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Effect of Hydroxyapatite Nanoparticles on the Behavior of Calcium, Silicate, and Phosphate in Cane Juice Treatment

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Abstract

In this study, hydroxyapatite nanoparticles (HAP), Ca5 (PO4)3(OH), were synthesized via wet-chemical precipitation methods. Physicochemical properties of nanoparticles were characterized using high-resolution Transmission Electron Microscope (HR-TEM), X-ray Diffraction (XRD). The application of the synthesized adsorbent in clarification of mixed cane juice "MJ", was investigated via batch experiments on a pilot scale. The effect of (HAP) on the behavior of dissolved nonsugars "calcium, silicate, and phosphate compounds", compared with the effect of the traditional sulfitation process was evaluated. The results show a significant difference in the removal of silica, 51.34% with using hydroxyapatite nanoparticles, whereas 36.25 % removal with the traditional sulfitation method. And 38.3% lower in the remaining calcium content in the clarified juice CJ was achieved. Moreover, 16 ppm of P_2O_5 content in CJ after using hydroxyapatite nanoparticles, compared with 6 ppm P_2O_5 in the CJ resulted from the traditional sulfitation process. These results mean a predicted soft scale formed in the evaporators, overcoming the hard-to-boiled massecuite "HTB" phenomenon, and lower sugar losses in final molasses. The results were discussed via, the physicochemical properties of hydroxyapatite nanoparticles, that affect coagulation and flocculation of flocs formed.

Keywords. Hydroxyapatite nanoparticles; HAP; Clarification; Mixed juice; Clear juice.

Introduction

The application of nanomaterials in the clarification processes in several industrial sectors has attracted significant attention. Clarification has been and still the key for development in sugar industry. Since it has a significant impact on the yield and quality of produced sugar. Despite the achieve of substantial improvement of cane and beet quality, still a relatively high content of non-sugar components (i.e. impurities) remains in the raw juice as produced from cane and beet. The presence of these non-sugars requires a rather complicated and costly purification process, in order to enable the production of white sugar of the right quality, as well to limit any unnecessary sugar loss to molasses (Madsen, 2009).

Traditional methods Treatment with lime in water or syrup (saccharate) solution remains the basic method of clarification, normally termed defecation, where the lime has been the universal chemical for neutralization of the acidic juice , and the process varies in the method and temperature of addition.

Variations of simple defecation have always the aim of lowering the color and turbidity of the clarified juice**.** In addition to simple defecation there are three traditional methods known as sulfitation, phosphatation and carbonatation among of all lime is used as a main clarification agent.

- In sulfitation, this combines treatments with sulfurous acid (from SO_2 gas) and treatment with lime solutions. Sulfitation may be carried out on cold or warm juice, as well, on evaporator syrup (double sulfitation).
- In phosphatation, small amounts of soluble phosphate may be added to juices to improve simple defecation. heavier addition would imply hosphatation" as a distinguishing term. Mainly though phosphatation techniques are applied to the clarification of raw and refinery syrups.
- In carbnatation, limed juice treatment with carbon dioxide followed by additional lime for neutralization is termed "carbonatation ".

The main goals of clarification is to remove the coarse and colloidal materials without losing sugar. These goals must be achieved via several control points involves:

- Formation flocs to trap all suspended matter which can be settled at a satisfactory rate .
- Provide conditions of temperature, pH and ion concentration which will maximize the precipitation of soluble impurities from the juice .
- Produce clarified juice of high quality, with a minimum turbidity, color and a low calcium (Ca^{++}) content. and carry out the above at minimum cost, minimum residence time, minimum loss of sucrose, and minimum formation of color (Rien, 2007).

A variety of chemical and physical reactions occur during the clarification process and these include:

- Coagulation/precipitation of amorphous calcium phosphate; denaturation of proteins, gums, pectin's and waxes; (Doherty et al., 2002).
- Inversion of sucrose due to the effect of both pH and temperature.
- Degradation of reducing sugars to organic acids caused by high pH and temperature.
- Hydrolysis of starch by natural amylase in sugar cane juice.
- Formation of color species through enzymatic and non-enzymatic reactions between natural colorants, color precursors and sugars.
- Flocculation of macro-flocs via particle bridging of calcium phosphate flocs impurities and copolymer flocculant , and adsorption of waxy-like materials and suspended solids with precipitate .

The aim of the present study was using prepared hydroxyapatite nanoparticles (HAP) as a novel clarifying agent in cane mixed juice clarification, and investigate its effect on the removal of inorganic (calcium, silicate, and phosphate) nonsugars, adding value to sugar production from sugar cane under condition of Egyptian sugar industry.

Materials and Methods

Preparation of hydroxyapatite nanoparticles

Hydroxyapatite Nanoparticles (HAP), $Ca_5(PO_4)_3(OH)$, were synthesized via wet-chemical precipitation methods as described by **Salah *et al.* (2014).** Firstly, 0.05 M calcium hydroxide ($Ca(OH)_2$, (Sigma-Aldrich)) was dissolved in deionized water under vigorously stirred at 1200 rpm/min for 2 h at 25 °C. 0.03 M of orthophosphoric acid (H_3PO_4, 85% solution, (Sigma-Aldrich)) was added to the calcium hydroxide solution at a rate of 1.5 ml/min under continuous stirring. At the end of the process, the hydroxyapatite nanoparticles precipitate was washed with deionized water three times and dried in an oven at 100 °C for 2 h.

- The suspension solution of 5 baumme from nano-clarifying agent was prepared to be used in the clarification ,where the dried powder was added at a rate which provided good dispersion to prevent agglomeration.
- Polarization of sugar juice was determined using polarimeter PolAAr 3001, England.
- Silica was determined as molybdosilicic acid using colorimetric method according to laboratory manual of ESIIC (1990).
- Calcium was determined by titration with EDTA according to ICUMSA method GS8/2/3/4-9 (2000).
- Batch settling test, initial settling rate, and final mud level were determined according to operating procedure for the SRI Settling test Kit method, SRI (1999).
- Turbidity of the CJ was determined by measuring the absorbance (A) at 975 nm in 1 cm cuvette cells against Mille-Q water (Luoisiana . 2009).

- The brix of juice samples was measured at ambient temperature using a digital refractometer (PTR 46, Index Instruments Ltd., UK).
- The pH of juices was measured using a pH/mv/temp pH meter (Jenway 3510, England) (027500).
- The % Sucrose or Pol in cane juice is typically determined by measuring the positive rotation of polarized light via the double polarization method, using a PolAAr 3001 (Optical Activity Ltd., UK).
- Phosphate, was determined colorometrically using ammonium molybdate according to laboratory manual for South African Sugar Factories(1999).
- Lime as milk of lime of baumme " ± 6" obtained from sugar mill.
- Anionic flocculent used in experiments was Magnafloc $LT_{27,}$ Acrylamide/ acrylate co –polymer, Samoral, MW18 x 10^6, and degree of hydrolysis 27. Flocculant solutions of 0.1 %(w/v) are more viscous. for good preparation method, disperse and dissolve the flocculent powder in deionized water by gentle stirring at a low shear rate of 50 rpm for 3 hr.

Hydroxyapatite nanoparticles (HAP) Clarification Procedure:

HAP clarification process has performed (Fig .1) according to the following steps :

30 L of MJ delivered to reaction tank, sample of 500 ml mixed juice was taken for analysis. Nano clarifying agent "HAP" added with 300 ppm dosage. Milk of lime "$Ca(OH)_2$ added to pH 7.5 at 75 ^{o}C, boiling at 103 ^{o}C. Allowing flashing of juice, 3ppm of Anionic flocculent injected to the juice after flashing, then settling in the clarifier through retention time 1.5 h. Sample of 500 ml clarified Juice collected as a sample for evaluating the efficiency of nano clarification. In each test the evaluation based on the comparison between values of brix, purity, Ca % brix, P_2O_5 ppm, SiO_2 ppm, turbidity, color and settling behaviour of clarified juice resulted from nano clarification and sulfitation were measured

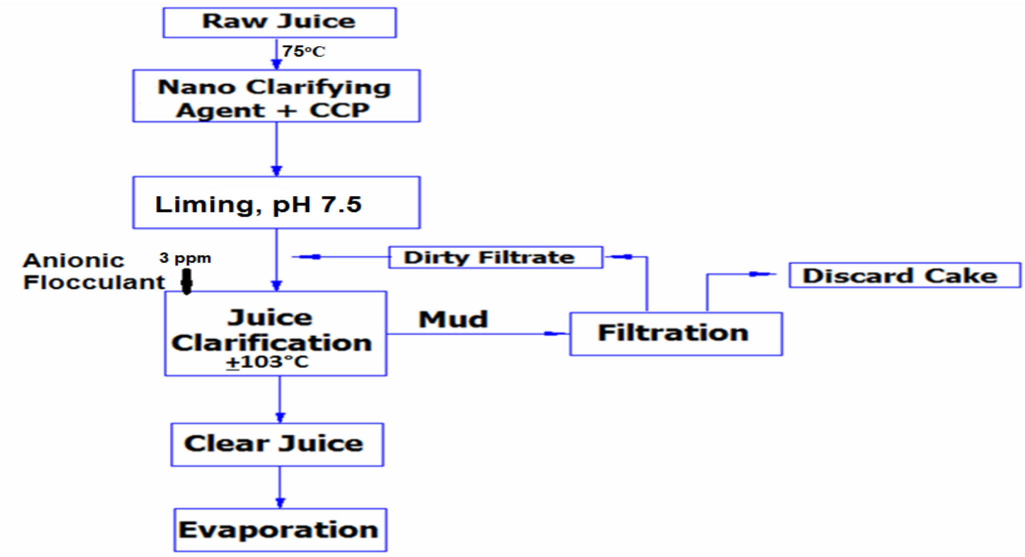

Fig. 1. Nano clarification process flow sheet

Sulfitation process

Sulfitation clarification process in factory (fig.2) was followed according to the following steps:

- Row juice delivered to reaction tank .
- Temperature of juice adjusted to 73 °C.
- Sample of juice before clarification has taken to pH, temperature, P_2O_5, silica , brix, purity and calcium determination.
- Phosphoric acid " 5% w/v" was added until 300 ppm P_2O_5 content in juice.
- In the clarification tower, lime " $Ca(OH)_2$ " was added to pH 9.8, flowed with injection of SO_2 gas until pH 7.3 . Allowing retention time 6 min for complete reaction between chemicals added.
- Temperature was raised to 103 °C.
- Flashing of Juice .
- Settling in clarifier via retention time 1.5 hr.

- About 500 ml of clarified juice were collected for analysis of brix. , pH , purity, turbidity, ash % brix , SiO_2 ppm, P_2O_5 ppm , colour, CaO % brix, and settling behavior .

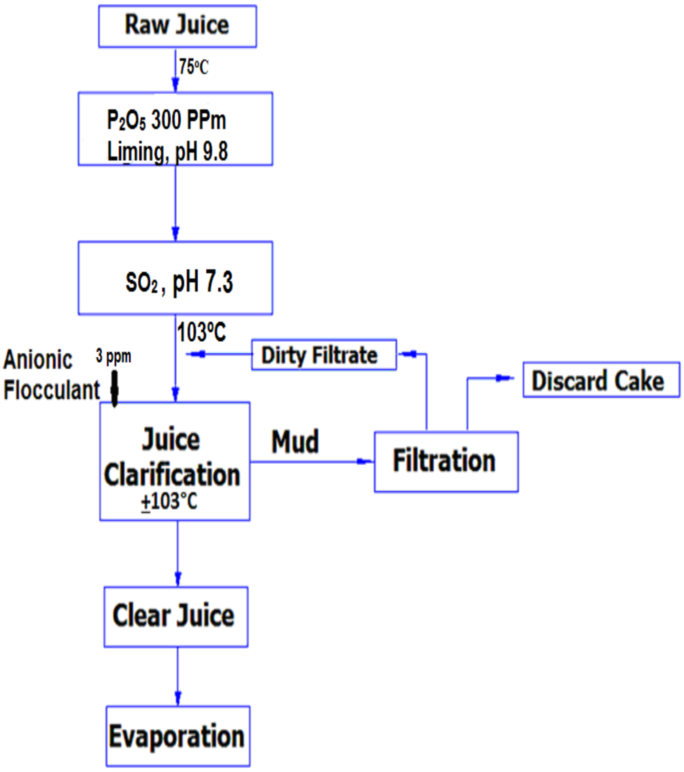

Fig. 2: Flow sheet of sulfitation process

Statistical Analysis

This was undertaken using Microsoft" Office Excel (2007). Statistical differences between two sets of data assuming equal variances were determined using T-test at the 5% probability level.

Results and Discussion

Characterization of synthesized calcium nanoparticles

a. Transmission electron microscopy (TEM)

Fig.3 displays a typical TEM image of hydroxyapatite nanoparticles (HAP). As clearly seen, HAP appeared in the form of thin short nanorods 12 nm in diameter and 20–40 nm in length. Apparently, there was a distinct separation between these HAP nanorods with a little aggregation, which might result instantly in the preparation procedure before the TEM measurements.

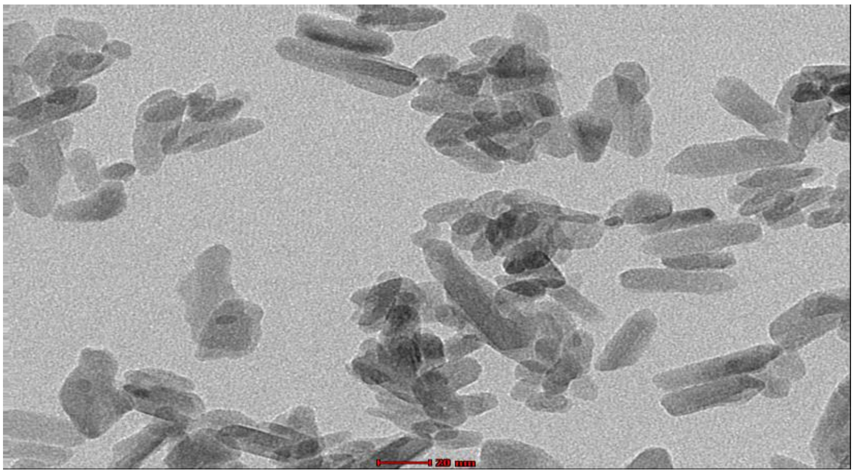

Fig.3: HR-TEM for calcium phosphate hydroxide nanoparticles

b. X-Ray diffraction (XRD)

The XRD was used to reveal the crystallography of the prepared HAP as illustrated in Fig.4. Interestingly, HAP exhibited distinct peaks at 2θ= 25.8°, 31.8°, 32.2°, 34.0°, 39.7° and 49.5°, corresponding to the diffraction planes (0 0 2), (2 1 1), (1 1 2), (2 0 2), (1 3 0) and (2 1 3), respectively. These results are in agreement with reference pattern card (JCPDS no.01-073-8417) and confirmed that the synthesized hydroxyapatite were of crystalline nature.

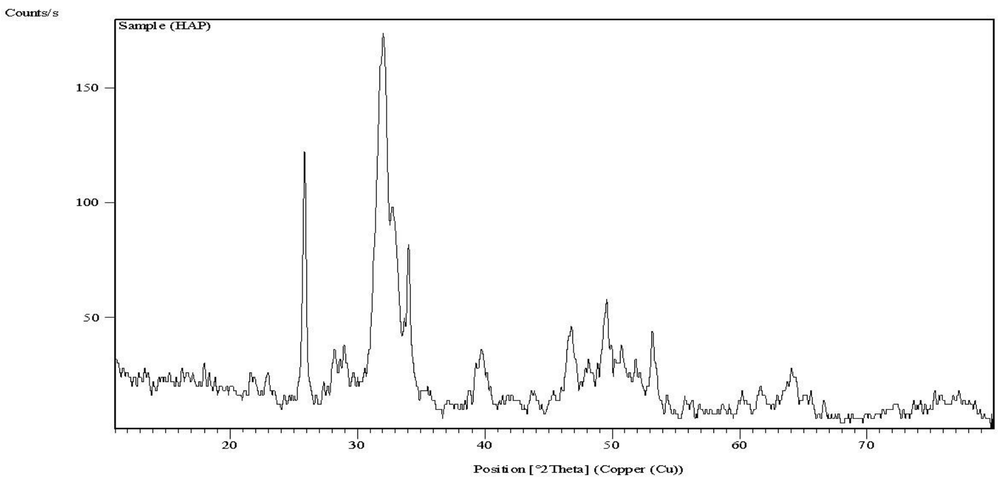

Fig .4: The graph represents the XRD pattern of synthesized nanoparticles shows the formation of hydroxyapatite nanorods on the comparison of their

XRD patterns with the standard pattern of $Ca_5(PO_4)_3(OH)$. Card number: (JCPDS no.01-073- 8417)

Dosage test

Using different dosages (200,300,500) of HAP clarification (fig. 1) were conducted. for determining the dosage which gives the best clarification performance, Turbidity, final mud level, initial settling rate of flocs, colour and levels of inorganic ion for untreated MJ & clarified juice CJ were measured .

Table 1: Results of M.J clarification at different dosage of Nano clarifying agent

Process Sample No.	M.J.	C.J at		
		200 ppm	300 ppm	500 ppm
Initial settling rate cm /min	-	22	30	29
Settling behavior	-	Moderate	Fast	Fast
Final mud level(%)	-	20% * ± 2	10%* ± 1	12% ± 2
Turbidity of CJ	-	24*	12*	14
CaO % Bx	0.66 ± 0.03	0.74 ± 0.04	0.71 ± 0.02	0.74 ± 0.03
P_2O_5 (mg/l)	160 ± 6	22 ± 3	18 ± 2	20 ± 4
SiO_2 (mg % g Bx)	238 ± 13	168* ± 10	119* ± 9	125 ± 7
Juice pH	5.4 ± 0.1	6.7 ± 0.1	6.7 ± 0.1	6.6 ± 0.1
Purity.	83.8 ± 0.3	83.4 ± 0.2	83.6 ± 0.1	83.6 ± 0.2
Color	-	10013 ± 170	8903 ± 150	8703* ± 200

***Correlation are significant at $p < 0.05$**

The effect of changed doses up on settling rate behavior, turbidity and the level of inorganic ions were followed (Table 1), 300 ppm added dosage from nano clarifying agent is the most proper one, since it resulted in the lowest final mud level (12 %) and the lowest calcium and silicate levels (0.71% and 119 ppm, respectively) in the clear juice.

Relatively high CJ turbidity results in each case, in spite of fast settling behavior with dosages 300 and 500 ppm this may due to the small flocs which attributable to high impurity load of M.J and the inability of the flocculant to effect bridging of the calcium phosphate flocs, thus using of cationic flocculant before addition of nano clarifying agent will facilitate the aggregation of colorant to be adsorbed on the surface of nano-hydroxyapatite.

- The color of C.J resulted from this process also adaptively moderate, where the dosages 200 and 300 ppm resulted CJ color" 8903and 8703 respectively ".
- A good advantages for nano clarification technique is the resulted moderate P_2O_5 level in the C.J at each dosages, (20, 18 and 20 respectively) this will followed and be explained later in detail.

Effect of HAP on inorganic ions

It has establish that high levels of inorganic components, particularly silicon, and calcium have been associated with scaling issues in the evaporators (Walthew et al., 1998). The high level of calcium and low level of phosphorus could imply calcium phosphate precipitates could be forming from the Ca^{2+} ions added from lime saccharate, hence inadequate phosphate ions are present to interact with excess calcium derived from trash which may hinder downstream processes.

For investigating the difference between HAP clarification and sulfitation clarification processe, several experiments in pilot scal, were conducted using sulfitation processe and clarification in the presence of HAP .

The comparison between these processes was followed in terms of calcium, silicate and phosphate behavior in each case .

Effect of HAP clarification on silica behavior

Table 2 shows a significant difference (P value < 0.05) in the percentage removal of silica from M. J to CJ after each clarification, a higher removal percentage (51.34 %) in case of HAP, this may explained according to the following:

- A higher content of P_2O_5 and high surface area exhibited by HAP which affects the stability of colloidal organosiliceous compound. Using co-polymer as a clarifying agent in case of HAP– clarification leads to precipitate a large scale of coloring matter before contacting with silica. It is well established that cane juice contains many phenolic compounds (Lionnet & Walth 2004).
- More open floc structures in the case of "HAP" clarification. Loosely bound and highly branched flocs are attributable to effective trapping of micro-flocs, and adsorption of particle impurities onto the surface of the floc network.
- In the case of using nano-hydroxyapatite, calcium phosphate has $Ca_5(PO_4)_3(OH)$ form. this different morphological structure appeared in the form of thin short nanorods, exhibits excellent adsorption ability because its large specific surface area, and thus an additional improvement in the performance of clarification process.

Table 2 : Effect of Nano & sulfitafion clarification on silica content

Process Sample No	M.J.	Process followed	
		Sulfitation	Nano clarification
1	220 ± 18	145 ± 11	105 ± 11
2	240 ± 18	151 ± 11	119 ± 9
3	225 ± 20	140 ± 13	112 ± 11
4	248 ± 22	160 ± 10	115 ± 12
5	220 ± 19	140 ± 9	110 ± 8
% Removal	-	36.25%	51.34%

- A low quantity of lime used in the case of nano clarification leads to a lower silica content deliver into the juice.
- In cane sugar juice, although binding of microflocs most likely proceeds primarily by calcium bridging of the charged acrylate group (Gress et al 1991) ,It is still possible that the other two mechanisms may be important

under some conditions. In the flocculation of colloidal silica present in cane sugar juice, similar effectiveness was seen with copolymers of acrylamide containing either a cationic or anionic co-monomer, suggesting that the uncharged polar amide groups are more important in binding to silica (Muhle 1990). Whatever the chemical basis of adsorption to particle surfaces, it is clear that the physical properties of the flocculant are responsible for the distinctive features of flocculation.

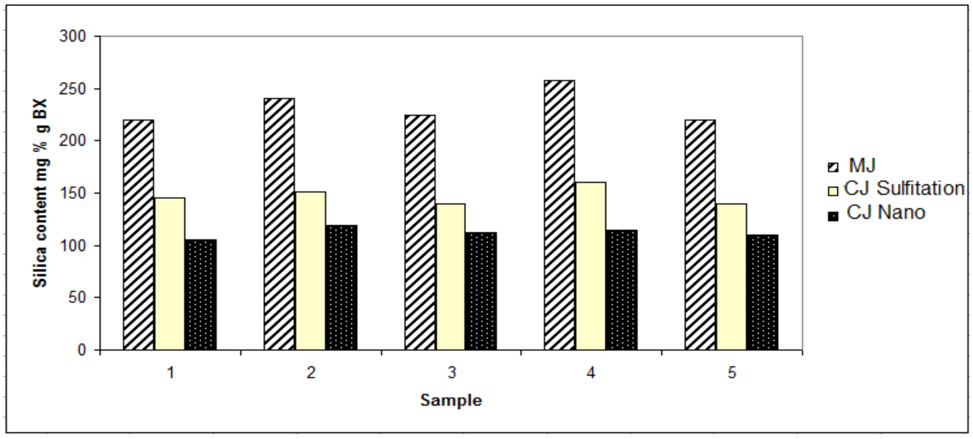

Fig. 5. Behavior of silica in case of sulfitation and nano clarification

Impact of silica on processes stream

It has been established that silica in industrial streams can originate from the cane itself, but that the contamination of cane by soil and clay can introduce silica in the factory; this contamination also introduces aluminum into the process. Experimental evidence shows that the presence of soil and clay interferes with clarification and could well result in poor sugar quality (Meyer & Keeping 2002). Therefore, it may be concluded that the presence of field soil increases silica in the juice. Furthermore, scaling in evaporators and heat-exchangers will be increased and also the mud-volume in settling, especially clay soils may aggravate these problems.

Effect of HAP clarification on calcium behavior

As it shown from Table (3) which represents the calcium as CaO % sugar in M.J & CJ in Quos sugar factory for 5 decades, CaO increases from 46 – 54 % during clarification, this is mainly caused by high amount of soluble inorganic and organic calcium salts. This increase excludes the precipitation of calcium ions as calcium sulphite, sulphate, ferrate and phosphate. In general it was reported that the increase in calcium during clarification varied from 51% to 54 % (Irvine, 1978)

Table 3: The CaO % sugar in MJ & CJ during sulfitation

M.J	**0.54 ± 0.03**	**0.52 ± 0.02**	**0.51 ± 0.01**	**0.54 ± 0.02**	**0.54 ± 0.03**
C.J	0.81 ± 0.2	0.80 ±0.02	0.78 ± 0.01	0.79 ± 0.01	**0.81 ± 0.02**
Iincrease in %	**50**	**54**	**53**	**46**	**50**

Table 4: Behavior of calcium content in case of phosphatation and sulfitation

Process Sample No.	Sulfitation		Phosphatation	
	M.J.	**C.J.**	**M.J.**	**C.J.**
1	0.52 ± 0.04	0.80 ± 0.03	0.61 ± 0.03	**0.67 ± 0.02**
2	0.56 ± 0.02	0.81 ± 0.02	0.62 ±0.01	**0.65 ± 0.01**
3	0.54 ± 0.01	0.81 ± 0.04	0.63 ± 0.02	**0.67 ± 0.01**
4	0.53 ± 0.03	0.81 ± 0.01	0.62 ± 0.04	**0.66 ± 0.03**
5	0.55 ± 0.02	0.83 ± 0.02	0.63 ± 0.03	**0.67 ± 0.04**
Increase in %	**50**		**6.5**	

This excess in calcium content in C. J. change mainly according to the clarification process adopted. In case of sulfitation (Quos sugar factory) equal 50 % whereas 6.5 % in case of phosphatation process (Geurga sugar factory) as it shown in Table (4) and Fig. 6.

- The excess of lime in clarified juice determined as CaO content, should be considered as being combined with newly formed acid decomposition product in the purification process. However, the lime content of the clarified juice due to the result of three factors: "a" lime present in the mixed juice, "b" neutralizing organic acids present in the original juice, and "c" lime combined acid decomposition products (Honig, 1954).

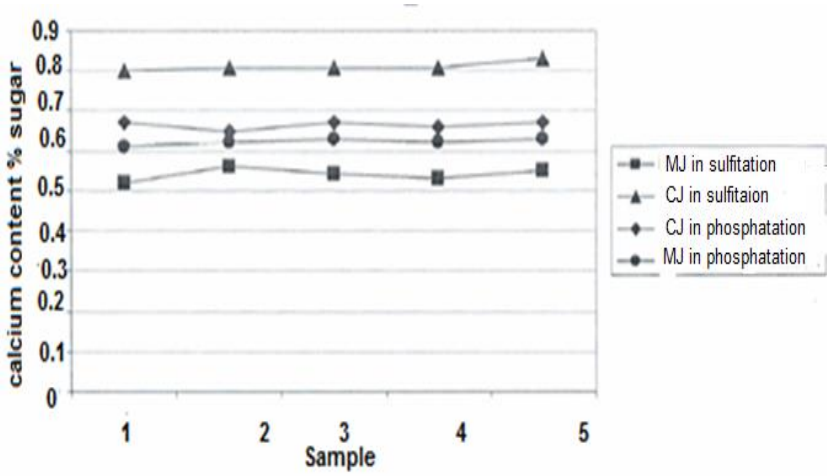

Fig. 6 : Behavior of calcium in case of sulfitation and phosphatation clarification.

Table 5: Behavior of calcium content in case of nano and sulfitation process

Process Sample No	M.J.	Residual calcium in C.J	
		Sulfitation	Nano.
1	0.55 ± 0.03	0.80 ± 0.02	0.60 ± 0.01
2	0.56 ± 0.04	0.81 ± 0.01	0.60 ± 0.02
3	0.56 ± 0.02	0.81 ± 0.03	0.61 ±0.03
4	0.54 ± 0.01	0.80 ± 0.04	0.60 ± 0.04
5	0.56 ± 0.03	0.82 ± 0.02	0.61 ± 0.03
Increase in %	-	+ 47.3%	- 9 %

As shown from results (Table 5), 47.3% increase in calcium content in the case of sulfitation whereas 9 % in the case of nano clarification due to**:**

- The use of HAP leads to low CaO consumption in the clarification, since the calcium oxide consumed in sulfitation about $\pm$ 0.16 % cane where as it is equal 0.1% cane in the case of HAP clarification. According to the fundamentals related to coagulation & flocculation (Fig.7), there are a good coagulation &flocculation mechanism in the case of HAP clarification due to much higher active sites of calcium available for bridging and flocculating with anionic copolymer, and additional adsorability for organosilicic compounds and proteins, resulted in decreasing in the remaining turbidity, calcium and silicate content.

In the case of using nano-hydroxyapatite, calcium phosphate forms exhibits a very high surface area, provides a higher bridging than traditional state which happens in the case of using lime and phosphate (Fig.7), thus an additional improvement in the performance of clarification process occurs .

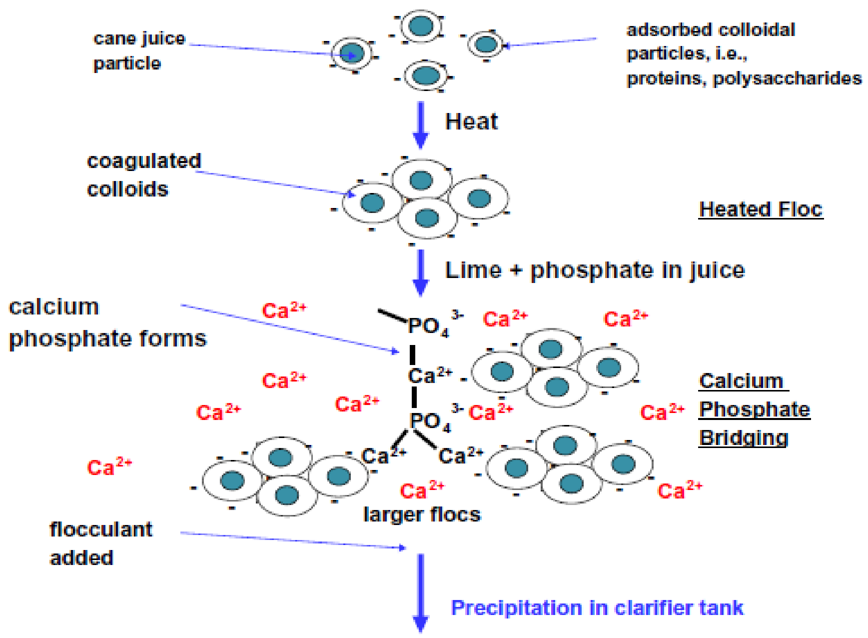

Fig. 7: Schematic mechanism for hot lime clarification of sugarcane juice (Eggleston et al. 2002).

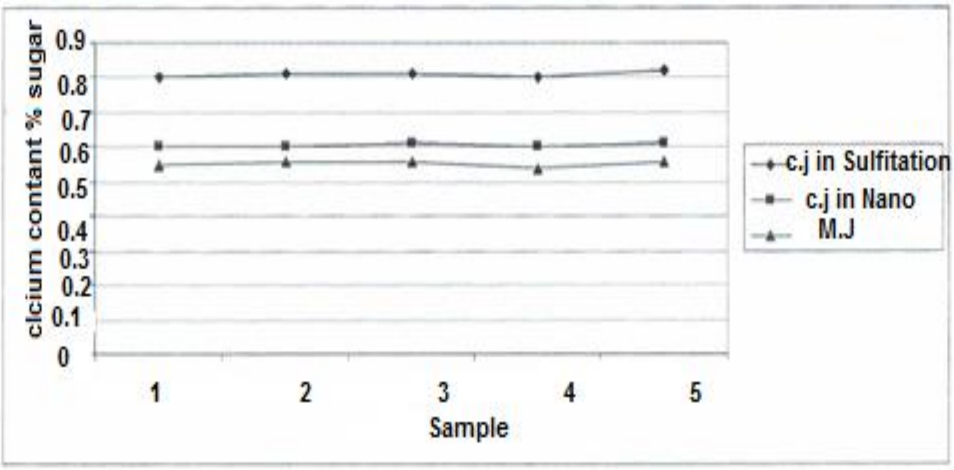

Fig. 8: Behavior of calcium in case of sulfitation and nano clarification

Impact of calcium on the process stream

- In evaporators, one of the most important effects resulted from using HAP clarification is the decrease in the remaining calcium in C.J, since its relation with quantity and hardiness of evaporator scales. The calcium content in clear juice has bearing on the economy of sugar factory, as it controls the extent of scale formation in evaporator bodies ,whereas the quantity of calcium content in CJ decrease the formation of precipitated calcium salts inside evaporator tubes. this will be decrease the scale thickness and heat transfer increase (Honig, 1954).
- In boiling house, Egyptian sugar cane mills sometimes suffer from a phenomenon known as "hard to boil" massecuite (HTB). During the 2012 grinding season, Edfo sugar factory episodes of a difficult to boil and slow to boil in A & B pan strikes, the hard to boil massecuite (HTB) samples included higher levels of calcium, as well as lower phosphate and polysaccharides. this was considered an indication that excess calcium may play an important role. The requirement to use extra lime for clarification due to high mud and polysaccharide levels, along with low natural phosphate in the juice, led to high levels of calcium carrying through the process with a deleterious effect on crystallization .It has

established that, a series of specific compounds were used as molecular probes to determine the causes of boiling difficulties, with an eye to improving the boiling characteristics of A-molasses, assuming that if a probe improved boiling, it could indicate the cause of the difficulty.

- Another factor that may cause HTB phenomenon is inhibition of heat transfer, caused by a fouling of the heating surfaces in evaporators (Gillian E., et al 2011) or the production of small bubbles throughout the massecuite, which interferes with heat transfer. The decrease in calcium content in clear juice after using of HAP will be add as a good molecular probes, and a good evidence that Hydroxyapatite Nanoparticles will overcome the hard to boil massecuite.
- In addition to HTB phenomenon, calcium is considered as a one of melassigenic compounds. These compounds are impurities found in massecuite that increase sucrose solubility and therefore carry sucrose into molasses, slowing crystallization in the process, and lowering yield. Among of the melassigenic compounds, calcium compounds are predominate where every molecule of calcium carry two molecule of sucrose to be lost in final molasses. Melassigenic coefficient is defined as the number of parts of sucrose that will be taken into molasses at saturation, per part of non- sucrose (Duffaut, & Godshall, 2004). Among the most melassigenic compounds, potassium and calcium salts having the highest coefficients in the order: K > Na > Ca > Mg. According to this fact, the use of HAP decreases the melassigenic phenomenon via decrease the calcium content in CJ.

Effect of Hydroxyapatite nanoparticles on phosphate behavior

Table 6: P_2O_5 content in M.J. and C.J during sulfitation and nano clarification .

Process Sample No.	M.J.	C.J resulted from	
		Sulfitation	Nano clarification

1	15 ± 6	4 ± 1	15 ± 4
2	160 ± 5	6 ± 2	18 ± 2
3	162 ± 7	6 ± 2	15 ± 3
4	170 ± 9	7 ± 3	16 ± 1
5	172 ± 4	8 ± 4	16 ± 2
6	160 ± 11	7 ± 2	15 ± 2

A significant difference in P_2O_5 content in the two cases (Table 6) where (16 ppm in the case of HAP and 6-7 ppm in the case of sulfitation). This difference in the phosphate content due to the properties of phosphate formed during clarification in the two cases which is a key for understanding any happens during clarification specially P_2O_5 and CaO content in CJ.

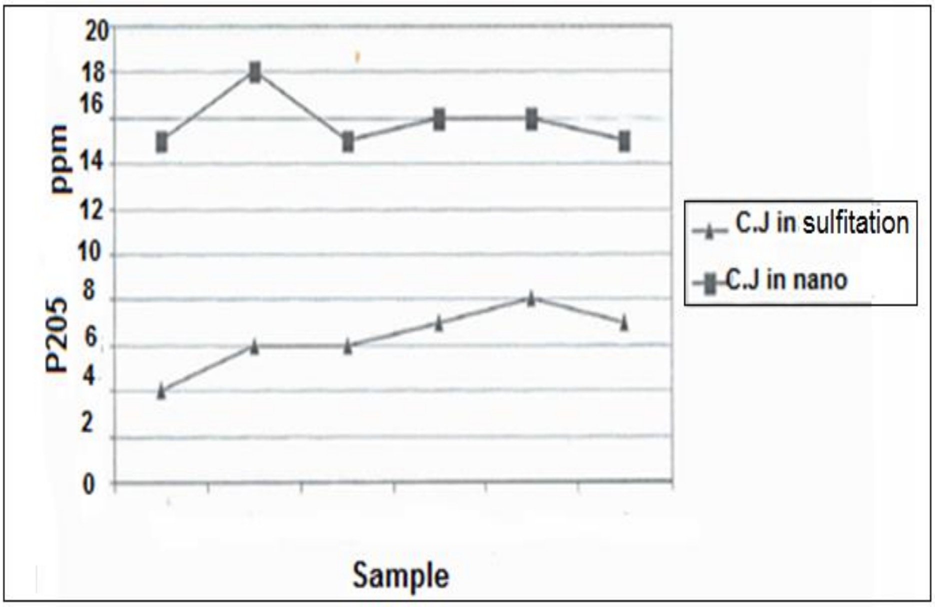

Fig. 9: Behavior of P_2O_5 in case of sulfitation and nano clarification

Calcium phosphate precipitation

Calcium phosphate particles are involved in the formation of flocs, and hence are pivotal in the clarification process. In aqueous solution, the main reactions that occur to produce calcium phosphates are:

$$Ca^{2+} + 2H_2PO_4^- \rightarrow Ca(H_2PO_4)_2(S) \quad (1)$$

(monocalcium phosphate,MCP)

$$Ca^{2+} + HPO_4^{2-} \rightarrow CaHPO_4(S) \quad (2)$$

(dicalcium phosphate ,DCP)

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)(S) \quad (3)$$

(tricalcium phosphate ,TCP)

$$2CaHPO_4 + 2Ca_3(PO_4)_2 \rightarrow Ca_8H_2(PO_4)_4)(S) \quad (4)$$

(Octaclcium phosphate,OCP)

$$Ca_3\ PO_4)_2 + HPO_4^{2-} + H \rightarrow Ca_5(PO_4)_3OH\ (s) + 2H^+ \quad (5)$$

(hydroxyapatite, HAP)

In addition, tetracalcium phosphate is formed because some of these reactions are sequential, i.e. some reaction products participate as reactants in further reactions, the distribution of calcium phosphate produced depend on the kinetics of each reaction. Thermodynamically, HAP is the most stable form (Doherty and Rackemann, 2009). The effectiveness of the juice clarification process would be considerably increased if a larger proportion of HAP was formed instead of TCP. In the case of HAP clarification, a moderate level of phosphate remaining in the clear juice (16) . This due to its morphological structure, which appeared in the form of thin short nanorods, exhibits excellent adsorption ability because its large specific surface area, and thus an additional improvement during HAP clarification process.

It has been established that the challenge is to develop conditions during clarification conductive for high proportion of HAP (Doherty and Rackeman 2009). Since HAP has largest service area thus it would remove a significant proportion of proteins and consequently reduce the formation of melanoidins.

Impact of phosphate on clarification

Whilst the basic chemistry of sugar juice clarification is understood, details of some of the interactions between various impurities remain unknown. The main reason stems from the complexity of the interactions between constituents of the juice and inconsistency in juice composition.

Juice composition depends on a variety of conditions such as the cane variety, age of the cane, geographical location and growing conditions, as well as on the harvesting and milling processes. The work by Naidoo and Lionnet (2000) on South African sugarcane clearly highlights the effect of cane variety and agricultural factors (e.g. cane age, ratoon number, rainfed and irrigation). Also, geographical location was statistically significant (5% level) on calcium and potassium, while cane variety was weakly statistically significant (10% level) with these elements. The phosphate level in sugar juice is a key parameter in the success of the clarification process by defecation. Juices with insufficient phosphate (-300 mg/l as P_2O_5) generally clarify poorly and produce hazy clarified juices (Deben, 1976; Steindl, 1998). Factory experience has shown that stale cane normally clarifies better when phosphate is added to juice prior to clarification. However, excessive phosphate in the clarified juice impacts negatively on sugar filterability (Bennett and Regnauth, 1960) and increases scaling of the evaporators. Conversely, if lime is added too much on the mixed juice, the clarified juice contains high levels of residual calcium, the clarified juice becomes dark, increased scaling occurs in the evaporators and pans, ash in sugar increases, and molasses exhaustion is less efficient. In many situations where the pH is appropriate and calcium level in mixed juice is adequate, maximum calcium phosphate precipitation will occurs, the variable that requires adjustment is the phosphate content of juice. Steindl (1998) found that extra phosphate should be added to mixed juice for optimum clarification performance. However, it is known that certain juice types may contain far in excess of the normal requirement of inorganic phosphate and yet clarify poorly.

Economic study for applicating HAP

Cost evolution of the HAP clarification for mixed cane juice

We assume a cane sugar factory processing 1500000 tons per crushing season according to our experiment ,for comparison between sulfitation and HAP clarification process from the stand point of cost evaluation , firstly the chemical aid and its consumption in each case were determined (Tables 7 and 8) the cost and the benefit were evaluated (Tables 9 and 10) according to the quantity of chemical consumed in each case.

Table 7: Chemical consumption % cane in case of sulfitation & HAP clarification

Chemical aid	Consumption in	
	Sulfitation	HAP clarification
CaO % cane	0.16 % cane	0.08% cane
H_3PO_4	0.03% can	-
Hydroxyapatite (HAP)	-	0.03% cane
Anionic fluctuant	0.0004% can	0.0004% cane
Sulfur	0.05% cane	-

Table 8: Quantity of chemical consumption per year in case of sulfitation and HAP clarification

Chemical aid	Quantity of chemical consumed	
	Sulfitation	HAP clarification
Calcium oxide	2400 ton	1200 ton
Ortho phosphoric acid	450 ton	-
Sulfur	750 ton	-
Anionic fluctuant	7.5 ton	7.5 ton
HAP	-	450 ton

Cost of chemical consumption in case of sulfitation and HAP clarification in million L.E were evaluated table.9

Table 9: Cost of chemicals in case of HAP & Sulfitation- clarification

Chemical aid	Cost	
	Sulfitation	HAP clarification
Calcium oxide	3.154.000 L.E	1.580.000 L.E
Ortho phosphoric acid	3.710.000 L.E	-
Sulfur	2.500.000 L.E	-
HAP	-	5.400.000 LE

Table 10: Total cost of HAP and the total benefits .

Cost	Benefit
HAP = 5.400.000 L.E	Removing of sulfur cost = 2.500.000
	minimizing of Cao cost to the half 1.580.000
	removing cost of phosphoric acid = 3.710.000 L.E
	In addition to maximize the recovery of crystallization pans, not calculated
	decreasing losses in final molasses not calculated
Total cost 5.400.000 L.E	Total Benefit 7.790.000 L.E

From the stand point of economic study the cost to benefit ratio 1:1.44, i.e. the net profit = 2.390.000 L.E per year, take in mind that the increase in sugar recovering not calculated. for all factories related to ESIIC the net profits per year = 14.34 m. L.E .

Conclusion

The work conducted in this paper has shown that the control points for applications of NHA as nano clarification in cane sugar industry in term of pH, doses, and retention time, were determined as 7.5, 300 ppm, and 1.5 hr respectively to be the most proper under conditions of Egyptian cane juice.

Since, under such parameters, the clarification of mixed juice using nano hydroxy apatite can be used as a good method instead of traditional sulfitation method, since it leads to brilliant CJ with a lower turbidity (4.n.t.u) and color (7166 mau), lower Ca.% sugar in CJ (0.6 %), a moderate P_2O_5 ppm (16 ppm) in CJ, and a lower SiO_2 ppm % BX (105) in CJ. These results mean a predicted soft scale formed in the evaporators, overcoming the hard to boiled massecuite phenomenon, removing the cost of sulfur, and minimize the cost of calcium oxide to the half .

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References

- Bennett, M. C., & Regnauth, J. M. (1960). The effects of calcium and phosphate in cane juice clarification. Int. Sugar Journal, 62, 13-16.
- Crees, O.L., Senogles, E. and Whayman, E. (1991) The flocculation of cane sugar muds with polyacrylamide-sodium acrylate copolymers. J. of Applied Polymer Science 42, 837-844.
- Deben, J. G. (1976). The chemistry of calcium phosphate precipitation in cane sugar juice clarification, Parts I, II and III. Int. Sugar Journal, 78,35-39 and 73-75.
- Doherty, W. O. S., & Rackemann, D. W. (2009). Some aspects of calcium phosphate chemistry in sugarcane clarification. Int. Sugar Journal, Ill, 448-454.

- Duffaut, E., & Godshall, M. A. (2004). Molecular probes for assessing the boiling difficulties. Pro. Sugar Processing Research Conference (pp. 403–416).
- Eggleston, G., Monge, A., and Pepperman , A.B., (2002) Pre-heating and incubation of cane juice prior to liming: A comparison of intermediate and cold lime clarification. J. Agric. Food Chem. 50, 484–490.
- ESIIC Laboratory manual, 1991.
- Gillian E., Gregory C., and Christopher S., (2011) New insights on the hard-to-boil massecuite phenomenon in raw sugar manufacture, Food Chemistry, 126, 21–30.
- Han M., Lawler D. F. (1992) An water works Assoc., 84, 79.
- Honig, p. (1953) principles of sugar Technology vol.1. Elsevier publishing Co. Payen, J.H chapter 13. Fundamental Reactions of the clarification. pp 501-535.
- International Commission for Uniform Methods of Sugar Analysis (2000) determination of calcium in sugar products by EDTA titration, Method GS 8/2/3/4-9, Bartens, 12-12.
- Irvine J. E. (1978), behavior of major inorganic cations during cane juice clarification, Sugar Journal, 41 (5), p:28.
- Laboratory manual for South African Sugar Factories, (1985), South African Sugar Technologests Association, phosphate determination, 8-261.
- Madsen Lee ,R. M., (2009), Iron mediated Precipitation of phenol: protein Aggregates from sugar cane juice, PhD Dissertation, Louisiana state university.
- Meyr J. H. & Keeping M. G., (2002) , Review of research into the role of silicon for sugar cane production, Proc. S. Afr. Sug. Tech. Ass. 74, 29-40.

- Muhle, K. and Domasch, K. (1990) Floc Strength in Bridging Flocculation. In: 'Chemical Water and Wastewater Treatment', Proceedings of the 4th Gothenburg Symposium, (Ed. H.H. Klute), Springer Verlag, Berlin: 105-115.
- Naidoo L and Lionnet G R E (2000) , The effect of cane variety and other agricultural factors in juice composition. Proc. S. Afr. Sugar Technol. Ass. 74, 19–24.
- Rein, P.W. (2007). Cane Sugar Engineering, 1st Ed. Verlag Dr. Bartens KG., pp 219-244.
- Salah, T. A.; Mohammad, A. M.; Hassan, M. a.; El-Anadouli, B. E. 2014, Development of nano-hydroxyapatite/chitosan composite for cadmium ions removal in wastewater treatment. J. Taiwan Inst. Chem. Eng. 45, 1571–1577.
- SRI (1999). Operating Procedure for the SRI Settling Test Kit. Mackay, QLD, Australia: Sugar Research Institute.
- Steindl, R.J. (1998) Dirt - its implications for the clarifier and filter stations. Proceedings of the Australian Society of Sugar Cane Technologists 20, 484-490.
- Walthew, DC, Khan, F and Whitelaw, R (1988). Some factors affecting the concentration of silica in cane juice evaporators. Proc S Afr Sug Technol Ass 72, 223-227.

الملخص العربي

أثر المعالجة باستخدام النانو هيدروكسى ابيتايت على سلوك الكالسيوم والسيليكا والفوسفات بعصير القصب

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لقد لاقت تطبيقات مواد النانو ضمن عملية المعالجة فى كثير من القطاعات الصناعية والزراعية انتباهاً واضحاً من الباحثين حديثاً، وفى هذا المجال تناول هذا البحث دراسة استخدام مركب النانو هيدروكسى ابيتايت (المحضر بمعمل تحضير وتوصيف مركبات النانو بمصر) كمادة معالجة للعصير الخام فى صناعة السكر .

يهدف البحث الى دراسة أثر استخدام مادة النانو هيدروكسى ابيتايت على المركبات الغير عضوية مثل الكالسيوم والسليكا والفوسفات والتى توجد بنسب مؤثره بعصير القصب. تم تقييم تطبيق المادة ضمن عملية المعالجة للعصير من خلال التجارب التي أجريت على نطاق معملى ونطاق نصف صناعى بمركز بحوث العمليات النصف صناعية التابع لشركة السكر .وقد وضحت النتائج التى تم الحصول عليها من التجارب بعد تحليلها باستخدام اختبار T الاحصائى أن هناك فروق ملموسة فى جودة العصير المعالج بتكنولوجيا النانو مقارنةً بالعصير المعالج بطريقة الكبرتة العادية، حيث لوحظ انخفاض فى محتوى الكالسيوم بالعصير الرائق الناتج من هذه الطريقة بمقدار 38.3% عنه فى حالة الطريقة العادية، وزيادة الإزالة للسيليكا التى

انخفضت بمقدار51.6% مقارنة بـ 36.2% فى حالة المعالجة بالكبرته بالإضافة الى الوصول الى محتوى معتدل من الفوسفات المتبقى بالعصيرالرائق الناتج، حيث كان 16 جزء/ مليون مقارنة بنسبة منخفضة (6 جزء/ مليون) فى حالة العصير الناتج من المعالجة العادية ، انخفاض فى فقد السكر بالمولاس والتغلب على ظاهرة صعوبة البلورة الناتجة عن الكالسيوم الموجود بالعصير. وقد نوقشت النتائج وتم تفسيرها اعتمادا على المفاهيم المتعلقة بخصائص مركبات الكالسيوم فوسفات وميكانيكية ارتباط وتجميع الغرويات من العصير التي تعتمد على مساحة سطح مواد المعالجة المستخدمة .