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Color removal of melanoidin-rich industrial effluent by natural manganese oxides

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A B S T R A C T

Melanoidin-rich industrial effluents, e.g. from coffee extraction plants and molasses distilleries, can cause potential environmental problems due to the high content of remnant dissolved organic carbon and dark color. It mainly consists of melanoidins and other organic colorants, which are recalcitrant to biological treatment. The current study was aimed to develop a polishing step after anaerobic digestion for the colorant elimination from melanoidin-rich wastewater (molasses distillery wastewater, MDW) using natural manganese oxides. Anaerobically digested MDW was used to test the removal of organic contents and color at different pH values. It was observed that the kinetics of colorant elimination was best described by the second order equation, with a significant dependence on pH. Furthermore, the liquid chromatography with organic carbon detection was applied to analyze the changes in molecular composition during the reaction. There was a preferential removal of low weight melanoidin molecules over higher weight molecules.

1. Introduction

Melanoidins are complex polymeric compounds which result from a non-enzymatic reaction called Maillard reaction. They are formed when amino acids and sugars are heated in basic conditions [1]. Melanoidins are the main organic contaminants responsible for dark color in several industrial effluents and account for over 2% of vinasse composition [2]. In sugar processing, melanoidins are formed during purification and evaporation steps. The composition of amino acids in beets is different from that of cane [1]; hence melanoidin contents from the two sources are different. Characterization of melanoidins is complex because Maillard reactions may involve different amino acids reacting at different proportions. The polymerization may also extend to different levels, and it occurs in complex ways. There are reports that melanoidins posse anti-oxidant activities [3] and are possible sources of antimicrobial activities in vinasse and coffee extraction effluents [2]. Besides melanoidins, caramels and alkaline degradation products of hexoses are organic colorants responsible for pollution in vinasse and effluents from associated industries [2]. However, for coffee extraction effluents, only melanoidins have been reported as the colored organic pollutants.

A medium distillery with molasses as its carbon source can release approximately 10 million litres of molasses distillery wastewater (vinasse) [2]. Despite its high nutrients contents, vinasse is not good for agricultural application because of its high salts and dark color, which interfere with the soil properties [4]. For safe disposal in the environment, it is required that the color and other recalcitrant should be removed first. Another industrial use of molasses is in white biotechnology as a cheap carbon source to manufacture products like lactic acid, pharmaceutical intermediates and yeast [2]. These industries release effluents with similar properties like those of vinasse. Development of an effective method to treat vinasse would be useful to these industries as well.

Coffee is one of the most widely consumed non-alcoholic beverages throughout the world. The treatment of coffee extraction effluent is not only important to the primary producers but also to the other countries which import bulks of semi-processed coffee for further processing. Melanoidin has been reported as the main pollutant in the coffee industry effluents [5,6]. In addition to causing dark color and high remnant COD, melanoidin in coffee has been reported to cause microbial inhibition [7] and may be responsible for the low biodegradability of the effluent. The formation of melanoidin in coffee processing occurs during the roasting process, where the sugars and amino acids in coffee products are exposed to high temperatures. Health problems have been reported in the vicinity of untreated coffee effluent disposal, and this was possibly caused by the pollution [8].

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Various methods have been tried to remove melanoidin color and recalcitrant COD. Biological processes employing bacteria [9], fungi [10], and enzyme [11] have been tried before to treat melanoidin-rich wastewater. Though biological processes are generally less costly than chemical or physical treatment methods, none of the reported methods can effectively remove the contaminants in melanoidin-rich wastewaters. Other methods like coagulation [12] and adsorption [13] have also been experimented by various groups. Use of advanced chemical oxidation methods has also been tried [14,15]. The limitation with chemical treatment methods is the high costs involved. The non-selectivity on treating chemicals means that high quantity of reagents is used to eliminate the organic matter; this raises the operation costs. Use of cheap and readily available chemicals would be advantageous in this regard.

Manganese oxides have been used before to oxidize hydroxylamines into nitrones with good yields [16]. Nitrones are synthetic tools for complex organic molecules and have advantages of high selectivity and reactivity mainly by nucleophillic or cycloadditions reactions [16]. In addition manganese dioxide has been reported to cause oxidation of phenols [17], the removal of organic pollutants [18] and pharmaceutical residues from the effluent [19,20]. Oxidation of alcohol by MnO_2 to either aldehydes or ketones under solvent free conditions has also been reported [21]. It was also reported that MnO_2 could oxidize aniline into aminobenzene [22]. Melanoidins have many amine groups in their structure, which indicate the possibility of the oxidation and decoloration by manganese oxides. In this study, a natural manganese oxide (MnOx) was investigated for the first time to eliminate dark color and recalcitrant DOC caused by melanoidins in molasses distillery wastewater after anaerobic digestion.

2. Materials and methods

2.1. Materials

The raw vinasse from molasses was obtained from Nordzucker AG, Braunschweig Germany. It had been concentrated by evaporation to about 600 g/l COD. The natural manganese oxide (3–5 mm) was purchased from Aqua-techniek, Netherlands, with the following composition: MnO_2 78%, Fe_2O_3 6.2%, SiO_2 5.2%, Al_2O_3 3.1%.

2.2. Anaerobic digestion

The pre-concentrated vinasse was diluted back to COD 12 g/l with tap water. The trace nutrients were added, including: calcium, nickel, cobalt, molybdate, zinc, manganese and copper salts. The pH value was adjusted to 7 with sodium hydroxide. The substrate was transferred to a 3-litre tank with a Rushton stirrer as an anaerobic bioreactor. The inoculums pellet sludge was obtained from a brewery wastewater treatment plant and was added to 30% of the bioreactor volume. The temperature of the bioreactor was controlled at 35 °C by a water jacket. The reactor was operated in a sequence batch mode with a daily substrate feed of 1.2 l. The anaerobically treated effluent was decanted after settling and stored at 4 °C for further tests. The properties of the anaerobically digested vinasse are shown in Table 1.

2.3. Removal of color and DOC

Anaerobically digested vinasse was adjusted to pH 7 with H_2SO_4 and NaOH. MnOx pellets were weighed (50 g, 75 g, 100 g and 125 g) and put into 500 ml conical flask containing 100 ml of vinasse. The flasks were shaken at 120 RPM. A sample 1.5 ml was taken during the course of reaction: 10 min, 30 min, 1.5 h, 4 h, 6 h and 8 h. The samples were centrifuged for 30 min at 3000 RPM before measuring the color, and DOC. The experiment was allowed to run overnight and the final DOC and pH values were recorded. The solution was finally filtered with 0.45 μm acetate filter and the filtrate was used to calculate the final color, DOC and manganese ions. The tests were conducted in duplicate.

Table 1
Characteristic of anaerobically digested vinasse.

pH	4–7
DOC, mg/l	480–550
COD, mg/l	1500–1900
TOC, mg/l	550–660
BOD_5, mg/l	>60
Conductivity, ms/cm	4.65
Turbidity, NTU	109
DON, mg/l	430
Color @ 475 nm	1.092

2.4. Sequence batch experiment

Two 500 ml conical flasks were filled with 100 g MnOx and 100 ml anaerobically digested vinasse of DOC 500–600 mg/l at pH 6. All flasks were placed on a shaker at 120 RPM at room temperature. After 24 h, the shaker was temporarily stopped and 50 ml of liquid was replaced with fresh vinasse at pH 6. The decanted liquid was filtered with 0.45 μm membrane for measuring the color at 475 nm, manganese residues, and DOC. The procedure was repeated up to the fifth day.

2.5. Analysis

DOC was analyzed by Analytik Jena Multi N/C 3100. COD was measured with Hach Lange kit and BOD analysis was conducted according to German Standard Methods (DIN EN 9408) with the OxiTop gadget from WTW Company. The color was measured on Hach Lange DR 500 spectrophotometer.

The distribution of molecular sizes were analyzed on a liquid chromatography equipped with a size-exclusion chromatography column HW-55S (GROM Analytik + HPLC GmbH, Germany) and an online DOC detector and a UV detector at 254 nm (UV254). The results were analyzed with the Fiffikus program.

3. Results and discussion

3.1. Color and DOC removal

Melanoidin-rich wastewater is preferably treated with anaerobic digestion due to the high organic contents. However, it is not effective for the removal of colorants and thus discharges dark effluent with recalcitrant DOC. In this study, a simple and cost-effective method has been investigated. Fig. 1 shows the profiles of color contents (measured as UV absorbance unit at 475 nm) along the course of reaction at different pH values (pH 4, 5, 6, 7) and with different amounts of MnOx. The C_o and C_t represents the contents of color or DOC at the initial and time t, respectively. A sharp decrease of color can be found at the initial phase (within 2 h) and a much slower but steady decrease thereafter. The color and DOC removal were compared by plotting C_t/C_o charts for the four pH values (Fig. 2). In general, it can be found that MnOx removed more color than DOC. And it is clear that a lower pH and more MnOx can promote the removal of both DOC and color.