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Mass transfer modelling of the extraction of antibiotics from aqueous solution using Biosurfactants

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***Abstract*— The objective of this work is to modelling a new separation technique based on the removal of antibiotics such as amoxicillin and ampicillin produced by antibiotical company Saidal Médéa (Algeria) from pharmaceutical effluents using biosurfactants and commercial surfactants.**

The kinetic distribution of amoxicillin and ampicillin between the two phases was modelled in order to well understand the mechanism governing the direct transfer of antibiotics from the aqueous phase to the micellar phase. The results were interpreted in terms of a two-film theory for flat interface.

The model of the kinetic transfer developed in this study provides excellent predictions. A very good correlation between predicted and experimental values was found : R2 = 0.98 for the sorption onto biosurfactant and R2 = 0.99 onto a synthetic surfactant. The model coefficients were used to estimate the overall combined mass transfer coefficient and the individual mass transfer coefficients.

Keywords—Modelling; two-film theory Mass Transfer; Extraction; Antibiotics

I. INTRODUCTION

The occurrence and fate of pharmaceutically active compounds in the aquatic environment has been recognized as one of the emerging issues in environmental chemistry [1]. Among pharmaceuticals, antibiotics are the most widely used family of drugs for improving human health, preventing and treating animals and plants infections as well as for promoting growth in animal farming and aquaculture operations [2,3]. All these applications made antibiotics to be released in large amounts in natural ecosystems [4]. They have been detected in many environmental samples worldwide including wastewater treatment plant effluents, hospital sewage water, surface water, seawater, rivers and groundwater [5,6,7].

The presence of antibiotics in the environment is a concern because they could change microbial ecology, increase the proliferation of antibiotic resistant pathogens, provoke toxic effect on aquatic species and negative effect on human health [8,9]. For these reasons, effluent containing antibiotics needs to be treated to prevent the adverse effects from contaminated water [2]. Several methods have been attempted for the removal of antibiotic drugs from different water matrix. These include coagulation, biodegradation, chlorination, oxidation processes, nanofiltration, ozonation and adsorption [9,10]. However, only a few reports have been published on the removal of antibiotics from wastewater using surfactants. These molecules are of great importance because of their amphiphilic structure which is responsible for causing them to concentrate at interface or to self-assemble to form various micellar structures [11]. In addition to these properties, biosurfactants offer the advantage of being biodegradable and nontoxic. Recently, micellar systems have attracted much attention as a novel method for separating many biological products. Boukhelkhal et al. [12] have investigated the elimination of amoxicillin antibiotic anionic surfactant.

The present work has for object to make a contribution to the purification of the aqueous environments contaminated by

antibiotics using a novel separation technique based on an aqueous surfactant extraction. To this end, we studied the treatment of a complex medium consisting of a mixture of both antibiotics amoxicillin and ampicillin using a synthetic surfactant and a biosurfactant. In order to understand the mechanism governing the forward transfer of antibiotics from the aquous phase to the micellar phase, a model was developed regarding the kinetic partitioning of amoxicillin and ampicillin between the two considered phases. Results were interpreted in terms of a two-film theory for flat interface.

II. Materials and Methods

A. Chemicals

The antibiotic drugs amoxicillin and ampicillin (see structures in Fig. 1) were kindly furnished by the pharmaceutical company SAIDAL of Medea (Algeria) and used as pharmaceutical effluents. The selection of these drugs for this study was made according to the most often prescribed antibiotics produced by SAIDAL company. Standard solution of AMX and AMP were daily prepared before use by dissolving the drugs in water. Water was distilled using water still apparatus (Model IM-100) and deionized by passing through Elga B114 deionizer to minimize its conductivity.

Anionic surfactant sodium dodecyl sulfate (SDS) 90% was purchased from FLUKA. Acetonitrile (HPLC grade) was obtained from Panreac. Methanol (HPLC grade) was obtained from Fluka. Potassium dihydrogen phosphate and phosphoric acid, all analytical grade, were purchased from Riedel-deHaèn.

B. Analysis

The amoxicillin and ampicillin concentrations in the solution was analyzed using high performance liquid chromatography with UV-visible detection. The HPLC system used was a Model Shimadzu LC-10A. It was equipped with an injector with a loop of 20 µL, on-line degasser (DGU-12A), a pump (LC-10 ADVP), a diode array detector (SPD-10AVvp) and a thermostated column oven. The column (125mm×4.6mm) was a reverse phase C18. An isocratic mobile phase consisted of a mixture of acetonitrile (90%) and aqueous buffer (10%) was used. Instrument control, data acquisition and data processing were carried out using CLASS VP software.

C. Adsorption study

Competitive adsorption experiments were conducted in binary antibiotic systems in order to study the capacity of biosurfactant to remove amoxicillin and ampicillin. An antibiotic solution at a concentration of 4 mg / l was prepared by dissolving antibiotics powder in deionized water. A sample of this initial solution was subjected to HPLC analysis. The adsorption tests were carried out in a batch system by adding 0,25 g of the biosurfactant to 100 ml of the antibiotics solution placed in a 250 ml Erlenmeyer flask and the solution was shaken at 100 rpm at 25°C for a given contact time. A sample of the residual solution was taken by means of a syringe and filtered through a syringe filter. The filtrate was transferred to a vial and 20µl of this solution was injected onto the HPLC system. The quantification was based on the peak area of each analyte.

III. Mass Transfer Model Development

The two-film theory described below (Fig. 1) is the most model used to describe the mass transfer in micellar systems.

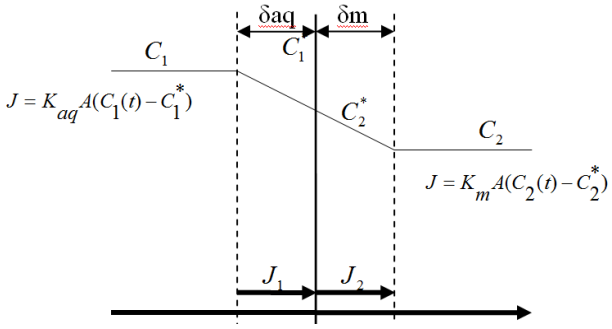


Fig. 1. Concentration profiles at the interface in the two-film theory

The extraction of antibiotics is governed by the transfer of amoxicillin and ampicillin molecules from the aqueous phase to the micellar phase. In fact, the two phases involved in this study are the aqueous phase (phase 1 with a volume V_1 and an amoxicillin concentration at time t of $C_1(t)$) and the organic phase (phase 2 with a constant volume V_2 and an antibiotic concentration $C_2(t)$). At the start of the extraction experiments, all the effluent reside in the aqueous phase, and thus the concentration of antibiotic in the two phases is $C_1(t)=C_1(0)$ and $C_2(t)=0$. So the mass balance of amoxicillin in the system at any given time is :

$$V_1 C_1(0) = V_1 C_1(t) + V_2 C_2(t) \quad (1)$$

At the equilibrium, the relative concentrations would be given by $C_1^* = mC_2^*$, where m is the equilibrium partition coefficient (assumed to be constant under given conditions). C_1^* and C_2^* are the equilibrium concentrations of antibiotic in phases 1 and 2, respectively. Therefore, the value of equilibrium partition coefficient is given by:

$$m = \frac{C_1(\infty)}{C_2(\infty)} \quad (2)$$

As a two-film model is used to describe solute transfer, the mass transfer rate is given by:

$$J = KA(C_1(t) - C_1^*) \quad (3)$$

where K is the overall mass transfer coefficient and A is the total interfacial area between the two phases. Thus:

$$V_1 \frac{dC_1}{dt} = -KA(C_1(t) - mC_2(t)) \quad (4)$$

In this study, the actual interfacial area between the two phases is unknown, and thus we can only obtain a combined mass transfer coefficient, KA, having units of m^3/s. Rearrange Eq. (1) in terms of $C_2(t)$ gives:

$$C_2(t) = \frac{1}{V_2}\left(V_1C_1(0) - V_1C_1(t)\right) \quad (5)$$

Then substituting $C_2(t)$ in Eq. (4) and rearranging gives:

$$\frac{dC_1}{dt} = -\frac{KA}{V_1}(1+mV_r)\left[C_1(t) - \left(\frac{mV_r}{1+mV_r}\right)C_1(0)\right] \quad (6)$$

Where Vr is the phase volume ratio (V_r=V_1/V_2).

Integrating Eq. (6) between the limits $C_1(0)$ and $C_1(t)$ and rearranging gives:

$$C_1(t) = C_0\left((1-\beta)\exp(-\alpha t) + \beta\right) \quad (7)$$

Where,

$$\alpha = \frac{KA}{V_1}(1+mV_r) \quad (8)$$

and,

$$\beta = \frac{mV_r}{1+mV_r} \quad (9)$$

The overall resistance to antibiotics transfer, as represented by KA, can be described as the sum of the resistances of both aqueous and micellar boundry films, then the overall combined mass transfer coefficient can be represented as :

$$\frac{1}{KA} = \frac{1}{K_{aq}A} + \frac{m}{K_mA} \quad (10)$$

Where,

$K_{aq}A$: Individual aqueous phase mass transfer coefficient.

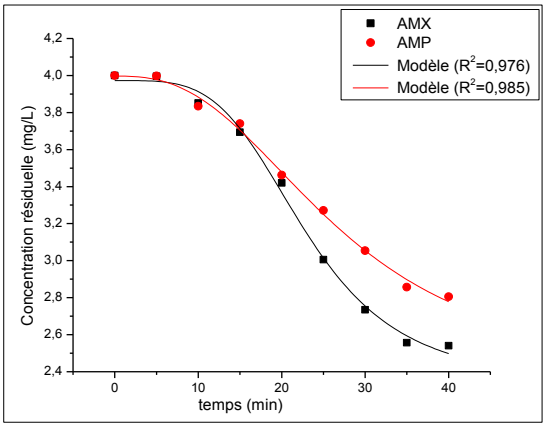
$K_{aq}A$: Individual micellar phase mass transfer coefficient.

It should then be probable to estimate the individual mass transfer coefficients ($k_{aq}A$ and k_mA) since a plot of $1/KA$ against m should yield a straight line of gradient $1/k_mA$ and intercept $1/k_{aq}A$.

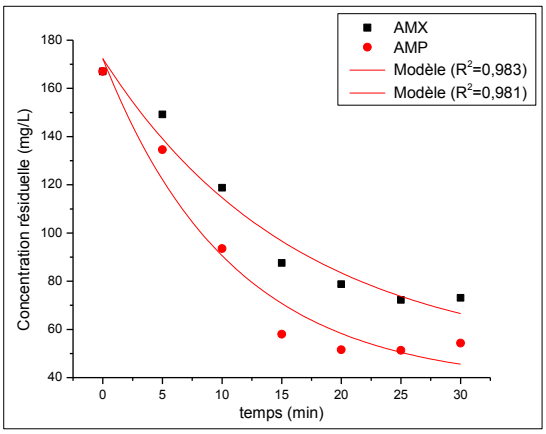
IV. Results and Discussions

After In order to verify that Eq. (7) described the antibiotic transfer from aqueous phase to micellar phase according to the two film model, the experimental results ($C_1(t)$ versus t data) were modelling using a microcomputer program. This program written in MATLAB language uses the "fminsearch" function to optimise the model coefficients according to the non-linear least-squares method.

The theoretical and experimental results are compared in Fig. 2 in which the solid lines represent the results of the two film model while the points with labels are the experimental results. It was found that the experimental results fit well the model with a correlation coefficient R^2 of 0.983 for amoxicillin and 0.981 for ampicillin.



(a)



(b)

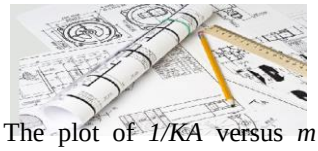
Fig. 2. Time-course of amoxicillin and ampicillin adsorption on SDS (a) and on biosurfactant (b)

The values of model coefficients α and β given by the program were then inserted into Eqs. (8) and (9) to calculate the combined mass transfer coefficient (KA) as shown in Table 1.

TABLE I. Values of model coefficients and combined mass transfer coefficent

		α	β	KA (m^3/s)	R^2
SDS	***AMX***	0,215	0,630	$3,89.10^{-6}$	0,976
	AMP	0,085	0,661	$1,61.10^{-6}$	0,985
Biosurfactant	***AMX***	0,087	0,214	$1,19.10^{-5}$	0,983
	AMP	0,054	0,249	$8,62.10^{-5}$	0,981

By comparing obtained overall combined mass transfer coefficients, we affirm the high aptitude of transfert of antibiotics molecules from the aquous phase to the micellar phase of biosurfactant.



The plot of *1/KA* versus *m* yield a straight line. These results allows to estimate the combined film mass transfer coefficients $k_{aq}A$ and k_mA wich are of 4.5331×10^{-6} m^3/s and 2.3771×10^{-5} m^3/s, respectively (Table II).

TABLE II. VALUES OF INDIVIDUAL MASS TRANSFER COEFFICENTS

		$K_{aq}A$ (m^3/s)	K_mA (m^3/s)
SDS	***AMX***	$1{,}32.10^{-6}$	$8{,}73.10^{-5}$
	AMP	$3{,}45.10^{-6}$	$5{,}11.10^{-5}$
Biosurfactant	***AMX***	$7{,}16.10^{-5}$	$3{,}53.10^{-4}$
	AMP	$4{,}32.10^{-5}$	$2{,}19.10^{-4}$

Since $k_{aq}A < k_mA$, the diffusion in the aqueous phase is the rate limiting step for the transfer of amoxicillin and ampicillin from aqueous phase into micellar phase.

V. CONCLUSION

In this study, the ability of a synthetic and a biological surfactants to remove amoxicillin and ampicillin antibiotics present in aqueous solution was tested using kinetic aspects.

The profiles of the transfer of the considered antibiotics between the aqueous phase and the micellar phase were studied at laboratory scale. In the aim to understand the mechanism governing the forward transfer of the considered antibiotics, a model was developed regarding the kinetic partitioning of amoxicillin and ampicillin between the two considered phases. It was shown that the transfer process was successfully modeled using the general two-film theory of mass transfer to flat interface with a correlation coefficient of 0,98 and 0,99 for the adsorption onto biosurfactant and synthetic surfactant, respectively. The model coefficients were used to estimate the overall combined mass transfer coefficient and the individual mass transfer coefficients.

The obtained values of overall combined mass transfer coefficients explain the high aptitude of transfert of antibiotics molecules from the aquous phase to the micellar phase of biosurfactant.

The obtained values of individual mass transfer coefficients affirm that the diffusion in the aqueous phase is the rate limiting step for the transfer of antibiotics molecules from aqueous phase into micellar phase.

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