



Thermochemolysis of winery wastewater particulates—Molecular structural implications for water reuse

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ABSTRACT

Environmental concerns have increased the interest in winery wastewater remediation and reuse. These practices require more detailed understanding of wastewater composition to ensure optimum usage, and to minimize the risk of long term soil degradation and grape contamination. Particulate organic matter is an important contributor to the carbon burden in winery wastewaters. This article investigates the molecular structure of particulates from the most common winery wastewater treatment processes via infrared spectroscopic and thermochemolysis-gas chromatography/mass spectrometry techniques. Study of the organic composition of both influent and effluent particles enabled further insight into which compounds could prove problematic during treatment and on discharge. The yield and molecular structure of desorbed or “guest” compounds were found to strongly correlate with those produced during pyrolytic cracking. These “guest” compounds and macromolecular fragments form a continuum whose separation is based on molecular size. Polyphenolic and lignin derived compounds tended to survive the water treatment processes within assemblages of microbial detritus. No evidence was found for particles adsorbing and concentrating other unrelated organics such as anthropogenic chemicals from winery wastewaters. Any release of particulates will require careful management to prevent localized accumulation of recalcitrant compounds to toxic levels.

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1. Introduction

Australian wineries face challenges in common with wineries all over the world, regarding wastewater treatment and disposal [1]. The universal aim of reducing cost and maximizing profit in wine production is compatible with the introduction of sustainable wastewater remediation processes [2]. One option for disposal is land discharge but the long term risk associated with this practice is not well understood [3]. Winery wastewaters (WWWs) present particular challenges for traditional wastewater treatments because of extreme seasonal variations in their volume and quality, high oxygen demands and the presence of recalcitrant polyphenols [4,5]. The sustainable reuse of treated WWWs for internal winery operations such as cleaning, externally for irrigation, or to supplement environmental flows requires detailed

knowledge of their chemical composition. The sparse literature on characterization of WWWs at the molecular level has focused on soluble species [6].

Suspended particulates represent a significant portion of the organic material in influents to WWW treatment plants. They arise primarily from natural sources (commonly grape marc and yeasts) and additives such as clays and filter aids [5]. The organic contribution to influent particulate material includes intact microbial cells and their debris, bio-polymeric compounds such as lignin and semivolatile natural or anthropogenic “guest” chemicals potentially including pesticides. Particulates provide significant surface area for physical and chemical interactions with solutes [7,8]. Given sufficient hydraulic retention time, particulates will equilibrate with dissolved compounds, acting as both sources and sinks for solutes [7].

A range of WWW treatment systems from simple lagoons to advanced bioreactors are in common use both in Australia and internationally [9]. Post treatment particulates are generally considered to comprise a blend of relatively unaltered inert particles, partly degraded and reformed material through to those particles completely synthesized in the treatment process [6]. Furthermore,

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insoluble particulates typically dominate the organics burden in WWWW treatment system effluents [9–11]. Differences in the structural composition of effluent versus influent particulates are still poorly understood. Research into the effects of microbial aerobic wastewater treatment technologies on the molecular chemistry of particulate material is sparse. The view that insoluble materials act as a molecular sponge trapping and concentrating soluble compounds [8,12–14] requires testing in the WWWW context; not least because particulates may act as the main source for environmentally deleterious compounds. A better understanding of the organic structure of particulates will assist in determining their possible desorption and decomposition products and potential for harm in application to soil or discharge to streams.

The bulk of WWWW analyses at the molecular level exclude suspended solids [5,15]. However, a number of techniques are available for characterizing solid material at the molecular level [16–18]. Fourier Transform Infrared spectroscopy (FT-IR) provides a broad functional group characterization when applied to WWWW particulates, with the advantage of probing their mineral, non volatile or thermally labile components which are not amenable to gas chromatography. FT-IR is well established for the characterization of intractable organic solids such as coals and kerogens [19].

A complimentary technique to the broad characterization afforded by FT-IR spectroscopy is the specific molecular structural information provided by thermochemolysis-gas chromatography/mass spectrometry (T-GC/MS) [17,18,20–23]. The sequential application of this technique enables the examination of “guest” compounds which volatilize or desorb at 340 °C, the remaining non volatile macromolecules are later subjected to pyrolytic (720 °C) cleavage, forming a char along with fragments representative of their molecular structure.

To address the poor understanding of the composition and fate of WWWW particulates, we have characterized the insoluble material present in both WWWW influents and effluents from five different treatment technologies. The impact of these different treatments on their chemical structure is examined with an emphasis on major contributors, particularly toxic or anthropogenic components. The desorbable species may be considered the most available and labile components in terms of toxicity whilst the environmental impact of the macromolecular material could be slow and prolonged. The results will be used to assign an origin to the organic component within these particulates and predict their likely fate and impact on the further remediation or reuse opportunities for WWWWs.

2. Materials and methods

The wastewater treatment technologies are described in Table 1. WWWW samples (1–5L) were collected in pre-rinsed polypropylene containers/amber glass bottles either via sampling ports at the Sequencing Batch Reactor (SBR) or directly from the ponds. The grab samples represent a snapshot in time at the individual plants. Given the open, passive nature of these biological treatment systems (excluding SBR) it was not possible to track a particular influent plume through each treatment process. The focus of the sampling was to provide a range of particulates from the most common WWWW treatments. Electrical conductivity (EC) and pH were performed in situ and the samples frozen until processed for FT-IR and T-GC/MS.

2.1. Solids

The particulates or Total Suspended Solids (TSS) were isolated via centrifugation at 6000 × g for 30 min and supernatant analyzed for DOC (dissolved organic carbon) using a Shimadzu TOC-V. The

crude pellet comprising the particulates was washed via ultrasonication with dilute (pH 2) HCl, and 18 MΩ lab grade water (re-centrifuged between contacts) and dried to constant weight at 50 °C.

2.2. FT-IR

Infrared spectra were obtained in absorbance mode (0.5% in KBr) using a Scimitar 1000 FT-IR (Varian Inc.). Insufficient effluent sample was available from the Passive Treatment system for FT-IR analysis. The discs were desiccated under vacuum with P₂O₅ for 3 days prior to analysis.

2.3. Thermochemolysis

Approximately 3 mg of the dried solids (weighed to 0.01 mg) was loaded into a quartz tube and spiked with the internal standard n-decylbenzene (10 ng) and 3 μL of 25% (wt/wt) tetramethylammonium hydroxide (TMAH) dissolved in methanol before insertion into the platinum coil of a Chemical Data Systems (CDS) 1000 coil pyroprobe unit. This unit was connected with a CDS 1500 interface directly to the GC/MS. Particulates were subjected to sequential thermal treatments (1 °C/ms ramp with 40 s dwell time) under helium. The first treatment involved desorption by heating to 340 °C to evolve volatile or guest compounds. Then additional internal standard and TMAH were added to the product residue from this 340 °C treatment prior to its sequential flash pyrolysis to 720 °C to produce fragments from the pyrolytic cleavage of residual macromolecules.

2.3.1. GC/MS

The GC/MS (CP8400 GC and Saturn 2200 ITMS; Varian Inc.) was fitted with a capillary column (VF-5 ms 30 m × 0.25 mm ID and 0.25 μm film thickness). Helium carrier gas programmed to a constant flow (1 mL/min) was used with the oven programmed between 0 °C and 325 °C. GC/MS experimental detail is presented in the [Supplementary Material \(SM\)](#).

2.3.2. Thermogravimetric analysis

The pyroprobe system in combination with a microbalance was also used to provide thermogravimetric data at 340 °C, 720 °C (both under helium) and 1200 °C in air (to determine ash yield).

3. Results and discussion

Whilst it is not possible to directly compare between the influent and effluent samples, one can however, compare the influents and effluents as groups, and to consider the general differences resulting from the treatment processes ([Table A-1, supplementary data](#)).

3.1. Physicochemical properties

Typically, the effluent waters exhibited more moderate pH values (pH 5.6–8.3), when compared with the influent (pH 3.5–12.4). This suggests that all treatment processes are generally effective at neutralizing the WWWW to a certain extent, which is likely due to increased blending of alkaline and acid WWWWs, and the treatment process itself. This pH moderation is especially important from a reuse perspective, to minimize damage to receiving environment, and ensure compliance with environmental guidelines [24,25]

Effluent waters also had much lower DOC concentrations (49–870 mg/L) compared with the influent samples (180–5200 mg/L). Given that the primary aim of WWWW treatment processes is to reduce the organic loading of the samples, typically via microbiological utilization of the organic molecules, this reduction suggests that the treatment processes are behaving

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