated on bipolar membrane (Fig. 1). The target pH value (decrease or increase in pH) determines specific electrodialysis stack configuration and number of the stack loops [1].

During deacidification anions (X^-—anions of organic and inorganic acids) are replaced by OH^- anion. Membrane stack consists of 3 circuits (beverage loop, acid loop and base loop) in this case and contains anion exchange and bipolar membranes (Fig. 2).

As an example of issues with too low pH, we can mention cider production from too acidic apples [5].

During acidification cations (K^+, Na^+, Ca^{2+}, etc.) are replaced by H^+ cation. Membrane stack consists of two circuits (beverage circuit and base circuit) and contains cation exchange and bipolar membranes (Fig. 3). Problem with pH being too high occurs during both, must and wine production.

The best method for evaluation of pH adjusting effect on organoleptic properties of product is sensory evaluation. Triangle sensory test and 9-point hedonic scale test were chosen as the most suitable methods. During the triangle sensory test, assessor decides which sample out of three is different. During the 9-point hedonic scale test, assessor evaluates partial (sweetness, acidity, colour, etc.) or whole sensory perception [5].

3. Experimental part

Aim of this study was to examine and verify pH adjustment of beverages using new heterogeneous bipolar membrane RALEX® BM.

Four series of experiments were carried out on unit P EDR-Z/3x (3 working loops) with modules EDR-Z/2x3-0.8 CBC and EDR-Z/3x10-0.8 BAAB—membrane ordering as mentioned above. Voltage was 2 V per membrane pair (in some cases increased to 2.4 V). Electrode rinse 0.25110 g/l K_2SO_4, flow rate was set on 50 l/h. All other streams of flow rate of 30 l/h. Membranes used were RALEX® AM(H)-PP, CM(H)-PP (specification on RALEX web page) and BM(H)-PP. BM used in tests was new type of heterogeneous bipolar membrane (Table 1).

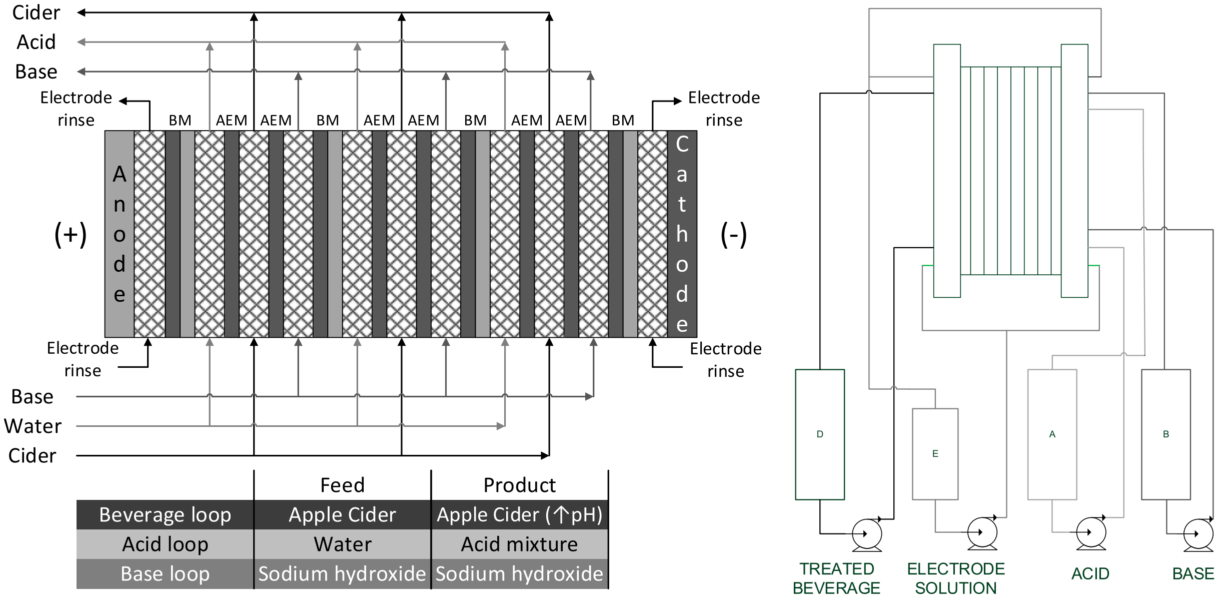

Fig. 2. Stack and circuit diagrams of electrodialyser for deacidification—pH increase.

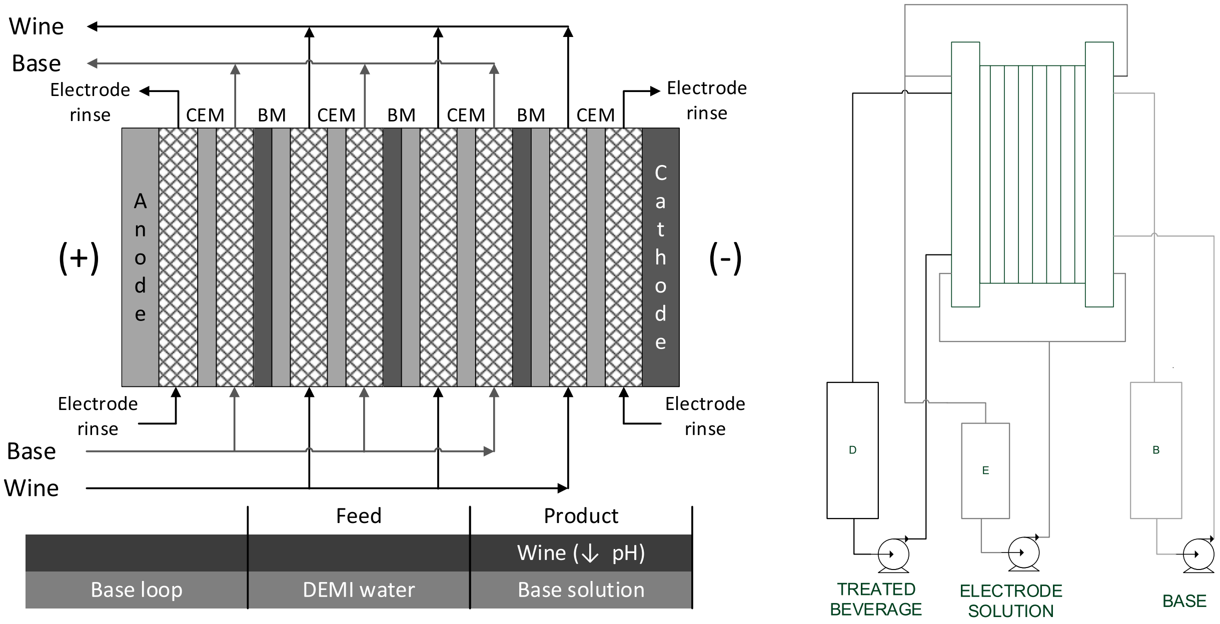

Fig. 3. Stack and circuit diagrams of electrodialyser for acidification–pH decrease.

CIP was carried out as required with 3% sulphuric acid, 3% sodium hydroxide and water.

To monitor conductivity and pH multimeter WTW 340 i was used. Voltage and current were measured on Fluke 189 True-rms Digital Multimeter.

Tested beverages were white wine (Sauvignon Blanc, 2012, Přikryl Winery), apple cider (Jablečný cider, F.H. Prager, alc. 4% vol.) and wine must (white, harvest 2013, no further details).

In consumer tests were original and modified samples put through triangle sensory test and 9-point hedonic scale test. In the assessment participated 10 untrained assessors, both men and women, age group 20–45 years.

Table 1
Properties of used bipolar membrane

Properties		Value
Mechanical properties		
Thickness of dry membrane, t_d (mm)		0.40 ± 0.05
Thickness of swelled membrane in demi water, t_w (mm)		0.50 ± 0.05
Swelled differences, Δ (in demi-water)	Thickness, Δt (%)	22 ± 2
	Length, Δl (%)	16 ± 2
	Width, Δw (%)	16 ± 2
	Weight, Δwt (%)	60 ± 5
Electrochemical properties		
Water splitting voltage (measured in 0.50 M NaCl; 13 mA/cm^2), U_m (mV)		1,200 ± 100
Other properties		
• Good thermal resistance: ○ Inside membrane stack under DC current 40℃, for a short time 45℃ • Hygiene and epidemiology certificate • Long-term stability at pH 0–14		

4. Results and discussion

4.1. Verification of EDBM capability for pH decrease

In the first series of experiments, we aimed to verify the capability of EDBM for increase in wine acidity. In each experiment, 1.5 l of Sauvignon Blanc with original pH 3.25 was used. Into base loop was added 0.5 l of demi water. The experiments continued until the required pH was achieved, specifically pH 2.75, 2.95, 3.05 and 3.15.

pH decrease is almost linear during the whole period of experiment (Fig. 4). The achieved velocity of pH drop decreases and the time required for specific pH value change increases with the number of experiments carried out, probably due to membrane scaling (like in the fourth case—Fig. 5).

From the obtained data was calculated energy consumption per wine unit and capacity related to membrane active surface per time unit (Table 2).

4.2. Determination of demineralized water consumption for base loop dilution

The aim of second series of experiments was to specify capacity estimation, determine amount of water for base loop dilution and determine frequency

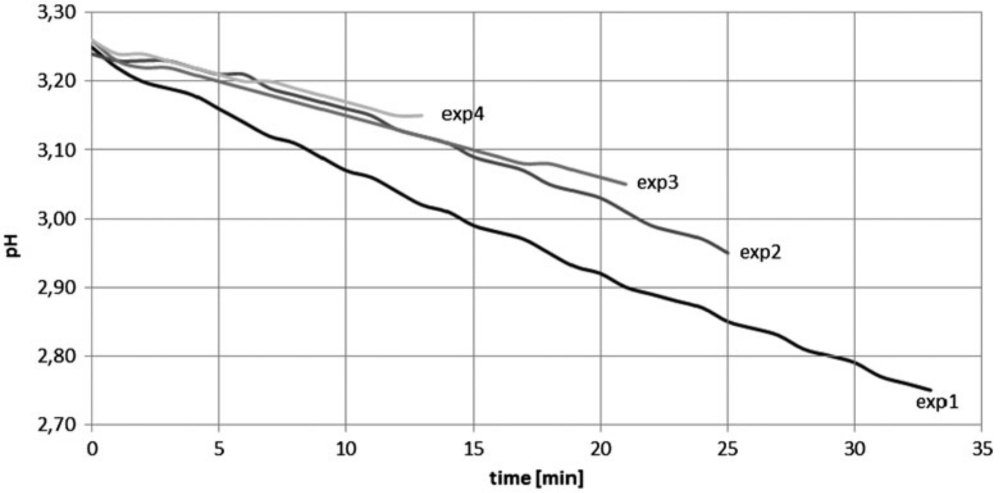

Fig. 4. Wine pH progress over time.

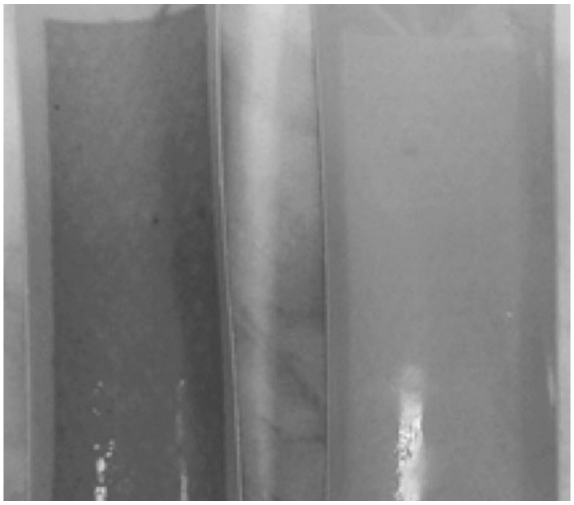

Fig. 5. Left—BM from concentrate loop; Right—New BM.

Table 2
Energy consumption and capacity of EDBM technology

pH decrease	0.20	0.10
Energy consumption (W h/kg of wine)	0.46	0.24
Capacity (l of wine/h m^{-2})	220	350

of CIP. Again, we used 2 l of Sauvignon Blanc for each experiment. The liquid volume in base loop was 0.9 l. In some cases demineralized water was used, in other concentrate from previous experiments was used (Table 3). Once pH 12 was reached, demineralized water was added to keep pH value constant. Experiment was finished once pH value of wine dropped by 0.2. Demineralized water was added during all experiments.

Average consumption of demineralized water for base loop dilution was 1,010 g per 1.96 kg of wine. This was calculated only from results of experiments in which concentrate from previous experiment was used.

4.3. *pH increase in cider*

In the third series of experiments we tested pH increase. For experiments was used apple cider with original pH of 3.51. Cider manufacturer complained about the taste being too sour. For each experiment was used 2 l of cider and experiment was terminated once the required pH was reached, specifically pH values of 3.75, 4.00, 4.25 and 4.50.

From pH progress of individual batches (Fig. 6 (left)) is obvious that EDBM technology is capable of pH increase in exact level in narrow interval. Almost linear increase in pH within tested interval may help with prediction of operation parameters of industrial scale technology. At the beginning of first experiment is very well obvious about the nonlinearity of pH progress. Time required for the pH to return to initial value and the system to regain stability is not negligible—it took almost half of the time required for the first batch to be processed. For production planning (determination of run-up time), it is necessary to further examine the dynamics of the processes.

Simultaneously were recorded pH values of acid concentrate from apple cider. During the experiments pH was decreasing (Fig. 6 (right)), which is indicative of acid concentration increase.

Once all the experiments were finished, the membrane stack was disassembled and membranes were checked for fouling. In case of AEM, on side where hydroxide anions were transported into cider, membrane was significantly fouled (Fig. 7(a)). The side of AEM from which were acid anions transported from

Table 3
Progress of experiments

Exp. No.	Type of concentrate (base loop)	Addition of demi water (g)
1	Fresh demi water	518
2	Concentrate from exp. 1	1,037
3	Concentrate from exp. 2	1,149
4	Fresh demi water	296
5	Concentrate from exp. 4	758
6	Concentrate from exp. 5	1,146
7	Concentrate from exp. 6	956
CIP carried out after exp. 7		
8	Mix of previous concentrates	968
9	Concentrate from exp. 8	1,074
10	0.5 L of C 8 + 0.5 fresh demi water	579

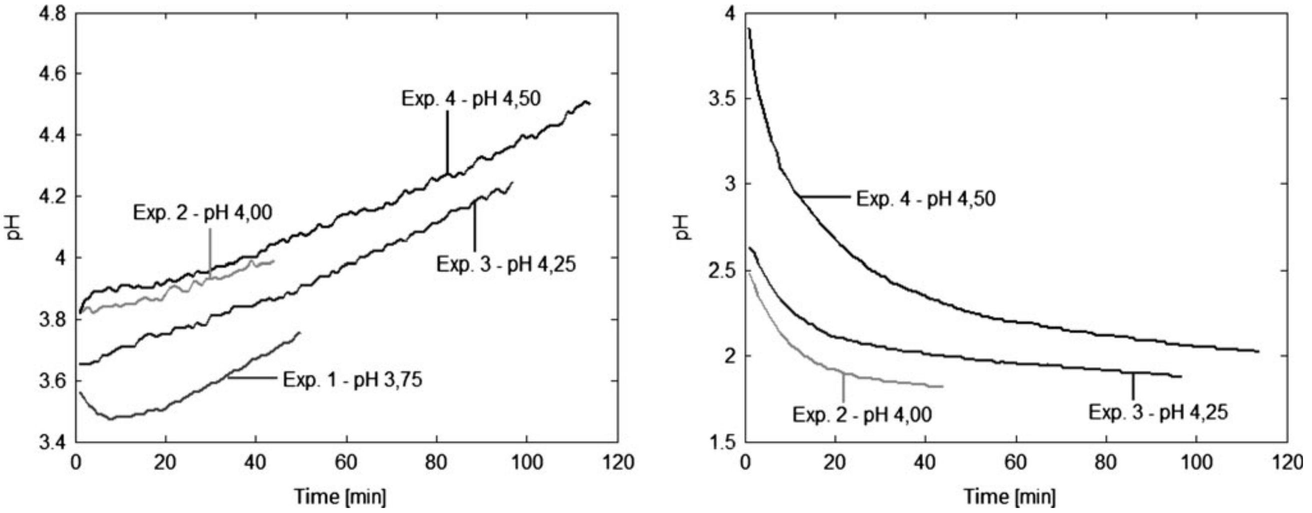

Fig. 6. pH progress for different final pH of apple cider batch (left) and acid concentrate (right).

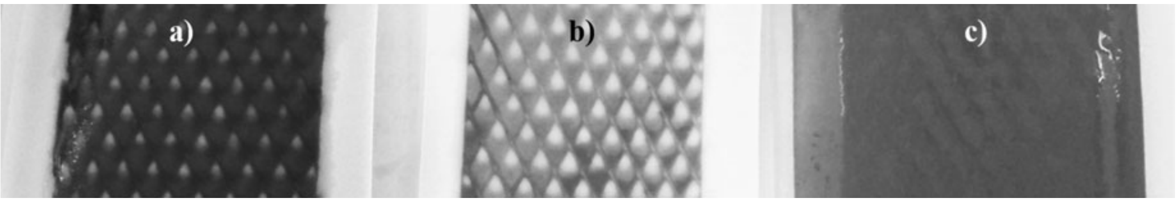

Fig. 7. Membrane fouling: (a) AEM donor of OH^-, (b) AEM acceptor of acid anions and (c) BM.

cider into demineralized water was less fouled (Fig. 7(b)). Anion exchange membranes protected by BM were without changes (Fig. 7(c)).

At higher pH accelerates browning of apple cider juice due to increased activity of tyrosinase oxidizing apple polyphenols. Based on the membrane fouling analysis, we can conclude that in the cider loop developes gradient of pH due to ion migration. This unequal membrane fouling will need to be taken into account for CIP frequency in case of real application. CIP with diluted sodium hydroxide solution was successful.

4.3.1. Sensory evaluation

Sensory evaluation of organoleptic properties of original and modified samples followed afterwards. Samples were refrigerated and tested within two days. The effect of pH modification on taste was evaluated by triangle sensory test. Test results are evaluated in Table 4. Based on the results, pH modification can be distinguished.

"Hedonic scale" sensory evaluation was also carried out. For our purpose were chosen following descriptors: sweet and sour taste and whole impression. Intensity of these was evaluated on 0–10 scale, where 10 was the maximum. Samples were tested in order of increasing pH. From results was calculated median of given descriptor. Trends of descriptors are represented above (Fig. 8).

It is clear that sensory sourness (sour taste) was decreased. The change of sourness also affects subjective perception of sweetness of apple cider. Based on these results, we can claim that it is possible to achieve better overall perception of apple cider through EDBM process (approx. by 20% compared to original sample).

Table 4
Triangle sensory test results

pH of modified sample	3.75	4.00	4.25	4.50
Relative abundance of correct answers	0.75	1.00	0.38	1.00

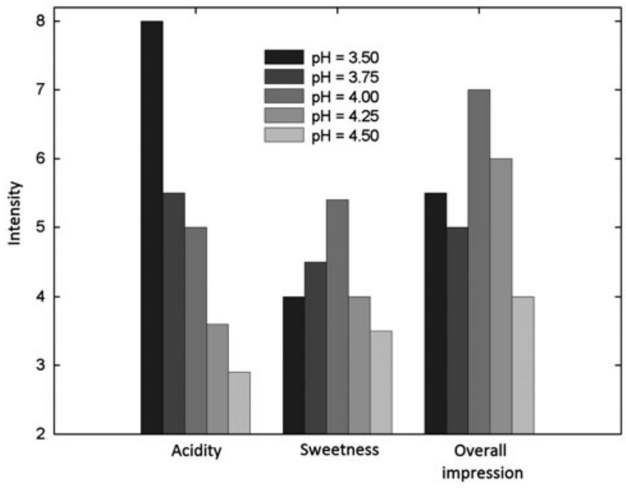

Fig. 8. Median intensity of chosen descriptors of organoleptic properties of apple cider at different pH.

4.4. *Necessity of filtration and determination of CIP parameters*

In the fourth series of experiments we decreased pH of wine must. The must was not filtered, only decanted with turbidity of 300 NTU and pH 3.22. For each experiment was used 2 l of must, the initial volume of liquid in base loop was 0.7 l. We used demineralized water in first experiment; in following experiments concentrate from previous experiment was used. The concentrate was diluted by demineralized water to constant value of pH 12. CIP with 3% solutions of sulphuric acid and potassium hydroxide was carried out after second, fourth and sixth experiment. During some experiments was stack voltage increased due to time pressure (Table 5).

Typical progress of pH change during deacidification is linear. Angular coefficient of pH decrease may be affected by potassium and other cations concentration. Membrane fouling by organic molecules has significant impact on the velocity of pH decrease. Processing of unfiltered wine must brings potential of ED stack clogging by solid particles.

Due to transport of both, monovalent and bivalent ions through CEM, concentration of Ca^{2+} in base loop is increasing (Table 6). The final concentrations of calcium cations may be up to 30-times higher than the concentration which considered safe for operation of EDBM unit—1 ppm. Around pH 12 starts coagulation of hydroxides of multivalent hydroxide on membrane surface. This process diminishes active surface of membrane and also impairs access of water to membrane. Access of sufficient amount of water is crucial for effective dissociation of water molecules at layer interface of bipolar membrane.

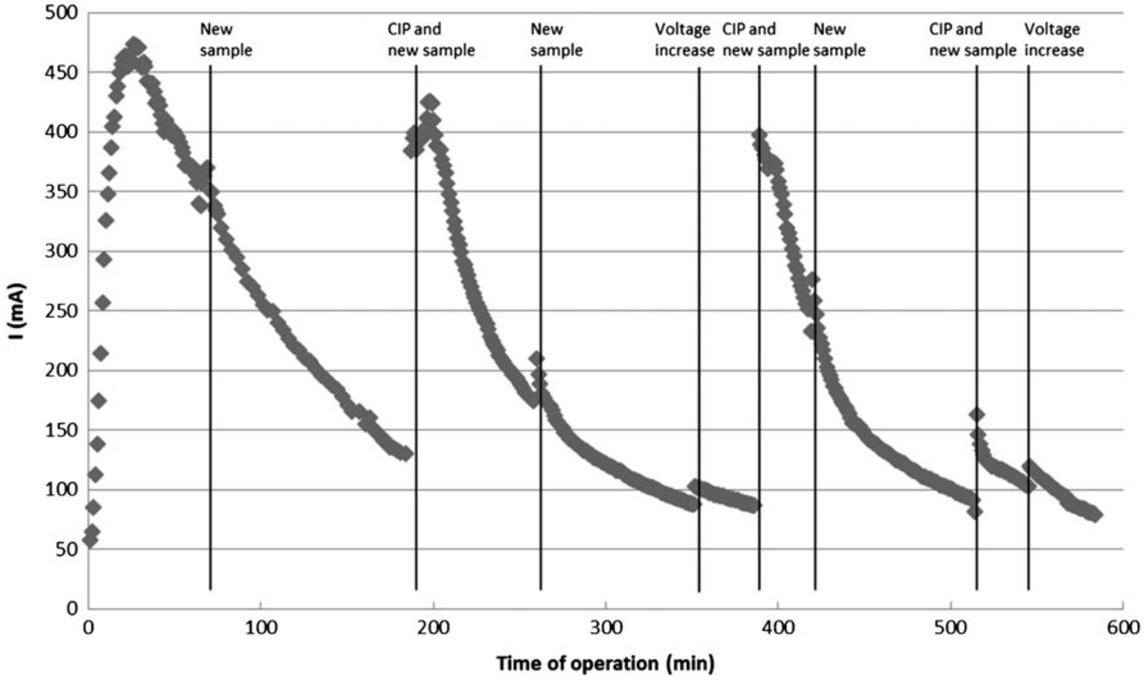

Fig. 9. Electric current progress in time and after CIP.

Table 5
Progress of experiments

Exp. No.	Change of diluate pH	Length of experiment (min)	Demi water (ml)	Notes
1	0.3	66	1,400	
2	0.3	107	1,030	
CIP				2.5 h
3	0.2	72	1,970	
4	0.2	113	500	From 91st min $U = 7.2$ V
CIP				1.5 h
5	0.1	31	320	
6	0.1	96	310	
CIP				30 min
7	0.1	71	240	From 31st min $U = 7.2$ V

Table 6
Ca^{2+} concentration in concentrate loop of EDBM

Sample no.	pH	Ca^{2+} (mg/l)
1	12.08	14.8
2	12.16	27.7
3	12.09	19.0
4	12.15	28.3
5	12.14	31.3
6	12.17	36.9
7	12.17	17.6

CIP parameters evaluation is crucial. The frequency of CIP must be so often to achieve average electric current of at least 0.2 A during the whole cycle between CIP.

In the case of unfiltered wine must CIP cycle took place after 180–220 min of EDBM operation. CIP frequency does not depend on required pH change.

It is clear from electric current progress (Fig. 9) that through CIP is possible effectively restore current density to original value. However, the cleaning process requires minimum length of time. There was no difference in efficiency of CIPs lasting 1.5 and 2.5 h. However, the CIP which lasted only 30 min was insufficient (Fig. 10).

The experiment also proved that decantation for clarification before EDBM process is insufficient. If unfiltered wine must is processed, diluate chamber will clog which will lead to hydraulic changes of flow and decrease in whole capacity. Filtration will be required to remove suspended solids and prevent spacer clogging.

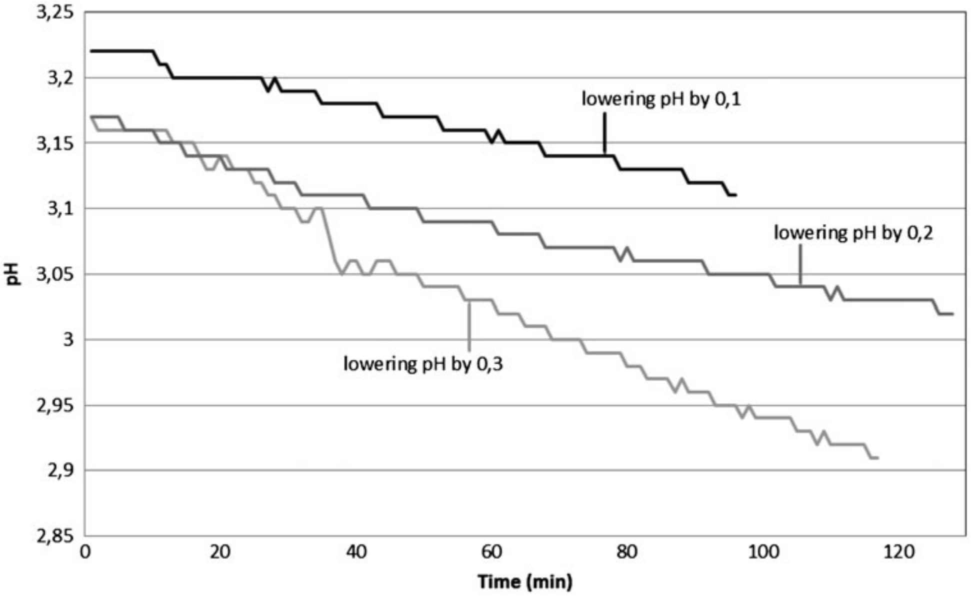

Fig. 10. pH progress during EDBM process.

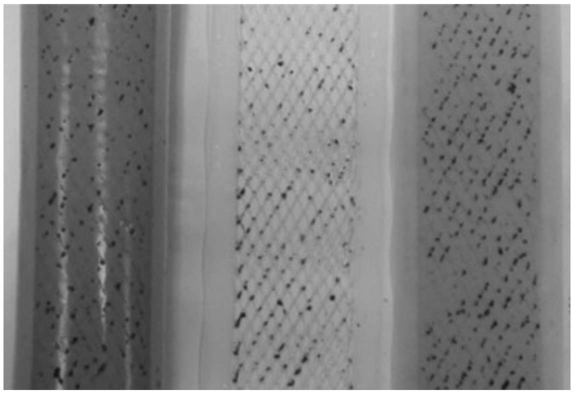

Fig. 11. Mechanical fouling in diluate chamber (from left: BM, spacer, CEM).

Above discussed facts suggest that this technology is demanding on cleaning process in both, time and material. Below is compared consumption of chemicals and demineralized water for CIP of EDBM unit and regeneration of IEX filter. Same amount of processed liquid was considered for this calculation (Fig. 11).

Chemicals required for CIP of EDBM:

(1) 1,000 l demi water for concentrate dilution.
(2) 100 l sulphuric acid (3% by weight) for CIP.
(3) 50 l sodium hydroxide (3% by weight) for CIP.
(4) 200 l demi water for CIP.

Chemicals required for regeneration of IEX filter [6]:

(1) 100–250 l drinking water for filter washing
(2) 25 l hydrochloric acid (10% by weight) for regeneration
(3) 150–400 l demi water for rinse (max. 7 l/l of ionex)

5. Conclusion

Application possibilities of EDBM technology were verified for acidification and deacidification of beverages. pH adjustment can be set with accuracy of 0.05 of unit to the extent of units. Progress of acidification/deacidification was linear enough to be able to predict operational parameters of industrial units.

It was proved that decantation is insufficient and filtration of raw liquid will be necessary as EDBM pretreatment.

To decrease wine pH by 0.2, 1 m^2 of active surface of bipolar membrane can process 100–250 l of wine per hour, depending on the processed liquid. Energy consumption for such pH change is 0.5 kWh/ton (energy calculated only for ion transport). Dilution of concentrate with demineralized water is required. Expected ratio is 1 l of demi water to 2 l of processed beverage.

CIP frequency of stack and unit depends significantly on processed material. In our tests, operation cycle of EDBM technology (period between CIPs) was 3–5 h.

Comparison of our results for EDBM technology with IEX technology [6] suggests that consumption of demi water and chemicals is in favour of IEX technology.

To extend lifecycle of bipolar membrane it is recommended to acquire cation exchange monovalent selective membrane to achieve higher concentration of potassium hydroxide and to prevent calcium coagulation on bipolar membrane.

Sensory evaluation proved that increase in cider pH by removal of acid anions has significant impact on its organoleptic properties. In our case, adjustment to pH 4 improved the overall impression of cider by 20%. We can claim that by pH adjustment through EDBM technology can be achieved better organoleptic properties.

Abbreviations

A	acid circuit
AEM	anion exchange membrane
B	base circuit
BM	bipolar membrane
CEM	cation exchange membrane
CIP	cleaning in place
D	diluate circuit
E	electrolyte circuit
ED	electrodialysis
EDBM	electrodialysis with bipolar membranes
IEX	ion exchange

Acknowledgments

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