



Novel Conducting Polymer Electrode for Clarification of Cane Juice

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ABSTRACT

In the present study removal of non-sugar constituents such as colloids, organic and inorganic salts and polyphenols from cane juice takes place. The study was therefore carried out to develop a novel polymer electrode for the clarification of cane juice. A method is described for the clarification of cane juice with other Physico-Chemical parameters. The process requires no chemicals for the removal of non-sugar impurities from cane juice. The proposed process is said to be an ecofriendly. Inorganic impurities were also removed by using the conducting polymer electrode.

Keywords: Conduction, clarification, non-sugar, cane juice, electrode.

INTRODUCTION

Sucrose commonly known as sugar is one of the substances manufactured on commercial scale in India. Sugar industry located in the rural areas is one of the largest agro based industry in India, next to cotton and textile industry. The annual value of the product of the sugar industry in India is about Rs. 600 billion. India is the largest cane sugar manufacturing country in Asia and occupies second position in the world [1]. The quantity of sugar produced for the last ten years in different states of India is remarkable [2]. Besides this, world sugar balance during last five years is available in terms of its production, consumption, surplus, import demand, export availability, end stocks and stocks consumption ratio in percent [3].

The principle raw material for the manufacture of sugar in India is sugar cane, while in European countries and in the United States of America, sugar is produced from beetroot. In India, sugar cane is crushed by means of different sets of rollers to extract juice. Sugar mills are rated by their crushing capacity. Factories crushing 2500 tons of cane per day are of average capacities and economically feasible in India. However, capacities of 10,000 tons per day crushing factories are also available in India in increasing trend factions. About 560 factories are in existence at various parts of India. Sugar cane is an important agro industrial crop in India. It is cultivated in an area of over 3.8 to 5 million hectares spread over a wide range of agro ecological situations. At present, the total production of sugar cane in the country is around 277.5 million tons and we are producing over 16 million tons of white sugar. Clones of different maturity play an important role in boosting cane productivity [4]. Literature [5] gives an appropriate estimate of the

composition of sugar cane though it is in variable quantities. The sucrose content of the cane is roughly in the range of 12-15 percent. The remaining part i.e. water, fiber, and non-sugar constituents exist in cane varies, within narrow limits, on account of number of factors, such as the variety of cane, climate and soils of the cultivation place, the mode of irrigation, the extent of growth and of cane maturity.

In India, the cane juice is converted into plantation white sugar at one-step basis by using lime and sulphur as clarification means. Whereas, globally it is first crystallized as raw sugar having 97.8 % purity without using sulphur and then it is refined after melting the raw sugar and purifying the melt for recrystallisation. In India the product contains 99.95 % sugar content i.e., purity where the refined sugar of 99.99 % purity. The manufacture of sugar from cane juice involves in general four main operations viz clarification, evaporation, boiling and crystal separation. It is for this reason that a factory is often referred to the clarification process adopted therein, thus a factory using lime and sulphur dioxide as the chemicals for clarification of juice, is referred to as sulphitation factory. The available electrolytes in a solution are responsible to conductivity measurement. In fact, conductance is the ability of a solution to conduct electric current, while conductivity is the conductance in given value. In fact, all substances possess some conductive properties. Generally, organic compounds such as benzene, alcohol, petroleum products etc., have very low conductivities while metals have very high conductivities. In electrolytic conductivity analysis for sugar samples which have complex matrices including acid water and salts. The role of conductivity of primary, mixed and clarified cane juice in a sugar factory were measured in terms of total non-sugar present in cane juice, which is responsible for conductivity generation. It may be pointed out that higher the non-sugar present in cane juice and sugar imparting less purity of cane juice. Such purity drop in cane juice is due to increasing amount of non-sugar showing higher conductivity value of cane juice and sugar [6-9].

Various processes are available for the effective clarification of cane juice [10-17]. Doss [18] observed that electrolysis of cane juice in acidic condition is more advantageous and beneficial than at higher pH. Use of phosphoric acid, active carbon and graphite electrode are good choice for the clarification of cane juice. Electrolysis means decomposition of electro active component or compound into its constituent's components and ions on applying potential differences by the process of oxidation and reduction. Oxidation and reduction are very effective methods for the destruction of non-sugars present in cane juice that can be separated from the mother liquor either by flocculation or settling, ultimately leading to the clarification of cane juice.

MATERIALS AND METHODS

Preparation of polypyrrole coated graphite electrode: The conducting polypyrrole coated graphite electrode was prepared in a special type of self-designed electrolytic cell which was fabricated at Indian Institute of Technology (IIT), Kanpur. The designed electrolytic cell is flat bottomed cylindrical in construction and has a gas inlet and two side arms with female quit frit joints, which are inserted with two male joints terminated with sintered glass frits. The conducting glass electrode is then attached to a crocodile clip with a long wire contact. This is so clipped that the crocodile clip is above the surface of liquid. The graphite electrode and saturated calomel electrode (SCE) are then placed in the side arms provided (separated from the solution by a sintered glass frit).

Electrochemical polymerization of pyrrole on graphite electrode: The electrochemical polymerization of pyrrole on graphite electrode produced a strongly adhered, durable film with enhanced and good electrode properties. Our interest to prepare of durable, conducting organic graphite electrode surface led us to this approach. Chemicals used for the deposition of polypyrrole on graphite electrode were pyrrole (Merk), Sodiumparatoluenesulphonate, calciumhydride obtained from Merk India Ltd. Electrolytic cell fitted with graphite rod, conducting glass electrode, saturated calomel electrode (SCE) is shown in fig.1. A

regulated constant D.C power supply source, Elnova was used for a constant potential in the circuit during the electrolysis.

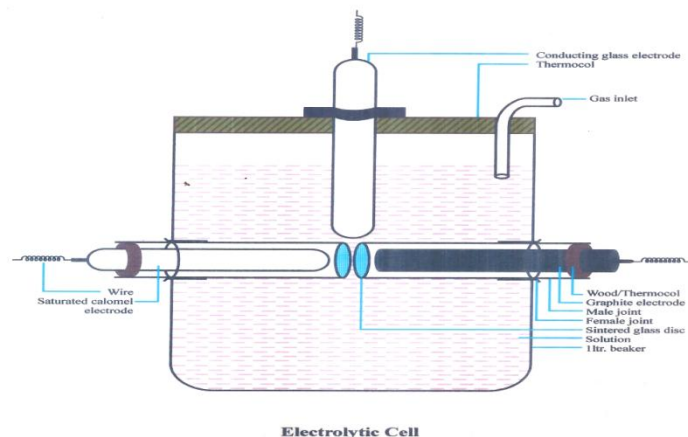
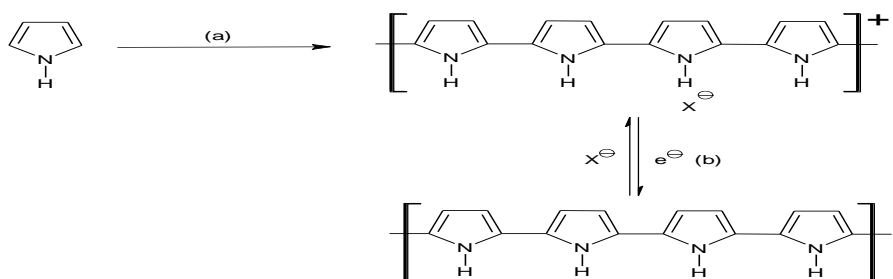


Fig.1: Polypyrrole coated graphite electrode

Method: A mixture of distilled pyrrole and sodiumparatoluenesulfonate solution was used as an electrolytic solution for the deposition of polypyrrole on the graphite electrode. The graphite electrode was attached to the positive terminal whereas both saturated calomel electrode and conducting glass electrode were attached to the negative terminal of the source. A constant potential of +1.0 V was applied to the graphite electrode with respect to saturated calomel electrode and electrolyzed for about one hour. A thick black film of polypyrrole was formed on graphite electrode. This result was further confirmed by spectral technique. The mechanism of the preparation of polypyrrole through oxidative polymerization of pyrrole (monomer) is shown in scheme 1. In this neutral state the polymer is not conducting and only becomes conducting when it is oxidized. The charge associated with the oxidized state is typically delocalized over several pyrrole units and can form a radical cation. The physical form of polypyrrole is usually an intractable powder resulting from chemical polymerization and an insoluble black thick film resulting from electro polymerization.



Scheme 1: (a) Electrochemical preparation of poly (pyrrole) and (b) separate redox between charged and uncharged forms.

Electrolysis of cane juice by polypyrrole coated graphite electrode: Freshly cut sugarcane was taken for the experiments from the farm of National Sugar Institute (Govt. of India), Kanpur. The sugarcane was crushed in electrically driven crusher in the laboratory. The first 500 ml of juice was rejected to avoid any contamination. The freshly crushed cane juice was filtered by an ordinary plastic sieve so as to remove the fine pieces of bagasse. The electrolysis of about two liter raw juice was carried out in a circular electrolytic cell (diameter=11cm, height=14cm) using polypyrrole coated graphite electrode. The fig. 2 shows the circuit diagram for the electrolytic clarification of cane juice.

The polypyrrole coated graphite electrodes were fitted tightly in high density polythene (HDPE) lid in order to maintain a constant separation. A rectifier that is regulated D.C power supply (ELNOVA) was used as a source of potential for electrolysis. A volt meter (range 0 - 30 volt) was connected across the electrodes to monitor the potential difference of the electrodes during the electrolysis. A multimeter (Model-PP 9007, Philips) was incorporated in the circuit for the measurement of current produced across the electrolytic cell. The purity, pole and brix were measured by sucromat (AUTOPOL 880, Rudolph) which is computerized and microprocessor based assembly of saccharimeter and refractometer. The change in pH and conductivity was monitored with the help of digital pH meter (Century CP 901) and conductivity meter (WTW LF 573, Germany). The color in term of absorbance of cane juice was measured at a wavelength 420 nm by double beam UV-visible spectrophotometer (Chemito, Spectrascan UV-2600).

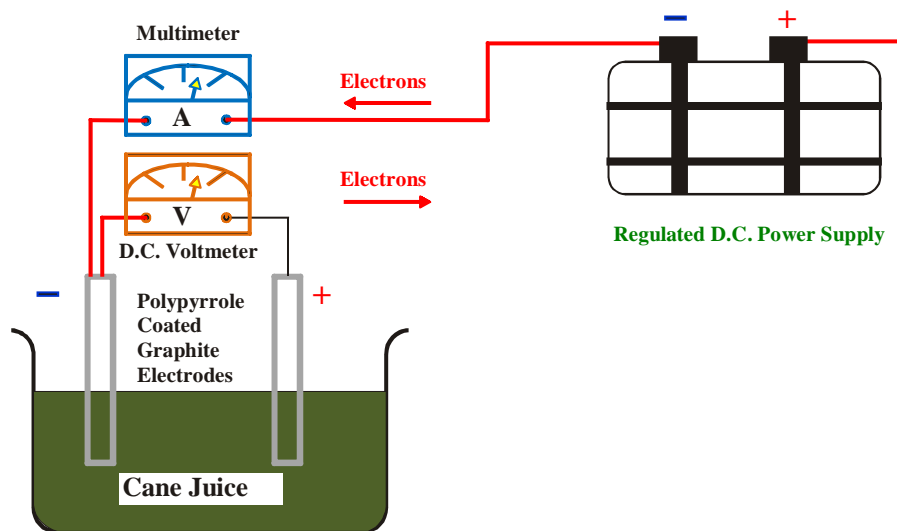


Fig. 2: Circuit diagram for the electrolytic clarification technique.

RESULTS AND DISCUSSION

Variation of purity with time : Incubation of reagent mixture used for the determining the purity in the presence of all the test compounds 0 to 60 minutes give high purity of cane juice. The results were in agreement with our concepts that increase in potential is necessary for the effective clarification of cane juice under our experimental condition (Figure 4 a-e).

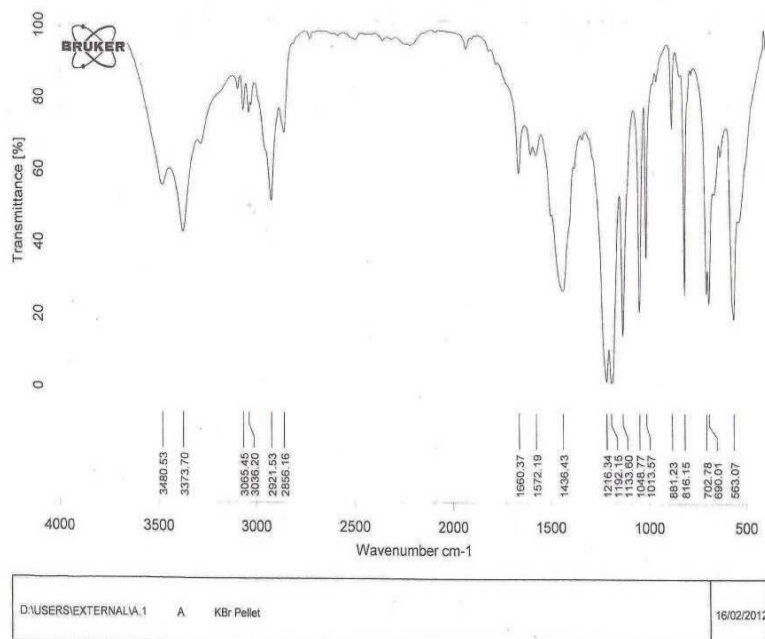


Fig 3: IR spectra of the film deposited on the graphite electrode.

Table 1: Interpretation of peaks of IR spectra of polypyrrole

IR absorption Frequencies	
Observed IR Frequency of Absorption, cm^{-1}	Assignment
3480.53	Nearest to 3400cm^{-1} i.e. the peak of secondary amine. Therefore it is confirmed that the peak at 3480.53 cm^{-1} is of N-H stretching.
3373.70	The N-H group has two spikes at 3373.70 cm^{-1} and another at 3200 cm^{-1} .
3065.45	This peak though not intense not sharp which is nearest to 3110 cm^{-1} . This is the IR frequency of C-H stretching. Here it is interesting that the CH bands are weak as they are in pyrrole dimer and trimer.
1600.37 to 563.7	This region of IR absorption frequency contains the pyrrole ring vibrations.

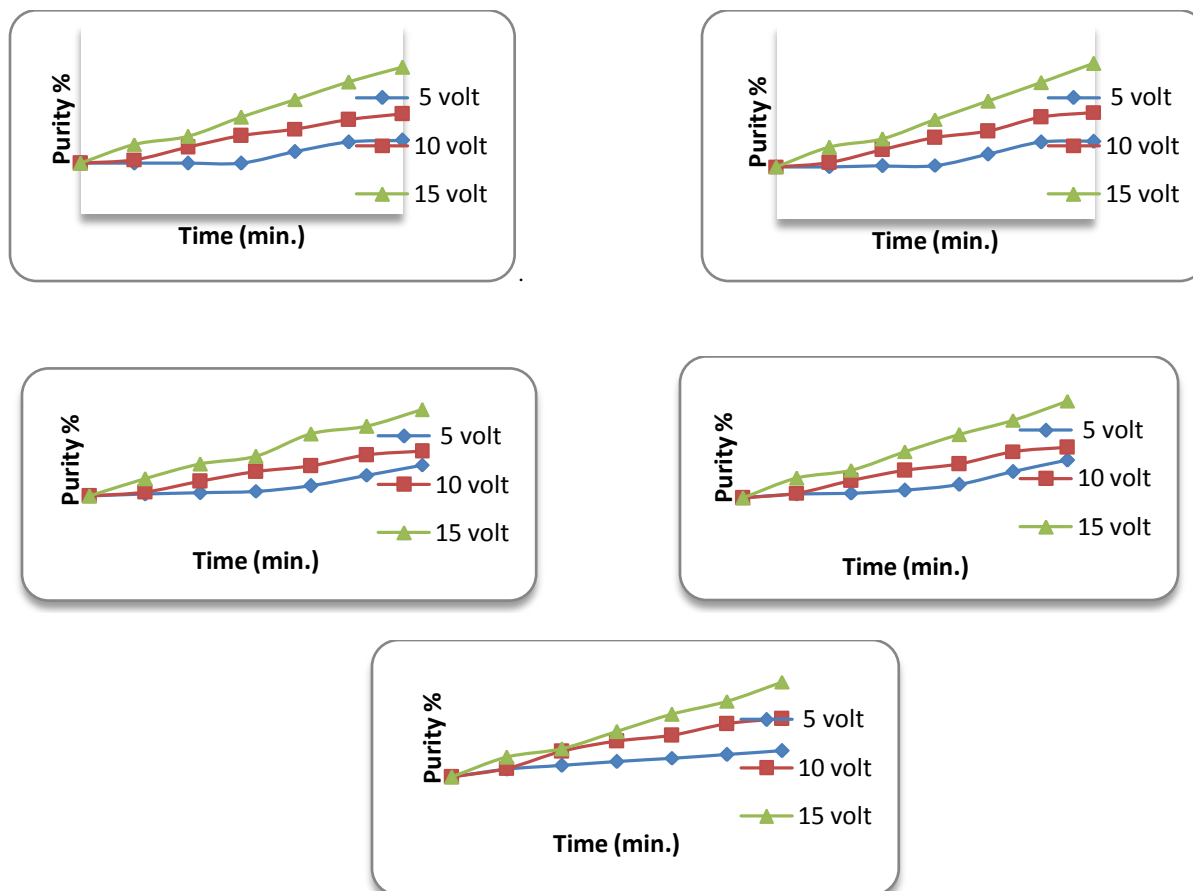
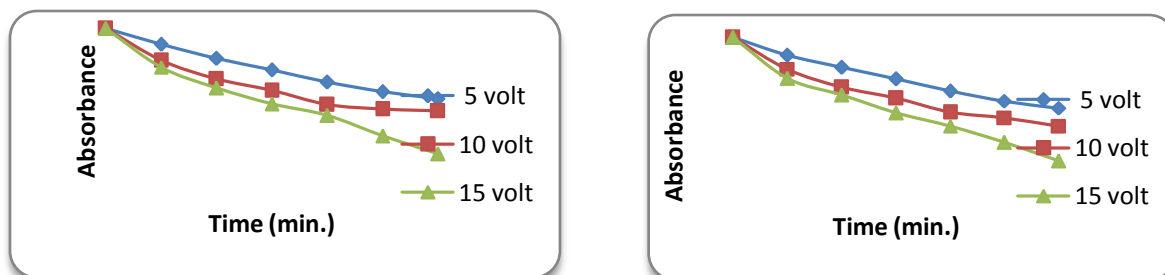


Fig. 4 : Variation of purity with time and potential at a. 30^oC temperature, b . 40^oC temperature, c. 50^oC temperature, d. 60^oC temperature and e. 70^oC temperature

Variation of color with time : A comparative study of the color production ability of cane juice at different potential is made. IR spectra of the film deposited on the graphite electrode shown in fig.3 (Table 1). It has been observed that color decreases as a function of time at different potential. The decrease in color may be attributed to the cathode reduction as some of the coloring impurities got deposited thereby decreasing the color. The decrease in color may be due to the neutralization and precipitation of colloidal coloring matters during electrolysis (Figure 5 a-e).



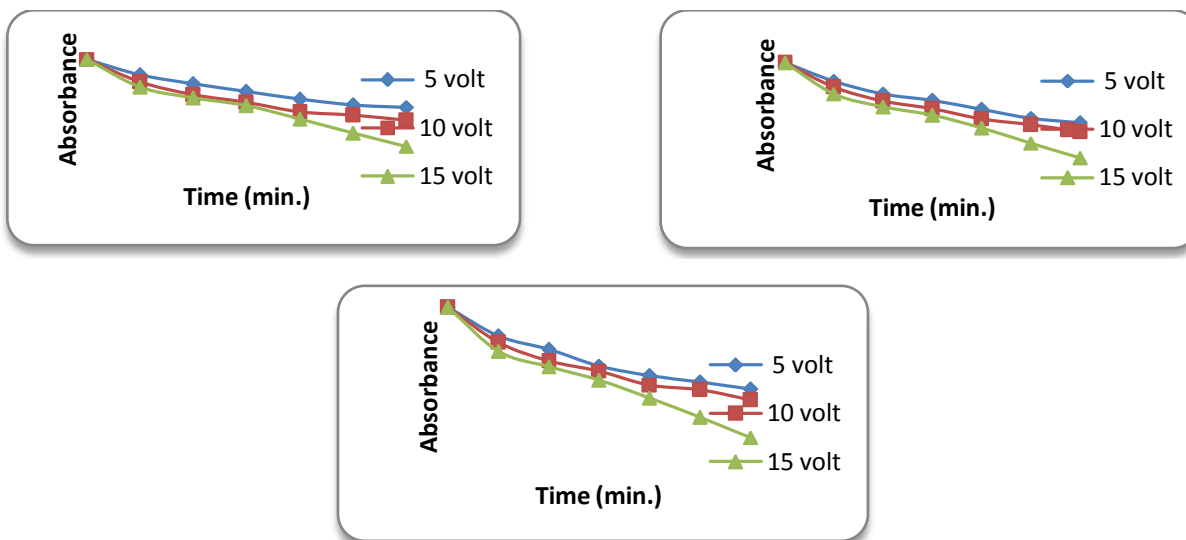
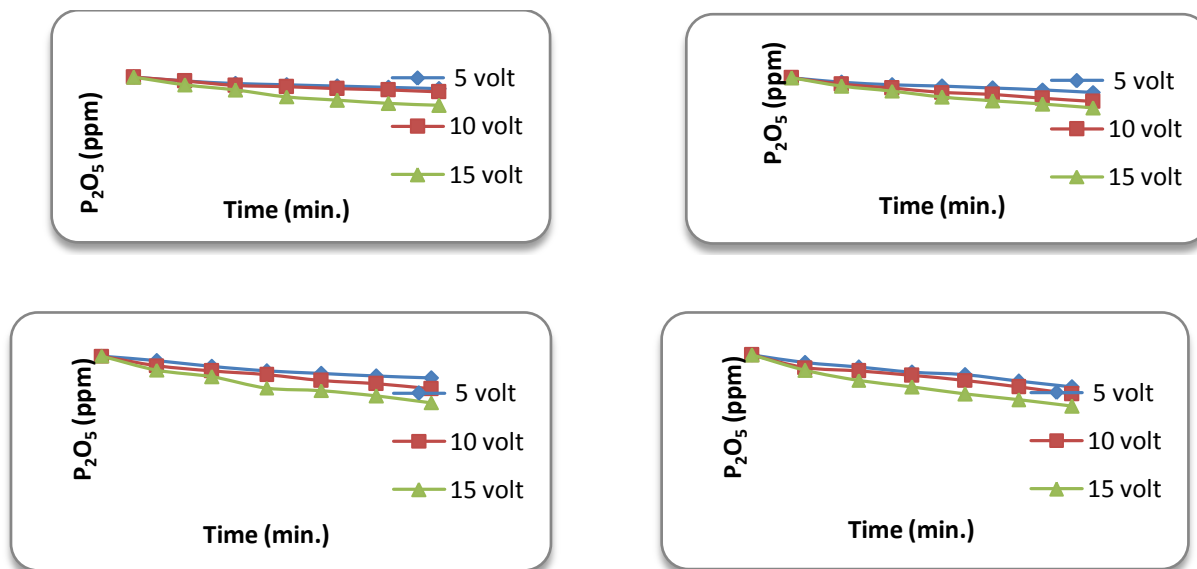


Fig. 5 : Variation of absorbance with time and potential at **a.** 30^oC temperature, **b.** 40^oC temperature, **c.** 50^oC temperature, **d.** 60^oC temperature and **e.** 70^oC temperature

Variation of P₂O₅ content with time: The formation of P₂O₅ content from cane juice was found to be both time and potential dependent. A nearly linearly relationship was found between the time of clarification of cane juice and amount of potential applied. The relationship between P₂O₅ production and time of cane juice was observed up to 0 to 60 minutes only. At higher time the linearity was disturbed (Figure 6 a-e).



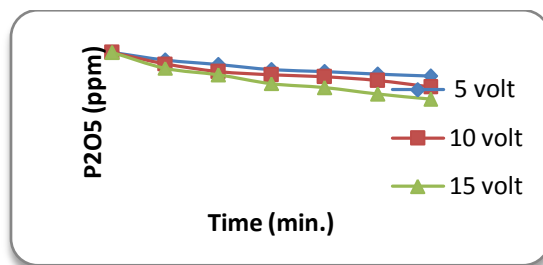


Fig. 6 : Variation P_2O_5 with time and potential a. at $30^\circ C$ temperature, b. at $40^\circ C$ temperature, c. at $50^\circ C$ temperature, d. at $60^\circ C$ temperature and e. at $70^\circ C$ temperature

Variation of CaO content with time: It was interesting to know that at 5 and 10 volts, the rate of decrease of CaO content was less than at 15 volt potential. At 5 and 10 volts, potential did not produce effective amount of clarification under similar conditions. The reason for the decrease in CaO is that the large no. of Ca^{++} ions were deposited on cathode during electrolysis [19]. Considerable quantities of calcium ions got precipitated due to the charge neutralization during the course of electrolysis. Some part of calcium is also involved in the precipitation with the phosphate content of the cane juice [20]. Considerable quantities of calcium ions got precipitated due to the charge neutralization during the course of electrolysis (7a-e).

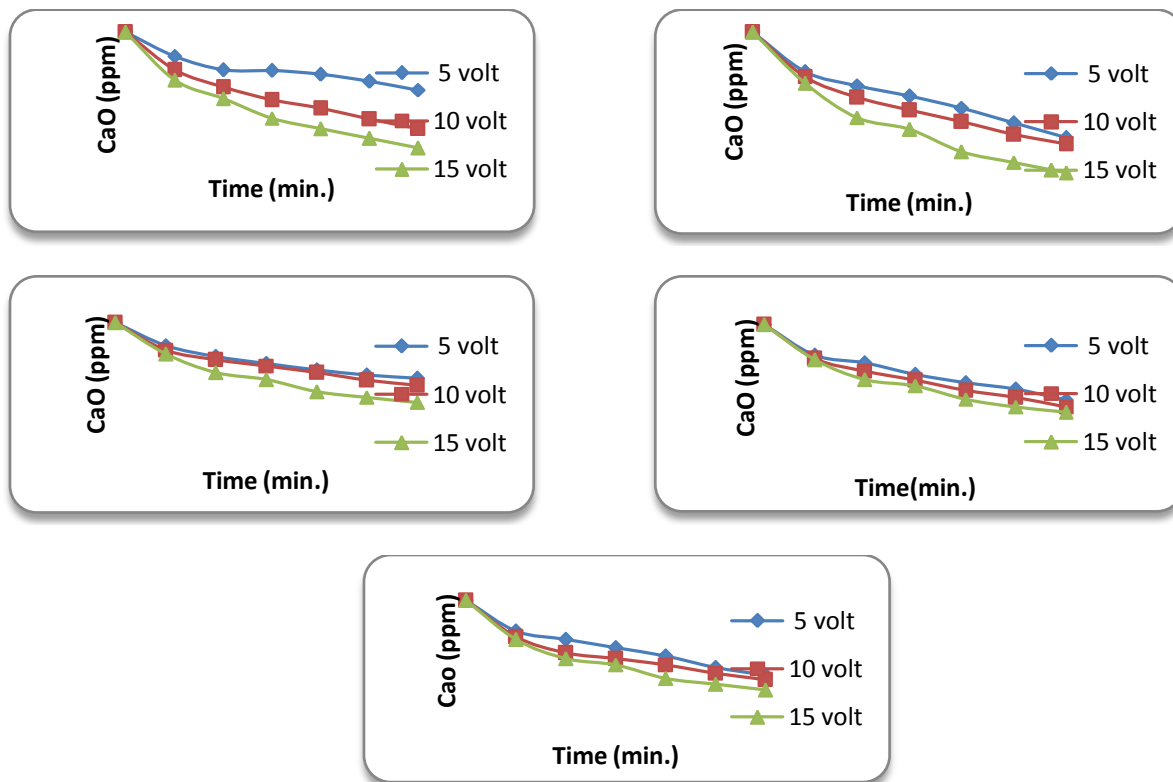


Fig. 7 : Variation CaO with time and potential at a. $30^\circ C$ temperature, b. $40^\circ C$ temperature, c. $50^\circ C$ temperature, d. $60^\circ C$ temperature, e. $70^\circ C$ temperature

It may be concluded from the present study that electrolytic clarification of cane juice can be improved by the use of polypyrrole coated graphite electrodes. The developed novel electrode gives precise and accurate results and expected to ensure better color of sugar crystal during sugar manufacture. The use of polypyrrole coated graphite electrodes for electrolytic clarification also has several advantages such as save of the power, easy maintenance of electrode materials etc., but the most significant advantage is that, it does not corrode due to which there is no additional contamination in the cane juice, which was the main limitation of earlier attempts made by different workers.

APPLICATIONS

The developed novel electrode gives precise and accurate results and expected to ensure better color of sugar crystal during sugar manufacture. The use of polypyrrole coated graphite electrodes for electrolytic clarification has several advantages such as save of the power, easy maintenance of electrode materials etc., but the most significant advantage is that, it does not corrode due to which there is no additional contamination in the cane juice, which was the main limitation of earlier attempts made by different workers.

CONCLUSIONS

The present study proves that the clarification of cane juice can be improved by the use of polypyrrole coated electrode at constant temperature and potentials. This techniques appears to ensure that increase in purity, minimum CaO content, minimum P₂O₅ concentration and decrease in absorbance during electrolysis is expected to ensure better color of sugar crystal during sugar manufacture.

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REFERENCES

- [1] Country wise world sugar balance 2010-2011. *Cooperative Sugar Journal*, **2011**, 42(7), 90-93.
- [2] Factories in operation, opening stocks, production, inputs, consumption and export of sugar during the last ten years. *Cooperative Sugar Journal*, **2010**, 1(8), 57.
- [3] World sugar balance during 2006- 2007 to 2010-2011. *Cooperative Sugar Journal*. **2011**, 42(7), 89.
- [4] Sugar cane, sugar and molasses production at a glance. *Cooperative Sugar Journal*. **2010**, 41(88), 56.
- [5] P. Honig, Principals of sugar technology, Elsevier Publishing Company. 295, **1953**.
- [6] Vikesh Kumar, Rashmi Upadhyay, P. Sanyal., *Sugar Tech*, **2012**, 14(2), 95-100.
- [7] Vikesh Kumar, Rashmi Upadhyay, P. Sanyal, *Sugar Tech*, **2011**, 13(2), 145-149.
- [8] Vikesh Kumar, S.K. Mitra, P. Sanyal, *Sugar Tech.*, **2010**, 12(2), 115-119.
- [9] Vikesh Kumar, S.K. Mitra, P. Sanyal, *Sugar Tech.*, **2009**, 11(4), 324-329.
- [10] L.P Tiwari, R Srivastav. *Proc. of Sugar Technologists Association of India*. **2007**, 28, 3-19.
- [11] P.P Chaturvedi, M.K Srivastava. *Proc. Sugar Technology Association of India*. **2005**, 66, M141-M155.
- [12] D.J.Walton, F.J.Davis, P.J.Langley, Polymer chemistry book. The School of Chemistry, Oxford University. 181, **2004**.
- [13] F Diaz, K.K Keiji. *Journal of Chemical Society, Chem. Comm.*, **1979**, 373, 635-636.
- [14] D.N Ghosh. *Indian Sugar*, **1952**, 14, 383-389.

- [15] S.N Gundu Rao, N.A Ramaiah. *Proc. Sugar Technology Association of India*. **1961**, M85-M96.
- [16] P. Hidi and R.I Nicholson, *International Sugar Journal*, **1959** 61, 9-12.
- [17] A. Lima. U.S Patent no. 1953653, **1934**.
- [18] K.S.G Doss. *Proceedings of Indian Academic Science, Section B*. **1956**, 38, 49-58.
- [19] N.A Ramaiah, J.K Sharma. *Proc. Sugar Technology Association of India*. **1960**, 28, 64-68.
- [20] R.B Nigam, S.K Gupta, S.K Mitra, P Sanyal. *Proc. of Sugar Technology Association of India.*, **2003**, 65, M3-M11.