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

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Abstract
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 melanoids 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]. Melanoids 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, melanoids 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 posses anti-oxidant activities [3] and are possible sources of antimicrobial activities in vinasse and coffee extraction effluents [2]. Besides melanoidins, carbons 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 bulk 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 nucleophilic 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 MnO2 to either aldehydes or acetate fillets 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 C0 and Ct 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/C0 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.

### 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 C0 and C represent the contents of color or DOC at the initial and time t, respectively.

<table>
<thead>
<tr>
<th>pH</th>
<th>DOC, mg/l</th>
<th>COD, mg/l</th>
<th>TOC, mg/l</th>
<th>BOD5, mg/l</th>
<th>Conductivity, ms/cm</th>
<th>Turbidity, NTU</th>
<th>DON, mg/l</th>
<th>Color @ 475 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-7</td>
<td>480–550</td>
<td>1500–1900</td>
<td>550–660</td>
<td>&gt;60</td>
<td>4.65</td>
<td>109</td>
<td>430</td>
<td>1.092</td>
</tr>
</tbody>
</table>

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.

### 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: MnO2 78%, Fe2O3 6.2%, SiO2 5.2%, Al2O3 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.

### 2.3. Removal of color and DOC

Anaerobically treated vinasse was adjusted to pH 7 with H2SO4 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,
3.2. LC-OCD

LC-OCD was used to analyse the distribution of molecular size in the anaerobic digested vinasses and after the reaction of MnOx (50 mg of MnOx in 100 ml wastewater, 24 h). It is worth mentioning that two LC-OCD samples were diluted with different ratios to finally form a similar DOC value (\( C_{24} \)). One can easily find in the LC-OCD chromatogram (Fig. 3) that the Peak d (low-molecule-weight acidic and neutral organics) in the anaerobically digested vinasse were completely eliminated by MnOx. The Peak c represents the low-molecule-weight melanoidins and is partly removed by MnOx.

3.3. Kinetics of color removal

The reaction with melanoidin can be described through the following equation, based on the surface binding model of manganese oxides for the reaction with organics by Stone and Morgan [17]:

\[
\cdot \text{MnOH} + \text{Me} \xrightarrow{k_{1}} \cdot \text{MnOH} + \text{H}_2\text{O}
\]

where \( \cdot \text{MnOH} \) is the concentration of the free active sites on the surface of MnOx pellets; \( \text{Me} \) is the melanoidin concentration; \( \cdot \text{MnMel} \) is a complex of melanoidin bonded on MnOx. The complex can be dissociated with the release of \( \text{Mn}^{2+} \) and reaction products:

\[
\cdot \text{MnMel} \xrightarrow{k_{2}} \cdot \text{Mn}^{2+} + \text{products}
\]

The total active site in a reaction system is given by the sum of free sites and the sites bonded to the melanoidin:

\[
[\text{Total sites}] = [\cdot \text{MnOH}] + [\cdot \text{MnMel}]
\]  

The general equation for the melanoidin removal is given by the equation below:

\[
\frac{d[\text{Mel}]}{dt} = -k_1[\cdot \text{Mel}]^n + k_{-1}[\cdot \text{MnMel}]^n
\]  

Assuming that the complex dissociation is fast, at any time the sites coverage is low then \( \cdot \text{MnMel} \) is negligible compared to the total number of free sites \( \cdot \text{MnOH} \) [18]. With this assumption, the following equation is obtained:

\[
[\text{Total sites}] = [\cdot \text{MnOH}]
\]

Eq. (4) therefore becomes:

\[
\frac{d[\text{Mel}]}{dt} = -k_1S_t[\cdot \text{Mel}]^n
\]

Since total sites, \( S_t \) is constant, Eq. (5) becomes:

\[
\frac{d[\text{Mel}]}{dt} = -K[\cdot \text{Mel}]^n
\]

For a first order reaction:

\[
\frac{d[\text{Mel}]}{dt} = -K[\cdot \text{Mel}]
\]

A plot of ln [Mel] against time is a straight line with the slope as \( K \).

For a second order reaction:

\[
\frac{d[\text{Mel}]}{dt} = -K[\cdot \text{Mel}]^2
\]
A plot of 1/[Mel] versus time gives a straight line with the slope as $K$. The [Mel], in this case, was taken as the color content measured (absorbance unit at 475 nm, AU) at time $t$: $C_t$. The color removal data can be well described with the second order kinetics (Eq. (8)), as presented in Fig. 4. A very good coefficient of determination was obtained for pH 4, 5, and 6 ($R^2 > 99\%$) while the coefficient for pH 7 was slightly lower ($\sim 94\%$).

The 2nd order kinetics constants per gram of MnOx are largely dependent on pH: $8.4 \pm 0.9$, $5.4 \pm 1.0$, $4.0 \pm 1.1$, $1.3 \pm 0.2$ mAU/h for pH 4, 5, 6, 7, respectively. Previous studies have found the following relation of the kinetics constant and the pH value [18]:

$$K_0 = K_{PH} \cdot \frac{[H^+]}{C_{H+}},$$

or

$$\log K' = \log K_{PH} + m \cdot [H^+]$$

$K'$ is the pH-independent kinetics constant; $K_{PH}$ is the pH-dependent kinetics constant; $m$ is a constant. Fig. 5 plots the logarithm of the initial reaction constant and the 2nd order kinetics constant against the pH values. The initial reaction constants $k$ for each pH value was obtained by from the slopes of the plots of absolute concentration against time for a very short time (1 h) after reaction. The figure clearly shows that the logarithm of $k$ values decrease when pH increases. The value of $m$ (0.26) for the 2nd order reaction is in the range of reported values [18]. However, the data for the initial reaction (0.08) is much lower. Moreover, the coefficient of determination for the initial reactions is much better than for the overall 2nd order reaction. This is possibly due to the variation of pH during the reaction and the accumulation of Mn$^{2+}$ in the system. After 24 h, several mg/l of Mn$^{2+}$ can be detected in the water phase: 6.50, 5.25, 0.71, 1.53 mg/L for pH 4, 5, 6, 7, respectively. In general, more Mn$^{2+}$ can be found at lower pH. However, it is very interesting to observe that pH 6 released a slight amount of Mn$^{2+}$. Therefore, pH 6 was selected for the sequence batch study.

Fig. 2. Comparison of color and DOC removal at different pH values after 24 h reaction. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. LC-OCD chromatograms of anaerobic effluent and MnO2 treated effluent: (a) biopolymers, (b) high molecular weight melanoidins/humics, (c) low molecular weight melanoidins/ acids, (d) low molecular weight neutrals.
3.4. Sequential batch tests

A very good removal of color, DOC, and TOC was found in the second day of the sequential batch operation. However, the removal was gradually decreased in the subsequent days, as shown in Fig. 6. This was probably due to decrease in hydrogen ions consumed in the reaction, as well as the deposition of organic matter on the solids by adsorption or/and precipitation, which blocks the access to free active sites in the manganese oxides. The dissolved Mn and pH values in the treated effluent were found to increase with time (Fig. 7).

It can also be noticed that the removal efficiencies of color, DOC, and TOC in all time were present in such a rank: color removal > DOC removal > TOC removal, which indicates that the color removal should involve a chemical reaction. The high color removal is most likely contributed by oxidation of the colored compounds to non-colored compounds but which still contribute to the DOC. The higher DOC removal compared to the TOC removal suggests that some DOC may have precipitated out of the solution probably due to the, polymerization or coagulation to less soluble compounds. There is also the possibility that some DOC was temporarily adsorbed on the surface of the manganese dioxide pellets.

It has been reported that manganese dioxide can oxidize aromatic amines to quinones and dimer products [22].

Fig. 4. Simulation of the color removal with 2nd order kinetics. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. The dependence of initial reaction and 2nd order reaction constants on pH.

Fig. 6. Removal of color, DOC, and TOC in the sequence batch test. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
oxide the long chain amines to nitrone, which may further dimerize to bigger compounds [23]. Melanoidins have several amines and aromatic groups, because they are formed from a reaction between amino acids and sugars [1]. Therefore, it is plausible that melanoidins in the studied wastewater were dimerized and precipitated out of the solution by MnOx; this may partly explain the less removal of TOC than DOC in the sequential batch test. However, a high DOC removal was observed in both batch and sequential batch tests. It is hardly attributed to the mineralization of organics since no obvious bubbles were found during all tests. It is also possible that most of the removed DOC was mainly due to the adsorption onto MnOx. Still, adsorption is essential for the surface reaction. Nevertheless, the chemical transformation of adsorbed DOC or colorants on MnOx seems to be suppressed in the sequential batch test. This led to a declined removal of color and organics in addition to the negative effects of accumulated Mn ions.

When it comes to application, a high manganese dosage (50–125) g/100 mL vinasse is recommended because it was more effective in color remediation. It is also important to consider some methods to restore the activity of MnOx after using. For example, if the active sites are covered by the precipitated polymers, it is feasible to remove the precipitates via backwashing or to avoid their formation via controlling an appropriate hydrodynamic condition in a reactor. One should also keep it in mind that the accumulated Mn\(^{2+}\) should be removed or oxidized in order to eliminate its negative influence.

4. Conclusions and outlook

The following conclusions can be deduced from the above results:

- TOC, DOC and color in the anaerobically digested vinasse were found to be effectively reduced by MnOx. The color removal was much higher than removal of TOC and DOC.
- The kinetics of colorants removal was found to follow the second-order kinetics. The kinetics constant was significantly dependent on the pH.
- The low-molecular-weight part of melanoidins was preferably removed over the high-molecular-weight one.

In addition, it is also highly feasible that the following mechanisms are involved: chemical transformation, polymerization and precipitation, adsorption. However, further studies are in need to confirm them.

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References


Fig. 7. Variation of pH and concentration of dissolved Mn ions in the sequence batch test.