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Membrane contactor for reactive extraction of succinic acid from aqueous solution by tertiary amine

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ABSTRACT

A hollow fibre membrane contactor (HFMC) made of microporous, hydrophobic, polypropylene (PP) fibres was used for removing dissolved succinic acid (SA) from aqueous streams. The Liquicel® HFMC module was operated in the liquid–liquid extraction (LLE) mode with aqueous SA as the feed solution. The aqueous feed was prepared by dissolving measured amounts of SA in deionised water, with concentrations varying from 5000 to 59 000 ppm. Two different types of organic extractant solutions were chosen to extract SA from aqueous streams: (a) 30% tripropylamine (TPA) dissolved in 1-octanol and (b) 30% trioctylamine (TOA)–TPA mixture in a 2:8 weight ratio and dissolved in 1-octanol. The aqueous feed was circulated through the lumens of the hollow fibres, and the extractant solution was passed through the shell side (i.e., inside the shell) of the HFMC module. Both liquids flowed counter-currently within the HFMC module and were recirculated continuously. Conditions such as SA-water flow rate, organic phase flow rate, and initial SA-water concentration were selected as the operating variables. The complexation reaction of SA with the amine was assumed at the aqueous–organic interface on the lumen side. The complex thus formed first diffused through the membrane pores filled with the organic phase (hereafter "organic-filled membrane pores") and was subsequently swept by the organic liquid flowing through the shell side of the module. The HFMC was observed to be highly efficient in removing SA from water, and a removal efficiency of more than 95% was obtained. A mathematical analysis was performed by considering the transport of SA molecules through the bulk aqueous phase and within the organic-filled membrane pores. The results of the model simulation were shown to be in agreement with the experimental data.

Keywords: Hollow fibre membrane contactor (HFMC); Reactive extraction; Succinic acid; Aqueous stream; Organic extractant; Reaction complex; Mathematical model

1. Introduction

Organic acids are often required to be separated from aqueous streams for various purposes. These acids are either recovered as a product from fermentation broths and reactor vessels or removed as pollutants from industrial effluents prior to discharge in natural aquifers. With respect to wastewater contaminated with organic acids, anaerobic treatment methods have been conventionally employed. However, these methods have various disadvantages such as long start-up times, requirement of alkalinity, and further aerobic biological treatment before discharge (Choi et al., 2008; Leitao et al., 2006). For overcoming these disadvantages, the use of membrane processes for treating such wastewater streams may be considered as an alternative strategy. When employed in an anaerobic bioreactor, microfiltration (MF) and ultrafiltration (UF) membranes have been shown to be effective, with a high removal rate of chemical oxygen demand (COD) and suspended solids (Bailey et al., 1994; He et al., 2005).

One of the carboxylic acids in the wastewater treatment process is succinic acid (SA), which has many important industrial applications. SA is employed in various scientific

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and manufacturing processes, as well as in the production of synthetic resins, pharmaceuticals, dyes, and biodegradable polymers (Jun et al., 2005; Zeikus, 1980). Additionally, it is used in the food industry. In certain manufacturing processes, SA is produced as an intermediate of the tricarboxylic acid cycle (Jun et al., 2005). Because of the huge demand for raw SA, conventional SA-production methods are now being replaced with advanced fermentation processes that use various bacterial strains. At the end of fermentation, SA is present in the aqueous broth along with contaminants such as proteins and cell by-products, organic acids such as acetic and pyruvic acids, carbon sources, and several salts, which should be removed from the final product (Jun et al., 2007). To achieve this end, a cost-effective fermentation method should accompany an efficient separation process. In addition to production losses, inadequate SA recovery from the fermentation broth may lead to increased acid concentration in the discharged wastewater. There are several methods for removing or recovering SA from aqueous solutions and controlling the quality of the final product obtained from the broth. Among these, the most commonly used methods include precipitation, crystallization, and acidification by ion-exchange resins, electrodialysis, distillation, and extraction (Jun et al., 2007; Kurzrock and Weuster-Botz, 2010; Tung and King, 1994). However, because of the high operational costs and complex procedures involved in these methods, it is necessary to explore other promising techniques (Huh et al., 2006).

Recently, Choi et al. (2008) successfully demonstrated the use of nanofiltration (NF) membranes for removing SA, as well as other organic acids, from wastewater with respect to various operating parameters; and achieved over 90% SA removal. Hollow fibre membrane contactor (HFMC)-based methods for wastewater treatment and recovery of valuable products are fast emerging as effective alternatives to conventional methods with high efficiency. The removal of dissolved gases such as CO_2, NH_3, and H_2S from aqueous effluents has been successfully carried out in the past (Agrahari et al., 2013, 2012, 2011). The application of HFMC to liquid–liquid extraction (LLE) operations has been reviewed by Schlosser et al. (2005). The reactive extraction of many organic acids such as acetic, citric, and aspartic acid from aqueous streams has been effectively achieved with HFMC application (Basu and Sirkar, 1991; Grzenia et al., 2008; Lin et al., 2006). There are several advantages associated with HFMC-based extraction methods, such as the prevention of loading and flooding, clear separation between two phases, independent flow control, compact operational setup, and good scalability (Agrahari et al., 2011; Grzenia et al., 2008). There is possibility of occurrence of instability, when treating biphasic liquid–liquid systems. However, such occurrence must be avoided by regular cleaning and drying of the membrane contactor following the prescribed procedure of the supplier (Liqui-Cel®). Hydrophobic membrane prevents the aqueous phase entering into the pores of the membrane, thereby minimizing the mixing of two phases within the pores, or the penetration of the aqueous phase into the shell side of the contactor. The membrane acts as a barrier to prevent loss of one phase into the other, since it provides a non-dispersive contact between the phases. The literature also shows several results (Dindore et al., 2004; Mosadegh-Sedghi et al., 2014) in which the problem of wetting of membrane with the polar phase has been addressed. Wetting can also be avoided by improvements in hydrophobicity of the membrane (Lv et al., 2010).

The present work demonstrates the application of a single HFMC module for separating SA from an aqueous medium. A synthetic SA-laden aqueous feed was prepared by dissolving measured amounts of SA in deionised (DI) water. The extractant phase consisted of a tertiary amine (TA), tripropylamine (TPA), diluted in 1-octanol. The use of tertiary amines diluted with miscible organic diluents for recovering carboxylic acids from aqueous solutions has been studied widely (Maurer, 2006). Because amines are highly basic in nature owing to their capacity to donate electrons, they show greater affinity towards reacting with negatively charged molecules. Such extracting compounds have been shown to enhance the efficiency of LLE operation for recovering SA and to offer better selectivity over other extractants (Pazouki and Panda, 1998). Furthermore, Hong and Hong (2000) have shown that a mixture of short- and long-chain tertiary amines has good extractability, similar to that of a single amine. The present work primarily involves using TPA dissolved in 1-octanol as the extractant phase; however, a comparative study was additionally undertaken for determining the removal efficiency of HFMC with mixed amines (diluted with 1-octanol) as the extractant phase. The extractant phase used herein comprised fixed amounts of trioctyl amine (TOA) and TPA dissolved in 1-octanol.

2. Theoretical considerations and model development

For the reactive extraction of SA using tertiary amines, it was assumed that the SA molecules form a reaction complex with the amine molecules. The complexation reaction was considered to occur at the aqueous–organic interface. Furthermore, the complex solubilized within the organic phase and was subsequently separated from the aqueous phase. The complexation reaction led to the transfer of protons or formation of ion pairs according to the nature of the amine and organic solvent (Hong et al., 2001; Kertes and King, 1986). Fig. 1 shows a schematic representation of the transport steps associated with the reactive extraction of SA in the HFMC module. As shown in figure, the entry of the aqueous phase with SA dissolved in water into the pores of the hydrophobic membrane is restricted. However, the extractant phase (organic) may enter the pores, fill them completely, and form an interface at the pore mouth at the lumen side. The SA molecules were thus partitioned between the aqueous and organic phase, and the complexation reaction between the SA and amine molecules occurred at the interface. Thus, the reaction complex, which was water insoluble, diffused and permeated through the membrane pores and was swept away by the bulk organic phase flowing on the shell side.

The solute (SA) molecules are partitioned into the organic phase. The concentration of SA in the organic phase, $C_{SA,or}$, is related to its aqueous phase concentration, $C_{SA,aq}$, by its partition coefficient (Basu and Sirkar, 1991):

$$C_{SA,or} = mC_{SA,aq} \tag{1}$$

where m is the partition coefficient of SA in 1-octanol, the organic phase. The partitioning of SA into the organic phase is represented as follows:

$$(SA)_{aq} \rightleftharpoons (SA)_{or} \tag{2}$$

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