SIT 2024 paper(final version)—Vancouver, Canada.

Value added antioxidants recovered/extracted from cane sugar production.

(Patent pending)

Chung Chi Chou. PhD. President, Dr Chou Technologies, Inc.(Cti)

Jeffrey Le Blanc. PhD, formerly Vice president of technologies, Cti.

Thevu Vu. PhD, formerly graduate student, Louisiana State University at Lafyette.

Abstract

A method for the recovery of ion exchange regenerant waste in a sugar plant is developed. The recovery method involves adjusting the pH of the ion exchange regenerant waste stream to change the characteristics of colorant facilitate the absorption the colorants from the waste with special activated carbon and/or adsorbent resins. The decolorized regenerant can be recycled to the plant for future regeneration steps. The removed colorants can be stripped off from the activated carbon and/or resins, purified by de-ashing, and concentrated into an antioxidant mixture, thus, producing a value added by-products from the ion exchange regeneration effluent. The method a) reduces operation cost, b) adds a value-added antioxidant product, and c) resolve the regenerant waste disposal problem.

Introduction

Ion exchange resins are commonly used in beet and cane sugar production as a method for decolorization etc. The technique is typically employed as a secondary decolorization of syrup solutions of 60-65 degrees brix. In the process, aromatic, phenolic, polyphenolic compounds, and acidic ionic colorants in the syrup adhere to and/or exchanged on to the porous ion exchange resin. The decolorized syrup is then crystallized to produced refined sugar. The effectiveness of the resin to remove color depreciated/degraded each time the resin is used.

Ion exchange resins must be periodically regenerated/reactivated to recover it's decolorizing capacity and sustain their operation. The methods of regenerating ion exchange resins for sugar processing have been documented in U.S. Patent No. 5,019,542 and U.S. Patent No. 3,791,866 and in more generic applications in U.S. Patent No. 9,186,665 and U.S. Patent No. 8,585,906. The method of using a caustic brine solution for reactivation resins is the most common industry practice because it is cheap and efficient. This caustic brine solution is also referred to as the "regenerant". The effluent from the regeneration process produces the regenerant waste contaminated with the aromatic, phenolic, polyphenolic compounds, and acidic colorant. For caustic brine solution to be re-use, these contaminates must be removed from the solution.

After regeneration, it is desirable to recover the caustic brine regenerant from the effluent in the interest of minimizing operational cost of the plant. The recovered caustic brine can be reused in future regenerations. Furthermore, If the regenerant waste is to be disposed of, the removal of caustic and salt, and colorants are necessary before disposal of the intensely dark effluent which is also an environmental issue. U.S. Patent No. 5,019,542 and U.S. Patent No. 3,791,866 present unique techniques for recovering regenerant from the effluent of the regeneration procedure.

The paper pertains to recovery of ion exchange regenerant from the waste stream of the resin's column regeneration process. The new method for recovery of the regenerate does not use ultrafiltration, nanofiltration, electrodialysis, chromatography, cationic or anion exchangers, gel permeation, freezing, osmosis, hydrophobic polymer absorbents, or elution with ethanol. The newly developed technique described herein offers lower capital and operating costs than such processes.

Brief summary of the recovery process

In sugar decolorization process, ion exchange resins have a finite color exchange and adsorption capacity and periodically needs to be regenerated with a sodium chloride (NaCl) and sodium hydroxide (NaOH) solution referred to as a caustic brine solution. During the regeneration process, about 85 to 95% of the colorants exchanged and adsorbed onto the resins are desorbed and concentrated into the caustic brine regenerant. The effluent from the regeneration is an intense dark color waste stream consisting of colorant that is approximately 6-10% NaCl and 0.5-1.5 % NaOH. The waste stream is environmentally hazardous and costly to dispose.

The recovery of regenerant waste and reuse of regenerated cautic brine solution involves adjusting the pH of the regenerant waste effluent, remove the colorant with special activated carbon and/or adsorbent resin, and then, separation of activated carbon and/or adsorbent resin via press filtration step. The treated/decolorized regenerant effluent after filtration, can be recycled to the plant for reuse. To add the value to the company's profit, the colorant can then be stripped off from the activated carbon and/or resin using sodium hydroxide. The desorbed colorant can be de-ashed with a weakly acid cation resin then concentrated through evaporation to create an antioxidant product. The concentrated antioxidant stream can be spray dried to form a dried powder antioxidant mixture of polyphenols, phytochemicals, and flavonoids. Finally, the weakly acid resin can be regenerated with hydrochloric acid from which yields sodium chloride which can then be use for ion exchange resins regeneration.

It is a principal objective of the present paper to provide a parallel process to 1) recover the regenerant from ion exchange waste streams for reuse and 2) recover antioxidant mixtures from ion exchange waste streams to increase the company's profit.

Example of the recovery process:

Ion exchange regenerant waste samples were obtained from a sugar refinery. (A) Before decolorization, the ion exchange regenerant waste were mixed and the pH was measured. The pH of the waste was between 6 and 7. (B) The solution was filtered through a 5-micron filter paper. (C) The pH of the filtered solution was adjusted to 7. (D) The brix of the solution was measured using a refractometer to be between 6 and 9. (E) The color of the solution was measured via the standard International Commission for Uniform Methods of Sugar Analysis (ICUMSA) method at 420 nanometer in a 1-centimeter cell to be 43,352 International Color Units (ICU).

(F) The high color solution was then decolorized using high-capacity powder activated carbon. Three different powder activated carbons (PAC) were used; neutral decolorizing PAC, high pH decolorizing PAC, and low pH decolorizing PAC. The solution was mixed with 5 or 10 grams of powdered activated carbon for 30 minutes at 80° Celsius. (G) To prepare the solution for filtration, 5 grams of diatomaceous earth was added and mixed for 5 minutes. The solution was filtered through a 1.6-micron filter. (H) The pH was adjusted to 7. (I) The brix of the solution was measured using a refractometer to be between 6 and 11. (J) The color of the solution was measured via the standard ICUMSA method at 420 nanometer in a 1-centimeter cell to be between 290 and 1,233 ICU.

The color reduction ranged from 97.16% up to 99.33% with different powdered carbons and carbon loadings. Higher loading of activated carbon provides better color reduction. The highest color reduction (99.33%) is achieved by using High pH carbon with a concentration of 10 grams per 100 milliliters.

The decolorized regenerant waste was to return to the process regeneration tank for reuse.

Brief description of the drawings

The accompanying drawings are provided for the purpose of illustration only and are not intended as a definition of the limits of the present processes.

FIG. 1 is a block flow diagram illustrating how colorant is removed from the regenerant then further processed to produce a concentrated antioxidant. After treating and filtering the regenerant with activated carbon and/or adsorbent resin, the clean regenerant is recycled back to the ion exchange column. The colorant is then desorbed from the activated carbon and/or adsorbent resin using a sodium hydroxide solution. The sodium hydroxide is removed from solution using a weakly acid ion exchange column. The deashed colorant solution is then concentrated using an evaporator and/or spray dryer. The final step shows how the weakly acid ion exchange can be regenerated with hydrochloric acid and product sodium chloride solution.

FIG. 2 shows the color of ion exchange regenerant at pH of 14.7 and 4 from left to right. The pH of the ion exchange regenerant is typical >11.
FIG. 3 shows the regenerant adjusted to a desired pH and treated with 0.3 and 0.6 weight percent powder activated carbon. The regenerant is clear.

Fig. 4 show characteristic of varies antioxidant extracts using florescence EEF technique.

Drawings

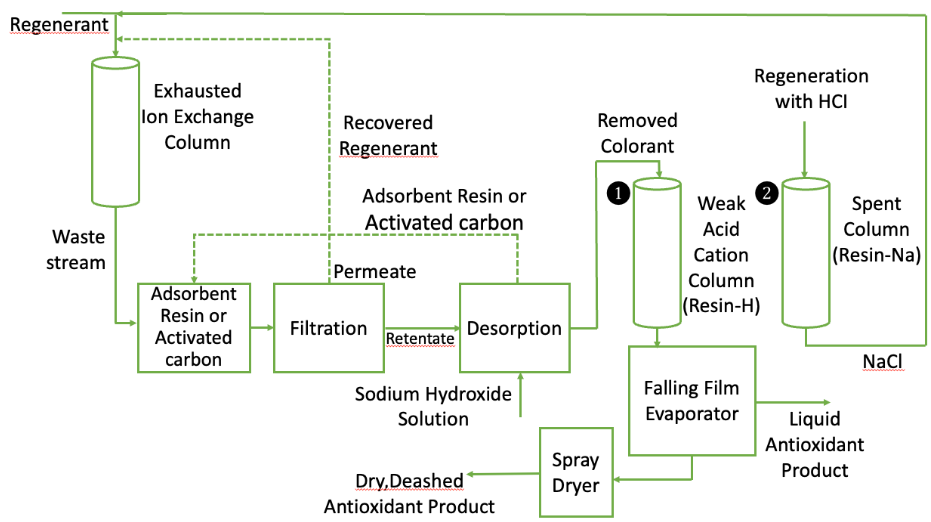
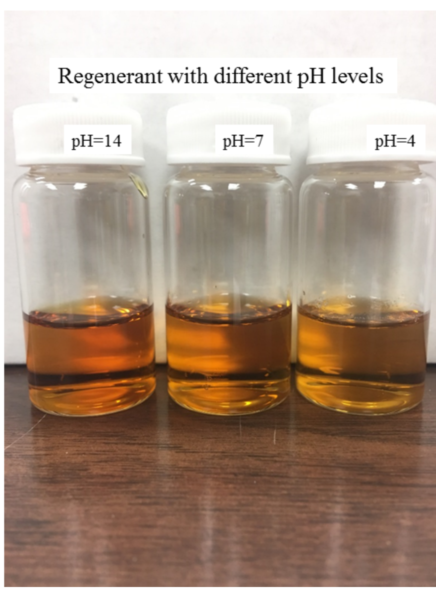


Figure 1



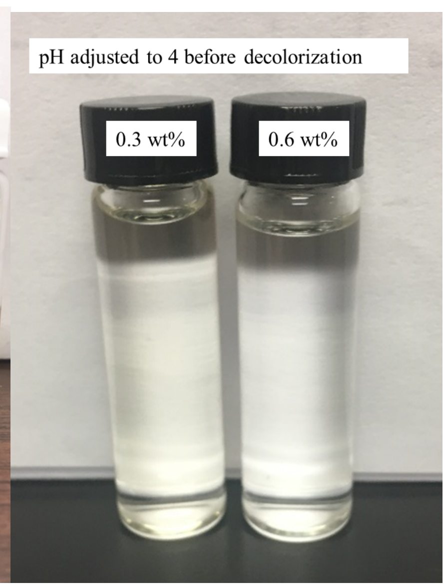


Figure 2

Figure 3

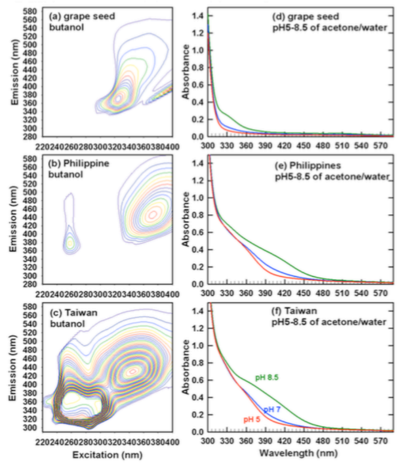


Figure 4. Fluorescence EEM in butanol (without dilution, a-c), and UV/vis spectra of acetone/water extracts set to pH3-8.5.

Major Benefits of sugar cane extract

(1) Antioxidant Activities

Antioxidants act to counter oxygen radicals which have been linked to a long list of life threatening diseases such as cancer, cardiovascular diseases, osteoporosis and degenerative diseases suggesting potential health benefits.(a,b)

(2) Caramel Coloring Replacement

Caramel has been shown to contain trace carcinogenic compounds. The Center for Science in the Public Interest (CSPI) is calling on the FDA to revoke the Generally Regarded as Safe (GRAS) status of caramel coloring, an ingredient found in many foods. Caramel coloring contains 4-methylimidazole (4-MI or 4-MEI), a known animal carcinogen. Refined sugarcane molasses can be used as a replacement for caramel coloring in the food and beverage industries.

(3) Potential Replacement for Synthetic Antioxidants as a Preservative

Butylated hydroxyanisole (BHA) and butylated hydorxytoluene (BHT) have been widely used in food application despite their suspected carcinogenic effect.(c,d) Refined sugarcane molasses is a potential replacement for these compounds.

(4) Cosmetic Applications

Compounds in the refined sugarcane molasses exhibit Tyrosinase inhibitory activities and play an important part in the cosmetic industry as they are incorporated in skin whitening creams.(e)

5) Lower the Glycemic Index (GI) of sugar

Obesity is a major health problem in many part of the world.
It has been shown that addition of sugarcane antioxidants(polyphenols) consistently reduce GI to below 55 as compared to 68 to 70 for white sugar (f)

Literature Cited

(a) Chung, Y. M., Wang, H. C., et al., Antioxidant and Tyrosinase Inhibitory Constituents from a Desugared Sugar Cane Extract, a By-Product of Sugar Production. Journal of Agricultural and Food Chemistry, American Chemical Society Publication, USA, 2011, 59, 9219 – 9225.

(b) Stohs, S. J., Bagchi, D. Oxidative Mechanisms in the Toxicity of Metal Ions. Free Radical Biol. Med. 1995, 18, 321 – 336.

(c) Whysner, J., Wang, C. X., et al., Dose Response of Promotion of Butylated Hydroxyanisole in Chemically Initiated Tumors of the Rat Forestomach. Food Chem. Toxicol. 1994, 32, 215 – 222.

(d) Williams, G. M., Latropoulos, M. J. et al., Safety Assessment of Butylated Hydroxyanisole and Butylated Hydroxytoluene as Antioxidant Food Additives. Food Chem. Toxicol. 1999, 37, 1027 - 1038.

(e) Kobayashi, T., Vieira W. D., et al., Modulation of Melanogenic Protein Expression During the Switch from Eu to Pheomelanogenesis. J. Cell Sci. 1995, 108, 2301 – 2309.

(f) David Kannar, Barry Kitchen and Richard Weisinger, Sugar Jounals, September, 2008