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Characterisation of foulants in membrane filtration of biorefinery effluents

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ABSTRACT

Effluents from biorefineries are highly coloured and carry a large organic load. Traditional treatment options, such as anaerobic and aerobic digestions are capable of reducing the biological oxygen demand, but cannot remove the residual chemical oxygen demand (COD) nor decolourise the effluent. Membrane filtration has been increasingly used for water recovery from industrial effluents, such as from these biorefineries. Different grades of membranes can be used to remove particular contaminants, such as suspended solids, organic macromolecules and salts from these effluents. Effluents were filtered by ultrafiltration (UF) and nanofiltration (NF) membranes and samples were analysed for traditional parameters, such as COD, dissolved organic carbon (DOC) and colour. While UF was capable of only partial removal of colour, COD and DOC, NF was shown to be capable of removing close to 100% of the organic content of the molasses and lignocellulosic effluents. Use of advanced analytical techniques, such as fluorescence excitation emission matrix analysis and liquid chromatography, helped to illustrate the difference between organic compounds found within molasses and lignocellulosic effluents. This was also useful in explaining the difference in membrane separation performance between the two effluents.

Keywords: Membrane filtration; Biorefinery wastewater; Membrane fouling; Foulant characterisation; Industrial wastewater treatment

1. Introduction

The use of molasses in the fermentation industry is associated with the generation of large volumes of effluent containing high concentrations of coloured compounds, such as melanoidins. This is a widely known industrial problem and hence a lot of research has been conducted on decolourisation and chemical oxygen demand (COD) removal from molasses wastewater [1–3]. This includes the use of biological treatment, oxidation, evaporation and coagulation amongst others. There has also been extensive research into the use of membranes in treating molasses effluents [4–6]. While there has been extensive progress in researching the treatment options for such effluent streams, analysis of these effluents rarely con-

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sists of more than general water quality parameters, such as COD/biological oxygen demand, colour, total dissolved solids, total suspended solids, nitrogen, phosphorous and potassium content and pH. A greater depth of knowledge into the compounds present in the effluent that contribute to these general parameters may improve the design of such systems as well as give clues to the better design of systems for superficially similar processes such as cellulosic ethanol. The growth of the biofuel industry has resulted in the competition for feedstocks, typically, sugar cane, sugar beet or corn, between the biofuel industry, livestock raising and food and beverage industries. This, along with the realisation that such easily fermentable sugars are limited in supply compared to cellulose has driven research into alternative feedstocks, particularly corn stover and sugar cane residues (bagasse and trash). As with molasses fermentation processes, lignocellulosic ethanol production results in large quantities of high strength effluent.

Cellulosic ethanol waste treatment has received limited research attention to date, with only a handful of papers and technical reports being published on the issue [7–15]. Producing ethanol at a high concentration and yield, and a low price remains an unsolved challenge; hence most research is focused in this direction. However, a comparison of design reports from National Renewable Energy Laboratory from 2002 to 2011, reveals that the estimated capital cost of the waste water treatment section of the plant to be $3.3 million and the annual operating cost to be $840,000 pa [7] whilst by 2011 these estimates had increased first to $49.4 million and $2.83 million pa., respectively [8], and then to a capital cost estimated between $67 million and $147 million and an operating cost of $12.6 million [16]. The waste treatment plant now accounts for a significant proportion of the plants' capital cost and as such is a serious impediment to the cost effective production of ethanol from cellulose. With a greater understanding of the separation performance of membranes in regard to lignocellulosic effluents, the estimates of operating and capital costs may become more accurate and more efficient and cost effective designs may be found.

The problems of cellulosic ethanol are superficially at least similar to those of molasses, high COD, Humbird et al. [8] estimate 80,000 ppm, high salinity due to the sulphuric acid used for hydrolysis and its neutralisation and high colour. However, due to the different nature of the compounds present in lignocellulosic effluent compared to molasses effluent, it is possible that the separation performance of membranes might be different as well.

This paper endeavours to analyse the membrane performance for colour and COD removal from molasses and lignocellulosic effluents, and then use more advanced techniques, such as fluorescence excitation emission matrix (EEM) analysis and liquid chromatography, to explain the separations achieved and the differences between the effluents.

2. Experimental methodology

2.1. Effluents

The effluents obtained for this study include effluents from cane and beet molasses fermentation plants and lignocellulosic ethanol effluent produced using sugar cane mulch feedstock (Table 1).

Although coming from very similar processes, there is a significant difference in the levels of compounds found in the cane and beet molasses effluents. The cane molasses effluent contains more organic suspended solids, contributing to a higher COD and colour measurement than the beet molasses effluent. Beet molasses shows a greater amount of inorganic solids, resulting in a high conductivity and osmolality than cane molasses.

The lignocellulosic effluent in some respects shows similar properties to the cane molasses effluent—similar levels of COD, osmolality and dissolved organic carbon (DOC). It does, however, contains a much lower colour reading and is more acidic than either molasses effluent, though this is due to the stream being tested being a dilute research lab effluent, not a more concentrated pilot scale effluent where a COD as high as 80,000 ppm may be expected, hence some values may be 5–6 times diluted.

2.2. Membrane pilot plant

The membrane filtration runs were performed using a small-scale Alfa Laval LabUnit M20 pilot plant run in batch mode, using 2.5´´ spiral wound membranes. The effluents were treated by a 2,000 molecular weight cut-off (MWCO) ultrafiltration (UF) membrane, and the filtrate was collected. The UF filtrate was then used as the feed for a second batch run using a nanofiltration (NF) membrane. This NF permeate was collected and samples of the feed, UF filtrate and NF permeate were taken for analysis (Fig. 1).

2.3. Water quality testing

COD was measured using Merck dichromate COD test kits. Osmolality was measured using an

Table 1
Typical characteristics of biorefinery effluents

	Cane molasses	Beet molasses	Lignocellulosic
COD (mg/L)	3,050	1,150	15,530
Conductivity (mS/cm)	8.9	14.9	6.7
Colour (PCU)	17,700	7,500	2,712
DOC (ppm)	855	316	995
pH	8.2	8.5	4.0
Osmolality (mOsm/kg)	161	275	199

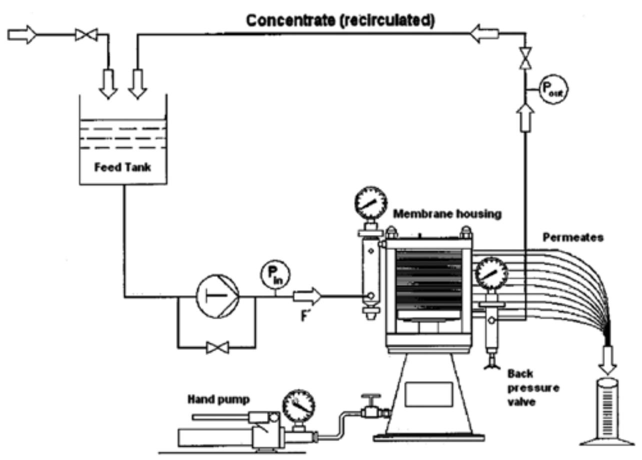

Fig. 1. Alfa Laval LabUnit M20 pilot plant.

Advanced Instruments model 3,320 micro-osmometer, using freezingpoint depression. DOC was measured using a Sievers 5310C TOC analyser. Colour was measured using an Aquanal-plus Spectro-Hazen spectrophotometer. The EEM spectra were obtained using a Perkin-Elmer LS55 fluorescence spectrometer. EEM analysis was performed

3. Results

Treatment of cane molasses effluent by a 2,000 MWCO UF membrane produced significant reduction in colour and organic content (DOC), but only slight reductions in inorganic components, as evidenced by conductivity and osmolality. Treatment by NF showed almost complete removal of organic content, by >99% reduction in colour and DOC. There has also been a significant reduction in conductivity and osmolality. The residual conductivity and osmolality do suggest a strong presence of monovalent ions, such as Na^+, K^+ and Cl^- (Table 2).

The results for beet molasses effluent showed strong similarities in reduction of DOC and colour, and therefore organic content, by UF. However, the reductions in conductivity and osmolality were significantly higher. The results for NF treatment again showed almost complete (>99%) removal of organic content in both colour and DOC. NF also showed significant reductions in conductivity and osmolality, but the permeate does retain significant residual levels of both suggesting a strong presence of monovalent ions.

The lignocellulosic effluent results show significant differences from the molasses effluents. UF showed much lower reductions in organic content, COD, DOC

Table 2
Membrane separation performance

	Conductivity (mS/cm)	COD (mg/L)	DOC (ppm)	Colour (PCU)	Osmolality (mOsm/kg)	% Reduction COD	% Reduction DOC	% Reduction Colour	% Reduction Osmolality
CM Feed	4.82	3,050	1900	15,000	82	–	–	–	–
CM UF	4.45	1,200	840	300	74	61.7	55.8	98.0	9.8
CM NF	1.96	30	17	9	34	99.1	99.1	99.9	58.5
BM Feed	14.89	1,150	316	7,500	275	–	–	–	–
BM UF	7.9	400	145	750	133	65.2	54.3	90.0	51.6
BM NF	4.22	0	0.4	19	69	100	99.9	99.7	74.9
LC Feed	6.7	15,530	1,065	4,000	199	–	–	–	–
LC UF	4.92	9,860	1,015	1,000	155	36.5	4.7	75.0	22.1
LC NF	0.6	1,475	15.3	7	35	90.5	98.6	99.8	82.4

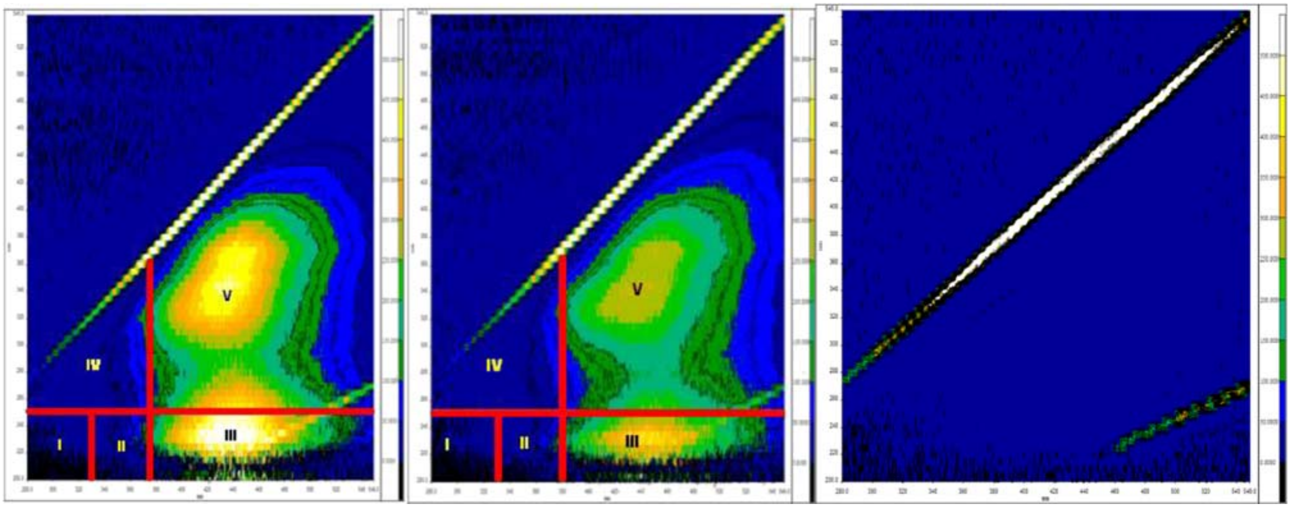

Fig. 2. EEM for (A) beet molasses effluent (left), (B) UF filtrate (middle) and (C) NF permeate (right).

and colour. There was also some reduction in both conductivity and osmolality. Treatment by NF showed significant reduction in organic content, >98% for both DOC and colour. However, the permeate retains significant residual COD. NF showed almost complete reduction in conductivity, suggesting that the inorganic content of the effluent was more predominantly polyvalent ions, rather than monovalent ions.

3.1. Fluorescence EEM results

Fluorescence EEM spectra are widely used for highly sensitive characterisation of organic components, such as proteins, polysaccharides, fulvic and humic compounds in water [17]. EEM analysis has recently been applied to effluents containing melanoidins [18,19]. EEM spectra can be divided into five regions, each associated with different groups of compounds. Regions I and II are associated with aromatic proteins, region III is associated with fulvic acid-like compounds, region IV is associated with soluble microbial products (SMPs) and region V is associated with humic acid-like compounds [17]. Melanoidins have been characterised as humic acid like compounds [18].

Fig. 2 shows the EEM results for UF/NF treatment of beet molasses effluent. The effluent feed (Fig. 2(A)) displays strong peaks in the humic acid-like (V) and fulvic acid-like (III) regions. One of the most prominent groups of compounds in molasses effluent is melanoidins. Melanoidins have been classified as humic compounds and have a large range of molecular weights. It is therefore more likely that the high concentration of melanoidins in the effluent, causing the high degree of colour, is responsible for the strong peaks shown in the EEM spectra. We observed similar results with cane molasses, with higher peak intensities in both humic and fulvic regions, correlating with higher COD, DOC and colour than beet molasses.

The molasses effluents were then filtered by a 2,000 MWCO UF membrane. Fig. 2(B) shows the EEM spectra for the filtrate. This spectrum shows the same “fingerprint” as for the raw effluent, however, the signal intensities have lowered significantly. This suggests that the majority of the organic content of the effluent has a molecular weight less than 2,000. The decrease in intensity also correlates well with the reduction in COD, DOC and colour after UF treatment. The UF filtrate was then treated by NF and the resulting spectra is shown in Fig. 2(C). This spectrum clearly shows complete removal of humic and fulvic compounds from the effluent. This again correlates well with very low levels of COD, DOC and colour in the NF permeate.

Fig. 3 shows the EEM spectra for the lignocellulosic (LC) effluent as well as the UF filtrate and NF permeate. While the cane and beet molasses effluents showed very similar “fingerprints” on their respective EEM spectra, the LC effluent showed differences. As with the molasses effluents, there are peaks present in the humic and fulvic acid-like regions, likely attributed to melanoidins or comparable colour producing compounds, however, the peak in the fulvic region extends into region II, associated with aromatic proteins, and another peak appears around the border between regions IV (SMPs) and V (humic acid-like compounds).

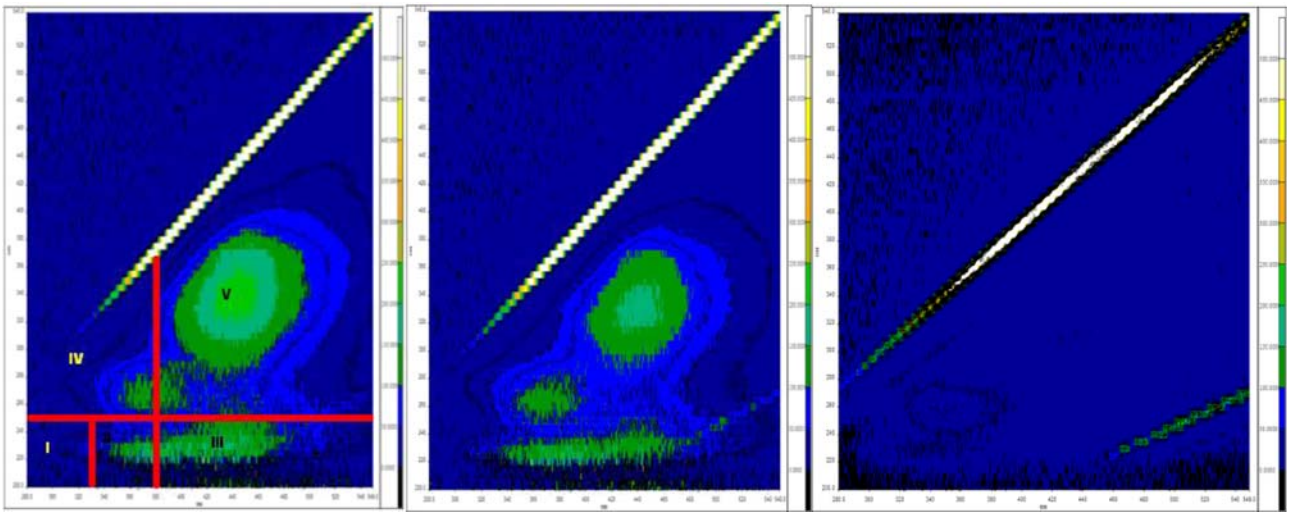

Fig. 3. EEM spectra for (A) LC effluent, (B) UF filtrate and (C) NF permeate.

After treatment by UF, slight reductions in intensity can be seen that correlate well with small reductions in DOC. A corresponding large drop in colour suggests that much of the organic material removed by UF contributes to colour, i.e. high molecular weight humic compounds. NF appears to remove all organic material, which correlates with almost complete removal of DOC and colour. Despite the apparent high removal of organic components, the permeate still shows a high level of residual COD.

3.2. Liquid chromatography

Liquid chromatography (LC-OCD) has been used extensively for the characterisation of organic matter in drinking water and wastewater [20–22]. Fig. 4 shows the chromatographs for beet molasses effluent and UF filtrate. The first small peak is seen at ~30 min and is attributed to biopolymers (>20,000 Da), high molecular weight organic compounds, such as polysaccharides or proteins. The low levels of biopolymer are to be expected due to the molasses undergoing fermentation followed by anaerobic and aerobic digestion, and hence most readily available biopolymers will have been consumed.

The most prominent peak, at ~40 min, represents humic compounds, such as melanoidins (500–20,000 Da). This is followed by a secondary peak at ~45 min representing building blocks (350–500 Da) from the decomposition of the humic compounds. The final peak is seen at ~50 min and is attributed to low molecular weight acids and humic compounds. Following this peak there is evidence of low molecular weight neutral compounds (<350 Da), such as mono or oligosaccharides, alcohols, aldehydes or ketones [20,21]. After UF, there is a significant reduction in the

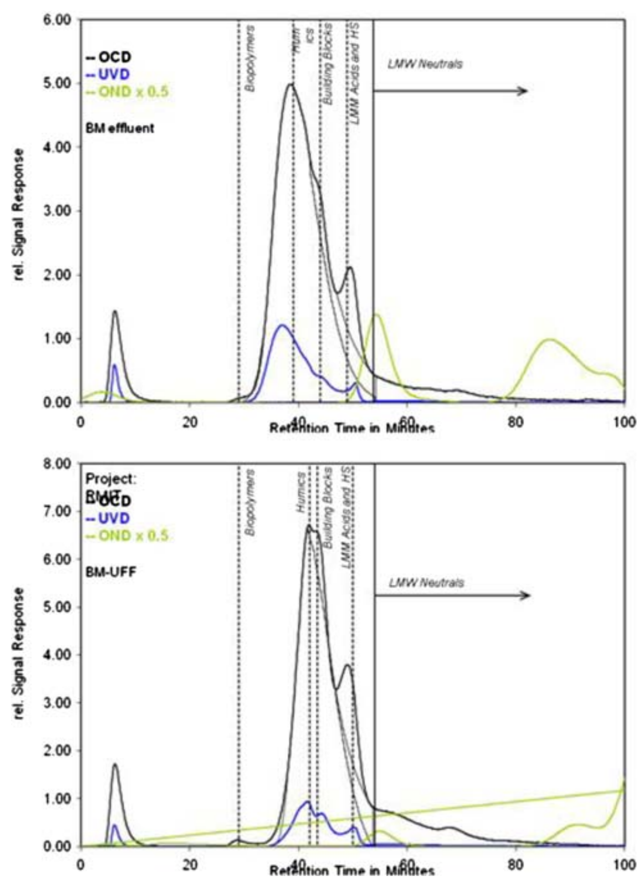

Fig. 4. Liquid chromatography results for beet molasses effluent.

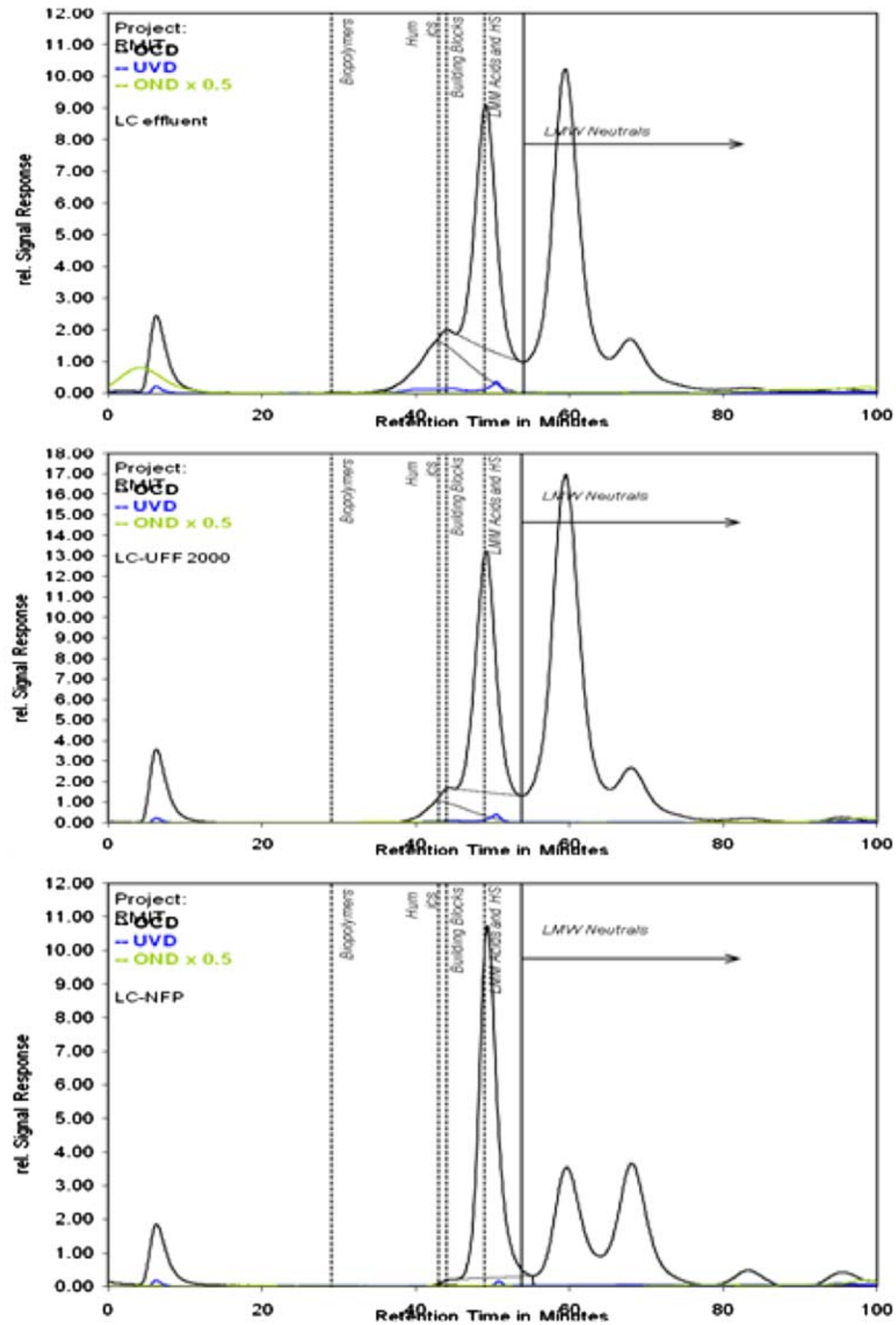

Fig. 5. Liquid chromatography results for lignocellulosic effluent.

humic compounds detected between ~30 and 40 min. This corresponds with similar reductions in humic and fulvic compounds in the EEM results, as well as reductions in COD, DOC and colour. This provides further evidence that the melanoidins present in the molasses effluents are mainly >2,000 Da. No results were obtained for the NF permeate due to very low organic content. Similar results were obtained for the cane molasses effluent.

Fig. 5 shows the liquid chromatography results for the lignocellulosic effluent. Unlike the molasses effluents, there is no evidence of biopolymers at the retention time of ~30 min. The first peak appears at the retention time of ~45 min and consists of both high molecular weight humic compounds (500–20,000 Da) and their derivatives (350–500 Da). Unlike the molasses effluents, this humic peak is not the most prominent peak. At ~50 min, a strong peak representing low molecular weight acids and humic compounds (<350 Da) is present. There is also a strong presence of low molecular weight neutral compounds (<350 Da) with a strong peak at ~60 min and a weak secondary peak at ~67 min.

The impact of UF is apparent only due to a slight reduction in the humic peak at 45 min. This suggests that the vast majority of the organic components in the lignocellulosic effluent consist of low to medium molecular weight compounds (<2,000 Da). The chromatograph of the NF permeate, shown at the bottom of Fig. 5, shows further rejection of the humic compounds in the peak at 45 min. This corresponds with a similar reduction in both DOC and colour. The other main impact of NF is a significant reduction in the signal response of the low molecular weight neutral peak at 60 min. The NF permeate showed significant residual COD and the chromatograph correspondingly shows residual low molecular weight acids and neutral compounds.

4. Conclusions/recommendations

Molasses and lignocellulosic effluents display similar water quality traits. They are both highly coloured, contain large amounts of organic compounds and have high salinity. However, these similarities are only superficial. Using fluorescence EEM analysis and liquid chromatography, it was revealed that while the nature of the organic content of cane molasses and beet molasses was very similar, they differ significantly from lignocellulosic effluent.

The effluents were treated by UF and NF membranes and the filtrates/permeates tested. It was shown that the separation performance of these membranes differed between effluents. UF, with a 2,000 MWCO, was shown to be capable of removing some of the organic material, particularly high molecular weight organic compounds, which contribute to colour. However, in both cases the residual colour and organic contents (COD and DOC) were both significant. NF was shown to be capable of almost complete removal of the organic content of molasses effluents and significant removal of the organic content of lignocellulosic effluent. The NF permeate displays a high amount of residual COD and it is unclear what compounds are contributing to this. Most indicators suggest that the organic content has been almost entirely removed. It is possible that high levels of sulphur, from the sulphuric acid used in the hydrolysis process, are affecting COD readings.

More work is required in analysing the contents of lignocellulosic effluent. Future work will include reverse osmosis performance in molasses and lignocellulosic effluent treatment, as well as more extensive water quality testing, including the use of inductively coupled plasma analysis for elemental composition and Fourier-transform infrared spectroscopy for further analysis of the organic compounds.

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