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# Mathematical model and experimental validation of the synergistic effect of selective enantioseparation of (*S*)-amlodipine from pharmaceutical wastewater using a HFSLM

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ABSTRACT

A case study on the synergistic enantioseparation of (*S*)-amlodipine from pharmaceutical wastewater by using hollow fiber supported liquid membrane (HFSLM) was examined. A chiral reaction flux mathematical model was applied. Optimum conditions achieved the highest percentages of extraction and stripping viz. 84% and 80%, respectively. Relevant parameters affecting the enantioseparation efficiency of (*S*)-amlodipine were determined. Standard deviation percentages were 2.31% for extraction and 1.26% for stripping. It was found that the mathematical model proved to be in good agreement with the experimental data.

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## 1. Introduction

Chemical synthesis-based pharmaceutical wastewater contains a variety of chemical contaminants e.g. solvents, additives, reactants and high-value pharmaceutically active compounds [1,2]. Although such compounds may be present in the environment at low concentrations, these drugs can nevertheless have an adverse effect on aquatic organisms [3]. These effects are chronic rather than acutely toxic [4]. Further, high-value drug substances can also be recycled for use in the pharmaceutical industry [5]. Currently, the recycling and reduction of waste materials has drawn much attention. One of the main purposes of wastewater treatment is the stripping of pharmaceutically active compounds [6–8]. In recent years, the use of a liquid membrane in wastewater treatment has become increasingly important. It offers several advantages, such as high selectivity, high efficiency of separation, high enrichment and less use of the organic phase, compared with the classical solvent extraction process [9].

The aim of this research is to design a HFSLM system for the separation and wastewater treatment processes in the pharmaceutical industry. HFSLM is an effective simultaneous process to extract and recover compounds from a very dilute solution of components in the feed phase by a single-unit operation [10]. In the past few years, researchers have been working on the enantioseparation for (*S*)-amlodipine using HFSLM [11–14]. HFSLM technique follows certain rules in the choice of a separation system [15–17]. This method has potential for large-scale production [18]. However, in order for it to be applied to industries, reliable mathematical formulae are required. These help to provide guidelines for mass transfer which describes the transport mechanism of the target species through HFSLM. A theoretical model of HFSLM system is urgently needed for the completion of an efficient stripping process.

The prime objective of this work is to provide a chiral mathematical model of the HFSLM process. Its aim is also to investigate the effect of operating parameters on selective enantioseparation of (*S*)-amlodipine from pharmaceutical wastewater. Prediction equations for enantioseparation of (*S*)-amlodipine via HFSLM are presented and validated by comparing theoretical results with experimental results.

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**Nomenclature**

| | |
|---|---|
| $A$ | cross-sectional area ($cm^3$) |
| $A$, $B$, $C$, $D$ | target enantiomer (A), Chiral selector (B), Chiral complex (C) and Chiral stripping compound (D) |
| $a$, $b$, $c$, $d$ | stoichiometric coefficients |
| $C$ | concentration (mmol/L) |
| $D$ | data results |
| $d_o$ | external diameter of the hollow fiber tube (cm) |
| HFSLM | hollow fiber supported liquid membrane |
| $J$ | flux ($mg\ cm^{-2}\ min^{-1}$) |
| $K_{ex}$ | equilibrium constant of the interfacial reaction in the feed phase |
| $K_s$ | equilibrium constant of the interfacial chemical reaction in the stripping phase |
| $K_f$ | dimensionless mass transfer coefficient in the feed layer |
| $k_{ef}$ | rate constant of extraction reaction in the feed phase ($min^{-1}$) |
| $k_m$ | rate of mass transfer coefficient in the membrane phase ($cm\ min^{-1}$) |
| $k_{sf}$ | rate constant of stripping reaction in the stripping phase ($min^{-1}$) |
| $L$ | length of the hollow fiber (cm) |
| $m$ | order of stripping reaction |
| $N$ | numbers of hollow fibers in the module |
| $n$ | order of extraction reaction |
| $Q_f$ | volumetric flow rate of feed solution ($mL\ min^{-1}$) |
| $R$ | universal gas constant |
| $R^2$ | coefficient of determination |
| $S$ | synergistic coefficient |
| $r_i$ | internal radius of the hollow fiber tube (cm) |
| $r_o$ | external radius of the hollow fiber tube (cm) |
| $r_{lm}$ | log-mean radius of the hollow fiber |
| $r_{ef}$ | rate of extraction reaction in the feed phase |
| $r_{sf}$ | rate of stripping reaction in the stripping phase |
| $T$ | absolute temperature (K) |

*Greek letters*

| | |
|---|---|
| $\tau$ | tortuosity of the liquid membrane |
| $\varepsilon$ | porosity of the membrane |
| $\mu$ | viscosity of the membrane (kg/(s m)) |

*Subscripts*

| | |
|---|---|
| $A$ | target compound |
| $aq$ | aqueous |
| $C$ | chiral complex |
| $Exp$ | experimental |
| $f$ | feed phase |
| $m$ | membrane phase |
| $Mod$ | model-calculated value |
| $org$ | organic |
| $s$ | stripping phase |

## 2. Theoretical background

### 2.1. Transport mechanisms of synergistic extraction of (S)-amlodipine

Transportation of (*S*)-amlodipine occurs as a consequence of the concentration driving force between the two opposite sides of the aqueous phase. The chiral organic selector or extractant is trapped in polymeric hydrophobic microporous fibers of the hollow fiber module by capillary action [18]. The supported liquid membrane lies between the aqueous solution which initially contains the racemic feed solution and the aqueous stripping solution. The feed phase, consisting of pharmaceutical wastewater containing (*S*)-amlodipine, together with the stripping solution are fed counter-currently into the tube and shell sides of the module, respectively. The transport mechanism of (*S*)-amlodipine in the microporous hollow fiber is presented schematically in Fig. 1. In the liquid membrane, the synergistic enantioseparation of (*S*)-amlodipine by a mixture of the chiral selector ((+)-DBTA) and the achiral selector D2EHPA occurs via two extraction reactions in the system.

The first reaction is the reaction between the chiral selector and the achiral selector to form the extractant complex (+)-DBTA–D2EHPA [19–21], as shown in Eq. (1). The second reaction is the reaction between the extractant complex and (*S*)-amlodipine, as shown in Eq. (2) [20]. The reaction takes place in the presence of proton transfer-chiral interactions i.e. (+)-DBTA–D2EHPA. This produces the derivative complex (*S*)-amlodipine-(+)-DBTA–D2EHPA. Thus, complex chiral compounds are formed and transported across the membrane phase to the other side. No transport of (*S*)-amlodipine passes this interface. At the interface, between the organic membrane phase and the stripping phase, the complex chiral compounds react with the stripping solution and release (*S*)-amlodipine to the stripping phase.

$$[(+)\text{-DBTA}]_m + [\text{D2EHPA}]_m \underset{k_2}{\overset{k_1}{\rightleftarrows}} [(+)\text{-DBTA}-\text{D2EHPA}]_m \quad (1)$$

$$2[(S)\text{-amlodipine}]_f + [(+)\text{-DBTA}-\text{D2EHPA}]_m \underset{k_4}{\overset{k_3}{\rightleftarrows}} [[(S)\text{-amlodipine}]_2 - [(+)\text{-DBTA}-\text{D2EHPA}]]_m \quad (2)$$

where $k_1$ and $k_2$ are the apparent rate constants of formed extractant and unformed extractant, and $k_3$ and $k_4$ are the apparent rate constants of feed–membrane and membrane–feed interfacial transport, respectively, of the amlodipine enantiomer. The suffixes f and m are defined as the feed phase and membrane phase, respectively.

The presence of $\beta$-cyclodextrin in the stripping phase produces higher stripping results by creating a complex with (*S*)-enantiomer via various electrostatic forces and hydrogen bonding [22,23]. The

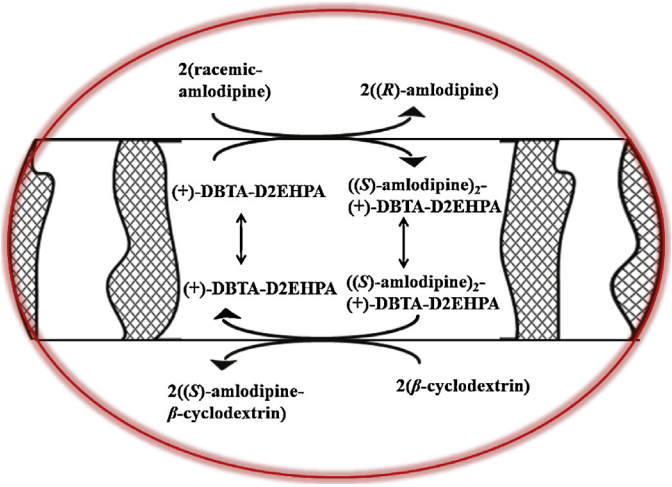


**Fig. 1.** Schematic of transport flux within HFSLM.

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