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Biodegradability of DOC and DON for UV/H_2O_2 pre-treated melanoidin based wastewater

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ABSTRACT

The aim of this study was to determine if preliminary treatment of melanoidin based wastewater by an advanced oxidation process (AOP) made the associated DOC and DON more biodegradable. UV-C irradiation of H_2O_2 was used to create the hydroxyl radical for chemical oxidation, while aerobic batch bioassays were used to assess the subsequent biodegradability of the DOC and DON associated with melanoidin. State-of-the-art natural organic matter identification techniques were used to identify melanoidin and study the subsequent degradation products throughout the chemical and biological oxidation processes.

Melanoidins are large (50–70 kDa), coloured, nitrogenous organic compounds that are refractory to sewage treatment plant (STP) biodegradation, but are susceptible to degradation by sunlight in receiving environments. This study showed that over an extended chemical oxidation period (72 h, which was sufficient to reach maximum chemical degradability) DOC and DON removal from a synthetic melanoidin wastewater were 92% and 48%, respectively. In comparison, the DOC and DON removal after 4 h of chemical oxidation followed by 7 days of aerobic biodegradation were 82% and 86%, respectively. Thus, the removal of organic bound nitrogen was drastically improved by using a combination of chemical and biological oxidation in place of the hydroxyl radical AOP alone.

Molecular weight fractionation results showed that the cleavage of the large nitrogenous melanoidin molecules, during chemical oxidation, produced small DON molecular weight compounds (<1 kDa) and ammonia, which were readily biodegradable. It was apparent that the small molecular weight DOC formed during the hydroxyl radical oxidation of melanoidin was biodegradable, but unlike the DON could also be chemically oxidised given sufficient exposure time to the hydroxyl radical.

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1. Introduction

The aim of this study was to use state-of-the-art analytical techniques to examine the organic products formed by UV/H_2O_2 oxidation of melanoidin and to determine the subsequent aerobic biodegradability of these products. Particular focus was placed on the removal of the organic nitrogen associated with the melanoidin.

Dissolved organic nitrogen (DON) is present in the effluent of all sewage treatment plants (STPs) much of which is humic and colloidal organic matter. Although refractory during the short biological retention times of STPs, evidence of nitrogen release from organics in the form of ammonia [1] in receiving environments due to sunlight degradation of these compounds is widely accepted [2]. This has forced effluent total nitrogen limits of STPs to become more stringent, and the presence of non-biodegradable DON in STP effluent is now a significant problem.

There are many sources of DON in wastewater [3]. This study focuses on DON associated with melanoidin. Melanoidins are most commonly present in the effluent of STPs if molasses by-product streams are fed to the STPs, as melanoidin is non-biodegradable. Melanoidin is the product of the Maillard reaction, a complex reaction which occurs during the heating of a sugars and amines. The resulting carbon chain is a cyclic based structure with nitrogen bound in amine rather than nitro forms [4].

Melanoidins are negatively charged, highly coloured humic organics [5]. Their colour, nitrogen and carbon content is related to the degree of polymerisation, aromaticity and saturation that occurs as a result of reaction conditions [6,7]. The charged nature of humic compounds such as melanoidin make treatment by adsorption [8] and coagulation [5] possible, but these treatment methods are non-destructive, transferring melanoidin from one phase to another.

The treatment of colour associated with melanoidin using the AOP is well documented [9–12]. The organic composition, in terms of the molecular weight, of the melanoidin molecules change after oxidation of the compounds [9,11,13], with small molecular weight

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carbon and nitrogen organics and ammonia produced as a result of the AOP [12].

AOP degradation of small amino compounds produces different nitrogenous by-products depending on the type of AOP used and the structure and charge of the organic in question. In the case of glycine, ozone preferentially directs the attack on the nitrogen functional group prior to the cleavage of the nitrogen of the alpha-carbon leading to the oxidation of the nitrogen to nitrate, while the hydroxyl radical directly attacks the nitrogen of the alpha-carbon yielding ammonia [14–16]. When using the hydroxyl radical to oxidise glycine, ammonia was the main by-product, but in the presence of oxygen, intermediates (oxamic acid) were formed which had the potential to be mineralised to nitrate by attacking the nitrogen functional group [16]. A competition between the nitrogen of the alpha-carbon and the carbon chain itself exists for amino compounds [16], with the attack of carbon bonds the cause of the formation of smaller molecular weight compounds. Due to the complexity of the nitrogen bound in large humic compounds, no studies have examined nitrogen by-products formed during AOP degradation.

AOP treatment of melanoidin produces smaller molecular weight organic compounds [12]. In general, AOP enhance the biodegradability of wastewater containing many different types of refractory organic compounds [17–19], with the partially degraded refractory organics more biodegradable post AOP treatment. However, this has not been shown for melanoidin.

A variety of novel characterisation techniques for the identification of DON associated with organic compounds are commonly used for water treatment [20–22]. Molecular weight characterisation by fractionation with surrogate measurements of DON, colour, DOC, UVA and fluorescence EEM can be used to identify the impacts of oxidation and biological degradation process on the melanoidin organics.

This study assesses the change to melanoidin by the UV/H_2O_2 AOP and its impact on the subsequent biodegradability of the produced DON and DOC. This is the first study to examine the nitrogenous end-products formed when using the hydroxyl radical to oxidise a large molecular weight nitrogenous organic such as melanoidin.

2. Material and methods

2.1. Synthetic melanoidin solution

A concentrated synthetic melanoidin solution was made from equal amounts of glucose and glycine with 0.5N of $NaCO_3$ added as a buffer. The solution was heated for 3 h at 121 °C [8]. A carbon to nitrogen ration of 7:1 was obtained. The initial concentration of melanoidin used for each of the AOP experiments was controlled by dilution with ultra pure water to obtain a colour concentration of 2000 mg-PtCo L^{-1}. The initial concentrations of DON and DOC were 22.9 and 135 mg L^{-1}. The solution was stored below 4 °C in its concentrated form.

2.2. Hydroxyl radical formation

Test water was recirculated through a 60 W mercury vapour lamp (UV-C, 253.7) annular photo-reactor with an observed flux of $I_0 = 2.4 \times 10^{-6}$ E s^{-1} L^{-1} [12]. Hydrogen peroxide was added as a 30% (w/w) solution to obtain a concentration of 3300 mg L^{-1} as this was the observed optimum H_2O_2 dose for this system at the described initial melanoidin concentration [12]. Temperature was controlled at 25 °C and the pH was controlled to 7 ± 0.25, by manual addition of 0.1 M NaOH and 0.1 M H_2SO_4.

2.3. Biological treatment

Batch bioassays were performed on 750 mL of solution for 168 h in conical flasks in the absence of light. The mixed solutions each contained 675 mL of test water, 10 mL of nutrient solution, and appropriate volume of concentrated activated sludge to obtain a MLSS of 1 g L^{-1} [23] and were made up to 750 mL with distilled water. Test water included non-AOP affected melanoidin solution, 0.5, 1, 2 and 4 h AOP oxidise melanoidin solution and a blank (distilled water filtered). Duplicate analyses of the test waters were performed.

The pH of the solution was adjusted to 7 and the temperature maintained at 22.5 ± 0.5 °C. The nutrient concentrate contained KH_2PO_4, K_2HPO_4, $Na_2HPO_4 \cdot 2H_2O$, NH_4Cl, $MgSO_4 \cdot 7H_2O$, $CaCl_2 \cdot 2H_2O$ and $FeCl_3 \cdot 6H_2O$ was added in accordance with international standards [23]. The mixed samples were shaken at 180 rpm to provide sufficient mixing and aeration [24]. Activated sludge was taken from Wetalla STP (Toowoomba, Australia), as Wetalla effluent contains melanoidin [12]. The sludge was rinsed with tap water and centrifuged multiple times in accordance with international standards [23]. Samples of 20 mL were drawn periodically (0, 3, 12, 24, 36, 48, 72, 120 and 168 h). Samples were centrifuged (4000 rpm for 5 min) and filtered with 0.45 μm Millipore filters to remove the biomass.

2.4. Analytical

Samples were removed using a pipette. Bovine catalyst (diluted C100, Sigma–Aldrich) was added to samples containing H_2O_2 to catalytically remove residual H_2O_2. The samples were filtered using 33 mm, 0.45 μm Millipore express filters prior to storage (4 °C) and analysis.

Total Kjeldahl Nitrogen (TKN) was measured using Lachat QuikChem Method 10-107-06-2-D. Ammonia was measured on a Lachat flow injection analyser as per the Lachat QuickChem Method 31-107-06-1-A. DON was calculated as the difference between dissolved-TKN and ammonia. DOC was calculated as the difference between dissolved total organic carbon and dissolved inorganic carbon, measured in accordance with standard methods [25] using a Dohrmann DC-190. Characteristic colour intensity was recorded in platinum–cobalt (PtCo) units. A ThermoSpectronic (Helios Beta) spectrophotometer at a wavelength of 475 nm was used to determine the absorbance in a 1 cm path length acryl cell and converted to colour units (PtCo). UVA was a measure of absorbance at 254 nm, measured in a 1 cm path length quartz cell.

2.5. Molecular weight fractionation

The dissolved organic compounds were fractionated using molecular sieves. Fractionation of samples was performed using a 200 mL stirred cell (Amicon 8200; Millipore Corp, MA). Three membranes made of regenerated cellulose with different molecular weight cut-offs were used: (1) PL 10,000 NMWL, (2) 5000 NWML and (3) 1000 NMWL. The initial volume was 200 mL. The samples were filtered through the membranes in series from (1) to (3); each time a measured volume of 50 mL was retained for analysis, while the volume that permeated the membrane was passed through the next membrane. DOC and DON were removed from the membranes by pre-rinsing in accordance with the manufacturer's instructions. Volumetric losses were negligible due to the use of wet membranes and insignificant hold-up volumes. The concentration of colour, DON, DOC, UVA and fluorescence intensity in each size range was calculated as follows, where χ[1–5 kDa] represents the concentration of the specific property

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