Use of Cobalt Nitroprusside Nanoparticles in the detection of Sulphites in Sugar

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Abstract— *Sulphite detection and removal is currently an important process in the manufacture of sugar. Our objective in this review paper is to explore the methods of detection of sulphites using Cobalt Nitroprusside nanoparticles.*

Cobalt Nitroprusside, also known as cobalt pentacyanonitrosylferrate has proved to be an excellent coordinate compound for the manufacture of its nanoparticles and usage of those nanoparticles in the detection of sulphite. The method proposed in our review paper involves using a carbon paste electrode modified with Cobalt Nitroprusside nanoparticles. Cobalt Nitroprusside being a transitional element complex and is used for the quantification of analytes, provides the industry with a wide potential window.

Sulphites in foods and most commonly in sugar, pose a threat to the health of individuals who consume processed foods regularly. Sulphites are known to cause allergic reactions on the face and eyes and vomiting, diarrhoea and cramps, it is essential to remove the sulphites in ingestible items.

Hence, it is an important process to detect the sulphites present in the sugar making process and taking the necessary steps to eliminate them from the sugar-manufacturing process.

Keywords— Sulphites; processed foods; sugar; cobalt nitroprusside nanoparticles.

I. INTRODUCTION

The sugar that is largely consumed across India is called,' Plantation White Sugar'. This 'Plantation White Sugar' is manufactured after operations such as affination, filtration and carbonation. It is because of these operations, the market gets flooded with the extra white, refined sugar. Most commonly, sulphur dioxide is used by sugar mills to lighten the colour of the molasses and extend its shelf life. This leads to residual sulphur remaining in the sugar in the form of sulphite, which is considered to be risky for human consumption and may cause health hazards towards sensitive individuals such as:

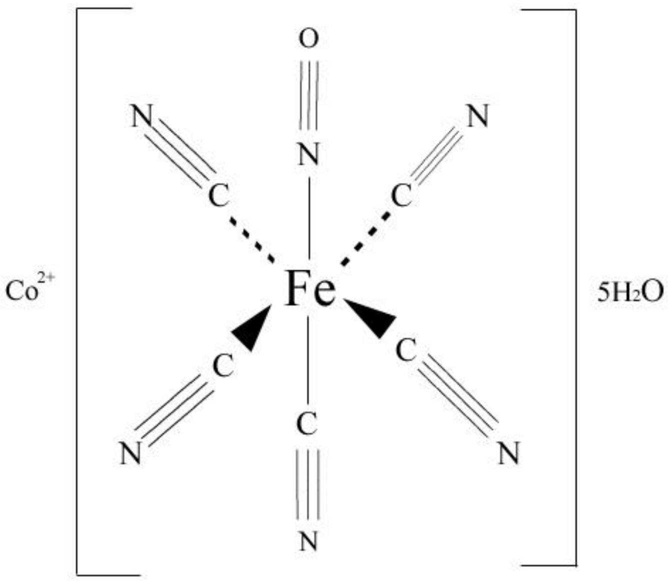
1. Dermatitis
2. Urticaria
3. Flushing
4. Hypotension
5. Abdominal Pain
6. Diarrhoea
7. Anaphylactic reactions

The sugar mills in India follow a process of double sulphitation for the plantation of white sugar. This causes the residual sulphur to be left behind in the manufactured sugar, which can be harmful to the human body. Traditionally, residual sulphur is removed by the method of evaporation and double distillation. This method leads to loss of yield and becomes uneconomical for the production of sugar. Moreover, the presence of residual sulphurous acid in the sugar, which is formed due to the reaction of excess sulphur dioxide with water after re-sulphitation of the unsulphured syrup obtained from the evaporator, increases the sulphur dioxide content of the sugar.

Hence, because of the health hazards being posed by the presence of sulphites in sugar, The Bureau of Indian Standard: 5982-1970, has kept the maximum sulphur dioxide content limit as 70 ppm, within the safe tolerance limit. For 'Plantation White Sugar' the safety limit has been fixed for 70 ppm and for refined sugar it has been fixed as 20 ppm. International Standard has fixed the safety tolerance limit at 10 ppm for refined sugar.

II. CRYSTAL STRUCTURE OF COBALT NITROPRUSSIDE.

The structure of Cobalt Nitroprusside, or as its chemical term refers to Cobalt Pentacyanonitrosylferrate, can be described as; the iron nucleus of the complex, octahedrally coordinated to five cyanide ligands and a nitrosyl group and the cobalt nucleus of the complex coordinated to 5 cyanide ligands and one water molecule. The cyanide ligands create a bridge (Fe-C≡N-Co) and link the metal centres. This provides a cubic framework and uncoordinated water molecules are held in position in crystallographically distinct environments by hydrogen bonding or van der Waals forces. This cubic framework characterizes unique vacancies and a high degree of disorder.



Cobalt Nitroprusside Structure

FIGURE 1: Properties of Nanoparticles Used

Recent globalization trends show that nanoscale metallic particles are being considered for their intriguing properties and potential application across various industries. Due to the large surface-to-volume ratio and superior properties of the nano-sized metal particles, these prove to be very useful candidates for electrochemical, food safety and catalytic studies than their bulk counterparts. The application of these nano-sized metallic particles involves the idea of carbon paste electrodes (CPE) being modified with nanoparticles. This method provides a considerably improved basis for the electrochemical behaviour in the respective compound.

In our case, Cobalt Nitroprusside nanoparticles (chemically referred to as Cobalt Pentacyanonitrosylferrate.). The ligand that forms the molecule mentioned above ([Fe(CN)5NO]2−) is an important one because of its ability to form complexes with most of the transitional metal ions. The advantage of nanoscale sizes factors in the improvement of dispersibility of Metal Nitroprussides in solvents.

The metal nitroprusside as stated above has to be modified into electrochemical sensors. This can be achieved by electrochemically coating the metal nitroprusside on the rigid electrode surface. According to some recent approaches, the CoNP nanoparticles have been used as a modifier in designing an electrochemical nanosensor for the quantification of sulphur. In this case, this CoNP nanosensor is used extensively for the detection of sulphites in sugar.

III. SYNTHESIS OF COBALT NITROPRUSSIDE

Cobalt nitroprusside synthesis can be achieved by three different procedures: 1. Drop-by-drop method, 2.sonication method, 3. bulk mixing method. This synthesized cobalt nitroprusside then has to be modified into catalytically oxidisable electrodes for the detection of sulphites. Out of the 3 methods mentioned above, according to Mr.S.Devaramani and Mr.P. Malingappa, drop-by-drop method shows the best catalytic activity.

The Cobalt Nitroprusside samples that are formed by the drop-by-drop method, sonication method and bulk mixing method have been designated as n-CoNP, s-CoNP, b-CoNP.

3.1 Drop By Drop Method

Through experiments conducted by Mr Devaramani and Mr Malingappa, the drop-by-drop method is initiated by using 10 m of the aqueous solution of 0.01 M sodium nitroprusside and added dropwise to 10 ml of 0.02 M aqueous solution of cobalt chloride. The thermostated beaker maintained at 5-10◦C, under vigorous stirring forms the turbid solution of cobalt nitroprusside complex. This turbid solution has to be then maintained in acidic condition and left untouched for 24 hrs. The supernatant liquid is then decanted and made to go through a routine process of centrifugation. The centrifuged compound of CoNP particles is then washed with water then alcohol and is now ready to be used as a modifying agent in carbon paste electrodes (CPE).

3.2 Electrode Preparation

The electrode preparation method specified by Mr Devaramani and Mr Malingappa proceeds by manually mixing dispersed graphite powder with the prepared n-CoNP at a 15:1 mass ratio. To this 38 % (m/m) of mineral oil has to be added. The resultant mixture has to be ground in an agate mortar for 10-15 minutes. This paste then has to be packed in a capillary tube and a copper wire has to be inserted from the opposite end to create an electrical contact. After being kept aside for 24 hrs, the electrodes would be ready for electrochemical sensing.

IV. MODIFIED CPE DETECTION OF SULPHITES

The n-CoNP CPE has to be tested for the detection of sulphite in a sample sulphite containing solution. According to the tests done previously, a solution of 0.5 KNO3 with the presence of 3.4 mM sulphite can be used for the detection of sulphite with the modified CPE. The CoNP nanoparticle here significantly improves the anodic current of the modified electrode in presence of sulphite. Hence, these CoNP nanoparticles are essential for the detection of sulphites in any sulphite containing solution.

V. USE OF THE N-CONP CPE IN THE DETECTION OF SULPHITE IN SUGAR

Sulphur dioxide remains an important constituent for sugar manufacture. It avoids browning of the raw sugar during the crystallization and evaporation process. It even prevents the enzymic oxidation of polyphenols and precipitation of calcium ions as calcium sulphite. This makes it important to the industries to take steps towards detection of sulphites in the sugar so that it does not exceed the parameters stated by National Legislations and adhere to the safety regulations set by the standard body of food safety in India, FSSAI (Food Safety and Standard Authority of India).

The steps towards the synthesis of sugar proceed as follows:

1. Obtaining a suitable carbohydrate source for extraction of its juice, eg. sugarcane, beet sugar, palm sap, etc.
2. Extraction of juice of the suitable carbohydrate source.
3. Sulphitation of the juice.
4. Post-sulphitation, the juice has to be settled to obtain clarity in the liquid.
5. Concentration of the juice to obtain syrup for the processing of crystallized sugar.

Here, the steps involved do not detect the sulphur content of the sulphitation undergone juice. The industries need to know the content of sulphur before concentration so that the sulphite content in it does not exceed the standard regulated 70 ppm for plantation white sugar or 20 ppm for refined sugar. Hence, the use of the n-CoNP CPE can be made to detect the amount of sulphite in sugar to ensure its treatment before being sent for concentration to syrup form.

The proposed reaction for the same will be given as follows:

$$2Co[Fe^{III}(CN)_5NO] + 2Ca^{2+} + HSO_3^{-} + H_2O \rightarrow 2KCo[Fe^{II}(CN)_5NO] + SO_4^{2-} + 3H^{+}$$

Steps for the desulphitation are proposed as follows:

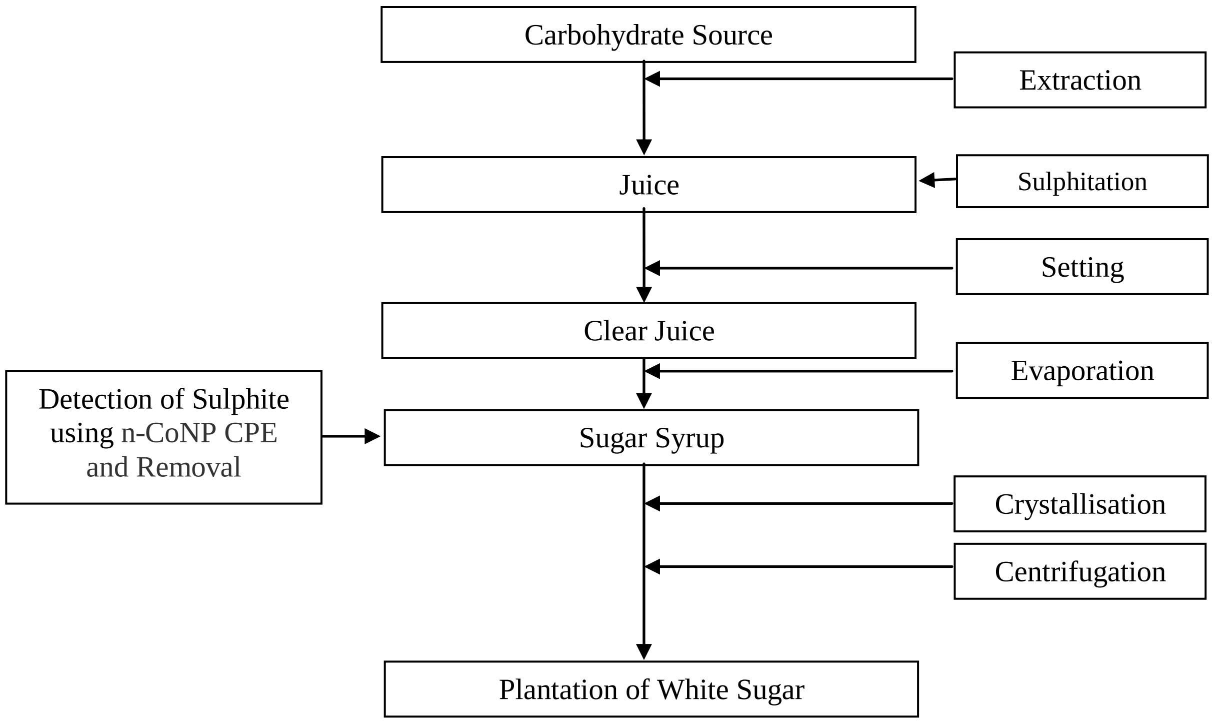


FIGURE 2: Steps for the desulphitation

Hence, using this methodology, the n-CoNP CPE can be effectively used for the detection of sulphur in sugar.

VI. CONCLUSION

Cobalt Nitroprusside is an important complex in the field of upcoming nanotechnology and nanoparticles. It is an extremely useful complex for the detection of compounds; sulphites, for instance. It has been used as a modifier in carbon paste electrode which in turn affects its electrochemical activity drastically. Even though the short term effects of sulphites are not usually an area of concern for the human body, its long term effects can be harmful. Alternate solutions like using the sonication method or bulk mixing method provide an insight on how the usage of Cobalt Nitroprusside nanoparticles in the detection of sugar can be modified. Having a low catalytic activity can even be preferable over a high catalytic activity producing CPE since the control over the process is more. The continued research in the removal of nanosensors and nanoparticles may also bring a change in the direction of our consumption of various products. Our review paper shall hopefully provide some knowledge to the researchers having an interest in the use of nanosensors and cobalt nitroprusside nanoparticles.

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