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CLARIFICATION OF SUGARCANE JUICE: REVIEW

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Abstract: The search for alternative methods to replace sulfur in the sugarcane juice clarification step has been increasing. The sulfur dioxide (SO2) produced in the combustion of sulfur is toxic and can cause environmental problems and risks to human health. This work aimed to analyze scientific articles on alternative methods to sulfitation published between 2011 and 2021, based on searches in the Portal de Periódicos Capes, Scielo and Web of Science. Among the 434 researched scientific articles, 296 were repeated and 138 were unique, of which 94 had the text available in full and 44, unavailable. Thirty were selected to compose this review, for reporting on alternative methods of clarification: carbonation (4), ozonation (6), peroxidation (5), microfiltration (6), natural flocculants (5), bagasse fly ash (1), centrifugation (1), lime, bentonite and activated carbon (1), lime saccharate, ammonium hydroxide (NH4OH) and sodium hydroxide (NaOH) (1). All methods proved to be effective and less polluting, in addition to reducing the consumption of chemical reagents.
Keywords: Carbonation, AOP, microfiltration, alternative methods for clarifying sugarcane juice.

INTRODUCTION

Sugarcane juice is a viscous, opaque, greenish-yellow liquid of varying composition (LOPES, 2011). It contains suspended materials (earth, sand, clay, bagasse, colloidal and insoluble compounds) and soluble solids, mainly sucrose, glucose, fructose, proteins and starches (ALBUQUERQUE, 2011; DOHERTY, 2011).

Clarifying the broth removes colloidal particles in suspension (JEGATHEESAN et al., 2012; THAI; BAKIR; DOHERTY, 2011; RODRIGUES; SPERANDIO; ANDRADE, 2018). The clarification of the mixed broth by sulfitation is represented in the flowchart **(Figure 1)**. In this process, the broth is sulphited with sulfur dioxide (SO_2), limed [addition of milk of lime – Ca $(OH)^2$] and heated. Heating reduces the density and viscosity, facilitating the flocculation of impurities. The flakes are precipitated, decanted and eliminated as a sludge and the clarified broth is removed from the upper part (LOPES, 2011).

The Zeta potential indicates the efficiency of the clarification (THAI; BAKIR; DOHERTY, 2012).

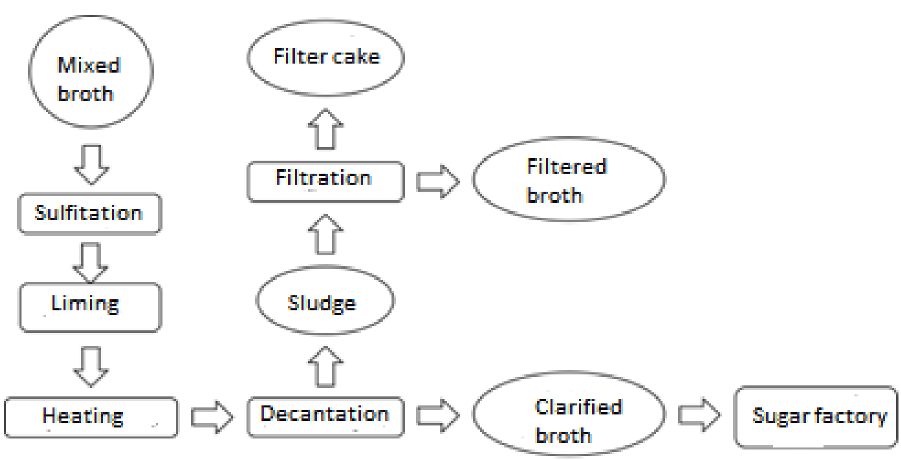

Figure 1. Flowchart of the sulfitation process.

Source: Adapted from Lopes, 2011

In Brazil, simple defecation and sulfitation predominate as clarification methods (MORENO; OLIVEIRA; BARROS, 2012). Defecation consists of adding lime (CaO) to the broth, followed by heating (DOHERTY, 2011). The pH is increased, precipitating inorganic salts such as calcium phosphate[$Ca_3(PO_4)_2$], that will carry suspended solids (EGGLESTON et al., 2014, THAI; MOGHADDAM; DOHERTY, 2015).

Sulfitation inhibits the formation of color by acidification of the broth with SO_2, decreasing the viscosity (MORENO; OLIVEIRA; BARROS, 2012). In column sulfitation, the combustion of sulfur in the rotary kiln releases SO_2, which is suctioned and cooled. The gas-broth contact takes place in perforated plates. The broth fed at the top of the column descends by gravity and absorbs the gas in counterflow. **(Figure 2)** (LOPES, 2011).

In multi-jet systems, SO_2 is cooled, suctioned and mixed with the mixed broth (LOPES, 2011). After acidification, it is neutralized by calcium oxide (CaO) (MORENO; OLIVEIRA; BARROS, 2012), producing the precipitated calcium sulfite ($CaSO_3$), which adsorbs colored compounds and impurities (MENG et al., 2019).

The use of SO_2 in the sugar and alcohol industry can affect the quality of white crystal sugar and cause environmental problems (HAMERSKI et al., 2012). The sulphite produced is not completely eliminated in decantation, and can be found in sugar. This information justifies the foreign market's demand for sulfur-free sugar (ARAUJO, 2017).

Carbonation is an alternative to using SO_2 in clarification. In this method, carbon dioxide (CO_2) is added to the broth with the milk of lime suspension, forming the precipitated calcium carbonate ($CaCO_3$), which will precipitate the impurities in suspension (HAMERSKI; AQUINO, 2014). Other less aggressive methods of clarification and that provide less loss of sugars are the advanced oxidative processes

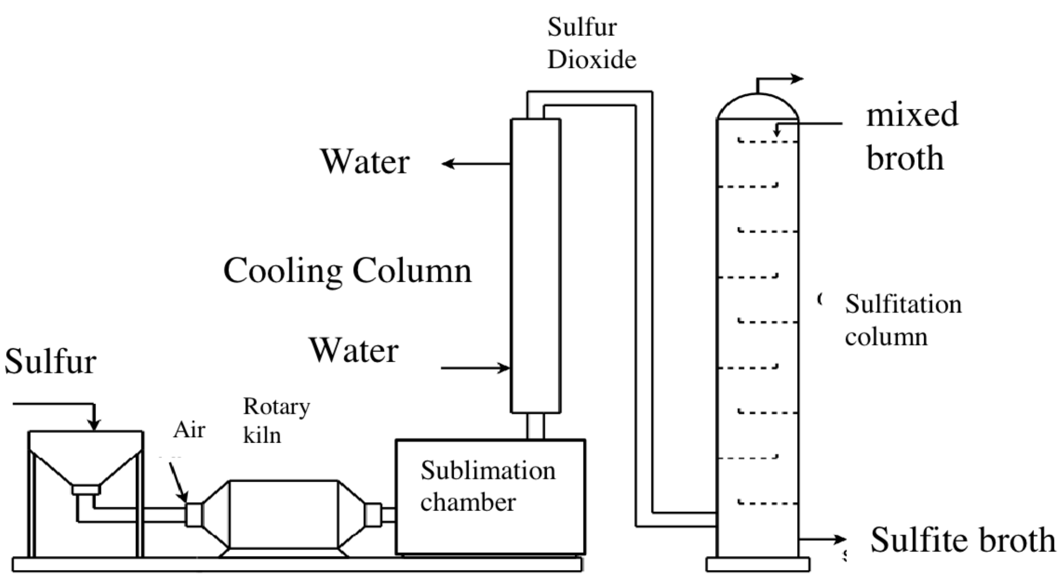

Figure 2. Column sulfitation process.

Source: Adapted from Lopes, 2011.

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(AOPs). They are: ozonation (application of O_3), peroxidation (application of H_2O_2) and incidence of ultraviolet radiation (UV), β, γ and accelerated electrons (MORILLA, 2015; SARTORI; MAGRI; AGUIAR, 2015; MANDRO, 2016; RODRIGUES; SPERANDIO; ANDRADE, 2018). AOPs oxidize complex compounds and generate hydroxyl radicals (·OH) that react with organic matter, converting it into H2O, CO_2 and inorganic ions (DANTAS et al., 2020). The formation of ·OH can occur by the combination of UV radiation with O_3 and H_2O_2, or by the catalytic decomposition of these oxidizing agents (SOUZA et al., 2019). In ozonation, O_3 oxidizes impurities in the broth (FONSECA, 2017). H_2O_2 can decompose into radical species or oxidize impurities (SOUZA et al., 2019). In peroxidation, the application of $H2O_2$ to the broth reduces the levels of colored compounds (SANTOS, 2020). UV, β, γ radiation or accelerated electrons decontaminate and reduce the ICUMSA color (ARAUJO, 2017). The method that involves the generation of ·OH from H_2 O_2 photolysis is the most efficient (MOHAMMED; FASNABI, 2016; SOUZA et al., 2019). In it, wavelengths from 200 to 300 nm are used, and UV radiation breaks the $H2O_2$ bond, originating ·OH radicals (SANTOS, 2020). The ionizing γ radiation is easily absorbed by the abundant water in the broth, promoting the formation of free radicals (LIMA, 2012).

Microfiltration (MF) is a separation method in which the suspended material is retained and sterilized at room temperature (MORENO; OLIVEIRA; BARROS, 2012).

This work deals with an analysis of alternative methods to sulfitation, through a review of scientific articles published between 2011 and 2021.

METHODOLOGY

Thirty scientific articles written in English, Spanish and Portuguese, published in journals between 2011 and 2021, were selected from the search in the database of the bases: Portal de Periódicos Capes, Scientific Electronic Library Online (Scielo) and Web of Science.

RESULTS AND DISCUSSION

ANALYSIS OF SELECTED SCIENTIFIC ARTICLES

The analysis of the articles indicated that the number of publications on alternative methods to broth clarification by sulfitation was higher in 2012 and 2019, with four and seven, respectively, totaling 37% (**Figure 3**).

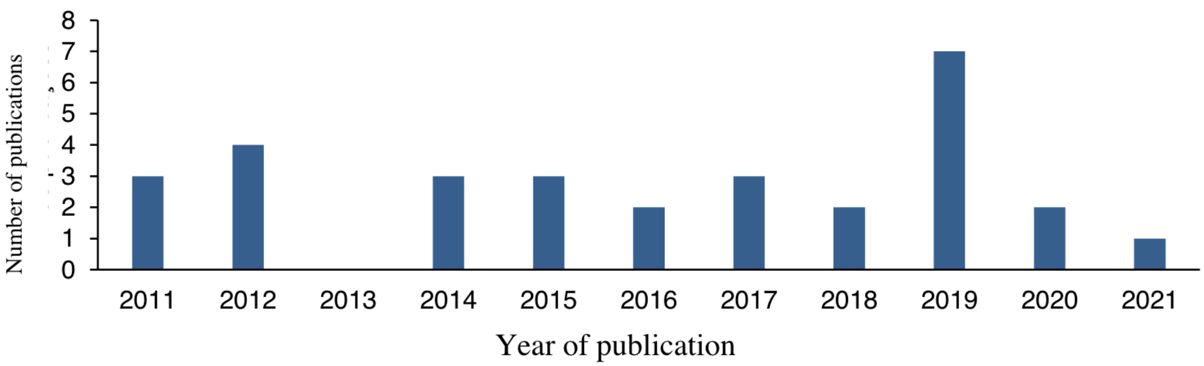

Figure 3. Number of publications on sulfitation between 2011 and 2021.

Source: From the authors, 2021.

These publications addressed carbonation, ozonation, peroxidation, microfiltration (MF), use of plant extract as a natural flocculant, bagasse fly ash (BFA), clarification by centrifugation, bentonite and activated carbon. No articles were published in 2013, three between 2020 and 2021.

CARBONATION

Only four articles dealt with carbonation.

Aquino and Ndiaye (2011) evaluated the effects of carbonation, varying the pH between 5.0 and 9.0. The best color reduction results were obtained in broths with a pH between 8.0 and 9.0.

Magazine	Authorship
Acta Scientiarum Technology	HAMERSKI; AQUINO; NDIAYE, 2011
	MORENO; OLIVEIRA; BARROS, 2012.
	GASCHI et al., 2014.
	FAVERO; HAMERSKI; AQUINO, 2014.
Food Science and Technology	COSTA et al., 2014.
	BERNARDI; JORGE; PARAÍSO, 2019.
	REZZADORI et al., 2014.
Sugar Tech	TIWARI et al., 2019.
	LI et al., 2017.
	LEITE; BARBOSA, 2021.
Ozone: Science & Engineering	SARTORI et al., 2019.
	FONSECA et al., 2017.
Brazilian Journal of Food Technology	SARTORI; MAGRI; AGUIAR, 2015
	AZEVEDO et al., 2019.
	NGUYEN; DOHERT, 2012.
Journal of Agricultural and Food Chemistry	DOHERTY, 2011.
Journal of Food Processing and Preservation	MAGRI et al., 2019.
Journal of Food Engineering	VU; LEBLANC; CHOU, 2020
International Journal of Food Engineering	SARTORI et al., 2017.
International Journal of Food Science and Technology	HAMERSKI et al., 2012.
International Food Research Journal	FERREIRA; COZAR; SCHMIDT, 2016.
Journal of Food Process Engineering	RODRIGUES; SPERANDIO; ANDRADE, 2018.
Revista Brasileira de Engenharia Agricola e Ambiental	COSTA, 2015.
Chemical and Process Engineering Research	SILVA; SARTORI; AGUIAR, 2015.
Proedia Technology	MOHAMMED; FASNABI, 2016.
Procedia Engineering	LAKSAMEETHANASAN et al., 2012.
Biotecnología en el Sector Agropecuario y Agroindustrial	ORTIZ et al., 2011.
Chemical Engineering Transactions	GALDINO et al., 2019.
International Journal of Food Microbiology	TEIXEIRA et al., 2019.
The Journal of Engineering and Exact Sciences	DANTAS et al., 2020.

Table 1. List of scientific articles by magazine.

Source: From the authors, 2021.

Hamerski et al. (2012) adopted a minimum pH limit of 6.5, and the results of the 2011 publication reported that there is little precipitate production at pH below 6.0, making broth clarification unsatisfactory. In this work, pH 9.5 was adopted as the maximum limit. Favero, Hamerski and Aquino (2014) adopted a minimum pH limit of 8.0 and a maximum of 9.0.

Hamerski et al. (2012) analyzed pH, temperature (40 and 80°C) and carbonation time (20, 40 and 60 min) in broths. They noted that higher concentrations of sucrose and lower concentrations of total soluble solids and reducing sugars were obtained in the carbonated broth at pH 9.5, 80°C and 60 min.

Hamerski, Aquino and Ndiaye (2011) obtained color removal of 66.5% at pH 8.0, temperature of 80°C and carbonation time of 40 min. Hamerski et al. (2012) achieved color removal of 93%, adopting pH 9.5, 80°C and 20 min of carbonation.

Favero, Hamerski and Aquino (2014) achieved color removal of 92.9 and 91.6% using carbonated broths with a flow rate of 200 NL h^{-1} and pH between 8.0 and 9.0.

OZONATION

Six articles dealt with the clarification of the broth using ozonation, highlighting the authors Juliana A. S. Sartori and Cláudio L. Aguiar, with publications in 2015 in the magazine *Chemical and Process Engineering Research* and 2019, at Ozone: *Science & Engineering.*

Silva, Sartori and Aguiar (2015) studied ozonation in heated and non-heated broth.

Fonseca et al. (2017) investigated ozonation in sucrose solutions and phenolic compounds. The flow of 30 L min^{-1}, under constant agitation, the phenolic compounds were degraded without loss of sucrose.

Sartori et al. (2019) evaluated the degradation of flavonoids and phenolic acids using solutions of rutin and caffeic acid prepared in methanol.

Rodrigues, Sperandio and Andrade (2018) analyzed the effects of ozonation on ICUMSA turbidity and color, resulting in a 12% reduction in the sample with a dosage of 21 mg min^{1} O_3, at 60°C for 60 min.

Azevedo et al. (2019) studied the effects of O_3 on the inactivation of the enzyme pholyphenol oxidase (PPO).

Bernardi, Jorge and Paraíso (2019) proposed a mathematical model to ensure O_3 saturation and avoid waste.

PEROXIDATION

Four articles dealt with clarification using peroxidation.

Sartori, Magri and Aguiar (2015) evaluated the efficiency of peroxidation in reducing ICUMSA color, and the best results were achieved for broths treated with 600 mg L^{-1} H_2O_2, at temperatures greater than 50°C and pH less than 7.0.

Nguyen and Doherty (2012) investigated the degradation of caffeic acid by peroxidation, at pH 3.0 and 60 min, 16.5% of caffeic acid was degraded.

Magri et al. (2019) clarified sugarcane juice using 1000, 5000 and 10000 mg L^{-1} H_2O_2. Color reductions of 39.7, 48.3 and 60.7% and BRIX, 63.9, 65.2 and 67.1% were observed.

Dantas et al. (2020) evaluated the peroxidation associated with UV radiation to clarify the broth. The ICUMSA color reduction was 55% and the authors concluded that radiation acts as a catalyst, accelerating clarification.

MICROFILTRATION

Six scientific articles reported on MF and ultrafiltration (UF), highlighting the work published in 2020 by Vu Thevu, Jeffrey Leblanc.

Moreno, Oliveira and Barros (2012) evaluated the effects of MF clarification on color and turbidity removal. Color reductions of over 16.4% were observed using the 0.2 μm and 2.0 bar membrane. MF reduced turbidity by 92.4%.

Gaschi et al. (2014) clarified broth by MF followed by UF of the permeate, and only by UF. MF followed by UF had the best performance (44.8% color removal).

Li et al. (2017) obtained satisfactory broth clarification results with tubular membranes of $ZrO_2/\alpha\text{-}Al_2O_3$, de 0,05 μm. UF achieved 50.5% color removal and reduced haze by 98.6%.

Rezzadori et al. (2014) studied MF clarification with 5% passion fruit pulp added to the juice to reduce acidity and minimize enzymatic browning.

Ferreira, Cozar and Schimidt (2016) evaluated the influence of temperature and pressure on the permeate flux obtained after clarification by MF.

OTHER METHODS

After analyzing the scientific articles, nine publications were identified that adopted alternative methods considered less common, and that can replace sulfitation in the clarification of sugarcane juice (DOHERTY, 2011; ORTIZ et al., 2011; LAKSAMEETHANASAN et al., 2012; COSTA et al., 2014; COSTA et al., 2015; GALDINO et al., 2019; TEIXEIRA et al., 2019; TIWARI et al., 2019; LEITE and BARBOSA, 2021).

CONCLUSION

The thirty articles in this review covered nine alternative methods to sulfitation. None of them presented an economic analysis, making it unfeasible, in a way, the application as substitute methods of sulfitation.

Carbonation proved to be effective for removing color and starch from the samples, under different physicochemical conditions.

Ozonation had better results for heated broth, and peroxidation removed phenolic compounds at acidic pH.

MF was effective in clarifying the broth, in addition to reducing the amount of chemical reagents. In this process, the pore diameter is a determining factor.

Natural polyelectrolytes acted effectively to remove color from the broth.

The nine mentioned methods are recommended to be used in substitution to the use of sulfur in the sugarcane juice clarification process.

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