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

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 \( \text{pH} \)-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 \( \text{pH} \) 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 \( \text{pH} \) value for achieving the minimum solution turbidity (\( \text{pH} \sim 7.5 \)). Both methods of measurement indicated that the \( \text{pH} \) 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, \( \text{pH} \), zeta potential, residual solution turbidity.

INTRODUCTION

Lime (\( \text{CaO} \)) 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 \( \text{pH} \) (Duan and Gregory, 2003; Sharp, 2005; Tipping et al., 2006; Wen-zheng et al., 2012). \( \text{Al}^3+ \) ions have a stable, highly positive charge over a wide \( \text{pH} \) range. Gregory and Carlson (2003) found the improved sedimentation and filtration performance of organic materials in water when coagulating with alum in the \( \text{pH} \) 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 \( \text{pH} 7 \), depending on the system (Sharp, 2005).
In previous papers, it has been found that the use of Al$^{3+}$ ions in the form of Al$_2$(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 Szulc-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/dm$^3$. (Kuljanin et al., 2010; Kuljanin et al., 2013). The suggested amounts of Al$_2$(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 Al$_2$(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, 2009). In order to achieve a pH similar composition at a constant pH = 7, it has been found that an optimal amount of 110 mg/l Al$_2$(SO$_4$)$_3$ is required to reach zero value of the zeta potential (Kuljanin et al., 2010). Under the same conditions, about 90 mg/l of Al$_2$(SO$_4$)$_3$ was required to achieve a minimal turbidity of the solution (Kuljanin et al., 2013). Therefore, Al$_2$(SO$_4$)$_3$ amounts were held constant at 110 mg/l.

**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 (Al$_2$(SO$_4$)$_3$ x 18H$_2$O) (“Zorka pharma”, Šabac, Serbia) was used as a precipitant for the preparation of the solutions with de-ionized water. The pH value of pectin solutions with Al$_2$(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 MA5740, Kranj, Slovenia) (500 rpm). The solutions were stirred for 30 min on a high-speed magnetic stirrer (TEHNIKA, 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.

A total of 1 g of pectin preparation was dissolved in 1 dm$^3$ of de-ionized water. Seven flasks were filled with 50 cm$^3$ of pectin solutions. Precipitants were prepared by dissolving 1 g Al$_2$(SO$_4$)$_3$ and an equivalent amount of Na$_2$CO$_3$ in 200 cm$^3$ distilled water. The adequate amounts of Al$_2$(SO$_4$)$_3$ and Na$_2$CO$_3$ solutions (cm$^3$) were added to 50 cm$^3$ 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 Al$_2$(SO$_4$)$_3$ were stirred for 30 min on a high-speed magnetic stirrer (TEHNIKA, 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 1. General characteristics of pectin preparations**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Solid content (g/100g)</th>
<th>Equivalent of free COOH groups, X · 10$^{-1}$</th>
<th>Equivalent of esterified COOH groups, Y · 10$^{-1}$</th>
<th>Content of galacturonic acid, Gal.A (%)</th>
<th>Degree of esterification, DE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$(SO$_4$)$_3$</td>
<td>80.25</td>
<td>21.83</td>
<td>18.55</td>
<td>71.31</td>
<td>45.94</td>
</tr>
</tbody>
</table>

A number of flasks were filled with 50 cm$^3$ of pectin solution 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, Δ$^T$) (Grbič 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 Al$_2$(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 Al$_2$(SO$_4$)$_3$ was required to achieve a minimal turbidity of the solution (Kuljanin et al., 2013). Therefore, Al$_2$(SO$_4$)$_3$ amounts were held constant at 110 mg/l.

**Table 2. The plan and conditions of the experiment**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>50 cm$^3$ flask with 0.1 % (w/w) pectin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of measurements</td>
<td></td>
</tr>
<tr>
<td>pH value</td>
<td></td>
</tr>
<tr>
<td>Al$_2$(SO$_4$)$_3$; Na$_2$CO$_3$ (mass ratio)</td>
<td>1 : 0.43 ; 1 : 0.57 ; 1 : 0.71 ; 1 : 0.86 ; 1 : 1.07 ; 1 : 1.14 ; 1 : 1.28</td>
</tr>
</tbody>
</table>

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 Helmoltz-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, Δ$^T$) (Grbič 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.

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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.

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 hydrolysis products of Al2(SO4)3 was required to neutralize the more negatively charged pectin. The method of measuring zeta potential proved to be more effective than the method of monitoring the residual turbidity of a pectin solution. In addition to dissolved organic matter and impurities, sugar beet juice contains various electrolytes. It is also possible that competing Al3+ 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 Al3+ ions as well as the hydrolysis products of these ions.

Fig. 1 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 (pHmin ~ 7.5) is slightly above the optimal pH for achieving the zero value of the zeta potential (pHIEP ~ 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 Al3+ 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 Al3(SO4)2+ (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 Al3+ ions and hydrolyzed products of Al2(SO4)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 Al2(SO4)3, indicated that the pH interval 6.6 - 7.5 provides the optimum condition for the highest pectin separation yield. Al2(SO4)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.

REFERENCES


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