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Melanoidins removal from simulated and real wastewaters by coagulation and electro-flotation

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HIGHLIGHTS

- Effective pre-treatment of molasses effluents by coagulation or electro-flotation.
- Effective post-treatment of molasses effluents by coagulation or electro-flotation.
- Effective re-use of the produced ferric hydroxide sludge from coagulation.

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ABSTRACT

Melanoidins are brown recalcitrant bio-polymers present in the effluents of fermentation processes due to their antioxidant properties. In this study, removal of melanoidin from simulated and real wastewaters (biologically treated and untreated) was investigated by coagulation/flocculation. The studied operating variables, based on the maximum removal of color expressed in ADMI units, were coagulant concentration, pH, mixing time and sludge re-use. The results show that coagulation experiments could achieve color removal 90% and higher, at pH = 5, for all wastewaters but with different ferric ion dose. Real effluents could be discolored by 100 mM [Fe^{3+}], while simulated by 300 mM [Fe^{3+}]. After flocculation, the generated ferric hydroxide sludge was washed, solubilized and re-used effectively in a new run. Melanoidin removal was also studied by electro-flotation. Color removal was 95%, 90% and 45% for real treated, real untreated and simulated wastewaters by applying 0.5 A current intensity. Furthermore, coagulation can reduce significantly the COD content of real effluents.

1. Introduction

Molasses is one of the by-products of the sugar production process and is the final residue from the sugar crystallization unit. It is used as a carbon source for animal feed and bio-fertilizer. Molasses is also the most common feedstock for fermentation industries such as backer's yeast production [1,2]. These industries generate huge amounts of wastewaters (vinasses) characterized by high concentrations of BOD_5, COD and a dark brown color. A medium size fermentation plant, which uses about 50 metric tons molasses per day, is estimated to produce approximately 1.5 tons of COD daily [3].

The biological treatment, typically a combination of anaerobic and aerobic processes, is effective in removing BOD from molasses effluents. However, the brown color remains due to the presence of melanoidin pigments [3]. The formation of melanoidins, which are high molecular weight colored polymers, consists of a set of sequential and parallel chemical reactions that take place between the amino compounds and carbohydrates during the non-enzymatic Maillard reaction [4]. Their structure is not yet fully understood but is considered not to have a defined structure. The elemental composition and chemical structure depends heavily on the nature and the molecular concentration of reactants and reaction conditions (pH, temperature, heating time and solvent) [5].

The antioxidant properties of melanoidins render them toxic to many organisms, such as those that are typically found in waste treatment systems and eventually enter the environment [6]. Conventional anaerobic–aerobic treatment processes can accomplish the degradation of melanoidins only up to 6% or 7% [6–9]. Therefore, it is necessary to study additional pre or post-treatment methods to remove color from molasses effluents. This can prevent serious environmental problems such as reduction of both photosynthetic activity and dissolved oxygen concentration that colored wastewaters can raise in river courses [9].

Most of the studies about melanoidins have been done on diluted model melanoidins, since natural and synthetic melanoidins both have similar elemental (CHON) compositions, spectroscopic properties and electrophoretic mobilities at various pH values

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[6]. Techniques that have been used with varying degree of success include among others: adsorption [1,6,10,11]; coagulation [3,12–14]; UV/H_2O_2 oxidation [15]; electrochemical methods [16,17]; ozone oxidation [4]; biological/enzymatic degradation [5] and combined biological–physicochemical [18,19].

Physicochemical treatment methods are effective in both color and COD removal. The drawbacks associated with these methods are excess use of chemicals, sludge generation with subsequent disposal problems, high operational costs and sensitivity to variable water input. Considering the advantages and the disadvantages of different treatment technologies, no single technology can be used for complete treatment of molasses wastewater. Hence, there is a need to establish a comprehensive treatment approach involving several technologies sequentially. If a higher degree of purification is required, biological purification can be used in combination with other processes such as physico-chemical [20].

The objective of this study was the removal of melanoidins from simulated and real effluents by two methods, either by coagulation/flocculation or electro-coagulation/electro-flotation. Ferric chloride, a conventional coagulant, was selected in this work because iron-based salts have been reported more effective and without additional risk of development of Alzheimer'disease than alum salts [21]. Several studies have been conducted on the discoloration of molasses wastewater by flocculation [3,12,14] and only few by electro-coagulation/electro-flotation [22]. The novelty of the current work is the comparison of the studied methods as pre or post-treatment complementary to conventional anaerobic–aerobic biological treatment. Additionally, a solution to the problem of sludge generation in coagulation was attempted by sludge re-use.

2. Materials and methods

2.1. Industrial molasses wastewater

Molasses wastewater was taken from a local industrial yeast manufacturing factory. The factory has a full-scale two-staged biological treatment facility. Raw molasses wastewater is initially mixed in a buffer tank before being fed to anaerobic systems comprising of a hydrolysis–acidification phase and an internal circulation reactor. Anaerobically treated effluent is then introduced to an activated sludge system. Samples under investigation were collected from the buffer tank (real untreated wastewater) and from the exit of aerobically treated effluents (real treated wastewater). All samples were kept in refrigerators at 5 °C before use [3].

2.2. Synthesis of simulated molasses wastewater

The synthetic melanoidins wastewater 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 [6,10,11].

2.3. Coagulation–flocculation experiments

Coagulation–flocculation experiments were conducted in a jar-test device (AZTEC, U.K.) for simulated and real wastewaters to evaluate the effect of pH, the amount of flocculant and the mixing time. For all of the testing, 250 mL of synthetic or real wastewater was rapidly mixed (400 rpm) for 2 min with the appropriate amount of analytical grade $FeCl_3{\cdot}6H_2O$ or other coagulant with pH adjustment and then slowly mixed (40 rpm) [3]. The suspension was allowed to settle and an aliquot of the supernatant was taken and filtered for measuring the color content.

2.4. Electro-coagulation/electro-flotation experiments

The electro-flotation experiments were carried out in a cylindrical flotation reactor equipped with two parallel perforated electrodes (8 cm diameter) at the bottom. The used electrodes were from aluminum (ASTM 7075) with an inter electrode gap of 0.5 cm. The power supply unit was a TF 21 58 Dual DC apparatus, purchased from Marconi Instruments.

The experimental procedure of electro-flotation was conducted by pouring a given amount of synthetic or real wastewater (250 mL) in the cell and applying a certain electrical current. Aliquots were collected periodically and centrifuged to measure the residual color content [23].

2.5. Measurement of color content

Melanoidins are negatively charged, high colored humic organics [15]. As that, the characteristic color is usually recorded by spectrophotometer at 475 nm [4,6,11–15,18]. Our preliminary analytical study has shown that the maximum absorbance of simulated effluent was found at 423 nm wavelength. However, this wavelength was not stable and sometimes was fluctuating depending on the dilution. Additionally, in another study the appropriate wavelength was found at 664 nm [1]. For this reason, we followed the ADMI (American Dye Manufacturers' Institute) Color Index, which has been developed to monitor the color of wastewater effluents as an indicator of water quality. The method relies on the measurement of transmittance in 31 wavelengths, from 400 to 700 nm, with 10 nm step [23]. Color was determined by using the Lovibond PFX 1495 Tintometer and found ($ADMI_0$) approximately 15,000, 15,000 and 16,800 for simulated, untreated and treated wastewaters, respectively [24].

2.6. FT-IR

Fourier transform infrared (FT-IR) spectroscopy was performed from 4000 to 500 cm^{-1} with a Perkin–Elmer Spectrum 2000 spectrophotometer. Freeze-dried samples of melanoidines wastewaters were mixed with special grade KBr to prepare the pellet for FTIR. All measurements were carried out at room temperature.

2.7. z-Potential

The zeta potential of the supernatants of the treated wastewater samples, with different coagulant dosage at pH = 6, was measured by a ZetaPALS, Zeta Potential Analyzer, Brookhaven.

3. Results and discussion

3.1. FT-IR spectroscopy of melanoidins

The identification of a compound using infrared (IR) spectroscopy is based on the existence of characteristic group frequencies that have roughly the same values regardless of the compound in which the functional group appears [25]. Fig. 1 shows the overlay of the IR spectra of untreated, simulated and treated melanoidins which appear quite similar.

The FTIR spectrum of the three melanoidin samples is characterized by an intense absorption around 3400 cm^{-1} (wide band