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Extraction of steviol glycosides using novel cellulose acetate pthalate (CAP) – Polyacrylonitrile blend membranes

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ABSTRACT

Tailor made membranes cast from blend of cellulose-acetate pthalate (CAP) and polyacrylonitrile (PAN) polymers for the extraction of steviol glycosides is the point of focus of this study. The mentioned blend is a highly non-ideal and immiscible and membranes formed using this blend is not reported in the literature. Various weight percent combinations of the polymers were dissolved in an aprotic solvent, viz., dimethylacetamide (DMAc) and membranes were cast using the phase inversion method. The obtained membranes were characterized on basis of molecular weight cut off (MWCO), hydraulic permeability, hydrophilicity, pore density, porosity, surface morphology and mechanical strength. It was found that a set of membranes of various MWCO was obtained ranging from 7 kDa to 104 kDa for various compositions of the blend. Stevioside and Rebaudioside were then recovered from water extract of dry Stevia leaf powder using these ultrafiltration membranes. The permeate flux decline was analyzed for each of the membranes, to study the fouling characteristics. The optimum membrane was identified in terms of steady state permeate flux, recovery and purity of glycosides. It was found that the 90 kDa membrane yielded the maximum steady state flux of 11 L/m^2 hr, recovery of 68% and purity of 34%.

1. Introduction

The search for low calorie sweeteners as a substitute for sugar is a challenge for the food industry. Nowadays, people are consuming more artificial drinks, energy drinks, carbonated beverages and artificial fruit juices. All these beverages, although different, have a common ground that they have large dosage of sugars, hence are loaded with calories. The sedentary life style and high calorie intake have coupled up giving rise to the number of diabetes, obesity and cardiovascular diseases all over the world (Zimmet et al., 2001). The need of the hour is low calorie, high intensity sweeteners (HIS), which can be at least 50–100 times sweeter than sucrose (Kim and Kinghorn, 2002). These can further be classified in two types: artificial and natural. The examples of artificial sweeteners are acesulfame-K, aspartame, neotame, saccharin, and sucralose. However, these compounds themselves can have a detrimental effect on the human body, e.g., saccharin is often associated with high risks of cancer and people suffering from phenylketouria must avoid aspartame (Grenby, 1991). On the other hand, there is the availability of naturally occurring sweeteners like, thaumatin, glycyrrhizin, xylitol, phyllodulcin, mogroside, and stevioside. Stevia is a herbaceous plant, belonging to the Asteraceae family, tribe Eupatoriae. It is indigenous to the South American continent, mainly Paraguay, where the native Guarany tribes have been using it as a sweetener for centuries (Puri et al., 2011). However, the importance of Stevia as a sweetener has increased manifold in recent years and more research is being carried out in the extraction and recovery process of steviol glycosides. The sweetness in the Stevia leaves is attributed to the presence of dipterene glycosides present in them, viz., Stevioside, Rebaudioside A, B, D, E, Dulcoside A and B (Leung and Foster, 1996). A lot of research has gone into investigating the possibility of replacing sugars by Stevioside in carbonated beverages (Chang and Cook, 1983; Prakash et al., 2012; Clos et al., 2008) and interaction studies of Stevioside with organic acids, coffee, tea and water soluble vitamins (Kroyer, 1999; Ye et al., 2013).

Typical extraction processes involved are addition of chelating agent followed by crystallization (Kumar, 1986); water extraction followed by centrifugation and treatment with calcium hydroxide (Giovanetto, 1990); ion exchange for removal of impurities from Stevia extract followed by methanol addition (Payzant et al., 1999); polymeric adsorption (Shi et al., 2002); adsorption by zeolite CaX (Moraes and Machado, 1999) and calcium zeolites (Mantovanelli et al., 2004). These processes are cumbersome, expensive, and time consuming. Moreover, excess usage of organic solvents makes these unsuitable for human consumption. In this context, membrane based separation processes prove to be of great use since, they can be carried out at room temperature, involves no phase change and external chemicals and easy to scale up (Kutowy

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Nomenclature

A	membrane surface area, m^2
C_P	concentration of permeate, kg/m^3
C_F	concentration of feed, kg/m^3
v_w	distilled water flux, m/s
l	membrane thickness, m
L_P	hydraulic permeability, L/m^2 h bar
n_c	pore density, number of pores/m^2
Q	volumetric flow rate, m^3/s
R	rejection, %
R_{irr}	membrane I/irreversible resistance, m^{-1}
R_m	membrane hydraulic resistance, m^{-1}
R_m^a	membrane resistance after the experimental run, m^{-1}
R_m^b	membrane resistance before the experimental run, m^{-1}
R_f	membrane fouling resistance, m^{-1}
r_{avg}	average pore size, m
V_w	total flux, m/s
w_o	weight of the dry membrane samples, kg
w_i	weight of the wet membrane samples, kg

Greek symbol

ε	membrane porosity (dimensionless)
μ	water viscosity, Pa s
ρ_w	density of water, kg/m^3
ΔP	transmembrane pressure drop, kPa
ΔT	sampling time, s

et al., 1998; Abou-Arab et al., 2010; Chhaya et al., 2012a,b; Rao et al., 2012). In this light, it is also worthwhile to mention that pure polyether-sulfone tailor made membranes have been used to purify glycosides (Vanneste et al., 2011). The blend membranes with improved properties can also be useful in this regard (Rahimpour and Madeini, 2007).

With the advance in research in materials science, it is possible to blend different polymers of either different or same nature to obtain a desired set of properties. The polymers, when cast on a fabric and put in a gelation bath, undergo phase inversion to yield a porous structure on a highly porous support (fabric). Sivakumar et al. (1999, 2000) examined the application of cellulose acetate–polyurethane blend membrane. CA based blend membranes were also fabricated and examined (Saljoughi and Mohammad, 2009). The other blends that have been reported are typical polysulfone–polyurethane blends (Arthanareeswaran et al., 2011), polysulfone-poly(1-vinylpyrrolidone-co-styrene) blends (Kim et al., 2002) and polysulfone-poly(vinyldene fluoride) blends (Wua et al., 2006) and several others. Effects of blending of cellulose acetate phthalate (CAP) in polyether sulfone on morphology, and antifouling characteristics have been studied (Rahimpour and Madeini, 2007).

The present work is an attempt to understand the science of polymer blend of cellulose acetate phthalate (CAP) and polyacrylonitrile (PAN) for its potential application in glycoside extraction and purification. The work is novel in a twofold manner. Firstly, membranes formed by a blend of CAP and polyacrylonitrile (PAN) are not reported thus far in the literature. This work also investigates the effect of blending a hydrophilic polymer (CAP) with a hydrophobic one (PAN) and thereby characterization of the blend. Secondly, the work deals with the extraction of glycosides with help of tailor made polymer blend membranes and not just pure polymers.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

Dry Stevia leaves powder was supplied by RAS Agro Associates, Maharashtra, India. Distilled water, used for extraction of glycosides, dissolving neutral polymers for measuring rejection, and as an anti-solvent in the gelation bath, was prepared by an in-house evaporator. High performance liquid chromatograph (HPLC) grade acetonitrile and water were supplied by Merck India Limited, Mumbai, India. Standard Stevioside and Rebaudioside A of 98% purity were obtained from Sigma–Aldrich, USA for calibration purpose. Polymers, cellulose acetate pthalate (average density 1.3 g/mL at 25 °C) was procured from GM Chemicals Company Limited. PAN (homopolymer average molecular weight of 150 kDa) was procured from Technorbital, Kanpur, India. Polyethylene glycol of (PEG) average molecular weight, 4 kDa, 6 kDa, 10 kDa, 20 kDa and 35 kDa and poly-ethylene oxide (PEO) of average molecular weight 100 kDa and 200 kDa was supplied by M/s, S R Ltd., Mumbai, India and dextran (average molecular weight: 70 kDa) was procured from M/s, Sigma Chemicals, USA. These polymers were used to find out the MWCO of the tailor made membranes. The solvent di-methyl acetamide (DMAc) was purchased from M/s, Merck (India) Mumbai Ltd. The casting fabric, a non-woven polyester fabric of thickness 118 ± 22.8 μm (product number TNW006013, was supplied by M/s, Hollytex Inc., New York, USA). The laboratory scale centrifuge (batch size of 200 mL; model number R-24) was supplied by Remi International Ltd., Mumbai, India. The stirred batch cell for conducting ultrafiltration was supplied by Gurpreet Engineering works, Kanpur, India. Digital tachometer was supplied by Agronic, Kolkata, India.

2.1.2. Membrane synthesis

Different weight percents of CAP and PAN were used to form the polymer blends. The total polymer was fixed at 20 weight%, since dissolving polymers in DMAc above this weight% made the solution highly viscous and was therefore difficult to cast. The membranes were made with weight percent of CAP (as supplied) varying from 0% to 20% in increments of 5, the rest being PAN. Thus five membranes were cast with the ratio of weight percentages being (CAP:PAN) 0:20, 5:15, 10:10, 15:5 and 20:0. The polymers with the respective weight percentages were dissolved in DMAc, under constant mechanical stirring at about 200 rpm and temperature was maintained at about 60 °C for 6 h to ensure complete mixing of the polymers. The polymer solution was cast on the non-woven fabric (attached to a glass plate), with the help of a stainless steel doctor's knife, set at a fixed gap of 150 μm, and the manual drawdown speed was 30 mm/s. The glass plate with the fabric and the cast polymer was immediately put in the distilled water gelation bath, to keep evaporation effects to a minimum. The membrane was kept in the bath for 24 h to ensure complete phase inversion. Therefore, it was kept in distilled water to remove traces of solvent.

2.1.3. Experimental set up

The experimental runs with Stevia extract were conducted in the stirred continuous cell, made of stainless steel and detachable in three parts. The top part included a flange with a stirring arrangement, the middle part comprised of the cylindrical shell