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AUTHORS: L. Peić Tukuljac, J. Krulj, J. Kojić, J. Šurlan, M. Bodroža-Solarov, B. Miljević, Z. Šereš, N. Maravić

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Biosorption of Na^+ , K^+ and Ca^{2+} from Alkalized Sugar Juice by Unmodified Pressed Sugar Beet Pulp in Closed-Loop Column System

Lidija Peić Tukuljac^{1,2} · Jelena Krulj² · Jovana Kojić² · Jelena Šurlan¹ · Marija Bodroža-Solarov² · Bojan Miljević¹ · Zita Šeres¹ · Nikola Maravić¹ 

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Abstract Sucrose crystallization process is greatly inhibited by high Na^+ , K^+ and Ca^{2+} content in the crystallizing medium—sugar juice. In this study, unmodified pressed sugar beet pulp was used as a weak polyfunctional cation exchanger for the removal of Na^+ , K^+ and Ca^{2+} from an alkalized sugar juice in a closed-loop column system. Cation removal effect was evaluated through the influence of temperature (30–70 °C), pH (8.5–12.5) and volume (150–300 ml) of alkalized juice. Sugar beet pulp exhibited the highest Ca^{2+} removal (56.58%) at 70 °C and pH value of 12.5, indicating strong impact of cation solubility, precipitation and valence. Milder conditions of alkalized sugar juice such as temperature (50 °C) and pH value (10.5) contributed to the maximum removal of Na^+ (15.07%) and K^+ (10.58%). Component analysis of the heteroporous sugar beet pulp with total porosity of 53% and specific surface area of 0.9 m²/g indicated hydroxyl and carboxyl groups as the main centers for an ion-exchange process in the material used, which was confirmed by FTIR analysis. This is the first time that unmodified pressed sugar beet pulp (PSBP) has been used as biosorbent for Na^+ , K^+ and Ca^{2+} removal in a closed-loop column system.

Keywords Alkalized sugar juice · Sugar beet pulp · Na^+ · K^+ and Ca^{2+} removal · Closed-loop column system · Ion-exchange

Introduction

Sugar industry is one of the key food industries recognizable by its high energy consumption. Sugar (sucrose) crystallization, besides sugar juice purification step, is the most important process in crystal sugar manufacturing. Furthermore, inefficient purification of the sugar juice strongly affects further crystallization of sucrose (Van der Poel 1998). Mineral components contained in the sugar juice could have major influence on the sugar production process, particularly crystallization and final energy consumption. If present in a relatively large amount in sugar juice, alkali metals (sodium and potassium) increase sucrose solubility and thus inhibit efficient crystallization, leading to higher amounts of sucrose in by-products (e.g., molasses) (Campbell 2002). Minerals, such as calcium, present in a large amount in sugar juice, represent a major problem in sugar industry due to the excessive limescale deposits on heat-exchange surfaces, located in evaporators and crystallizers. Reduced heat transfer causes increased energy consumption and prolonged time of evaporation, leading to undesirable color of sugar juice and sugar crystal (Maravić et al. 2015). Alkalized sugar juice, obtained at high temperature (70 °C) and pH value (10.5), represents the most valuable intermediate product in a juice purification stage essential for mineral removal process (Asadi 2006). Stage in the production when alkalized juice as intermediate sugar juice product is obtained represents the most suitable position for installation of the additional processes for the sugar juice purification. After

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✉ Nikola Maravić
maravic@uns.ac.rs

¹ Faculty of Technology, University of Novi Sad, Bul. Cara Lazara 1, 21000 Novi Sad, Serbia

² Institute of Food Technology in Novi Sad, University of Novi Sad, Bul. Cara Lazara 1, 21000 Novi Sad, Serbia

alkalization juice has been obtained, process of carbonation and alkalization is followed.

The sugar juice “softening” with ion-exchange resins has proved its potential and become a standard unit operation in beet sugar industry (Kochergin and Tzschatzsch 2005) <https://www.sciencedirect.com/science/article/pii/S0260877409005871>—bib11. On the other hand, possibility of removing juice color and cations, such as Na^+ , K^+ and Ca^{2+} from sugar juice by using plant-based sorbents, e.g., sugar beet pulp, in batch conditions showed promising results in the alkaline pH region (Peić Tukuljac et al. 2022). Therefore, in order to avoid undesirable changes regarding the quality of the sugar juice, in the current research, experiments were conducted in strong alkaline pH region. Sugar beet pulp was the third most important product from the sugar industry with annual production of around 200 million tons in the EU (Elsayed et al. 2022). Crystal sugar from the sugar beet was manufactured in the amount of 14.2 million tons during the campaign 2020/21 in the EU with an increasing potential in the 2021/22 year campaign to 16 million tons (CEFS 2022). Specific structural composition of sugar beet pulp, based on dietary fibers such as hemicellulose, cellulose, pectin (about 85% on dry matter basis) and lignin, expands the possibilities for successful application as cation-exchange biosorbent (Altundogan et al. 2007). Column filled with fibers could have features as an adsorption column with an ion-exchange properties (Eastwood 1974). Nowadays, sugar beet pulp represents advanced biosorbent for the removal of heavy metals from different effluents: lead or cadmium (Pehlivan et al. 2008), toxic mercury (Ma et al. 2016), nickel and copper (Reddad et al. 2002) or zinc (Castro et al. 2017).

The purpose of the current study was to investigate the possibility of Na^+ , K^+ and Ca^{2+} removal from an alkalized sugar juice by using unmodified sugar beet pulp as a cation-exchange biosorbent in a closed-loop column system. The main aim was to introduce additional closed process loop into the purification stage of the sugar juice and therefore minimize by-product (PSBP) and recover alkalized sugar juice. Central composite design (CCD) was applied to evaluate impact of operating parameters pH (8.5–12.5), temperature (30–70 °C) and volume of alkalized juice (150–300 mL) on Na^+ , K^+ and Ca^{2+} removal efficiency. In this investigation, the aim was to approach to the mechanism of cation removal efficiency by comprehensive textural analysis of the used biosorbent (FTIR, SEM, porosity and specific surface area measurements). Valorization process of the PSBP (native industrial residue) as feasible alternative to commercial cation-exchange resins was described.

Materials and Methods

Materials

Pressed sugar beet pulp (PSBP) and alkalized sugar juice were provided by Serbian sugar factory during 2019 year campaign. Pressed sugar beet pulp was collected in a sugar factory after cutting sugar beet into noodles, extracting sugar from them and finally pressing excess water and used in an unmodified form (Maravić et al. 2018). Alkalized sugar juice, as an intermediate product of sugar juice purification stage, was collected after first lime-carbonating process and subsequent cloth filtering. Alkalized sugar juice with 15.6% dry matter content has pH value of 10.5 and total amount of molassigenic metals: Na^+ , K^+ and Ca^{2+} 3076.92, 10,128.21 and 12,115.38 mg/kg dry matter, respectively (Peić Tukuljac et al. 2022). Both PSBP and alkalized juice were stored at $-18\text{ }^\circ\text{C}$ before conducting experiments.

Closed-Loop Column Biosorption Process

Flow-through column experiments included ion-exchange process performed in a column loaded with a predetermined amount (17 g) of PSBP. The amount of the PSBP in the column was determined during preliminary tests. Peristaltic pump (Ecoline, Ismatec Germany) was used in order to ensure controlled alkalized juice flow in the direction from the bottom to the top of the column. The flow rate was kept constant at 6.5 L/h in all experiments. Contact time was 60 min. Scheme of closed-loop column ion-exchange system of custom-made equipment is presented in Fig. 1.

Textural Characterization of PSBP

The surface of PSBP was analyzed by using a Fourier transform infrared spectroscopy (FTIR). The infrared spectra were recorded on Alpha Bruker Optics instrument (Bruker Optics, Germany) with attenuated total reflection technique (ATR). Spectra were recorded within a region $400\text{--}4000\text{ cm}^{-1}$, resolution 4 cm^{-1} and scanning frequency 24 times. Data were processed with OPUS 7 software (Bruker Optics, Germany).

Grinded and dried PSBP samples were placed on an appropriate stub and coated with a thin layer of gold under the vacuum, photographed and examined under a scanning electron microscopy (SEM) Vega 3 LM (Tescan, Czech Republic).

Mercury intrusion porosimetry was performed by using the instrument AutoPore IV 9500 (Micromeritics, USA) measuring the cumulative intrusion as a function of pore size up to the maximal intrusion pressure of 228 MPa.

Specific surface measurements of the PSBP sample were performed by using the gas adsorption porosimeter Surfer

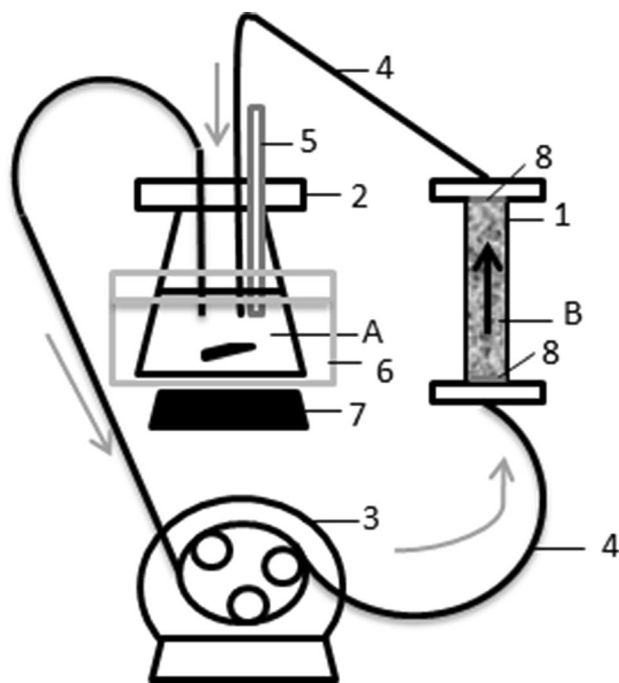


Fig. 1 Closed-loop column system 1.column; 2. vessel; 3. peristaltic pump; 4. pipes; 5. thermometer; 6. water bath; 7. magnetic stirrer; 8. filters; A alkalized juice; B PSBP

(Thermo Fisher Scientific Inc., Italy) and liquid nitrogen was used at its boiling temperature (77 K). Specific surface of PSBP was measured after drying the sample at 60 °C for 3 h in vacuum. The Brunauer–Emmett–Teller (BET) calculation method was employed.

Na⁺, K⁺ and Ca²⁺ Contents in Alkalized Sugar Juice

Na⁺, K⁺ and Ca²⁺ contents in alkalized sugar juice were detected and quantified by atomic absorption spectrometer (varian spectra AA 10, varian techtron pty limited, Australia). Analytical method for metal content determination was in accordance with the standard (SRPS EN ISO 6869/2008, 2008). All measurements were conducted in triplicate and mean values were given. Mixture of air and acetylene gas was used in all experiments. Cathode lamps for potassium, sodium and calcium determination were used for radiation. The sensitive wavelength, for Na⁺ at 330.3, K⁺ at 404.4 and Ca²⁺ at 422.6 nm, were used with slit-band width at 0.5 nm in all cases.

Removal effect (*R*) was calculated by the following expression:

$$R(\%) = \frac{C_i - C_f}{C_i} 100 \quad (1)$$

where C_i and C_f were initial and final concentration of corresponding metal (Na⁺, K⁺ and Ca²⁺) in alkalized juice and PSBP (mg/kg on dry basis), respectively (Arslanoglu and Tumen 2012).

Experimental design

A central composite design (response surface methodology) was used to investigate the effects of three independent variables (temperature, pH and volume of alkalized juice) at three levels ((30, 50 and 70 °C; X_1), (8.5, 10.5 and 12.5; X_2) and (150, 225 and 300 ml; X_3)), on the depended responses Na⁺, K⁺ and Ca²⁺ removal in alkalized juice. Levels of variables were determined according to preliminary research. The lowest, medium and highest values of the three selected independent variables were presented with coded values in the graphs (0, 0.5, 1; respectively). Twenty-three experiments were conducted with three replicates in central point. The relationship between removal effect of K⁺, Na⁺ and Ca²⁺ and selected independent variables was assessed by the second-order polynomial model function:

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_{ii}^2 + \sum b_{ij} X_{ij} \quad (2)$$

where Y —the response (dependent variable); b_0 —intercept term; b_i , b_{ii} , b_{ij} —the linear, quadratic and interaction term, respectively; X_i and X_j —the independent variables, and ε —the standard error. The experimental design and multiple linear regression analysis were performed using design-expert 6.0.5 Trial (Stat-Ease, USA). The results were statistically tested by analysis of variance (ANOVA) with the significance level of 5%. The significance of the model was evaluated by model p values, R values and lack-of-fit testing.

Results and Discussion

PSBP Textural Characterization

The FTIR spectra of PSBP before and after ion-exchange process were observed (Fig. 2). The accessible functional groups for Na⁺, K⁺ and Ca²⁺ removal were identified. The broad band absorbance at 3200–3500 cm⁻¹ (peak at ~ 3277 cm⁻¹) was attributed to the O–H stretching modes of vibration in hydroxyl functional group. The absorption peak at 2910 cm⁻¹ (2900–3000 cm⁻¹) corresponded to C–H aliphatic or alicyclic stretching vibration modes in the hydrocarbon chains. The FTIR spectra band at 1700–1800 cm⁻¹ (peak at 1733 cm⁻¹) referred to the stretching vibrations of the carbonyl functional group (C=O) in aldehydes (Castro et al. 2017). The absorption spectra band (1320–1364 cm⁻¹) was attributed to O–H and -CH₃ functional groups of the amino acids: Leu, Ile, Ser and Ala, typical for the sugar beet

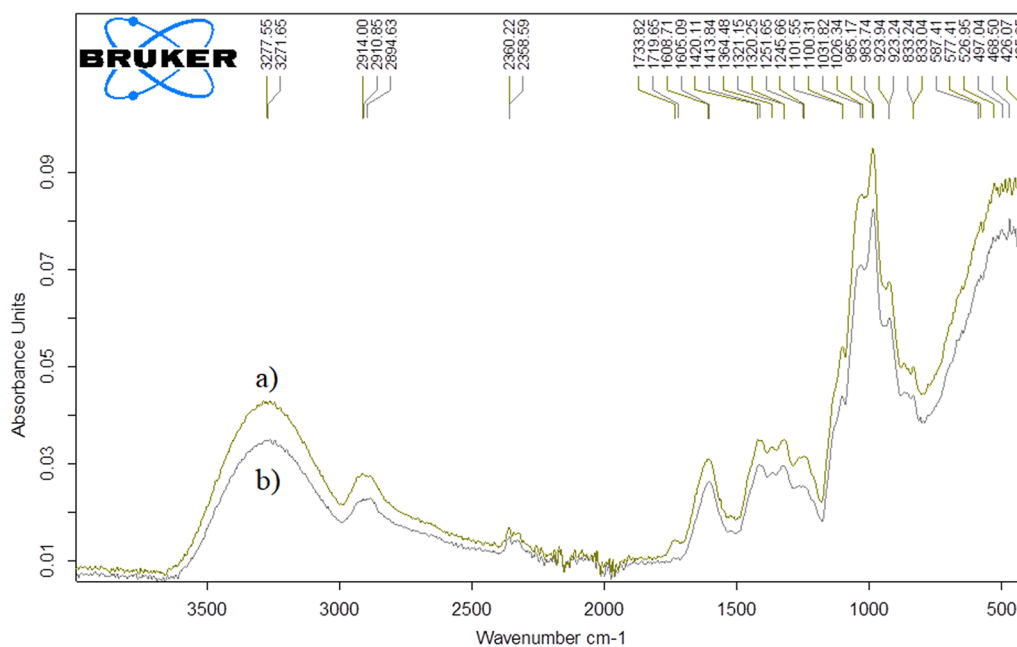


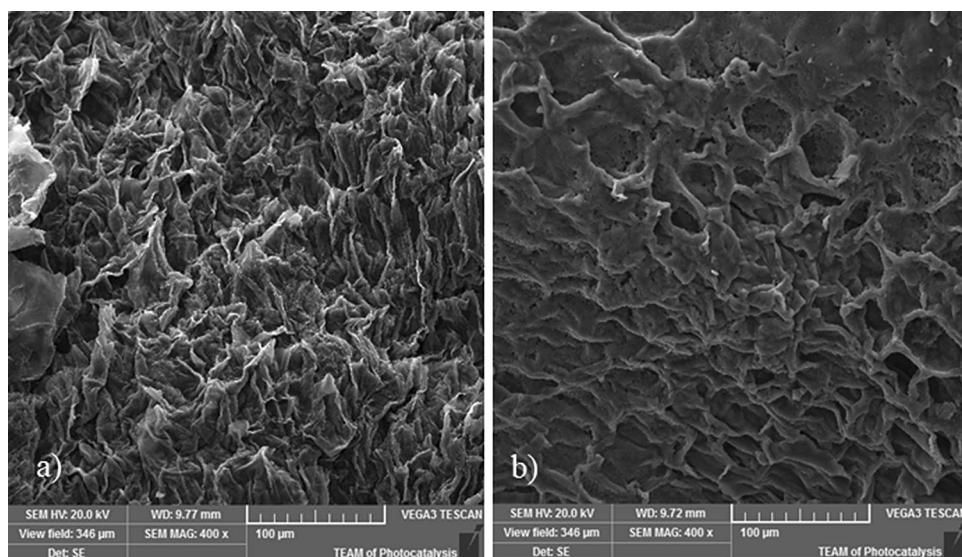
Fig. 2 FTIR spectra of PSBP: **a** before **b** after ion-exchange process

pectin (Maravić 2019). At the wavenumber region between 1200 and 1300 cm^{-1} , C=O bonds from the carboxyl group were identified originating from the characteristic proteins or the polygalacturonic acid chain. The region between 980 and 1100 cm^{-1} could be assigned to β -glycosidic linkages between sugar units (Ma et al. 2016; Castro et al. 2017). Comparing these two spectra from Fig. 2a and Fig. 2b, it is evident that intensity of bands in the spectra decreased in PSBP after ion-exchange process. From the obtained spectra, it could be assumed that dominant cation-exchange groups in the proposed ion-exchange material (PSBP) belong to O–H

band of hydroxyl and carboxyl groups. Ma et al. (2016) reported similar results regarding mercury removal from an aqueous solution by using sugar beet pectin gels. Pehlivan et al. (2008) previously concluded that the surface of sugar beet pulp is dominated by negatively charged centers, mainly carboxylate groups suggesting possible metal removal properties. Therefore, sugar beet pulp loaded with various functional groups on a surface could act as a polyfunctional ion-exchange material particularly favorable for cation removal.

An irregular rugged surface with a lot of folds and shrinks was observed in both SEM micrographs (Fig. 3).

Fig. 3 SEM micrographs of PSBP **a** before and **b** after ion-exchange process



Micrographs of PSBP cellulose hollow fibers were visible presenting a possible successful filter for undissolved particles in alkalized juice. Micrographs showed no cracks after the process and no visible physical changes on the surface of PSBP where metals were potentially placed. Castro et al. (2017) reported similar conclusions regarding sugar beet pulp with no physical changes after a biosorption of zinc from an industrial effluent. Shrink density was similar before and after the treatment with alkalized juice. The structure was in some parts smoother, more compact and uniform after the ion-exchange process. This effect could appear due to fiber rehydration and high water retention capacity (7.95 ml/g) and water swelling capacity (7.82 g/g) resulting in fibers swelling (Peić Tukuljac et al. 2022).

Textural characteristics of the natural biosorbents were directly correlated with the capacity and surface accessibility of biomaterials, bioavailability and physical properties (Worch 2012). The morphological structure is one of the main characteristics regarding prediction of the metal ions removal effectiveness and generally adsorption ability (Bellahsen et al. 2021). Total porosity of the PSBP sample measured by mercury intrusion porosimetry was 53%. Gupta et al. (2020) confirmed similar range of the total porosity for the sugar beet pulp and wheat straw (41.8–57.3%). The obtained graph (Fig. S1) shows the pore size distribution of the measured PSBP. The biggest share of 24.44% belongs to relatively big pores with the radius bigger than 100 μm , and then very small pores with the radius below 5 nm (share of 18.82%). Beside these two fractions, there is a continuous decrease in shares with decrease in the pore radius to about 10 μm . Middle range pore radius corresponds to almost equally distributed contributions below 5%. Finally, the increase in shares starts with decrease in pore size below 16 nm. A result obtained in this study regarding heteroporosity of sugar beet pulp is well correlated with characteristics generally specific for the natural plant cellulosic materials (Mladenović et al. 2018). Amount and size of the particles significantly influenced removal efficiency of the metal ions from the liquid (Altundogan et al. 2007). In the study of Šćiban et al. (2016), particle diameter of the sugar beet pulp was the most present in the range of 224–400 μm indicating certain potential for the heavy metal ions removal (Šćiban et al. 2016). Similar particle size range (> 100 μm) was also the most dominant in the pressed sugar beet pulp used as biosorbent in current work.

PSBP's specific surface area of 0.9 m^2/g was calculated from the linear part of BET plot as presented in the graph (Fig. S2). Surface area of raw, depectinated and hydrolyzed sugar beet pulp was similar and also very low (lower than 1 m^2/g) (Šćiban et al. 2016). Compared to other biosorbents, especially activated carbon from sugar beet pulp (187.9–328.8 m^2/g), surface area of PSBP was significantly smaller (Özer and Tumen 2003). Due to low amount of the

micropores, specific surface area of sugar beet pulp is small. Low specific surface area is directly correlated with higher amount of present mesopores.

Impact of Input Parameters on Obtained Responses—Removal Efficiency of Ca^{2+} , K^+ and Na^+ From an Alkalized Sugar Juice

The obtained responses after 23 conducted experiments with variation of the temperature, pH and volume of the alkalized sugar juice are presented in Table 1. The monitored responses were: removal effect of Na^+ , K^+ and Ca^{2+} .

Ca^{2+} removal efficiency ranged from 9.03 to 56.58% (Table 1). Obtained result concerning Ca^{2+} removal efficiency in the closed-loop system was significantly higher comparing to batch biosorption experiments conducted at the similar processing parameters regarding pH and temperature of the alkalized juice (30.20%) (Peić Tukuljac et al. 2022). The pH value of alkalized juice strongly influenced solubility, distribution and dissociation of both metal ions in solutions and active groups in the solid phase ($p < 0.001$, Table S1). Removal effect of Ca^{2+} linearly increased by increasing pH value of tested alkalized juice (Fig. S3c). By increasing pH of alkalized juice from 8.5 to 12.5, removal effect of Ca^{2+} significantly increased, in all conducted experiments. However, the presence of the functional groups on the PSBP surface could not guarantee efficient removal of selected metals due to numerous interfering factors. Regression coefficients (Eq. 5) and p values (Table S1) confirmed the strongest impact of pH upon the Ca^{2+} removal effect (on the level $p < 0.001$). Özer and Tumen (2003) confirmed that removal efficiency of cations is strongly dependent of liquid pH value. pH value also influenced the surface distribution of the metal cations on the biosorbent (Mahvi et al. 2008). It can be assumed that higher pH values lead to stronger electrolytic dissociation of charged active groups toward the release of H^+ ions and thus increasing the ion-exchange capacity of investigated material toward Ca^{2+} cations. Electrostatic repulsive forces between the H_3O^+ and Ca^{2+} are stronger at lower pH values (Özer and Tumen 2003). Due to strong repulsive forces between cations and competition of H^+ and Ca^{2+} ions for the active sites available for the adsorption was avoided acidic pH of the alkalized juice in current work. Malekbala et al. (2012) also reported positive impact of higher pH value on the removal of cation dyes using sugar beet pulp. Furthermore, increased pH significantly affected polygalacturonic backbone of the pectin macromolecule present in the PSBP. Sugar beet pectin structure, as polyelectrolyte, is susceptible to conformational changes when the pH of the surrounding solvent is changed. Therefore, with the increase of pH, polygalacturonic chains tend to uncoil, stretch and form more linear structure, as a consequence of intermolecular electrostatic repulsive force. The

Table 1 Independent variables and responses

Run	X_1 T (°C)	X_2 pH	X_3 V(ml)	Responses R_K (%)	R_{Na} (%)	R_{Ca} (%)
1	50.00	12.50	225.00	7.41	6.00	34.32
2	30.00	12.50	300.00	-7.10	-5.61	18.97
3	50.00	10.50	225.00	3.69	3.93	25.20
4	30.00	10.50	225.00	2.87	0.04	26.47
5	70.00	8.50	300.00	-1.89	-2.79	35.82
6	50.00	10.50	225.00	4.55	8.14	32.44
7	70.00	8.50	150.00	-3.11	3.68	11.37
8	50.00	8.50	225.00	-0.83	0.10	11.66
9	50.00	10.50	300.00	0.51	2.66	27.42
10	30.00	8.50	150.00	6.18	7.90	19.27
11	50.00	10.50	150.00	10.58	15.07	32.49
12	30.00	8.50	300.00	6.54	1.76	7.78
13	70.00	12.50	300.00	-3.07	5.02	42.30
14	70.00	10.50	225.00	5.20	4.87	38.98
15	30.00	12.50	150.00	4.34	5.84	37.29
16	70.00	12.50	150.00	8.16	12.12	56.58
17	50.00	10.50	225.00	5.62	0.33	27.06
18	70.00	12.50	225.00	4.90	6.73	50.06
19	50.00	12.50	300.00	0.22	6.19	41.10
20	70.00	10.50	300.00	-1.92	1.00	38.20
21	30.00	8.50	225.00	3.78	-1.13	7.92
22	50.00	8.50	150.00	-0.61	5.73	18.78
23	30.00	10.50	150.00	9.74	6.75	25.74

R_K —removal effect of K^+ , R_{Na} —removal effect of Na^+ , removal effect of Ca^{2+}

conformational change increased potential for the formation of Ca^{2+} bridges between the polygalacturonic backbone chains previously hindered by specific coiled structure of sugar beet pectin (Farnane et al. 2017). Therefore, due to the significant changes of PSBP ion-exchange characteristics at different pH values, PSBP could be classified as a weak ion exchanger. The removal effect of Ca^{2+} from alkalized sugar juice was also greatly influenced by temperature of the solution (Fig. S3c and $p < 0.001$, Table S1). Higher temperatures significantly decreased solution viscosity and increased alkalized juice fluidity, hence promoting larger number of contacts between Ca^{2+} and PSBP functional groups. Therefore, better mobility of Ca^{2+} due to the lower viscosity could have positive influence on total removal effect (Asadi 2006). However, positive impact of higher temperatures on Ca^{2+} removal efficiency was probably influenced by lower solubility of calcium ions at higher temperatures, leading to Ca^{2+} irreversible precipitation on PSBP cellulose hollow fibers. Thus, besides dominant ion-exchange process as the main driving force, undissolved Ca^{2+} ions tend to precipitate on the PSBP surface involving adsorption as an important Ca^{2+} removal process. Özer and Tumen (2003) and Mahvi et al. (2008) concluded that higher temperatures in combination with alkaline pH values can influence metal ion precipitation, especially in the form of the hydroxide.

Metal ion precipitation, characteristics of divalent metal ions, appeared as a consequence of the changed concentration and formation of the soluble metal species accessible for the adsorption. Increased temperature also caused increase in PSBP porosity. Polysaccharide porous matrix, as a result of intensive swelling, became wider, matrix pores deeper and possibly increased total active surface which could interact with the targeted metal ions (Altundogan et al. 2007). Combined positive effect of increased temperature and pH resulted in the most efficient Ca^{2+} removal (Fig. S4c). The results presented in Table 1 suggested positive influence of volume decrease toward Ca^{2+} removal effect. The corresponding positive effect could mainly be attributed to the larger amounts of active material per juice volume (ranging from 0.05 to 0.1 g PSBP/mL of alkalized juice) capable to interact with metal ions present in the alkalized juice. Therefore, it can be concluded that the further increase of PSBP amount in the column could lead to the higher removal effects. Besides, lower juice volumes, at the constant pump feed rate, lead to the higher number of flow cycles through the column, thus increasing the number of contacts with active material and promoting the possibilities of successful removal through ion-exchange or filtration process (at higher temperatures). Stronger influence of volume factor on Ca^{2+} ions removal effect was particularly emphasized at higher

temperatures and pH values (Fig. S4c). Higher temperatures in combination with lower juice volume promoted positive impact of Ca^{2+} ions removal. Combined impact can be explained as a consequence of several mutually dependent variables (lower juice viscosity \rightarrow higher number of cycles through the column \rightarrow better sedimentation due lower Ca^{2+} solubility). The combined impact of pH value and volume was noticed at all tested pH values (Table 1). However, the most significant impact was noticed at the lowest temperature (30 °C) with obtained relative increase of Ca^{2+} removal ranging from 17 to 111%. Lower juice volume compensated the negative impact of low temperature on juice viscosity and general availability of Ca^{2+} ions by increasing the number of juice cycles through the column. Furthermore, lower juice temperature increased Ca^{2+} solubility and hence cation availability for ion-exchange process which is additionally promoted by lower juice volume as previously discussed. Therefore, required number of contacts between Ca^{2+} ions, present in the juice, and the active sites of the material, are enabled and hence, the removal effect is considerably increased.

Average removal effect of Ca^{2+} was significantly higher than the removal effect of Na^+ and K^+ . Removal effect of Na^+ ranged from -3.79 to 15.07% , whereas K^+ removal effect was in the range from -6.11 to 10.58% (Table 1). Nevertheless, the removal efficiency regarding Na^+ and K^+ from alkalized sugar juice were also higher in comparison with results obtained at the similar processing parameters in batch system (11.00 and 9.30% , respectively) (Peić Tukuljac et al. 2022). Negative values indicated transfer direction of ions from PSBP to alkalized juice. The influence of juice pH values on K^+ and Na^+ removal effect was observed; however, the effect was less intensive and significant differences compared to Ca^{2+} removal are noticed. A comparative study regarding Na^+ , K^+ , Ca^{2+} and Mg^{2+} removal efficiency by applying different biosorbents and biosorption type is given in Table 2.

The findings from this study make several noteworthy contributions to the currently available literature. The PSBP, used in this work, was unmodified and biosorption type applied for the molassigenic metal ions removal was closed-loop continuous column system. By avoiding pre-treatment and modification of the PSBP used as a biosorbent, economic, energetic, technological and ecological requirements were met. Additionally, bio-waste material was minimized by reusing PSBP in the form of biosorbent. Without a doubt, utilization of the synthetic cation-exchange resins showed absolute removal of the divalent Ca^{2+} (100%) which is almost impossible to achieve with natural, industrial by-products (Table 2). Current research supported circular bioeconomy concept and closed cycle of material and energy flow by conducting experiments in the closed-loop system until total utilization of components.

Usage of the material as long as possible contributed to the closed loop of the resource flows and increased efficiency. In the current research, experiments were conducted mostly in strong alkaline pH conditions (pH = 12.5). Most of the other researches were conducted until pH value of the solution reached almost 9, which is significant difference in comparison to current research (Table 2). The reason for the more successful Ca^{2+} removal effect compared to Na^+ and K^+ could be found in precipitation effect of Ca^{2+} , due to the significantly lower Ca^{2+} solubility at higher temperatures (van der Poel 1998). Furthermore, the formation of calcium bridging effect formed by stoichiometric union with two adjacent COOH^- groups has also contributed. The removal of Na^+ ions from the alkalized juice showed positive impact of the rising juice pH values. The removal capacities of the PSBP increased as the pH increased affecting the increased degree of the ionization on the PSBP surface. The ionic state of the functional groups on the surface is determined by the pH value. PSBP pectin was characterized by high content of anhydrogalacturonic acid which was around 28,700 units/molecule, and therefore, it can be assumed that the same amount of $-\text{COOH}$ groups are available for the ion exchange with molassigenic metals from the alkalized juice (Pinho and Macedo 2005). Supposed removal mechanism of the molassigenic metal ions along with the pectin units of the PSBP is presented in Fig. 4.

The values of the obtained removal increased up to five times with the pH value increase from 8.5 to 12.5. Previously discussed impact of pH on the structure and electrolytic properties of active material (PSBP) significantly contributed to the higher values obtained in the removal of Na^+ and K^+ . However, the corresponding positive effect was significantly dependent on the juice temperature. Positive effect on Na^+ removal was noticed at 50 and 70 °C but not at the lowest tested temperature of 30 °C. Similar effect was also detected regarding K^+ removal. As presented in Figure S3 and Fig. S4a, negative impact of increased temperature is particularly emphasized regarding K^+ removal. Furthermore, negative values (mostly regarding K^+ removal) were obtained in the experiment where temperature was set to the highest value (70 °C), indicating transfer direction of ions from PSBP to alkalized juice. The temperature effect on the obtained removal could be explained through the characteristic solubility of the K^+ and Na^+ compounds at the tested temperatures. Solubility of K^+ and Na^+ , mostly present in the form of carbonate, sulfate and chloride salts in the alkalized juice, significantly increases with the increase in temperature (Jahed et al. 2014). The solubility increase is almost exponential regarding K^+ compounds. Therefore, concentration gradient, as one of the most important driving forces of the process, is greatly decreased. Moreover, the corresponding change in the solubility triggered the opposite process and certain amounts of K^+ and Na^+ ions, naturally

Table 2 A comparison of the Na⁺, K⁺, Ca²⁺ and Mg²⁺ removal by different biosorption techniques and biosorbents

Biosorbent	Liquid	Metal ions	Pretreatment	Biosorption type	Conditions	Removal effect (%)	Reference
Sugar beet pulp	Alkalized juice (Na ⁺ = 3076.82 mg/L; K ⁺ = 10,128.21 mg/L; Ca ²⁺ = 12,115.38 mg/L)	Na ⁺ , K ⁺ , Ca ²	Without (unmodified)	Closed -loop column	T = 50–70 °C pH = 8.5–12.5 V = 150–300 ml Eq.time = 40 min	Na ⁺ = 15.02–12.12 K ⁺ = 10.58–8.15 Ca ²⁺ = 32.48–56.58	Current research
Sugar beet pulp	Alkalized juice (Na ⁺ = 3076.82 mg/L; K ⁺ = 10,128.21 mg/L; Ca ²⁺ = 12,115.38 mg/L)	Na ⁺ , K ⁺ , Ca ²	Without (unmodified)	Batch	T = 70 °C pH = 10.5 V = 300 ml Eq.time = 90 min	Na ⁺ = 10.9 K ⁺ = 9.1 Ca ²⁺ = 30.2	Peić Tukuljac et al. (2022)
Sugar beet pulp	Thin juice (Na ⁺ = 404 mg/L; K ⁺ = 247 mg/L; Ca ²⁺ = 1190 mg/L)	Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺	Neutralized form of the citric acid and NaOH treated (~ 61.5 h)	Batch	T = 20–60 °C pH = 9 ± 0.05 Dose = 2.5–20 g/L Eq.time = 60 min	Na ⁺ = 5.7 K ⁺ = 15.8–31.6 Ca ²⁺ , Mg ²⁺ = 7–49.1	Arsianoglu and Tumen (2012)
Kind of a beet pulp	Alkaline salt solution (Ca ²⁺ = 467.3 mg/L)	Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺	Alkali lye hybrid reaction and FeCl ₃ reaction (6–12 h)	Batch	T = 30–80 °C pH = 5–9 Dose = 5–30 g/L Time = 30–120 min	Ca ²⁺ = 27.87–80.76 Mg ²⁺ = 43.04 K ⁺ = 63.72	CN107262050A (2017)
Resin Lewatit S 8528 in H + form	Thick juice and 2nd carbonated juice (150 mg CaO/L)	Ca ²⁺	Cross-linked polyacrylate matrix whereas Amberlite SR IL Na has a styrene divinylbenzene matrix	Column	T = 20–80 °C pH = 9.1 ± 0.1 Flow = 11.9–40.6 BV/h	Ca ²⁺ = 84.4–100%	Coca et al. (2010)
Grafted potato starch	Hard water (Ca ²⁺ , Mg ²⁺ = 547 mg/L)	Ca ²⁺ , Mg ²⁺	Peroxydisulfate initiated synthesis under microwave irradiation	Batch	T = 30–90 °C pH = 2–12 Dose = 0.5–4.5 g/L Eq. time = 80 min Time = 20–120 min	Ca ²⁺ , Mg ²⁺ = 44.64–80.70%	Mgombezi and Vegi (2020)
Baker's yeast	Metal solutions prepared by taking NaCl, KCl, CaCl ₂ , MgSO ₄	Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺	Deactivated by heating in an oven and eluted with acids	Batch	Dose = 1 g/L pH = 3–7	Ca ²⁺ = 1 meq/g Mg ²⁺ = 0.36 meq/g Na ⁺ = 0.125 meq/g K ⁺ = 0.1 meq/g	Vasudevan et al. (2002)

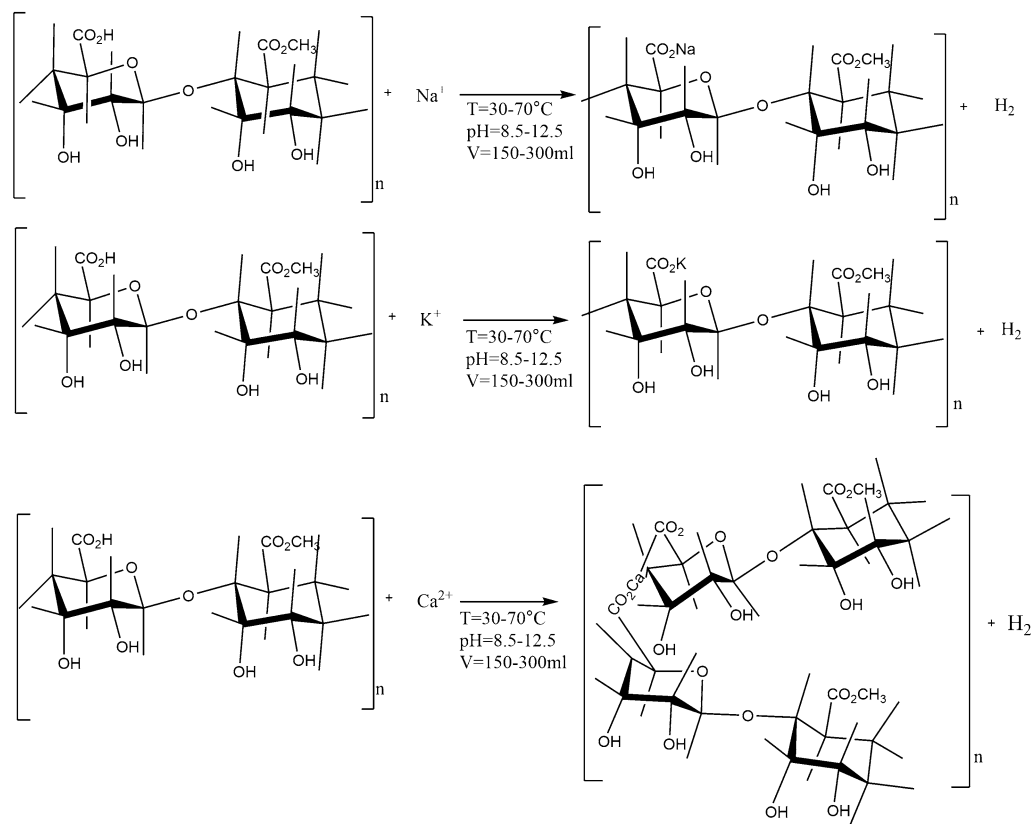


Fig. 4 Potential removal mechanism reactions of the Na⁺, K⁺ and Ca²⁺ from the alkalized sugar juice by using sugar beet pulp with insight into polygalacturonic pectin chains

present in the material, were transferred to the juice from the PSBP. Negative influence of higher tested temperature on Na⁺ removal is more pronounced with the rising values of juice volume. Increased juice volume negatively affected the removal effect of Na⁺ in all conducted experiments. Furthermore, juice volume showed the most significant impact on Na⁺ and K⁺ removal effect compared to other input factors (juice pH value and temperature) confirmed by the lowest *p* values (Table 2). The removal effect of Na⁺ ions at the highest tested volume showed the lowest values, coupled with the trend of decrease as the juice temperature increased (Fig. S4b). Considering solubility characteristics of Na⁺ and K⁺ in the alkalized juice, filtration, as an important mechanism for Ca²⁺ removal, was not assumed, and the process was most likely completely ion-exchange mechanism. Therefore, juice pH value was highly important factor affecting ionic distribution of PSBP active groups responsible and able to perform ion exchange. At the lowest tested juice pH value, changes in volume of alkalized juice had no influence on the removal effect of K⁺. However, with increase in juice pH value, juice volume significantly affected removal trend of K⁺. At the highest juice pH value, decrease in juice volume increased the K⁺ removal effect by more than three times (Table 1). The corresponding effect could be a result

of higher number of juice cycles through the column (i.e., higher number of successful contacts of K⁺ and Na⁺ compounds with the active groups), combined with the increased material capacity to conduct ion exchange at the tested juice pH values.

On the other hand, at the highest juice volume values, reversible trend of K⁺ transfer from the PSBP to alkalized juice was detected, due to increased capacity to dissolve more K⁺ compounds in higher juice volume. Therefore, it can be concluded that the combined effect of higher juice volume and temperature redirected the process toward extraction of K⁺ and Na⁺ compounds from PSBP to alkalized juice (Van der Poel 1998).

RSM was applied to evaluate the effects of temperature (X₁), pH (X₂) and volume of alkalized juice (X₃) on molasses-igenic metals (K⁺, Na⁺ and Ca²⁺) removal effect (%). The models were developed in order to discuss influence of the operating parameters on the particular responses. A second-order polynomial (SOP) models were developed in terms of the three coded independent variables:

$$K^+ \text{ removal}(\%) = +5.15 - 2.99X_3 + 3.17X_1X_2 - 3.04X_2X_3 \quad (3)$$

$$\text{Na}^+ \text{ removal}(\%) = +4.60 + 1.87X_2 - 3.95X_3 + 3.14X_1X_2 \quad (4)$$

$$\text{Ca}^{2+} \text{ removal}(\%) = +28.51 + 7.97X_1 + 11.15X_2 + 4.25X_1X_3 - 4.40X_2X_3 \quad (5)$$

The obtained models were statistically significant with a p value lower than 0.05 (0.0015; 0.0007; <0.001, respectively) and insignificant lack-of-fit values. The SOP regression models indicated good fitting of the experimental results. Adequacy of proposed models was also confirmed by high values of R^2 coefficients (Table S1).

The plots with second-order polynomial model were used to illustrate single and combined impact of the input parameters on the removal effect of molassigenic metals (Fig. S3 and S4). Plots represented function of coded values of input variables (juice temperature, pH and volume) and the removal effect of K^+ , Na^+ and Ca^{2+} .

Conclusions

The evaluation of temperature, pH and volume of alkalinized sugar juice impact on the removal efficiency of Na^+ , K^+ and Ca^{2+} using unmodified sugar beet pulp in a closed-loop column system was presented. Sugar beet pulp was identified as weak ion exchanger due to the significant impact of pH value of alkalinized juice on molassigenic metals ion-removal efficiency. Removal of Na^+ and K^+ (15.07% and 10.58%, respectively) using sugar beet pulp as cation ion-exchange material was significantly lower compared to Ca^{2+} removal (56.58%) indicating strong impact of both, input parameters and cation valence. Alkalinized sugar juice temperature (50–70 °C) showed the most significant influence on Na^+ , K^+ and Ca^{2+} removal efficiency due to the strongest impact on corresponding metal cations solubility. Absolute removal (100%) of the investigated metal ions was almost impossible by using natural biosorbents. However, FTIR spectra showed that cation removal appeared on the carboxyl and hydroxyl groups of the PSBP and included both ion-exchange and adsorption processes depending on the applied operating parameters. Heteroporous PSBP with total porosity of 53% had low specific surface area (0.9 m^2/g), but typical for the cellulosic-based biomass. At the same time, circular bioeconomy requirements were satisfied regarding by-product reuse and waste reduction. Usage of the material as long as possible contributed to the closed loop of the resource flows and increased efficiency. Current research has closed cycle of material and energy flow by conducting experiments in the closed-loop system until total utilization of components. Presented research was valuable contribution to the improvement of juice purification stage in sugar processing with a hope of shedding some light for an industrial

level scale-up. Sugar beet pulp obtained after the process of sodium, potassium and calcium biosorption could serve as a value-added animal feed product providing increased amounts of corresponding electrolytes in animal nutrition.

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Authors' contribution Lidija Peić Tukuljac was involved in investigation, writing—original draft, methodology; Jelena Krulj helped in conceptualization, writing—original draft; Jovana Kojić contributed to validation, writing—review & editing; Jelena Šuran was involved in investigation; Marija Bodroža-Solarov helped in visualization, funding acquisition; Bojan Miljević contributed to investigation; Zita Šereš was involved in conceptualization, methodology; Nikola Maravić helped in conceptualization, methodology, writing—review & editing.

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Declarations

Conflicts of interest The authors have no conflict of interests.

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