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Kinetic of Alkaloids Extraction from Plant by Batch Pertraction in Rotating Discs Contactor

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Abstract

A liquid membrane process of Alkaloids extraction from Datura Innoxia solution was studied applying pertraction process in rotating discs contactor (RDC). Decane as a liquid membrane and dilute sulphuric acid as stripping solution were used. The effect of the fundamental parameters influencing the transport process, e.g. type of solvent used, effect of disks speed, amount of liquid membrane and effect of pH for feed and strip solution. The transport of alkaloids was analysed on the basis of kinetic laws of two consecutive irreversible first order reactions. Thus, the kinetic parameters (k_1, k_1, R_m^{max}, t_{max}, $J_F^{max}$and J_S^{max}) for the transport of alkaloids were determined. The effect of organic membrane type on percentage of Alkaloids transport was found to be in the order (n-decane> n-heptane> n-hexane> ethyl ether). The results showed that the highest alkaloids extraction was obtained when using two stages, (10 rpm) discs speed, (pH=9.5) of feed solution and (pH=2) of acceptor solution in n-decane. Observation showed that the membrane entrance rate constant k_1 and percentage of alkaloids transported in strip phase increased with increasing numbers of stages but the exit rate constant k_2 decreased. The alkaloids extraction ratio increased with increasing the disks speed from 5 to 10 rpm but decreased at 15 rpm and decreased when increasing the volume of membrane. Also pH of feed and strip solution affected the extraction ratio and rate constants.

Keywords: extraction, batch pertraction, liquid membrane, alkaloids, kinetic, rotating disc contactor.

Introduction

Plants have been used as medicine for a long time. Many of the natural products in plants of medicinal value offer new sources of drugs which have been used effectively in traditional medicine [1].

For medicinal interest, atropine alkaloid (chemical structure is shown in Fig. 1) is found in plants of the *solanaceae* family, such as *Atropa, Datura, Duboisia and Hyoscyamus*. Atropine is the chief alkaloid in *Atropa belladonna*. It can be extracted from the plant as free bases using basic aqueous solution or as salts using acidified solution [2].

The liquid membrane technology has been effectively used to treat aqueous streams contaminated with metal ions [3].

The liquid membrane extraction was introduced as an alternative separation technique to the liquid-liquid

extraction and to separation by means of solid polymeric membrane [4].

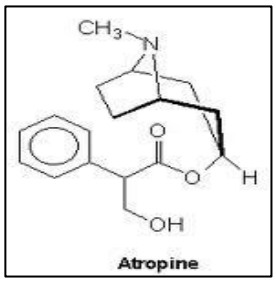

Fig. 1: Chemical structure of Atropine Alkaloid

This property of membranes makes them useful in the textile and food industries, in hydrometallurgy, medicine, biotechnology, environmental protection, in the separation of hydrocarbons and gases, and in the concentration and separation of amino acids, metal ions and other mixtures and suspensions [5] [6]. This method provides low cost, simplicity, high efficiency and energy saving in comparison to other process. In the recent years, a remarkable increase of the application of liquid membranes has included bulk liquid membrane (BLM), emulsion liquid membrane and supported liquid membrane [7].

A kinetic study of alkaloids transport through a liquid membrane was studied. The influence of pH in the aqueous feed solution and pH of stripping solution were also studied and the effect of stirring speed of disks, type and amount of liquid membrane on the transport of atropine through a BLM were studied. The consecutive irreversible first- order apparent rate constants, k_1 and k_2, have been determined.

In the present work, transport of Alkaloids n-decane bulk liquid membrane was studied. Different experimental conditions, such as the effect of pH in feed and stripping solution, the rate of stirring speed and effect of time were also investigated.

Experimental Work

1. Chemicals and Reagents

Studies of Alkaloids permeation through the liquid membrane were carried out using atropine aqueous solutions. The atropine was extracted from *Datura innoxia* seeds (collected in 2011, from the region of the College of Agriculture- University of Baghdad-Iraq) applying solid–liquid extraction. Various reagents were used in this work as liquid membrane, n-decane (99% BDH), n-hexane (95% ALDRICH), n-heptane (99.5 HOPKIN and WILLIAMS) and ethyl ether (99% Fluka AG). Ammonia (25% CHEM-SUPPLY) and sulfuric acid (98% GCC) were used to adjust the acidity of the aqueous solutions.

2. Instruments

The concentration of atropine alkaloids in the strip solution was measured by UV-spectrophotometer SP-3000 (OPTIMA INC) at wave length λ=257 nm. The pH values of the aqueous solutions were measured by means of the laboratory pH meter (CRISON, MM40).

3. Three Phase Experiment

3.5 grams of *Datura innoxia* seeds were milled to fine powder and leached by 250 ml of buffer solution of (NH_3-$(NH_4)_2SO_4$) adjusted to appropriate pH. This solution was shaken for half an hour and filtered to obtain the feed solution.

The stripping solution was adjusted to appropriate pH using few drops of sulfuric acid. Using this type of acid and at the membrane/receiver interface, conditions were appropriate for atropine stripping and its accumulation in the receiver phase as atropine sulphate, which is insoluble in the organic liquid membrane.

N-decane, n-hexane, n-heptane and ethyl ether were used as organic liquid membrane.

4. Bulk Liquid Membrane

Among the large variety of liquid membrane technique, the pertraction in rotating discs contactor (RDC) model was selected due to its stability [8, 9]. Kinetic of atropine alkaloids in three phases system was studied in laboratory RDC, presented schematically in Fig. 2. The lower part of the contactor is divided into four compartments: two for the feed and two for the stripping solution. The liquid membrane covers both aqueous solution and occupies the common upper part of the contactor. Four hydrophilic membrane disks (1mm thickness and 18 cm in diameter) were fixed on a horizontal shaft and their lower parts immersed to compartments, with disks, in which aqueous phases (feed or strip) were immersed and due to rotation, were contacted with the LM phase. Two peristaltic pumps were used to circulate both aqueous solutions to homogenize the aqueous solutions and to eliminate the dead zone or minimize it. For constant shaft rotating in small rpms, DC-motor (50 rpm) and variable DC power supply were used. The hydrophilic disks for each stage were made from stainless steel because of its resistance against the acids and bases with the added advantages of being very hygienic and easy to clean.

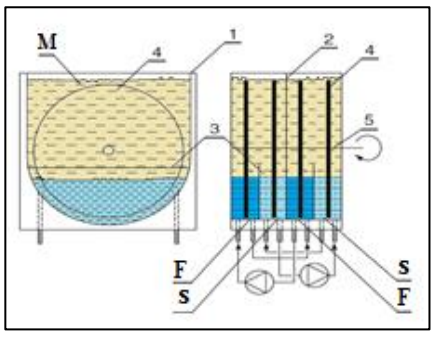

Fig. 2: Scheme of a rotating film contactor: (1) Body, (2) Stage wall, (3) Feed/Stripping solution separating walls, (4) Rotating discs, and (5) Common shaft

5. Kinetic Procedure

Variation of atropine alkaloids concentration with time was directly determined on both feed (g/cm^3) and strip (g/cm^3) phases using UV-spectrophotometer SP-3000 at wave length λ=257 nm. The corresponding change of atropine concentration in the membrane phase was determined from the material balance between the phases. For practical reason, dimensionless reduced atropine alkaloids concentration in the feed (R_F), membrane (R_m) and strip (R_S) phases were used [10, 11].

$$R_F = \frac{C_F}{C_{F0}}, R_m = \frac{C_m}{C_{F0}}, R_S = \frac{C_S}{C_{F0}} \quad \ldots(1)$$

Where C_{f0} is the initial concentration of Atropine Alkaloids in the feed (donor) phase while C_F, C_m, and C_S, are the atropine concentration in feed (donor), membrane and strip (acceptor) phases, respectively. From this expression, the material balance can be established as $R_F + R_m + R_S = 1$. When R_F, R_m and R_S values are inspected, the results suggest that atropine alkaloids transport obeys the kinetics of two consecutive irreversible first order reactions according to the kinetic scheme [11].

$$C_F \xrightarrow{k1} C_m \xrightarrow{k2} C_S \quad \ldots(2)$$

Where k_1 and k_2 are the pseudo-first apparent rate constants for the membrane entrance and exit, respectively. The kinetic scheme for consecutive reaction systems can be described by considering the reduced concentrations as follows [11, 12]:

$$\frac{dR_F}{dt} = k_1 R_F = J_F \quad \ldots(3)$$

$$\frac{dR_m}{dt} = k_1 R_F - k_2 R_m \quad \ldots(4)$$

$$\frac{dR_S}{dt} = k_2 R_m = J_S \quad \ldots(5)$$

Where J is the flux when $k_1 \neq k_2$ and the integration of the above differential equation gives:

$$R_F = \exp(-k_1 t) \quad \ldots(6)$$

$$R_m = \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \quad \ldots(7)$$

$$R_S = 1 - \frac{1}{k_2 - k_1}[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \quad \ldots(8)$$

Where t is the time elapsed.
Substituting Eqs. 6 – 8 into Eqs. 3 – 5, Ji can be expressed as:

$$J_F = -k_1 \exp(-k_1 t) \quad \ldots(9)$$

$$J_m = \frac{k_1}{k_2 - k_1}[k_2 \exp(-k_2 t) - k_1 \exp(-k_1 t)] \quad \ldots(10)$$

$$J_S = \frac{k_1 k_2}{k_2 - k_1}[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t) \quad \ldots(11)$$

When J_m (Eq. 10) is equal to zero, the maximum fluxes of metal transport across BLM are achieved as follows [13]:

$$J_F^{max} = -k_1 \exp(-k_1 t_{max}) \quad \ldots(12)$$

$$J_m^{max} = \frac{k_1}{k_2 - k_1}[k_2 \exp(-k_2 t_{max}) - k_1 \exp(-k_1 t_{max})] = 0 \quad \ldots(13)$$

$$J_S^{max} = \frac{k_1 k_2}{k_2 - k_1}[k_2 \exp(-k_1 t_{max}) - k_1 \exp(-k_2 t_{max}) \quad \ldots(14)$$

Where J_F^{max} and J_S^{max} are the maximum fluxes of atropine transport in feed and stripping phases, respectively, while t_{max} is the time at which the maximum fluxes are accomplished. From Eq. 13, t_{max} is derived as [13]:

$$t_{max} = \frac{\ln(\frac{k_1}{k_2})}{k_1 - k_2} \quad \ldots(15)$$

Substituting Eq. 15 into Eq. 7, the value of R_m at t_{max}, i.e. R_m^{max} , is obtained as follows [13].

$$R_m^{max} = (\frac{k_1}{k_2})^{-k_2/(k_1 - k_2)} \quad \ldots(16)$$

Since J_m^{max} is equal to zero (Eq. 13), the system is in steady state and, hence, J_F^{max} (Eq. 12) and J_S^{max} (Eq. 14) are equal to each other but of opposite signs, i.e.

$$-J_F^{max} = J_S^{max} \quad \ldots(17)$$

Results and Discussion

1. Effect of Type of Solvent (Liquid Membrane)

The transport study of atropine alkaloid was carried out in different solvents; n-decane, n-heptane, n-hexane and ethyl ether, at pH of feed (pH_F =9.5), pH of strip (pH_S= 2), stirring discs speed= 10 rpm and volume of membrane =500 ml.
The transport efficiency of atropine alkaloid was found to be good when using n-decane. But the transport efficiency was found to be less with n-heptane, n-hexane and ethyl ether as shown in Fig. 3 and Table 1. About 75.41% of atropine was transported to the striping solution.

Table 1: The Kinetic parameters for the extraction of Atropine at different solvents

Type of solvent	k_1 (min^{-1})	k_2 (min^{-1})	t_{max} (min)	R_m^{max} (--)	J_F^{max} (min^{-1})	J_S^{max} (min^{-1})	%Atropine in S phase
n-decane	0.00817	0.087	30	0.073	-0.00639	0.00639	75.41
n-heptane	0.00422	0.065	45	0.052	-0.00349	0.00349	71.06
n-hexane	0.00304	0.074	45	0.036	-0.00266	0.00266	24.61
Eth. Eth.	0.01742	0.005	30	0.043	-0.01033	0.01033	20.47

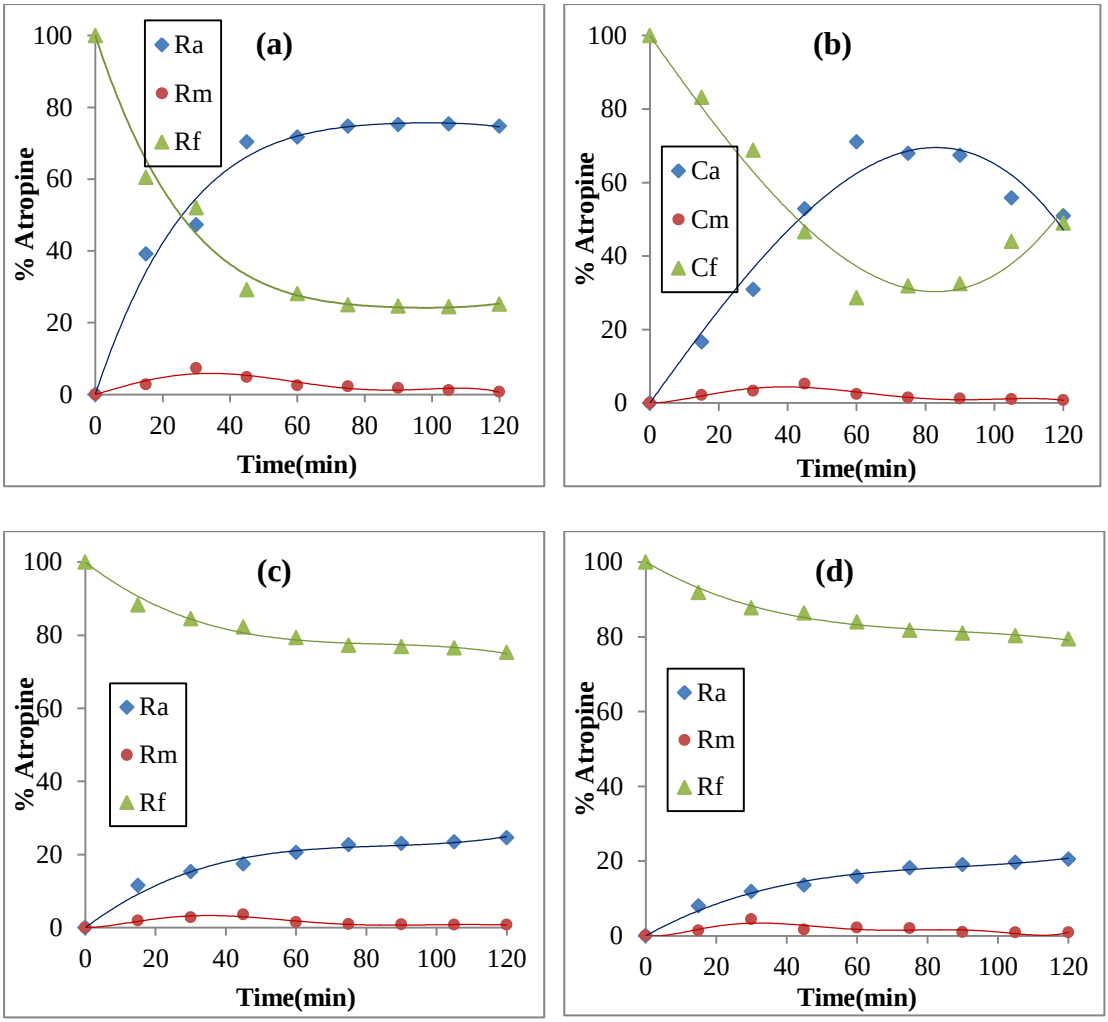

Fig. 3: Effect type of solvent on Atropine; a. n-decane b .n-heptane c. n-hexane d. Ethyl Ether (experimental conditions: pH_F=9.5, pH_S=2, 10 rpm and one stage at 27 ℃)

2. Effect of Agitation Speed

It is well known that hydrodynamic conditions play an important effect in mass transfer from one phase to another phase at the interface between two liquid phases. In order to examine the effect of hydrodynamics on the atropine extraction, experiments were carried out with different agitation speeds, 5, 10 and 15 rpm at pH of feed (pH_F =9.5), pH of strip (pH_S = 2), stirring discs speed= 10 rpm and volume of membrane =500 ml. The percentage of atropine extracted is plotted versus time at different agitation speeds in Fig. 4. Higher rotation speed was not applied because of the increased risk of droplet formation and process deterioration [14].

The rate constant k_1 and k_2 were determined from Equations 15 and 16 and are shown in Table 2.

Table 2: The kinetic parameters for the extraction of Atropine at different agitation Speed

Agitation Speed(rpm)	k_1 (min^{-1})	k_2 (min^{-1})	t_{max} (min)	R_m^{max} (--)	J_F^{max} (min^{-1})	J_S^{max} (min^{-1})	%Atropine in S phase
15 rpm	0.00367	0.0688	45	0.045	-0.00311	0.00311	17.62
10 rpm	0.00817	0.0870	30	0.073	-0.00639	0.00639	75.41
05 rpm	0.00336	0.0475	60	0.057	-0.00275	0.00275	22.64

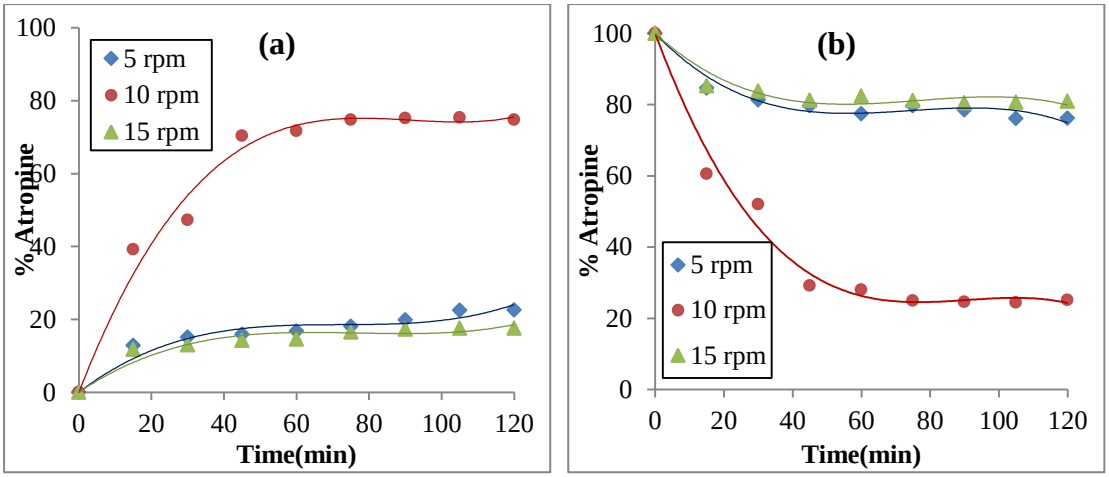

Fig. 4: Effect of agitation speed; a. %Atropine in stripping phase b. %Atropine in Feed phase (experimental conditions: pH_F=9.5, pH_S=2, one stage and 500ml of n-decane as liquid membrane)

3. Effect of pH of Feed Solution

The pH of feed solution plays an important effect on the extraction of atropine. In order to study the effect of pH in the feed phase (pH_F) on the mass transfer performance of pertraction process, pH in the feed phase is adjusted with ammonia buffer solution. Experimental studies were carried out at various pH values from 7 to 12.

Preliminary tests were carried out to find the optimum pH_F solution. The results of the atropine extraction experiments are shown in Fig.5. It is to be concluded that the best pH for the feed solution that gave good extraction is around 9.5.

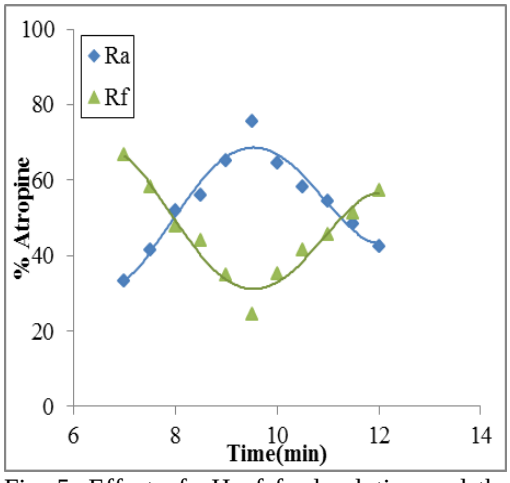

Fig. 5: Effect of pH of feed solution and the best pH for extraction of Atropine (experimental conditions: pH_S=2, 10 rpm, one stage and 500ml of n-decane as liquid membrane)

4. Effect of pH of Striping Solution

The effect of pH of striping solution (pH_S) was studied for the range 1.5 – 3 and the results of atropine transport is shown in Fig. 6. The percentage of atropine alkaloid extracted in striping solution were 43.76, 75.41 and 52.08 at pH=1.5, pH=2 and pH=3 for striping solution, respectively. The results showed that higher extraction ratio for atropine was at pH_S=2.

It is observed that the pH of the aqueous acceptor phase played an important role on the extraction of atropine values when all the experimental conditions were kept constant except for the pH value of acceptor solution.

5. Effect of Number of Stages

Increasing the number of stages in RDC design plays an important role to increases the extraction efficiency. The results of atropine extraction using one and two stages are presented in Fig. 7.

Using two stages mean four hydrophilic discs and this will increase the surface area in contact with the feed solution. Therefore, atropine alkaloid exhausting from seeds increases and the same increase occurs in membrane. On the other hand, increasing the number of stages leads to an increase in surface area in contact with the striping solution. Thus H_2SO_4

molecules in membrane are increased. Therefore, using two stages gave higher %atropine extract than that from one stage.

Table 3 shows that increasing the number of stages decreases the rate constant exit k_2 while the rate constant entrance k_1 increases.

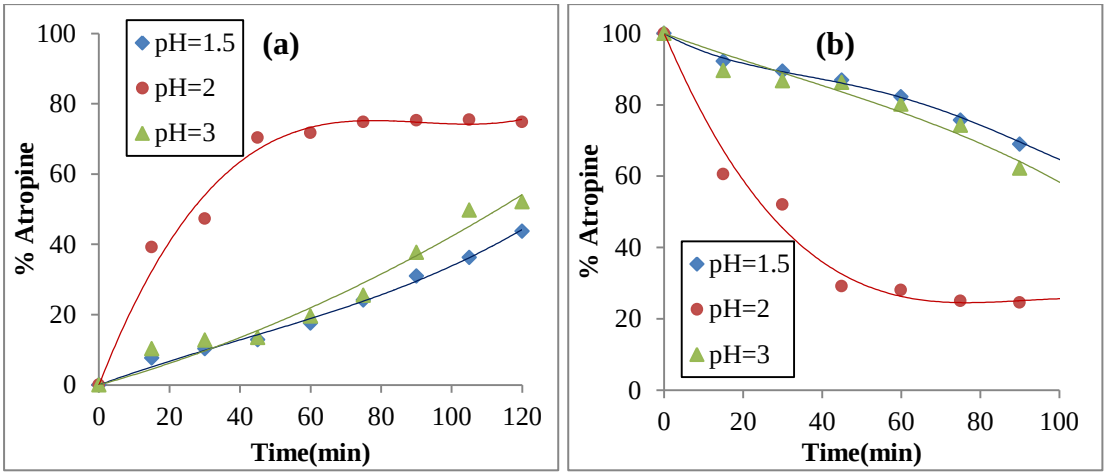

Fig. 6: Effect of pH of stripping solution; a. %atropine in striping phase b. % atropine in feed phase (experimental conditions: pH_F=9.5, 10 rpm, one stage and 500 ml of n-decane as liquid membrane)

Table 3: The Kinetic parameters for the extraction of Atropine at different number of stages

Number of Stages	k_1 (min^{-1})	k_2 (min^{-1})	t_{max} (min)	R_m^{max} (--)	J_F^{max} (min^{-1})	J_S^{max} (min^{-1})	%Atropine in S phase
One stage	0.00817	0.0870	30	0.073	-0.00639	0.00639	75.41
Two Stage	0.00837	0.0860	30	0.075	-0.00652	0.00652	89.93

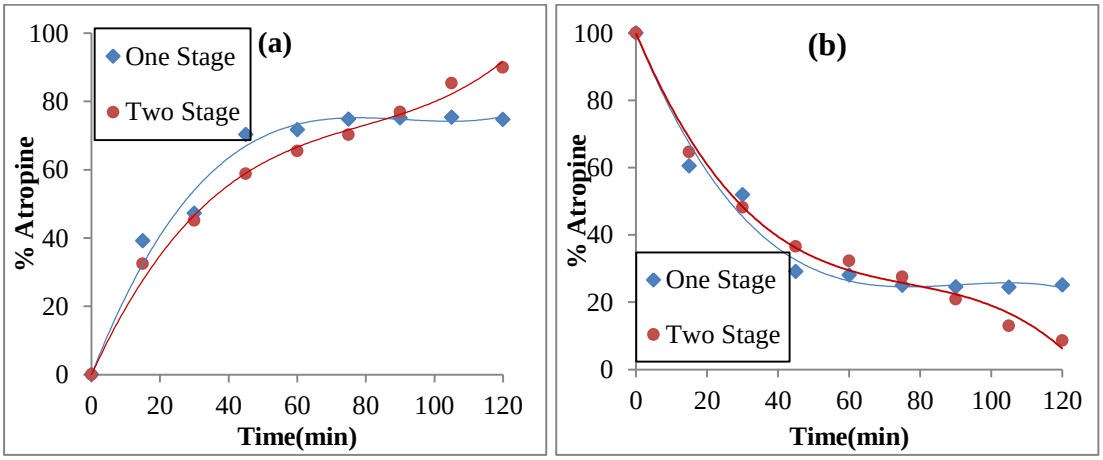

Fig. 7: Effect of number of stages; a. %atropine in striping phase b. % atropine in feed phase (experimental conditions: pH_F=9.5, 10 rpm and 500 ml of n-decane as liquid membrane)

6. Effect of the Amount of Liquid Membrane

The pertraction study of atropine was carried out in two amounts of liquid membrane 500 and 1000 ml. It can be seen from Figure 8 and Table 4 that the increase of liquid membrane volume gave negative effect if the surface area is kept constant. If surface area was increased, it may lead to increasing percentage atropine extract because more time is needed for the atropine and sulphate ion to meet together in the membrane to form atropine sulphate. This is shown in Figure 8 and Table 4.

Table 4: The Kinetic parameters for the extraction of Atropine at different amount of organic liquid membrane

Amount of membrane	k_1 (min^{-1})	k_2 (min^{-1})	t_{max} (min)	R_m^{max} (--)	J_F^{max} (min^{-1})	J_S^{max} (min^{-1})	%Atropine in S phase
500 ml	0.00817	0.0870	30	0.073	-0.00639	0.00639	75.41
1000ml	0.00722	0.0504	45	0.103	-0.00522	0.00522	19.63

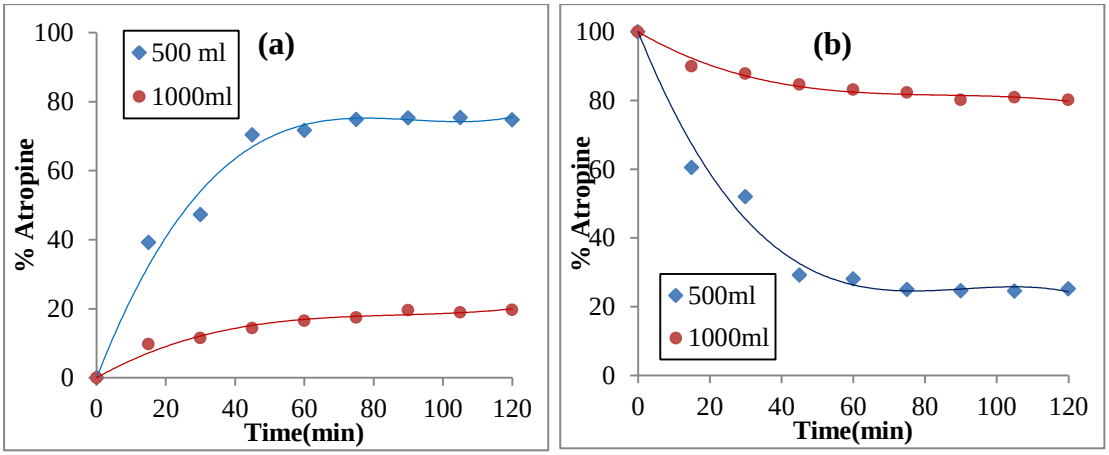

Fig. 8: Effect of amount of liquid membrane a. %atropine in striping phase b. % atropine in feed phase (experimental conditions: pH_F=9.5, 10 rpm and n-decane as liquid membrane for one stage)

Conclusion

Atropine alkaloid can be transported and extracted by RDC through organic liquid membrane. The percentage of atropine alkaloid extracted by RDC depends on many important parameters such as rate of stirring speed of discs, type of liquid membrane, volume of liquid membrane and pH of feed and striping phases. The extraction efficiency of atropine alkaloid increased with increasing discs rotation speed from 5 to 10 rpm. Increasing it to 15 rpm, the percentage of atropine alkaloid decreased because of the increased risk of droplet formation and process deterioration. 89.93 % of atropine was transported when two stages were used. The apparent rate constants, k_1 and k_2, interfacial transport of extraction and re-extraction are determined on the basis of a scheme implying two consecutive irreversible first order reactions. This method offers important advantages such as simplicity and economy.

Nomenclature

Notation	Description
RDC	Rotating Disc contactor
F	Feed
S	Stripping
k_1	Entrance rate constant
k_2	Exit rate constant
pH_F	pH of feed solution
pH_S	pH of striping solution
rpm	Revolution per Minute.
DC-motor	Direct Current Motor.
UV	Ultraviolet Visible.
C_F	Concentration of atropine in feed solution
C_{F0}	Initial concentration of atropine in feed solution
C_m	Concentration of atropine in liquid membrane
C_S	Concentration of atropine in striping solution
R_F	Dimensionless concentration in feed solution
R_m	Dimensionless concentration in membrane solution

R_S	Dimensionless concentration in striping solution
J	Flux
J_F^{max}	The maximum fluxes of atropine transport in feed phase
J_S^{max}	The maximum fluxes of atropine transport in stripping phase
λ	wave length
t_{max}	The time at which the maximum flux
R_m^{max}	Maximum dimensionless concentration in membrane solution
Eth. Eth.	Ethyl Ether

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