Colour removal from beet molasses by ultrafiltration with activated charcoal

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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 ºC. A colour reduction of over 98% was achieved at equilibrium using a 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%.

Keywords: Beet molasses; Colour removal; Ultrafiltration; Activated charcoal; Regeneration

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 polymerization 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 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 ºZ and reproducibility of ± 0.01 ºZ [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 di-hydrogen phosphate, with a flowrate of 1 mL/min. Maleic acid was used as

an internal standard. Samples were analyzed in triplicate under identical conditions. The error in the HPLC analytical method was ± 0.01 mol/m^3.

The colour reduction (%D) of beet molasses and co-adsorption (%A) of species i (i= sucrose, lactic acid, citric acid or betaine) were calculated as follows:

$$\%D = 100 \text{ x } \left(1 - \frac{Abs_{DM}}{Abs_F}\right) \quad (1)$$

$$\%A_i = 100 \text{ x } \left(1 - \frac{C_{i_{DM}}}{C_{i_F}}\right) \quad (2)$$

where Abs is the absorbance of samples measured at 475 nm, C is the concentration expressed in mol/m^3, the subscripts F and DM refer to the feed molasses (initial condition) and the decolourized molasses after treatment with activated charcoal. The error in %D was ranged from ± 0.02 to ± 0.8%.

The pH of aqueous solutions (molasses and regeneration solutions) was measured using a Crison GLP 22 pH-meter fitted with an ATC 55 31 temperature compensator and a Crison 52-08 electrode with an analytical error of ± 0.01 pH units.

The antioxidant capacity of the feed molasses and the total permeate from the charcoal chemical regeneration was experimentally measured at a pH of 11 using a Hitachi U-2000 spectrophotometer at 517 nm and the DPPH (1-diphenyl-2-picrylhydrazyl) method, according to the method of Cheng *et al*. [1,8,22] with TROLOX as standard. A blank was prepared for each sample. Samples were analyzed in triplicate under identical conditions. The error in the analytical method was ± 0.1 mmol/g of sample.

2.3. Adsorption equilibrium isotherms

All adsorption equilibrium isotherms were performed at 25 ± 0.1 ºC using 10 mL of the molasses diluted with water (50 g molasses/L) at a pH of 3.0 and 7.1 and different activated charcoal concentrations (1-10 g/L). Scharlau granular activated charcoal (SGAC), Scharlau powdered activated charcoal (SPAC), Norit powdered activated charcoal (NPAC) and NPAC after

regeneration (by chemical and thermal methods) were used. Samples (molasses with activated charcoal) were shaken at 200 ± 1 rpm for 12-24 hours in an Innova 2000 orbital shaker (New Brunswick Scientific Co) until equilibrium conditions had been achieved. The activated charcoal was separated by centrifugation (Eppendorf 5804 centrifuge) at 7500 rpm for 15 minutes. The decolourized molasses was also filtered to remove any remains of charcoal. The separated phases (decolourized molasses and exhausted charcoal) were stored at 4 ºC. The feed molasses and decolourized molasses were analyzed experimentally to determine the colour reduction (Eq. 1), the co-adsorption of species i (Eq. 2) and pH changes. The loss of colour reduction capacity for activated charcoals after regeneration was estimated using the following equation:

$$\text{Loss of } \%D = 100 \text{ x } \left(1 - \frac{\%D_2}{\%D_1}\right) \tag{3}$$

where %D is the colour reduction of beet molasses calculated using Eq. 1 and subscripts 1 and 2 refer to the first decolouration stage with new activated charcoal and second decolouration stage with regenerated activated charcoal, respectively. The error in the loss of %D was below ± 3%.

2.4. Exhausted NPAC regeneration experiments

An adsorption equilibrium experiment at 25ºC using 0.5 L of the dilute molasses at pH 3 with 5 g/L of NPAC was used to obtain exhausted NPAC. Regeneration of the exhausted NPAC was carried out by thermal, chemical, and combined chemical/thermal processes. Prior to regeneration, the exhausted NPAC was washed with water to avoid clumping due to the presence of sucrose, then dried in an oven (JP Selecta desktop oven to 250 ± 0.25 °C) at 105 ± 2 °C.

Several dry exhausted-NPAC concentrations (5–50 g/L) and different desorption agents (water, ethanol and sodium hydroxide solutions) were used for chemical regeneration. Samples (desorption agent with the charcoal) were shaken at 200 rpm for 6-12 hours at 25 ºC until equilibrium desorption conditions had been reached. The exhausted activated charcoal was then separated by centrifugation at 7500 rpm for 15 minutes. Liquid samples were also filtered to remove traces of

activated charcoal and the colour was experimentally measured. Equation 4 was used to determine the recovery of the colour compounds ($\%R_{colour}$) in desorption solutions (S) at equilibrium with respect to the initial colour in the feed dilute molasses, prior to decolouration.

$$\%R_{colour} = 100 \text{ x } \left(\frac{Abs_S}{Abs_F} \right) \quad (4)$$

Thermal regeneration of the dry exhausted-NPAC (0.3 g) was performed in an oven at two temperatures (450 and 550 ºC) for several different times (0.5, 1, 2 and 5 hours). Charcoal weight loss after thermal treatment was determined gravimetrically using a Sartorius LA620S electronic scale (±0.001 g). The experimental conditions for thermal regeneration experiments are collected in Table 1. Regeneration of the dry exhausted NPAC was also performed by chemical treatment with sodium hydroxide followed by thermal treatment at 450 ºC for 30 minutes following the aforementioned procedure.

2.5. Ultrafiltration of beet molasses with NPAC

The experimental setup shown in Fig. 1 was used in ultrafiltration experiments. Filtanium ceramic membranes (Tami Industries) with an active layer of TiO_2 supported on titania and a cut-off from 10 to 300 kDa were used. These membranes consist of a single tubular module (length of 254 mm, and inner and outer diameters of 6 and 10 mm, respectively) with an effective membrane area, as stated by the manufacturer, of 47 cm^2. The feed solution (acid water or molasses with NPAC) at 25 ± 2 ºC was pumped from a batch stirred glass tank (Pobel) to the membrane module using a Masterflex peristaltic pump (HV-7520-57, with a Masterflex L/S Easy-Load II Head HV-77201-62). Silicone tubing (Masterflex L/S 15) was used. Prior to ultrafiltration, the feed solution (molasses with NPAC) was recirculated through the system without pressure for 30 minutes. The feed flowrate and transmembrane pressure were then adjusted to the desired values using a variable speed drive (from 1 to 100 rpm) for the pump and a valve placed after the membrane module. The pressures at the inlet and outlet of the membrane module were measured using two pressure gauges.

Experiments were performed in concentration mode (the retentate was recycled back to the feed tank and the permeate was collected in the permeate tank). The activated charcoal concentration was increased progressively throughout the experiment. Permeate fluxes (J_p) were determined gravimetrically using a Sartorius LA620S electronic scale (±0.001 g) under different operating conditions of transmembrane pressure (TMP = 50 and 100 kPa), feed flowrate (Qf = 1.86 and 4.24 L/h), pH (1, 3 and 7.1) and initial NPAC concentrations (C_{NPAC} = 1.5-5 g/L). Two identical experiments with 3 and 5 g/L of NPAC were performed in concentration mode to verify the reproducibility of the results. The permeates collected were also analyzed in order to determinate the colour removal (Eq. 1), co-adsorption of species i (Eq. 2), and changes in pH and membrane fouling. The initial conditions for ultrafiltration kinetic experiments are summarized in Table 2.

The ceramic membrane was cleaned at room temperature after each ultrafiltration run following a procedure that involved rinsing with soapy water and deionized water in order to remove the molasses and NPAC, cleaning with a 20 g/L of NaOH solution in deionized water for 60 min at 30 kPa, rinsing again with deionized water, and cleaning again with a 0.17 vol.% aqueous H_3PO_4 solution at 30 kPa for 60 minutes. The membrane was then rinsed with freshly deionized water and the permeate flux was measured at 25 ºC to check membrane cleaning.

Additional experiments with two consecutive ultrafiltration runs using several initial NPAC concentrations were performed to decolour the molasses at pH 3. In the first run, the molasses plus NPAC (3 or 1.5 g/L of NPAC1) mixture was crossflow ultrafiltered at 25 ± 1 °C under the optimal conditions identified previously (Qf = 4.24 ± 0.06 L/h and TMP = 100 ± 1 kPa). Ultrafiltration was performed in concentration mode for 3-4 hours to reach a total permeate (decolourized molasses) of 0.35 L. The equipment and ceramic membrane were then cleaned following the procedure detailed above. The decolourized molasses was again added to the feed tank with a new quantity of weighed NPAC (3 g/L of NPAC2), then ultrafiltered in concentration mode under the same experimental conditions as the first ultrafiltration run. Permeate fluxes (J_p) were also determined gravimetrically and analyzed using the aforementioned analytical methods.

2.6. Decolouration of beet molasses with NPAC and NPAC after regeneration in the continuous charcoal/ultrafiltration process

Experiments with several ultrafiltration stages for decolouration of beet molasses and subsequent NPAC regeneration were performed. In the first decolouration stage, the feed of dilute molasses with NPAC (2.5 and 5 g/L) at pH 3 was crossflow ultrafiltered (Fig. 1) at 25 ± 2 °C using a feed flowrate of 4.24 ± 0.06 L/h and a TMP of 100 ± 1 kPa. Ultrafiltration was performed in concentration mode for 1.7 hours to reach a total permeate (decolourized molasses) of 0.5 L. The equipment containing exhausted NPAC was then rinsed with 2 L of water in order to remove traces of the molasses and sugars. Four NPAC regeneration runs were then carried out using sodium hydroxide solutions (1 mol/L) for 4 hours. The equipment containing regenerated NPAC was then rinsed with 1 L of water and 2 L of aqueous H_3PO_4 solution at pH 3 to restore the charge of the membrane and the adsorbent surface [7,14,23]. This operation was sufficient to achieve membrane cleaning. New dilute molasses at pH 3 was then added to the feed tank and crossflow ultrafiltered under the same experimental conditions as the first decolouration run. In the experiment with an initial NPAC concentration of 5 g/L, two additional NPAC regeneration and molasses decolouration cycles were performed under the aforementioned conditions to evaluate the operational life of the activated charcoal. Prior to any ultrafiltration, solutions with NPAC were recirculated for 30 minutes without pressure. Two identical experiments were performed to verify the reproducibility of the results.

Permeate fluxes (J_p) were determined gravimetrically and also analyzed using the aforementioned analytical methods. Colour reductions and loss of colour reduction capacity for the NPAC charcoal after regeneration were calculated using Eqs. 1 and 3, respectively. Equation 4 was used to determine recovery of the colour compounds ($\%R_{colour}$) in sodium hydroxide desorption solutions.

3. Results and discussion

3.1. Operating conditions for colour removal from beet molasses

The pH is one of the main factors that affect the activated charcoal adsorption capacity due to the modification of its charge and the ionization equilibrium of many organic compounds dissolved in the feed aqueous molasses [14,23]. Preliminary equilibrium experiments were performed to select the most suitable activated charcoal and to determine the influence of pH on its colour adsorption capacity. The results of adsorption equilibrium isotherms using SGAC, SPAC and NPAC at a pH of 3 and 7.1 are shown in Figs. 2 and 3. Figure 2 shows that the best colour reduction was achieved using NPAC concentrations higher than 3 g/L at pH 3, with no co-adsorption (Fig. 3) of betaine and sucrose and a low co-adsorption of citric acid (8.50 ± 0.03%–10.00 ± 0.05%) and lactic acid (15.71 ± 0.02%–16.77 ± 0.04%) at equilibrium. In comparison with NPAC, a lower %D (Fig. 2) and high co-adsorptions (not shown) of sucrose (45.03 ± 0.08%–56.1± 0.1%) and citric acid (35.0 ± 0.1%-44.1 ± 0.3%) were obtained with Scharlau powdered charcoal at pH 3. Therefore, %D for SPAC is affected by the high co-adsorption of sucrose and citric acid, so that we can conclude that Scharlau charcoal affinity by dark colour compounds is affected by the presence of other adsorbable compounds of the molasses. As such, NPAC was selected for subsequent experiments.

The particle size distribution of NPAC charcoal (see Fig. 4) was measured using laser light diffraction (Mastersizer 2000, Malvern Instruments Ltd.) and n-propanol (99%, Prolabo) as dispersant medium. A particle size distribution (Fig. 4) from 0.8 to 500 μm was obtained for NPAC with a volume mean diameter of 50.2 ± 0.4 μm. Consequently, a tubular ceramic membrane with a 100 kDa cut-off was used for crossflow ultrafiltration experiments to ensure total retention of NPAC.

The following step focused on evaluating the feasibility of continuous crossflow ultrafiltration with NPAC in order to select the optimal operating conditions for colour reduction in molasses of more than 90%. Ultrafiltration permeates (decolourized molasses) were found to have the same pH

and concentrations of species i as the feed molasses (experiments 3-11 of Table 2), thus indicating that these species i were not adsorbed by NPAC present in the molasses due to its higher affinity by the dark colour compounds. Figure 5 shows the effects of the feed pH, feed flowrate, initial NPAC, TMP and several feed types (F = water, molasses, molasses with NPAC) on permeate flux (Fig. 5(a)) and colour removal (Fig. 5(b)) for the experiments of Table 2.

Constant permeate fluxes of 109.8 ± 0.7 kg/m^2 h and 98 ± 3 kg/m^{2}h were obtained for systems with water at pH 3 without NPAC (experiment 1) and with 3 g/L of NPAC (experiment 2), respectively, as shown in Fig. 5(a). However, a continuous sharp decrease in J_p is observed in Fig. 5(a) for experiments 3-11 with beet molasses, increasing slightly upon increasing the initial NPAC concentration from 0 to 5 g/L (experiments 4-6 and 11), TMP from 50 to 100 kPa (experiments 6 and 9), feed flowrate from 1.86 to 4.24 L/h (experiments 6 and 10) and at pH 3 (experiments 6-8). These results indicate that the permeate flux is mainly affected by the molasses and, to a lesser extent, by the presence of NPAC in the feed solution, feed flowrate, TMP, or pH.

Experiments 4-11 with beet molasses and NPAC (Fig. 5(b)) show that %D also depend on the different operating conditions (pH, TMP, Qf and C_{NPAC}) used. Thus, a comparison of experiments 6 (pH 3), 7 (pH 1) and 8 (pH 7.1) shows that %D are higher at pH 3 (%D = 86.74 ± 0.01%–89.08 ± 0.01%) than at pH 1 (%D = 58.2 ± 0.7–71.0 ± 0.6%) or 7.1 (%D = 70.93 ± 0.01%–72.02 ± 0.01%). These kinetic results agree with the equilibrium results previously shown in Fig. 2.

It should be pointed out that permeates obtained in experiment 3 (molasses without NPAC) kept the same colour as the feed molasses, which indicates that the removal of coloured compounds (%D) from the molasses is only due to their adsorptions on the activated charcoal, with no colour retention by the membrane. The effects of initial NPAC, TMP, and feed flowrate depicted in Fig. 5(b) indicate that %D also increase with increasing initial NPAC concentration from 1.5 to 5 g/L (experiments 4-6 and 11), TMP from 50 to 100 kPa (experiments 6 and 9) and, to a lesser extent, upon increasing the feed flowrate from 1.86 to 4.24 L/h (experiments 6 and 10). A %D about 97.24

± 0.01% after 3 hours is achieved using a pH of 3, initial NPAC concentration of 5 g/L, TMP of 100 kPa and a feed flowrate of 4.24 L/h, as can be observed from Fig. 5(b).

In addition, the linear fit (solid lines) of %D experimental data (symbols) versus time is also shown in Fig. 5(b). The intercept and slope of the linear fit indicate, respectively, the colour reduction at the beginning of ultrafiltration and the colour removal rate, which can be assumed to be constant for each ultrafiltration experiment. The linear regression coefficients (r) and values for the slope (v) and intercept (%Do) are also summarized in Table 2. A comparison of experiments 4-11 shows that v is mainly affected by the feed pH, with values close to 1 h^{-1} (from 0.60 to 1.44 h^{-1}) for systems with pH 3, whereas %Do depends on the pH, initial NPAC and TMP. This result confirms that, in experiments at pH 3, %D increases with increasing %Do, reaching a maximum value of 95.80 ± 0.02% at a TMP of 100 kPa and initial NPAC concentration of 5 g/L.

Membrane fouling was also evaluated for the experiments of Table 2. Considering a resistance-in-series model, the total resistance of the membrane can be written as [7,24]:

$$R_t = \frac{\rho\ (TMP)}{\mu\ J_P} = R_m + R_S \tag{5}$$

where ρ and μ are the experimental density and viscosity of the solutions (water and molasses) listed in Table 2, R_m is the membrane hydraulic resistance expressed in m^{-1} and R_S is the secondary resistance due to concentration polarization and membrane fouling, expressed in m^{-1}. As $R_t = R_m$ in systems with water, R_m was measured experimentally for ultrafiltration of water and acidified water at pH 3 under different TMP values (10-100 kPa) at 25 ºC. A similar linear relationship between J_p and TMP was observed for water and water at pH 3. The experimental density and viscosity values for acidified water at pH 3 were 997.0 ± 0.1 kg/m^3 and 0.89 x 10^{-3} ± 0.01 x 10^{-3} Pa s, respectively. R_m obtained from the slope of the linear fit of J_p with TMP (not shown) was 3.66 x 10^{12} m^{-1}, with a linear regression coefficient of 0.9998. The same value for R_m (3.67 x 10^{12} ± 0.05 × 10^{12} m^{-1}) was obtained from the experimental data of experiment 1 in Table 2. The time evolution of R_t and R_s was calculated for experiments 2-11 in Table 2 using Eq. 5. The contribution of the secondary

resistance during each ultrafiltration experiment, expressed as $\%(R_s/R_t)$, is shown in Fig. 6 and Table 2. Figure 6 shows that R_s increases with time for experiments with beet molasses at pH 3. Similar results were obtained for the ultrafiltration of beet molasses at pH 1 and 7.1, as shown in Table 2. As expected, R_s is considerably higher than R_m for these experiments with molasses, decreasing slightly upon increasing the initial NPAC from 0 to 5 g/L at pH 3, thus indicating that the molasses is the predominant contribution to the resistance (more than 60% for experiments at 100 kPa). This result reflects the formation of a dynamic membrane due to the activated charcoal deposited on the ceramic membrane surface, decreasing the effects of concentration polarization and ceramic membrane fouling promoted by the molasses [25-28]. As expected, TMP is an important parameter in the membrane fouling [28], increasing by about 40% upon increasing from 50 to 100 kPa. However, as higher values of J_p and %D were achieved with a TMP of 100 kPa, this value was selected for subsequent experiments, as discussed above. As an additional disadvantage, variations in TMP were detected in the experiment at 50 kPa over time, thus meaning that TMP had to be readjusted to 50 kPa throughout this experiment.

Figure 7 shows the colour reduction (%D) of beet molasses at pH 3 over time for experiments with two consecutive ultrafiltration runs using the molasses with 1.5 or 3 g/L of NPAC (NPAC1) as feed in the first run and the permeate (decolourized molasses) from the first run with 3 g/L of NPAC (NPAC2) as feed in the second run (ratios of NPAC1/NPAC2 = 1.5/3 and 3/3). As expected, the %D results for the first decolouration run were identical to those shown in Fig. 5(b) for experiments 4 and 6 of Table 2. In this first run, the molasses was decolourized by about 88.08 ± 0.05% and 60.4 ± 0.4% with an initial NPAC concentration of 3 and 1.5 g/L, respectively. A linear behaviour in %D is also observed in the second decolouration run with values of 98.64 ± 0.01%–99.20 ± 0.01% and 95.60 ± 0.08%–96.10 ± 0.08% for experiments with NPAC ratios of 3/3 and 1.5/3, respectively. Final molasses decolourization of 99.17 ± 0.01% and 96.04 ± 0.08% was achieved for experiments with NPAC ratios of 3/3 and 1.5/3, respectively, thus showing a high colour reduction in beet molasses even when using 1.5 g/L of NPAC in the first ultrafiltration run.

3.2. Regeneration conditions for NPAC

An important aim of this study is to evaluate the regeneration of the exhausted adsorbent by chemical and thermal methods for its reuse. As it was mentioned, chemical desorption experiments was carried out by using different exhausted NPAC concentrations (5–50 g/L) and several desorption agents (water, ethanol, 0.5 mol/L NaOH solutions, and 1 mol/L NaOH solutions). A negligible desorption was obtained with water and ethanol, an increased desorption ($\%R_{colour}$ = 69.97 ± 0.01, 71.97 ± 0.03, 20.4 ± 0.3, 17.28 ± 0.02, and 5.61 ± 0.01 for exhausted NPAC concentrations of 5, 10, 20, 40 and 50 g/L, respectively) was achieved with 0.5 mol/L NaOH solutions, whereas the use of 1 mol/L NaOH solutions using several exhausted NPAC concentrations gave the best desorption results ($\%R_{colour}$ = 95.04 ± 0.05, 145.85 ±0.08 and 201.84 ± 0.03 for exhausted NPAC concentrations of 5, 10 and 20 g/L, respectively) for the dark coloured compounds. The removal of coloured compounds from the exhausted NPAC is then affected by the concentration of NaOH desorption solution and the concentration of exhausted NPAC used.

Thermal regeneration of exhausted NPAC was performed at two temperatures (450 ºC and 550 ºC) and several different times (0.5–5 hours). The degree of decolouration ($\%D_1$ and $\%D_2$, Eq. 1) and loss of NPAC capacity values (Eq. 3) for colour removal after thermal regeneration under several experimental conditions are listed in Table 1. Some loss of activated charcoal was observed upon calcination, especially at 550 °C. A high loss of %D (about 50%) was observed after the thermal regeneration at 550 ºC for 0.5-1 hours and at 450ºC for 5 hours. As shown in Table 1, the best regeneration results were achieved at 450 ºC with times of less than 1 hour. The loss of NPAC adsorption capacity after this thermal regeneration was about 20% and 10% for NPAC concentrations of 3 g/L and 5 g/L, respectively.

Figure 2 also shows a comparison of the adsorption equilibrium isotherms at 25 ºC for the dark colour removal of beet molasses at pH 3 using NPAC and NPAC regenerated by chemical (with 1 mol/L NaOH solutions), thermal (at 450 ºC for 0.5 hours) and combined thermal/chemical

processes (with NaOH solutions and at 450 ºC for 0.5 hours). Similar equilibrium results were obtained by NPAC regenerated using thermal, chemical and combined thermal/chemical processes. These results show that the use of a thermal method at 450 ºC with times of less than 1 hour does not provide significant improvements in terms of NPAC regeneration, which can be due to a low oxidation of NPAC with slight modifications in its surface activity and porosity [15].

Chemical regeneration method using 1 mol/L NaOH solutions and 10 g/L of exhausted NPAC was selected for subsequent experiments to regenerate the exhausted activated charcoal, and also to recover the coloured compounds due to their high antioxidant capacity. Furthermore, differences in %D for experiments with NPAC and regenerated NPAC were decreased upon increasing the initial NPAC concentrations from 1 to 5 g/L. The loss of NPAC decolouration capacity at equilibrium after these regeneration types was 33 ± 3%, 25 ± 2% and 11 ± 1% using regenerated NPAC concentrations of 1, 3 and 5 g/L, respectively. These results confirm that regeneration of activated charcoal depends on the initial NPAC concentration irrespective of the regeneration type used. Moreover, the loss of NPAC decolouration capacity after regeneration indicates that desorption is not completed and that the regeneration method may cause inactivation of active centres on the adsorbent particle [15,29].

3.3. Decolouration capacity for NPAC and NPAC after regeneration in the continuous charcoal/ultrafiltration process

In the first decolouration stage, the permeate flux and colour reduction ($\%D_1$ = 81.50 ± 0.03–83.68 ± 0.02 and 95.82 ± 0.01–97.35± 0.02 for experiments with C_{NPAC} = 2.5 and 5 g/L, respectively) values over time were identical to those shown in Fig. 5(b) for experiments 5 and 11. The molasses was about 82.52 ± 0.03% and 96.51 ± 0.01% decolourized for systems with an initial NPAC concentration of 2.5 and 5 g/L, respectively. As expected, %D for the second decolouration stage with regenerated NPAC was slightly lower and beet molasses achieved a lower colour reduction ($\%D_2$ = 66.10 ± 0.04% and 91.72 ± 0.04% for experiments with C_{NPAC} = 2.5 and 5 g/L,

respectively). In Fig. 8 is depicted the time evolution for loss of decolouration capacity for NPAC after regeneration as calculated using Eq. 3. The loss of NPAC decolouration capacity varied from 1.83 ± 0.07% to 9.09 ± 0.05% in the system with 5 g/L NPAC and from 7.31 ± 0.05% to 23.00 ± 0.08% in the system with 2.5 g/L NPAC. These results are in good agreement with the equilibrium data for regenerated NPAC shown in Fig. 2. A colour reduction ($\%D_3$ = 91.1 ± 0.1% and $\%D_4$ = 91.4 ± 0.2%) for molasses similar to the $\%D_2$ (91.72 ± 0.04) value was achieved in two successive decolouration stages using the system containing 5 g/L of NPAC. These results show that, even after several regeneration cycles, NPAC maintains the slight loss in colour reduction capacity obtained in the first regeneration run.

Regeneration of exhausted NPAC after the first adsorption stage was performed by ultrafiltration using four desorption runs with sodium hydroxide solutions (1 mol/L). The colour of desorption permeates (Abs_S) was measured experimentally throughout the ultrafiltration experiment. Figure 9 shows the recovery of the coloured compounds ($\%R_{colour}$, Eq. 4) in NaOH desorption solutions.

Similar colour-desorption were obtained for both systems studied, with any differences being due to the different degree of exhaustion of the activated charcoal after the first decolouration stage. Good NPAC regeneration was obtained in these experiments, as shown in Fig. 9. A value higher than 50% for the first desorption run and a total desorption close to 93.6 ± 0.1 % were achieved for the experiment with an initial NPAC concentration of 5 g/L. An important feature was that the total permeate from the first desorption run containing 40-50% of the dark colour of the feed molasses had about 20% (17.5% and 25%, respectively, for experiments with C_{NPAC} = 2.5 and 5 g/L) of the antioxidant capacity of the molasses. Similar desorption results were obtained in the subsequent regeneration cycles for the system with 5 g/L NPAC (not shown).

Moreover, as J_p was completely restored without additional cleaning cycles, we can conclude that this continuous process allows a high decolouration of beet molasses and good NPAC regeneration without the need for equipment disassembly or other membrane-cleaning cycles.

4. Conclusions

The capacity of several activated charcoals to adsorb dark colour compounds from dilute beet molasses was studied in equilibrium experiments and NPAC was selected. A fast colour removal of more than 97% after 3 hours, with no co-adsorption of sucrose, betaine, citric acid or lactic acid, was achieved for the crossflow ultrafiltration experiment using feed molasses at pH 3, an initial NPAC concentration of 5 g/L, a 100 kDa TiO_2 tubular ceramic membrane, a TMP of 100 kPa, and a feed flowrate of 4.24 L/h. The removal of coloured compounds was only due to their adsorption on NPAC dynamic membrane formed onto the ceramic membrane surface, which also helped to the decrease of concentration polarization and ceramic membrane fouling promoted by the molasses. Experiments with several ultrafiltration stages for the decolouration of beet molasses with an initial NPAC concentration of 2.5 or 5 g/L and subsequent regeneration of the exhausted NPAC with NaOH solutions were performed under the optimal operating conditions. The molasses was decolourized by about 96.5% in the first adsorption stage when using an initial NPAC concentration of 5 g/L. A good NPAC regeneration was also obtained, with a loss of its colour removal capacity lower than 10% for three consecutive ultrafiltration runs, with no need for equipment disassembly or other membrane-cleaning cycles. Moreover, the lower cost of activated charcoals compared with other adsorbents, together with their good regeneration capacity with NaOH solutions suggest the use of this NPAC/ultrafiltration process from a technical, economic, and environmental viewpoint.

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^2h)
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})
Rs	secondary resistance due to concentration polarization 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

Acknowledgements

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Figure captions

Figure 1. Experimental setup for ultrafiltration experiments with activated charcoal.

Figure 2. Adsorption equilibrium isotherms at 25 ºC for the colour removal from dilute beet molasses (50 g of molasses/L) at two pH values (3 and 7.1) with several activated charcoals (SGAC, SPAC, NPAC and NPAC regenerated by chemical (with NaOH solutions), thermal (at 450 ºC for 0.5 hours) and combined thermal/chemical processes) and different activated charcoal concentrations (1-10 g/L).

Figure 3. Equilibrium co-adsorption of species i (i = sucrose, betaine or carboxylic acids) for experiments of Fig. 2 with NPAC at pH 3 and 7.1.

Figure 4. Particle size distribution for Norit powdered activated charcoal (NPAC).

Figure 5. Time evolution of (a) the permeate flux (J_p) and (b) colour reductions (%D) for ultrafiltration kinetic experiments 1-11 in Table 2. Experimental values of %D (symbols) calculated using Eq. 1 and their linear fit (lines). Linear regression coefficients, slopes and intercepts of the linear fit can be found in Table 2.

Figure 6. Comparison of the contribution of secondary resistances (%(R_s/R_t)) calculated using Eq. 5 for ultrafiltration experiments 2-6, 9 and 11 in Table 2 using a 100 kDa cut-off TiO_2 monochannel tubular ceramic membrane.

Figure 7. Colour reductions (%D) for beet molasses at pH 3 over time for experiments with two ultrafiltration runs using 1.5 or 3 g/L NPAC (NPAC1) in the first decolouration run and 3 g/L NPAC (NPAC2) in the second decolouration run. Operating conditions for ultrafiltration runs were: 100 kPa of TMP, 4.24 L/h of Qf and 25 °C.

Figure 8. Loss of decolouration capacity for NPAC after the first regeneration stage calculated using Eq. 3 for the ultrafiltration experiments with successive stages for the decolouration of beet molasses at pH 3 and subsequent charcoal regeneration. Experimental conditions for ultrafiltration runs: 100 kPa of TMP, 2.5 or 5 g/L of C_{NPAC} and 25ºC.

Figure 9. Comparison of recovery of coloured compounds ($\%R_{colour}$, Eq. 4) from the exhausted NPAC in sodium hydroxide desorption solutions for the experiments depicted in Fig. 8.

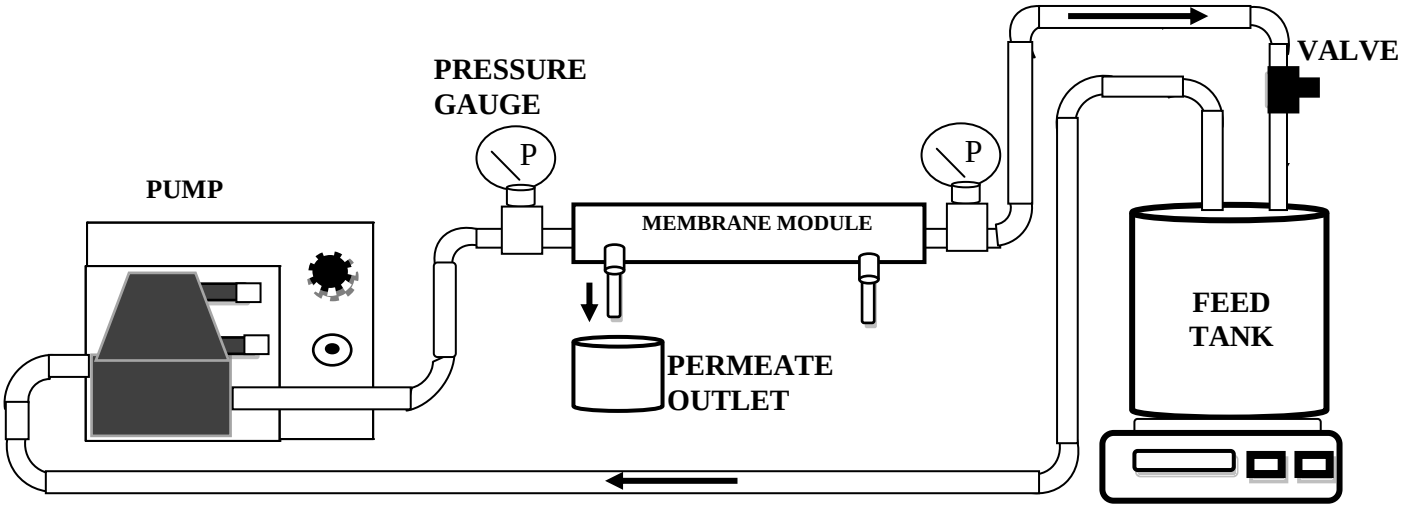
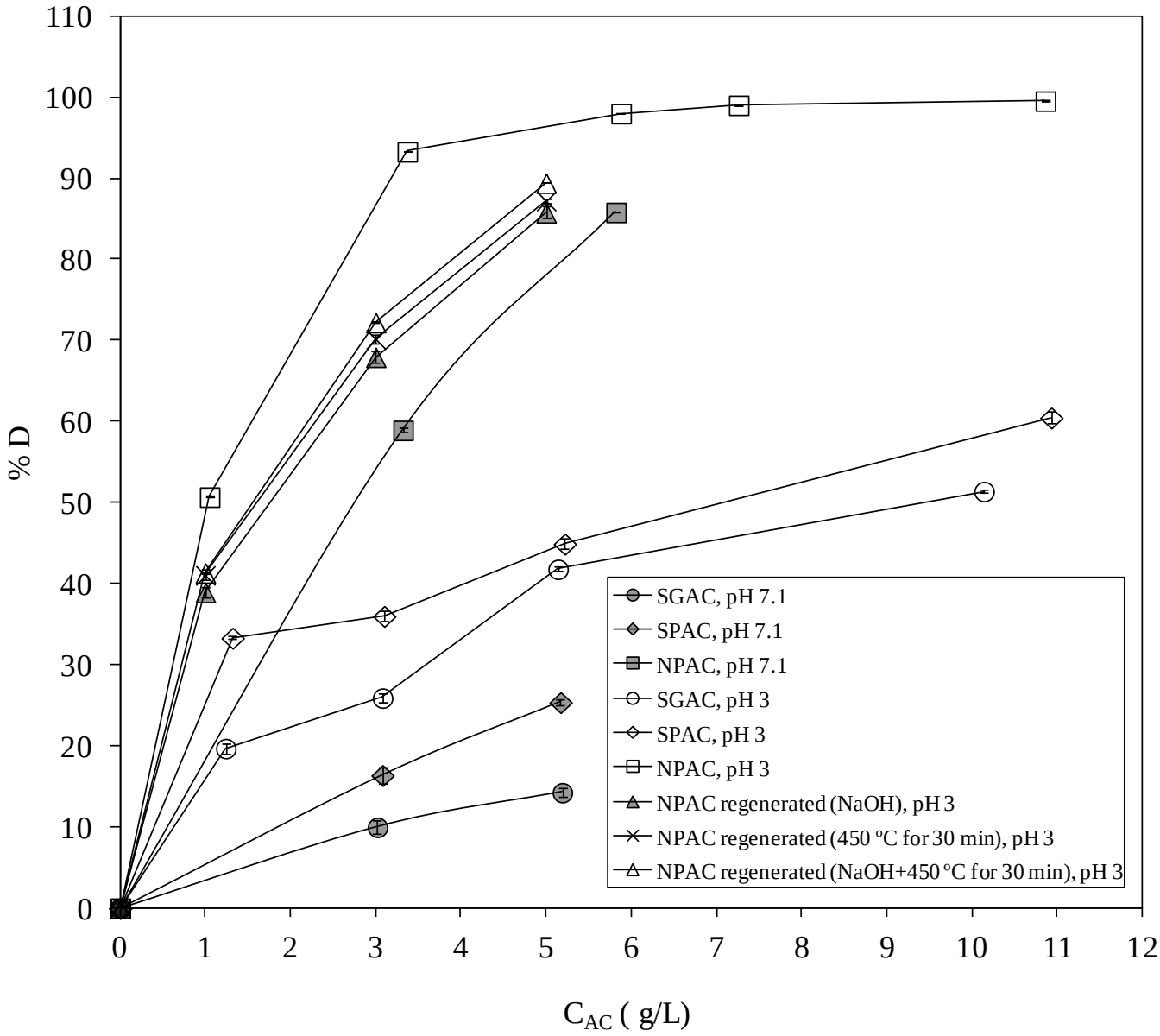

PRESSURE
GAUGE
P
P
VALVE
PUMP
MEMBRANE MODULE
FEED
TANK
PERMEATE
OUTLET

Figure 1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100
90
80
70
60
50
40
30
20
10
0
% D
0
1
2
3
4
5
6
7
8
9
10
11
12
C_AC (g/L)
SGAC, pH 7.1
SPAC, pH 7.1
NPAC, pH 7.1
SGAC, pH 3
SPAC, pH 3
NPAC, pH 3
NPAC regenerated (NaOH), pH 3
NPAC regenerated (450 ºC for 30 min), pH 3
NPAC regenerated (NaOH+450 ºC for 30 min), pH 3

Figure 2

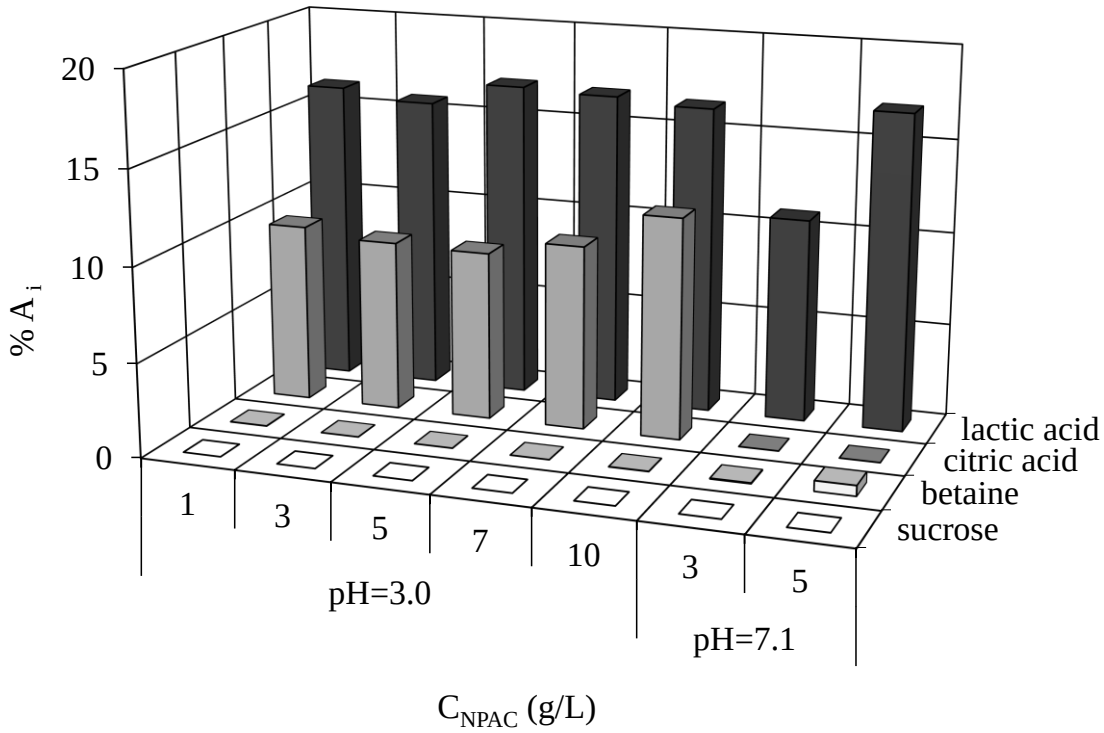
20
15
10
5
0
% A i
1
3
5
7
10
3
5
pH=3.0
pH=7.1
C NPAC (g/L)
lactic acid
citric acid
betaine
sucrose

Figure 3

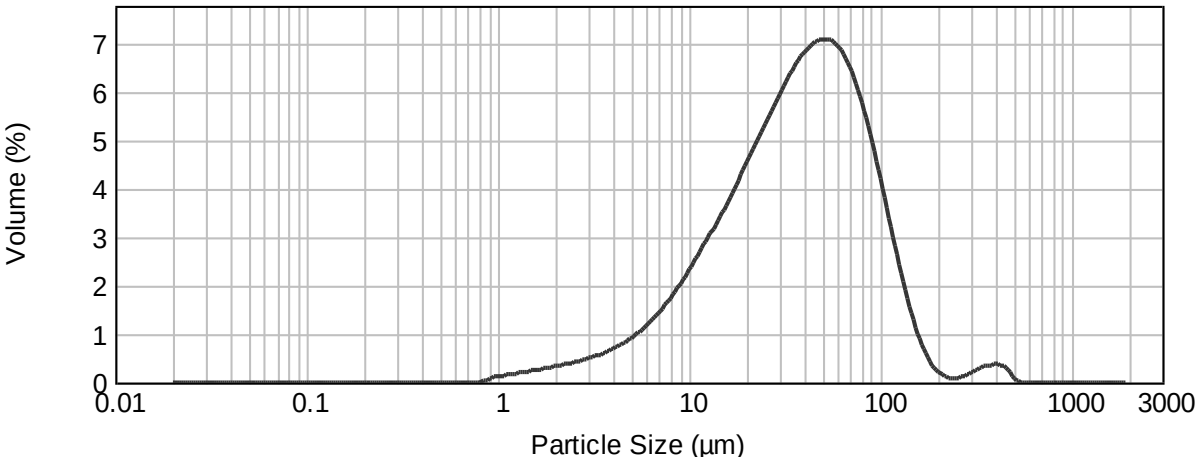

Figure 4

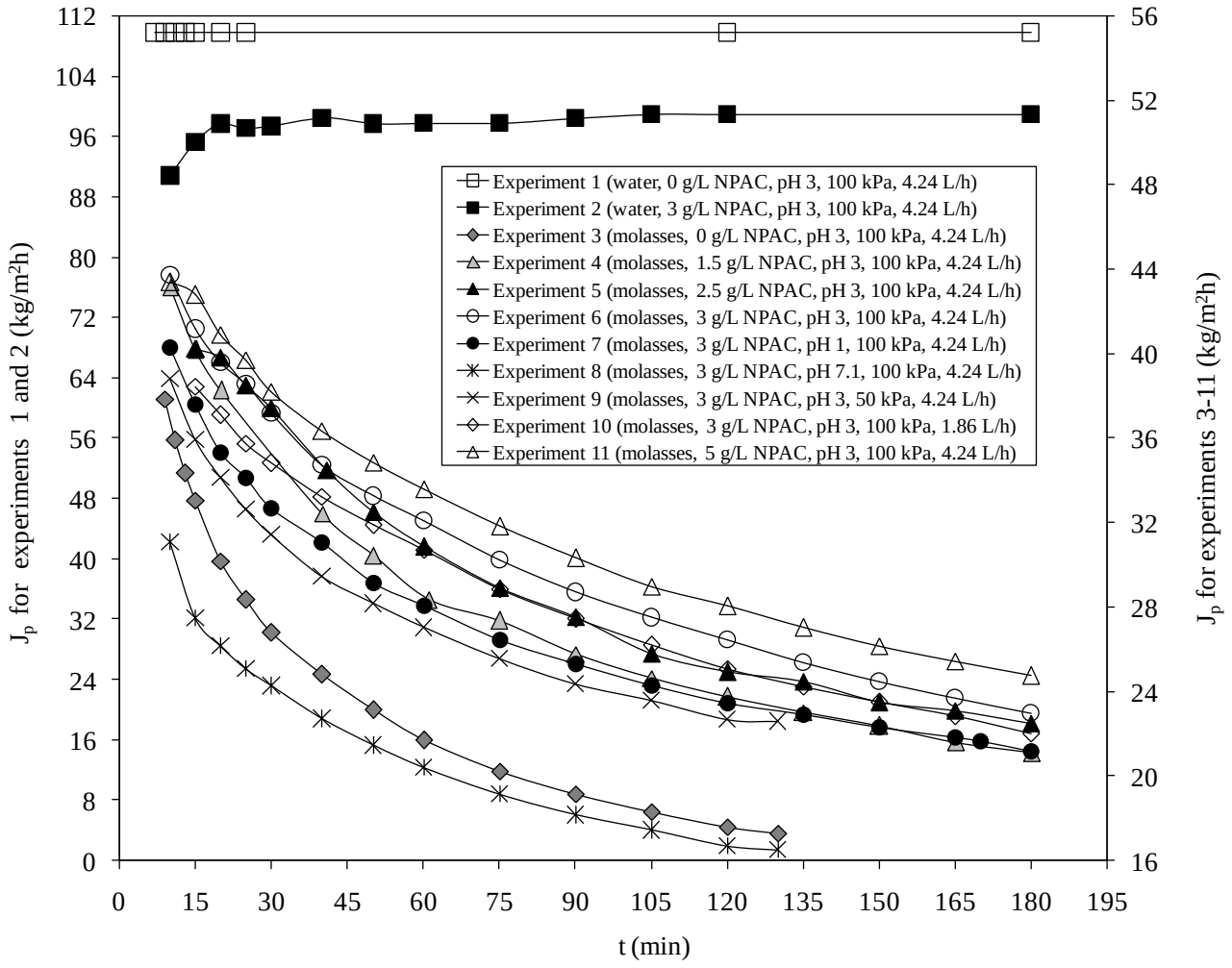
Experiment 1 (water, 0 g/L NPAC, pH 3, 100 kPa, 4.24 L/h)
Experiment 2 (water, 3 g/L NPAC, pH 3, 100 kPa, 4.24 L/h)
Experiment 3 (molasses, 0 g/L NPAC, pH 3, 100 kPa, 4.24 L/h)
Experiment 4 (molasses, 1.5 g/L NPAC, pH 3, 100 kPa, 4.24 L/h)
Experiment 5 (molasses, 2.5 g/L NPAC, pH 3, 100 kPa, 4.24 L/h)
Experiment 6 (molasses, 3 g/L NPAC, pH 3, 100 kPa, 4.24 L/h)
Experiment 7 (molasses, 3 g/L NPAC, pH 1, 100 kPa, 4.24 L/h)
Experiment 8 (molasses, 3 g/L NPAC, pH 7.1, 100 kPa, 4.24 L/h)
Experiment 9 (molasses, 3 g/L NPAC, pH 3, 50 kPa, 4.24 L/h)
Experiment 10 (molasses, 3 g/L NPAC, pH 3, 100 kPa, 1.86 L/h)
Experiment 11 (molasses, 5 g/L NPAC, pH 3, 100 kPa, 4.24 L/h)
J_p for experiments 1 and 2 (kg/m²h)
J_p for experiments 3-11 (kg/m²h)
t (min)
0
8
16
24
32
40
48
56
64
72
80
88
96
104
112
16
20
24
28
32
36
40
44
48
52
56
0
15
30
45
60
75
90
105
120
135
150
165
180
195

Figure 5(a)

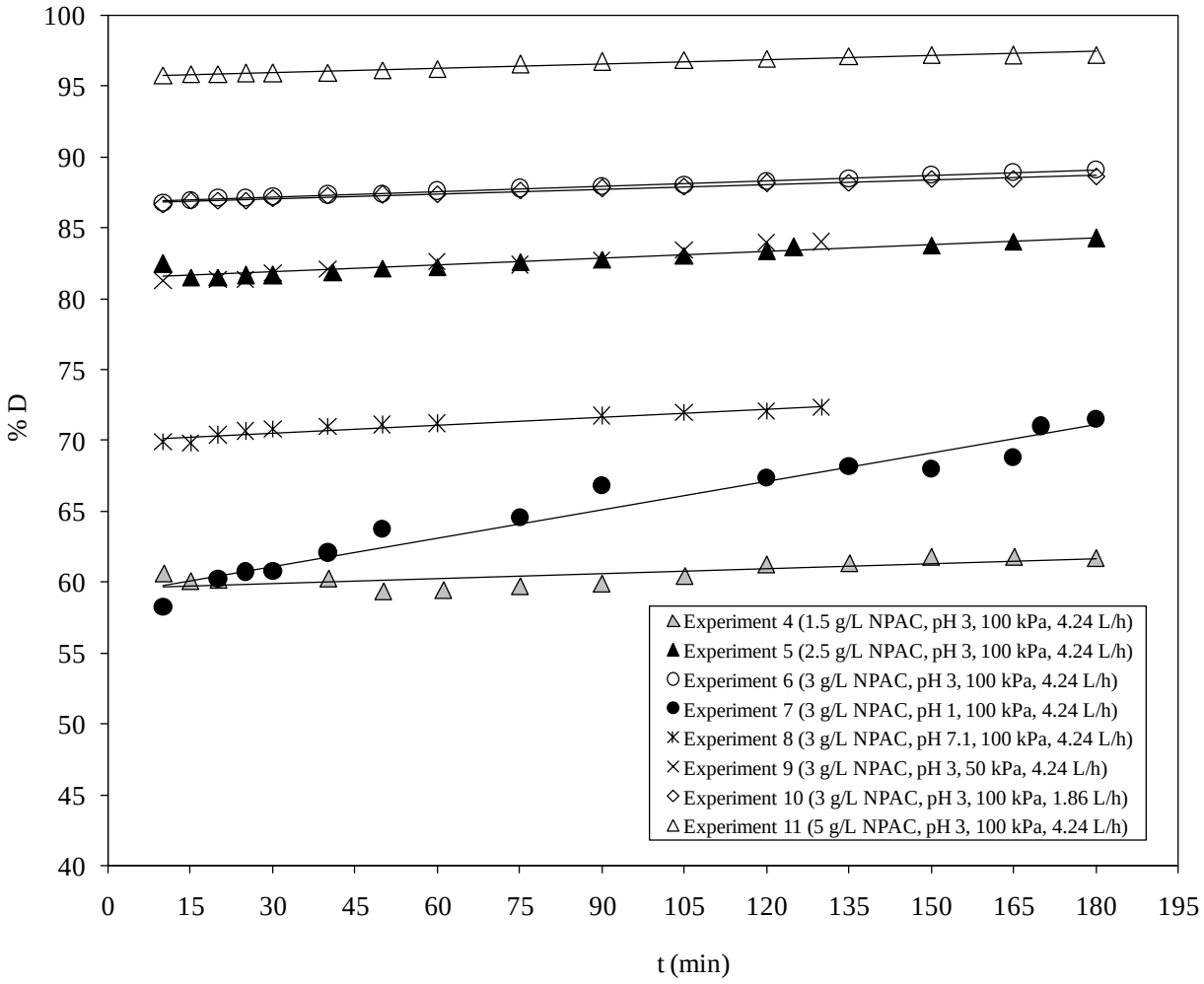
100
95
90
85
80
75
70
65
60
55
50
45
40
% D
0
15
30
45
60
75
90
105
120
135
150
165
180
195
t (min)
Experiment 4 (1.5 g/L NPAC, pH 3, 100 kPa, 4.24 L/h)
Experiment 5 (2.5 g/L NPAC, pH 3, 100 kPa, 4.24 L/h)
Experiment 6 (3 g/L NPAC, pH 3, 100 kPa, 4.24 L/h)
Experiment 7 (3 g/L NPAC, pH 1, 100 kPa, 4.24 L/h)
Experiment 8 (3 g/L NPAC, pH 7.1, 100 kPa, 4.24 L/h)
Experiment 9 (3 g/L NPAC, pH 3, 50 kPa, 4.24 L/h)
Experiment 10 (3 g/L NPAC, pH 3, 100 kPa, 1.86 L/h)
Experiment 11 (5 g/L NPAC, pH 3, 100 kPa, 4.24 L/h)

Figure 5(b)

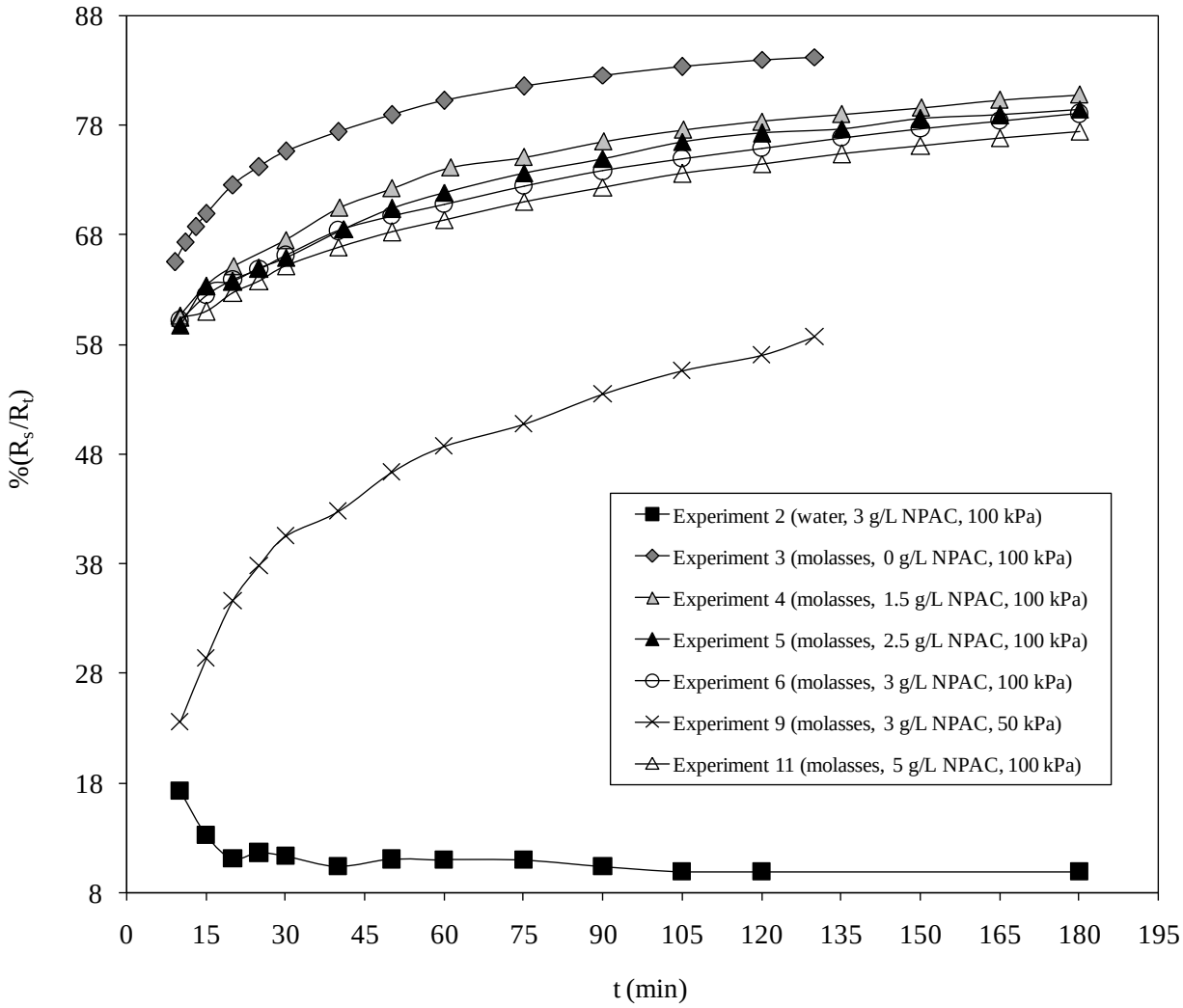
88
78
68
58
48
38
28
18
8
%(Rs/Rt)
0
15
30
45
60
75
90
105
120
135
150
165
180
195
t (min)
Experiment 2 (water, 3 g/L NPAC, 100 kPa)
Experiment 3 (molasses, 0 g/L NPAC, 100 kPa)
Experiment 4 (molasses, 1.5 g/L NPAC, 100 kPa)
Experiment 5 (molasses, 2.5 g/L NPAC, 100 kPa)
Experiment 6 (molasses, 3 g/L NPAC, 100 kPa)
Experiment 9 (molasses, 3 g/L NPAC, 50 kPa)
Experiment 11 (molasses, 5 g/L NPAC, 100 kPa)

Figure 6

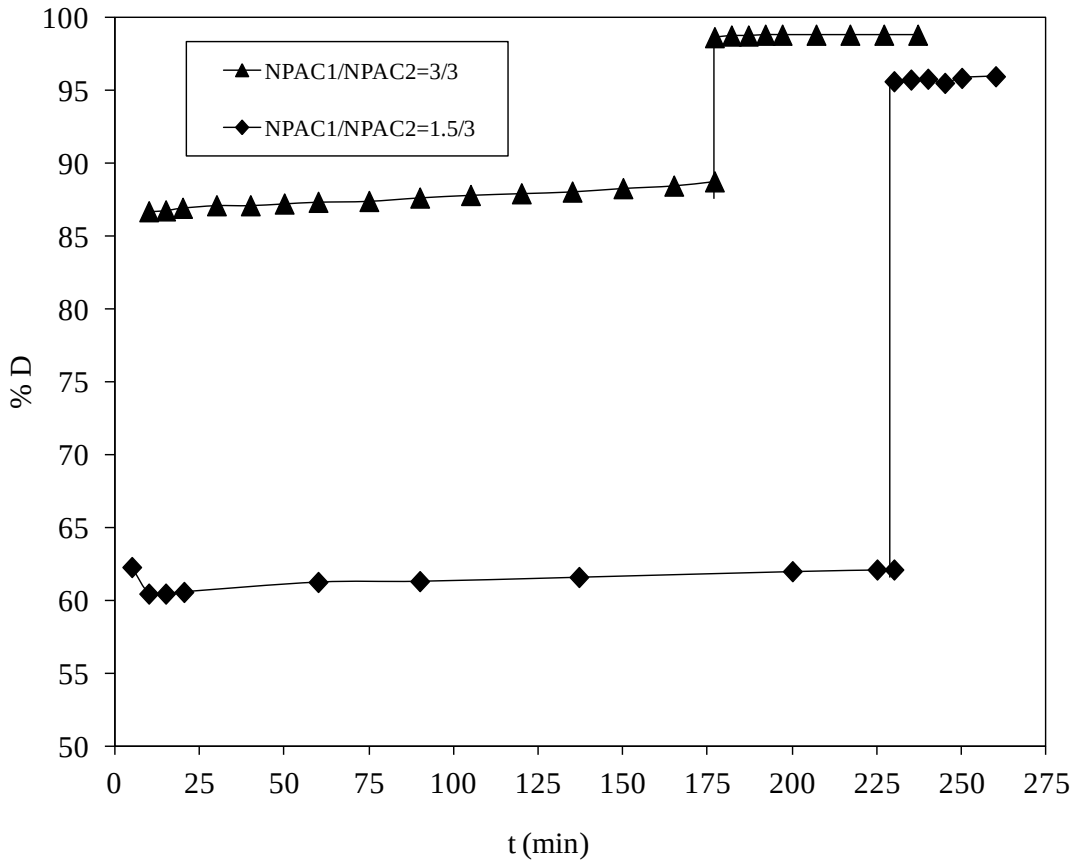
NPAC1/NPAC2=3/3
NPAC1/NPAC2=1.5/3
% D
t (min)
100
95
90
85
80
75
70
65
60
55
50
0
25
50
75
100
125
150
175
200
225
250
275

Figure 7

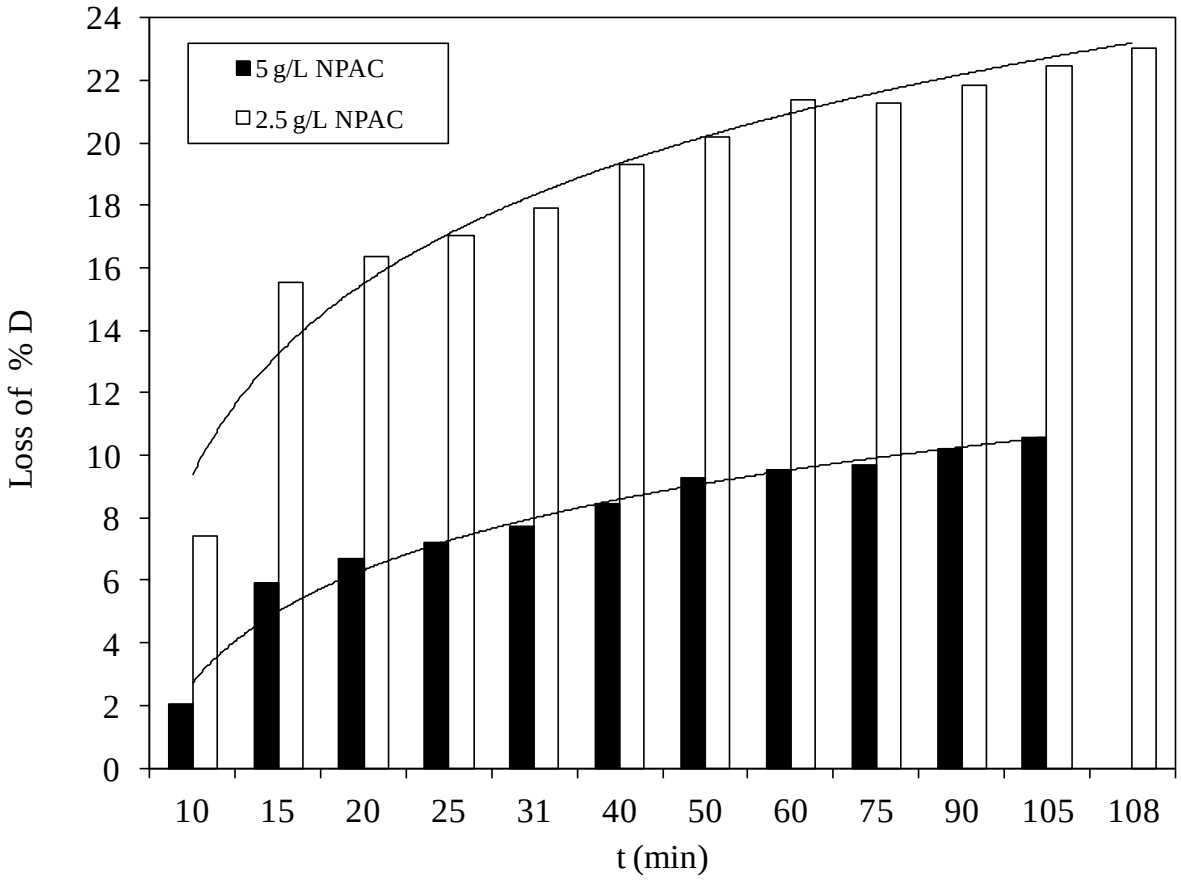
5 g/L NPAC
2.5 g/L NPAC
Loss of % D
0
2
4
6
8
10
12
14
16
18
20
22
24
10
15
20
25
31
40
50
60
75
90
105
108
t (min)

Figure 8

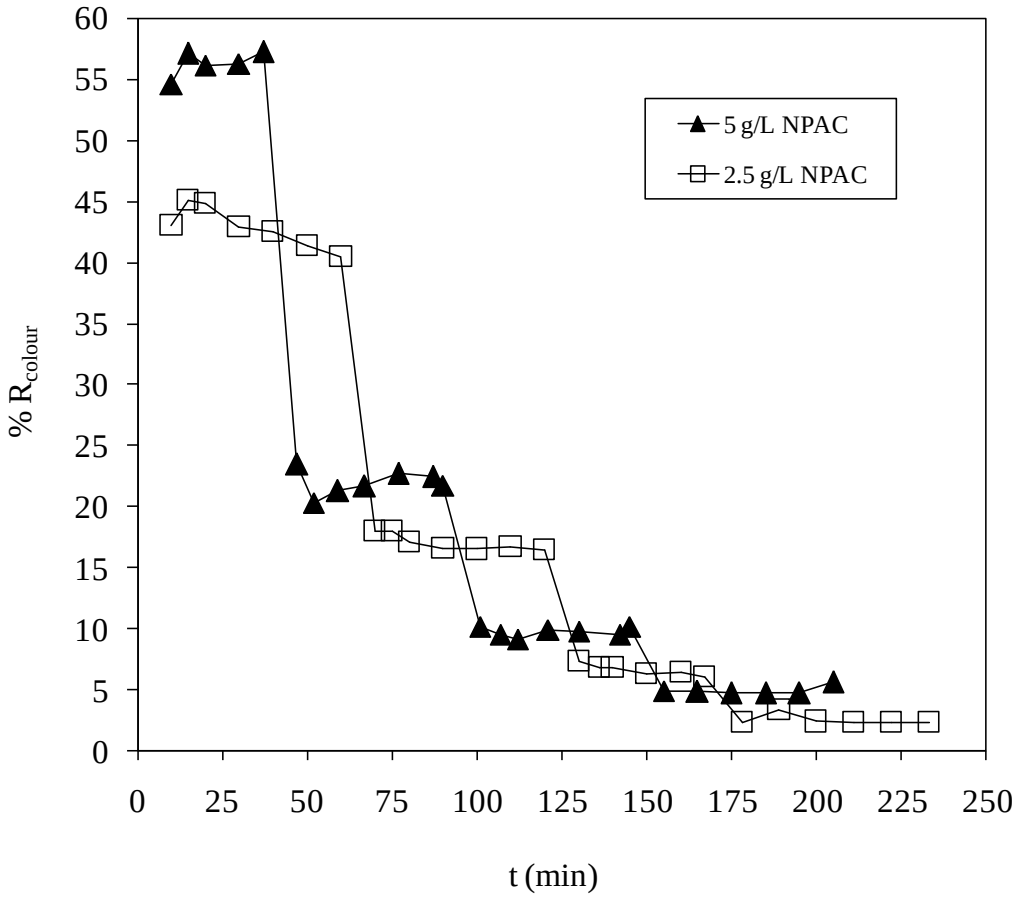
60
55
50
45
40
35
30
25
20
15
10
5
0
% R colour
0
25
50
75
100
125
150
175
200
225
250
t (min)
5 g/L NPAC
2.5 g/L NPAC

Figure 9

Table 1. Colour reduction of beet molasses at equilibrium using NPAC ($\%D_1$) and NPAC after thermal regeneration ($\%D_2$), and loss of NPAC decolouration capacity after thermal regeneration at several experimental conditions.

Thermal regeneration conditions for exhausted NPAC		Experimental conditions of the equilibrium experiments with NPAC and regenerated NPAC				
t (h)	T (ºC)	C_{NPAC} (g/L)	pH / T (ºC)	$\%D_1$ (Eq. 1)	$\%D_2$ (Eq. 1)	Loss of %D (Eq. 3)
0.5	450	5	3 / 25	98.0	87.2	11 ± 2
0.5	450	3	3 / 25	93.3	70.9	24 ± 1
0.5	550	3	3 / 25	93.3	49.4	47 ± 1
1	450	5	3 / 25	98.0	88.2	10 ± 1
1	450	3	3 / 25	93.3	71.6	23 ± 1
1	550	3	3 / 25	93.3	48.5	48 ± 2
3	450	3	3 / 25	93.3	56.9	39 ± 3
5	450	3	3 / 25	93.3	49.4	47 ± 1

Table 2. Experimental results for ultrafiltration experiments with different feeds (F) and operating conditions ($C_{NPAC,}$ TMP, Qf and pH), at 25 ± 1 °C**.** The contribution of the secondary resistance (%(R_s/R_t)) was calculated by Eq. 5. %Do and v are, respectively, the intercept and slope of the linear fitting of %D experimental data. These straight lines are shown in Figs. 5(b) and r is the linear regression coefficient.

Experiment	C_{NPAC} (g/L)	TMP (kPa)	Qf (L/h)	%(R_s/R_t) from 15 to 120 min	v (h^{-1})	%Do	r
1 (F=water)	0.0	100	4.24	-	-	-	-
2 (F=water at pH 3)	3.0	100	4.24	10.8	-	-	-
3 (F= molasses at pH 3)	0.0	100	4.24	69–83	-	-	-
4 (F= molasses at pH 3)	1.5	100	4.24	68–80	1.14	58.21	0.970
5 (F= molasses at pH 3)	2.5	100	4.24	62–75	0.96	81.41	0.995
6 (F= molasses at pH 3)	3.0	100	4.24	62–75	0.78	86.76	0.996
7 (F= molasses at pH 1)	3.0	100	4.24	66–77	4.20	59.15	0.971
8 (F= molasses at pH 7.1)	3.0	100	4.24	75–84	10.80	70.29	0.983
9 (F= molasses at pH 3)	3.0	50	4.24	29–56	1.44	80.95	0.971
10 (F= molasses at pH 3)	3.0	100	1.86	65–76	0.66	86.72	0.992
11 (F= molasses at pH 3)	5.0	100	4.24	61–73	0.60	95.70	0.982