PECTIN SEPARATION FROM SUGAR BEET JUICE AS AFFECTED BY THE pH, AMOUNT OF $\text{Al}_2(\text{SO}_4)_3$ AND USE OF ZETA POTENTIAL/RESIDUAL TURBIDITY MEASUREMENT

UTICAJ pH VREDNOSTI I KOLIČINE ALUMINIJUM SULFATA NA IZDVAJANJE PEKTINA IZ SOKA ŠEĆERNE REPE – PRIMENA METODE ZETA POTENCIJALA/REZIDUALNE MUTNOĆE RASTVORA

Tatjana KULJANIN, Biljana LONČAR, Vladimir FILIPOVIĆ, Milica NIČETIN, Violeta KNEŽEVIĆ
University of Novi Sad, Faculty of Technology, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia
e-mail: kuljanin@uns.ac.rs

ABSTRACT

Impurities in the diffuse juice of sugar beet, especially pectins, interfere with the crystallization of sucrose. The purpose of this paper is to examine the properties of $\text{Al}_2(\text{SO}_4)_3$ as an alternative coagulant, considering that the use of lime in the sugar industry requires a large amount of this commercial coagulant. The optimal pH-value interval in a pectin solution (0.1 % wt.) was obtained for producing stable, highly charged forms of hydrolysis of $\text{Al}_2(\text{SO}_4)_3$, which facilitate a successful pectin precipitation. The measurements of residual solution turbidity and zeta potential were performed in the study.

In the pH range of 3 to 9, the zero zeta potential at which the pectin particles were discharged was $\text{pH} \sim 6.6$. This value was less than the pH value for achieving the minimum solution turbidity ($\text{pH} \sim 7.5$). Both methods of measurement indicated that the pH range 6.6 - 7.5 provided the optimal condition for the highest yield of pectin separation. Measuring the zeta potential was found to be a more effective method than monitoring the turbidity of pectin solution.

Key words: aluminium sulphate, pectins, pH, zeta potential, residual solution turbidity.

REZIME

Prisustvo nesaharoznih jedinjenja u difuznom soku šećerne repe, posebno pektini, znatno smanjuje količinu proizvedenog šećera. Istraživanje je usmereno ka proučavanju osobina alternativnog koagulanata, $\text{Al}_2(\text{SO}_4)_3$, pošto je za čišćenje soka šećerne repe potrebna velika količina kreča kao komercijalnog koagulanata. Poznato je da aluminijumove soli u vodenom rastvoru daju katjonske oblike hidrolize velikog naelektrisanja. Time se ubrzava njihova adsorcija i razelektrisanje površine negativno naelektrisanih pektinskih čestica. Sulfatni joni su takođe veoma efikasni jer smanjenjuju hidrataciju pektinskih čestica što pospešuje njihovu koagulaciju i taloženje u soku šećerne repe.

Eksperimentalno je ispitivan optimalni interval pH vrednosti pektinskih rastvora pri kome bi se stvarali stabilni visoko naelektrisani oblici hidrolize $\text{Al}_2(\text{SO}_4)_3$. Model rastvori pektina (0,1% mas.) tretirani su sa rastvorom $\text{Al}_2(\text{SO}_4)_3$ pri različitim pH vrednostima. U eksperimentu su korišćene metode merenja zeta potencijala i rezidualne mutnoće rastvora.

U prethodnim ispitivanjima, pri konstantnoj vrednosti $\text{pH} = 7$, utvrđene su optimalne količine $\text{Al}_2(\text{SO}_4)_3$ za postizanje minimalne mutnoće pektinskog rastvora (oko 90 mg/dm^3) kao i za postizanje nulte vrednosti zeta potencijala (oko 110 mg/dm^3). U intervalu pH vrednosti od 3 do 9, nulti zeta potencijal, tj., razelektrisanje pektinskih čestica je postignuto na $\text{pH} \sim 6,6$. Ta vrednost je bila nešto manja od izmerene pH vrednosti za postizanje minimalne mutnoće rastvora ($\text{pH} \sim 7,5$). Obe metode, ukazuju da se u intervalu pH vrednosti od 6,6 do 7,5, mogu ostvariti optimalni uslovi za efikasnu separaciju pektina iz soka šećerne repe. Metoda merenja zeta potencijala se pokazala efikasnija od metode praćenja rezidualne mutnoće rastvora.

Ključne reči: aluminijum sulfat, pektini, pH, zeta potencijal, rezidualna mutnoća rastvora.

INTRODUCTION

Lime (CaO) is used in the conventional purification process of sugar beet diffuse juice, wherein pectins claim the largest share of non-sucrose matter (approximately 60 %). Pectins and other impurities impede the crystallization of sucrose, which significantly reduces the amount of sugar produced. At this stage of sugar beet juice processing, large amounts of lime are required, which can cause soil alkalisation in the immediate vicinity of the sugar factory. In order to create conditions for a more efficient coagulation and precipitation of pectin, the possibility of discharging these particles by chemical means, i.e. by adding cations of greater valence, was studied (Schneider et al., 2011). $\text{Al}_2(\text{SO}_4)_3$ is often used in the treatment of beverages and wastewaters. When an aluminum salt is added to water, the negative charge of the organic material in water is reduced or reversed. The dominant mechanism for coagulation depends on

the coagulant dose and pH (Duan and Gregory, 2003; Sharp, 2005; Tipping et al., 2006; Wen-zheng et al., 2012). Al^{3+} ions have a stable, highly positive charge over a wide pH range. Gregory and Carlson (2003) found the improved sedimentation and filtration performance of organic materials in water when coagulating with alum in the pH range from 6.1 to 7.4. The measurements of zeta potential and solution turbidity were performed in the present study. A change in zeta potential can be used to indicate a change in the charge of colloidal particles, whereas turbidity measurements indicate the amount of colloidal and suspended particles. The oppositely charged polyvalent ions can decrease or even change the sign of the zeta potential (Jianbo et al., 2015; Delgado et al., 2007; Kuljanin et al., 2010; Kuljanin et al., 2013). The zeta potential of hydrophilic organic material with surface confined acidic groups is likely to exhibit charge reversal at approximately pH 7, depending on the system (Sharp, 2005).

In previous papers, it has been found that the use of Al^{3+} ions in the form of $\text{Al}_2(\text{SO}_4)_3$ is more effective in the separation of pectin compared to compounds with Ca^{2+} ions (Kuljanin et al., 2014; Kuljanin et al., 2014a). Al^{3+} ions, according to Szulce-Hardy's rule, lead to a faster discharge of the negatively charged surface of pectin particles. In addition, the SO_4^{2-} anions cause hydrophobization, or reduce the hydration of the macromolecular surface of pectin, which are naturally hydrophilic (so-called the effect of isolation). This contributes, in addition to discharge, to a faster agglomeration and increased rate of precipitation of pectin (Koper, 2007). A number of preliminary tests were conducted to determine the optimum Al^{3+} ion concentration at pH = 7. The doses obtained ranged from 80 to 120 mg/dm³. (Kuljanin et al., 2010; Kuljanin et al., 2013). The suggested amounts of $\text{Al}_2(\text{SO}_4)_3$ converted to the average daily intake of sugar were significantly less than the tolerable daily intake for aluminum (Stahl et al., 2011).

When an aluminum salt is added to water, the aluminum ion hydrolyses with water, producing a series of cationic dissociation products with a relative abundance varying with pH. In a certain pH value interval, highly charged cationic forms of hydrolysis $\text{Al}_2(\text{SO}_4)_3$ are formed, which are most effective in neutralizing the surface area of pectin particles and thereby creating the most favorable conditions for the pectin deposition (Duan and Gregory, 2003). This paper highlights the range of pH required for a high-quality treatment of sugar beet juice.

MATERIAL AND METHOD

A pectin preparation was extracted from sugar beet juice obtained in the industrial processing of sugar beet (Sugar factory Žabalj, Serbia). Aluminium sulphate in the crystal hydrate form ($\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$) ("Zorka pharma", Šabac, Serbia) was used as a precipitant for the preparation of the solutions with de-ionized water. The pH of pectin solutions with $\text{Al}_2(\text{SO}_4)_3$ was measured by a pH METER (Iskra MA5740, Kranj, Slovenia). The pH value varied from 3 to 9 before the measurements of zeta potential and residual turbidity. A pectin preparation was isolated by extraction using the standard laboratory procedure AOAC (2000). The extraction was conducted in an extractor (TALBOYS INSTRUMENT CORP., model 102), which was designed at the Faculty of Technology, Novi Sad, Serbia. The extraction of pectin was performed under the following conditions: pH = 3.5, $t = 85^\circ\text{C}$, $\tau = 2.5$ h. A detailed description of the pectin extraction can be found elsewhere in the literature (Kuljanin et al., 2010). The pectin solution used in the experiment was of similar concentration to the sugar beet juice concentration (about 0.1 % w/w). The general characteristic of pectin extracted were defined and presented in Table 1 (AOAC, 2000). The purity of the preparation was expressed through the content of galacturonic acid. The degree of esterification was determined relative to the equivalents of free (X) and esterified carboxyl groups (Y) (Yapo, 2009). In order to achieve a pH value in a given interval from 3 to 9, an equivalent amount of the base (in our case, Na_2CO_3) must be added due to the incomplete hydrolysis of $\text{Al}_2(\text{SO}_4)_3$ (Kuljanin et al., 2010). The values obtained are displayed in Table 2.

Table 1. General characteristics of pectin preparations

Solid content, SC (g/100g)	80.25
Equivalent of free COOH groups, $X \cdot 10^5$	21.83
Equivalent of esterified COOH groups, $Y \cdot 10^5$	18.55
Content of galacturonic acid, Gal.A (%)	71.31
Degree of esterification, DE (%)	45.94

A total of 1 g of pectin preparation was dissolved in 1 dm³ of de-ionized water. Seven flasks were filled with 50 cm³ of pectin solutions. Precipitants were prepared by dissolving 1 g $\text{Al}_2(\text{SO}_4)_3$ and an equivalent amount of Na_2CO_3 in 200 cm³ distilled water. The adequate amounts of $\text{Al}_2(\text{SO}_4)_3$ and Na_2CO_3 solutions (cm³) were added to 50 cm³ of pectin solutions (Table 2). Finally, the pH of the solutions was adjusted to a variable value in the range between 3 and 9. The tested solutions containing $\text{Al}_2(\text{SO}_4)_3$ were stirred for 30 min on a high-speed magnetic stirrer (TEHNICA, MM-520 Železniki, Slovenia) (500 rpm). The solutions were thereafter slowly and manually stirred for 5 min and left to rest for another 5 min.

Table 2. The plan and conditions of the experiment

Parameters	50 cm ³ flask with 0.1 % (w/w) pectin						
Number of measurements	I	II	III	IV	V	VI	VII
pH value	3	4	5	6	7	8	9
$\text{Al}_2(\text{SO}_4)_3$: Na_2CO_3 (mass ratio)	1 : 0.43	1 : 0.57	1 : 0.71	1 : 0.86	1 : 1.07	1 : 1.14	1 : 1.28

Zeta potential was evaluated by electrophoresis using a Zeta Meter ZM-77. The method of measuring zeta potential has been explained in previous papers (Kuljanin et al., 2010). An average value of the 20-particle time was used to derive the zeta potential in the tested solutions using a diagram based on the Helmholtz-Smoluchowski equation (Lyklema, 2003).

A method for determining the optimal coagulation in the first carbonation process used in sugar production was employed to measure residual turbidity. The absorbance of decant before and after filtration was also measured. The optimal coagulation was achieved with a minimum difference between these two absorbance values (minimal turbidity of the solution, $\Delta \tau$) (Grbić et al., 2003; Kuljanin et al., 2013). The measurements were performed by spectrophotometry using a SPEKOL 202 spectrophotometer at a wavelength of 560 nm. Prior to filtration and measuring the absorbance, the pectin solutions were aging at 25 °C for 10 h to reach an equilibrium state for the pectin- Al^{3+} system. The measurement of residual turbidity was performed under the same conditions as the measurement of zeta potential. All the experiments were assayed in three replicates, and the means of the replicate values were calculated.

RESULTS AND DISCUSSION

Relative to previous studies on the pectin preparation of a similar composition at a constant pH = 7, it has been found that an optimal amount of 110 mg/l $\text{Al}_2(\text{SO}_4)_3$ is required to reach zero value of the zeta potential (Kuljanin et al., 2014a). Under the same conditions, about 90 mg/l of $\text{Al}_2(\text{SO}_4)_3$ was required to achieve a minimal turbidity of the solution (Kuljanin et al., 2013). Therefore, $\text{Al}_2(\text{SO}_4)_3$ amounts were held constant at 110

mg/l for measuring the zeta potential, and 90 mg/l for measuring the minimum solution turbidity. Fig. 1-2 shows the zeta potential and residual turbidity profiles at different pH values.

Fig. 1. Influence of pH on the zeta potential of pectin solution (the concentration of $\text{Al}_2(\text{SO}_4)_3$ - 110 mg/l)

Fig. 2. Influence of pH on the residual turbidity of pectin solution (the concentration of $\text{Al}_2(\text{SO}_4)_3$ - 90 mg/l)

Changes in the zeta potential and pectin coagulation were strongly affected by the pH in the range 3 – 9 (Fig. 1-2). The dissociation of pectin functional groups increases with the pH level, leading to an increase in the negative charge density of pectin surface. Therefore, a larger amount of the positively charged hydrolyzed products of $\text{Al}_2(\text{SO}_4)_3$ was required to neutralize the more negatively charged pectin. At the pH 3.0 – 5.5, the solution zeta potential decreased rapidly. The reason for a large slope of the zeta potential curve in that pH range can be attributed to the rapid adsorption of Al^{3+} ions, primarily highly charged cationic hydrolysis products $\text{Al}_2(\text{SO}_4)_3$ and H^+ ions on the negatively charged pectin surface. A slight decrease in the zeta potential value was recorded in the pH range of 5.5 – 8 (from +3 to -2 mV). In addition to the adsorption of positively charged ions and hydrolysis products, the adsorption of negatively charged hydrolysis products $\text{Al}_2(\text{SO}_4)_3$ and OH^- ion from the solution on the positively charged sites on the pectin surface (HII) is also carried out in this pH interval. Moreover, it might result from the reaction of OH^- ions with Al^{3+} ions or other cations, which are present in small amounts in the pectin solution. The sign of the zeta potential is reversed at pH ~ 6.6

(Fig. 1). The zero value of zeta potential, i.e. the isoelectric point (IEP), is attributable to charge neutralization of the pectin surface. At this pH value, the resulting pectin – $\text{Al}_2(\text{SO}_4)_3$ complex is uncharged and highly hydrophobic, so it can be easily separated from the pectin solution. Changing the sign of the zeta potential from "+" to "-" leads to a conclusion that the adsorption of hydrolysis products of $\text{Al}_2(\text{SO}_4)_3$ has a key role in the process (in addition to the dominant mechanism such as the neutralization of the charge by electrostatic forces). Specifically adsorbed ions can be recognized by their ability to reverse the sign of the zeta potential (Kuljanin et al., 2010). A sharp decrease in the zeta potential at pH 8 – 9 (Fig. 1) is the result of the formation of a larger amount of negatively charged hydrolysis products of $\text{Al}_2(\text{SO}_4)_3$ in this pH region.

In addition to dissolved organic matter and impurities, sugar beet juice contains various electrolytes. It is also possible that competing Al^{3+} ions and other trivalent electrolytes are present in small amounts in diffuse sugar beet juice, which can exert a reducing effect on the absorption of Al^{3+} ions as well as the hydrolysis products of these ions.

Fig. 2 indicates that the optimal coagulation takes place at a value of pH ~ 7.5, which corresponds to the minimal solubility of the solution. By comparing the results shown in Figures 1 and 2, it can be concluded that the optimal pH for achieving the minimum residual turbidity ($\text{pH}_{\text{tmin}} \sim 7.5$) is slightly above the optimal pH for achieving the zero value of the zeta potential ($\text{pH}_{\text{ZPO}} \sim 6.6$). Previous research suggests that the optimal pH interval for the removal of organic matter from water is slightly lower (pH 5 – 6). The minimum solubility of aluminum salts in water is achieved at pH = 6.3, whereas the measured isoelectric point of the aqueous solution of aluminum sulfate is at pH = 8.0. In this field, the cationic forms of hydrolysis of Al^{3+} ions are dominant (Duan and Gregory, 2003). The experimentally obtained interval of pH values from 6.6 to 7.5 is within the range of pH (6.3 – 8.0), which confirms the creation of highly charged cationic hydrolysis products $\text{Al}_2(\text{SO}_4)_3$ (which would be most effective for depositing pectin from sugar beet juice). It is also noteworthy that the isoelectric point of the pectin solution (pH ~ 6.6) was recorded at a pH that is close to the minimum solubility of aluminum salts when the highest amount of precipitate is generated. The comparison of both methods indicates that the method of measuring zeta potential is more efficient. Turbidity monitoring is not effective for control due to a lag time of 10 hours between the coagulant addition and filtration. The results obtained indicate the existence of an operational interval of zeta potential (+3 to -2 mV) within which pectin removal efficiencies are high.

CONCLUSION

The pH level significantly affects the binding of Al^{3+} ions and hydrolyzed products of $\text{Al}_2(\text{SO}_4)_3$ to pectin. The method of measuring the zeta potential proved to be more effective than the method of monitoring the residual turbidity of a pectin solution. Both methods of measurement, using the previously determined optimal amount of $\text{Al}_2(\text{SO}_4)_3$, indicated that the pH interval 6.6 – 7.5 provides the optimum condition for the highest pectin separation yield. $\text{Al}_2(\text{SO}_4)_3$ proved superior to the conventional coagulant CaO in sugar beet juice clarification at a laboratory level. Further research should be conducted under both laboratory and industrial conditions.

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