Aluminium and calcium ions binding to pectin in sugar beet juice – model of electrical double layer

Tatjana A. Kuljanin[1], **Lidija R. Jevrić**[1], **Biljana Lj. Ćurčić**[1], **Milica R. Nićetin**[1], **Vladimir S. Filipović**[1], **Jasna P. Grbić**[2]

[1]University of Novi Sad, Faculty of Technology, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia
[2]University of Novi Sad, Institute for Food Technology, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia

Abstract

In sugar industry, there is a problem with the presence of undesirable macromolecules such as pectins in sugar beet juice. Removal of these compounds is done mostly by CaO. Calcium may cause undesirable process of alkalization of soil in the proximity of sugar factory. The theoretical basis of new juice purificatin method based on the application of $Al_2(SO_4)_3$, $CaSO_4$ and their mixtures are presented. Two model solutions of pectin (0.1%, w/w) are investigated using method of measuring zeta potential. Pure salts $Al_2(SO_4)_3$ and $CaSO_4$, showed better binding with pectin than mixtures. Amount of all studied pure salts and mixtures of Al^{3+} and Ca^{2+} were significantly less (142–710 mg/g_{pectin}) than the average amount of CaO used in classical process (about 9 g/g_{pectin}). Mechanism of discharge of pectin macromolecules in the presence of mixtures of these ions using a model of double electric layer is suggested.

Keywords: pectin, sugar beet, $Al_2(SO_4)_3$, $CaSO_4$, zeta potential, double electric layer.

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One of the most convenient parameters to determine the sugar beet juice purification efficiency is the lime consumption. The lime consumption varies depending on the quality of sugar beet. CaO consumption of individual factories may vary significantly between 1 and 3% depending on the quality of beets. Due to the large quantity of CaO (about 15 g CaO/100 g dry matter of sugar beet juice), calcium may cause undesirable process of alkalization of the soil in the proximity of sugar factory [1]. It is possible to reduce lime consumption down to 1%, but at the same time it would change color and lime salts content of the purified juices as well as the inferior filterability of the juices [2]. There are different improved methods of the purification of sugar beet juice, such as ion exchange, electrolysis, reverse osmosis, ultrafiltration, nanofiltration, etc., but they are at disadvantage due to the high maintenance cost [3,4].

About 60% nonsugar matter of the beet juice are pectin macromolecules. Pectins are ionic plant polysaccharides consisting almost entirely of D-galacturonic acid and galacturonic acid methyl ester residues, acetylated to some degree [5,6]. Coagulation and precipitation of pectins can be performed by process of chemically induced discharging. Due to the dissociation of carboxylic acid groups of galacturonic acid, pectic substances have the negative charge on the surface. These groups can take a part in the binding of divalent or trivalent cations [7,8]. There is a selectivity order of the binding affinity of various divalent cations by citrus and sugar-beet pectins [9–11]: $Cu^{2+} \approx Pb^{2+} >> Zn^{2+} > Cd^{2+} \approx \approx Ni^{2+} > Ca^{2+} > Mg^{2+}$.

There are many studies of applying ions with greater number of positive charges such as Al^{3+}. Al^{3+} is often used in form of hydrolyzed salt $Al_2(SO_4)_3$ for treatment of fresh and waste water [8,12,13]. Previous study [14] has given a simplified scheme of Al^{3+} hydrolysis. With the increase of pH value and concentration of ions, different products of hydrolysis are being formed including nonhydrolyzed ions, monomeric, dimeric and polymeric.

Ion binding to natural organic matter in water expressed as $H^+/Me^{2+,3+}$ molar exchange ratios varied strongly with metal ion: Al^{3+} (2.1–2.7) and Ca^{2+} (0.2–0.5). The bonding strength of Al ions with humic materials compared with divalent metal ions and the order of preference for ion binding are shown: $Al^{3+} > > Cu^{2+} > Pb^{2+} > Cd^{2+} > Ca^{2+}$ [15]. In accordance with this selectivity order, it is clear that applying of Al^{3+} will be efficient in sugar beet juice purification in relation to classical process that utilizes Ca^{2+} compounds [16]. Published research that studied the deposition of macromolecules from juices and by-products of sugar production (in order to determine their quality), gave priority to Al salts from economical and ecological point of view [17,18]. Studying the influence of Al^{3+} during the chemical processing of molasses, established the optimum amount of $Al_2(SO_4)_3$ (0.2–0.4 mol/l) [19]. In [14], studied was the influence of 100% $Al_2(SO_4)_3$ and $Al_2(SO_4)_3$

Correspondence: T.A. Kuljanin, University of Novi Sad, Faculty of Technology, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia.
E-mail: kuljanin@uns.ac.rs

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with different shares of $CuSO_4$ on the efficiency of sugar beet pectine separation. It has been proven that the most effective was pure $Al_2(SO_4)_3$ (142–182 mg/g_{pectin}).

In the research presented, the efficiency of ion binding was determined by elektrokinetical method by measuring zeta potential. 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. According to this, zeta potential measurements should be effective for the control of discharging pectin and protein particles.

The very important are cation binding characteristics of pectins themselves since the total capacity of pectins to bind metal cations is directly related to the degree of methyl-esterification, degree of polymerization and galacturonic acid content [11,20]. Also, one of the influencing factors, concerning cation binding by pectins, is the remaining part of the coagulant molecules. Anions with greater charge, such as sulfates, have a high tendency to coordinate with metal ions [8]. Therefore, in this paper, were compared activity of $CaSO_4$ with the activity of CaO (in the form of $Ca(OH)_2$) used in the classical treatment of beet juice purification.

It is known that the adsorption of metal ions also influences the presence of the other ions of the same or different valence [14,21]. Also, an aspect ratio of ion size present in solution must not be neglected. The influence of ion size is greater at higher concentrations of ions whose valence is ≥2 and for systems with large electric charge of the colloidal particles [22].

Herein, the efficiency of binding of Al and Ca ions (from $Al_2(SO_4)_3$ and $CaSO_4$) in their mixtures with pectin was studied. The aim of the mixtures investigation was to determine whether the efficiency of coagulation is proportional to the concentrations of Ca^{2+} and Al^{3+} or discrepancies might occur.

Theoretical part

All electrokinetic phenomena are related to the development of electrical double layer (EDL) at the particle/electrolyte interface. EDL consists of two layers: the adsorbed (Stern) and mobile diffuse layer. The potential at the boundary between the Stern layer and the diffuse layer (where hydrodynamic movement of ions is still possible, Figure 1 – shear plane) can be easily measured and it is known as the electrokinetic or zeta potential (ζ) [23–25].

According to the Gouy-Chapman-Stern-Graham's (GCSG) model of EDL, Figure 1 illustrates the structure of EDL on the surface of macromolecule of pectin in the presence of divalent and trivalent salts ($CaSO_4$ and $Al_2(SO_4)_3$) in the aqueous solution. This model is characterized by the localization of ions (Ca^{2+}; Al^{3+}; H^+; SO_4^{2-}; OH^-) in the fixed (Stern) layer and also in the diffuse layer of the solid-liquid interface.

According to the GCSG model, the fixed layer is assumed to be bound by two planes: the Inner Helmholtz plane (IHP) and Outer Helmholtz plane (OHP), which are characterized by the potentials, ψ_{IHP} and ψ_{OHP}. The surface potential of pectin particles (ψ_0) occurs due to the presence of COO^-. According to the GCSG model, the potential change, ψ, between the IHP and OHP is linear, depending on the number, size and

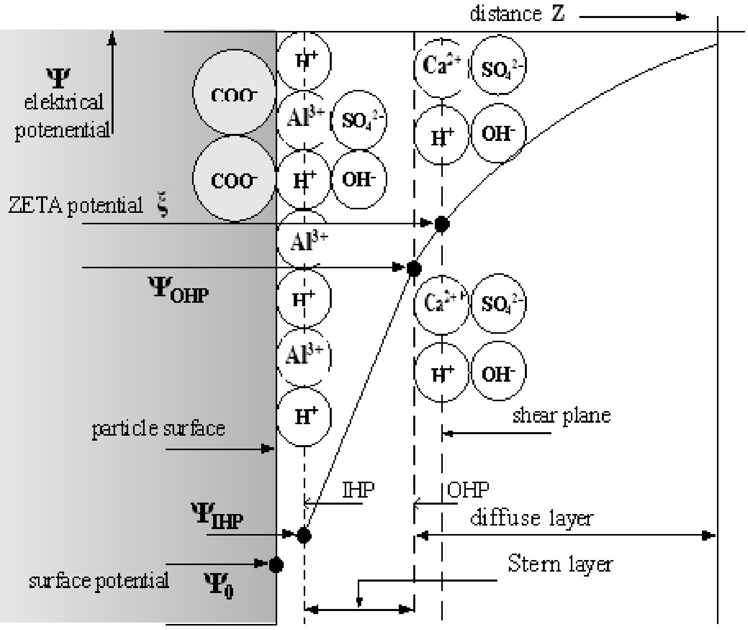

Figure 1. A schematic illustration of the structure of double electric layer (EDL) on surface of macromolecule of pectins according to GCSG model [23].

hydration of Ca^{2+} and Al^{3+}. In the diffuse layer, an exponential potential drop is observed in accordance with the Boltzmann distribution [26].

Adding polyvalent cations leads to release of negative charge on the pectin surface and decrease of zeta potential. By keeping zeta potential close to zero, pectin colloidal particles will discharge and the conditions for effective coagulation and sedimentation of particles will be achieved [25]. Zeta potential measurement method has limitations in theory and technique of work. Because of the wide range of sizes and masses of these colloids, it is impossible to have all zeta potential values of the interval ±5 mV (as attested in the water treatment practice) and total sedimentation cannot be achieved. However, the control of zeta potential based on the average size of the colloid is sufficient to obtain diffuse juice with significantly smaller share of undesirable macromolecules.

EXPERIMENTAL

Material

Pectin preparations were extracted from cossettes (dry matter 72.5%) obtained in the industrial processing of sugar beet (factory Žabalj). Salts, $CaSO_4$ and $Al_2(SO_4)_3$ in crystal hydrate form ($CaSO_4 \times 2H_2O$ and $Al_2(SO_4)_3 \times 18H_2O$), “Zorka Pharma”, Šabac (purity of both salts was 99.0%, w/w) were used for preparation of the studied solutions in deionized water. The pH 7 of $Al_2(SO_4)_3$ solutions was regulated before each experiment, using the equivalent amount of Na_2CO_3.

Method of isolation of pectin preparation

Two kinds of pectin preparations were isolated by extraction in acidic conditions in accordance with a standardized laboratory procedure [27]. Extraction conditions were: pH 1.0, 75 °C for 1.0 h, P_1 preparation, while for the P_2 preparation were: pH 3.5, 95 °C and 1.5 h. Extraction of each preparation was repeated three times. Due to differences in the extraction conditions, the resulting pectin preparations had different composition and degree of esterification. High molecular colloidal fraction was isolated from extract by multistep precipitation with 70% ethanol. Extraction procedure has been described in previous work [28].

Determination of molar mass, degree of polymerization and esterification

Basic parameters of the pectin preparation were determined according to standard methods of AOAC [27]. Content of galactouronic acid was calculated using the equation:

$$Gal.A = \frac{m_{\mathrm{g}}100}{g} \left[\frac{\mathrm{g_{gal.kis.}}}{100\ \mathrm{g_{S.M.}}}\right] \tag{1}$$

Where the mass of pure galactouronic acid (*Gal.A*) is expressed through equivalents of free (*X*) and esterified carboxy groups (*Y*): $m_{\mathrm{g}} = 176X + 190Y$ (g). In this equation, the values 176 and 190 are the molar masses of dehydrated galactouronic acid and methyl-esterified galactouronic acid (g/mol) [5].

Degree of esterification (DE) was calculated using equation [5,14]:

$$DE = \frac{Y}{X+Y}100 \tag{2}$$

Average molar mass was determined refractometrically and spectrophotometrically by measuring 5 different concentrations of pectin preparations: 0.0025, 0.005, 0.010, 0.015 and 0.020 g/cm^3 [29]. Degree of polymerization (DP) was calculated by dividing the mean molar mass of the preparation with the molar mass of dehydrated *Gal.A*. The affinity of binding of metal ions depends primarily on the number of binding sites at macromolecule. The number of binding sites (primarily COO^- groups) on the surface of pectin macromolecule was calculated through form [30]:

$$n = DP\left(\frac{Gal.A}{1000}\right)\left(\frac{1-DE}{100}\right) \tag{3}$$

The cation binding capacity of pectin macromolecules, CBC_t, was calculated on the basis of simplified equation [31]:

$$CBC_{\mathrm{t}} = \frac{Gal.A\left(1-\frac{DM}{100}\right)}{176} \left[\frac{\mathrm{mmol}}{\mathrm{g_{SM}}}\right] \tag{4}$$

In this paper it is accepted that only free carboxyl group of the galacturonic acid take part in the binding of cations.

In determining the composition of pectin preparation, measurements were repeated twice. If the difference between the two results of the same experiment was more than 5%, measurements were repeated several times.

Plan of the experiment

Experiments were performed in a model-pectin solutions P_1 and P_2 (0.1%, w/w). This concentration corresponds to the mean concentration of pectin in sugar beet juice [24]. Solutions were obtained by dissolving 1 g of pectin preparation in 250 cm^3 of distilled water and leaving it overnight to swell. After that, distilled water was added to 1 dm^3 and for each measurement 50 cm^3 of solution was taken. At each measurement, the pipette was used to add correct volume (in cm^3) of coagulant (pure solutions of $Al_2(SO_4)_3$, $CaSO_4$ or their mixtures) in order to obtain the required concentrations of coagulants (mg/dm^3).

Solutions $Al_2(SO_4)_3$ and $CaSO_4$ were obtained by dissolving 1 g of salt in 200 cm^3 of distilled water. Mixtures of these solutions were prepared in the following proportions of $CaSO_4$ and $Al_2(SO_4)_3$, respectively (calculated according to the pure salt mass): 20:80 (II); 40:60 (III); 60:40 (IV) and 80:20 (V) (%, w/w). From these solutions adequate volume (cm^3), using pipette, was added to 50 cm^3 of 0.1%, w/w, of pectin preparation solutions to obtain the corresponding concentration of coagulants. The range of these concentrations was from 50 to 500 mg/dm^3. Due to incomplete hydrolysis of $Al_2(SO_4)_3$, during preparation of coagulant, the equivalent amount of base must be added to obtain pH 7 solution [19]. In this study, Na_2CO_3 was added in equivalent mass ratio to the pure $Al_2(SO_4)_3$ (1:1.07).

It is known from the literature that the ability of surface complexation of metal ions with polysaccharides increases in the pH range of 3–7 [20]. All measurements were performed at pH 7. At neutral pH value, main cationic form of hydrolysis is Al^{3+} [8]. Also, at pH 7, ions Al^{3+} and Ca^{2+} have limited solubility (minimum solubility of $Al_2(SO_4)_3$ and $CaSO_4$ are 0.36 and 0.24 g/100 ml water at 20 °C). The pH of the solutions was measured using pH Meter MA 5740 at one hour intervals, counting from the moment of their preparation.

After adding the provided amounts of coagulants (I–VI) in the samples of preparations, pH adjusted solutions were stirred for 30 min on a high-speed magnetic stirrer (500 rpm). Then, the solution was stirred for another 5 min at low speed of maximum 20 rpm, to prevent the disaggregation of the already formed floccules. The solution was then allowed to settle down for 5 min. An aliquot taken from the supernatant was used to measure the zeta potential. Measurements were performed at room temperature for 10 different solution concentrations.

Zeta potential measurement

The electrokinetic potential was evaluated by means of electrophoresis using a Zeta Meter ZM-77 [32]. The instrument consists of an electrophoretic cell with platinum electrodes connected to direct current and a stereoscopic microscope equipped with a special ocular micrometer. After adjusting the voltage, an electric recording device was used to measure time needed for a colloidal particle to pass a distance of a standard micrometer division.

From the measured value of 20 particles, an average value was used to derive the zeta potential in the tested solutions using a diagram based on the Helmoltz–Smoluchowski equation for electrophoretic mobility of colloidal particles. 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 [32].

RESULTS AND DISCUSSION

In accordance with the described extraction conditions, preparations of different composition and degree of esterification were obtained. These properties depend on the biological origin of raw material, sugar beet ripeness, extraction conditions and experimental procedure. The results are shown in Table 1. Along with results for the average molar masses, the calculated values of the degree of esterification, degree of polymerization, number of binding sites and the cation binding capacity are shown (Table 1).

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. Degree of esterification of pectin preparations, P_1 and P_2 (72.21 and 39.50, respectively), is inversely proportional to the number of binding sites (124.5 and 217.8). Also, it can be seen from Table 1 that the cation binding capacity (1.045×10^{-3} and 2.480×10^{-3} mmol/g) is proportional to the equivalent of free COOH groups (10.60 and 24.58) which are responsible for the surface charge of pectin particles.

Table 1. Basic physicochemical composition, number of binding sites and the cation binding capacity of pectin preparation

Preparation	P_1	P_2
Solid content, *SC*, g/100 g	82.25	80.35
Equivalent of free COOH groups, $X\times10^5$	10.60	24.58
Equivalent of esterified COOH groups, $Y\times10^5$	27.55	16.05
Content of galacturonic acid, *Gal.A*, %	66.31	72.24
Degree of esterification, *DE*	72.21	39.50
Mean molar mass, M_{Wsr} (g/mol)	87720	119048
Degree of polymerization, *DP*	676	498
Number of binding sites, *n*	124.5	217.8
Cation binding capacity, $CBC_t\times10^3$, mmol/g	1.045	2.480

As coagulants, most efficient are salts that give catonic hydrolysis products of the higher charge, such as $Al_2(SO_4)_3$. At pH below the effective isoelectric point of the metal hydroxide (pHzpc 8), the predominant Al species are positively charged and charge neutralization can be achieved. At pH ~ 7, Al^{3+} can form hydroxyl complexes such as $Al(OH)_2^{+}$, $Al(OH)^{2+}$ and $Al(OH)_3$. In the vicinity of the isoelectric point, colloidal hydroxy-Al polymers with high charge are also created, that are more efficient in the charge neutralization of the surface of pectin particles [8].

Addition of $Al_2(SO_4)_3$ and $CaSO_4$ reduces steadily the zeta potential of pectin macromolecules. Charge inversion of zeta potential was observed within the whole series of tested coagulant concentrations (Figures 2 and 3). Therefore, in addition to the simple charge neutralization mechanism and ion exchange, a mechanism of specific adsorption occurs. If ions possess a special affinity for the solid surface, but are not chemisorbed, they are known as specifically adsorbed ions. Specifically adsorbed ions adsorb strongly to the surface because of covalent bond forming and solvation effect [23]. Therefore, the specific adsorption of ions will change the surface charge and surface potential of colloidal particles, which may cause the charge inversion. Charge inversion is the occurrence of EDL in which, as measured by electrokinetics, there is more counter charge than charge on the surface. The phenomenon of charge inversion, where changes in the sign of the zeta potential (in our case, "–" to "+"), has not been yet sufficiently clarified from the physical–chemical point of view [33].

According to the GCSG model, specific adsorption takes place in the Inner Helmholtz layer (Figure 1). By analyzing the proposed model in the presence of Ca^{2+}, Al^{3+}, SO_4^{2-} in aqueous solution, the following can be observed:

- The inner Helmholtz plane (IHP) is passing through the centers of Ca^{2+} and Al^{3+} specifically adsorbed (and H^{+} adsorbed from the solution) on the negatively charged glycosyl-residues on the pectin macromolecule surface.
- Anions (SO_4^{2-} and OH^{-}) form a secondary layer due to electrostatic attraction with the ions of Ca^{2+} and Al^{3+} from the Stern layer.
- The outer Helmohltz plane (OHP) is passing through the centers of Ca^{2+}, Al^{3+} and H^{+} that are attracted only by the electrostatic forces (Coulombic attraction). Also present are SO_4^{2-} and OH^{-} from the solution, attracted by the electrostatic forces as oppositely charged ions.

According to the presented model, it is assumed that the increase in Ca^{2+} and Al^{3+}, increases the proportion of specific adsorption of these ions as compared to the proportion of electrostatic Coulombic attractions.

The low amount of Al^{3+} were compared to the amount of Ca^{2+} (from $Al_2(SO_4)_3$ and $CaSO_4$) to achieve the charge inversion on the surface of pectin macro-

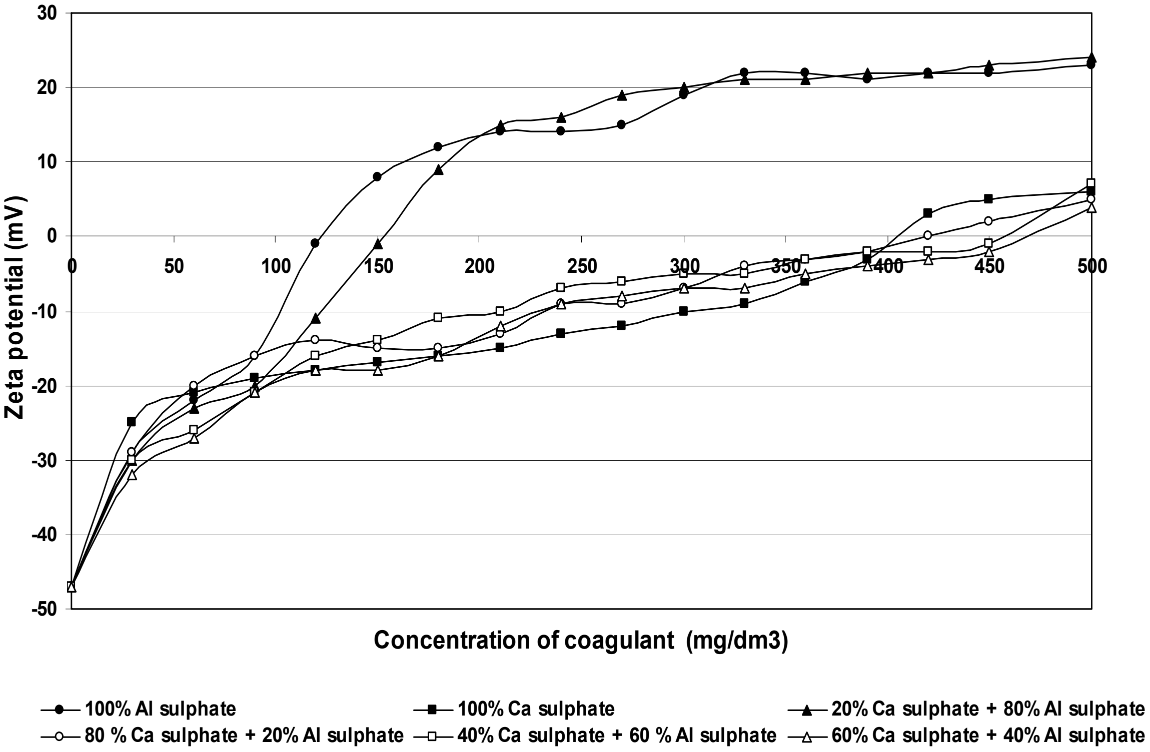

Figure 2. The influence of $Al_2(SO_4)_3$, $CaSO_4$ and their mixtures to the change zeta potential of the pectin preparation P_1.

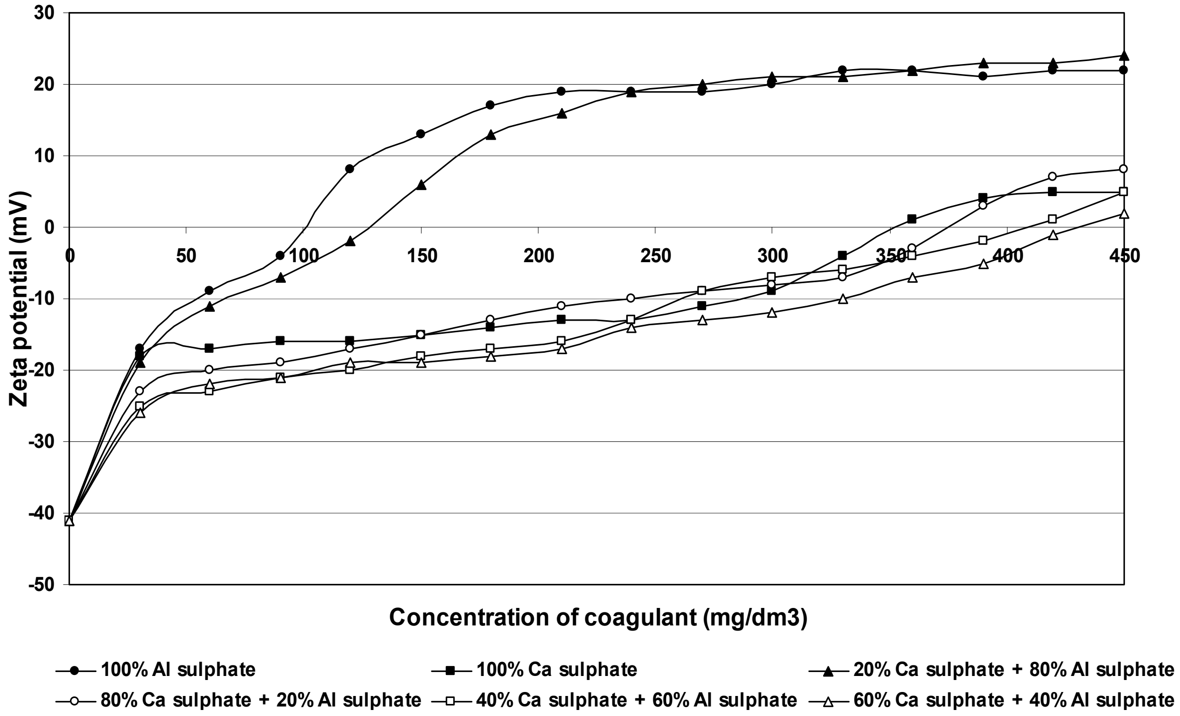

Figure 3. The influence of $Al_2(SO_4)_3$, $CaSO_4$ and their mixtures to the change zeta potential of the pectin preparation P_2.

molecules (Figures 2 and 3). For both tested preparations, about 3.5 times smaller amount of Al^{3+} (120 mg/dm^3 or 182 mg/g$_{pectin}$ for P_1 and 102 mg/dm^3 or 142 mg/g$_{pectin}$ for P_2) are needed compared to Ca^{2+} (405 mg/dm^3 or 610 mg/g $_{pectin}$ for P_1 and 355 mg/dm^3 or 490 mg/g $_{pectin}$ for P_2) for the value of zeta potential to reach zero (Table 2). This can be explained by weaker, electrostatic binding of Ca^{2+} (Coulombic attractions). Since Ca^{2+} are in the last place of the affinity binding scale of divalent ions with biological material [15], specific adsorption of these ions is much smaller compared to the electrostatic binding. In recent literature, the binding of Ca^{2+} with humic materials is explained by gradual formation of humic acid–Ca-OH complex (although the presence of such a complex has not be proven so far) [34,35]. In this way, the mechanism of specific absorption and charge inversion of pectin molecule surfaces in the presence of Ca^{2+} probably occurs *via* the creation of Gal.A–Ca-OH complexes.

It is known that Ca^{2+} have a large dehydration effect of hydrophilic macromolecules such as pectin. The ions with the smaller hydrated radius such as Ca^{2+} will be able to approach the surface closely. The distribution of these ions is faster so they are easily stored, primarily in the diffusion part of EDL. However, in the charge inversion process, valence of counterion is very significant [26]. Al^{3+} have a larger hydrated radius, carry higher charge, reduce zeta potential to zero point at much lower concentrations. This is in accordance with Schulze–Hardy rule and literature [15,36]. From the literature data, Al^{3+} have three times higher binding constant to the cell walls of plant origin (4.36) in relation to the Ca^{2+} (1.44) [34]. Also, due to the high density of Al^{3+} (the density of Al^{3+} is 2.70 g/cm^3, whereas of Ca^{2+} is 1.54 g/cm^3), their electrophoretic mobility is higher, which enables easier location in the Stern layer and neutralization of the negative charge on the surface of pectin macromolecules.

Table 2. Amounts of $Al_2(SO_4)_3$ and $CaSO_4$ (I and VI) and their mixtures (II–V) required for neutralization of the charge of pectin macromolecules

Pure salts and mixtures: $Al_2(SO_4)_3$, $CaSO_4$		Preparation P_1		Preparation P_2	
		mg/dm^3	mg/g$_p$	mg/dm^3	mg/g$_p$
I	100% $Al_2(SO_4)_3$	120	182	100	142
II	20% $CaSO_4$ + 80% $Al_2(SO_4)_3$	155	234	130	180
VI	100% $CaSO_4$	405	610	355	490
V	80% $CaSO_4$ + 20% $Al_2(SO_4)_3$	420	634	370	512
III	40% $CaSO_4$ + 60% $Al_2(SO_4)_3$	460	695	410	568
IV	60% $CaSO_4$+ 40% $Al_2(SO_4)_3$	470	710	435	602

The results show that amount of $Al_2(SO_4)_3$ needed to achieve zero zeta potential of pectin preparations is significantly lower (142–182 mg/g pectin), compared to the removal of humic substances from water [8]. Zeta potential of humic substances in water reached zero value at a concentration about 3 g_{Al} / g_{DM} (pH 7).

Comparing the activity of coagulants with the same cation and different anions, $Al_2(SO_4)_3$ has proved to be significantly more effective than $AlCl_3$ studied in previous work under the same experimental conditions [7]. To achieve a zero value of zeta potential, it was necessary to add 350–390 mg/dm^3 of $AlCl_3$, which is about 3.5 times the amount of $Al_2(SO_4)_3$ (120 mg/dm^3 for P_1 and 102 mg/dm^3 for P_2). However, $CaSO_4$ showed a slight difference compared to the effect of $CaCl_2$ (300–400 mg/dm^3 $CaCl_2$ or 350–420 mg/dm^3 $CaSO_4$ to achieve zero zeta potential) [7]. In the present study, SO_4^{2-} did not have influence on the coagulation effect of Ca^{2+}.

The amount of adsorbed ions in the mixtures depends on the equilibrium between adsorption competition from of the ions, ionic size and stability of bonds between metal ions and surface macromolecules [36]. Using mixtures with different proportions of Al^{3+} and Ca^{2+}, caused a change in adsorption properties and ion binding affinity. The required quantities of $Al_2(SO_4)_3$ (I), $CaSO_4$ (VI) and their mixtures (II–V) to achieve zero zeta potential values, sorted by size, are shown in Table 2.

Pure salt of $Al_2(SO_4)_3$ and $CaSO_4$, proved to be the most effective in neutralizing the charge of pectin macromolecules (Table 2, I and VI). From the tested mixtures, compounds with the highest proportion of Al^{3+} (80% $Al_2(SO_4)_3$ + 20% $CaSO_4$), as expected, showed the highest affinity for binding ions. In order to reach zero zeta potential value, necessary amount was 234 mg_{mix}/g_{pectin} for P_1 and 180 mg_{mix}/g_{pectin} for P_2. This confirms earlier presented conclusions on the impact of Al^{3+} on the surface charge modification of colloidal particles. The charge inversion from negative to positive for the investigated concentrations in mixtures of $Al_2(SO_4)_3$ and $CaSO_4$ infers, that besides ionic exchange and decrease in the surface potential, ψ_0, caused by charge neutralization, marked specific adsorption of Al^{3+} occurs at active sites of pectin macromolecules (COO^-).

The most unfavourable proved to be a mixture with approximately equal shares of Al^{3+} and Ca^{2+} (Table 2, compounds III and IV). Lower strenght of bonding ions in this case, can be explained by the mutual competition of Ca^{2+} and Al^{3+} for the same adsorption site (COO^-) on the surface of pectine macromolecules. This is most likely because of phenomenon that occurs in the presence of salts which differ in their physical and chemical properties. This phenomenon is known in literature as "ion antagonism", when the coagulation ability of the salt mixture is usually less than coagulation capabilities of individual components [37].

The effect of ion size ratio was observed at ion valence ≥ 2, most likely due to small concentrations of these ions and a small charge of pectin macromolecules.

As for the pure salts, also in the case of mixtures, the compound P_2 showed better cation-binding characteristics in relation to the product P_1 ($CBC_{T(P2)}$ = = 2.37×$CBC_{T(P1)}$). This is as expected, since the product P_2 has a higher content of galacturonic acid (72.24%), a lower degree of esterification (39.50) and a higher molar mass, *i.e.*, greater length of polygalacturonic chains (119048 g/mol).

Based on these studies it can be concluded that in the presence of a mixture of Al^{3+} and Ca^{2+}, binding mechanism of ions and mechanism of discharge of pectin macromolecules are more complex. In addition to the concentration, size, and charge of ions, the pH of the solution, the number of binding sites on the surface of pectin macromolecules and other factors play a role as well. These are, above all, ion competition for the same adsorption site, the possibility of partial dehydration of ions and the possibility of overlapping hydration layers of ions in the Stern part of the EDL.

In the case of mixtures, GCSG model was proposed to illustrate the accomodation and interactions of Ca^{+2}, Al^{+3} and H^+ in the EDL (Fig. 1.)

In the sugar industry in clarification stage of sugar beet juice, about 2.2%, w/w, CaO is used (calculated to the mass of juice). Extracted sugar beet juice contains about 14%, w/w, of dry matter or 15 g_{CaO}/100 g_{DM}. Calculated to the pectin mass that represents about 60% of dry matter, content of juice is about 9 $g_{CaO}/g_{pectins}$. This means that the amounts of $Al_2(SO_4)_3$ and $CaSO_4$, determined in this study, individually or in mixtures, are significantly lower (142–710 mg per g pectin) compared with the amount of conventional coagulant CaO.

CONCLUSION

Multivalent cation Al^{3+} exerts a greater influence on the zeta potential of pectin than divalent cation Ca^{2+}. The binding of Ca^{2+} and Al^{3+}, appeared to be regulated by following mechanisms:

- elctrostatic bonding with a small share of specific adsorption (Ca^{2+}),
- surface complexation, solely through the mechanisam of specific adsorption, with a small portion of electrostatic bonding (Al^{3+}) and
- competition of ions for adsorption sites (mixtures of Ca^{2+} and Al^{+3}).

Compared to conventional process where approximately 9 g CaO per g of pectin is used, the amount of $Al_2(SO_4)_3$ and $CaSO_4$ (in the form of mixtures or pure salt) were significantly lower, ranging in the interval 142–710 mg per 1 g of pectin.

GCSG model has been proposed to illustrate the placement and interactions of Ca^{2+}, Al^{3+} and H^{+} on the surface of the pectin particles.

Control of the zeta potential and appropriate dosing of Ca^{2+} and Al^{3+}, could very efficiently remove the pectin from sugar beet juice. The significance of this method is that it achieves significantly higher cleaning efficiency of sugar beet juice compared to the conventional method. With certain improvement in techniques and methods of work and further study of the electrokinetical phenomenon, better results could be obtained.

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

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IZVOD

VEZIVANJE ALUMINIJUMOVIH I KALCIJUMOVIH JONA SA PEKTININIMA SOKA ŠEĆERNE REPE – MODEL DVOJNOG ELEKTRIČNOG SLOJA

Tatjana A. Kuljanin[1], Lidija R. Jevrić[1], Biljana Lj. Ćurčić[1], Milica R. Nićetin [1], Vladimir S. Filipović[1], Jasna P. Grbić[2]

[1]Tehnološki fakultet, Univerzitet u Novom Sadu, Srbija
[2]Naučni Institut za prehrambene tehnologije, Univerzitet u Novom Sadu, Srbija

(Naučni rad)

U industriji šećera, u fazi čišćenja soka šećerne repe, najčešće se koristi CaO u obliku $Ca(OH)_2$. Količine upotrebljenog kreča su jako velike i iznose 1–3 mas.% na suvu masu šećerne repe. $Ca(OH)_2$ može prouzrokovati neželjen proces alkalizacije zemljišta u neposrednom okruženju fabrike šećera. Izneta je teorijska osnova nove metode čišćenja soka šećerne repe koja se bazira na primeni soli $Al_2(SO_4)_3$ i $CaSO_4$ kako čistih, tako i njihovih smeša u cilju smanjenja količine otpadnog materijala. Proučavana su dva model-rastvora pektina čija koncentracija odgovara srednjoj koncentraciji pektina u soku šećerne repe (0,1 mas.%). Koristeći elektroforetsku metodu merenja ceta potencijala, utvrđeno je da Al^{+3} imaju bolji afinitet vezivanja sa pektinskim makromolekulima u poređenju sa jonima Ca^{2+}. Utvrđeno je da čiste soli $Al_2(SO_4)_3$ i $CaSO_4$ poseduju bolje karakteristike vezivanja jona nego njihove smeše. Smanjena jačina vezivanja jona u slučaju smeša može se objasniti međusobnim takmičenjem Al^{+3} i Ca^{+2} za adsorpciono mesto (COO^-) na površini makromolekula pektina. Najnepovoljnije su se pokazale smeše sa približno jednakim udelima Ca^{+2} i Al^{+3} (antagonizam jona). U poređenju sa klasičnim postupkom čišćenja soka šećerne repe gde se koristi približno 9 g CaO po g pektina, ustanovljene količine $Al_2(SO_4)_3$ i $CaSO_4$ (u vidu smeša ili čistih soli) su znatno manje i kreću se u intervalu od 142–710 mg po g pektina. Korišćen je *Gouy–Chapman––Stern–Graham*-ov (GCSG) model dvojnog električnog sloja da bi se prikazala raspodela Al^{+3} i Ca^{+2} na površini makromolekula pektina. Ustanovljeni su sledeći mehanizmi razelektrisanja pektinskih makromolekula: elektrostatičko vezivanje (Ca^{+2}), površinska kompleksacija – isključivo preko mehanizma specifične adsorpcije (Al^{+3}) i kompeticija jona za adsorpciono mesto (smeša Ca^{+2} i Al^{+3}). Kontrolom zeta potencijala uz pravilno doziranje $Al_2(SO_4)_3$ i $CaSO_4$, moglo bi se postići efikasnije uklanjanje pektina iz soka šećerne repe u poređenju sa konvecionalnom metodom. Predloženi koagulanti su povoljni ne samo iz ekonomskih razloga, nego i zbog očuvanja životne sredine. Preporučuje se delimična ili potpuna zamena tradicionalnog koagulanta CaO sa predloženim koagulantima $Al_2(SO_4)_3$ i $CaSO_4$.

Ključne reči: Pektini • Šećerna repa • $Al_2(SO_4)_3$ • $CaSO_4$ • Zeta potencijal • Dvojni električni sloj