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# Melanoidin removal from molasses effluents by adsorption

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ABSTRACT

Melanoidins, classified as nitrogenous brown biopolymers, are present in the wastewaters of fermentation industries, which use molasses as feedstock. In this study, removal of melanoidins from simulated and real (untreated and biologically treated) molasses effluents was investigated by adsorption onto powdered activated charcoal (PAC). The influence of solution pH, contact time and adsorbent concentration was evaluated in batch adsorption experiments. The Freundlich isotherm and the pseudo-second order model were used to fit equilibrium and kinetic data, respectively. The maximum experimental adsorption capacity was found to be approximately 10–12 g/g. Melanoidin loaded PAC can be regenerated by sodium oleate, providing reasonable melanoidin recovery for seven successive cycles of adsorption–desorption. Fixed bed dynamic studies showed that the breakthrough curves of melanoidin adsorption followed the characteristic "S" shape with good fit of the Thomas model.



## 1. Introduction

Melanoidins are the high molecular weight compounds, which are formed at the last stage of the Maillard reaction. The latter is a non-enzymatic reaction in thermally treated foods and takes place between the amino group of a free or protein-bound amino acid and reducing sugars. Melanoidins have commercial, nutritional and toxicological significance because they have considerable effect on the quality of food. They exhibit antioxidant, antiallergenic, antimicrobial and cytotoxic properties. Maillard reaction products (MRPs) may offer substantial health promoting effects acting as reducing agents, metal chelators and radical scavengers [1–3].

Besides the existence of melanoidins in food products, significant amounts are found in wastewaters from various agro-based industries especially from cane molasses based distilleries and fermentation industries. These industries generate huge amounts of wastewaters characterized by high concentrations of $BOD_5$, COD and a dark brown color due to the presence of melanoidins [1]. The biological treatment, a typical combination of anaerobic–aerobic processes, is able to reduce $BOD_5$ and COD from effluents to acceptable levels, however the brown color persists, because only 6–7% of melanoidins is biodegraded by these conventional processes [4]. Thus, the wastewaters released from such industries are a major source of soil and aquatic pollution.

Hence, removal of melanoidins and their recovery is very important both for ecological reasons and commercial use. Techniques that are applied for melanoidin removal, with varying degree of success, include: adsorption [5]; coagulation [6]; UV/$H_2O_2$ oxidation [7]; electrochemical methods [8]; ozonation [9]; membrane treatment [10]; and evaporation. Most of the studies have been done on model (simulated) melanoidins or diluted real effluents [11].

This work focuses on the recovery of melanoidin from (i) simulated, (ii) biologically untreated and (iii) biologically (anaerobic–aerobic) treated baker's yeast undiluted effluents. Adsorption onto activated carbon was evaluated as a pre or post-treatment process to conventional anaerobic–aerobic biological treatment. To the best of our knowledge this is the first study which deals with melanoidins recovery and encompasses all types of effluents. The main objectives of this study were (a) to identify the optimum pH value of adsorption on activated carbon, (b) to reduce the sorbent dosage as low as possible while maintaining sufficient color removal and (c) to investigate the regeneration of the melanoidin loaded activated carbon by elution, in order to reuse the adsorbent in successive cycles and achieve melanoidin recovery. Thereby, the specific novelty of the carried research refers toward the evaluation of commercial activated carbon as sorbent for melanoidins from simulated and real undiluted effluents along with melanoidin recovery and carbon regeneration.

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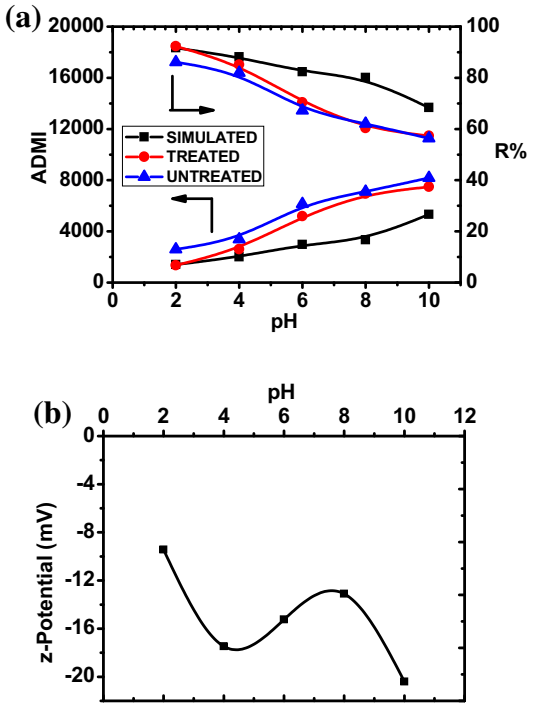


**Fig. 1.** (a) Effect of adsorption pH on residual color and color removal percentage for simulated, treated and untreated wastewaters: [PAC] = 4 g/L, $t$ = 24 h.; (b) $z$-potential of PAC vs pH.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Industrial molasses effluents

Real molasses effluents were taken from a local baker's yeast manufacturing factory in the region of Thessaloniki. The factory has a full-scale two-stage biological treatment facility. Raw molasses wastewater is initially mixed in a buffer tank before being fed to anaerobic system, comprising a hydrolysis–acidification phase and an internal circulation reactor. Anaerobically treated effluent is then fed to an aerobic activated sludge system. Samples under investigation were collected from the buffer tank (denoted as untreated) and from the exit of aerobically treated effluents (denoted as treated). All samples were kept in refrigerators at 5 °C before use [12].

#### 2.1.2. Synthesis of simulated molasses effluents

The simulated melanoidins wastewater (denoted as simulated) was prepared by mixing 4.5 g glucose (Sigma–Aldrich), 1.88 g glycine (Sigma–Aldrich) and 0.42 g sodium bicarbonate in 100 mL of deionized water. The mixture was placed in an oven for 7 h at 95 °C. During the heating various reactions were carried out leading to the formation of melanoidins that are responsible for the dark brown color of the solution. After removing the solution from the oven, and leaving it to come to ambient temperature, another 100 mL of deionized water were added [12].

#### 2.1.3. Sorbent material

The commercial activated carbon, powdered activated charcoal from Panreac Applichem (PAC, Applichem GmbH, Darmstdt, Germany), was evaluated as a sorbent material for the treatment of molasses effluents. The porosity characteristics of PAC were determined by $N_2$ adsorption–desorption experiments performed at −196 °C on an Automatic Volumetric Sorption Analyzer (Autosorb-1, Quantachrome) using static sorption procedure. Samples were outgassed at 150 °C and $1.0 \times 10^{-3}$ mbar for a minimum of 12 h prior to analysis. BET surface areas were calculated from the linear part of the BET plot. Pore size distribution was estimated from the adsorption branch of the isotherm by the BJH method. The specific surface area for the PAC area is 1092 $m^2/g$, the external surface area 343 $m^2/g$, the pore volume 0.791 $cm^3/g$, and the average pore diameter 1.05 nm. Measurement of the zeta potential of the sorbent was conducted using a zeta analyzer (ZetaPALS, Brookhaven Instruments Corporation, Holtsville, NY).

**Table 1a**
Parameters of the pseudo-second order kinetic model for adsorption of simulated, treated and untreated effluents onto activated carbon.

| Effluent | pH | $q_e$ (g/g) | $k_2$ (g/g min) | $R^2$ (−) | APE (%) |
|---|---|---|---|---|---|
| Simulated | 2 | 5.56 | 0.282 | 0.999 | 0.006 |
| | 4 | 4.44 | 0.215 | 0.999 | 0.001 |
| | 6 | 3.11 | 0.199 | 0.999 | 0.003 |
| Treated | 2 | 4.63 | 0.242 | 0.999 | 0.005 |
| | 4 | 4.23 | 0.100 | 0.997 | 0.001 |
| | 6 | 3.53 | 0.081 | 0.995 | 0.120 |
| Untreated | 2 | 4.23 | 0.190 | 0.998 | 0.002 |
| | 4 | 3.80 | 0.038 | 0.988 | 0.610 |
| | 6 | 3.34 | 0.022 | 0.979 | 2.110 |

### 2.2. Methodology

#### 2.2.1. Melanoidin analysis

The residual melanoidin concentration in the liquid phase followed the ADMI (American Dye Manufacturers' Institute) Color Index. This method measures the transmittance from 400 to 700 nm, in 31 wavelengths with a 10 nm step [13]. The experimental error was estimated through recovery experiments in spiked solutions, since no certified reference material was available. The relative error was 3.1%, assuming 100% purity of synthetic melanoidin.

After completing the adsorption process, at 20 ± 2 °C, the suspensions were centrifuged for 15 min at 3000 rpm and an aliquot of the supernatant was taken for the measurement of residual color. Blank experiments were performed to check the extent of adsorption by the falcon tubes. The adsorbed amount of melanoidin, $q$ (mg/g) was calculated using Eq. (1)

$$q = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

where, $C_0$: initial concentration of melanoidin in solution (g/L); $C_t$: concentration of melanoidin in solution at time $t$ (g/L); $V$: solution volume (L); and $m$: mass of carbon (mg). The percentage of removed melanoidin in solution was calculated using Eq. (2)

$$R\% = \frac{(C_0 - C_t) \times 100}{C_0} \quad (2)$$

#### 2.2.2. Batch adsorption studies-effect of pH

The effect of pH was studied over a pH range 2–10 out in 50 mL falcon tubes containing 25 mL wastewater and 0.1 g of PAC. The pH of the suspensions was monitored and kept constant using HCl and NaOH. The falcon tubes were placed on a rotary mixer for 24 h. The adsorbed amount of melanoidin, $q$ (mg/g) was calculated using Eq. (1).

#### 2.2.3. Batch adsorption studies-effect of contact time—kinetic model

The kinetic experiments were carried out in 50 mL falcon tubes containing 25 mL wastewater and 0.1 g of PAC at pH 2, 4, 6. The falcon tubes were placed on a rotary mixer for various time intervals within 7 h to reach equilibrium in accordance with results obtained from preliminary experiments. The adsorbed amount of