Utilization of Sugar Beet Pulp as Biosorbent for Molassigenic Metal Ions: Kinetic Study of Batch Biosorption

Lidija Peić Tukuljac1,2*, Jelena Krulj2, Lato Pezo3, Nikola Maravić1, Jovana Kojić2, Zita Šereš1

1 Faculty of Technology Novi Sad, University of Novi Sad, Bulevar Cara Lazara 1, 21000 Novi Sad, Serbia
2 Institute of Food Technology in Novi Sad, University of Novi Sad, Bulevar Cara Lazara 1, 21000 Novi Sad, Serbia
3 Institute of General and Physical Chemistry, University of Belgrade, Studentski Trg 12-16, 11000 Belgrade, Serbia

* Corresponding author, e-mail: lidija.peictukuljac@fins.uns.ac.rs

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Abstract

The sugar industry is facing problems with high amount of molassigenic metal ions remained after the purification step in sugar juice. In this investigation the application of unmodified sugar beet pulp as a weak monofunctional cation-exchange biosorbent for molassigenic metal ions (Na+, K+ and Ca2+) removal from the alkalized sugar juice was studied. The batch biosorption experiments were performed at temperature (70 °C) and pH (10.5) of alkalized sugar juice similar to industrial conditions. The highest removal efficiency was noticed for divalent Ca2+ (30.2%), while monovalent Na+ and K+ ions were removed with 10.9 and 9.1% efficiency, respectively. Biosorption equilibrium was established in 90 min for all tested metals. Sugar beet pulp characterization from the perspective of cation-exchange material was conducted. The structure of the biosorbent and an insight of the functional groups were also characterized by scanning electron microscopy and Fourier transform infrared spectroscopy. The biosorption data were analyzed using four non-linear kinetic (pseudo-first order, pseudo-second order and Elovich) and diffusion models (Weber-Morris). The time course data of biosorption processes fitted well to the pseudo-first and the pseudo-second-order kinetic models indicating ion-exchange and chemisorption as dominant mechanisms for metal ions removal from the alkalized juice. HNO3 as a desorption reagent showed the highest average molassigenic metal ions desorption efficiency (54.4%). Utilization of sugar beet biomass as cation-exchange material imposes as a potential solution for more successful sugar juice purification.

Keywords

sugar beet pulp, alkalized juice, biosorption, molassigenic metal ions

1 Introduction

In the sugar industry, the conventional method based on the liming-carbonation process is mandatory directed for high-purity sugar juice production [1]. However, after the juice purification step, sugar juice still contains inorganic compounds responsible for the scales on evaporators and crystallizers, consequently decreasing sugar juice quality [2]. Molassigenic metal ions (such as Na+, K+, Ca2+ and Mg2+) present in the sugar juice cause an adverse effects on the sucrose yield by creating complex compounds with sucrose and therefore increasing their solubility. During the recent years, certain sugar plants introduced the juice-softening process (by using cation-exchange resins), with satisfactory results produced regarding the complete removal of Ca2+ ions [3]. The alkalized juice, acquired after one lime-carbonation cycle and fine filtration, represented an intermediate product with the most adequate characteristics for the application of an additional purification step on the industrial level.

Besides sucrose and molasses, sugar beet pulp (SBP) represents the third most important product of the sugar industry. Furthermore, SBP is most important solid by-product with around 9.7 million tons/year produced in the Europe which is around 4.6–5% of the whole sugar beet production in 2019 in Europe (194.15 million tons/year) [4, 5]. In Serbia, all sugar production is based on sugar beet (Beta vulgaris L.) processing. SBP remains after the extraction of sugar from sugar beet cossets [6]. Afterward, SBP is pressed, dried and sold as a valuable ruminant feed component. Nowadays, SBP is used as a raw material for bioethanol and biogas production strengthening the emerging concept of biorefinery and also as a biosorbent for entrapped heavy metals (nickel, mercury, cooper etc.) removal from the industrial wastewater [7,
First of all, SBP represents source of the fibers, oligosaccharides and pectin isolates, namely used as stabilizer, gelling and thickening agent [9]. Lignocellulosic materials, such as SBP, have the ion-exchange capacity and general sorptive characteristics, which are derived from their structure, composed of polysaccharides [10]. Since the current conventional methods are limited regarding adequacy and cost, biosorption technique has received increasing attention for low cost, high efficiency, environmentally-friendly, non-secondary pollution, and superiority in the treatment of low concentration residual metal effluents [11]. However, there is still lack of investigations regarding alkali and alkaline earth metals removal. Nowadays, natural by-products in the form of biosorbents have been successfully used for the biosorption of cadmium on sugar beet pulp pectin [12] and citrus peel [13], lead on the sugar beet pulp [14], barley straws [10], and Myrophyllum spicatum L. [15], copper on the sugar beet pectin gel [16], banana peel [17] or barley straws [10].

Desorption from the biomass is important for identification of adsorption mechanism, which also contributes in the decreasing of process cost, recovery of contaminants, and reduction of secondary wastes [18]. Desorption can be performed by proton exchange using acids (HNO$_3$, H$_2$SO$_4$, HCl), bases (NaOH), by exchange with other ions (NaCl, KCl, CaCl$_2$), using chelating agents (EDTA) or water [13, 14, 19]. The main criteria of a successful desorption is the proper selection of eluents which strongly depends on the biosorbent type, removed metal ions and the biosorption mechanism [20].

The main aim of the present study was to assess the potential of unmodified SBP as an ion-exchange biosorbent for the removal of molassigenic metal ions (Na$^+$, K$^+$ and Ca$^{2+}$) from alkalized juice in the batch system. The present work is the first study to investigate the utilization of unmodified pressed sugar beet pulp in native form for removing the molassigenic metal ions for the purpose of alkalized juice purification. These findings enhance understanding of the sugar beet pulp ion-exchange feature. Additionally, by avoiding utilization of the additional chemicals for the modification of sugar beet pulp economic and ecological benefits were evident. The examined conditions were similar to the industrial referring to two the most important alkalized juice performances: temperature (70 °C) and pH value (10.5). The non-linear kinetics and diffusion models including pseudo-first, pseudo-second, Elovich and Weber Morris models were applied to examine the mechanism, reaching the equilibrium and behavior of biosorption process. Furthermore, SBP was chemically characterized before and after the applied biosorption process. The most effective desorbent for the molassigenic metal ions elution from the SBP was determined by the desorption process conducted with selected reagents (HNO$_3$, H$_2$SO$_4$, NaOH, EDTA and HCl).

2 Material and methods
2.1 Preparation and characterization of biosorbent and alkalized juice
SBP and alkalized juice were provided by sugar plant in Republic of Serbia. Samples were taken directly from the sugar beet plant, and then stored at −20 °C in a freezing chamber until biosorption study. SBP was used in unmodified form. The obtaining procedure of the pressed sugar beet pulp from the sugar industry was mentioned in the study of Maravić et al. [6]. Determined ion-exchange properties of the SBP were: water sweling and retention capacity [21], apparent density [22] and cation exchange capacity [23]. Chemical characterization of SBP before and after the biosorption process included determination of dry mass and the content of ash, sucrose, protein, cellulose and total dietary fiber. pH value, ash and dry matter content of SBP and alkalized juice were determined according to International Commission for Uniform Methods of Sugar Analysis methods [24]. Protein (Official Method No. 950.36), total dietary fiber, (Official Method No. 958.29), insoluble dietary fiber (Official Method No. 991.43) and soluble dietary fiber content (Official Method No. 991.43) were analyzed in order to determine fibrous composition of SBP [25]. Further, representation of the functional groups in unmodified SBP and surface morphology characterization of SBP before and after biosorption were determined by Fourier transformation infrared spectra (FTIR) by using Alpha Bruker Optics instrument (Bruker Optics, Germany) with attenuated total reflection technique (ATR) in the region 400–4000 cm$^{-1}$ and Scanning electron microscope (SEM) (Hitachi TM 3030 tabletop, Japan) at 20keV. Alkalized sugar juice, used in this research, contained 15.6% dry matter, pH value of 10.5 and Na$^+$, K$^+$ and Ca$^{2+}$ content: 3076.92, 10128.21 and 12115.38 mg∙kg$^{-1}$ dry matter, respectively.

2.2 Biosorption experiments
Biosorption experiments were conducted in the batch regime in a series of conical vessel (500 mL, containing 300 mL alkalized juice and predetermined amount of 17 g SBP). Alkalized juice (pH = 10.5) was in the contact with SBP for 5–240 min, agitated using magnetic stirrer
(IKA, Germany) to avoid sedimentation. The temperature of the alkalized juice was maintained at 70 °C by using the water bath. Samples of the alkalized juice were taken from the series of conical vessels for kinetics studies at various time intervals between 5 and 240 min. Each experiment has been performed in duplicate.

The final metal content in alkalized juice and SBP was quantified by atomic absorption spectrometer (Varian spectra AA 10, Varian Techtron Pty Limited, Australia) using standard method [26]. The biosorption capacity of the SBP, for the removal of Na⁺, K⁺ and Ca²⁺ was quantitatively evaluated using the amount of metal retained on weight unit of biomass q (mg g⁻¹):

\[ q = \frac{(C_i - C_f) \times v}{m}, \]  
\[ \text{(1)} \]

while metal removal efficiency \( R \) (%) was calculated using the following equation:

\[ R = \frac{C_i - C_f}{C_i} \times 100, \]  
\[ \text{(2)} \]

where \( C_i \) and \( C_f \) were initial and final concentration of Na⁺, K⁺ and Ca²⁺ in alkalized juice (mg L⁻¹), respectively, \( C_f \) was amount of Na⁺, K⁺ and Ca²⁺ at time \( t \) (mg L⁻¹), \( v \) (L) volume of the alkalized juice and \( m \) (g) mass of the biosorbent [2, 13, 27].

2.3 Kinetic models

Equation used for calculation of biosorption behavior of SBP for the pseudo-first model could be defined as:

\[ y = q_e \times (1 - \exp(-k_1 \times t)), \]  
\[ \text{(3)} \]

where \( q_e \) is the amount of adsorbate in solution at equilibrium (mg g⁻¹); \( y \) is amount of adsorbate in solute at exact time (mg g⁻¹); \( t \) is the time of the biosorption process (min); \( k_1 \) is the constant of the pseudo-first order adsorption rate (min⁻¹) [28].

The pseudo-second model of adsorption could be represented according to the following equation:

\[ y = \frac{t}{k_2 + q_e} + \frac{1}{q_e}, \]  
\[ \text{(4)} \]

where \( y \) is amount of adsorbed metals at exact time (mg g⁻¹); \( q_e \) is second-order amount in solution at equilibrium (mg g⁻¹); \( k_2 \) is second-order rate constant (g mg⁻¹ min⁻¹); \( t \) is biosorption time (min) [28, 29].

The Elovich model of adsorption behavior could be calculated according to equation:

\[ y = \frac{1}{b} \ln (a \times b) + \frac{1}{b} \ln (t), \]  
\[ \text{(5)} \]

where \( y \) is amount of adsorbate in the solute at the specific time (mg g⁻¹); \( a \) is initial adsorption rate (mg g⁻¹ min⁻¹) and \( b \) is constant associated with the extent of surface coverage; \( t \) is the exact time of the adsorption duration (min) [30].

The in-particle diffusion (Weber-Morris) model of adsorption could be presented by the equation:

\[ y = k_{\text{ad}} \times \sqrt{t} + C, \]  
\[ \text{(6)} \]

where \( y \) is amount of adsorbate in solute at time (mg g⁻¹); \( t \) is the adsorption time (min); \( k_{\text{ad}} \) is the intra-particle constant (mg g⁻¹ min⁻¹/²); \( C \) is the thickness of the boundary layer (mg g⁻¹) [30, 31].

2.4 Desorption studies

The molassigenic metal ions-loaded SBP was rinsed with deionized water, filtered through strainer filter and immersed in a 300 mL desorption solution of 0.1 M of HCl, H₂SO₄, HNO₃, EDTA and NaOH. The desorption experiments was maintained at 70 °C. Desorption efficiency (\( DE \% \)) of Na⁺, K⁺, Ca²⁺ ions migration from the SBP was calculated by the following equation:

\[ DE = \frac{q_{\text{ad}} - q_{\text{de}}}{q_{\text{ad}}} \times 100, \]  
\[ \text{(7)} \]

where \( q_{\text{ad}} \) and \( q_{\text{de}} \) were amount of Na⁺, K⁺ and Ca²⁺ ions adsorbed and remained on the SBP after desorption process (mg g⁻¹), respectively [13]. The positive values for the removal and desorption indicated a release of molassigenic metals, whereas negative values indicated enrichment of SBP and alkalized juice in molassigenic metal ions.

3 Results and discussion

3.1 Chemical composition and properties of biosorbent

In order to examine changes that have occurred after the biosorption process, characterization of SBP before and after the applied process was conducted (Table 1). In this study SBP was used as unmodified, raw, pressed sugar beet pulp in the form produced directly in the sugar factory after sweet water extraction of sucrose and pressing the remaining water. Utilization of the unmodified sugar beet pulp for the biosorption studies is desirable from the aspect of time management and also more suitable from the environmental aspect. Therefore, toxic and expensive chemicals were avoided for the modification of SBP, contributed to the reduction of harmful emissions into the environment. The dry matter content of SBP was 27.0%, which indicated a successful dewatering capabilities.
and a proper sucrose extraction from sugar beet during appropriate technological process in the sugar plant. These results were in agreement with those presented by Maravić et al. indicated dry matter content of sugar beet pulp was 31.50% [6]. Additionally, Doležal et al. reported dry matter of pressed sugar beet pulp was 23–24% and still containing small amount of sucrose 3.50% A small extent of sucrose is still expected to remain in the SBP after the extraction and pressing process [32]. Due to certain amount of residual sucrose in the SBP there are possibilities for emerging technologies as bioethanol production and biorefinery [33, 34].

The total dietary fiber (TDF) content of SBP is usually between 70 and 80%, and is mainly composed of cellulose, hemicellulose, pectin and lignin [35]. Cellulose, pectin and hemicellulose consists of approximately one third of the SBP amount [33]. A high cation exchange capacity and good sorption characteristic was expected from the SBP due to significant total dietary fiber content (73.7%). SBP is mostly fibrous structure, indicating biosorbent potential for molassigenic metal ions removal [8]. Additional physicochemical analysis (water retention-WRC and swelling capacity-WSC, apparent density and cation exchange capacity-CEC) of SBP has been conducted and obtained results were shown in Table 2. Cation exchange behave capacity is characteristic of fibrous materials which affects as a cation-exchange material. In this study was obtained optimal CEC value (0.84 meq g⁻¹) and density (1.02 g L⁻¹) of the SBP which was in favour of the high ion-exchange property of the SBP. Experimental values of CEC of the SBP are in a good agreement with previously reported by Altundogan et al. (0.86 meq g⁻¹) [36] and Arslanoglu and Tumen (0.93 meq g⁻¹) [2].

### Table 1 Chemical properties of SBP before and after biosorption process

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Before biosorption</th>
<th>After biosorption</th>
<th>% dry matter</th>
</tr>
</thead>
<tbody>
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<td>Dry matter</td>
<td>27.0 ± 0.1</td>
<td>23.8 ± 0.0</td>
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<td>Ash</td>
<td>4.3 ± 0.1</td>
<td>7.4 ± 0.1</td>
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<td>Protein</td>
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<tr>
<td>Total dietary fiber</td>
<td>73.7 ± 1.4</td>
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<tr>
<td>Insoluble dietary fiber</td>
<td>62.4 ± 4.5</td>
<td>62.4 ± 4.5</td>
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<tr>
<td>Soluble dietary fiber</td>
<td>9.0 ± 0.9</td>
<td>4.8 ± 0.2</td>
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### Table 2 Physicochemical properties of the pressed SBP

<table>
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<th>Property</th>
<th>SBP</th>
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<tr>
<td>Water retention capacity, WRC (mL g⁻¹)</td>
<td>7.95</td>
</tr>
<tr>
<td>Water swelling capacity, WSC (g g⁻¹)</td>
<td>7.82</td>
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<tr>
<td>Apparent density (g L⁻¹)</td>
<td>1.02</td>
</tr>
<tr>
<td>Cation exchange capacity, CEC (meq g⁻¹)</td>
<td>0.84</td>
</tr>
</tbody>
</table>

in aqueous solution, due to the carboxyl residues of galacturonic acid [7]. Lower amount of soluble dietary fibers (4.8%), mostly pectin after the biosorption process indicated occupancy of the functional groups from the SBP pectin with molassigenic metal ions. Slightly lower content of total dietary fibers (67.7%) obtained after the biosorption process in this study can be also attributed to the high process temperature (70 °C) and strong alkaline conditions (pH = 10.5), leading to fibers decomposition [37]. For these reasons, slightly lower amount of the total dietary fibers (especially the soluble fibers) was gained after the biosorption experiment. The homogalacturonan region of pectin also may be degraded into small fragments when exposed to alkaline conditions, leading to the loss of galacturonic acid, but at much higher temperatures between 200-300 °C [38]. Therefore, this reduction in fiber content indicated that experimental temperature set at this study (70 °C) would not degrade pectin into smaller fragments composed of amide groups and galctourinoic chains [39]. Acidic pH values (1.5–2) are convenient for degradation of pectin from SBP and destroying homogalacturonan regions [40]. Hydration capacities (WRC=7.95 mL g⁻¹, WSC=7.82 g g⁻¹) are in satisfactory range and also similar to previously mentioned studies. Water holding capacities are difficult to compare due to huge impact of the operating parameters (pH, temperature, centrifugation) [41]. Apparent apparent density of the SBP was 1.02 g L⁻¹. This result is in accordance with Rezić et al. who obtained apparent density of SBP from 1.11–1.22 g L⁻¹ depending on particle size of the SBP [22]. SBP powders with high apparent density were good source of fibers and also nutritionally valuable ingredient [42]. Small and negligible change in protein content (17.2%) from the SBP was detected in this research. Some researchers reported that the protein-polysaccharide linkages in the SBP were unstable in alkaline solutions. Therefore, alkaliized juice and the proteins may be partially present in their free form [43]. The presence of proteins in sugar beet pectin structure resulted in better surface-active properties, metal ion removal and biosorption
Higher ash content after biosorption process could emphasize adsorbed metal ions (Na\(^+\), K\(^+\) and Ca\(^{2+}\)) on the SBP surface which increased mineral composition of SBP.

### 3.2 Fourier transform infrared spectroscopic measurements

Fourier transform infrared (FTIR) spectrum of pressed sugar beet pulp was determined in order to get insight into present functional groups on the biosorbent (SBP) surface responsible for the metal ions removal. Obtained spectra at 400–4000 cm\(^{-1}\) of the raw pressed sugar beet pulp was presented in Fig 1.

As mentioned earlier in this study, sugar beet pulp was rich in cellulose, lignin, hemicellulose and pectin, therefore broad band at 3300–3400 cm\(^{-1}\) attributed to –OH groups were expected [30, 44]. Hydroxyl groups were available for the metal ion bonding via ion-exchange process. Another peak at 2900 cm\(^{-1}\) is assigned to stretching form of the –CH vibrations in lignin and hemicellulose [45]. A small band appeared at 2300 cm\(^{-1}\) indicated presence of the C≡C groups. Another important peak was in the range of 1200-1800 cm\(^{-1}\) and related to carboxyl groups in pectins, same as free and esterified with methyl groups [44, 45]. Broad band at 1031 cm\(^{-1}\) was assigned to the C-O-C glycosidic linkage in polysaccharides, such as hemicellulose [37]. Furthermore, in all sugar beet pulp spectra always appeared peak at 1015 cm\(^{-1}\) related to the C–O groups associated with sugars [46]. From the FTIR spectrum could be concluded that different present functional groups as carboxyl, hydroxyl were mostly involved in metal ions binding. For the cation-exchange studies, pH value of the liquid is the most important. Protonation of the functional groups was directly related to the pH value of the liquids influencing ion-exchange mechanism. For the biosorption studies, carboxyl groups play an important role, since in a broad range of the pH values were deprotonated [47].

### 3.3 SEM analysis

Scanning electron microscopy (SEM) method of analysis provides results of morphology, porosity and structural changes of biosorbent after the applied biosorption process [44]. SEM micrographs of pressed sugar beet pulp before and after the applied biosorption process were presented in Fig. 2. From the Fig. 2 can be noticed porous, rough, irregular surface with numerous shrinks. Porous, heterogenous structure of the surface of sugar beet pulp was beneficial for the sequestering of the metal ions from liquids, especially for the ion-exchange process [30]. After the applied biosorption process, morphology of the SBP was not destructed. From the reutilization point of view this phenomena represented a good perspective for desorption of entrapped metal ions in order for repeated biosorbent utilization. Slightly lower roughness of SBP after the biosorption process could be attributed to the water retention and swelling capacity and decreased dry matter content after biosorption process (23.8%, Table 1).

### 3.4 SBP removal efficiency and kinetic study

One of the most important information in evaluation of a new ion-exchange biosorbent and its application is time needed for reaching the equilibrium, binding kinetics and the adsorption mechanism [40]. Biosorption kinetics and dynamics can be analysed by applying various kinetic and diffusion models to experimental data. The effect of contact time of the SBP and alkalized sugar juice on the removal efficiency of molassesigenic metal ions (Na\(^+\), K\(^+\) and Ca\(^{2+}\)) are presented in Fig. 3. Ca\(^{2+}\), as a divalent cation, was removed from the alkalized juice in a greater amount (30.2 %) than monovalent cations: Na\(^+\) (11.0 %) and K\(^+\) (9.3 %), all after 90 min. Kukić et al. obtained similar results regarding reaching equilibrium after 90 min in
the study of removing Cr (VI) onto activated and non-activated biochar from brewer’s spent grain [29]. Successful adsorption of the brewer’s spent grain can be attributed to high adsorption capacity of the biosorbent and at the same time high specific area. Liu et al. also reported that more contact time (90 min) was mandatory for reaching equilibrium with Cu(II) removal on a shell of rape straw powders due to thick and tough morphology, similar to the sugar beets’ [28]. Pehlivan et al. reported that 70 min was sufficient for reaching equilibrium while removing divalent cadmium and monovalent lead with 70–75% removal efficiency onto sugar beet pulp [4]. In the study of Mgombezi and Vegi Ca\(^{2+}\) was removed mostly from the hard water after 100 min, which is in accordance with our study [52]. As the time of the biosorption lengthens, efficiency is reducing which is in accordance with monolayer adsorption theory [30]. Slightly decreasing in removal efficiency after reaching the plateau of maximal adsorption of metals was noticed in current research. Higher removal efficiency of the Ca\(^{2+}\), than Na\(^+\) and K\(^+\), indicated an additional biosorption mechanism such as precipitation effect on the polysaccharides which contain carboxyl groups (pectin) [16]. Slightly decrease in the pH value of the alkalized juice from the 10.5 to 9.9 was attributed to an ion-exchange process. Effect of the pH should be highlighted in the approaching into ion-exchange mechanism [49]. Ion-exchange appears when the pH of the solution decreased after the biosorption process [50]. Decrease in pH solution after the Na\(^+\), K\(^+\) and Ca\(^{2+}\) sorption is related to release of H\(^+\) ions from SBP and their displacement into the alkalized juice. Besides ion-exchange mechanism, Ca\(^{2+}\) was removed from the alkalized juice also with precipitation mechanism resulting in higher removal efficiency compared to two other examined metals. Study of Arslanoglu and Tumen showed slightly lower removal efficiency regarding Na\(^+\) (5.7%) and K\(^+\) (5.8%) whereas removal of divalent Ca\(^{2+}\) was 7% [2]. Non-modified, dried and grinded SBP was used as biosorbent with biosorbent dose three times lower than in our study. In the mentioned research, equilibrium was obtained earlier (60 min) compared to this study. It may be attributed to higher purity of the thin sugar juice obtained later in the sugar factory in comparison to purity of alkalized sugar juice, obtained one step earlier in the sugar juice purification stage.

Experimental data were fitted to kinetic models (pseudo-first, pseudo-second, Elovich) and intra-particle diffusion model in order to evaluate the behavior of SBP for Na\(^+\), K\(^+\) and Ca\(^{2+}\) removal. The model parameters of the four applied kinetics models are presented in Table 3. The calculated constants of all kinetic models \((k_1, k_2, a, b, k_d)\) were obtained according to the Eqs. (3)–(6), using non-linear solvers. Regarding high coefficient of determination (average \(R^2 \geq 0.910\)) for the biosorption of K\(^+\), Na\(^+\) and Ca\(^{2+}\) onto biomass of the SBP, the pseudo-first and pseudo-second order models provided satisfactory fitting (Table 3).

The pseudo-first model described the adsorption mechanism between adsorbate and adsorbent [51]. The experimental \(q_{exp}\) and predicted \(q_e\) values are well correlated, especially in the case of pseudo-first kinetic model for K\(^+\) (0.82), Na\(^+\) (1.22) and Ca\(^{2+}\) (1.80). The biosorption rate constants of the pseudo-first model were 0.023, 0.050 and 0.015 min\(^{-1}\) for the Na\(^+\), K\(^+\) and Ca\(^{2+}\), respectively. Low values of the biosorption rate constants indicated that the uptake of the metals onto the SBP was rapid and favorable [30]. The pseudo-second order kinetics equation refers to adsorption behavior which was controlled by one rate-controlling step. Biosorption process is addressed to chemical sorption involving electronic exchange between adsorbate (metal ions) and adsorbent (functional groups from the SBP) [52]. Applicability of the pseudo-second model indicates chemisorption and ion-exchange as a dominant mechanism for the biosorption process [53]. Šostarič et al. reported that the biosorption of Cu(II), Pb(II) and Zn(II) on apricot shell also occurs as ion-exchange and complexation [54]. Elovich model describes homogeneity of the adsorption system and indicates presence of the chemical adsorption. The calculated multiplication of constants \(a\) and \(b\) from the Elovich model regarding K\(^+\) and Ca\(^{2+}\) with low values (≤ 1) suggested that there are no more available binding sites for the biosorption of metal ions (all
available binding places are occupied with the metals) [30]. The intra-particle diffusion model describes the adsorption mechanism which takes place inside a biosorption mechanism and also defines multi-linerarity of the system [53]. The data of molassigenic metals removal by sugar beet pulp were fitted excellent to the diffusion model with $R^2$ approximately equal than 1 (average $R^2 = 0.999$). Graphical presentation of experimental and predicted parameters and models are shown in Fig. 4. The intercept value in the Weber Morris's intra-particle diffusion model (C) indicated a thickness of the boundary layer. Higher value of C constant is indicated by the higher boundary layer. The effect of boundary layer is considered as stronger when the constant C has greater values. The effect of boundary layer were in order: $K'^ +$ (9.14)$ > Ca^{2+}$ (1.61)$ > Na^+$ (1.25). According to Weber Morris model, plot t versus q is not a straight line passing through the origin, therefore the rate-limiting step is not only the intraparticle diffusion and other mechanisms were also included. Vučurović et al. obtained similar results regarding involvement of different diffusion mechanisms while utilizing sugar beet pulp as biosorbent for cationic dyes removal [55].

### Table 3 Kinetic parameters for biosorption process

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<th>Variable</th>
<th>Estimate</th>
<th>Element</th>
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<td>$R^2$</td>
<td>0.893</td>
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#### Elovich model

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<tr>
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<td>$k_i$ (mg g$^{-1}$ min$^{-1}$)</td>
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*$^*$Statistically significant at $p < 0.05$ level
of molassigenic metal ions adsorption showed multilinearity with intra-particle diffusion model. The adsorption process of Na\(^+\), K\(^+\) and Ca\(^{2+}\) onto the SBP has been conducted following two stages. Two stages were also noticed while removing Zn(II) onto sugar beet pulp [56]. Results obtained by Alakhras et al. showed also multilinear plot of the Weber Morris equation while removing Na\(^+\), K\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) from the brine water by electrodialysis with two cation-exchange membranes. For the monovalent and divalent cations were not intra-particle removal the rate-determining step and the whole process was determined by two or more other mechanisms [57]. Two steps are related to the dissociation of the metal ions from the solution and attaching metal ions onto biosorbent. The first segregate phase is attributed to the diffusion of adsorbate through liquid and surface binding on the biosorbent and represents external surface adsorption, while the second phase is attributed to the equilibrium of the biosorption process onto SBP [29].

### 3.5 Desorption study

After the biosorption process, elution of metal ions is important for the reutilization of exhausted biomass. Success in application of desorbing solution: HNO\(_3\), NaOH, HCl, EDTA and H\(_2\)SO\(_4\) in removing molassigenic metal ions from the SBP can be seen in Fig. 5. The desorption potential of the eluents is compared for one sorption/desorption cycle to select the most successful desorbing reagent. Desorbing reagent solution (HNO\(_3\)) at concentration of 0.1 M showed the most promising result for the desorbing eluent of cadmium, lead and copper from SBP [58]. Also, this concentration was selected due to the fact that the high acid concentration damaged the overall structure of biomass [13].

All applied desorbing agents were able to achieve over 70% removal efficiency for Ca\(^{2+}\) removal from the SBP within first 20 min or less. HCl as a desorbing reagent achieved 98.1% desorption of Ca\(^{2+}\) and was the most efficient eluent regarding Ca\(^{2+}\) desorption. Successful use of the HCl as a desorbing agent indicated that the ion-exchange mechanism are dominant in adsorption process due to competition between H\(^+\) and metal ions for the binding sites [54]. Similar and high percentage of desorption efficiency with HCl were obtained also for cadmium (96.3%), copper (99.9%) and zinc (91.9%) desorption from the multi-metal binding biosorbent composed of combination of tea waste, maple leaves and mandarin peels with a certain proportion [59]. Besides successful application of the HCl as desorbing reagent, SBP was disintegrated into smaller pieces after desorption experiment with HCl which makes it less desirable reagent for SBP regeneration. The 0.1 M HNO\(_3\) showed optimum performance for desorption of Na\(^+\), K\(^+\) and Ca\(^{2+}\) from the SBP, achieving the highest desorption efficiency in the first 20 min. Using HNO\(_3\) as a desorbing reagent, Na\(^+\) was desorbed in the amount of 26%, whereas K\(^+\) and Ca\(^{2+}\) were released with 74% and 71% desorption efficiency, respectively (Fig. 3). Study of Mata et al. confirmed that 0.1 M HNO\(_3\) is the most successful eluting agent for copper elution from the sugar beet pectin gel with 98% desorption efficiency while lead desorption from Hydrilla verticillata (L.F.) were desorbed with 100% efficiency using this desorption agent [12, 58]. Chemisorption is the main driving force of adsorption if desorption is conducted using an organic acid [60]. Acid can generate high desorption efficiencies.
for the mechanisms of ion-exchange and complexation. HNO₃ as a successful desorption reagent directed to the adsorption mechanism combined of both, ion-exchange and chemisorption. After the applied biosorption process metal ions were adsorbed on carboxyl-binding groups by electrostatic interaction. Acid solutions (e.g. HNO₃) would regenerate the Ca²⁺-loaded biosorbents since the concentration of H⁺ increases giving place to ion exchange with the adsorbed Ca²⁺ [61]. It was obvious that H₂SO₄ was very ineffective for releasing adsorbed metal onto the SBP, especially in term of Na⁺ (4.0%) and K⁺ (−1.5%) desorption efficiency. H₂SO₄ was the weakest desorbing agent for the all observed metals and also damaged the overall structure of the SBP. The adsorption mechanism is based on the ion-exchange and physical adsorption if sulfuric acid or alkaline solution was used as desorption reagent [18]. NaOH showed weaker potential for removing adsorbed metal in comparison with the acids. Na⁺ and K⁺ were desorbed in the amount smaller than 40% (Fig. 5). Similar results regarding inefficient desorption efficiency with NaOH were obtained using multi-metal binding biosorbent for desorption of the following metal ions: Cd, Cu, Zn and Pb [30]. EDTA, as a complexing agent did not damage SBP after the desorption process and showed average desorption abilities regarding three molassigenic metals release from the SBP with desorption success of the K⁺ and Ca²⁺ in the range 70-80% efficiency (Fig. 5). EDTA has the highest stability constant for formation of complexes or produces fewer structural modifications than acid or the alkaline solution without color change of the biosorbent [62]. EDTA formed stable complexes over broad range of the pH with heavy metal ions, but this desorbing agent is not easily affordable in nature [30].

4 Conclusion
The results of this study indicated that the raw, non-modified SBP, by-product obtained after sugar extraction, was successfully used as biosorbent for the molassigenic metal ions (Na⁺, K⁺ and Ca²⁺) removal from alkalized sugar juice. By using SBP in the form of biosorbent was closed the cycle of their utilization from the process of obtaining from sugar beet, to utilization directly in the sugar plant in order to increase the purity of alkalized juice. Rich in fiber SBP demonstrated high cation exchange capacity (0.84 meq g⁻¹) which is in accordance with 73.7% total dietary fiber content. The experiments were performed in the batch system under the pH (10.5) and temperature (70 °C) of the alkalized juice identical to an industrial and obtained results indicated higher removal efficiency of the divalent Ca²⁺ (30.2%), than monovalent Na⁺ (10.9%) and K⁺ (9.1%). Additional removal mechanism was present with divalent metal ions removal, such as precipitation. The pseudo-first and pseudo-second order kinetics models were defined with high value of the coefficient of correlation (R² ≥ 0.910) and describe biosorption process satisfactorily by abstracting an ion-exchange and chemisorption as dominant mechanism for metal ions removal. Hydroxyl and carboxyl groups detected on the SBP surface had the most significant role in ion-exchange process with molassigenic metal ions from alkalized juice. Desorption of molassigenic metals from the SBP by using HNO₃ was performed the most promising without deteriorating the biosorbent structure. Scanning electron microscopy analysis after the applied process confirmed intact morphology of the SBP. Successful desorption of metal ions from sugar beet pulp, indicated the possibility of their reutilization and revalorization. The present study makes noteworthy contribution to the juice purification stage at the laboratory level with beneficial potential for scaling-up to an industrial level. Future biosorption studies will be conducted on laboratory level towards continual column biosorption process.

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References


