A study of sugar colourants through ion exchange and salt regeneration

By Carla Guimarães*, Luis San Miguel Bento* and Manuel Mota**

Summary

In order to study the refinery ion-exchange process for colour removal, some synthetic colourants were passed through a strong base anion exchange resin. The effect of sodium chloride concentration on their subsequent removal from the resin was also studied.

Caramels were retained less by the resin than melanoidins or HADP's (hexose alkaline degradation products). Melanoidins were the best removed during salt regeneration, but only about 50% of the caramels and HADP's were removed. HADP's were the major colourants to be fixed irreversibly to the resin.

Luis San Miguel Bento

Carla Guimarães

Manuel Mota

Introduction

Colour in the sugar industry consists of a complex mixture of organic compounds that can have their origins in the sugarcane plant or in the extraction and refining process. The cane plant colourants include compounds such as flavonoids and phenolics. They tend to be charged, more so at high pH, and, if unreacted, are in the low to mid molecular weight range[1]. Of the colourants developed in the process, the three subclassifications[2] are Caramels, Melanoidins and Alkaline Degradation Products of reducing sugars. Caramels are thermal degradation products of sucrose, only slightly charged, and of increasing molecular weight with increasing time, temperature and development. Melanoidins are, in general, Maillard reaction products of amine compounds with a sugar group. Melanoidins vary considerably in their properties according to the conditions of their formation, but are recognised as being acidic and polymeric, containing nitrogen and being a highly complicated mixture. They have some charged nature, usually negative at process pH's. The alkaline degradation products are usually formed in the refinery, where the pH is on the basic side. They are medium to high molecular weight anionic compounds[1,3-5].

At RAR - Refinarias Açúcar Reunidas, in Portugal, parts of the colourants are removed from the sugar liquor by strong base anion exchange resins. The subsequent removal of colourants from the loaded resin is achieved by regeneration with sodium chloride solutions[6] at two concentrations: 50 and 100 g/l.

There has been considerable research on sugarcane colourants (phenolics and flavonoids) and their behaviour through refinery systems[1,2,7-10] but little is known about the fate of caramels, melanoidins and alkaline degradation products through the process.

In this work we are concerned with the behaviour of these colourants, through the decolourization and regeneration processes. The affinity of synthetically prepared colourants towards strong base anion exchange resins was analysed, together with the influence of sodium chloride concentration (50 and 100 g/l) in their removal from the resin.

Materials and methods

Ion exchange resin (Lewatit MP500A) in chloride form was packed in a 150 ml jacketed column. The resin, 75 ml, was washed with distilled water prior to being charged with 40 BV (bed volumes) of colourant solution in a down flow direction at 2 BV/h. After loading the colourants, the resin was washed with 10 BV of distilled water at 5 BV/h. Desorption of the colourants was achieved by regeneration of the resin, which was carried out in two steps, as in the refinery. In the first step, 1.5 BV of 50 g/l NaCl were passed through the resin by down flow at 1.0 BV/h. In the second step, 2.25 BV of 100 g/l NaCl were passed through the resin at 1.5 BV/h. Finally, the resin was washed with distilled water at 1.5 BV/h until no colour was observed in the effluent. Colourants charging and the washings were performed at room temperature and regeneration at 38°C. A new resin was used for each colourant experiment. Effluent fractions (10 ml) were collected during the regeneration. Sodium chloride concentration, colour and absorbance were determined for each fraction. Absorbance was measured at the characteristic absorption wavelength for each colourant : 330 nm for melanoidins, 283 nm for caramels and 264 nm for HADPs.

Analytical procedures

Sodium chloride content was measured by the Mohr titration method[11]. Colour was measured at 420 nm, after pH adjustment to 9.0, in a Perkin-Elmer LC-55 spectrophotometer. Colour was expressed as attenuation:

$$\text{Attenuation} = (\text{Absorbance} \times 1000)/\text{cell length, cm}$$

The absorbance at characteristic absorption wavelength and UV-VIS absorption spectra were determined at pH 9.0 in a GBC 916 spectrophotometer with a one centimetre cell, using water as blank solution.

Preparation of colourant solutions

Melanoidins were prepared from glucose and glycine (pH 11.0), and caramels from sucrose and alkaline degradation products from fructose, as described by Shore *et al.* [12]. Each colourant was

diluted with distilled water in order to have an attenuation at 420 nm of approximately 680 (pH 7.0), which corresponds to a typical carbonated liquor colour (800 ICUMSA, with 65°Brix). Before loading the resin, each colourant solution was adjusted to pH 8.5, in order to have the same conditions as in the refinery.

Results and discussion

Colourants removal by anion exchange

In order to evaluate the amount of colourant retained by the resin, the colour of the solution eluted during the resin loading was measured and related to the colour of the feeding colourant solution. Colour was considered to be proportional to the amount of colourant present.

The percentage of colour retained by the anionic resin increases from 62.8% for caramels, to 97.5% for melanoidins and 98% for HADPs (Fig. 1). Similar results were observed for the removal of melanoidins (glycine) and HADPs by Amberlite IRA 900 resin[13].

It is known that sugar colourants are fixed to strong base anionic styrenic resins by ionic bonding and/or by hydrophobic inter-actions. In the first case, the ionic bond is formed between the negative polar part of the colourant and the resin fixed ion. In the second case, the hydrophobic part of the colourant is forced against the resin matrix by hydrophobic inter-action.

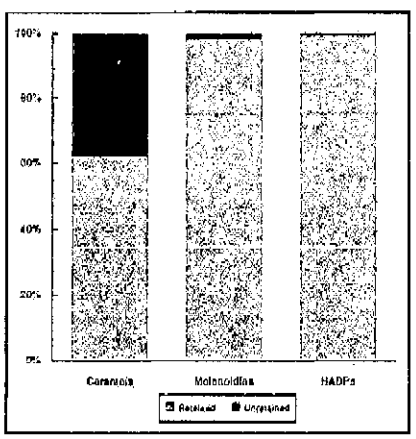

Fig. 1. Decolourization with anion exchange resin

Our results indicate that caramels are the least retained by the resin. This could be explained by the fact that caramels are relatively uncharged[1] whereas melanoidins and HADPs are anionic in an alkaline medium[4,5,13]. Hydrophobic inter-actions could account for some of the retention observed. However, as there is no precise information about sugar colourants' hydrophobicity, it is difficult to explain the results on this basis.

Behaviour during regeneration

After being loaded with the colourant, the resin was regenerated in two steps: 1) low density regeneration (LDR), with NaCl 50 g/l, and 2) high density regeneration (HDR), with NaCl 100 g/l. In order to characterise the regeneration effluent, samples (10 ml) of it were taken during regeneration and analysed for sodium chloride concentration, colour and absorbance at the characteristic absorption wavelength for each colourant. The elution profiles for the three colourants are in Fig. 2.

Concerning HADPs (Fig. 2a), two peaks were observed, the first one leaving the column in the LDR step corresponding to compounds strongly absorbing in the UV region. The other one was eluted in the beginning of the HDR step and corresponds to the more coloured compounds.

For both melanoidins and caramels (Figs. 2b and 2c), a single peak was observed, which was eluted in the low density regeneration step, and involves colourants absorbing in the UV and visible ranges.

By integrating the colour profiles below and above 50 g/l of NaCl, we obtained the total coloured components eluted in each regeneration step (Fig. 3). It was observed that 80.6% of the melanoidins were eluted during the first step of regeneration and the remaining 19.4% left the column during the next step. The corresponding fractions were 62.1% and 37.9% for caramels, and 38.9% and 61.1% for HADPs.

In conclusion, melanoidin colour and caramel colour were mainly

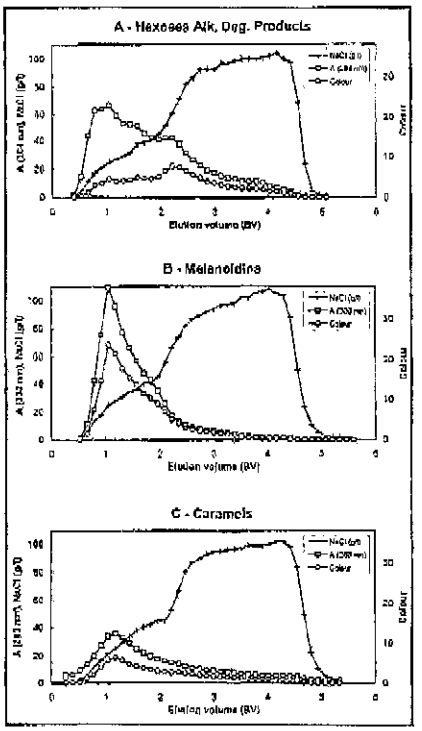

Fig. 2. Elution profiles of the regeneration effluent

removed with NaCl 50 g/l and HADP colour mainly with NaCl 100 g/l.

UV-VIS absorption spectra

UV-VIS absorption spectra were determined in order to make a qualitative evaluation of the colourants in the different phases of decolourization and regeneration.

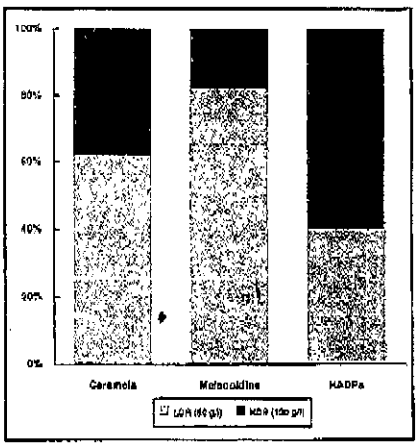

Fig. 3. Colourants eluted in each regeneration step (50 and 100 g/l).

The UV-VIS spectra of the colourants before and after the anion exchange resin are illustrated in Fig. 4, curves a and b, respectively. The spectrum profile of the feed HADPs is quite different from the one obtained for the colourant eluted from the resin (Fig. 4 - top), the first one showing a single peak at 264 nm and the second showing two shoulders at 231 and 260 nm. The profiles of the spectra obtained for melanoidin are also different (Fig. 4 - middle), whereas, for caramels they are very similar (Fig. 4 - bottom), showing sharp maxima at 226 and 283 nm.

The UV-VIS spectra of the colourants, in each of the two regeneration steps (LDR and HDR), are shown in Fig. 4, curves c and d, respectively. It was observed that the UV-VIS absorption spectra profiles of the LDR and HDR fractions were similar, both for melanoidins and caramels. However, concerning HADPs, the profiles obtained were quite different. The spectrum of the LDR fraction presents a peak at 264 nm, which is not present in the spectrum of the HDR fraction, indicating the presence, in the LDR fraction, of compounds strongly absorbing in the UV region (more precisely at 264 nm), as was described above.

Distribution of the colourants

A global colourants balance was done to summarise the results obtained. Starting with 100 base units for each colourant, a diagram was drawn illustrating the distribution of each colourant through the decolourization and regeneration processes used in a sugar refinery (Fig. 5).

It was observed that 37.2% of the caramels loaded were not retained by the resin and the remaining 62.8% were distributed in the following order: 29.6% stayed irreversibly fixed to the resin; 20.6% were eluted in the LDR fraction and 12.6% in the HDR fraction. Caramels were neither well retained by the resin nor well regenerated.
Only a small part of the melanoidins were not retained by the resin (2.5%) or stayed irreversibly fixed to the resin (9.0%). The main part (71.3%) was eluted in the low density fraction of the regeneration effluent. Of the three colourants studied, melanoidins were the best regenerated.

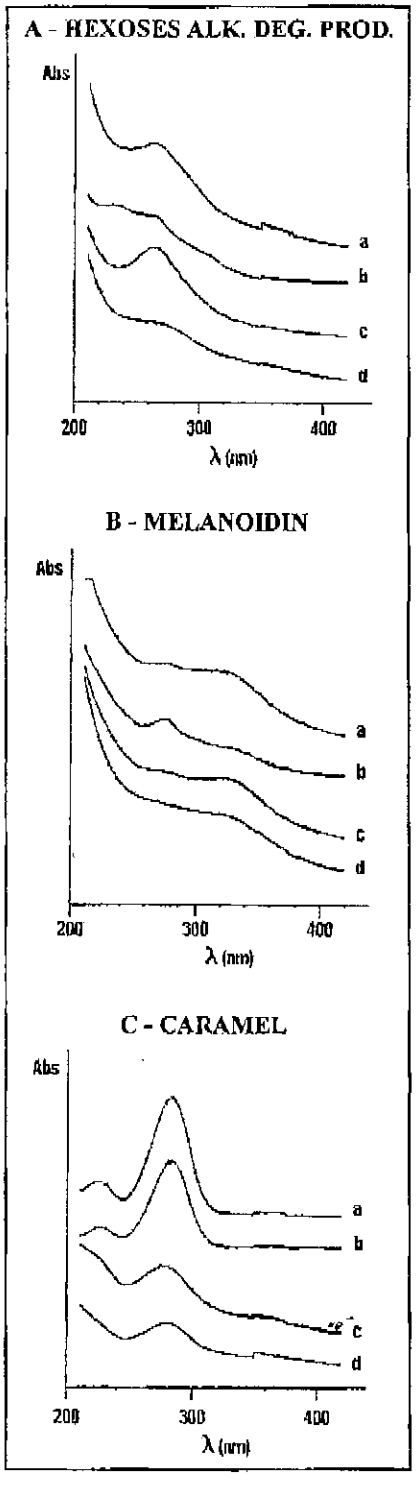

Fig. 4. UV-VIS absorption spectra of the colourants in the different phases. Decolourization: feed colourant (a) and eluted colourant (b). Regeneration: LDR fraction (c) and HDR fraction (d)

The distribution of HADPs through the decolourization and regeneration processes was the following: 48.1% remained in the resin, irreversibly fixed; 30.5% in the HDR; 19.4% in the LDR and, finally, 2.0% in the fine liquor. HADPs were quite well retained by the anion exchange resin, but not so well regenerated, a great part remaining fixed to the resin. These results suggest that, HADPs are probably the major contributors to the fouling of the anionic resin, among the three families studied.

The irreversible retention of HADPs could be due to the "switch effect" described by Bento[14]. During salt regeneration some colourants can switch from an ionic bond mechanism to surface sorbing mechanisms, which increases the difficulty of their removal.

An irreversible retention of hexose degradation products by anionic resins, was also described by Parker[13].

Treatment of regeneration effluent

With this study we were able to characterise the predominant colourants in the two fractions of the salt regeneration effluent. This will allow their treatment to be improved. The first fraction of the effluent, with a low salt concentration, will be treated by the action of microorganisms[15], and the second fraction, with a higher salt concentration and containing the more anionic charged colourants, by precipitation with calcium hydroxide[14].

Acknowledgements

The authors wish to thank PEDIP and STRIDE Programs for the financial support, JNICT for the grant conceded to C. Guimarães and finally the RAR staff, especially colleagues of DID.

Investigación de colorantes mediante el intercambio iónico y regeneración *(Resumen)*

Con el fin de examinar el proceso de intercambio iónico para remover color

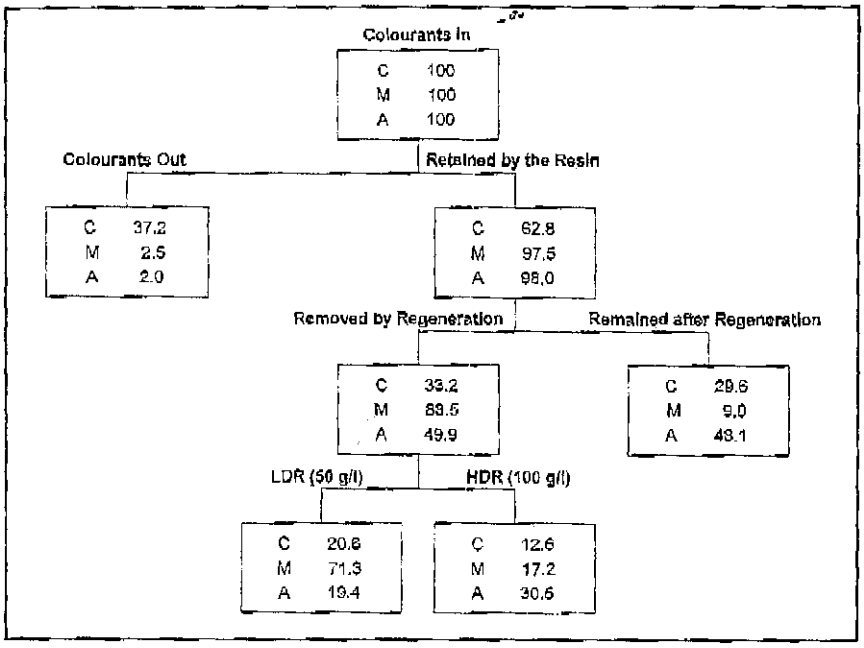

Fig. 5. Distribution of the colourants through resin decolourization and regeneration processes
A - Hexoses alkaline degradation products; M - Melanoidins; C - Caramels

en una refinería azucarera, algunos colorantes sintéticos fueron sometidos a la acción de una resina intercambiadora de aniones. Se examinó también el efecto de la concentración del cloruro sódico sobre la remoción de los colorantes.

Se observó un nivel inferior de retención de caramelos que de melanoidinas o HADP (productos de hexosa a degradación alcalina). Las melanoidinas se removieron mejor durante la regeneración salina, pero sólo se removió el 50% de los caramelos y HADP. Los HADP fueron los colorantes principales en fijarse de modo irreversible en la resina.

Etude des colorants au moyen de l'échange d'ions et des procédés de régénération *(Résumé)*

Afin d'étudier le procédé de décoloration par échange d'ions dans une raffinerie de sucre, on a soumis des colorants synthétiques à une résine échangeuse d'anions. On a étudié aussi l'effet de la concentration de chlorure de sodium sur la séparation des colorants de la résine.

Les teintures de caramel ont été retenues par la résine moins efficacement que les mélanoïdines et les HADP (produits d'hexose à dégradation alcaline). On a réussi à mieux séparer les mélanoïdines pendant la régénération de sel, mais on n'a enlevé que 50% des teintures de caramel et des HADP. Les HADP sont les colorants principaux à se fixer irréversiblement à la résine.

Eine Studie der Zuckerfarbstoffe durch Ionenaustausch und Erneuerungsverfahren *(Zusammenfassung)*

Um den Ionenaustausch für Entfarbung in Raffinerien zu studieren, werden einige künstliche Farbstoffe durch einen festbasigen Anionenaustauschharz gegossen. Die Wirkung der Natriumchloridkonzentration auf ihre nachfolgende Entfernung wird auch studiert.

Karamele wurden weniger vom Harz als von Melanoidinen oder HADP (hexose alkalische Abbauprodukte) gehalten. Am besten werden Melanoidinen durch Salzerneurerung entfernt, aber nur 50% der Karamele und HADP wurden entfernt. Die HADPs waren die Hauptfarbstoffe, die am Harz irreversibel befestigt waren

* RAR - Refinarias de Açúcar Reunidas, Apt. 1067, 4101 Porto Codex, Portugal.
** Dep. Eng. Biológica, Univ. Minho, Largo do Paço, 4719 Braga Codex, Portugal.

1 Clarke *et al.: Proc. Sugar Ind. Tech.*, 1985, 53 - 87.
2 Smith & Gregory: *Proc. 16th Congr. ISSCT*, 1971, 1415 - 1425.
3 Kort: "Sugar: Science and Technology", Ed. Birch & Parker (App. Science Pub., London), 1979, pp. 97 - 130.
4 Alekseenko *et al.: Tr. Vses. Naueh.-Issled. Inst. Sakhar. Prom.*, 1972, **18**, 161-170.
5 Chou *et al.: Proc. Tech. Session Cane Sugar Refining Research*, 1972, 8 - 22.
6 Bento: *Proc. 49th Meeting Sugar Ind. Tech.*, 1989, 176 - 200; *I.S.J.*, 1990, **92**, 116 - 125.
7 Farber *et al.: I.S.J.*, 1971, **73**, 170 - 173.
8 Kennedy & Smith: *Proc. 35th Meeting Sugar Ind. Tech.*, 1976, 156 - 160.
9 Linecar *et al.: Proc. Tech. Session Cane Sugar Refining Research*, 1978, 81 - 91.
10 Paton and Smith: *Proc. 42nd Meeting Sugar Proc. Res.*, 1982, 1 - 23; *I.S.J.*, 1983, **85**, 102 - 145.
11 Vogel: "A text-book of quantitative inorganic analysis including elementary instrumental analysis", (Longman, London), 1961, pp. 259 - 260.
12 Shore *et al.: Sugar Technol. Rev.*, 1984, **12**, 1 - 99.
13 Parker: *Tate & Lyle Ltd. Res. Centre Ann. Rept.*, 1967, 57 - 85.
14 Bento: *Proc. 51st Meeting Sugar Ind. Tech.*, 1992, 201 - 220.
15 Guimarães *et al.: Proc. Conf. Sugar Proc. Res. Inst.*, 1994, 103 - 119.