

# CaSO<sub>4</sub> and cationic polyelectrolyte as possible pectin precipitants in sugar beet juice clarification

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## Abstract

Three pectin preparations were isolated from fresh sugar beet pulp during the 150 min of extraction, at pH values of 1, 3.5 and 8.5. CaSO<sub>4</sub> precipitant was added to 100 cm<sup>3</sup> of 0.1 wt.% solution of pectin. Studies were performed with 9 different concentrations of CaSO<sub>4</sub> solution (50–450 mg dm<sup>-3</sup>) with the addition of a cationic polyelectrolyte (cationic PAM) in concentrations of 3 and 5 mg dm<sup>-3</sup>. The efficiency of pectin precipitation was monitored by measuring the zeta potential of pectin preparations. Optimal amounts of precipitant CaSO<sub>4</sub>, without the use of a cationic polyelectrolyte, were as follows: 490–678 mg CaSO<sub>4</sub>/g pectin. After the use of a cationic polyelectrolyte, the optimal amounts of CaSO<sub>4</sub> were smaller (353–512 mg/g pectin). These quantities are significantly lower than the average amount of CaO used in the conventional clarification process of sugar beet juice (about 9 g/g pectin of sugar beet juice).

**Keywords:** clarification, pectin, sugar beet juice, CaSO<sub>4</sub>, cationic polyelectrolyte, zeta potential.

Available online at the Journal website: <http://www.ache.org.rs/HI/>

SCIENTIFIC PAPER

UDC 664.126:544.6:66

Hem. Ind. 69 (6) 617–625 (2015)

doi: 10.2298/HEMIND141015085K

Removal of impurities from sugar beet juice by clarification is an essential part of the process of raw sugar manufacture. Application of CaO, in its Ca(OH)<sub>2</sub> form in sugar beet juice clarification is very well known. However, huge quantities of lime are used in everyday sugar production. This might have negative influence on the area that surrounds sugar factory. Calcium is known for its good absorption characteristics that can cause undesired alkalisation process in the soil [1].

Precipitation of pectins can be performed by process of discharging, *i.e.*, carboxylic acid groups of acids from pectins can take a part in the complexation of divalent and trivalent cations from various compounds [2–4]. It is known that the colloidal particles in the solution surrounded by an electric double layer that is composed of a stationary (Stern's) and diffuse layer. The potential at the interface between these layers is easily measurable size and it is known as zeta potential ( $\zeta$ ). By keeping zeta potential close to zero, pectin colloidal particles will discharge and the conditions for effective precipitation of particles will be achieved [5,6]. According to the selectivity order of the binding affinity of various divalent cations by citrus and sugar-beet pectins, it is evident that Cu<sup>2+</sup> are more efficient than Ca<sup>2+</sup> due to marked surface complexation ability [7,8]. On the other hand, it is known that Ca<sup>2+</sup> with the

smaller hydrated radius have a large dehydration effect. Therefore, hydrophilic macromolecules (such as pectin) hydration considerably decreases in the presence of Ca<sup>2+</sup> which is an important prerequisite for coagulation besides charge neutralisation [9]. In the presence of Ca<sup>2+</sup>, electrostatic interactions are performed between the negatively charged side chains of polysaccharide, leading to formation of "egg-box" structure. This binding takes place preferably between the side chains of the same macromolecule forming the intramolecular complexes [10].

Investigation performed in paper [18] suggests that salts: CaCl<sub>2</sub>, CuSO<sub>4</sub> and AlCl<sub>3</sub>&NaHCO<sub>3</sub> are more efficient in pectin precipitation than commonly used CaO. Also, in previous paper (Kuljanin and others, in press) was proved that Ca<sup>2+</sup> bounded with SO<sub>4</sub><sup>2-</sup> has greater affinity to complexation than Ca<sup>2+</sup> bonded with (OH)<sup>1-</sup>.

The total capacity of pectin polysaccharide to complex metal cations was directly related to the degree of methyl esterification, degree of polymerisation and glycosil residue composition of pectins [11]. The cation binding capacity of pectin macromolecules (CBC) can be calculated on the basis of simplified equation [12]. It is accepted that only free carboxyl group of the galacturonic acid take part in the binding of cations:

$$CBC = \frac{Gal.A \left(1 - \frac{DE}{100}\right)}{176} \left[ \frac{\text{mmol}}{\text{g}_{SM}} \right] \quad (1)$$

where *Gal.A* corresponds to the content of pure galactouronic acid, *DE* denotes degree of methyl esterific-

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Paper received: 15 October, 2014

Paper accepted: 8 December, 2014

ation, value 176 denotes molar masse of dehydrated galactouronic acid [13,14].

Another mechanism that causes the coagulation and precipitation of the macromolecules is interparticle bridging. Interparticle bridging occurs using high molecular weight polyelectrolytes where colloids are adsorbed into the polymers branches or share ions directly to form ionic bridges [19–21,24]. The mechanism of cationic polyelectrolyte action is more complex: At the beginning of the process attractive electrostatic forces (mechanism of charge neutralization) are active and when their action stops, destabilization occurs by mechanism of interparticle bridging. The mechanism of this process is related to the density of the charges on the polyelectrolytes vis-à-vis the density of charges on the pectin macromolecule surfaces [22]. Earlier studies in application of polyelectrolytes, cationic or anionic, were related to purification of waste water [22,21]. Also, cationic and anionic polyelectrolytes have been claimed to enhance the flocculation of sugar cane juice. The best results in clarification of sugar cane juice were obtained by adding cationic polyelectrolytes with low molar mass in quantities of 40–200 mg dm<sup>-3</sup> in combination with anionic flocculant with high molar mass, concentration of 3 mg dm<sup>-3</sup> [19]. It has been also studied the use of cationic polyelectrolytes and polyacrylamide flocculants in sugar beet juice clarification according to classical method (application of CaO). Industrial trials confirmed the technological and economic justification of this method in the phase prior to defecation [23,24]. Investigation performed in paper [18] suggests that three salts: CaCl<sub>2</sub>, CuSO<sub>4</sub> and AlCl<sub>3</sub> and NaHCO<sub>3</sub> are more efficient in pectin precipitation than commonly used Cano. Cationic polyelectrolytes in combination with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and CuSO<sub>4</sub>, were studied in the paper [25]. By measuring the zeta potential it has been proven that the efficiency of precipitation of pectin and protein particles in the presence of polyelectrolyte increases.

Although Al<sup>3+</sup> due to its high charge have greater bonding strength to natural organic matter than Ca<sup>2+</sup> (the H<sup>+</sup>/Me<sup>2+,3+</sup> molar exchange ratios ranging of 2.1–2.7 and 0.2–0.5, for Al<sup>3+</sup> and Ca<sup>2+</sup>, respectively) [26], the reason for CaSO<sub>4</sub> selection was primarily acceptable solubility in water and not expansive for eventual industrial application.

Beet juice has a concentration of undesirable colloids as most of the waste and contaminated water (about 1 wt.%). Previous practice in the modern plants for the improved water treatment showed that zeta potential control enhances the removal of colloids [27]. According to this, zeta potential measurements should be effective for the control of discharging pectin particles [28,17,19].

The aim of this study was to investigate the effect of CaSO<sub>4</sub> and cationic polyelectrolyte concentration, as well as the pectin type on sugar beet juice clarification. The reason for CaSO<sub>4</sub> selection was primarily acceptable solubility in water and not expensive for eventual industrial application. Since cationic polyelectrolytes additionally neutralize the charge of pectin particles, applying them would decrease the amount of CaSO<sub>4</sub>. That would further reduce the cost of cleaning sugar beet juice while protecting the environment.

Simple regression models, using second order polynomial and Response Surface Methodology (RSM) have been proposed for calculation of zeta potential capabilities as function of proposed process parameters (CaSO<sub>4</sub> concentration, polyelectrolyte concentration and the pectin type). Analysis of variance (ANOVA) has been applied to show relations between applied assays.

## MATERIALS, METHODS AND PLAN OF EXPERIMENTS

### Materials

Three pectins were isolated from pressed sugar-beet slices (*Beta vulgaris L. ssp. vulgaris var. Latissimi Dell*) from Vojvodina – region situated at the Panonian basin (factory Žabalj), Serbia. Then, three model solutions were prepared, concentration of which was 1 g dm<sup>-3</sup>. The metal salt CaSO<sub>4</sub>, in crystal hydrate form (CaSO<sub>4</sub>×2H<sub>2</sub>O), was used for preparation of the solutions with de-ionized water (Zorka Pharma, Šabac, Serbia; purity of salt was 99.0%). For the adjustment of pH values, aqueous solutions of HCl and NaOH were used.

Magnafloc LT24 is a high purity (99%) cationic polyacrylamide (PAM) purchased from Henan, Shandong China (Mainland). Cationic PAM is made by a vinyl monomer and cationic acrylamide copolymer [–CH<sub>2</sub>–CH(CONH<sub>2</sub>)<sub>n</sub>]. It is one kind of high molecular weight of linear polymer (5×10<sup>6</sup>–15×10<sup>6</sup> million g mol<sup>-1</sup>), solid content: ≥ 90% and ion degree: 30–80%. It is described as a white, low dusting powder containing less than 0.05% free acrylamide.

### Methods

#### Isolation of pectins

Pectins were isolated by the extraction, under the acidic conditions (pH 1 and 3.5) and under the alkaline conditions (pH 8.5), according to the standardized laboratory scale procedure [29,30] presented in Fig. 1. Each extraction was carried out three times. Because of the differences among the extraction conditions, three pectin samples were of different composition and degree of esterification.

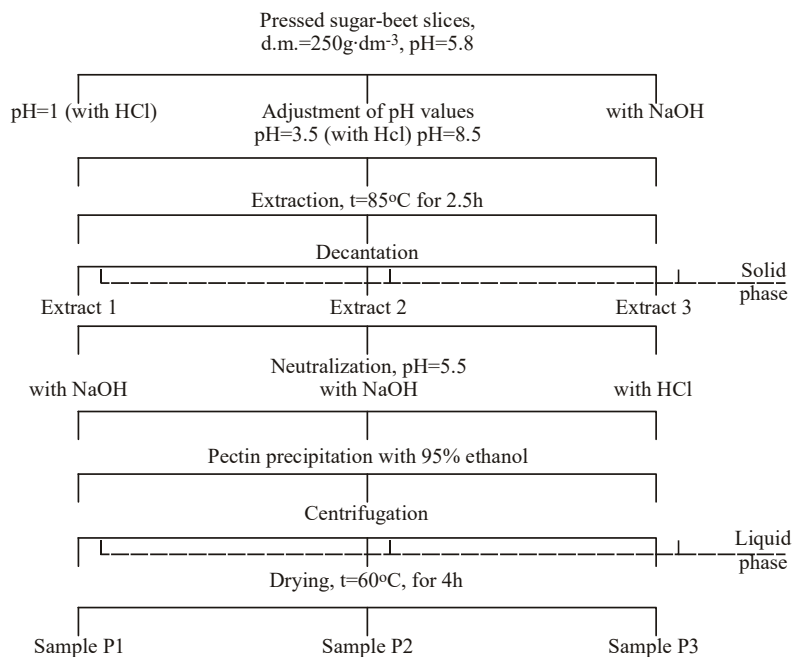


Figure 1. Laboratory scale extraction procedure [18].

#### Determination of content of galacturonic acid

For the quantitative determination of the purity of pectin preparations using the content of galacturonic acid, the titration method was applied. The principle of this method was the determination of the volumetric equivalent of total carboxyl groups of galacturonic acids. The equivalent of free carboxyl groups was determined by potentiometric titration of solution of pectin preparations with 0.01 M NaOH. The content of galacturonic acid, *Gal.La*, i.e., purity of pectin preparations, was calculated using the equation [31]:

$$Gal.A = \frac{100m_g}{g} \left[ \frac{g_{gal.A}}{100 g_{D.M.}} \right] \quad (2)$$

Weight of pure galacturonic acid, mg, expressed by the equivalent of free ( $X$ ) and the equivalents of methyl-esterified carboxyl groups ( $Y$ ), is given by Eq. (3) where: 176 and 190 – the molecular weights of anhydrous free galacturonic or methyl-esterified galacturonic acid (g / mol):

$$m_g = 176X + 190Y \text{ [g]} \quad (3)$$

#### Determining the degree of esterification

Ester-linked carboxyl groups were determined by adding 0.1 M NaOH to a solution of pectin mixture while stirring. After aging and addition of HCl, the potentiometric titration with 0.01 M NaOH solution was carried out. From the expenditure of a base, the content of associated ester groups was calculated. The degree of esterification ( $DE$ ) of pectin sample, was calculated using equation [31]:

$$DE = \frac{100Y}{X + Y} \text{ [%]} \quad (4)$$

#### Zeta potential

Charge of particles in a colloidal solution was expressed by the zeta potential value determined by applying Zeta-meter ZM-77 and well-known equation of Helmholtz–Smoluchowski:

$$\zeta = (4 \pi \eta / D_t) EM \quad (5)$$

where  $\zeta$  denotes zeta potential,  $\eta$  corresponds to the solution viscosity,  $D_t$  signifies its dielectric constant, while  $EM$  represents electrophoretic mobility. From the measured  $EM$  value of 20 particles, an average value was used to derive the zeta potential in the tested solutions using a diagram based on the Helmholtz–Smoluchowski equation. Experiments were conducted at 6-fold magnitude on a stereoscopic microscope and voltage adjusted at 150 V. Just before zeta potential measurements, solution temperatures were measured. Zeta potential was read from the diagram and multiplied by a correction factor for a given temperature.

#### Plan of experiments

Experiments were performed in accordance with the plan presented in Table 1. Nine flasks were filled with the model solutions of pectin (0.1mass%). After the adjustment of pH value, in 1–9 flasks, pectin solution was treated: *i*) with a CaSO<sub>4</sub> solution and *ii*) with CaSO<sub>4</sub> solution with added cationic polyelectrolyte (Magnafloc LT24) concentrations of 3 and 5 mg dm<sup>-3</sup>.

Table 1. Plan of experiments with pectin solutions P1, P2 and P3; precipitants: flask, each filled with 50 cm<sup>3</sup> of pectin solution (0.1 mass%), at pH 7

CaSO <sub>4</sub> and cationic polyelectrolyte (0, 3, 5 mg dm <sup>-3</sup> )	1	2	3	4	5	6	7	8	9
Concentration of CaSO <sub>4</sub> , mg dm <sup>-3</sup>	50	100	150	200	250	300	350	400	450
Volume of CaSO <sub>4</sub> solution, cm <sup>3</sup>	0.625	1.250	1.875	2.500	3.125	3.750	4.375	5.000	5.625

The zeta potential values of colloidal particles were measured after the induced precipitation. The process of agglomeration and precipitation lasted for 10 h, so as to enable precipitants to react with pectin as complete as possible. This experimental plan was performed three times, once for each particular pectin solution.

## RESULTS

The results of the measurements are presented in Table 2 and Figure 2.

Table 2. Zeta potential, experimental data, mV

CaSO <sub>4</sub> concentration mg dm <sup>-3</sup>	Pectin type								
	P1			P2			P3		
	Floculant concentration, mg dm <sup>-3</sup>								
	0	3	5	0	3	5	0	3	5
50	-21	-19	-19	-22	-19	-20	-18	-15	-14
100	-20	-17	-16	-18	-13	-15	-17	-11	-11
150	-19	-14	-13	-17	-10	-10	-15	-9	-9
200	-17	-9	-8	-16	-8	-7	-13	-5	-4
250	-14	-6	-5	-13	-4	-4	-12	-1	-1
300	-11	-3	-1	-10	-1	-1	-9	4	3
350	-7	3	3	-7	2	3	-1	6	6
400	-3	6	5	-1	5	4	4	7	8
450	2	7	6	4	6	6	5	7	8

## Statistical analyses

Simple regression models, using second order polynomial and response surface methodology (RSM) have been proposed for calculation of zeta potential capabilities as function of proposed process parameters (CaSO<sub>4</sub> concentration, polyelectrolyte concentration and the pectin type).

The experimental data used for the study of experimental results were obtained using a 9×3 experimental design, with 27 runs, for three types of pectin, according to RSM. It was used to design tests for sugar beet juice clarification, considering two factors: CaSO<sub>4</sub> and cationic polyelectrolyte (used as flocculant) concentration, and the type of used pectin (P1, P2 and P3).

The following second order polynomial (SOP) model was fitted to the data [32,33]. The model of the following form was developed to relate one response (*Y*) and three process variables (*X*):

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^3 \sum_{j=i+1}^3 \beta_{ij} X_i X_j \quad (6)$$

where  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$ ,  $\beta_{ij}$  are constant regression coefficients; *Y* - zeta potential; *X*<sub>1</sub> - CaSO<sub>4</sub> concentration; *X*<sub>2</sub> - flocculant concentration; *X*<sub>3</sub> - pectin type, numbers 1, 2 and 3 represent types of tested preparations P1, P2 and P3 (Figure 2).

Descriptive statistical analyses for all the obtained results were expressed as the mean ± standard deviation (*SD*). The evaluation of one-way ANOVA analyses of the obtained results was performed using StatSoft Statistica 10.0® software.

## Pectin isolation and characterization

Isolation of pectins from fresh sugar beet was performed with the aim to obtain pectins similar to those appeared in sugar-beet processing. Also, acidic and alkali conditions were applied due to broadening characteristics of investigated pectins. As it is well known, beet pectins contain galacturonic acid, rhamnose, arabinose and galactose as the major sugar constituents. Typical for beet pectins is also presence of both acetyl and ferulic acid, linked arabinose residues in the arabinan chains and galactose residues in (1-4)-linked galactans [29,34]. The presence of ferulic acid contributes to cross-linking of particular components thus increasing molar mass of pectins. By acidic extraction a degradation of arabinan side chains takes place as well as a loss of feruloyl groups, which causes a significant decrease of molar mass of pectins [35]. Under alkali conditions, similar processes occur. By alkali treatment the ester bonds, such as linkages between ferulic acid and arabinan or galactan, can be partially or completely cleaved [36], resulting in severe decrease of molar mass. Probably because of that, our alkali extracted pectin (P3) has molar mass approximately 64 500 g mol<sup>-1</sup> (pH 8.5, *t* = 85 °C,  $\tau$  = 2.5 h), which is significantly smaller than the value of 118000 g mol<sup>-1</sup>, obtained for both pectins P1 and P2, extracted by acidic process (pH 1, *t* = 85 °C,  $\tau$  = 2.5 h and pH 3.5, *t* = 85 °C,  $\tau$  = 2.5 h, respectively). The molar mass was determined by rather approximate viscosity method, but the results are in acceptable agreement with the results for alkali conditions (75 100 g mol<sup>-1</sup>, 2% NaOH, *t* = 45 °C,  $\tau$  = 3 h), and results for acidic conditions (119000 g mol<sup>-1</sup>, pH 1, *t* = 45 °C,  $\tau$  = 1.5 h and 122000 g mol<sup>-1</sup>, pH 3, *t* = 45 °C,  $\tau$  = 1.5 h) [35,36]. Due to differences in the conditions

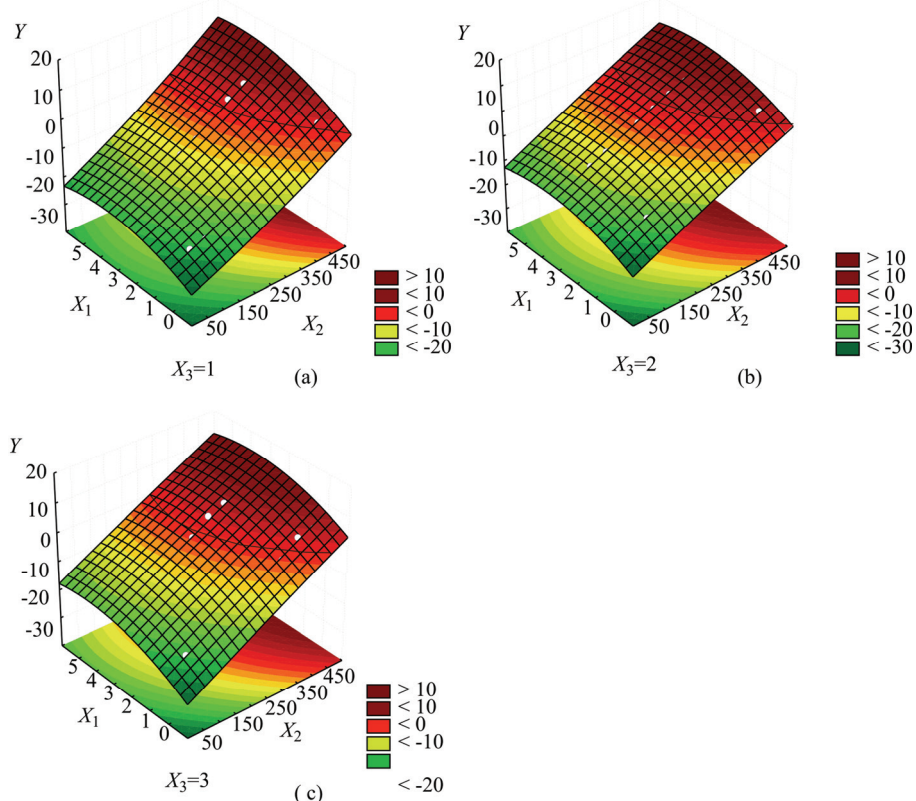


Figure 2. The effect of the precipitant concentration, flocculant concentration and the type of pectin on the charge of zeta potential: a) pectin type P1, b) pectin type P2 and c) pectin type P3. Y-zeta potential (mV);  $X_1$  – CaSO<sub>4</sub> concentration (mg/dm<sup>3</sup>),  $X_2$  – flocculant concentration (mg/dm<sup>3</sup>),  $X_3$  – pectin type.

of extraction, the obtained pectin preparations had a different composition and degree of esterification (Table 3).

Table 3. Basic physicochemical composition and the cation binding capacity of pectin preparation

Pectin solution	P1	P2	P3
Solid content, SC / (g/100 g)	81.55	82.25	80.35
Equivalent of free COOH groups, $X \times 10^5$	16.83	10.60	24.58
Equivalent of esterified COOH groups, $Y \times 10^5$	19.74	27.55	16.05
Content of galacturonic acid, Gal.A / %	63.45	66.31	72.24
Degree of esterification, DE	53.98	72.21	39.50
Mean molar mass $M_{Wsr} / g \text{ mol}^{-1}$	118000	118000	64 500
Cation binding capacity $CBC_t / \text{mmol g}^{-1}$	0.1659	0.1048	0.2480

The content of galacturonic acid in the tested preparations is in accordance with the mean content of pectin found in raw sugar beet juices from diffuser reported in literature [17,18]. As set out in Eq. (1), the degree of esterification of pectin P1, P2 and P3 (53.98, 72.21 and 39.50, respectively) is inversely proportional to the cation binding capacity (0.1659, 0.1048 and

0.2480 mmol/g, respectively). The cation binding capacity is proportional to the equivalent of free –COOH groups (16.83, 10.60 and 24.58 respectively for P1, P2 and P3) which are responsible for the surface charge of pectin particles [12,17].

#### RSM analysis

Analysis of variance was performed for comparison of zeta potential for different process parameters. The measured values of zeta potential, under different processing conditions, are presented in Table 2, and statistically significant differences for observed data were found in almost all samples, using Tukey HSD test.

Investigated samples are characterized by relatively low zeta potential, especially in case of increased flocculant concentration. According to ANOVA analysis (Table 4), response variable Y is mostly affected by CaSO<sub>4</sub> concentration, statistically significant at  $p < 0.001$  level. The flocculant concentration is also influential, while pectin type has been the least important variable for zeta potential calculation. Linear terms have been found most influential for mathematical model developing (Eq. (6)), and according to ANOVA, these terms have been found statistically significant at  $p < 0.001$  level, 95 % confidence limit. The quadratic term in SOP model for CaSO<sub>4</sub> concentration has been

found statistically insignificant, while the quadratic terms for flocculant concentration and pectin type have been found statistically significant for zeta potential calculation, but not very influential. The influence of all interchange (nonlinear) terms has been found statistically insignificant.

The average error between the predicted values and experimental values (calculated by Eq. (6)) was below 10%. Values of average error below 10 % indicate an adequate fit for practical purposes. To verify the significance of the models, analysis of variance (ANOVA) was conducted and the results indicate that all models were significant with minor lack of fit, suggesting that they adequately represented the relationship between response and factors.

Table 4. ANOVA calculation for zeta potential; \* – significant at  $p < 0.001$  level, \*\* – significant at  $p < 0.01$  level, 95% confidence limit, error terms were found statistically insignificant

Variable	dF	Zeta potential (Sum of squares)	F test	p
$X_1$	1	5274.32*	1830.01	<0.001
$X_1^2$	1	0.18	0.06	0.80
$X_2$	1	600.00*	208.18	<0.001
$X_2^2$	1	109.38*	37.95	<0.001
$X_3$	1	195.13*	67.70	<0.001
$X_3^2$	1	18.67**	6.48	0.01
$X_1 \times X_2$	1	4.10	1.42	0.24
$X_1 \times X_3$	1	4.01	1.39	0.24
$X_2 \times X_3$	1	0.00	0.00	0.99
Error	71	204.63		
$r^2$		0.969		

Table 5 shows the regression coefficients for the (SOP) model of zeta potential calculation, used by Eq. (6). The three-dimensional graph has been plotted for experiment data visualization (white coloured points) and for the purpose of observation the fitting of regression models to experimental data, Figure 2.

Table 5 is also used in calculation the optimum values of CaSO<sub>4</sub> and flocculant concentration, for each of the pectins in order to obtain zero zeta potential. It seems that zeta potential reaches zero most promptly when using pectin P3 (this is due to relatively high  $\beta_{33}$  regression coefficient). Other two parameters, CaSO<sub>4</sub> and flocculant concentration, also contribute to final value of zeta potential. Zero zeta potential is reached with higher CaSO<sub>4</sub> concentration (300–400 mg dm<sup>-3</sup>, depending on pectin used). All these observation coincide very well to obtained experimental results. Zero zeta potential curves have been drawn on 3D surfaces for each used pectin representing sugar beet clarification process, Figure 2.

Table 5. Regression coefficients for zeta potential calculation; \* – significant at  $p < 0.001$  level, \*\* – significant at  $p < 0.01$  level, 95% confidence limit, error terms were found statistically insignificant

Coefficient	Regr. coeff.	SD	t test	p
$\beta_0$	-27.060*	1.992	-13.586	<0.001
$\beta_1$	0.063*	0.008	8.151	<0.001
$\beta_2$	3.186*	0.443	7.192	<0.001
$\beta_{22}$	-0.414*	0.067	-6.160	<0.001
$\beta_{33}$	1.019**	0.400	2.545	0.013

### Precipitation and cation-binding characteristics

Charge inversion of zeta potential was observed within the whole series of tested coagulants concentrations (Table 2 and Figure 2). This indicates that in addition to the simple charge neutralization mechanism and ion exchange, a mechanism of specific adsorption occurs.

The beneficial effect of SO<sub>4</sub><sup>2-</sup> is well known from the literature on the coagulation of colloidal particles [27]. However, by comparing the binding efficiency of the CaSO<sub>4</sub> and CaCl<sub>2</sub> with pectins under the same experimental conditions [18], it can be seen that the Ca<sup>2+</sup> bounded with SO<sub>4</sub><sup>2-</sup> have no better affinity to complexation than Ca<sup>2+</sup> bounded with Cl<sup>-</sup>. In this case, the influence of anion size present in solution (SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>) cannot be neglected, which requires additional testing. The influence of anion size is greater at higher concentrations of ions whose valence is  $\geq 2$  and for systems with large electric charge of the colloidal particles [37].

In the experiment, the used concentrations of the polyelectrolyte were in range from 3 to 5 mg dm<sup>-3</sup>, since they have proved to be the most favourable in the experiments with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and CuSO<sub>4</sub>. However, cationic polyelectrolytes applied with the precipitant Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and CuSO<sub>4</sub> showed lower efficiency in the deposition of pectin and protein particles (the amount of Al<sup>3+</sup> and Cu<sup>2+</sup> necessary to bring to zero zeta potential values decreased by 15 mg dm<sup>-3</sup>) [25]. With the application of a cationic polyelectrolyte of the same type, the amount of CaSO<sub>4</sub> is necessary to bring to zero zeta potential values decreased to about 100 mg dm<sup>-3</sup> (Table 6). This means that the cationic polyelectrolyte can function as both coagulant (through charge neutralization) and flocculant (through interparticle bridging) of pectin solutions. The results indicate that such a complexation–flocculation process is of potential interest for the removal of pectins during sugar beet juice clarification.

Cationic polyelectrolyte (cationic PAM) concentration of 5 mg dm<sup>-3</sup> shows slightly higher removal efficiency of pectin from the tested model-solutions, suggesting that the cationic polyelectrolyte with large molar mass (over 100000 g mol<sup>-1</sup>) targets a pectin macromolecules with different molar mass.

The pectin preparation P3 showed better cation-binding characteristics in relation to the pectin P1 and P2 (from Table 3:  $CBC_{(P3)} = 2.37CBC_{(P2)}$  and  $CBC_{(P3)} = 1.49CBC_{(P1)}$ ). This is understandable, since the pectin P3, besides at least the value of mean molar mass (64500 g mol<sup>-1</sup>), has the highest content of galacturonic acid (72.24%) and the lowest degree of esterification (39.50).

Compared with conventional process where is approximately used 9 g CaO per g of pectin, the amount of CaSO<sub>4</sub> (in the form of pure salt or salt with cationic electrolyte) was significantly lower, ranging in the interval of 353–678 mg per g pectin (Table 6).

Table 6. CaSO<sub>4</sub> and cationic polyelectrolyte concentration for zero zeta potential of pectin solutions obtaining Zero zeta potential (0 mV)

Precipitant	P1		P2		P3	
	mg dm <sup>-3</sup>	mg g <sub>p</sub> <sup>-1</sup>	mg dm <sup>-3</sup>	mg g <sub>p</sub> <sup>-1</sup>	mg dm <sup>-3</sup>	mg g <sub>p</sub> <sup>-1</sup>
CaSO <sub>4</sub> + 0 mg dm <sup>-3</sup> cationic polyelectrolyte	430	678	410	618	355	490
CaSO <sub>4</sub> + 3 mg dm <sup>-3</sup> cationic polyelectrolyte	320	512	320	482	260	360
CaSO <sub>4</sub> + 5 mg dm <sup>-3</sup> cationic polyelectrolyte	310	504	315	475	255	353

## CONCLUSION

The assumption that a small amount of a cationic polyelectrolyte will have an influence on the improvement of coagulation characteristics of Ca<sup>2+</sup> in CaSO<sub>4</sub> as precipitant extracting pectin, has proved to be true. Cationic polyelectrolyte achieves additional charge neutralization. This mechanism is combined with mechanism of interparticle bonding. The optimal amount of cationic polyelectrolytes was found to be (cationic PAM) 3 mg dm<sup>-3</sup>. Addition of increased amounts of cationic polyelectrolyte did not give an improvement, suggesting that the cationic bridging polyelectrolyte targets pectin macromolecules with different molar mass.

The quality of precipitation of pectin is affected by precipitant concentration (CaSO<sub>4</sub>) the most, which is confirmed by ANOVA calculation, (RSM) and standard score evaluation.

With an adequate dosing of CaSO<sub>4</sub> and cation polyelectrolyte along with zeta potential control, significant economic effect can be achieved. It has been found that the consumption of this coagulant is about 20 times lower in comparison with the consumption of a conventional coagulant CaO. In this way, the contamination of soil would be reduced to a minimum.

However, reliable comparison between the proposed compounds and traditional coagulant CaO, requires additional testing under industrial conditions of sugar beet juice processing.

## Acknowledgement

The Ministry of Education, Science and Technological Development of the Republic of Serbia financially supported this work (Project TR -31055).

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## IZVOD

**CaSO<sub>4</sub> I KATJONSKI POLIELEKTROLITI KAO MOGUĆI PRECIPITANTI PEKTINA PRI PREČIŠĆAVANJU SOKA ŠEĆERNE REPE**Tatjana Kuljanin<sup>1</sup>, Biljana Lončar<sup>1</sup>, Lato Pezo<sup>2</sup>, Milica Nićetin<sup>1</sup>, Violeta Knežević<sup>1</sup>, Rada Jevtić-Mučibabić<sup>3</sup><sup>1</sup>*Tehnološki fakultet, Univerzitet u Novom Sadu, Srbija*<sup>2</sup>*Institut za opštu i fizičku hemiju, Univerzitet u Beogradu, Srbija*<sup>3</sup>*Naučni Institut za prehrambene tehnologije, Univerzitet u Novom Sadu, Srbija*

(Naučni rad)

U toku industrijske obrade šećerne repe, jedna od najvažnijih faza je čišćenje soka šećerne repe. U tu svrhu, najčešće se koristi CaO u obliku Ca(OH)<sub>2</sub>. Pošto kalcijumovi joni iz ovih jedinjenja imaju relativno mali afinitet vezivanja sa pektinima soka šećerne repe, potrebne su vrlo velike količine kreča (oko 15 g CaO/100 g soka). Zbog toga je razmatrana mogućnost izdvajanja pektina procesom razelektrisanja čestica dodavanjem jedinjenja sa dvo- i trovalentnim katjonima kao i katjonskog polielektrolita. U ovom radu, izneta su istraživanja i date su teorijske osnove nove metode čišćenja soka šećerne repe koja se bazira na primeni CaSO<sub>4</sub> i katjonskog polielektrolita. U toku trajanja ekstrakcije od 150 min, na pH vrednostima od 1, 3.5 i 8.5, iz rezanaca sveže šećerne repe izolovana su tri pektinska preparata. Precipitant CaSO<sub>4</sub> u vidu vodenog rastvora, dodavan je u 100 cm<sup>3</sup> 0.1 % (mas) rastvora pektina. Ispitivanja su vršena sa 9 različitih koncentracija rastvora CaSO<sub>4</sub> (u intervalu 50–450 g/dm<sup>3</sup>) bez dodavanja katjonskog polielektrolita i uz dodatak katjonskog polielektrolita koncentracije 3 i 5 mg/dm<sup>3</sup> (cationic PAM). Efikasnost taloženja pektina praćena je merenjem zeta potencijala model-rastvora pektinskih preparata. Izmerene vrednosti zeta potencijala za različite procesne parametre upoređivane su statistički, primenom RSM analize. Optimalne količine precipitanta CaSO<sub>4</sub>, bez primene katjonskog polielektrolita, iznosile su: 490–678 mg CaSO<sub>4</sub>/g pektina. Nakon primene katjonskog polielektrolita, optimalne količine CaSO<sub>4</sub> su bile manje (u intervalu 353–512 mg/g) što znači da je katjonski polielektrolit uticao na poboljšanje koagulacionih karakteristika jona Ca<sup>2+</sup> iz CaSO<sub>4</sub>. U ovom slučaju, došlo je dodatne neutralizacije naelektrisanja – mehanizam neutralizacije naelektrisanja je udružen sa mehanizmom međučestičnog povezivanja. Utvrđena je optimalna doza katjonskog polielektrolita (cationic PAM) od 3 mg/dm<sup>3</sup> dok veća doza (5 mg/dm<sup>3</sup>) nije značajno uticala na povećanje taloženja pektina. Ove količine su znatno manje od prosečne količine CaO upotrebljenog u klasičnom postupku čišćenja soka šećerne repe (oko 9 g/g pektina soka šećerne repe). Delimičnom ili potpunom zamenom klasičnog koagulant sa CaSO<sub>4</sub> uz primenu katjonskog polielektrolita, smanjili bi se troškovi uklanjanja pektina iz soka šećerne repe uz očuvanje životne sredine.

*Ključne reči:* Čišćenje • Pektini • Sok šećerne repe • CaSO<sub>4</sub> • Katjonski polielektrolit • Zeta potencijal