Chemical reagents for intensification of diffusion juice purification

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Keywords:

Phosphate
Hydroxyapatite
Diffusion
Juice
Purification

Article history:

Received 06.09.2013
Received in revised form
20.12.2013
Accepted 23.12.2013

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ABSTRACT

Introduction. Further improvement of the technological scheme is possible by increasing the effect of treatment directly in the extraction process, the intensification of chemical and adsorption processes, at different stages of treatment using high-molecular coagulants, flocculants and cheap natural sorbents.

Materials and methods. The traditional physical and chemical methods of researches are used in accordance with operative standarts. Rassing and decision of tasks optimization were conducted with the help of packet applied programmes MathCAD and Microsoft Excel.

Results and discussion. Investigations showed considerable advancement in the efficiency of raw juice purification by means of using $NH_4H_2PO_4$ on the primery and on the final stage of purification. That allows to intensify chemical and adsorption processes as a result of formation hydroxyapatite with a high specific surface area. Addition of 0,2% $NH_4H_2PO_4$ on filtered preliming juice permits to increase degree of precipitation and flocculation of high-molecular compounds on 84,0%, calcium salts and precipitation of anions which form insoluble lime salts – on 93,0%, colour – on 27,0%. Thin juice had purity on 2,0 units higher. Addition of 0,10…0,15% $NH_4H_2PO_4$ on filtered juice of 1st carbonatation at zone pH 11,5…9,0 degree of presipitation anions acids and calcium salts increased on 85,0%, colour – on 55,0%, high-molecular substances as protein – on 70,0%. Thin juice had purity on 2,0 units higher. The mechanism of formation of hydroxyapatite in the lime juice purification are suggested.

Conclusion. The use of ammonium dihydrogen phosphate in the first or final purification step of the raw juice helps to intensify the chemical and adsorption processes in consequence the formation of hydroxyapatite with a high specific surface area, to improve cleanliness and to reduce the viscosity of the purified juice and syrup, to increase the yield and quality white sugar. The local criterions of optimization were selected and task of optimization the ammonium dihydrogen phosphate consumption to purification were solved.

Introduction

Increasing requirements to quality of sugar, the increased energy prices, lime stone and auxiliary materials set tasks of continuous improvement of the technological scheme of production for workers of beet sugar industry.

Further improvement of the technological scheme is possible by increasing the effect of treatment directly in the extraction process, the intensification of chemical and adsorption processes, at different stages of treatment using high-molecular coagulants, flocculants and cheap natural sorbents.

The juice purification using the lime/carbonic acid treatment may be subdivided into a number of chemical reactions which ultimately affect of main target, i.e. improving the white sugar recovery and sugar quality.

The main reactions are:

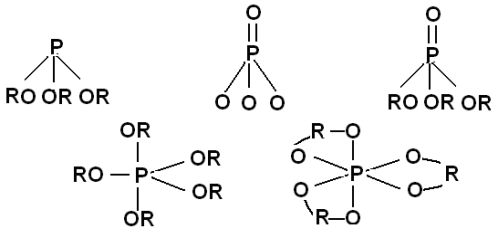
- precipitation of high molecular compounds such as proteins, pectins and anions wich form insoluble or partly insoluble lime salts by addition about 0,25…0,30% lime on juice during preliming;
- alkaline degradation of invert sugar and amides to organic acids;
- elimination of nonsugars by adsorption when main part of the added calcium hydroxide is precipitation as calcium carbonate by addition of CO_2.

Using the lime and carbonic acid treatment one is able to remove up to 40 %, but under technical conditions mostly only 30 to 34 %, of nonsugars present in raw juice.

To improve the quality of purified juice were proposed use of cheap natural sorbents: bentonit, filtroperlit [1, 2].

The main criterions to make a good choise of sorbent – this is a high developed surface, presence a great amount of OH groups and high free energy of surface.

The phosphates of calcium can have three, four, five or six atoms of oxygen, connected with central atom of phosphorus, they possess high free energy of surface and well adsorb organic matters.



The phosphates of calcium received a wide application as at the instrument-making (lyminophores, pezoelectrics, sorbents for a chromatography) and also as of food additions, sorbents of heavy metals and radionuclides.

The special place among the large class of compounds of phosphorus occupies hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, which with some assumptions it is possible to consider the crystallochemical analogue of mineral constituent of fabrics of skeleton of animals and people and which successfully serves as the base component of synthetics materials for orthopaedy of stomatology.

Materials and methods

The traditional physical and chemical methods of researches are used in accordance with operative standarts.

Rassing and decision of tasks optimization were conducted with the help of modern methods of the mathematical processing of data with the use of computer technologies statistical treatment of results of experimental researches, the construction of charts was executed by means of packet applied programmes MathCAD Professional 2000 and Microsoft Office Excel 2003.

Results and discussion

Methods of purifying diffusion juice are suggested, which allow to intensify chemical and adsorption processes at the first and final stages of purification by introducing in the filtered preliming juice or filtered juice 1st carbonatation chemical reagent - ammonium dihydrogen phosphate [3, 4].

After studying various methods for possible mechanisms formation of calcium phosphorus and phosphorus compounds [5, 6] we suggested the mechanism of formation of hydroxyapatite in the lime juice purification [7] using ammonium dihydrogen phosphate:

1. First, monocalcium phosphate of the least stable is formed ($Ca(H_2PO_4)_2$) :

$$Ca(OH)_2 + 2\ NH_4H_2PO_4 = Ca(H_2PO_4)_2 + 2\ NH_4OH$$

2. Monocalcium phosphate is dissolved in a large excess of water and hydrolyzed to phosphate dicalcium $CaHPO_4$:

$$Ca(H_2PO_4)_2 \xrightarrow{nH_2O} CaHPO_4 + H_3PO_4$$

3. Dicalcium phosphate forms oktacalcium phosphate - $Ca_8(HPO_4)_2{\cdot}(PO_4)_4{\cdot}5H_2O$ during hydrolysis in a narrow zone of neutral values pH:

$$8Ca(HPO_4)(s.p.) + 2Ca(OH)_2 + H_2O \rightarrow Ca_8(HPO_4)_2{\cdot}(PO_4)_4{\cdot}5H_2O + 2\ CaHPO_4$$

4. Metastable oktacalcium phosphate, alike as an amorphous calcium phosphate is a precursor (formed as an intermediate product) in obtaining more stable phases, such as hydroxyapatite $Ca_{10}(PO_4)_6{\cdot}(OH)_2$:

$$Ca_8(HPO_4)_2{\cdot}(PO_4)_4\ 5H_2O + 2\ Ca^{2+} + 4\ OH^- \rightarrow Ca_{10}(PO_4)_6{\cdot}(OH)_2 + 2\ H_2O$$

It is ascertained that addition $NH_4H_2PO_4$ in alkaline medium at zone pH 11,5…9,5 at the high ionic correlation Ca/P as 1,67 generated hydroxylapatite with the big specific surface ($100 m^2/g$).

Addition of 0,2% $NH_4H_2PO_4$ on filtered preliming juice permits to increase degree of precipitation and flocculation of high-molecular compounds on 84,0%, calcium salts and precipitation of anions which form insoluble lime salts – on 93,0%, colour – on 27,0%. Thin juice had purity on 2,0 units higher. Dependence of the quality indicators of filtered preliming juice from consumption of reagent are presented on *Fig. 1*.

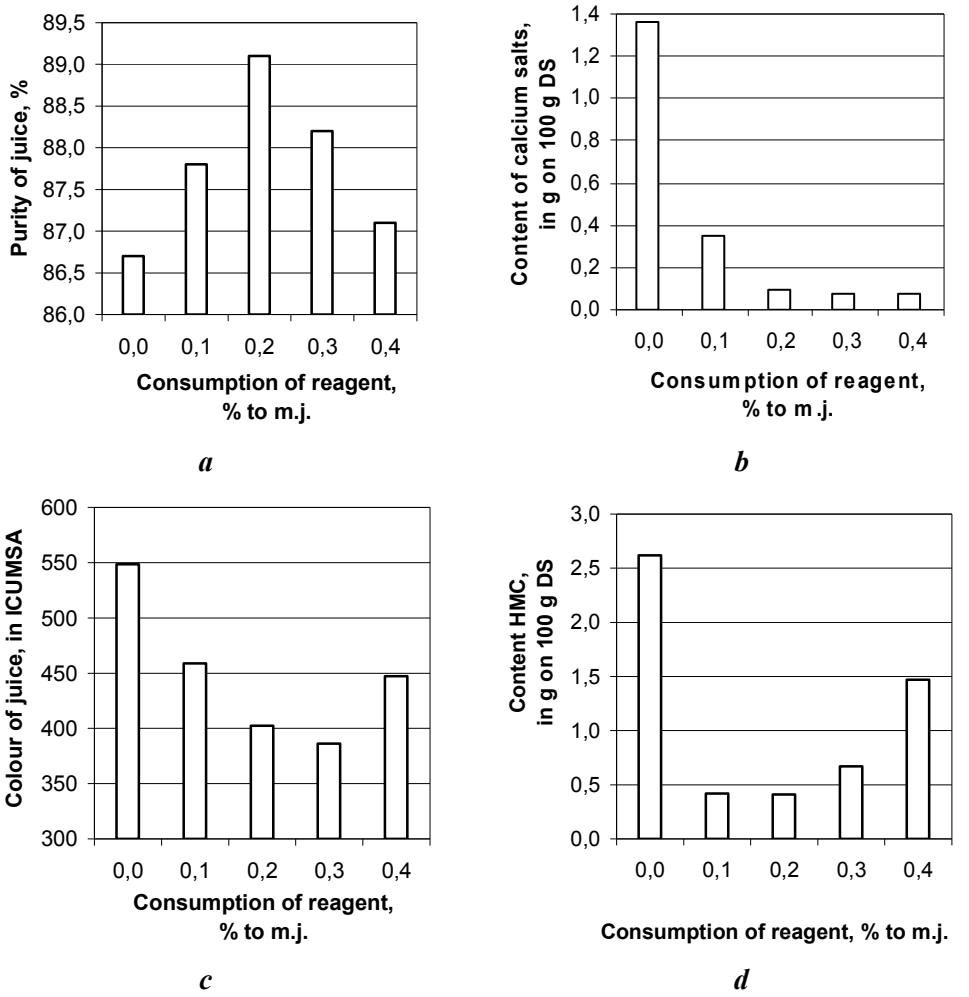


Fig 1. Dependence of the quality indicators of filtered preliming juice from consumption of ammonium dihydrogen phosphate:
a - purity of juice; b - content of calcium salts; c - colour of juice; d - content of HMC

The optimum consumption of ammonium dihydrogen phosphate for purification filtered preliming juice varies depending on its purity. This dependence is presented on *fig. 2.*

Addition of 0,10…0,15% $NH_4H_2PO_4$ on filtered juice of 1st carbonatation at zone pH 11,5…9,0 degree of presipitation anions acids and calcium salts increased on 85,0%, colour – on 55,0%, high-molecular substances as protein – on 70,0% (on *Fig. 3*). Thin juice had purity on 2,0 units higher.

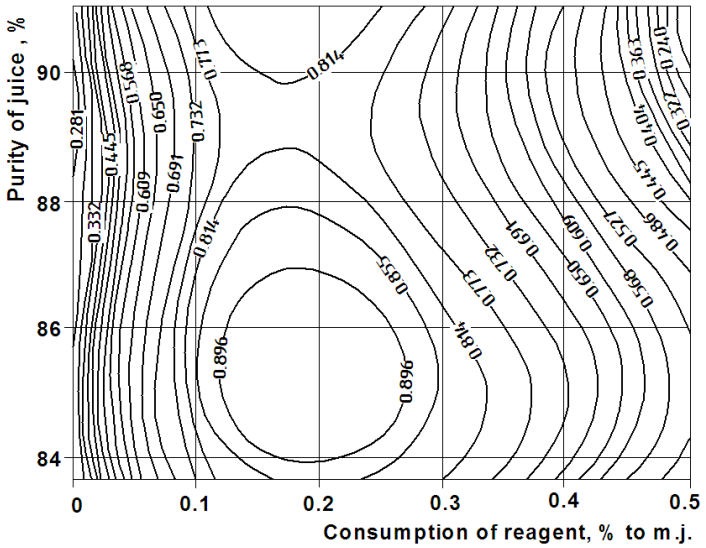


Fig. 2. Level lines of the generalized criterion of optimization in coordinates purity of filtered preliming juice - consumption of ammonium dihydrogen phosphate.

Using the massif of experimental obtained data aproksymated them in packet applied programmes, obtained the following equations of local optimality criterias (increase purity of juice, content of calcium salts, colour of juice from parameters of optimization):

- increase purity of juice 1st carbonatation from parameters of optimization:

$$\mathbf{\Delta P}_{\text{juice 1}^{st}\text{ carbonatation}} = 1{,}96\cdot10^{5} + 79{,}79\cdot G - 6{,}51\cdot10^{3}\cdot P + 8{,}85\cdot10^{-3}\cdot G\cdot P - 7{,}49\cdot G^{2} + 72{,}17\cdot P^{2} + 0{,}228\cdot G^{3} - 0{,}27\cdot P^{3}, \quad (1)$$

where G – pH_{20} of juice of 1st carbonatation after introduction of ammonium dihydrogen phosphate;

P – purity of juice 1st carbonatation, %.

- content of calcium salts of juice 1st carbonatation from parameters of optimization:

$$\mathbf{Salts\ Ca}^{2+}_{\text{juice 1}^{st}\text{ carbonatation}} = -6{,}31\ 10^{4} - 1{,}20\cdot G + 2{,}10\cdot10^{3}\cdot P - 0{,}03\cdot G\cdot P + 0{,}31\cdot G^{2} - 23{,}2\cdot P^{2} - 8{,}38\cdot10^{-3}\cdot G^{3} + 0{,}09\cdot P^{3}, \quad (2)$$

- colour of juice 1st carbonatation from parameters of optimization:

$$\mathbf{C}_{\text{juice 1}^{st}\text{ carbonatation}} = -5{,}31\cdot10^{7} + 7{,}11\cdot10^{3}\cdot G + 1{,}76\cdot10^{6}\cdot P + 4{,}90\cdot G\cdot P - 794{,}13\cdot G^{2} - 1{,}95\cdot10^{4}\cdot P^{2} + 27{,}68\cdot G^{3} + 72{,}06\cdot P^{3}, \quad (3)$$

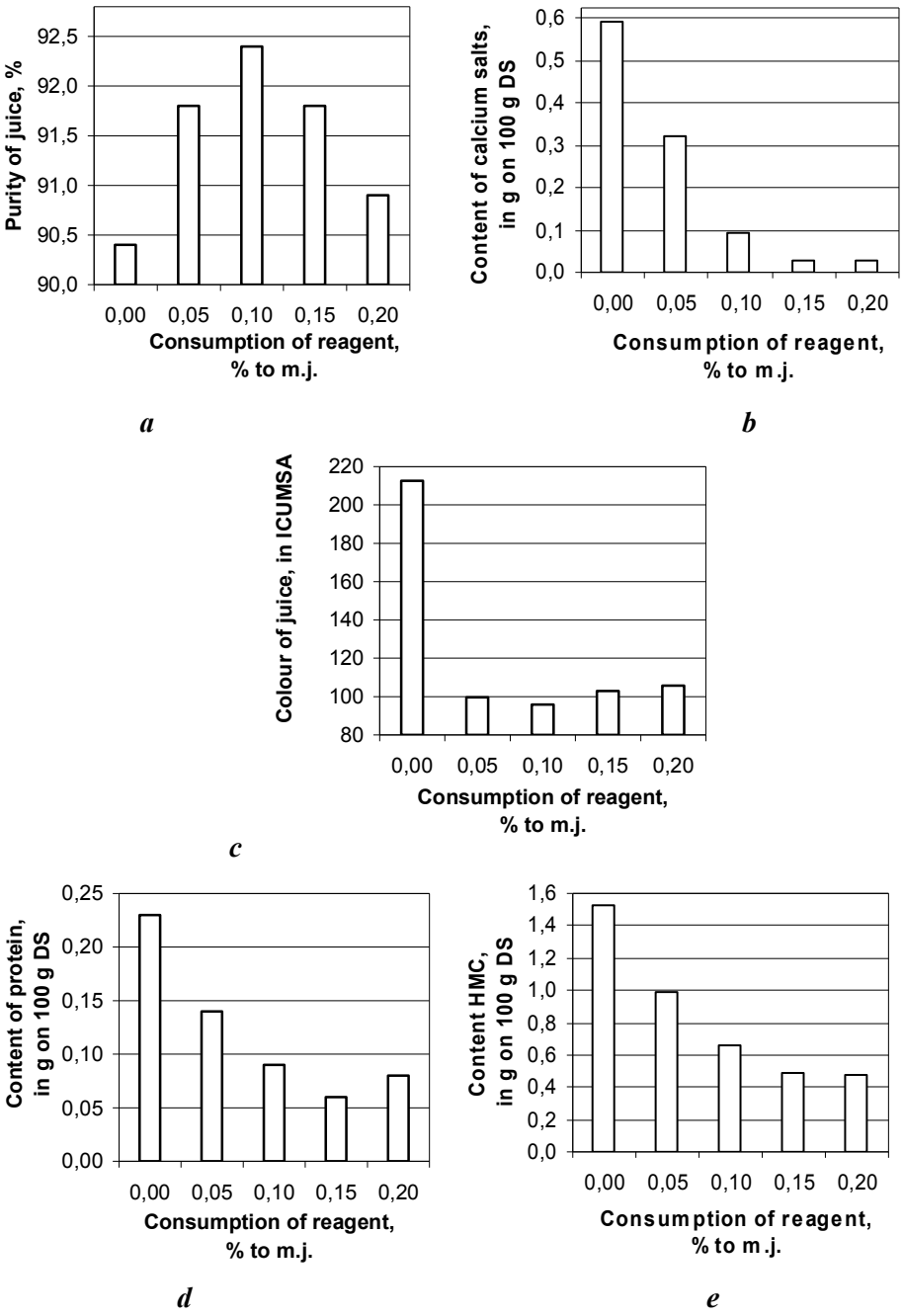


Fig 3. Dependence of the quality indicators of filtered juice of 1st carbonatation from consumption of ammonium dihydrogen phosphate:
a - purity of juice; b - content of calcium salts; c - colour of juice;
d - content of protein; e - content of HMC

To find the general criterions of optimization local criterions of optimalnost transferred into stretch form by means of method Harrington.

The optimal significance of parameters optimization – pH juice after introduction of $NH_4H_2PO_4$ and purity juice of 1st carbonatation find with the help of maximum significance of special function by using method nets.

The optimum pH of filtered juice of 1st carbonatation after introduction of ammonium dihydrogen phosphate varies depending on its purity. This dependence is presented on *Fig. 4*.

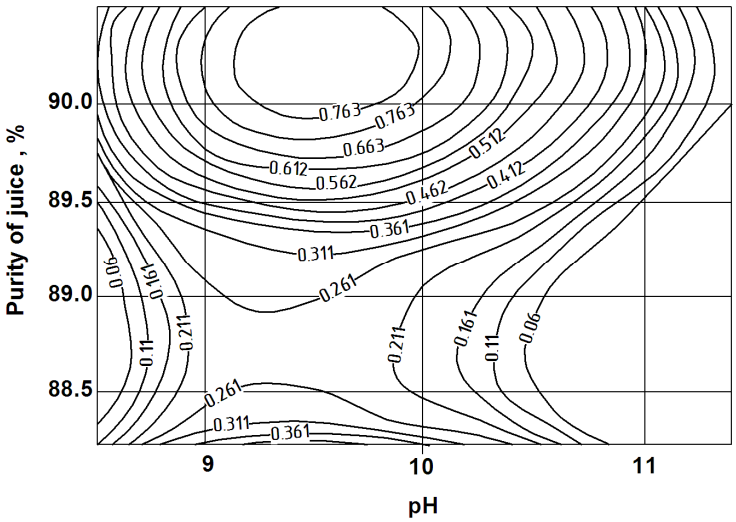


Fig. 4. Level lines of the generalized criterion of optimization in coordinates purity of filtered juice of 1st carbonatation - pH of juice of 1st carbonatation after introduction of ammonium dihydrogen phosphate

Obviously, that optimal significance of pH_{20} juice it is 9,2…9,5 (starting purities of juices were 88,4; 89,5; 90,6; 91,3; 91,5; 91,6%).

Thus, the use of ammonium dihydrogen phosphate in the first or final purification step of the raw juice helps to intensify the chemical and adsorption processes in consequence the formation of hydroxyapatite with a high specific surface area, to improve cleanliness and to reduce the viscosity of the purified juice and syrup, to increase the yield and quality white sugar.

Conclusions

1. Investigations showed considerable advancement in the efficiency of raw juice purification by means of using $NH_4H_2PO_4$ on the primary and on the final stage of purification.

2. It is ascertained that addition $NH_4H_2PO_4$ in alkaline medium at zone pH 11,5…9,5 at the high ionic correlation Ca/P as 1,67 generated hydroxyapatite with the big surface area.

3. The mechanism of formation hydroxyapatite by means of using $NH_4H_2PO_4$ is suggested.

4. The local criterions of optimization were selected and task of optimization the ammonium dihydrogen phosphate consumption to purification were solved.

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