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Colour removal from beet molasses by ultrafiltration with activated charcoal

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HIGHLIGHTS

- Activated charcoal/ultrafiltration process has been used for molasses decolouration.
- Activated charcoal is an efficient decolouration agent for beet molasses.
- Process optimisation is discussed in terms of the charcoal decolouration capacity.
- Good regeneration of exhausted charcoal is obtained using NaOH solutions.
- The loss of decolouration capacity for NPAC after regeneration has been evaluated.

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ABSTRACT

The feasibility of an activated charcoal/ultrafiltration process for the decolouration of beet molasses, and subsequent regeneration of the exhausted charcoal by thermal and chemical methods, has been examined. Several activated charcoals were assayed prior to the selection of Norit powdered activated charcoal (NPAC). The affinity of NPAC for the adsorption of dark colour compounds was studied at 25 °C. A colour reduction of over 98% was achieved at equilibrium using an NPAC concentration of 5 g/L from the beet molasses at pH 3, with no betaine or sucrose co-adsorptions. Crossflow ultrafiltration experiments with NPAC were performed using a 100 kDa TiO_2 tubular ceramic membrane, in order to select the optimal operating conditions. Experiments with several ultrafiltration stages for the decolouration of beet molasses, and subsequent regeneration of the exhausted NPAC with sodium hydroxide solutions, were also performed under the conditions identified previously. A high colour reduction in the molasses of over 96.5%, with no adsorption of sucrose, betaine, citric acid or lactic acid, was achieved in the first decolouration stage at pH 3, with an initial NPAC concentration of 5 g/L, a transmembrane pressure of 100 kPa and a feed flowrate of 4.24 L/h. A good NPAC regeneration was obtained, with a loss of its colour removal capacity lower than 10%.

1. Introduction

Beet molasses is mainly used as a supplement for livestock feed or as a substrate in fermentation processes, especially for ethanol and bioethanol productions [1–4]. This byproduct of sugar-beet processing plants is a highly viscous, dark brown syrup, which is characterised by a high content of fermentable sugars (50–55 wt.%) and several non-sugar organic compounds, such as betaine, lactic acid, amino acids, minerals, phenolic compounds, and dark colour compounds (6 wt.%) [1,5–7]. At least 80% of the colour of beet molasses is provided by melanins, melanoidins and hexose alkaline degradation products (HADPs), which can take part in sucrose hydrolysis and in many complex reactions such as Maillard reactions, with the formation of new melanoidins, and different polymerisation reactions [2,6,8]. Removal of the dark colour compounds can be highly profitable in order to avoid changes to the composition and colour of beet molasses during storage and use [1,3,7].

Activated charcoal has been extensively applied to remove colour and the colour precursors from several types of juices, coffee and tea infusions, sugar beet vinasses, vinegar, and syrups or liquors [9–15]. This adsorbent generally provides a high colour adsorption capacity without modifying the odour and flavour of the foods processed [9,11].

Ultrafiltration with activated charcoal can be proposed as an alternative to conventional adsorption process in batch tanks or porous and fluidized beds in order to improve separation yield and to reduce processing costs. This hybrid technology combines

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Nomenclature

Abs	absorbance of samples (molasses and desorption samples) measured at 475 nm
A_i	co-adsorption of species i on the activated charcoal defined in Eq. (2)
C_i	concentration of species i (mol/m^3)
C_{NPAC}	concentration of Norit powdered activated charcoal (g/L)
D	colour reduction of the molasses defined in Eq. (1)
Do	colour reduction at the beginning of the ultrafiltration with activated charcoal
J_p	permeate flux (kg/m^{2}h)
NPAC	Norit powdered activated charcoal
ρ	experimental density (kg/m^3)
Qf	feed flowrate (L/h)
r	linear regression coefficient
R_{colour}	recovery of colour compounds from the exhausted activated charcoal defined in Eq. (4)
R_m	membrane hydraulic resistance (m^{-1})
R_s	secondary resistance due to concentration polarisation and membrane fouling (m^{-1}) defined in Eq. (5)
R_t	total resistance of the membrane (m^{-1}) defined in Eq. (5)
SGAC	Scharlau granular activated charcoal
SPAC	Scharlau powdered activated charcoal
t	time (min)
TMP	transmembrane pressure (kPa)
μ	experimental viscosity (Pa s)
V	volume (m^3)

Subscripts

1	first decolouration stage of the molasses with new activated charcoal
2	second decolouration stage of the molasses with regenerated activated charcoal
AC	activated charcoal
F	feed beet molasses
i	species i (sucrose, lactic acid, citric acid or betaine)
S	desorption samples in the regeneration experiments
DM	decolourized beet molasses

the adsorption of coloured compounds by activated charcoal with an ultrafiltration to separate the decolourized stream and exhausted activated charcoal in a single stage. In this process both the membrane used to ensure total retention of the adsorbent and the regeneration process to allow reuse of the exhausted activated charcoal must be carefully selected. The most common techniques for regeneration of exhausted activated charcoal are thermal and chemical methods [10,11,16–20]. Thus, a temperature above 300 °C is usually used in thermal method [15] and water [11,18,19], sodium hydroxide solutions [19,20] or various alcohols [18,19] as desorption agents in chemical methods.

The main aim of this study was to evaluate the use of an activated charcoal/ultrafiltration process for the decolouration of beet molasses, and regeneration of the exhausted charcoal to recover the coloured compounds, thus allowing the activated charcoal to be reused. Colour removal from beet molasses can be useful to avoid changes in its composition during storage and to improve recovery processes for non-sugar compounds of market value such as betaine, lactic acid or phenolic compounds. Preliminary adsorption equilibrium isotherms were determined in order to select the type and minimum concentration of the activated charcoal, and the most suitable regeneration method for the exhausted activated charcoal. Continuous crossflow ultrafiltration experiments were performed using a tubular ceramic membrane, and the effects of transmembrane pressure (TMP), feed flowrate (Qf), feed pH, initial NPAC concentration (C_{NPAC}) and several feed types (water, molasses, molasses with NPAC) on the permeate flux, membrane fouling and colour reduction of beet molasses were investigated in order to select the optimal operating conditions. Experiments with ultrafiltration stages for the decolouration of beet molasses and subsequent chemical regeneration of the exhausted NPAC were also performed under the conditions identified previously. The colour reductions, co-adsorptions and loss of activated charcoal capacity after regeneration were calculated for this continuous process.

2. Experimental section

2.1. Materials

Anhydrous betaine (>98% purity, Fluka), lactic acid (>90% purity, Fluka), citric acid (>99.5% purity, Fluka), disodium hydrogen phosphate dodecahydrate (>98%, Panreac), potassium dihydrogen phosphate (>99.5%, Merck), maleic acid (99%, Fluka), methanol (HPLC grade, HiPerSolv Chromanorm), sodium hydroxide (97%, Panreac) and sucrose (99%, Fluka) were used for analytical methods and cleaning processes. Laboratory grade chemicals without further purification were used as supplied in all cases. Solutions were prepared using Milli-Q water (Millipore, USA). Beet molasses containing 46.7 wt.% sucrose, 3.8 wt.% glucose, 4.0 wt.% fructose, 7.6 wt.% betaine, 4.1 wt.% lactic acid, 2.5 wt.% citric acid, 1.0 wt.% phenolic compounds, and 16 wt.% of moisture was supplied by a local sugar-beet factory. The molasses were diluted with water to 50 g/L, in order to lower their liquid density from 1408.0 ± 0.4 g/L to 1015.0 ± 0.1 g/L and their viscosity to 0.0011 ± 0.0003 Pa s. The composition of the feed dilute molasses was 24.62 ± 0.04 mol/m^3 lactic acid, 7.15 ± 0.02 mol/m^3 citric acid, 30.30 ± 0.01 mol/m^3 betaine, and 70.13 ± 0.05 mol/m^3 sucrose, with an absorbance value of 1.30 ± 0.01 at 475 nm, and a pH of 7.10 ± 0.06. Phosphoric acid (85%, Sigma–Aldrich) was added to modify the pH of the dilute molasses from 7.1 to 1 or 3.

Scharlau granular activated charcoal (Scharlau CA0346, Scharlab S.L), Scharlau powdered activated charcoal (Scharlau granular crushed with a volume mean diameter of 48.0 ± 0.7 μm) and Norit powdered activated charcoal (Norit 97876, Sigma–Aldrich) were used to decolour the dilute molasses.

2.2. Analytical methods

The sucrose content of the molasses was measured by polarimetry at 880 nm using an Anton Paar MPC500 Sucromat polarimeter with a precision of ±0.01 °Z and reproducibility of ±0.01 °Z [7]. The colour of the feed molasses, decolourized molasses and exhausted charcoal regeneration solutions was determined spectrophotometrically at 475 nm using a Hitachi U-2000 spectrophotometer [21]. Total concentrations of betaine, lactic acid and citric acid in the molasses (feed and decolourized) were determined by liquid chromatography using a Beckman System Gold HPLC [7]. A reverse phase column ACE 5C18 (ACE HPLC columns), and a UV–vis detector at 216 nm were used. The mobile phase was an aqueous solution of 0.17 vol.% phosphoric acid and 0.16 wt.% potassium dihydrogen phosphate, with a flowrate of 1 mL/min. Maleic acid was used as an internal standard.