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$CaO\&CaSO_4$ and $CaO\&Al_2(SO_4)_3$ as Pectin Precipitants–Model of Overlapping Diffuse Layers

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Abstract

This work is concerned with the theoretical basis of novel sugar beet juice purification method using binary systems $CaO\&CaSO_4$ and $CaO\&Al_2(SO_4)_3$. The Gouy–Chapman–Stern (GCS) model of overlapping of diffuse layers of EDLs on pectin surface and that on Ca^{2+} and Al^{3+} ions, theoretically explains this method. The change of the zeta potential was used to quantitatively indicate overlapping of diffuse layers. For the experiment two model solutions of pectin (0.1 % w/w) were prepared, while the concentrations of $CaO\&CaSO_4$ and $CaO\&Al_2(SO_4)_3$ in the range of 50–500 g dm^{-3} were used. The greater decrease in the absolute value of zeta potential indicated greater overlapping of diffuse layers between pectin particles and Ca^{2+} and Al^{3+} ions and faster coagulation of pectin. The overlapping degree increased with increased concentration of these binary systems. Pectin with a greater surface charge and multivalent Al^{3+} from $CaO\&Al_2(SO_4)$, exerted a greater impact on the zeta potential. Optimal quantities of the applied binary mixtures were as follows: 256–640 mg g^{-1} pectin. This is much lower than CaO commonly used in the conventional process of sugar beet juice purification (about 9 g g^{-1} pectin).

Keywords

calcium oxide, aluminum and calcium sulfates, pectin, zeta potential

1 Introduction

In sugar industry there is a problem of the presence of non-sugar matters in the sugar beet juice. About 60 % of non-sugar matters in beet juice are pectins. Due to the dissociation of carboxylic acid groups of galacturonic acid, pectic substances have the negative charge. These groups can take a part in the binding of polyvalent cations from various compounds [1-4]. Ca^{2+} ions have low efficiency of binding with pectin [5-7]. It is known that Ca^{2+} ions have a large dehydrating effect. This is, besides discharging, an important prerequisite for sedimentation of pectins [6, 8]. On the other hand, Al^{3+} ions have high binding affinity with organic matter because they give the hydrolysis products of high charge [9, 10]. The more dense the charge, the more hydrolysis take place. The adsorption of the metals in the multi-element system differs from their corresponding behavior in the single–element system. The mobility of metal ions in various colloidal solutions is governed largely by competitive adsorption and desorption reactions at solid–liquid interfaces [11-15]. Competitive effects of the trivalent metal ions are expected to be more pronounced than in the case of divalent metals. It can be expected that increasing the amounts of the more strongly bonded Al^{3+}, reduced the number of sites available for Ca^{2+} ions adsorption [14, 15]. From the literature is well known beneficial effect of SO_4^{2-} anions on the coagulation of colloidal particles. By comparing the binding efficiency of the $CaSO_4$ and $CaCl_2$ with pectins under the same experimental conditions, it can be seen that the Ca^{2+} cations bounded with SO_4^{2-} anions have no better affinity to complexation than Ca^{2+} cations bounded with Cl^- anions [16]. In the previous works [17, 18], the amounts of $Al_2(SO_4)_3$ and $CaSO_4$, which were used to precipitate pectin, individually or in mixtures, were significantly lower compared with the amount of conventional coagulant CaO. Even better results were achieved using $CaSO_4$ in combination with cationic polyelectrolytes. Also, these flocculants showed good results in the in classical method of sugar beet juice clarification (application of CaO) [18].

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It is known that in a liquid environment, the electrical double layer (EDL) surrounding colloid particles. EDL exists as two parts: a Stern layer where the ions are strongly bonded to the particle surface and a diffuse layer where they are less intensely associated. Adsorption, distribution and the competition of Ca^{2+} and Al^{+3} ions on the pectin surface can be explained in accordance with the Gouy–Chapman–Stern (GCS) model of overlapping of diffuse layers [19-22]. From the Stern layer to the diffuse layer, the charge density of cations gradually decreases, but that of anion increases. Within the diffuse layer there is a notional boundary in which the ions form a stable entity [17, 18]. The potential at this boundary (shear plane) is easily measurable size and it is known as the Zeta potential (ζ). Therefore, the change in zeta potential of colloidal particles can be used to characterize the interaction degree of diffuse layers between oppositely charged particles. Moreover, the oppositely charged polyvalent ions can decrease the thickness of EDL and consequently cause a reduction in the zeta potential. In addition to the ion concentration, the valence of the surrounding cations contributes significantly to the reduction of the thickness of EDL and the zeta potential [23, 24].

In the research of soil colloids and Fe/Al oxides, based on the change of zeta potential, the results confirmed the interaction of the diffusion layers as related to the surface charge characteristics; i.e., the higher the charge density of the colloid particles, the stronger the interaction of the diffusion layers between them [24, 25]. It was concluded that the interaction of the diffusion layers increases with the increase in the ratio of soil colloids to Fe/Al oxides. The interaction also relates to the charge characteristics on the Fe/Al oxides.

Unlike previous GCS models that represented the phenomenon of discharging to the surface of pectin particles [17], a novelty in this work is the application of a different model based on overlapping of EDL diffuse layers between pectin particles and surrounding ions.

2 Materials and methods

2.1 Materials

Pectin preparations were extracted from pressed sugar-beet slices (*Beta vulgaris* L. ssp. *vulgaris* var. *altissima* Doell) obtained in the industrial processing of sugar beet (factory Žabalj, Serbia). The lime, in the form of white, dry powder provided from "Jelen Do", Požega, Serbia, purity of 90.0 % – 98.50 % CaO and 1 % - 2 % MgO was used for preparation of the binary solutions with de-ionized water. Also, the salts, $CaSO_4$ and $Al_2(SO_4)_3$ in the crystal hydrate form ($CaSO_4$ x $2H_2O$ and $Al_2(SO_4)_3$ x $18H_2O$), produced by "ZorkaPharma", Šabac, Serbia, were used for preparation binary solutions. Purity of both salts was 99.0 % w/w. For the adjustment of pH values of solutions, aqueous solutions of HCl and NaOH were used [26]. The pH of the solutions was measured on a pH Meter MA 5740, "Iskra", Kranj, Slovenia. The pH of solutions with $Al_2(SO_4)_3$ was corrected at 7 before each experiment, using the equivalent amount of Na_2CO_3.

2.2 Methods

2.2.1 Isolation of pectins

Two pectin preparations were isolated by extraction in acidic conditions in accordance with a standardized laboratory procedure [27]. Pectin preparations were extracted under the following conditions: pH = 1, t = 85 °C, τ = 2.5 h; pH = 3.5, t = 85 °C, τ = 2.5 h. Extraction procedure given at Fig. 1 has been schematically presented by Kuljanin et al. [18]. Extraction of each preparation was carried out three times. Due to differences in the extraction conditions, the pectin preparations were of different composition and degree of esterification.

2.2.2 Pectin characterization

The dry matter content was determined gravimetrically by drying the samples within 12 hours at 105 °C. The purity of pectin preparations was determined by the content of galacturonic acid. Titration method was applied [28]. Degree of esterification was calculated using equivalents of free (modified method of Deuel) and esterified carboxy groups (method of Shultz) [28].

2.2.3 Zeta potential

The zeta potential of particles in a pectin solution was measured by means of electrophoresis using a Zeta Meter ZM-77 [29]. The process of measuring of zeta potential and general arrangement of Zeta Meter Unit was explained in the work [30].

2.2.4 Plan of experiments

Two model-pectin solutions were prepared by dissolving 1 g of pectin preparation in 250 cm^3 of distilled water and leaving it overnight. For each measurement, 50 cm^3 of pectin solution was taken. Binary solutions were obtained by dissolving 0.5 g of CaO and 0.5 g $CaSO_4$ or $Al_2(SO_4)_3$ in 200 cm^3 distilled water. Ten flasks filled with the model solutions were treated with the binary solutions: (i) CaO&$CaSO_4$ (1:1 w/w) and (ii) CaO&$Al_2(SO_4)_3$ (1:1 w/w).

A series of precipitant concentrations in the range from 50 to 500 mg dm^{-3} were prepared [9, 17, 18]. Then, the solutions were stirred for 30 min on a high-speed magnetic stirrer (TEHNICA, Železniki, MM-520, Slovenia) at 500 rpm. After that, the solutions were slowly manually stirred for 5 min and left to rest another 5 min. The process of precipitation lasted for 10 h, so as to enable precipitants to react with pectin [27]. The zeta potential of clear part of the solution was measured. All measurements were repeated three times. The measurements were carried out at pH 7.

3 Results and discussion

3.1 Scheme of the electrical double layers overlapping

The schematic illustration of the EDL on the surface of pectin in the presence of $CaSO_4$ and $Al_2(SO_4)_3$ is presented by the Kuljanin et al. [17]. In this work, Fig. 1 displays the schematic representation of the EDLs of negatively charged pectin particles and Ca^{2+} and Al^{3+} ions before (a) and after (b) the overlapping based on the GCS model [19]. GCS model is characterized by the localization of ions, both in the fixed (Stern) layer and in a diffuse layer of the solid-liquid interface. For the purpose of better clarity, EDLs of other ions present in the solution were not shown in Fig. 1.

Fig. 1 presents presented the change in electrical potentials (surface potential, Ψ, and electrokinetic or zeta potential) on the surface of pectin particles before (a) and after (b) the overlapping of the diffusion layers. The surface potential of pectin particles (ψ_p) occurs due to the presence of COO^- groups. According to the GCS model, the electrical potential change in Stern layer is linear. After overlapping of the diffuse layer on the pectin surface with the diffuse layer of Al^{3+}/Ca^{2+} ions, the absolute value of the surface potential of pectin particles slightly dropped (ψ_{p1}, Fig. 1b) as a consequence of charge neutralization on pectin surface. In the diffuse layers of pectin particles and Al^{3+}/Ca^{2+} ions, an exponential potential change is observed in accordance with the Boltzmann distribution [31]. Shear planes on the Al^{3+}/Ca^{2+} ions and pectin surface are presented with dashed lines. After overlapping of diffuse layers between pectin and Al^{3+}/Ca^{2+} ions, under the assumption on the occurrence of charge inversion from "-" to "+", the change in zeta potential is marked as $\Delta\xi$.

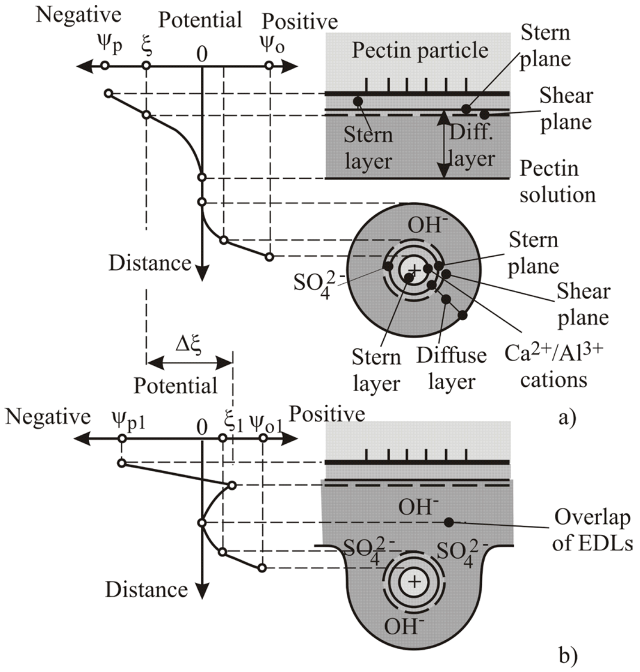

Fig. 1 Schematic illustration of the electrical double layers of negatively charged pectin particles and Ca^{2+}/Al^{3+} ions, before (a) and after (b) the overlapping based on the GCS model.

3.2 Surface charge characteristics of pectins

Isolation of pectin from fresh sugar beet was performed with the aim to obtain pectins similar to those appeared in sugar beet processing. Due to differences in the extraction conditions, the obtained pectin preparations had a different composition, degree of esterification and different structural features of pectin macromolecules (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 the diffuser, reported in literature [32]. As explained, the proton and metal ion binding can be influenced by the surface charge (macroionic effect). The surface charge characteristics of pectin affect the interaction degree of the diffusion layers between pectin and Ca^{2+}/Al^{3+} ions in solution. The equivalent of free $-COOH^-$ groups are responsible for the pectin surface charge (Table 1). The degree of esterification of pectin preparations is inversely proportional to the cation binding capacity [17]. The quantity of CaO&$CaSO_4$ and CaO&$Al_2(SO_4)_3$ needed to achieve optimum zeta potential ($\xi = 0$) was different for the pectin preparations P1 and P2. From Table 1, it can be seen that pectin preparation P2 showed slightly better coagulation properties. This is understandable, since

Table 1 Basic physico-chemical composition of pectin preparation

Pectin solution	P1	P2
Equivalent of free COOH groups, X · 10^5	16.83	24.58
The equivalent of esterified COOH groups, Y · 10^5	19.74	16.05
Content of galacturonic acid, Gal. A (%)	63.45	72.24
Degree of esterification, DE	53.98	39.50

the preparation P2 had a higher content of galacturonic acid and a lower degree of esterification. In addition to the fact that the surface complexation between metal ions and –COO$^-$ groups are facilitated at lower degree of esterification (higher amount of free COOH groups), there was an increase in the ionic exchange with the cations present in the pectin macromolecule as well as in the hydrogen bond formation. It can be reasoned out that related mechanisms are: specific adsorption (primarily for the Al^{+3} ions), electrostatic adsorption (primarily for the Ca^{2+} ions), competition between Ca^{2+} and Al^{3+} ions for adsorption sites, surface complexation and even micro-deposition of Al^{+3} and Ca^{2+} ions on the pectin surface.

3.3 Results of the measurements of zeta potential

Changes in zeta potential for two pectin solutions with different Ca^{2+} and Al^{3+} contents from binary solutions $CaO\&Al_2(SO_4)_3$ and $CaO\&CaSO_4$ (w/w : 1/1) are presented in Fig. 2. The obtained zeta potential data for binary mixtures were compared to the results from previous studies on the effects of pure, mono compounds $CaSO_4$ and $Al_2(SO_4)_3$ (thin dark blue points) [9, 17, 18]. Binary mixtures are presented with light blue points while contour lines represent the mathematical models. Investigations were performed under the same conditions for all pectin solutions.

In both cases, charge inversion, i. e. change in the sign of the zeta potential, occurred over the experimental concentration range. This means that there was an increase in the magnitude of the total charge carried by the Al and Ca ions in these mixtures (including H^+ ions from the solution). The phenomenon of charge inversion has not been yet sufficiently clarified from the physical-chemical point of view [33]. Charge inversion is schematically illustrated below Fig. 1b as a maximum (ξ_1) on the curve representing the change in the electric potential on pectin surface. For charge inversion to occur, besides a decrease in surface potential Ψo, it is necessary a specific adsorption of cations in the EDL [30]. More noticeable specific adsorption of Al^{3+} ions is in accordance with Schulze-Hardy rule and literature [12] due to ability of Al^{3+} ions to form strong covalent bonds. According to the GCS model of EDL, specific adsorption of Al^{3+} ions takes place mainly in the Stern region due to the higher density of these ions. The density of Al^{3+} ions is 2.70 g cm^{-3}, whereas of Ca^{2+} is 1.54 g cm^{-3} [9, 17]. However, the adsorption reactions are usually slower than the electro-diffusion transport processes in EDL [34]. Accordingly, it can be expected that the rate of Al^{3+} and Ca^{2+} ion distribution in the diffuse region of EDL will be higher than the rate of their adsorption in the Stern layer on the surface of pectin macromolecules.

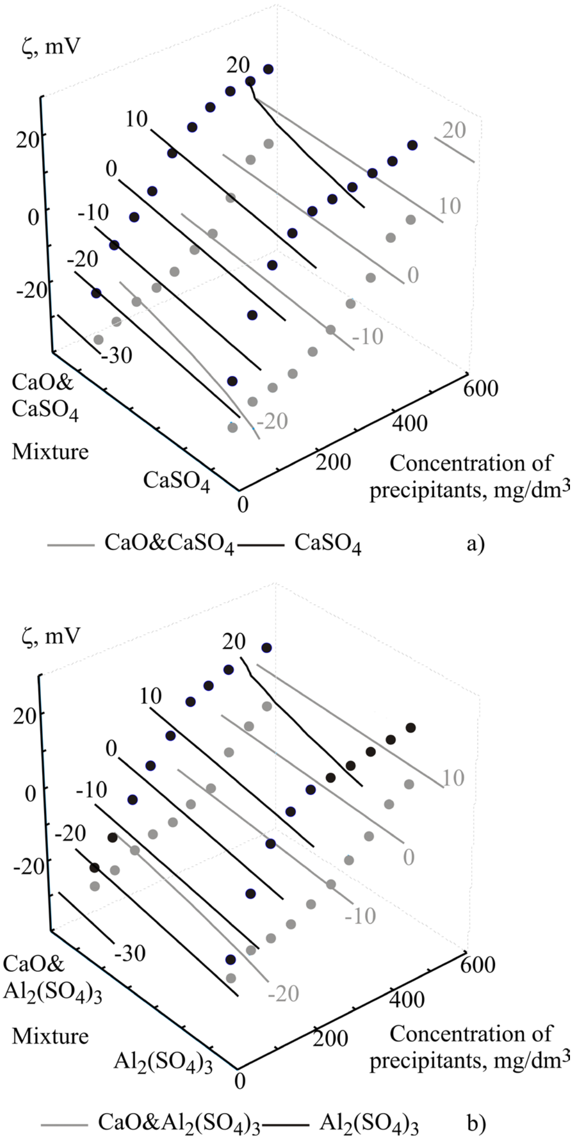

Fig. 2 (a) The influence of $Al_2(SO_4)_3$, $CaSO_4$ and mixtures $CaO\&Al_2(SO_4)_3$, $CaO\&CaSO_4$ (w/w: 1/1) on the change in zeta potential pectin solution P1, (b) The influence of $Al_2(SO_4)_3$, $CaSO_4$ and mixtures $CaO\&Al_2(SO_4)_3$, $CaO\&CaSO_4$ (w/w: 1/1) on the change in zeta potential - pectin solution P2

When the contents of Ca^{2+}/Al^{3+} ions from both mixtures are increased, then the number of adsorbed H^+ ions from solution becomes less. It is known that trivalent Al ions have a positive role in the delayed coagulation because of their hydrolysis and complexation in relatively low concentrations. Ca^{2+}, Al^{3+} ions as well as positively charged products of hydrolysis of Al^{3+} ions which failed to adsorb on the surface of pectin will attract ions of opposite charge from the diffuse layer such as OH^-, SO_4^{2-} and negatively charged products of Al hydrolysis. Consequently, there is a shift in the shear plane between the Stern and diffuse layer directed towards the diffuse layer of pectin. According to the literature data, in the presence of higher concentrations of highly positively charged hydrolysis products of Al ions, the thickness of the EDL diffusion region on pectin surface is pronouncedly reduced [30, 31]. Specific adsorption induced greater interaction of its diffuse layers with pectin particles. This indicates more overlapping of diffuse layers of pectin and Al^{3+} ions, primarily their positively charged hydrolysis products. The electrostatic adsorption and hydration of Ca^{2+} ions reduces to a lesser extent the thickness of EDL pectin, which leads to the weaker overlapping of diffuse layers of pectin and Ca^{2+} ions [35].

Based on the previous explanation, the presence of Al^{3+} ions (binary mixture $CaO\&Al_2(SO_4)_3$), would occur more efficient precipitation of pectin. In this experiment, this assumption was confirmed by attaining zero zeta potential at much lower concentration of mixture with Al^{+3} ions (190 mg dm^{-3} $CaO\&Al_2(SO_4)_3$ for pectin P1 and 180 mg dm^{-3} for pectin P2) in comparison to the mixture that contains only Ca^{2+} ions (425 mg dm^{-3} $CaO\&CaSO_4$ for P1 and 380 mg dm^{-3} for P2). The tested mixtures reduced zeta potential of pectin solution to zero point of higher concentration than the pure $CaSO_4$ and $Al_2(SO_4)_3$ (Table 2).

It means that the strength of the binding of Ca^{2+} and Al^{3+} ions in the tested mixtures with pectin, is weaker than the strength of binding of Ca^{2+} and Al^{3+} ions from pure salts $CaSO_4$ and $Al_2(SO_4)_3$.

Weaker bonding strength of ions of different valences, such as ions Ca^{2+} and Al^{3+} from $CaO\&Al_2(SO_4)_3$ compared with the Al^{3+} ions from the 100 % $Al_2(SO_4)_3$, can be explained by the mutual competition of these ions for the same adsorption site (COO^- groups) on the surface of pectin [9, 17]. This means that the adsorption of Al^{3+} ions is reduced in the presence of Ca^{2+} ions under pH neutral condition. This is most likely because of the phenomenon that occurs in the presence of compounds which differ in their physical and chemical characteristics. This phenomenon is known in the literature as "ion antagonism" when the ion bonding strength of the mixture is usually less than the bonding strength of individual ions [12].

Table 2 Quantities of $Al_2(SO_4)_3$, $CaSO_4$, $CaO\&Al_2(SO_4)_3$ and $CaO\&CaSO_4$ to achieve zero zeta potential values

Precipitants:	Preparation P1: mg dm^{-3} mg g$_p^{-1}$	Preparation P2: mg dm^{-3} mg g$_p^{-1}$
100 % $Al_2(SO_4)_3$	120 182	100 142
$CaO\&Al_2(SO_4)_3$ (w/w : 1/1)	190 288	180 256
100 % $CaSO_4$	405 610	355 490
$CaO\&CaSO_4$; (w/w : 1/1)	425 640	380 525

p-pectin

3.4 Statistical analyses

In this work, the evaluation of one-way ANOVA analyses of the obtained results was performed using StatSoftStatistica 10.0® software. Analysis of variance was performed for comparison of zeta potential for different concentrations of precipitants. Statistically significant differences for observed data were found in almost all samples, using Tukey HSD test. According to an ANOVA analysis (Table 3), zeta potential is mostly affected by the type of binary system, statistically significant at $p < 0.001$ level. The CaO concentration is also influential for zeta potential calculation.

It may be concluded that in the presence of a mixture of Al^{3+} and Ca^{2+} ions, binding mechanisms and mechanism of discharge of pectin are more complex. The adsorption could be influenced by a number of factors, such as concentration, size and charge of ions, contact time, agitation speed, temperature, pH of the solution, the number of binding sites on the surface of pectin, ion competition for the same adsorption place, the possibility of partial dehydration of ions and the possibility of overlapping hydration layers of ions in the Stern EDL layer [36]. Also, mechanism of surface precipitation is possible if there is a considerable accumulation of Ca^{2+} and Al^{3+} ions within the diffuse part of pectin electrical double layer [11].

However, it is very difficult to separate the relative contribution of the overlapping of diffuse layers and charge neutralization of pectin surface to the change of zeta

Table 3 ANOVA calculation of zeta potential

		Zeta potential	
	df	P1	P2
Type	1	0.02	0.40
C	1	3427.37^+	5604.85^+
C^2	1	124.12^+	870.61^+
CaO	1	65.03^+	270.40^+
Type × C	1	0.01	0.15
Type × CaO	1	0.22	0.10
C × CaO	1	0.01	61.97^+
Error	32	52.99	203.02
r^2		0.986	0.971

$^+$ Significant at $p < 0.001$ level, df - degrees of freedom, Type - the type of binary system ($CaO\&CaSO_4$ and $CaO\&Al_2(SO_4)_3$), C- concentration of binary system, CaO^- concentration of CaO, P1,P2 - precipitation, r^2 - coefficient of determination potential – since the overlapping of these layers between the pectin and Ca^{2+}/Al^{3+} ions (especially the hydrolysis products of Al^{3+} ions) does not last long as it leads to mutually coagulation [19, 35].

The quantity of investigated binary systems $CaO\&CaSO_4$ or $CaO\&Al_2(SO_4)_3$ used as precipitants, would be significantly reduced (approximately from 14 to 35 times) compared with the quantity of lime used in the classical sugar beet juice processing where is approximately used 9 g pure CaO per g of pectin. With this, significant economic and environmental effect would be achieved. However, more reliable results require additional testing under industrial conditions.

4 Conclusion

The assumption that an equal amount of CaO and $CaSO_4$ or $Al_2(SO_4)_3$ will have an effect on the improvement of sedimentation characteristics of lime as a conventional precipitant for separating pectin in sugar beet juice, has been confirmed.

The mechanism of action of the $CaSO_4$ and $Al_2(SO_4)_3$ is explained using a GCS model of overlapping of diffuse layers between pectin particles and surrounding ions. The zeta potential method has proved to be useful to monitor discharging of pectin particles.

The use of these compounds combined with CaO would reduce the consumption of lime and concomitantly reduce the amount of energy necessary to obtain CaO in furnaces for lime burning, thus contributing to a significant economic effect.

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