International Food Research Journal 25(4): 1391-1396 (August 2018)
Journal homepage: *http://www.ifrj.upm.edu.my*

Evaluation of remaining blankit in refined Iranian sugar products through ion exchange resins

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Article history

Received: 16 April 2017
Received in revised form: 13 June 2017
Accepted: 14 June 2017

Keywords

Sugar
Blankit
Sodium dithionite
Ion exchange resin

Abstract

Sodium dithionite with blankit trade name is being used as bleaching material in sugar industry. This is noticeable that the application of this material in food industries is led to irreparable side effects such as cancer. Therefore, the evaluating remaining blankit is one of the most important factors in sugar quality control. Recently, ion exchange resins are replaced with old methods to decrease the remaining blankit in sugar. Accordingly, in this study, amount of blankit in various sugar factory products of Tehran province was evaluated after using ion exchange resins. Results of this research showed that the use of double or triplex tanks containing these resins decrease blankit less than 6 ppm. Indeed, this method effectively was led to remove blankit and produced white sugar.

Introduction

Sulfur compounds have been widely used in food industries as healthy materials for many years. Blankit ($Na_2S_2O_4$) belongs to this group of compounds which is used as bleaching material in different industries (Kreber *et al*., 1999) such as sugar (Canadian Sugar Institute., 2011), nuts, paper (Carreira *et al*., 2012) and textile (De Carvalho *et al*., 2002). In sugar industry, this bleaching agent is used to refine syrup and eliminate remaining colors of sugar beet, sugarcane and created color compounds during production process. Sugar decolorization by blankit depends on its ability in redox reactions. In fact, the use of blankit produce sulfur dioxide which avoid production of color compounds in syrup through blocking Maillard reaction (Shibamoto *et al*., 1977). Sometimes, this material remains in sugar and its overdose lead to gastrointestinal disease through its effects on stomach villi and intestinal villus and in long term may result to elimination of anti-oxidants (Meng, 2003).

Dry blankit is a stable compound but during the heating process of syrupin temperatures higher than 90°C and in presence of oxygen, it decomposes and dithionite ($S_2O_4^{2-}$) remains in solution. Dithionite is an anionic compound that in various pH and through redox reactions can be converted into different sulfur products including; sulfurous anhydride, sulfite, hydrogen sulfite, thiosulfate, sulfate and sulfur dioxide (Helio *et al*., 2012). It should be pointed out that high consumption of dithionite can result to cancer (Meng and Zhang, 1999; Meng, 2003).

Many people prefer sugars and candies with white appearance (Iraie *et al*., 2014). Therefore, some sugar factories use blankit more than authorized limit for decolorization. In these factories, blankit are added in several stages to diluted syrups (before operation), concentrated syrup (before crystallization), refined syrup (after carbonation) and or wastes after crystallization process. Also, using blankit in this industry is caused to decrease viscosity of mother liquor which facilitate centrifugation of massecuite (mixture of sugar crystals and molasses produced during the manufacture of sugar) and crystallization of sugar (Hinkova *et al.,* 2002).

Since this material has irreparable effects on human health, evaluation of remaining blankit in sugar is one the most important factors in its quality control. Today, usage of blankit has been limited because it causes to final products outside of standard. In Iran, evaluation of remaining blankit is performed according to Iranian National Standards (standard numbers: 3666, 3679 and 3680) and its acceptable range must be lower than 10 ppm in sugar products and candies (Sani *et al*., 2009).

Therefore, replacing healthy and economic methods for decolorization of sugar is imperative (Mohseni *et al*., 2015). Sulphitation, filtration soils (fossil soils and diatomaceous earth) with

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decolorization capacity, active carbon or coal filtration, and ion exchange resin (active resin) are various filtration and decolorization methods of raw syrup which are performed in many factories for the purpose of better purification of syrup. Accordingly, depending on the circumstances of each company, the choice of purification methods will be different (Hinkova *et al.*, 2002; Eggleston, 2008).

Indeed, syrup sulphitation is a main decolorization process in sugar industry. After sulphitation, different decolorization techniques can be used to remove remaining colors from the sugar syrup containing: activated carbon, bone char and polymeric media (Lindeman and O'Shea, 2004; Zagorodni, 2006). The powdered activated carbon (usually termed as PAC) and granular activated carbon (GAC) are the most common types for sugar syrup decolorization. Also, pyrolyzed ground animal bones have a high surface area which adsorbs color. On the other hand, polymeric media such as ion exchange resins has been developed as a novel technique for the decolorization of sugar syrup (Cane sugar refining with ion exchange resins, 2009).

An ion-exchange resin is a resin which acts as a medium for ion exchange. It is an insoluble matrix in the form of small microbeads with 0.25–0.5 mm radius that is made from an organic polymer substrate. The porous beads provide a large surface area which trap ions. Consequently, the resin can selectively exchange cationic and anionic ions with other ions in a solution. Ion exchange resins can also function as adsorbents in addition to exchange ions. There are various types of ion-exchange resins that use in different purification, separation, decontamination and decolorization processes (Zagorodni, 2006). Currently, the ion exchange (active resin) method is one of the most important complementary operations of refining and decolorization of raw syrup (Hinkova *et al.*, 2002). Of course attention must be paid that lack of appropriate planning in applying ion exchange systems may lead to problems including increase of wastes, refining problems, bacterial activities in syrup and leak of chemical wastes especially through decomposition of sucrose (inversion: inverted sugar) (Zagorodni, 2006).

It is important to note that ion exchange resins have suitable thermal stability, high resistance to thermal shocks and very high absorption capacity. So they can be active in high temperatures and different pHs. The resins have various types which include Purolite, Hydrolite, Pertolite resines. Purolite has higher usage among others (Dardel *et al*., 2008). For instance, Purolite-A500PS is a macroporous poly (vinylbenzyl-trimethylammonium) exchanger which has designed for decolorization of sugar syrups. (Purolite - Model A500PS, 2017). This type of anion-exchange resin has high absorptive capacity for the complex color materials which occur in sugar syrups. The resin is used in the chloride salt form, and can remove 85-90% of the color from concentrated syrup at the high temperatures.

Ion exchange tests can be done with the columns or thanks which be filled with these resins and distilled water without any bubbles. The solution that flows into the column is called input flow and the flow which exits is called output flow. Decolorization system through these resins can be done in a single stage or multistage manner. Multistage systems usually have several column or tanks which are connected to each other in parallel shape. In this research, the decolorization systems containing single, double and triple tanks were designed and used. In multistage systems,next tank containing fresh resins was led to more bleaching effect.

Materials and Methods

Materials

In order to estimate rate of remaining blankit in sugar's samples of Tehran province, nine manufacturing units were evaluated. Three samples were chosen from each unit according to sampling method of the Institute of Standards and Industrial Research of Iran (standard number:3679) and the remaining blankit was evaluated according to Standard Number: 69. All chemical compounds were purchased from Merck Company.Purolite-A500PS was purchased from the Purolite company. The calibration certificate of all equipments was approved by Iranian Standard Organization.

Sample preparation and solutions

In order to prepare sugar samples for test of remaining blankit, rosaniline colorimetric method (Iranian Standard Number: 14519) was applied. In this method, the required solutions were: decolorized rosaniline solution, sucrose, sulfite standard solution 60.86 μg/ml, sodium thiosulfate 0.1 mol/l, sodium hydroxide 0.1 mol/l, iodine solution 0.05 mol/l, hydrochloric acid 1 mol/l, starch glue 1% and formaldehyde 2 g/l. A saturated rosaniline hydrochloride solution was prepared to suspend 1 g of pararosaniline hydrochloride or rosaniline hydrochloride in 10 ml distilled water and shacked. After 48 hours, solution was filtered by Whatman 42 filter paper. Fresh decolorized rosaniline solution (100 ml) were prepared to mix 4 ml of filtered rosaniline solution, 6 ml of concentrated hydrochloric acidwith density:1.9 and 90 ml of distilled water.

Pure sucrose solution was obtained through dissolving 100 g of sucrose without sulfite in 1000 ml of distilled water. Then, sulfite standard solution (500 ml) was prepared to dissolve 2.5 g of sodium sulfite heptahydrate in the sucrose solution.

25 g of potassium iodide without iodate was dissolved in 40 ml of distilled water and transferred to a volumetric flask containing 12.69 g of iodine (laboratory purity grade), this solution was shaken to dissolve iodine completely and then distilled water was added up to considered volume (1000 ml). Sodium thiosulfate solution (0.1 mol/l) was prepared to dissolve 24.817 g of sodium thiosulfate pentahydrate in 1000 ml distilled water.

Titration of solutions

10 ml of hydrochloric acid (1 mol/l), 100 ml of distilled water and 25 ml of iodine solution (0.05 mol/l) were mixed and shaken. Then, 25 ml of sulfite standard solution was added to the mixture and extra iodine was titrated with sodium thiosulfate solution until straw color was appeared. Afterward, starch solution was added and titrated until blue color disappeared. So, titration number (T) was determined by this method. Then, 5 ml of sulfite standard solution was diluted by sucrose solution up to 100 ml. In conclusion, accurate amount of sulfite (C) from titration (T) was calculated according following equation (1):

$$C= (25-T) \times 3/203 \times 2 \quad (\mu g\ SO_2/ml) \qquad (1)$$

Where:

C: concentration of sulfite (µg/ml)

T: calculated titration number (ml)

In the following, 100 ml of sugar sample (20 g) was prepared to add 4 ml of sodium hydroxide (0.8 mol/l) and distilled water. Then, 2 ml of fresh decolorized rosaniline solution and 2 ml of formaldehyde (0.002%) were added to 10 ml of sugar solution and was kept in room temperature for 30 minute. The absorption of the solutions was determined through UV-visible spectrophotometer (560 nm) and distilled water was applied as control.

Amount of sodium dithionite in 1 kg of sample (mg) = [sodium dithionite in curve (µg) ×10] /mass of sugar sample (mg) (2)

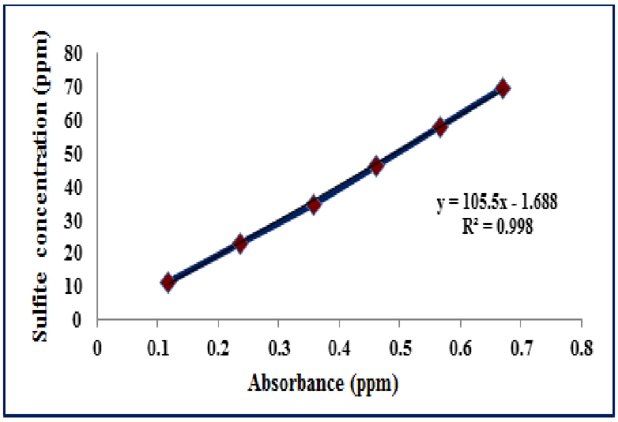

Figure 1. The curve of absorption based on sulfite concentration.

Determination of standard curve

The standard curve was determined based on different amounts of diluted sulfite standard solution in following order; 1, 2, 3, 4, 5 and 6 ml in six volumetric flask (100 ml). Then 4 ml of sodium hydroxide solution 0.1 mol/l was added to each flask and their volume reached to 100 ml with pure sucrose solution. In the following, 10 ml of each solution with 2 ml of decolorized rosaniline solution and 2 ml of formaldehyde solution was delivered to a clean tube and mixed. These solutions were kept in room temperature and then absorption of each sample was determined. The standard curve were drawn by excel (Figure 1). Amount of SO_2 for each tube was calculated based on following equation (3):

$$\text{Amount of } SO_2(\mu g)= C \times N / 10 \qquad (3)$$

Where:

C: accurate amount of calculated sulfite through equation 1 (µg/ml)

N: volume of diluted sulfite standard to each 100 ml volumetric flask (ml)

Figure 1 shows relation between absorption and sulfite concentration. Linear curve of absorption for each sample was specified by excel and then standard curve for tested samples was drawn. Afterward, amount of blankit was calculated using absorption/ concentration curve through equation 3. The linear curve shows that in tubes 1 – 6, absorption increase with amount of blankit linearly and confirms test accuracy (Figure 1).

Statistical analysis

Control and test data in the present study were analyzed using SPSS (version 22.0, 2012). One-way ANOVA was used to test the statistical differences for three doses within a group, followed by Tukey's test

Table 1. The amount of sulfite in studied units based on number of decolorizing resin tanks.

Factory*	Sample 1 (ppm)	Sample 2 (ppm)	Sample 3 (ppm)	Average of three samples of each unit (ppm)
A	16	14	12	14
B	13.5	12	10.5	12
C	12.5	9	8.5	10
D	7	6	5	6
E	6.5	5	3.5	5
F	5	4	3	4
G	4	3	2	3
H	3.5	2.5	1.5	2.5
I	3.25	1.75	1	2

*A-C were the samples with one declorizing resin tank; D-F were the samples with two declorizing resin tank; G-I were the units with three decolorizing resin tanks.

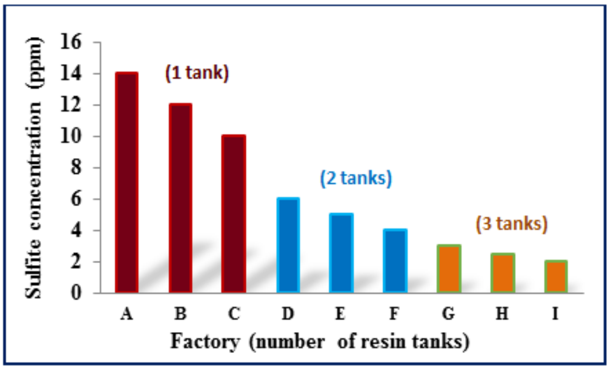

Figure 2. Comparison of the amount of remaining sulfite based on number of tanks.

for pairwise comparisons. $P \leq 0.05$ was considered statistically significant.

Results and Discussion

Over the years, different processes have been developed to achieve efficient and affordable color removal techniques in order to produce white sugar. There are various types of sugar colorants such as plant pigments, caramels, melanoidins, melanin, and alkaline degradation products of fructose (ADF). Refining processes can remove these colors. But choosing and operating these processes is very important in color removal because any process may remove different types of sugar colors.The findings show a number of overlapping areas and several differences between color removal techniques in sugar industry (Davis, 2001). For example, phenolics, flavonoids, and melanoidins is removed by sulphitation. While, ion exchange resins can remove melanoidins and ADFs.

On the other hand, there is the synergistic effect between various color removal techniques (Davis, 2001). The findings presented high color removal with the combination of two process. The best methods were carbonatation or phosphatation followed by activated carbon. The combination of carbonataion with ion exchange resins denotes a process benefit. In fact, there is a synergistic effect which shows the result of the carbonataion improves the implementation of the second process. The combination of processes can produce the best quality refined sugar.

Due to the benefit of the processes combination, in this study were used ion exchange resins and sulphitation for the preparation white sugar. For this purpose, ion exchange resins in packed bed columns was caused to decolorize syrup. In the next step, blankit was used as syrup bleaching agent. This method gave a benefit in terms of color removal, indeed with different processes were removed various types of color. While, less blankit was used for syrup bleaching andobtained white sugar product. This is notable that an advantage of the polymeric materials is that the adsorbed species can potentially be recovered for future use. Indeed, the application of decolorization resin in sugar industry is a low cost alternative instead traditional methods such as activated carbon or bone char. On the other hand, this method can solve environmental pollution problems. Accordingly, in this study was used ion exchange resin Purolite-A500PS for all columns at temperature 50-60ºC. At the end of this combination processes, amount of sulfite in nine sugar production units (A-I) was evaluated (Table 1).

In factories A-C with one resin tank, average of blankit in sugar samples of units A:14 ppm , B:12 ppm and C:10 ppm were measured. In factories D-F with two tanks, average of blankit in samples of units D, E and F were 6, 5 and 4 ppm, respectively. Eventually, the factories G-I with three tanks presented average of blankit of 3, 2.5 and 2 ppm in sugar samples of units G, H and I, respectively.

Figure 2 shows the amount of blankit in the studied units based on number of used tanks. The factories (A-C) with one resin tank showed high amount of blankit in a range of 10-14 ppm. In factories (D-F) with double resin tanks, amount of blankit reduced compared to one tank in range of 4 – 6 ppm. The assessment result of factories (G-I) with three tanks showed lowest amount of blankit in range of 2-3 ppm. In conclusion, high quality and white products was obtained with three decolorizing resin tanks.

Table 1 shows evaluated sulfite’s amount in nine sugar products. According to Iranian Standard Organization, authorized amount of blankit in sugar is 1 to 10 ppm. Based on primary study, in three factories (A-C), syrup delivered to one decolorizing resin tank. The study average of blankit's amount in sugar samples of these units (A-C) showed that remaining blankit was higher than standard limits (Table 1, Figure2). The second study was about factories with double resin tanks. At first, syrup was delivered to first tank and then decolorized syrup was delivered to second decolorizing resin tank again for more decolorization. At the end, average of blankit in sugar samples of units (D-F) showed which remaining blankit was equivalent to standard limit. Therefore, high quality products obtained in comparison to factories with one tank (Table 1, Figure 2).

The third study was about factories with triplex resin tanks. At first, syrup was delivered to first decolorizing tank. Then, decolorized syrup was delivered to second and third tank, respectively. In this study, average of blankit in sugar samples of units (G-I) presented excellent results. The remaining blankit was even lower than standard limit and these factories had desirable products in comparison to factories with one and two tanks (Table 1, Figure 2). The Figure 3 shows schematic triplex resin tank in addition to cross- section of tank.

The result of statistical analysis between the demonstrated groups showed significant difference between factories with one and two tanks ($P < 0.05$). Also, factories with one and three tanks showed very highly significant difference ($P < 0.001$). While, no difference was found between factories with tow and three tanks (($P > 0.05$). This analysis confirm which using double or triplex tanks have close results.

In the present study, absorption of sulfite solutions were evaluated through spectrophotometry in designed methods with single, double and triple decolorizing resin tanks. The results showed which using the ion exchange resins were caused to decrease blankit consumption in studied samples according to increasing of tanks number. In fact, the use of ion exchange resin was caused to syrup decolorization. Therefore, low amount of blankit was used in next decolorization process.

Indeed, increase of resin tanks and syrup circulating in each tank make it possible to have better decolorization and more pure syrup. So, white sugar with high quality is produced. The biggest advantage of this method is significant decrease of blankit which leads to reduce side effects and consequently suitable effect on health of society. As a result, this research showed that using one resin tank could not have appropriate effect on decrease of blankit. While using two or three declorizing resin tanks was led to greater elimination of blankit in final products and more desirable products were achieved. Science using double resin tanks presented good response in authorized range and for economic justification in decolorization process, this method can be applied in sugar companies.

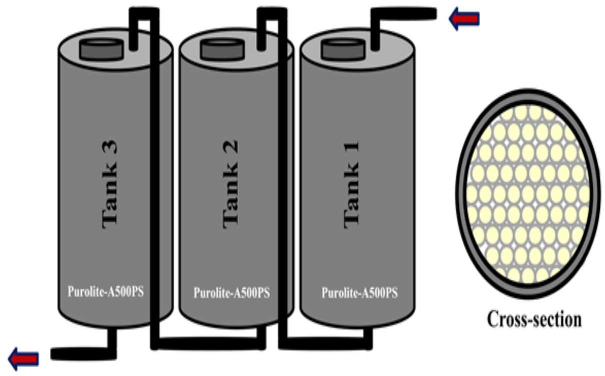

Figure 3. Schematic view of a triplex resin tank and its cross-section.

Conclusion

Ion exchange resins decrease blankit in final products of sugar industry. The result of this research showed that blankit in Iranian sugar products (10-15 ppm) was higher than standard limit with use of one ion exchange resin tank. But in two and three time use of resin tanks it caused to decrease blankit less than 6 ppm. It is remarkable that using double resin tanks has economic justification in decolorization process. Therefore, this method can be applied in sugar companies to produce white sugar whit high quality.

Acknowledgments

This research was performed in laboratory of Sugar Co. located at Tehran province (project of ion exchange resin tank) so we appreciate managing director of this group, Mr. Hasanali Hasani. Also, the authors are grateful to Dr. Fateme Nowroozi.

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