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Recovery of antioxidants from sugarcane molasses distillery wastewater and its effect on biomethanation

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ABSTRACT

Antioxidants (melanoidins and polyphenols) present in sugarcane molasses distillery wastewater are not readily biodegradable. However, these compounds exhibit potential physiological properties which may be tapped for food, cosmetics and pharmaceutical applications. Recovery of these compounds from distillery wastewater could thus lead to products of commercial interest while improving the conventional biological (anaerobic) treatment step. Three processes viz. ultrafiltration (UF), adsorption-desorption and solvent extraction were investigated for antioxidants recovery from distillery wastewater and selected fractions were subjected to biomethanation (anaerobic digestion). The effect of different adsorbents and solvents as well as operational parameters on antioxidants recovery was studied and the separated fractions were analyzed for melanoidins content, polyphenols content and antioxidant activity. UF through 100 kDa membrane resulted in an antioxidant rich retentate (245 mM TEAC) but the permeability was low. Solvent extraction with methyl ethyl ketone (MEK) led to 113 mM TEAC recovery in organic phase. Adsorption on XAD16 resin followed by desorption with acidified ethanol enabled antioxidants recovery of 192 mM TEAC. Antioxidant removal from the wastewater improves biomethanation. Overall, adsorption on XAD16 resin followed by biomethanation (74% COD reduction and 71% methane in biogas within 25 days) appears to be promising for improving the existing biomethanation facility while recovering antioxidants with potential commercial value. Further analysis of the antioxidants fraction is required to ascertain the content of specific commercially viable polyphenols.

1. Introduction

Sugarcane molasses based alcohol distilleries generate 7–15 L effluent/L alcohol, that is characterized by high chemical oxygen demand (COD) of 80,000–1,40,000 mg/L and biochemical oxygen demand (BOD) of 40,000–65,000 mg/L, low pH and intense brown color [1]. The dark color is imparted by complex compounds like melanoidins, caramel, polyphenols as well as carotenoids, chlorophyll, anthocyanins, tannins etc. that are recalcitrant (difficult to biodegrade) and inhibit biological activity [2–4]. Owing to the high COD/BOD ratio (1.11–1.25) [5], biomethanation (anaerobic digestion) with biogas generation is conventionally employed as the primary treatment step. However, anaerobic conditions cause the melanoidins color to intensify [6], making decolourization of the effluent even more difficult.

Melanoidins are formed through Maillard reaction between sugars and amino acids in the sugar manufacturing process. They are a key component in sugarcane molasses used for ethanol production. Melanoidins are difficult to characterize due to their varying sizes and types of sugars and amino acids involved in their formation. There has been extensive work on degradation and removal of melanoidins from biomethanated molasses distillery effluent, exploring both biological [7,8,4] and physico-chemical methods [9,10]. Other options such as microbial fuel cell for electricity generation have also been tested with distillery wastewater diluted with sewage [11].

It is established that phenolic compounds in wastewater are major contributors to toxicity and antibacterial activity [12,13], limiting its microbial degradability. Melanoidins isolated from various sources have shown antimicrobial activity against different microbial species [14,15]. In molasses distillery wastewater, polyphenols are present in lower concentration (~7467 mg/L) compared to melanoidins (~16,600 g/L) [16]; however, at a given concentration, the polyphenols exhibit higher antimicrobial effect than melanoidins [4]. Presence of polyphenols above 1 g/L is known to inhibit methanogenesis [17], thereby negatively affecting COD removal and methane production. Therefore, removal of melanoidins and polyphenols prior to, rather than after biomethanation, would be more appropriate.

Melanoidins and polyphenols obtained from various sources exhibit useful biological effects. Besides antioxidant and antimicrobial

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properties, melanoidins (obtained from coffee brews etc.) and polyphenols (obtained from artichoke, kiwifruit juice, apple waste etc.) have shown antihypertensive [14,18], anti-inflammatory [19], anticarcinogenic [20,21] and antiglycative [22] properties. These properties make melanoidins and polyphenols valuable for food, cosmetics and pharmaceutical applications. Thus, the recovery of these compounds from natural botanic sources and agro-industrial wastewaters becomes of interest.

Several approaches have been investigated for isolation of melanoidins and polyphenols. Synthetic melanoidins and those obtained from coffee brews have been purified by ultrafiltration (UF) through 100 kDa, 30 kDa and 10 kDa membranes [23,14]. Adsorption on various synthetic resins e.g. anionic resin Lewatit S6328 A, polystyrenic resin Lewatit 6368, and sulphate and styrene divinyl benzene copolymer based resin has been studied for melanoidins recovery [24–26]. Acrylic ester based Amberlite XAD7 and styrene divinyl based XAD16 resins have been successfully employed for solid phase recovery of polyphenols from grape pomace [27,28], apple waste [29] and olive mill wastewater [30,31]. Melanoidins have been adsorbed on waste/natural materials such as bagasse bottom ash [32], carbon fraction from bagasse ash after activation [33], chitin nanofibres from shrimp shell waste [34] and natural zeolites [35]. Solvent extraction using isopropyl alcohol has been studied for melanoidins isolation from biomethanated distillery effluent [36]. Solvents of different polarity have been investigated for extraction of polyphenols from olive mill wastewater [37,38].

Review of literature indicates that antioxidant compounds present in molasses distillery wastewater have been identified and scattered data are available for the recovery of these compounds. However, no systematic study appears to have been done on developing a sustainable process, for antioxidants recovery from distillery wastewater and assessing its effect on the primary biomethanation step.

In this work, we have studied UF, adsorption-desorption and solvent extraction for the recovery of antioxidants (melanoidins and polyphenols) as value added products from sugarcane molasses distillery wastewater. This was followed by anaerobic treatment of the antioxidants depleted stream. Based on the results, the potential of applying combined processes for resource (antioxidants, energy) recovery from distillery wastewater has been assessed. The aim was to understand (a) which process leads to maximum recovery of antioxidants from distillery effluent, (b) if removal of antioxidants improves the biomethanation potential of the distillery effluent, and (c) if the antioxidants recovery method has any influence on the biomethanation performance.

2. Materials and methods

2.1. Materials

Sugarcane molasses distillery wastewater (pH 4.2, 130,000 ± 6000 mg COD/L, total suspended solids or TSS 156,000 ± 5000 mg/L) was collected from Brajnathpur distillery unit of Simbhaoli Sugars Limited, U.P., India. The wastewater was passed through 30 μm mesh (Hi Tech Enterprize, New Delhi) and centrifuged at 8000 rpm for 30 min to remove most of the suspended solids. It was then stored in the refrigerator.

Polyethersulfone UF membranes stable between pH 2–11 with molecular weight cut-off rating of 100 kDa (Tri Sep) and 10 kDa (GE Osmonics) were procured from Sterlitech, Mumbai. Resins Amberlite FPX66 and FPA98Cl were purchased from Virmani Brothers Pvt. Ltd., New Delhi; XAD7 and XAD16 were from Sigma Aldrich, New Delhi. All other chemicals viz. 2,2′-Azobis-(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), ethyl acetate, diethyl ether, chloroform, methyl ethyl ketone, methyl isobutyl ketone and isopropyl alcohol were purchased from Sigma Aldrich, New Delhi and used as-received. Sodium chloride, disodium hydrogen phosphate and potassium hydrogen phosphate required for phosphate buffer saline (PBS) were obtained from Fischer Scientific, New Delhi.

2.2. Recovery of antioxidants

Three different approaches viz. UF, adsorption-desorption and solvent extraction were tested for recovery of antioxidants components. The compounds analyzed were melanoidins and polyphenols, cumulatively referred to as antioxidants in the text henceforth. All experiments were performed in triplicate.

2.2.1. Ultrafiltration (UF)

The distillery wastewater was ultrafiltered in a dead-end filtration cell (Sepa ST, Osmonics, USA) with an effective filtration area of 16.9 cm^2. 100 mL of sample was concentrated 4-fold through 100 kDa membrane at 2 bar. The permeate fraction (< 100 kDa) was further passed through 10 kDa membrane. The retentate and permeate fractions (of 100 and 10 kDa membranes) were analyzed for antioxidants concentration and antioxidant activity (radical scavenging activity as per ABTS assay).

2.2.2. Solid phase extraction

Four different polymeric resins viz. XAD16, XAD7, FPX66 and FPA98Cl (Table 1) were tested. All the resins were activated using acidified ethanol to remove salts attached to their adsorption sites. 50 mL distillery wastewater was mixed with 10 g of activated resin in 100 mL conical flasks and kept in a shaker (Orbitek, Scigenics Biotech, India) at 160 rpm for 24 h at 25 °C. One set of flasks without adsorbent addition was maintained as control. The suspension was filtered through 0.45 μm filter (Millipore, Mumbai) and the filtrate analyzed for antioxidants concentration. The solid phase concentration was normalized relative to the concentration in the control (Eq. (1)) to adjust for variation among different batches of distillery wastewater.

$$\text{Normalized solid phase concentration} = (C_o - C_e)/C_o \quad (1)$$

where C_o and C_e are the concentration of antioxidants in the control and at equilibrium respectively.

The effect of different temperatures (25 °C–45 °C) and time (2 h–8 h) on adsorption was studied. Adsorption-desorption cycle was examined at 25 °C over 5 consecutive cycles. Adsorption (24 h) was followed by desorption (acidified ethanol for 24 h followed by water for 24 h). The adsorption capacity was calculated as per Eq. (2),

Table 1
Properties of resins[a].

Parameters	XAD16	XAD7	FPX66	FPA98Cl
Matrix	Styrene-divinylbenzene	Aliphatic ester	Macroreticular aromatic polymer	Acrylic macroreticular structure
Surface area (m^2/g)	900	450	> 700	-
Average particle size (mm)	0.63	0.56-0.71	0.60-0.75	0.63-0.85
Specific density (kg/L)	1.04	1.06-1.08	1.015-1.025	-
Polarity	Non-polar	Moderately polar	Non-polar	Anionic

[a] Based on product data sheet provided by the supplier.