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REMOVAL OF SODIUM, POTASSIUM AND CALCIUM METAL IONS FROM ALKALIZED SUGAR JUICE USING SUGAR BEET PULP: A FIXED-BED COLUMN BIOSORPTION STUDY

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Abstract: This study investigates the possibility of applying continuous biosorption as an additional step in the sugar juice purification process to reduce the content of metal ions in alkalized juice. The response surface methodology (RSM) was used to examine the influence of the biosorption parameters: bed height of the biosorbent in the column, flow rate of the alkalized juice, and granulation of the biosorbent on molassigenic metal ions (K^+, Na^+ and Ca^{2+}) removal efficiency. At a flow rate of 4.75 mL/min, a biosorbent bed height of 15 cm, and biosorbent granulation <1 cm, the achieved reduction of Na^+ and Ca^{2+} ions in the alkalized juice was 74.19% and 62.78%, respectively. Slightly lower removal efficiency of K^+ ions (50.69%) was achieved at a flow rate of 6.75 mL/min, a bed height of 15 cm, and biosorbent granulation >5 cm. Therefore, the biosorption process is highlighted as a desirable process in the thin juice purification stage. By repurposing the by-product of the sugar industry, the concept of circular economy and zero waste emission is achieved. An additional step in the juice purification process in the sugar industry results in higher juice purity, thereby enabling greater sugar extraction and yield.

Key words: *fixed-bed column biosorption, sugar beet pulp, alkalized juice, metal ions*

INTRODUCTION

Today, the scientific community is confronted with a global environmental pollution crisis and is actively working towards sustainable development by exploring green technologies, harnessing renewable resources, and restoring environmental systems (Kukić et al., 2023). Each year, large quantities of low-value lignocellulosic residual agro-industrial biomaterial are generated during sugar production (Singh et al., 2021). The accumulation of significant amounts of this material leads to disposal problems including environmental pollution, land use issues, high costs, biodegradability challenges and regulatory concerns. A potential solution is using biomaterials in the form of biosorbents (Kulkarni, Golder & Ghosh, 2018).

Biosorption is an adsorption process using biomaterials such as bacteria, fungi, algae, yeasts,

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biopolymers, agricultural and industrial biowastes as an adsorbent (Pham, Kim,Chang & Chung, 2022; Yaashikaa, Palanivelu & Hemaavathy, 2024; Parades-Aguilar et al., 2025, Gupta, Prajapati & Kumar, 2025). Various research studies implicate biosorption potential on metal ions removal, which could cause adverse effects on human health or the environment and interfere purification processes of different industrial effluents (Peić Tukuljac et al., 2023; do Nascimento, Otaviano, de Sousa, de Oliviera & Hung, 2024; Romano, Corne, Azario, Centurión & García, 2025).

Biosorbents could form complexes with metal ions through their ligands or functional groups (Reddad et al., 2002). In the biosorption process, the significant interaction of the biomaterial with the metal ions being removed is crucial. Interactions such as ion exchange, complexation, electrostatic interactions, chemisorption, physisorption, microprecipitation, and reduction are types of biosorption mechanisms (Nathan, Jain & Rosengren, 2022). Factors such as pH, temperature, contact time, mixing speed, initial metal concentration, ionic strength of the metal ions, duration of mixing between the biosorbent and liquid and the amount of biosorbent are key factors that are optimized to enhance the efficiency of the biosorption process (Ciobanu, Lucaci & Bulgariu, 2024; Xie, 2024). Additionally, functional groups present on the surface of the biosorbent—such as carboxyl, amino, phosphate and sulfonate groups—also have a significant impact on metal ions removal (Gadd, 2009; Perović, 2024).

The principle of batch (discontinuous) biosorption is relatively simple. Batch biosorption typically occurs in a glass reaction vessel that is filled with a specific volume of liquid that needs to be purified, i.e. freed from the present ions (Castro, Blázquez, González, Muñoz, & Ballester, 2017). Batch biosorption provides fundamental information about the performance of the biosorbent and its affinity for the metal ions that need to be removed. However, considering the goal of enhancing the biosorption process in terms of the liquid volume, continuous biosorption certainly represents a step towards that objective (John et al., 2024).

There are three types of continuous column adsorption: fixed-bed adsorption, fluidized bed adsorption, and continuous flow of adsorbent and water (Šćiban & Klašnja, 2011; Blagojev, 2019). The most commonly used form of continuous adsorption is fixed-bed adsorption (Blagojev et al., 2019). The performance of the column is explained through the concept of a breakthrough curve, which is obtained by plotting the relationship between metal ion concentration over time (t) and initial concentration (C/C_0) against time (t). The breakthrough time is an indicator of the biosorbent saturation, along with the biosorption efficiency, representing the key variables that can be determined from the breakthrough curve (Patel, 2019).

The available scientific literature does not provide sufficient data on the removal of molassigenic metal ions (sodium, potassium and calcium) from various industrial effluents and intermediates in the sugar industry. Molassigenic metal ions, present in the alkalized juice, have a negative contribution to the sugar yield and formation of a complex with sucrose, thus enhancing its solubility. In the study by Arslanoglu and Tumen (2012), sugar beet pulp was used for the purification of raw juice with the aim of removing non-sucrose components: colouring substances and molassigenic metal ions (Na^+, K^+, Ca^{2+}, and Mg^{2+}). A relatively low amount of metal ions was removed (5.7-7%), when using unmodified sugar beet pulp.

This study aimed to evaluate the interaction of the biosorbent bed height in the adsorption column, flow rate of the alkalized juice and granulation of the biosorbent on molassigenic metal ion removal from the alkalized juice in the continuous fixed-bed column.

The parameters of the biosorption breakthrough curve the time when the breakthrough of the curve occurs (t_b), the time when the biosorbent is completely exhausted (t_{tot}), the total amount of metal ions removed (q_{tot}), the total amount of metal ions that pass through the column (m_{tot}), the biosorption capacity (q_e), and the efficiency of metal ion removal (R) have also been determined. Therefore, the main goal of this research was to optimize the continuous biosorption process in order to approach closer to industrial conditions.

MATERIALS AND METHODS

The samples of pressed sugar beet pulp and alkalized juice were obtained from the local sugar industry in Serbia.

Continous biosorption

Continuous biosorption experiments were conducted in an opaque stainless steel column (internal diameter: 2.3 cm and length: 15 cm) filled with a fixed bed level of biosorbent (Fig. 1). The alkalized juice is introduced into the column from the bottom in an upward flow regime using a peristaltic pump (Ecoline, Ismatec, Germany). The flow rate of the juice through the column is adjusted. A pre-defined mass of adsorbent is transferred into the column onto set mesh screens for sample retention. Sampling frequency was every two minutes during the first 30 minutes of the experiment, afterward sampling was done every 5 minutes (10 mL aliquots) until reaching 99% of biosorbent saturation. The experiments were carried out at a temperature of 70°C and a pH value of 12.5, indicating the most effective conditions for removing molassigenic metal ions during experiments conducted in a closed-loop biosorption system (Maravić et al., 2024).

Determination of metal ion amounts in alkalized juice

Detection and quantification of metal contents in samples were performed using a flame atomic absorption spectrometer (Varian Spectra AA 10, Varian Techtron Pty Limited, Australia) with a flame of acetylene and air, according to the Standard method (SRPS EN ISO 6869, 2008). The operating conditions that needed to be adjusted on the device before starting work (setting up the halogen lamp for the examined metal in operational position, adjusting the wavelength, slit size, and flame intensity) were set according to the manufacturer's instructions (Varian SpectrAA-10/20 Analytical methods, 1989).

The biosorption capacity (q) of the tested biosorbent for the removal efficiency of molassigenic metal ions was determined by the difference between the amount of molassigenic metal ions present in the alkalized juice before and after the applied biosorption process. The formula for calculating the biosorption capacity is:

$$q = \frac{(C_i - C_f) * V}{m},$$

where:

q - biosorption capacity (mg/g);
C_i - initial concentration of metal ions in the alkalized juice (mg/L);
C_f - final concentration of metal ions in the alkalized juice (mg/L);
V - volume of alkalized juice (mL);
m - mass of the biosorbent (g).

The removal efficiency (%) of molassigenic metal ions from the alkalized juice is determined by the formula: $E = \frac{C_i - C_f}{C_i} * 100$.

Parameters of continous biosorption

The volume of effluent (mL) that has passed through the system for continuous biosorption is calculated using the formula:

$V_{eff} = F * t_{tot}$,

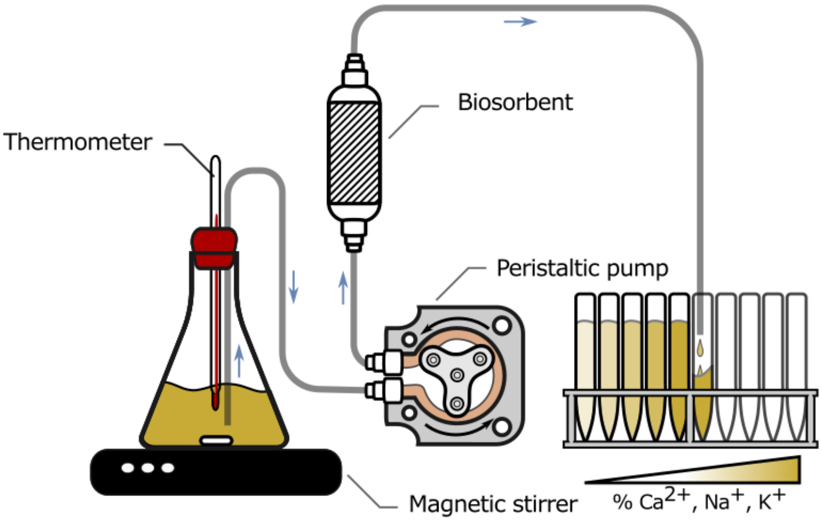

Figure 1. Apparatus for fixed-bed continous biosorption

where F is the effluent flow rate (mL/min) and t_{tot} (min) is the total time required for the total effluent volume to pass through system. The total mass of biosorbate adsorbed onto the biosorbent (mg) is calculated as:

$$q_{tot} = \int_{t=0}^{t=tot} Ca * dt,$$

where Ca is the concentration of adsorbed biosorbate and is calculated as:

Ca (mg/L) = $C_0 - C_t$,

where:

C_0 is the initial adsorbate concentration,

C_t is the adsorbate concentration at time t.

The amount of biosorbate adsorbed onto the biosorbent at equilibrium represents the biosorption capacity (mg/g) and can be determined using the formula:

$$q_{eq} = \frac{q_{tot}}{m},$$

where m is the amount of biosorbent (g) used in the study.

The total amount of biosorbate (mg) introduced with the liquid into the column is calculated using the equation:

$$m_{tot} = \frac{Co * F * t_{tot}}{1000}.$$

The removal efficiency (R) of the biosorbate (%) from the alkalized juice is calculated as the ratio of the total amount of biosorbate adsorbed onto the biosorbent surface to the total amount of biosorbate introduced into the system, using the formula:

$$R\ (\%) = \frac{q_{tot}}{m_{tot}} * 100.$$

Response surface methodology

The experimental design was created using Design-Expert version 7.0.0 statistical software (Stat-Ease Inc., Minneapolis, USA). The Central Composite Design (CCD) was chosen to minimize the maximum number of required experiments (23 experiments) with 3 repetitions at the center point (all inputs at middle level) (Sen, Nandi & Dutta, 2018). Mathematical and statistical processing of results was performed using Response Surface Methodology (RSM). The input factors for continuous biosorption experiments are: bed height of the biosorbent material (X_1, variation range 5 cm), flow rate (X_2, variation range 2 mL/min), and granulation of sugar beet pulp (X_3, variation range 5 cm). Outputs or dependent variables are removal efficiencies for Na^+ (Y_1), K^+ (Y_2), and Ca^{2+} (Y_3) (Table 1). All variables were given an equal significance factor.

RESULTS AND DISCUSSION

The effect of alkalized juice flow through the column on the removal efficiency of K^+, Na^+ and Ca^{2+}

Alkalized juice flow through the column is an important parameter that affects the performance of the continuous biosorption process. The flow rate directly determines the time that metal ions will spend in alkalized juice and the duration they will be in contact with the biosorbent (Acheampong, Pakshirajan, Annachhatre & Lens, 2013). Therefore, the flow rate of alkalized juice was varied at three levels: 4.75, 6.75, and 8.75 mL/min. Along with varying the flow rate of alkalized juice, both the granulation of the biosorbent and the bed height of the biosorbent in the column were also different. The temperature (70°C) and pH value (12.5) of alkalized juice were maintained constant as optimal conditions established during biosorption in a closed-loop when achieved removal efficiency for Na^+, K^+ and Ca^{2+} was 15.07%, 10.58% and 56.58%, respecttively (Peić Tukuljac et al., 2023).

Table 1.
Central composite design–dependent and independent variables

Independent variables	Level		
	Low (-1)	**Medium (0)**	**High (1)**
X_1: bed height of biosorbent (cm)	5	10	15
X_2: alkalized juice flow (mL/min)	4.75	6.75	8.75
X_3: granulation of biosorbent (cm)	<1	1-5	>5
Dependent variables:			
Y_1: removal efficiency Na^+ (%)			
Y_2: removal efficiency K^+ (%)			
Y_3: removal efficiency Ca^{2+} (%)			

Biosorption in batch conditions as the lowest optimised system provided the lowest removal efficiency for K^+, Na^+ and Ca^{2+} (9.30%, 11.00% and 38.2%, respectively) (Peić Tukuljac et al., 2022). In current research, after improving and optimizing process conditions, the highest removal efficiency for the mentioned three molassigenic metal ions (Na^+, K^+ and $Ca^{2+)}$ was achieved (74.19%, 50.69% and 62.78%, respectively).

At the same time, changes in layer height as well as granulation were monitored to assess both their individual effects and any synergistic impacts among these parameters. The breakthrough curves for removing Ca^{2+} ions at three different flow rates (4.75, 6.75, and 8.75 mL/min) are shown in Fig. 2. The time required to reach a breakthrough decreased from 25.36 minutes to 12.57 minutes when increasing flow from 4.75 to 8.75 mL/min while maintaining constant bed height (15 cm) and using large granulated sugar beet pulp (>5 cm). A similar result was reported by El Messaoudi et al. (2016) during Congo Red biosorption, where breakthrough time decreased from 60 minutes to 30 minutes (a twofold reduction), following an increase in flow rate from 2.8 mL/min to 6.4 mL/min.

The same trend of reduced breakthrough time while increasing flow rate was also observed by Zhao, Shang, Xiao, Dou & Han (2014) when using modified wheat straw as a biosorbent. As the flow rate increases, the amount of metal ions that end up in the effluent rises rapidly, resulting in a much steeper breakthrough curve, as seen in Fig. 2. This behaviour occurs because at high liquid flow rates feeding the column, the contact time between metal ions and biosorbent is significantly shorter.

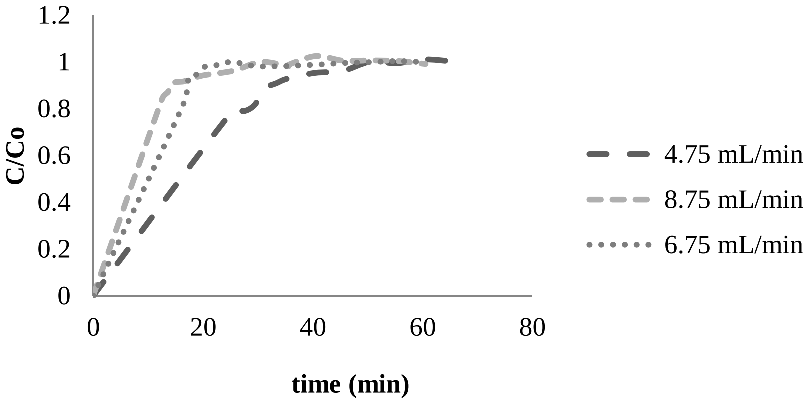

Figure 2. Breakthrough curves for the removal of Ca^{2+} ions at different flow rates of alkalized juice: 4.75 ml/min (experiment no. 7), 6.75 ml/min (experiment no. 19), and 8.75 mL/min (experiment no. 17)

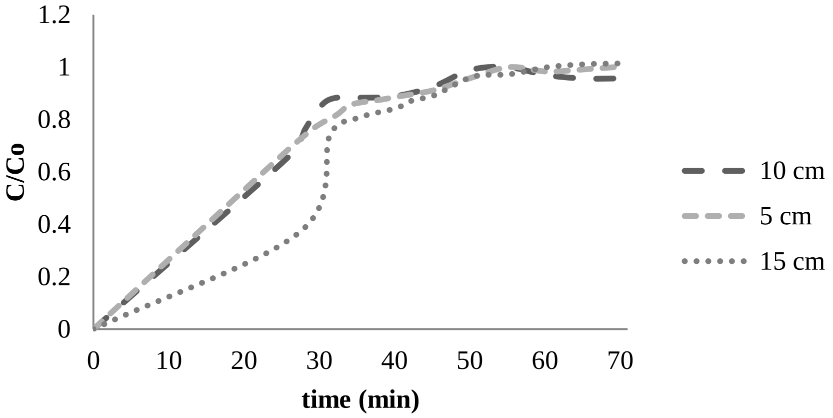

Figure 3. Breakthrough curve for Ca^{2+} removal at biosorbent bed heights of 5 cm (experiment no. 13), 10 cm (experiment no. 23), and 15 cm (experiment no. 10)

Consequently, metal ions have considerably less time to attach to active sites on the biosorbent and to diffuse into its open pores. The column with a fixed-bed of biosorbent thus receives a significantly larger quantity of metal ions in a shorter period before achieving adsorption equilibrium.

The time required for saturation of the biosorbent increases if liquid flow is reduced (Kojić, Vučurović, Lukić, Karadžić & Popović, 2017). At lower liquid flows, significantly higher removal efficiencies for metal ions are also achieved. Therefore, lower flows are desirable for more efficient purification of alkalized juice. At a flow rate of 4.75 mL/min, an efficiency of removal for Ca^{2+} ions is achieved at 21.02%, while at a flow rate of 8.75 mL/min, this efficiency drops significantly to 15.70% (Appendix 3). Considering Na^+ removal, increasing flow rate from 4.75 mL/min to 8.75 mL/min while keeping other parameters constant (bed height: 15 cm and granulation >5 cm), the removal efficiency decreases from 43.62% to 28.32% (Appendix 2). Under similar parameters and increasing flow rate, potassium ion removal efficiency decreases from 39.28% to 14.37% (Table S1).

Lower flow rate ensures longer residence time for mass transfer into adsorbent pores; thus, more metal ions will bind to active sites. The time at which the breakthrough occurs happens faster at higher flows. With increased flow rates, external mass diffusion to the biosorbent surface accelerates and ions accumulate on its surface, leading to significantly faster saturation of that surface. Reducing linear liquid flow contributes to enhanced diffusion within biosorbent particles due to longer residence times resulting from an increased number of contacts between liquid and adsorbent. At lower flows, intraparticle diffusion takes precedence as external mass transfer controls overall mass transfer processes over external diffusion itself (Hasan, Ranjan & Talat, 2010; Riazi, Keshtkar & Moosavian, 2016).

The influence of the bed height on the removal efficiency of K^+, Na^+, and Ca^{2+}

In order to investigate the efficiency of molassigenic metal ions removal using sugar beet pulp, the column was filled with different masses of biosorbent (5.7 g, 12.1 g, and 17.0 g), indicating biosorbent layer heights of 5 cm, 10 cm, and 15 cm, respectively. The breakthrough curves become sharper with lower bed heights, indicating an increased proportion of metal ions in the effluent leaving the column. The saturation of the whole layer occurs more quickly when the bed height is lower and fewer metal ions are adsorbed onto the biosorbent (Tables S1-S3). Fig. 3 shows breakthrough curves for removing Ca^{2+} ions when flow rates are fixed at 4.75 mL/min and granulation is less than 1 cm to examine how changes in bed height affect metal ion removal efficiency and removal trend.

From the Table S3, it is clear that the removal efficiency of 62.78% for the Ca^{2+} was achieved at the highest bed height. However, under the same conditions, when the bed height was reduced to 10 cm and 5 cm, the removal efficiency dropped to 33.78% and 33.01%, respectively. For all three metal ions (Na^+, Ca^{2+}, and K^+), the best removal efficiency was achieved at the highest biosorbent bed height (15 cm), as evident from the tables in Appendices 1, 2, and 3. If an insufficient biosorbent height is established in the column while simultaneously having a high flow rate of alkalized juice through the biosorbent layer, metal ions start appearing in the effluent right from the start. It is also necessary to conduct the biosorption process at a flow rate lower than the critical flow rate. The bed height of this biosorbent layer must be greater than a critical height below which it should not fall, so that large amounts of metal ions do not end up in the effluent.

By increasing the layer height of biosorbent in the column, both specific surface area and number of active sites for binding metal ions increase as well. A greater bed height results in longer contact time between liquid and biosorbent layers, leading to a higher percentage of metal ion removal. The time at which the breakthrough occurs increases from 25.29 minutes to 27.5 minutes due to an increase in biosorbent bed height from 5 cm to 15 cm (experiments numbered 13 and 10; Appendix 3). As the amount of biosorbent in the column increases, the number of free active sites available for binding metal ions also increases. Increasing layer heights from 5 cm to 15 cm directly affects the increased mass transfer zone size, resulting in sharper-shaped breakthrough curves as visible in Fig. 3. As bed height increases, mass transfer through diffusion becomes more dominant than the axial dispersion phenomenon (Riazi et al., 2016). Biosorption yield increases with increasing loading, thereby allowing metal diffusion deep into the pores of biomass (Marín et al., 2009). As bed height increases, the effect of axial dispersion on mass transfer decreases, leading to enhanced diffusion rates of metal ions into the layers. Thus, liquid has enough time to diffuse throughout each pore while remaining longer within a column (Hasan et al., 2010; Lodeiro, Herrero & de Vicente, 2006).

At a lower bed height value (5 cm), the C/C_0 ratio increases more rapidly than at a bed height of 15 cm (Rajeswari et al., 2013). A larger number of active sites is available when the filling within the column is greater (El Messaoudi et al., 2016). The time at which complete exhaustion of the biosorbent occurs is later, and the mass transfer zone also increases. Complete exhaustion of the biosorbent during Ca^{2+} removal occurs significantly later when the filling height is 15 cm (60.4 min), while at a filling height of 5 cm (55.29 min), complete exhaustion happens earlier. With a greater quantity of biosorbent present, there are more functional groups available, allowing for a higher number of ion exchange processes to take place (Pilli, Goud & Mohanty, 2012; Lodeiro et al., 2016; Kojić et al., 2017). The shape and gradient of the breakthrough curve change significantly with variations in fill height (Muhamad, Doan & Lohi, 2010).

The slope of the breakthrough curve is smaller with a lower bed layer height, especially when the liquid flow rate is reduced. Figure 3 shows that as bed height decreases to 5 cm in biosorption columns during Ca^{2+} ion removal under experimental conditions specified in experiments numbered 10 and 13 (Table S3), this leads to smaller slopes.

In some cases, if the bed height is very high, the possibility of its complete exhaustion is difficult, and in those cases, the effect of the so-called "tailing" is absent, i.e. the towing of the curve after reaching the complete saturation of the biosorbent.

Certainly, if the liquid containing a small proportion of metal ions is purified, and the bed height of the biosorbent layer is extremely high, the saturation of the biosorbent occurs slowly. The wide end of the breakthrough curve in the form of tailing may be a consequence of the non-ideal flow of the liquid through the biosorbent, as well as the limiting rate of diffusion within the particles (Lodeiro et al., 2016).

For these reasons, the experiment must be properly designed, taking into account both the characteristics of the liquid to be purified and the capabilities of the adsorption column. Dimensioning of the experiment itself must be adequately conducted and adapted to the liquid purified by the biosorbent.

After the breakthrough time is reached, that is the time for regeneration or desorption of the biosorbent. When the biosorption process is considered for scaling-up of the whole system, it is necessary to consider the length of unused bed (LUB), mass transfer zone ($\Delta t = t_{tot} - t_b$) and stoichiometric time (t*). Stochiometric time represents the moment when the influent concentration is equal to one-half of the effluent concentration. LUB measured the length of the mass transfer zone, which is unused for the biosorption process:

$$LUB = Z(1 - \frac{t_b}{t^*}),$$

where Z is bed height (cm).

In the majority of biosorption processes, the removal of metal ions primarily occurs in the initial section of the adsorption bed, concentrated within a narrow zone. The consideration of the unused portion of the adsorption bed is important when designing a continuous biosorption process.

Total bed length must be the sum of the total height of the packing and the unusable capacity. After the active sites are filled at the beginning, the mass transfer zone descends to the higher parts, and at the end, in the outlet liquid similar amount of metal ions is found as at the beginning liquid (Cazón, Viera, Donati & Guibal, 2014, Kulkarni, Shetty & Srinikethan, 2024).

In current research, LUB, t* and Δt for optimal experiment regarding all three monitored molassigenic metal ions (K^+, Na^+ and Ca^{2+}) were calculated and depicted in Table 2.

Considering the obtained results, a very short length of the bed is unused. LUB for K^+ is 0.4 cm, whereas for Na^+ is 1.05 cm and for Ca^{2+} is 0.6 cm, indicating well well-planned experiment for the considered alkalized juice and molassigenic metal ions.

Table 2.
Critical design factors

Metal ion	Experiment No.	LUB (cm)	t* (min)	Δt (min)
K^+	19	0.4	17	30
Na^+	10	1.05	29.5	23
Ca^{2+}	10	0.6	28.5	33.1

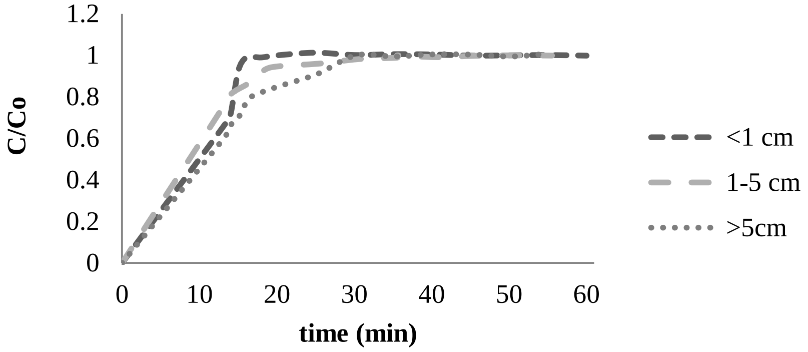

Figure 4. Breakthrough curves for Na^+ removal at a fixed bed height (15 cm), flow rate (8.75 mL/min), and particle sizes <1 cm (experiment no. 2), 1–5 cm (experiment no. 18), and >5 cm (experiment no. 17)

Effect of biosorbent particle size on Na^+, K^+ and Ca^{2+} removal efficiency

Particle granulation of the biosorbent represents a limiting and controlling parameter when it comes to continuous biosorption. The granulation of the biosorbent particles is an extremely important parameter that directly affects the specific surface area of the biosorbent and the availability of free active sites for molassigenic metal ion binding. In this study, sugar beet pulp fractions of three different sizes were used: <1 cm, 1-5 cm, and >5 cm.

In industrial conditions, pressed sugar beet pulp represents a combination of the three men-tioned dimensions. The comparison results of Na^+ removal efficiency of three different fractions of sugar beet pulp (<1 cm, 1-5 cm, and >5 cm) at the constant filling height (15 cm) and the constant flow rate (8.75 mL/min) yielded the following results shown in Fig. 4. The graph shows that the removal efficiency is highest when the biosorbent granulation is smallest (<1 cm), while increasing the granulation to a size >5 cm, the Na^+ removal efficiency decreases from 51.72% to 28.32%. When the smallest flow rate (4.75 mL/min), which is the most favourable in terms of biosorption efficiency, is fixed, the differences in Na^+ removal efficiency become even greater. With the increase in granulation, the Na^+ removal efficiency decreases from 74.19% to 46.62%. In this boundary example, it is evident how the difference in granulation also affected a larger volume of effluent treated and a higher biosorbent capacity. The volume of effluent processed until the saturation of active sites on the biosorbent at a granulation of <1 cm was 215.13 mL, while under the same experimental conditions, at a granulation of >5 cm, the processed volume of alkalized juice was 183.26 mL (Table S2). The decrease in removal efficiency is directly proportional to the reduction in the specific surface area of the biosorbent layer. Therefore, reducing the granulation of the biosorbent layer results in a potentially longer residual retention time of the alkalized juice within the column due to the greater number of contacts between the juice and the biosorbent (El Messaouidi et al., 2016). Thus, the time required for complete exhaustion of the biosorbent during K^+ removal was 45.29 minutes at a granulation of <1 cm, while at a granulation of >5 cm, it was 38.58 minutes.

The granulation of biosorbent should not drop below the critical, limiting granulation; no significant changes were observed in the efficiency of metal ion removal, nor in the appearance of the breakthrough curve. In porous materials, such as sugar beet pulp, whose total porosity is 53%, the contribution of the external surface to the total surface area is limited (Perović, 2024). The most significant influence comes from the number and size of pores. Since reducing the particle size of the biosorbent does not increase its porosity, but rather its external specific surface area, the contribution to reducing the granulation of the biosorbent is not significant. Furthermore, in these types of materials, the removal of metal ions is controlled by the ion exchange mechanism, which makes it independent of the size of the external surface of the biosorbent. In the study by Marín et al. (2009), orange peel was used as a biosorbent, which contains a high proportion of exchangeable ions such as Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}. In this research, the same ion exchange process occurs, but the mentioned ions are present in the alkalized juice and exchanged with H^{+} ions from the surface of the biosorbent.

CONCLUSIONS

Removal efficiency of molassigenic metal ions from alkalized juice was strongly influenced by alkalized juice flow. The highest metal ion removal efficiency was achieved at 4.75 mL/min. At a lower flow, the break point in the curve occurs later, and the curve is less sharp. The highest removal efficiency of molassigenic metal ions is at 15 cm bed height. The more sugar beet pulp in the column, the more active sites there are for metal ion binding, making adsorption more effective. Following the influence of varying granulation, i.e. of the size of sugar beet pulp at three levels (<1 cm, 1-5 cm and >5 cm), the highest efficiency of removing Na^{+}, K^{+} and Ca^{2+} ions was achieved at the smallest granulation of sugar beet pulp (<1 cm). Smaller granulation of sugar beet pulp in the column leads to a larger volume of alkalized juice that flows through the column until the moment of complete saturation of the biosorbent with metal ions, as well as to a longer residual retention time of the alkalized juice in the column.

AUTHOR CONTRIBUTIONS

Conceptualization, investigation, writing–original draft, methodology, L.E.P.; Conceptualization, methodology, J.A.M. and N.R.M.; Investigation, J.D.Š, I.K.Z.; Formal analysis, visualization, R.C.J-M.; Validation, writing-original draft preparation, N.R.M.; Writing-review and editing, J.A.M.; Supervision, visualization, Z.I.Š.

DATA AVAILABILITY STATEMENT

Data contained within the article.

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CONFLICT OF INTEREST

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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SUPPORTING INFORMATION

This article contains additional supporting material in Appendix.

Table S1. Independent variables, dependent variables, and calculated parameters of continuous biosorption of K^+ ions from alkalized juice

Table S2. Independent variables, dependent variables, and calculated parameters of continuous biosorption of Na^+ ions from alkalized juice

Table S3. Independent variables, dependent variables, and calculated parameters of continuous biosorption of Ca^{2+} ions from alkalized juice

BIOSORPCIJA JONA NATRIJUMA, KALIJUMA I KALCIJUMA REZANCIMA ŠEĆERNE REPE POMOĆU KONTINUALNE BIOSORPCIJE SA FIKSNIM SLOJEM BIOSORBENTA

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Sažetak: Primena biosorpcije u industrijskim i laboratorijskim uslovima u industriji šećera je slabo istražena. Ovaj rad prikazuje primenu rezanaca šećerne repe u vidu biosorbenta u industriji šećera, za prečišćavanje alkalisanog soka i smanjenje nesaharoznih materija. Korišćen je kontinualni postupak biosorpcije kako bi se simulirali industrijski uslovi. Primena *Central Composite Design* eksperimentalnog plana korišćena je za optimizaciju parametara biosorpcije: visine sloja biosorbenta, protoka alkalisanog soka i granulacije biosorbenta. Procesom biosorpcije se smanjuje sadržaj jona Na^+ i Ca^{2+} u alkalisanom soku za 74,19% i 62,78%, pri protoku 4,75 ml/min, visini sloja punjenja biosorbenta 15cm i granulaciji biosorbenta <1cm. Sadržaj jona K^+ se smanjuje za 50,69% pri protoku 6,75 ml/min, visini sloja punjenja 15cm i granulaciji biosorbenta >5cm. Ovime se potvrđuje doprinos valorizacije rezanaca šećerne repe u vidu biosorbenta, koji predstavlja sporedni proizvod prerade šećerne repe. Prenamenom sporednog proizvoda industrije šećera zadovoljava se koncept cirkularne ekonomije i nulte emisije otpada.

Ključne reči: *kontinualna biosorpcija sa fiksnim slojem biosorbenta, rezanci šećerne repe, alkalisani sok, joni metala*

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Appendix

Table S1.
Independent variables, dependent variables, and calculated parameters of continuous biosorption of K^+ ions from alkalized juice

Exp. number	**Flow (mL/min)**	**Bed height (cm)**	**Granu-lation (cm)**	**t_b (min)**	**t_{tot} (min)**	**V_{eff} (mL)**	**m_{tot} (mg)**	**q_{tot} (mg)**	**q_{eq} (mg/g)**	**R (%)**
1	6.75	10	<1	15.00	35.27	238.07	215.69	61.18	5.06	28.37
2	8.75	15	<1	13.40	20.04	175.35	154.13	21.57	1.27	13.99
3	6.75	10	>5	15.19	25.19	170.03	107.97	25.76	2.13	23.86
4	6.75	10	1-5	16.36	25.36	171.18	178.54	56.49	4.67	31.64
5	4.75	10	1-5	31.55	39.55	187.87	196.69	68.38	5.65	34.77
6	4.75	5	>5	23.58	38.58	183.26	17849	31.89	5.59	17.86
7	4.75	15	>5	25.36	40.36	191.71	194.20	76.30	4.49	39.28
8	8.75	5	<1	13.12	28.12	246.05	308.54	64.47	11.31	20.89
9	6.75	10	1-5	17.07	30.07	202.97	152.97	61.29	5.07	40.07
10	4.75	15	<1	27.50	42.40	201.40	233.62	103.72	6.10	44.39
11	6.75	5	1-5	19.38	23.38	157.81	175.33	48.77	8.55	27.81
12	6.75	15	1-5	16.14	45.14	304.69	381.17	95.37	5.61	25.02
13	4.75	5	<1	25.29	45.29	215.13	322.69	143.69	25.21	44.53
14	6.75	10	1-5	14.35	25.35	171.11	138.26	40.89	3.37	29.59
15	8.75	10	1-5	12.45	45.45	397.69	387.75	91.08	7.52	23.48
16	8.75	5	>5	11.80	27.15	237.56	286.74	99.30	5.84	34.63
17	8.75	15	>5	12.57	25.57	223.74	238.28	34.24	2.01	14.37
18	8.75	15	1-5	13.21	30.21	264.34	320.91	127.67	7.52	33.79
19	6.75	15	>5	16.36	40.36	272.43	354.16	179.53	10.56	50.69
20	8.75	10	>5	12.10	30.10	263.38	3444.95	855.97	70.74	24.85
21	4.75	5	1-5	28.23	40.00	190.00	289.75	55.48	9.73	19.15
22	6.75	5	<1	18.00	22.00	148.50	159.19	49.59	4.09	31.16
23	4.75	10	<1	26.10	40.10	190.47	236.37	37.72	3.11	15.95

Table S2.
Independent variables, dependent variables, and calculated parameters of continuous biosorption of Na^+ ions from alkalized juice

Exp. number	**Flow (mL/min)**	**Bed height (cm)**	**Granulation (cm)**	**t_b (min)**	**t_{tot} (min)**	**V_{eff} (mL)**	**m_{tot} (mg)**	**q_{tot} (mg)**	**q_{eq} (mg/g)**	**R (%)**
1	6.75	10	<1	15.00	25.27	170.57	1497.63	728.35	60.19	48.63
2	8.75	15	<1	13.40	25.04	219.10	1792.24	926.79	54.52	51.72
3	6.75	10	>5	15.19	25.19	170.03	1428.27	464.19	38.36	32.50
4	6.75	10	1-5	16.36	25.36	171.18	1417.37	657.33	54.32	46.37
5	4.75	10	1-5	31.55	39.55	187.86	1604.35	732.67	60.55	45.67
6	4.75	5	>5	23.58	41.58	197.51	2000.75	707.07	124.05	35.34
7	4.75	15	>5	25.36	45.36	215.46	1753.84	764.88	44.99	43.62
8	8.75	5	<1	13.12	28.12	246.05	2192.31	834.11	146.33	38.04
9	6.75	10	1-5	17.07	35.07	236.72	2142.34	752.78	62.21	35.14
10	4.75	15	<1	27.50	50.40	239.40	3581.42	2657.34	156.31	74.19
11	6.75	5	1-5	19.38	30.38	205.07	3457.39	1207.83	211.90	34.93
12	6.75	15	1-5	16.14	30.14	203.44	3305.98	1295.95	76.23	39.20
13	4.75	5	<1	25.29	55.29	262.63	4559.21	1964.45	344.64	43.09
14	6.75	10	1-5	14.35	28.35	191.36	1544.29	331.05	27.36	21.44
15	8.75	10	1-5	12.45	35.45	310.19	2884.74	1209.11	99.93	41.92
16	8.75	5	>5	11.80	37.15	325.06	3465.16	1053.2	61.95	30.39
17	8.75	15	>5	12.57	40.57	354.99	3233.94	915.87	53.87	28.32
18	8.75	15	1-5	13.21	30.21	264.34	3806.46	1509.37	88.79	39.65
19	6.75	15	>5	16.36	40.36	272.43	3705.05	1059.75	62.34	28.61
20	8.75	10	>5	12.10	40.10	338.85	3308.75	607.01	50.17	18.35
21	4.75	5	1-5	28.23	65.00	308.75	3856.28	707.04	124.04	18.33
22	6.75	5	<1	18.00	30.00	193.50	3069.90	943.65	77.99	30.74
23	4.75	10	<1	26.10	55.10	261.73	4360.33	2670.42	220.69	6.25

Table S3.
Independent variables, dependent variables, and calculated parameters of continuous biosorption of Ca^{2+} ions from alkalized juice

Exp. number	Flow (mL/min)	Bed height (cm)	Granu-lation (cm)	t_b (min)	t_{tot} (min)	V_{eff} (mL)	m_{tot} (mg)	q_{tot} (mg)	q_{eq} (mg/g)	R (%)
1	6.75	10	<1	15.00	35.27	238.07	176.41	59.76	4.94	33.87
2	8.75	15	<1	13.40	20.04	175.35	123.78	40.51	2.38	32.72
3	6.75	10	>5	15.19	25.19	170.03	140.10	32.31	2.66	23.06
4	6.75	10	1-5	16.36	25.36	171.18	137.79	39.00	3.23	28.45
5	4.75	10	1-5	31.55	51.55	244.86	180.71	96.23	7.95	53.25
6	4.75	5	>5	23.58	38.58	183.25	143.85	34.63	6.07	24.08
7	4.75	15	>5	25.36	50.36	239.21	183.23	38.51	2.27	21.02
8	8.75	5	<1	13.12	28.12	246.05	183.97	58.33	10.23	31.71
9	6.75	10	1-5	17.07	30.07	202.98	112.98	43.84	3.62	38.08
10	4.75	15	<1	27.50	60.40	286.90	233.54	146.61	8.62	62.78
11	6.75	5	1-5	19.38	30.38	205.06	190.92	32.41	5.68	16.97
12	6.75	15	1-5	16.14	25.14	169.69	144.41	41.04	2.43	28.67
13	4.75	5	<1	25.29	55.29	262.63	248.18	81.94	14.37	33.01
14	6.75	10	1-5	14.35	28.35	191.36	138.16	36.74	3.03	26.59
15	8.75	10	1-5	12.45	45.45	397.68	279.61	51.89	2.46	18.56
16	8.75	5	>5	11.80	32.15	281.31	220.75	44.08	2.59	19.97
17	8.75	15	>5	12.57	30.57	267.49	212.92	33.44	1.97	15.70
18	8.75	15	1-5	13.21	30.21	264.34	237.11	54.72	3.22	23.08
19	6.75	15	>5	16.36	25.36	171.18	141.91	26.09	1.53	18.38
20	8.75	10	>5	12.10	40.10	350.88	247.63	37.18	3.07	15.00
21	4.75	5	1-5	28.30	40.00	190.00	186.20	73.34	12.87	39.38
22	6.75	5	<1	18.00	40.00	270.00	253.80	81.81	6.76	32.23
23	4.75	10	<1	26.10	55.10	261.73	235.55	79.56	6.57	33.78