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The abrasion effects of natural organic particles on membrane permeability and the size distribution of recalcitrants in a colored effluent

Milton M Arimi [a,b,*], Saul S. Namango [b], Gesine Götz [a,**], Yongjun Zhang [a], Kirimi Kiriamiti [b], Sven-Uwe Geißen [a]

[a] *Technische Universität Berlin, Department of Environmental Technology, Chair of Environmental Process Engineering, Secr. KF 2, Straße des 17. Juni 135, 10623 Berlin, Germany*

[b] *Moi University Main Campus, Faculty of Technology, P.O. Box 3900, Eldoret, Kenya*

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ABSTRACT

The refractory substances and foulants are the main hindrance in treatment of many organic effluents. The aim of the study was to characterize the distribution of COD particles in molasses distillery wastewater (MDW) and their effects in membrane fouling. The factors analyzed include: permeate flux, conductivity, trans-membrane pressure, pH, color, biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total nitrogen (TN). Further analysis was done using high performance liquid chromatography (HPLC) and the liquid chromatography–organic carbon detection (LC–OCD) technologies. The permeate flux and permeability for 100 kDa membrane test were found to increase with time when the feed was not pre-filtered with Whatman paper. This was caused by the abrasion effects of huge particles on the active surface of the membrane. The microbial products were found to play a significant role as foulants for the digested effluent. A possible treatment process for MDW would start with biological digestion followed by microfiltration to remove huge particles before ultrafiltration and finally nanofiltration. The process eliminates more than 80% remnant COD and increases its BOD5/COD ratio from 0.07 to 0.3. An alternative process should entail membrane pretreatment of raw MDW before anaerobic digestion with 50 kDa membrane because of its reasonable permeate flux.

1. Introduction

In order to design an efficient membrane treatment system for common wastewaters, it is important to understand their COD fractional composition, size distribution and the effects of these fractions on the filtration system. For example, through studying the COD particle size distribution (PSD), it is possible to establish where the bulk of COD lies. After characterization of COD fractions by sizes, further analysis of these COD particles according to their biodegradabilities is possible. The readily biodegradable portion of the COD and their metabolites are quickly consumed, thus achieving a high COD removal. However, the slowly biodegradable portion has the COD first broken into smaller compounds like sugars, which are further metabolized by microbes [1]. The prior knowledge of biodegradability of COD fractions enables the determination of an appropriate treatment process in membrane bioreactors.

The COD portions can be categorized by size as; soluble, colloidal or particulate COD. In wastewater, it is generally presumed that the COD particles with diameters less than 0.45 μm are soluble while those with larger ones are treated as particulate. The conventional methods for characterizing dissolved organic particles include; gel permeation chromatography, size exclusion chromatography and membrane filtration. Gel permeation methods are laborious and time consuming; furthermore, they are being replaced by new and faster methods. Ultrafiltration and nanofiltration have been widely used and still command huge application in wastewater characterization [2,3]. Modern chromatographic methods are well advanced with wide applications in separation. They include versatile instruments like HPLC and the high performance size exclusion chromatography (HPSEC). Other

* Corresponding author at: Technische Universität Berlin, Department of Environmental Technology, Chair of Environmental Process Engineering, Secr. KF 2, Straße des 17. Juni 135, 10623 Berlin, Germany.

** Corresponding author.

E-mail addresses: Milton.m.marimi@campus.tu-berlin.de (M. Arimi), gesine.goezt@tu-berlin.de (G. Götz).

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technologies for characterizing dissolved organic particles include; the LC–OCD and the flow field flow fractionation methods.

The particulate COD in the feed solution have different effects on the membrane permeability and rejection depending on their sizes, nature and the properties of the membrane used [4]. They may form an active layer over the membrane which increases the rejection but decreases the permeate flux. They may also form a porous layer over the membrane that prevents the transport of the rejected material back to the feed tank: this results in a decrease of the rejection and an increase in the permeate flux. The particles may also cause abrasion effects on the membrane thus breaking its active layer. This results in the increase of the permeate flux and a decrease of the rejection [4].

Particle size distribution can be used to study the particles that cause fouling in the filtration processes. The fouling of membranes in the wastewater treatment is mainly dependent on; the properties of the particles of the feeds, the membrane characteristics, biomass characteristics and the operating conditions [5]. It has also been reported that organic loading also determines the membrane fouling [6]. In the study, sub-micron particles were found to highly influence tfouling of the membrane in the treatment of activated sludge effluent [6]. Fouling by particles occurs either through forming a cake above the membrane or by foulant particles blocking the pores. The main causes of membrane fouling in wastewater treatment include; natural organic matter, macromolecules, inorganic salts and microbial products. The foulants can be temporary or permanently attached to the membrane. The temporary foulants are mainly microbial products, which can be removed by backwashing, while the permanent foulants would require chemical treatment of the membrane to be removed. Microbial products in wastewater treatment are biological matter originating from biomass in the reactor and are part of its contents. They contribute highly to membrane fouling in membrane bioreactors. They are either soluble or insoluble particles [7]. Microbial products in wastewater can also be classified as: biomass associated products, utilization associated products or extracellular polysaccharides. Some of the products released by the microbes after biological treatment of wastewater include; organic acids, humic and fulvic substances, polysaccharides, proteins, antibiotics, enzymes, steroids etc.. Their formation and degradation in wastewaters are well documented [8,9]. Knowledge of the nature and the sources of foulants are necessary for the design of good membrane processes for wastewater treatment.

Particle size distribution has been studied in several wastewaters; pulp and paper mill effluent [10], textile effluent [11], tannery wastewater [12] and domestic wastewater [13]. A study of COD particle distribution in tannery effluent reported that 60% COD was particulate, 25% was soluble while the rest were in a colloidal form [12]. In domestic wastewater, only 29% was reported to be soluble COD while the rest was in particulate form [13]. Another study tested the relationship between particle size distribution and the quality of wastewater treated with different biofilm technologies [14].

There is no documentation of the PSD studies for industrial effluents rich in melanoidins like molasses distillery wastewater [15], which have very complex characteristics. This is because of their high refractory COD and the dark color which remains even after biological treatment. These effects are caused by the melanoidins and their related compounds in the molasses distillery wastewater (MDW) [16], and also coffee processing effluents [17]. Melanoidins are complex organic polymers with varying molecular sizes ($<$ 100 kDa) [18]. They are formed by reaction between amino acids and sugars in alkaline conditions [16]. These factors are present in processes like the making of instant coffee and sugar processing. Molasses is a by-product of the latter. It is used as a fermentation substrate in the production of other products like ethanol, yeast biomass or other biopharmaceutical products [19]. The wastewaters released by these processes have similar properties characterized by a dark color and a high recalcitrant COD which is caused by melanoidins and their related compounds. Due to the complexity of melanoidins, their properties have not been characterized.

The goal of the present work was to characterize organic particles including the refractory substances in MDW before and after biological treatment. The change in MDW biodegradability after membrane filtrations was also studied in addition to in depth analysis of the common parameters like COD, BOD and TOC. HPLC and LC–OCD were used to determine how different particles were eliminated during biological treatment and membrane filtration. Based on the knowledge acquired, a feasible process for the treatment of raw MDW involving biological treatment and membrane filtration was proposed.

2. Materials and methodology

2.1. Materials

The supplier of the raw MDW was Nordzucker AG (Braunschweig, Germany). The COD of the raw MDW was very high (600 g/L) because it had been concentrated by evaporation before packaging. The flat membranes used were donated by Berghof (Berlin, Germany) and a new membrane was used for each test. Each membrane was pretreated to increase the hydrophilic properties of its surface by soaking it for one hour in 25% solution of isopropanol. It was then rinsed and soaked in distilled water for another one hour. The membrane was finally stored in fresh distilled water overnight before use.

2.2. Anaerobic digestion

The MDW was diluted back to COD 10–20 g/l by adding tap water. The following trace nutrients were added: calcium, nickel, cobalt, molybdate, zinc, manganese and copper salts before adjusting the pH to 7 with sodium hydroxide. The substrate was transferred to a 3-L tank with a Rushton stirrer as an anaerobic bioreactor. The properties of the diluted MDW are shown in Table 1.

The sludge used was in the form of pellets. It was obtained from a plant treating brewery effluent was added to one third of the reactor volume with 2 L working volume. The reactor had a water jacket which was used to control the temperature at 35 °C and was operated on sequence batch mode. After decantation and filtration by a piece of cloth to remove the flocs and huge particles, the digested MDW was stored at 4 °C. The characteristics of the biologically treated water are given in Table 2.

Table 1
The Characteristics of MDW feed.

Parameter	Value
BOD_5, mg/l	12,000–13,000
Dissolved organic carbon (DOC), mg/l	5500–6200
COD, mg/l	16,000–17,000
Density, g/l	1020
pH, dimensionless	7.5
Conductivity, mS/m	4.0
Absorbance @ 475 nm, /cm	3.1
Turbidity, NTU	1.9
TN, mg/l	800–1000