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Optimization of the Ultrasound-Assisted Extraction Process of Aspartic Acid from Molasses and its Anti-scaling Capability in Sugar Industry Evaporators

M. Mokhtarian [a], ***M. Honarvar*** [b*], ***M. Mizani*** [c], ***M. Ghavami*** [c]

[a] PhD Research Student of the Department of Food Science and Technology, Science and Research Branch, Islamic Azad University, Tehran, Iran.
[b] Associate Professor of the Department of Food Science and Technology, Science and Research Branch, Islamic Azad University, Tehran, Iran.
[c] Professor of the Department of Food Science and Technology, Science and Research Branch, Islamic Azad University, Tehran, Iran.

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ABSTRACT: This study aimed to optimize the extraction of aspartic acid from sugar beet molasses using an ultrasound-assisted extraction method and its use as a green anti-scaling agent in the evaporator tubes of the sugar industry. The results of ultrasound-assisted extraction showed that the linear model is the best model to describe the behavior of aspartic acid extraction. It was determined that the optimal conditions for extracting aspartic acid using the ultrasound-assisted method include an extraction temperature of 25.09 °C, pH of 7.00, ultrasound power of 69.99%, and no ethanol. The extracted aspartic acid under optimal conditions was applied with various concentrations (10, 25, and 50 mg/100g) and temperatures (60, 90, and 120 °C) on the scales of the sugar industry evaporators. The highest anti-scaling efficiency for all three processes was related to the treatment performed at 90 °C with a concentration of 50 mg/100 g. Field emission scanning electron microscopy images showed that by increasing temperature up to 90 °C and increasing concentration up to 50 mg/100g, the scales formed on the evaporator tube changed from crystalline and uniform state to porous with fine particles. Energy dispersive spectroscopy analysis showed that by increasing the temperature to 90 °C and increasing the concentration to 50 mg/100g, the calcium and silica content in the scales of the evaporator tubes decreases. Fourier-transform infrared spectroscopy analysis showed that by applying aspartic acid as an anti-scaling of stable crystals, the scales become smaller and more unstable crystals.

Keywords: Aspartic Acid, Green Anti-scaling, Molasses, Optimization, Ultrasound-Assisted Extraction.

Introduction

The sediments deposited on the evaporator tube during the concentration of syrup in the sugar industry act as a limiting factor for further concentration of the syrup. These sediments prevent further concentration of raw syrup by reducing the heat transfer coefficient (Madaeni *et al.*, 2004). Mineral salts that are present in raw syrup and have low solubility are deposited on the evaporator walls as a result of the cooking process of the syrup and will lead to a decrease in the heat transfer coefficient (Djordjević *et al.*, 2018). Silicon, iron, sulfur, phosphorus, and calcium are the most important

[*]Corresponding Author: m.honarvar@srbiau.ac.ir

elements in the sediments of the evaporator walls, which reduce the thermal efficiency of the stove bodies and syrup heaters (Smith & Taylor, 1981). However, the most negative effect of these deposits is on the evaporator walls, leading to the formation of hard scales, and their composition depends on the nature of the primary syrup. There are currently several methods (chemical and physical) of descaling that lead to damage to evaporators (Coombs, 1986).

Since the formation of sediments on the evaporator walls is an inevitable thing, sodium hydroxide (caustic soda) is used industrially to solve this problem, which will lead to the softening of the sediments. Therefore, after softening the sediments, water jets are used to remove the resulting sediments (Drennan *et al*., 1995; Phakam *et al*., 2018). However, the main problem related to the physical and chemical removal of sediments from the tubes of the evaporators is to provide conditions for the corrosion of the tubes. Although the corrosion of evaporators and cooking bodies leads to significant economic costs, using anti-scaling chemicals has many negative effects on human health (Ghosh & Balakrishnan, 2003).

Therefore, researchers recommend the use of plant metabolites with a green nature and safe methods of extraction to reduce the adverse effects of chemical compounds. Plant metabolites are biodegradable and non-toxic compounds that can be used as natural sediment inhibitors. The lack of biological accumulation of plant metabolites qualifies their use as natural anti-scaling agents (Chaussemier *et al*., 2015).

By processing sugar beet and extracting sugar from it, molasses is produced as waste, which can be used in various industries as a cheap source of bioactive compounds with unique properties. By extracting these bioactive compounds from molasses, products with high added value can be produced that can be used for different purposes (Varaee *et al*., 2019). In our previous study, it was proved that the aspartic acid extracted from molasses is able to remove scales from the surface of the evaporator tubes. In the last research, aspartic acid was extracted from molasses using a microwave-assisted process and applied to the scales of evaporator tubes under different conditions. The results showed that aspartic acid can transform scales with stable crystals into unstable crystals, which will lead to the formation of porous and fine sediments (Mokhtarian *et al*., 2022).

Traditional common methods for extracting and separating products have disadvantages. In centrifugation and sedimentation, the size and density of the material are involved. Therefore, optimal separability is not achieved. The energy cost is very high, especially for viscous solutions. Chromatographic methods such as column chromatography or high-pressure liquid chromatography, although specific, can transfer only a small part of the feed (Aguilar & Rito-Palomares, 2010). In recent years, the use of ultrasound as a new method with its advantages, high efficiency, convenience, and low maintenance costs has gained an important place in the food industry.

The term ultrasound refers to sound waves whose frequency is higher than the range of human hearing (about 20 Hz to 20 kHz). When the liquid medium is affected by ultrasonic radiation, microbubbles form, grow, and oscillate rapidly and finally explode with full force (if the sound pressure is high enough). The bubbles created inside the media are the cavitation phenomenon, which is responsible for the effect of ultrasound. When the size of the bubbles reaches a

critical point, they explode during the compression cycle, releasing a large amount of energy. The temperature and pressure at the moment of explosion are estimated to be around 5000 K and 5000 atmospheres. The creation of these hot spots can significantly accelerate the speed of chemical reactions in the desired media (Kumar *et al*., 2021). Therefore, this study not only aims to optimize aspartic acid extraction from sugar beet molasses using the ultrasound-assisted method but also to explore its potential use as a natural anti-scaling agent in the sugar industry evaporators.

Materials and Methods

Aspartic acid standard, methanol, acetic acid, and HPLC grade acetonitrile were purchased from Merck Co. Darmstadt, Germany. Molasses was obtained from Hegmatane Sugar Company, Hamadan, Iran.

- Ultrasound-assisted extraction

In order to extract aspartic acid from sugar beet molasses according to the method proposed by Patil *et al*. (2021) with some modifications in the ultrasound-assisted extraction process. Sugar beet molasses was extracted by the response surface method and the Box-Benken design. The variables include the concentration of ethanol (0, 25, and 50 % v/v), temperature (25, 40, and 55 °C), pH (3, 5, and 7), and ultrasonic power (30, 50, and 70 % of 20 kHz) (Table 1). In order to carry out the object, an ultrasound machine (Bandelin - AMMM - M.P.I. Germany) consisting of a 20 kHz ultrasound generator and a cylindrical probe was used for 15 min. Molasses samples were mixed with water and water/ethanol at a ratio of 1:30, and the desired pHs were adjusted by 0.1 N HCl and 0.1 N NaOH. After adjusting the pH of the solution, the probe of the ultrasonic device was placed inside the samples, and the extraction operation was performed using different ultrasonic ranges. It should be noted that the thermal jacket system connected to the device was used to adjust the extraction temperature (Kumar *et al*., 2021).

- Determination of aspartic acid content

High performance liquid chromatography (HPLC) was used to determine the aspartic acid content in the samples extracted from sugar beet molasses. To determine the inhibition time of aspartic acid, the aspartic acid standard was injected into the device separately. Then the samples extracted from sugar beet molasses were injected into the HPLC device. During this research, an HPLC device equipped with a fluorescence detector was used. HPLC analysis was performed with the SGE Hypersil ODS C18 column on a laboratory scale (250 × 4.6 mm i.d.) and a particle size of 5 µm. HPLC conditions were as follows: mobile phase A, ammonium phosphate (pH 6.5) 30 mM in methanol with 85:15 ratio v/v; water; mobile phase B, 15: 85 v/v methanol; water; mobile phase C, 90: 10 v/v acetonitrile; water. The washing gradient (min/A%/B%/C%) was as follows: 13:63:0.24, 46:43:11.32, 46:43:11.34, 100:0:0.05 /34, 100: 0: 0/5/36, 13: 63: 24/55/36, 13: 63: 24/50. The flow rate was constant and equal to 1.1 ml/min and the ambient temperature was maintained at 38 °C. Finally, the extraction yield was calculated using the following equation (Sánchez-Machado *et al*., 2010).

Extraction Yield (% w/w) = [Weight of extracted aspartic acid (mg) ÷ Weight of molasses (g)] × 100

Table 1. RSM design related to different levels of ultrasound-assisted extraction process variables and response (extraction yield)

Run	Ethanol (%)	Temperature (°C)	pH	Power (%)	Extraction Yield (mg/100 g sample)
1	25	55	7	70	52.33
2	25	25	5	50	56.61
3	50	40	3	30	48.41
4	25	55	5	30	55.68
5	25	25	5	70	55.67
6	25	40	3	50	61.57
7	25	25	3	50	45.2
8	0	55	5	50	64.02
9	50	40	7	70	45.95
10	0	40	5	50	49.61
11	50	25	5	50	42.03
12	25	40	5	50	59.34
13	0	40	7	30	52.76
14	25	40	7	30	61.09
15	50	40	5	50	43.38
16	25	40	5	50	45.38
17	25	25	7	70	62.61
18	25	40	7	30	61.16
19	0	40	5	70	44.06
20	25	55	5	50	57.92
21	0	40	3	70	52.6
22	50	40	5	50	62.5
23	0	25	5	50	57.73
24	50	55	5	30	44.74
25	25	40	3	50	44.57
26	25	55	3	50	40.02
27	25	40	5	50	59.54

- **Anti-scaling activity of extracted aspartic acid**

To investigate the anti-scaling activity of aspartic acid extracted from sugar beet molasses under optimal conditions of three different concentrations of aspartic acid solution (10, 25, and 50 mg/l) with three different temperatures of 60, 90, and 120 °C at pH equal to 8 was applied on the evaporator tube of the sugar industry for 6 h.

- **Anti-scaling efficiency**

To check the efficiency of anti-scaling, the difference in the weight of scales on the evaporator tubes before and after anti-scaling was evaluated. For this purpose, sugar industry evaporator tubes were cut with the same dimensions (length 1.5 cm) and the scales deposited on the primary pipes were gently scraped and completely collected. The weight of the scraped scales before anti-scaling was recorded as the initial weight. Then the intact pipes were subjected to different treatments of anti-scaling operations and the weight of the scales after descaling was recorded as secondary weight. Finally, the anti-scaling efficiency is calculated with the obtained weight difference (Jampílek *et al*., 2019).

- **Morphological characteristics and Energy dispersive spectroscopy analysis (EDS) analysis**

Field emission electron microscope (FESEM; MIRA3, TESCAN, Czech Republic) is used to investigate the microstructural characteristics of scales

before and after applying aspartic acid with different concentrations and different temperatures (Rezaeinia, Ghorani, *et al*., 2020). Before analysis, the scales were coated with a thin layer of gold by a sputter coater (K-450X, EMITECH, England) for 150 s at 20 mA. Also, for elemental analysis and ensuring the change of composition of elements after applying aspartic acid as an anti-scaling agent, FESEM equipped with EDS was used (Xie *et al*., 2020).

- **Fourier transform infrared spectroscopic analysis**

FTIR device (Bruker Alpha FTIR, US) was used to investigate the possibility of reaction between different compounds of scales and aspartic acid as well as change the type of bonds. The FTIR spectrum of each of the samples was obtained in the wave number range of 4000 to 400 cm^{-1} (Rezaeinia, Emadzadeh, *et al*., 2020).

- **Design of experiments and statistical analysis**

To investigate the effect of each of the variables of the ultrasound-assisted extraction process, i.e., concentration of ethanol, temperature, pH, and ultrasonic power, on the extraction efficiency, Box-Benken and response surface methodology were used by Design Expert 10.0 software. In addition, the comparison of average data was made by one-way ANOVA using Duncan's multiple range test and by IBM SPSS statistics software (version 22.0, IBM Corp., USA) at a probability level of 5%.

Results and Discussion

- **Ultrasound-assisted extraction**

The ultrasound-assisted extraction process was used to extract aspartic acid from molasses. For this purpose, the parameters of ethanol concentration (0, 25, and 50% v/v), temperature (25, 40, and 55 °C), pH (3, 5, and 7), and ultrasound power (30, 50, and 70%) were used. Aspartic acid extracted from each sample was analyzed using HPLC and its amount was determined (Table 1). The obtained results showed that the linear model (Eq. 1) between the data is the best model to describe the behavior of aspartic acid extraction from sugar beet molasses.

$$Y_i = A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_4X_4 \quad \text{Eq.1}$$

Where, Y_i is the dependent variable (Y_1: aspartic acid extraction efficiency), A_0 is the response index fitted at the center point of the plot which is equivalent to the point (0, 0, 0), A_1, A_2, and A_3 are linear coefficients, and X are independent variables (X_1: the concentration of ethanol, X_2: extraction temperature, X_3: solvent pH, and X_4: ultrasound power). The significance test was performed based on the total error at the 95% confidence level. The efficiency of the model was calculated and evaluated by R^2 and adjusted R^2.

The results of this study to investigate the effect of extraction process conditions (ethanol concentration, temperature, pH, and ultrasonic range) on the efficiency of aspartic acid extraction from sugar beet molasses are presented in the form of two-dimensional images (Figure 1). The results of analyzing the variance of the data (ANOA) related to each answer as well as the coefficients of the regression model of the first order equation for the extraction efficiency of aspartic acid are shown in Tables 2 and 3, respectively.

Based on the results obtained from data variance analysis and ANOA table, it was found that the extraction efficiency of aspartic acid is significantly (p<0.05) influenced by the ultrasound-assisted extraction (ethanol concentration, temperature, pH, and ultrasound power).

Therefore, as shown in Table 2, the extraction efficiency of aspartic acid is significantly (p<0.05) influenced by the concentration of ethanol used as a solvent, pH and ultrasonic power, but the extraction efficiency is significantly (p<0.05) was not affected by process temperature (Table 2). Also, the data dispersion and their normality compared to the proposed model are shown in Figure 2, which shows the appropriate data dispersion and their normality. Figure 1 shows the effect of ultrasound-assisted extraction process variables on the recovery of aspartic acid from molasses in two dimensions plan. As shown in Figure 1, with the increase of extraction temperature from 25 to 55 °C, the extraction efficiency of aspartic acid from molasses decreases, but this decrease is not statistically significant (p<0.05). However, increasing the concentration of ethanol from 0 to 50% v/v significantly (p<0.05) led to a decrease in the extraction efficiency of aspartic acid from molasses. It was also found that increasing the pH from 3 to 7 and increasing the ultrasonic power from 30 to 70% significantly (p<0.05) increases the recovery of aspartic acid from molasses by the ultrasound-assisted method. The increase in the extraction efficiency of aspartic acid from molasses using the ultrasound-assisted extraction process as a result of increasing the pH from 3 to 7 and also increasing the ultrasound power from 30 to 70% can be attributed to the increase in the solubility of aspartic acid as a result of the ultrasound-assisted extraction process. Based on the studies, it has been determined that amino acids and proteins have higher solubility in the pH range higher or lower than their isoelectric pH. Because aspartic acid has an isoelectric pH of about 3, therefore, by increasing the pH of the solvent from 3 to 7, because the pH of the solvent moves away from the isoelectric point of aspartic acid, therefore, the solubility of aspartic acid in the media increases and the efficiency of extracting aspartic acid from molasses using the ultrasonic extraction process is enhanced. It has also been found that increasing the ultrasonic power, due to the high energy it creates, improves the mass transfer process and causes more aspartic acid to penetrate the solvent from the molasses matrix, and as a result, the extraction efficiency will increase. In addition, studies have shown that aspartic acid has very little or insoluble solubility in alcohol (ethanol) and alcohol-based solvents. Therefore, it can be expected that by increasing the percentage of ethanol in the solvent to extract aspartic acid from molasses, the recovery efficiency of aspartic acid will decrease. Carrera *et al*. (2015), studied the optimization of amino acid extraction from grapes. Based on the results obtained by these researchers, it was found that by increasing the ultrasonic power and moving away from the isoelectric point of amino acids, the extraction efficiency of amino acids from grapes increases (Carrera *et al*., 2015).

Table 2. ANOA table related to the effect of ultrasound-assisted extraction process variables on the extraction efficiency of aspartic acid from sugar beet molasses

Source	Extraction Yield (mg/100 g)
Model	< 0.0041
A (Ethanol)	< 0.0478
B (Temperature)	0.3331
C (pH)	< 0.0032
D (Power)	0.0439
R^2	0.92
Adj-R^2	0.86
CV	10.75
Lack of Fit	0.9350 (not significant)

Table 3. Regression coefficients of linear equation for aspartic acid extraction by ultrasound-assisted extraction

Source	Yield (mg/100 g)
Intercept	52.38
A_1 (Ethanol)	-2.81
A_2 (Temperature)	-0.43
A_3 (pH)	3.63
A_4 (Power)	3.74

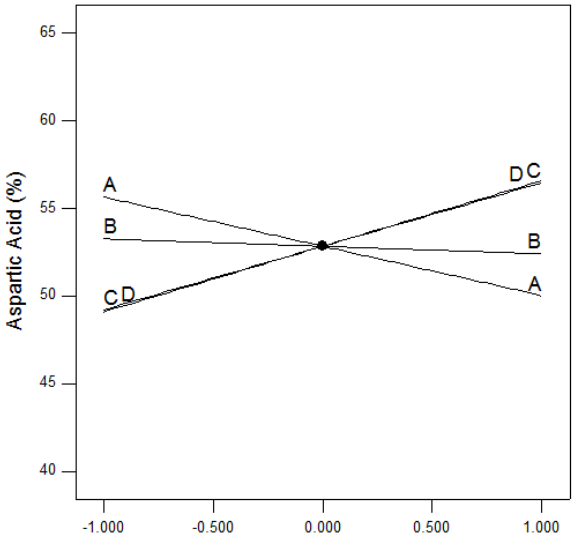

Fig. 1. Two-dimensional diagram of the effect of ultrasound-assisted extraction process variables on aspartic acid extraction (A: ethanol, B: temperature, C: pH, and D: power)

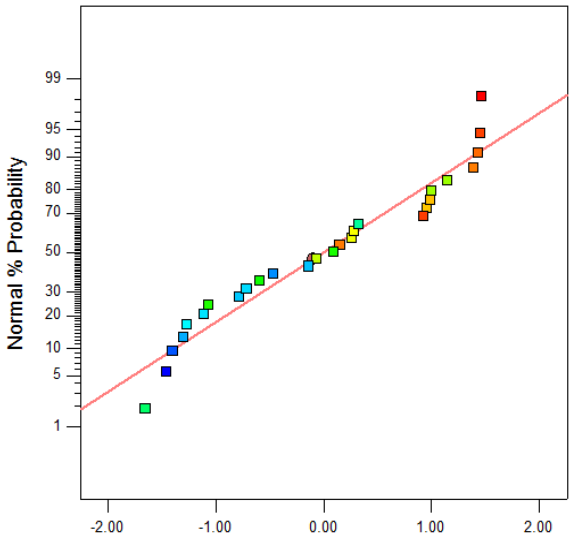

Fig. 2. Normal distribution diagram of aspartic acid extraction data in the ultrasound-assisted extraction

- **Optimization of aspartic acid extraction**

Based on the results obtained during this phase of the research and the effect of each process variable on the extraction efficiency of aspartic acid, the extraction conditions were optimized to maximize the extraction efficiency of aspartic acid. For this purpose, extraction of aspartic acid was performed by applying extraction conditions of ultrasound-assisted in three levels of ethanol as a solvent (from 0 to 50% v/v), three levels of temperature (25, 40, and 55 °C), three levels of pH (from 3 to 7), and three levels of ultrasonic range (from 30 to 70%) and the content of aspartic acid extracted from each molasses sample was evaluated using HPLC. According to the obtained results, the optimization was done based on the maximum efficiency of aspartic acid extraction, and the optimal conditions were selected based on the desirability function, and hence the limitations of the process for extracting aspartic acid from molasses samples are shown in Table 4. For this reason, the highest extraction efficiency of aspartic acid from sugar beet molasses was chosen as the optimization target, and the results of the optimization of the level of the variables are shown in Table 5 in the form of predicted data and experimental data. Therefore, it can be concluded that the optimal conditions for the highest extraction efficiency of aspartic acid from sugar beet molasses include 00.00 % ethanol, 25.09 °C temperature, 7.00 pH, and 69.99 % ultrasonic power (Table 5). Therefore, under the optimal conditions of ultrasound-assisted extraction mentioned above, the amount of aspartic acid extracted from beet molasses was 65.03 mg/100g (Table 5). The results obtained from the extraction efficiency of aspartic acid from beet molasses showed that there

is a very small difference between the experimental data and the predicted data from the regression model used in the RSM method. This indicates that the predicted model during this research to evaluate the data and optimal conditions for extracting aspartic acid from beet molasses with the highest efficiency is well fitted and the data is consistent with the predicted model. Sánchez-Zurano *et al*. (2020), studied the optimization of protein extraction from bacteria. Based on the results obtained by these researchers, it was found that there is not much difference between the experimental data and the predicted data. For this reason, these researchers stated that the proposed model for protein extraction from bacteria using the ultrasonic process fits well (Sánchez-Zurano *et al*., 2020).

- **Anti-scaling efficiency**

The results of the anti-scaling efficiency of aspartic acid extracted from molasses using the ultrasound-assisted extraction process with concentrations of 10, 25 and 50 mg/100g and different temperatures (60, 90 and 120 °C) on the sediments of sugar industry evaporators and comparing the average data based on

Table 4. Limitations of the optimization process of aspartic acid extraction from sugar beet molasses by the ultrasound-assisted extraction method

Name	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
Ethanol (%)	In range	0	50	1	1	3
Temperature (°C)	In range	25	55	1	1	3
pH	In range	3	7	1	1	3
Power (%)	In range	30	70	1	1	3
Yield (mg/100 g)	Maximize	40.02	64.02	1	1	3

Table 5. Optimal level of variables, predicted responses and experimental results for extraction of aspartic acid from sugar beet molasses by ultrasound-assisted extraction method

Variable	Optimal variable level	
Ethanol (%)	0.00	
Temperature (°C)	25.09	
pH	7.00	
Power (%)	69.99	
Response	Predicted value	Experimental value
Yield (mg/100 g)	63.44 ± 1.25^{a}	65.12 ± 1.16^{a}

* The same case showed no significant difference (p>0.05).

Table 6. Descaling efficiency of the solutions containing aspartic acid extracted from an optimum condition of the ultrasound-assisted extraction method

Treatment	Concentration (mg/L)	Temperature (°C)	Descaling efficiency (%)
1	10	60	24.24 ± 1.11^{i}
2	25	60	45.28 ± 1.21^{f}
3	50	60	70.38 ± 1.15^{b}
4	10	90	46.62 ± 1.18^{g}
5	25	90	55.49 ± 1.34^{d}
6	50	90	74.37 ± 1.42^{a}
7	10	120	29.50 ± 1.14^{h}
8	25	120	49.21 ± 1.08^{e}
9	50	120	65.34 ± 1.23^{c}

* Different letters indicate significant differences (p<0.05).

Duncan's multi-range test, it is shown in Table 6. Based on the results of data variance analysis, it was found that the anti-scaling efficiency is significantly (p<0.05) dependent on the amount of extracted aspartic acid and the process temperature. Therefore, as shown in Table 6, by increasing the concentration of aspartic acid from 10 to 50 mg/100g, the anti-scaling efficiency increases significantly (p<0.05) from 40 to 50%. It was also found that increasing the temperature of the anti-scaling process by aspartic acid extracted from molasses from 60 to 90 °C significantly (p<0.05) increased the anti-scaling efficiency. However, increasing the process temperature from 90 to 120 °C significantly (p<0.05) decreased the anti-scaling efficiency (Table 6). Aspartic acid, due to its active and reactive groups (amino group and acid group), has the ability to react with positively and negatively charged elements and ions in the structure of sediments, and in this way, it blocks the active sites of sediments for their accumulation, which leads to an increase in its anti-scaling efficiency (Chauhan *et al*., 2012). Therefore, it is obvious that by increasing the concentration of the anti-scaling agent, its ability to block the active sites of sediments to prevent the formation of crystals is blocked (Jafar Mazumder, 2020). Similarly, Hamdona *et al*. (2021) used lysine and glutamic acid as natural antifouling agents to prevent the formation of deposits. They stated that with the increase in the concentration of the antifouling agent, the efficiency of de-fouling increases, which they considered to be due to blocking the active sites of the deposits and preventing the formation of strong and compact crystals (Hamdona *et al*., 2021).

- **Morphological characteristics and EDS analysis**

The effect of using different concentrations of aspartic acid extracted from molasses using the ultrasound-assisted extraction process on the morphological characteristics of evaporator tube sediments at different temperatures was investigated. After applying 6 h of aspartic acid with concentrations of 10 to 50 mg/100g at temperatures of 60, 90, and 120 °C on the sediments of the evaporator tubes, the morphology of the sediments changed as shown in Figure 3. Based on the obtained results, it was found that the sediments of the reference sample have a uniform, regular and compact surface that has a crystalline state (Figure 3-Control). By applying aspartic acid extracted from molasses using an ultrasound-assisted process, the sediment morphology was transformed into a porous state and smaller particles (Figure 3.-1-9). By increasing the concentration of aspartic acid from 10 to 50 mg/100g, the sediments that were compact and crystalline (Figure 3-1, Figure 3-4, and Figure 3-7) turned into sediments with a porous structure and many pores, which were smaller in size (Figure 3-3, Figure 3-6, and Figure 3-9). In addition, changes in the temperature of the sedimentation process also changed the morphology of the sediments. Therefore by an increase in the temperature of the sedimentation process from 60 to 90 °C, the uniform and integrated structure of the sediments (Figure 3-1, Figure 3-2, and Figure 3-3) turned into a porous structure with smaller pieces (Figure 3-4, Figure 3-5, and Figure 3-6). However, increasing the temperature of the anti-scaling process from 90 to 120 °C reduced the porosity of the sediments and their particle size (Figure 3-7, Figure 3-8, and Figure 3-9). By reacting with the active sites of

sediments and blocking the active points of these sediments to prevent the accumulation and formation of sediments, anti-scaling agents disrupt the formation of crystals and as a result, sediments with a porous and fine structure are formed. By blocking the active points of sediments and the reaction of anti-scaling materials with the constituent elements of sediments, the growth of sediment crystals will be disrupted, which will be accompanied by a decrease in the size of sediments (Yu *et al*., 2019). Similarly, Khaled (2021), by using natural anti-scaling materials to prevent the formation of sediment, determined that by preventing the formation of sediment crystals and preventing their growth, anti-scaling materials cause the formation of small crystals that have a porous structure. This researcher considered the reason for this to be due to the reaction of sediment-forming elements with the active functional groups of the natural anti-scaling agent (Khaled, 2021).

The EDS analysis of the sediment samples treated with aspartic acid extracted with molasses was carried out to investigate the change in the composition of sediment constituents compared to the composition of control sediments (Table 7). The EDS analysis on the initial sediments of the evaporator tubes, which had not been subjected to any process, showed that oxygen, carbon, and calcium elements were the most abundant constituents of these sediments, which have values equal to 48.54%, 33.71%, and 16.08, respectively. In addition to these elements, small amounts of elements such as iron, silicon, potassium, and aluminum were observed in the structure of the control sediments, which had values equal to 0.54%, 0.52%, 0.4% and 0.21%, respectively. After using aspartic acid extracted from molasses with different concentrations and temperatures on the sediments on the surface of the evaporators, it was found that the composition of the elements forming the sediments was also dependent on the concentration and temperature of the process so the sediments treated with aspartic acid extracted with molasses contain calcium, iron, silica, potassium, and aluminum were less than the control sample. However, by applying aspartic acid to the sediments, the content of carbon and oxygen in them increased. Therefore, based on the results obtained from the EDS analysis of sediments, it was found that increasing the concentration of aspartic acid led to a decrease in the percentage of calcium and silicon elements

Table 7. Composition of elements (% w) of control sample scales in comparison with scales treated with aspartic acid extracted by the ultrasound-assisted extraction method (the codes on the table refer to the row numbers of Table 6)

Treatment	C	O	Al	Si	K	Ca	Fe
Control	33.71	48.54	0.21	0.52	0.4	16.08	0.54
1	37.12	42.52	0.18	0.17	0.18	15.54	0.84
2	35.36	45.44	0.17	0.32	0.19	13.24	1.84
3	39.41	43.52	0.18	0.17	0.29	10.94	1.62
4	35.65	44.09	0.15	0.13	0.34	14.78	1.02
5	38.43	45.34	0.21	0.19	0.24	11.41	1.28
6	41.37	41.12	0.16	0.16	0.22	9.22	1.12
7	37.15	42.66	0.12	0.14	0.20	15.33	1.28
8	38.12	44.45	0.13	0.14	0.25	12.38	1.14
9	37.42	45.37	0.12	0.15	0.30	11.45	2.07

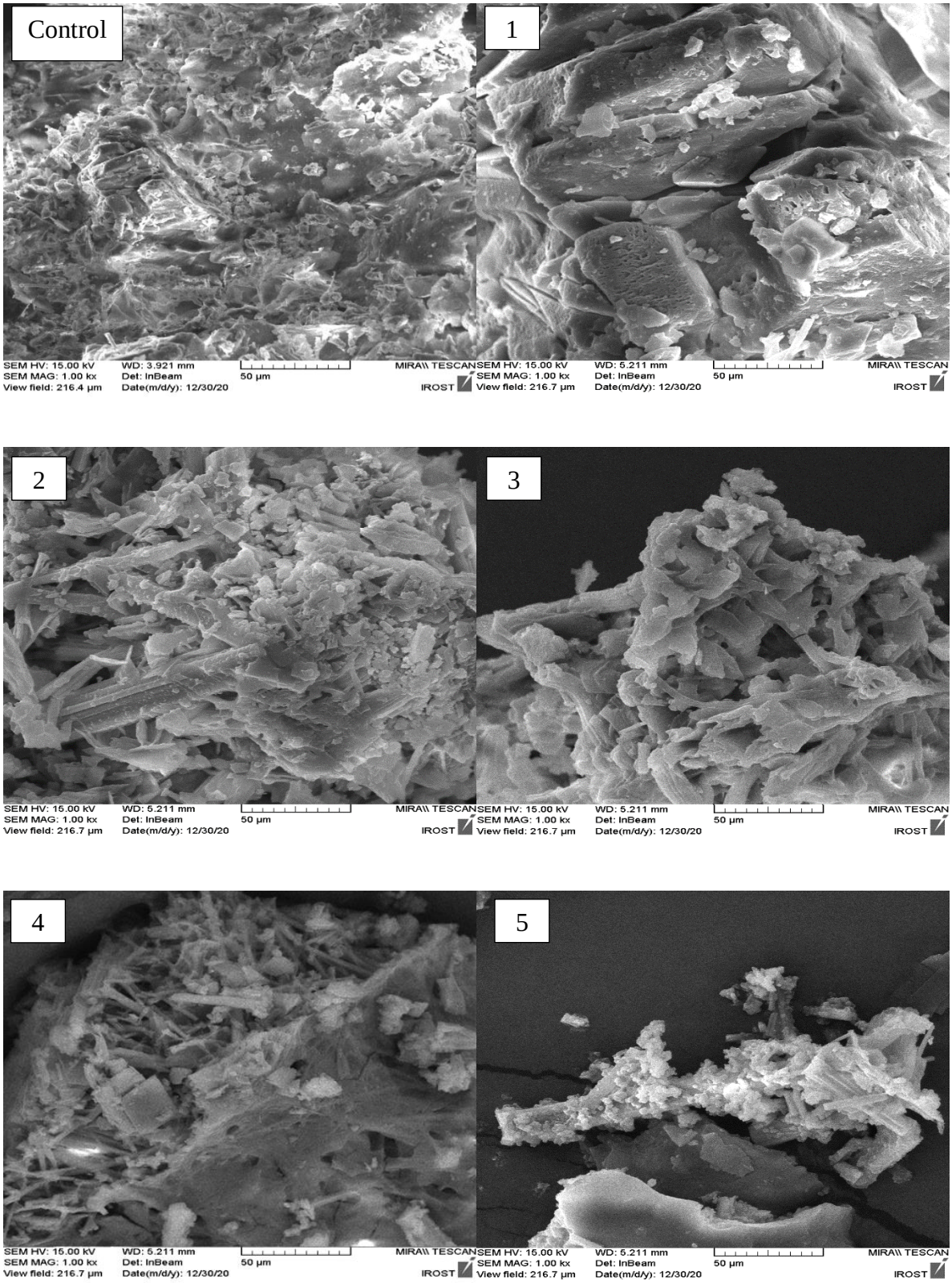

Fig. 3. The FESEM images of control sample scales compared to scales treated with aspartic acid extracted by the ultrasound-assisted extraction method (the codes on the table refer to the row numbers of Table 6) (*continued*).

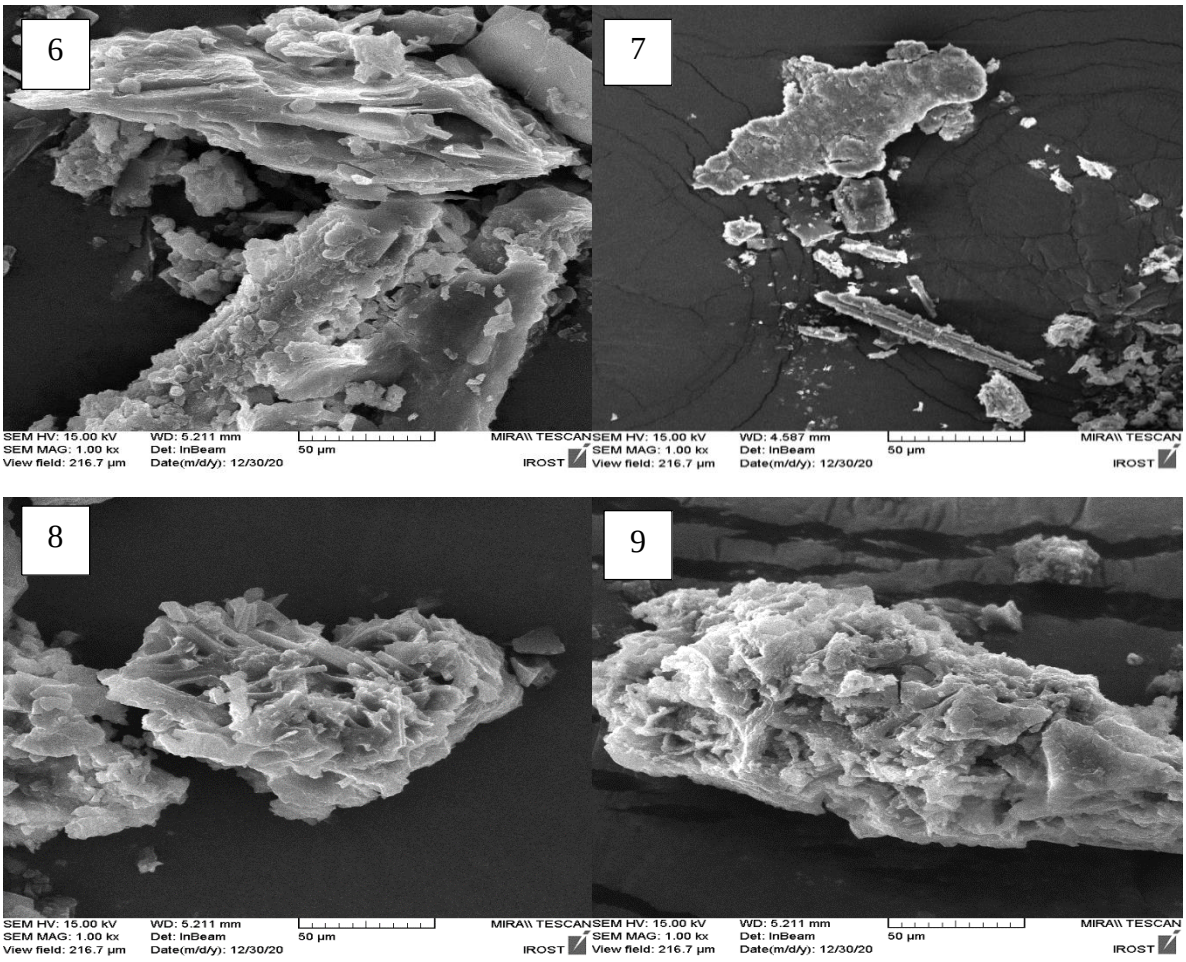

Fig. 3. (*continue*)The FESEM images of control sample scales compared to scales treated with aspartic acid extracted by the ultrasound-assisted extraction method (the codes on the table refer to the row numbers of Table 6).

in the structure of sediments. By increasing the temperature of the anti-scaling process from 60 to 90 °C in the presence of aspartic acid as an anti-scaling agent, the content of calcium and silica decreased significantly, but with the increase of the anti-scaling temperature in the presence of aspartic acid from 90 to 120 °C, the amount of calcium and silica decreased. This is probably due to the reaction of aspartic acid with elements such as calcium and silicon. Aspartic acid can react with these elements through active functional groups and remove them from the reaction media by forming a complex between these substances. However, high temperatures (higher than 90 °C and up to 120 °C) may lead to the denaturation of aspartic acid and reduce its anti-scaling effect (Chen *et al.*, 2019).

–FTIR analysis

The FTIR spectrum of the primary sediments shows a broad absorption peak at 3392.4 cm^{-1}, which corresponds to the O-H stretching vibration (Figure 4). Also, in primary sediments, there are four specific peaks in the regions of 850.8 (out-of-plane vibrations CO_3^{-2}), 6.600 (in-plane vibrations O-C-O in calcium carbonate crystals ($CaCO_3$)), 1062.4 (Si-O symmetric stretching vibrations), and

1311.9 cm^{-1} (Si-O asymmetric bending vibrations) were observed (Figure 4). The addition of aspartic acid as an anti-scaling at different concentrations and temperatures caused a change in the location and intensity of the specific peaks of the primary sediments-by increasing the concentration and temperature of the descaling process, stable calcium carbonate crystals and silicon-containing crystals turned into unstable and weak crystals. Similarly, researchers have shown that by using Al_2O_3 as an anti-scaling agent, calcium carbonate sediments can be changed. This change is a change in the stable crystal of calcite and its transformation into unstable crystals of aragonite and vaterite (change in the position of the 700, 713, 853, and 1083 cm^{-1} peaks) (F. Wang *et al*., 2019). Also, the study showed that the anti-scaling of the landfill leachate piping system using polymer materials would change the sediment crystals in the range of 700 to 1600 cm^{-1}, which leads to an increase in descaling (Li *et al*., 2020).

Conclusion

Molasses is one of the main wastes of sugar factories, usually used to produce products with low added value. Therefore, using new extraction methods to extract its bioactive compounds can be a promising way to use these compounds. In this study, aspartic acid was first extracted from molasses as one of the bioactive components of molasses with the ability to be used as a natural anti-scaling by the ultrasound-assisted extraction method. Then, the extracted compound was used under optimal conditions as a natural anti-scaling agent on sugar industry evaporator

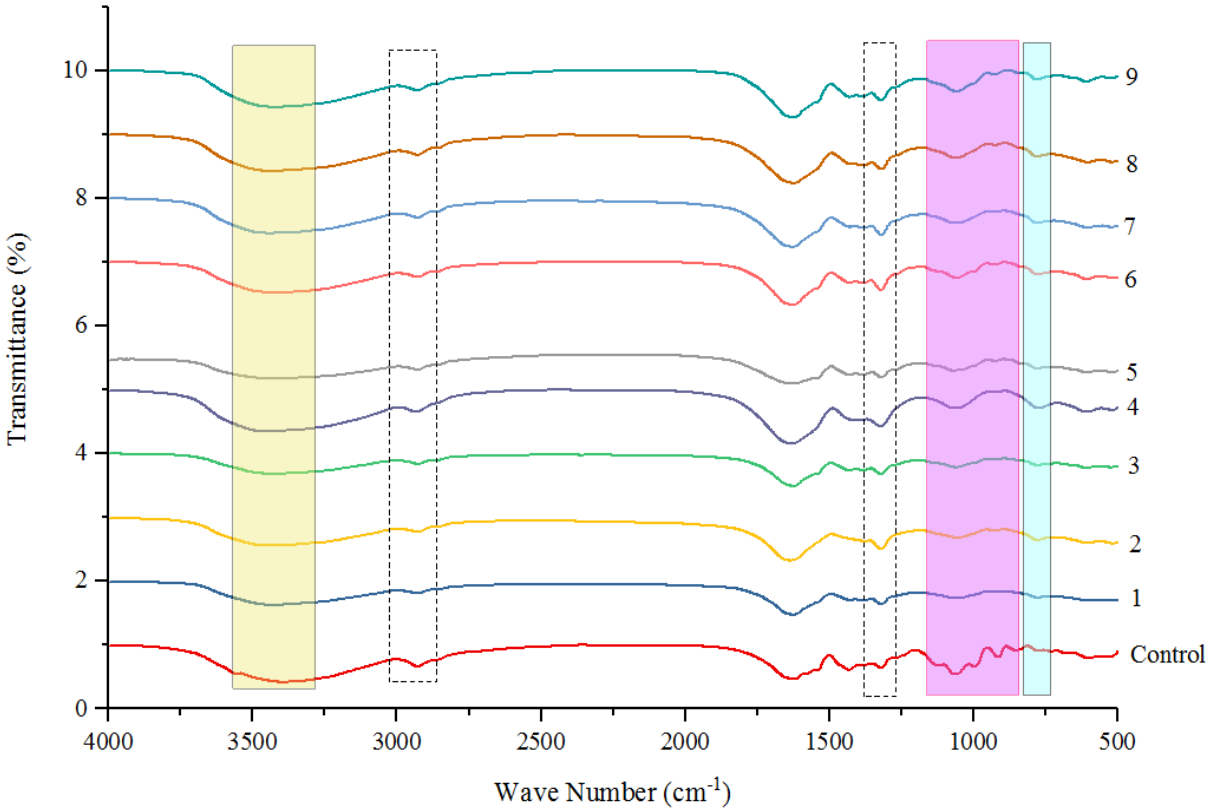

Fig. 4. FTIR spectra of control sample scales in comparison with scales treated with aspartic acid extracted by the ultrasound-assisted extraction method (the codes on the table refer to the row numbers of Table 6).

tubes. The results of the ultrasound-assisted extraction showed that the linear model is the best model to describe the behavior of aspartic acid extraction from sugar beet molasses. The optimal conditions for extracting aspartic acid using the ultrasound-assisted method include an extraction temperature of 25.09 °C, pH equal to 7.00, ultrasound power of 69.99%, and no ethanol. Aspartic acid extracted under optimal conditions with three different concentrations (10, 25, and 50 mg/100g) at three different temperatures (60, 90, and 120 °C) was applied to the sediments of sugar industry evaporator tubes. In general, the results showed that using a concentration of 50 mg/100g of aspartic acid extracted from molasses under optimal conditions at a temperature of 90 °C for 6 h effectively removes sediment from the evaporator tube. The change in the structure of the sediments formed on the tubes of the evaporators was well shown by the results of FESEM images and FTIR spectroscopy. The results of the EDS analysis also showed the change in the composition of sediments on the evaporator tubes as a result of applying aspartic acid as a natural anti-scaling agent. The use of aspartic acid at the concentration of 50 mg/100 g at the temperature of 90 °C as a natural anti-scaling agent for descaling the pipes of evaporators and heat exchangers are recommended.

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