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Enantiomeric and racemic effect of tartaric acid on polysulfone membrane during crystal violet dye removal by MEUF process

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ABSTRACT

The enantiomeric and racemic effect of tartaric acid was studied on the properties of polysulfone (PSn) ultrafiltration membranes. Dextro-tartaric acid (D-TA) and DL-tartaric acid were used as additives in the present study. Investigation was done in terms of permeation and rejection behaviour of fabricated membrane for crystal violet dye, with and without an anionic surfactant sodium dodecyl sulphate from aqueous media. Morphological study of the prepared membranes was done by field-emission scanning electron microscope, scanning electron microscope and atomic force microscopy. Whereas, contact angle, equilibrium water content, hydraulic resistance, porosity and ion exchange capacity were measured for finding the hydrophilicity (HPCT) of these membranes. The measurements of water contact angle provide evidence that the HPCT of PSn membrane increases by addition of the D-TA in the casting solution. This study shows that addition of D-TA in membrane results in enhanced pure water flux and rejection as well as higher permeation compared to ordinary PSn membrane.

1. Introduction

Dyes are integrated part of different industries such as paper, paints and textile. These industries release effluent which is contaminated with harmful dyes and subsequently it is responsible for many ecological problems. So, proper treatment and handling of coloured wastewater is necessary before throwing away. Even small amount of dye present in the water is able to be seen which affects the clearness of water and also the aquatic life since it hinders the path of sunlight [1]. Its complex nature made it difficult to satisfactorily treating a dye effluent. Many decolorization methods including physical [2,3], chemical and biological processes have been reported [4,5] in last decades. However, performance of combination of two methods is proven to be more satisfactory than that of single one.

Micellar enhanced ultrafiltration (MEUF) is one of the potential methods for the removal of organic dyes from coloured effluent. MEUF have certain advantages over other membrane based separation processes which includes higher removal efficiency, lower operating cost and higher permeate flux [6]. In this process, micelle formation occurs by the addition of surfactant in aqueous medium at the same or higher critical micelle concentration (CMC) level. Then, the oppositely charged solute molecules are solubilized over the micellar surface. Thus, by the increment of size the solutes separated after trapping with the micelles [7]. Recovery of surfactant in MEUF is a well established technique; Purkait et al. have done work on aromatic alcohols separation and dye removal from water using MEUF and further recovery of surfactant [8,9].

PSn is widely used polymer for membrane fabrication. Hydrophobic character of PSn is its major drawback because it is responsible for the adsorption of organic molecules on the membrane surface; this fact is known as membrane fouling. There are many ways to protect the membrane from fouling. Surface modification of PSn based membrane is a common technique for increasing the HPCT of membrane, consequently reducing the fouling. Literature shows that even a small amount of organic acid can change the HPCT of polymeric membrane. So, blending of different organic acids with PSn can be used for surface modification and consequently increasing the hydrophilic properties of the membrane. Kumar et al. [10] prepared polysulfone-chitosan blend ultrafiltration membranes with 1% acetic acid. Their observation resulted with improved antifouling property of bovine serum albumin (BSA) rejection through modified membrane. Xenobiotics removal at different solution pHs was studied by Ghaemi et al. [11]. They investigated the effect of various concentrations (0.25 to 1 wt%) of three different organic acids on the morphology and per-

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Table. 1
Literatures related to crystal violet dye removal.

Type of membrane	Flux (L/m^2h)	Pressure (kPa)	Rejection (%)	Ref.
NF	7.55	415	95	[19]
Composite hollow fiber NF	5.57	70	99.2	[20]
Liquid emulsion membrane	–	–	95	[21]
NF	11	700	98	[22]
Advanced oxidation process followed by MF	13.2	276	100	[23]
MEUF	14.1	150	99	Present work

formance of PSn membrane. They observed that citric acid offered highest retention efficiency of the solutes compared to other two acids (i.e. ascorbic acid and maleic acid). Ghaemi et al. [12] also studied the effect of amphiphilic fatty acids (palmitic, oleic, and linoleic acid) on the structure and performance of cellulose acetate nano filtration membranes. They observed that addition of palmitic acid represent highest rejection of nitrophenols compared to other fatty acids. Mansourizadeh et al. [13] used polyethylene glycol and ethanol, glycerol and acetic acid as the additives in porous PSn hollow fibre membranes for CO_2 absorption. They found that all the additives resulted in enhanced surface porosity. Wei et al. [14] studied the effect of preadsorption of citric acid on surface modification of PSn ultrafiltration membrane. They observed that after modification the membrane surfaces became more hydrophilic and permeability also improved. Acrylic acid (AA) was also used with different hydrophilic polymers [15]. Sinha et al. [16] synthesized polyurethane macromolecules (PU) with end capping of citric acid, maleic acid, lactic acid and 4-hydroxy benzoic acid. Membranes blended with PU showed improved pore density, HPCT and pure water flux compared to plain PSn membrane.

Solubility of Dextro-tartaric acid (D-TA) and racemic tartaric acid (DL-TA) is different in water [17]. This fact can change the diffusion rate of solvent and non-solvent in coagulation bath (i.e. water) during wet phase inversion process and it can subsequently change the porosity of the membrane. Dissociation constants of acids are also slightly different which can affect the surface charge of the PSn membrane. Some literatures are available, addressing the enantiomeric and racemic effect of organic acid on membrane. Yang et al. [18] studied extractive resolution of racemic mandelic acid through a bulk liquid membrane containing binary chiral carrier. They developed a complex of di(2-ethylhexyl) phosphoric acid and O, O′-dibenzoyl-(2R, 3R)-tartaric acid (L-(-)-DBTA) for the extractive resolution of racemic mandelic acid and observed a separation factor (α) of 2.74. It appears from the literatures review that although lots of works have reported on several organic acids to increase the HPCT of PSn membrane, but no work has been reported on the investigation of enantiomeric and racemic effect of tartaric acid (TA) on the HPCT of PSn membrane.

Therefore, in the present study an attempt was made to investigate the effects of addition of D-TA and DL-TA into the casting solution of PSn membrane; i.e. blending of D-TA and DL-TA in PSn membrane and their performance in the removal of crystal violet dye (CVD) from aqueous solutions. However, different membrane processes were studied for the removal of CVD from aqueous medium (Table 1). Enantiomeric and racemic effects of TA on the membrane morphology, HPCT, water flux as well as permeation and rejection behaviour were examined and explained well.

2. Experimental

2.1. Materials and reagents

Polysulfone (average molecular weight of 30,000 Da) was procured by Sigma–Aldrich Co., USA, and was taken as base polymer in the membrane casting solution. Dimethyl acetamide (DMAc) (supplied by LOBA Chemie, India) was used as solvent. PVP (average molecular weight of 40,000 Da), D-tartaric acid ($pK_a = 2.98$) and DL-tartaric acid ($pK_a = 3.03$) with average molecular weight of 150 Da for both TAs; were supplied by Otto Chemie Private Limited India. CVD with molecular weight of 407.9 Da was purchased from CDH Laboratory, India and surfactant SDS (MW 288.38) has been procured from SISCO Research Laboratories, India. Chemical structure of tartaric acid, PVP and PSn are shown in Fig. 1.

2.2. Membrane preparation

Wet phase inversion technique was used for the fabrication of flat film PSn membranes. PVP with D-TA and DL-TA were used as additives and DMAc (79–80 wt%) was used as solvent (Table 2). A constant concentration 18 wt% of the PSn was taken for all the membrane casting solutions. Membranes with varying compositions were defined as M1, M2 and M3. The casting solution was stirred (at 350 rpm) at room temperature with the help of a magnetic stirrer for 8 h. Detailed preparation procedure is explained in our previous work [24]. Thickness of the film was maintained as 100 μm. Finally, the sheets were air dried for 24 h at room temperature. After that, membranes were cut in the circular shape of required diameter 0.03 m and placed inside the membrane cell for filtration experiments.

2.3. Characterization of membranes

All the fabricated membranes were characterized through permeation experiments as well as morphological analysis. Morphological analysis of the prepared membranes was done by microscopic observations. The permeation and rejection capacity of each membrane was studied in terms of compaction factor (CF), equilibrium water content (EWC), porosity, pure water flux (PWF), percentage rejection (%R) of CVD, ion exchange capacity (IEC) of the membranes, water contact angle (for finding the HPCT of membrane) and hydraulic resistance (R_m). All the characterization techniques are explained well in literature [24].

Table. 2
Composition of PSn casting solutions of the membranes.

Serial no.	Membrane	PSn (wt%)	PVP K-30 (wt%)	DMAc (wt%)	D-TA (wt%)	DL-TA (wt%)
1	M1	18	2	80	–	–
2	M2	18	2	79	1	–
3	M3	18	2	79	–	1