Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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L. Boyadzhiev[a]; S. Alexandrova[a]
[a] INSTITUTE OF CHEMICAL ENGINEERING BULGARIAN ACADEMY OF SCIENCES, SOFIA, BULGARIA

To cite this Article Boyadzhiev, L. and Alexandrova, S.(1992) 'Dephenolation of Phenol-Containing Waters by Rotating Film Pertraction', Separation Science and Technology, 27: 10, 1307 — 1317
To link to this Article: DOI: 10.1080/01496399208019427
URL: http://dx.doi.org/10.1080/01496399208019427

SEPARATION SCIENCE AND TECHNOLOGY, 27(10), pp. 1307–1317, 1992

Dephenolation of Phenol-Containing Waters by Rotating Film Pertraction

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L. BOYADZHIEV and S. ALEXANDROVA
INSTITUTE OF CHEMICAL ENGINEERING
BULGARIAN ACADEMY OF SCIENCES
SOFIA 1113, BULGARIA

Abstract

The mass transfer of phenol in a rotating film (RF) pertractor was studied and the optimum performance regime for the system phenolic water–*n*-nonane–sodium hydroxide solution was obtained. The distribution coefficient of phenol between the hydrocarbon used and water is measured experimentally for various initial concentrations of the solute, and the corresponding relationship for 22°C is derived. A mathematical model is developed to describe the batch process of phenol removal in an RF pertractor. Based on the experimental results obtained and on the mathematical model proposed, the local mass transfer coefficients were evaluated and the effect of disc rotation speed was studied.

INTRODUCTION

Many chemical and pharmaceutical plants worldwide generate large amounts of phenol-containing wastewaters. Phenol concentrations in various effluents of that kind vary in a wide range from several ppm to 2–3%.

Regarding subsequent wastewater treatment, various purification techniques are employed, depending on the particular process objectives. Some processes are aimed at phenol recovery and concentration for further reuse and generally involve extraction, adsorption, and evaporation operations. Other cases pursue degradation of phenolic contaminants and involve biological or incineration processes.

One of the most effective and widely practiced methods for water dephenolation is based on solvent extraction using polar organic solvents with high distribution coefficients of the solute. An important disadvantage of this method, however, is the relatively high solubility of these solvents in the raffinate (*1*). To remove the solvent, additional purification steps are usually required, which increases the purification costs. This can be overcome if solvents, exhibiting very low solubility in water, for example, normal paraffins of nine or more carbon atoms in the chain, are used. But paraffins are rarely used in solvent extraction since the distribution coefficients of phenol between the hydrocarbon and water phases are low. However, if the liquid–liquid extraction process is replaced by a liquid membrane process, the low distribution coefficients no longer present a problem for phenol removal (*2*).

The interest in liquid membrane, or pertraction techniques, has grown considerably in recent years. All three groups of pertraction methods [namely, emulsion liquid membranes (ELM), supported liquid membranes (SLM), and bulk liquid membranes (BLM)], have been the subject of intensive studies. The last group of liquid membrane methods, which includes the creeping film (CFP) (*3*) and the rotating film pertraction (RFP) (*4*) techniques, avoids the main shortcomings of the ELM and SLM methods.

A large number of membrane liquids have been used for phenol pertraction: various hydrocarbons or hydrocarbon mixtures, isoparaffins (*6*, *8*, *14*), normal paraffins (*3*, *7*, *10*), silicone oil (*5*), kerosene (*12*, *13*, *15*), methyl isobutyl ketone (*9*, *11*, *15*), mono-*n*-alkylbenzene (*10*), mineral oil (*7*), xylene (*9*), *n*-butanol (*9*), etc.

The receiving or acceptor phase in all studies has been a water solution of sodium or another alkaline hydroxide, capable of transforming phenol irreversibly into a phenolate. The latter cannot be transferred back across the organic phase, and thus the phenol is concentrated in the acceptor solution.

The aim of the present work is to study the transfer of phenol using *n*-nonane as the membrane phase in a rotating film pertractor.

TRANSFER MECHANISM

Phenol is transported in the three-liquid phase system being studied according to the transfer mechanism illustrated in Fig. 1. This mechanism is regarded as a typical case of an "uphill transfer" or a "transfer against the apparent concentration gradient" (*2*).

The nondissociated phenol molecules present in the donor aqueous solution F are dissolved in the membrane liquid S and, following the concentration gradient, are subsequently transferred into the acceptor liquid R. In this phase, phenol reacts with sodium hydroxide to produce sodium phenolate which, as an ionic compound, is insoluble in the membrane liquid.

Let us consider the process shown schematically in Fig. 1. The three liquids, namely F, S, and R, have constant volumes V_F, V_S, and V_R, re-

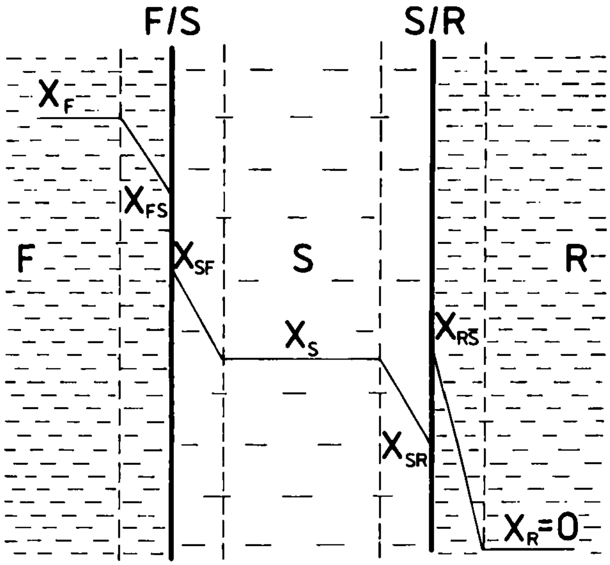

FIG. 1. Scheme of phenol transport and its simplified concentration profiles in the W-O-W three-liquid-phase system.

spectively. Their cores are completely homogenized and therefore the mass transfer resistances are located only in the boundary layers, adjacent to the interfaces F/S and S/R.

The time course variation of phenol concentration in the donor phase F is given by

$$V_F \frac{dx_F}{dt} = -K_F a_F (x_F - x_S/m_F) \tag{1}$$

Similarly, the variation of the solute in the membrane phase S is described by

$$V_S \frac{dx_S}{dt} = K_F a_F (x_S - x_S/m_F) - K_R a_R (x_S/m_R - x_R) \tag{2}$$

where the first term accounts for the solute flux in the extraction step, while the second one accounts for the stripping step.

From the overall material balance of the three-phase system, the amount of phenol, as phenolate, in the acceptor phase R is given by

$$V_R x_{RPh} = V_F (x_F^0 - x_F) - V_S x_S \tag{3}$$

Regarding the principle of resistance additivity, the overall mass transfer coefficients K_F and K_R are related to the film mass transfer coefficients as follows:

$$\frac{1}{K_F} = \frac{1}{k_F} + \frac{1}{m_F k_S} \tag{4}$$

$$\frac{1}{K_R} = \frac{1}{k_R} + \frac{1}{m_R k_S} \tag{5}$$

By assuming equilibria at the interfaces, it follows that

$$x_{FS} = x_{SF}/m_F \qquad \text{and} \qquad x_{RS} = x_{SR}/m_R \tag{6}$$

Since no mass is accumulated at the interfaces, the following relationships for phenol fluxes hold:

$$N_F = k_S(x_{SF} - x_S) = k_F(x_F - x_{FS}) \tag{7}$$

$$N_R = k_S(x_S - x_{SR}) = k_R(x_{RS} - x_R) \tag{8}$$

Due to the similar physical properties of the aqueous layers in contact with the organic membrane, the distribution coefficients of phenol, m_F and m_R, are considered to be equal, i.e., $m_F = m_R = m$. In addition, from the apparatus geometry it follows that both the mass transfer areas in the system considered are also equal:

$$a_{FS} = a_{SR} \tag{9}$$

Similarly, due to identical flow conditions in the solutions adjacent to both oil–water interfaces and the above mentioned similarity in the physical and chemical properties of the aqueous solutions F and R, it can be assumed that

$$k_R = k_F = k_W \tag{10}$$

Substituting Eqs. (4), (5), (6), (7), (8), and (10) into Eqs. (1), (2), and (3), and assuming that $x_R = 0$ due to the instantaneous chemical reaction between phenol and hydroxide, the following model for a batch pertraction process is obtained:

$$\frac{dx_F}{dt} = -\frac{k_W k_S a}{V_F(mk_S + k_W)}(mx_F - x_S) \tag{11}$$

$$\frac{dx_S}{dt} = \frac{k_W k_S a}{V_S(mk_S + k_W)}(mx_F - 2x_S) \tag{12}$$

$$V_R x_{RPh} = V_F(x_F^0 - x_F) - V_S x_S \tag{13}$$

The initial conditions are:

$$\text{at } t = 0: \quad x_F = x_F^0;\ x_S = 0 \tag{14}$$

EXPERIMENTAL

1. Reagents and Analytical Methods Used

The donor (feed) solution of phenol in distilled water was prepared with pure grade phenol (Loba Feinchemie). Similarly, the acceptor solution in distilled water was prepared with sodium hydroxide, analytical grade (Merck). Pure grade *n*-nonane (Fluka) was used as the membrane liquid.

The concentration of phenol in the donor solution was measured spectrophotometrically by a SPECORD UV/VIS (Carl Zeiss, Jena) in the UV region at a wavelength of 270 nm. In the range $0.5 < x_F < 100$ mg/L, the accuracy was 0.2 mg/L. The concentration data were obtained by means of a calibration curve derived at constant temperature (22°C) and pH value (pH 5). The photometric measurements were carried out in parallel to blank assays which contained distilled water saturated with *n*-nonane at the same temperature.

2. Experimental Setup

The experiments were carried out in a 2.2-L laboratory RF pertractor made of organic glass, as shown schematically in Fig. 2. Its body was divided by means of Wall 7 into two sections of equal volume (1.1 L). The lower part of each section contained two compartments separated by Baffles 3, intended for the donor and the acceptor solutions respectively. The maximum volume occupied by each aqueous phase was 0.35 L. The compartments containing identical solutions were interconnected by Grooves 6 and 6′. Each section had two connections, 4 and 5′, for the donor liquid, and two connections, 5 and 4′, for the acceptor liquid. The free space over the aqueous solutions in both sections contained the membrane liquid, S.

There were two pairs of stainless steel discs 2, 1 mm thick and 0.18 m in diameter supported by a common shaft. The lower part of each was immersed in the corresponding aqueous solution F or R. The rotating discs provided both moving interface formation and membrane phase agitation. The disc surface was coated by a hydrophilic coating made of viscose and

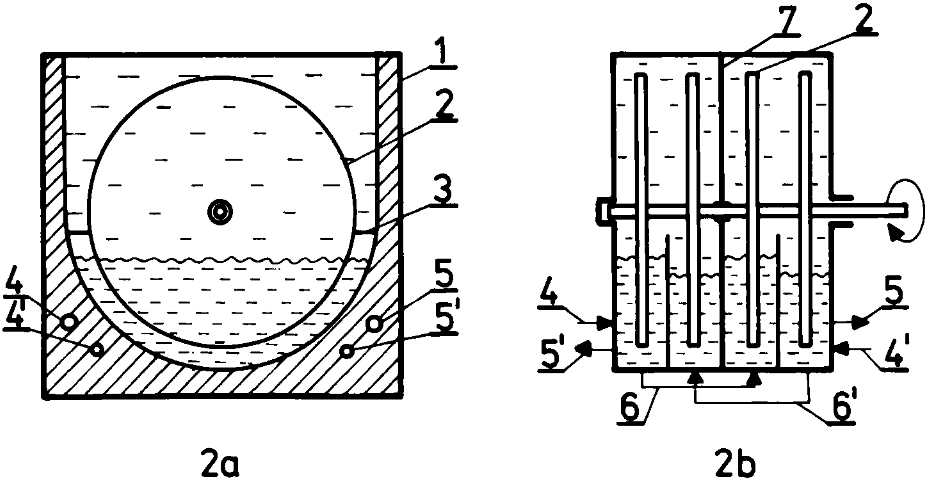

FIG. 2. Scheme of the rotation film pertractor. 1: Pertractor body. 2: Rotating hydrophilic discs. 3: Separating half-walls (baffles). 4, 4', 5, 5', 6, and 6': Interconnecting grooves, inlets and outlets. 7: Compartment separator.

intended to stabilize continuously the renewed films of donor and acceptor liquids. The discs were set in rotation by an electric motor combined with a reducing gear.

An option was envisaged to interconnect the compartments in such a way as to provide countercurrent flow of phases F and R. Otherwise, the apparatus operated as a one-stage batch contactor.

A constant temperature of 22°C was maintained by means of a thermostat.

RESULTS AND DISCUSSION

1. Equilibrium Studies

The distribution coefficient of phenol was measured for various phenol concentrations of the aqueous phase, ranging from 10 to 100 mg/L at 22°C with a constant pH value of 5.

Equilibrium was attained after intensive shaking of the liquids in separating funnels for 10 min at an aqueous-to-organic phase ratio of 1:5. For complete phase separation in all runs, the mixture was settled for more than 20 min.

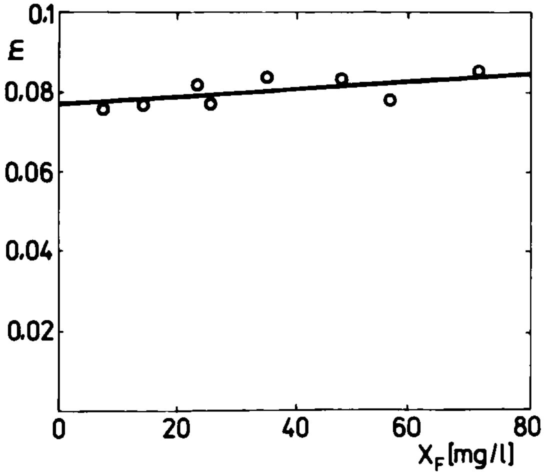

FIG. 3. Effect of concentration (x_F) on phenol distribution coefficient (m) between n-nonane and water (pH 5).

The effect of the aqueous phase phenol concentration on the distribution coefficient is shown in Fig. 3. As seen from the figure, it was linear and conformed to the equation

$$m = 0.0771 + 9.74 \times 10^{-5} x_F \tag{15}$$

2. Effect of the Donor Phase Amount in the Apparatus

During these and all further runs, a phenol solution in distilled water, 100 mg/L at pH 5, was used as the donor solution. All runs were carried out according to a batch operation scheme. In order to homogenize the donor solution and to take small representative samples from both sections, it was recirculated slowly by means of a peristaltic pump. The acceptor (stripping) phase was a 4 g/L sodium hydroxide solution in distilled water.

These experiments were carried out at a constant speed of disc rotation of 20 rpm changing the amount of feed F and therefore changing the ratio of the disc areas immersed in the aqueous solution and in the membrane liquid, respectively. The maximum pertraction efficiency was observed at V_F = 0.275 L, which means that 81% of the disc surface was immersed in the organic liquid. By using a larger donor liquid volume with less membrane liquid, the active contact area between the donor and the membrane phases decreased. In the opposite case, the aqueous films formed on the rotating surfaces are not renewed properly. All further experiments were carried out at the quoted optimum value.

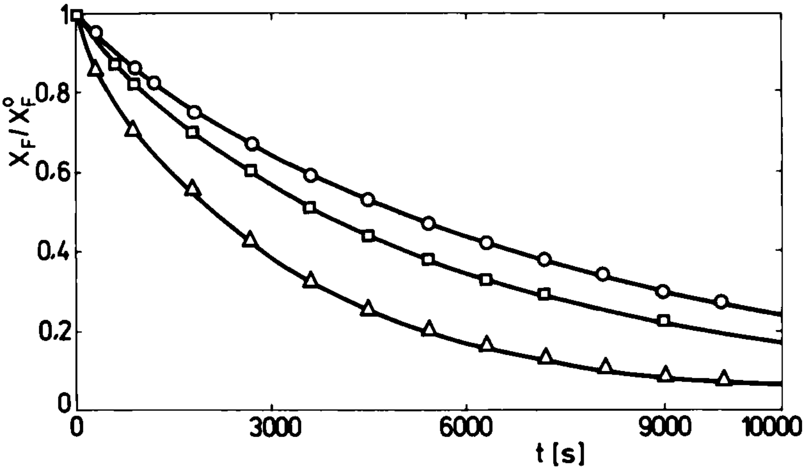

FIG. 4. Dimentionless phenol concentration in the donor solution (x_F) as a function of time (t).

3. Effect of Rotation Speed on Mass Transfer Efficiency

The rate of phenol recovery at constant feed volume depends on disc rotation speed. As seen from Fig. 4, the mass transfer rate increases with the speed of disc rotation. This is due both to the higher rate of contact area renewal and to the intensification of the hydrodynamics in both phases. The experiments were carried out at peripheral rotation speeds of 0.0471, 0.0940, and 0.1885 m/s. Any further increase in rotation speed is undesirable, since drops of acceptor solution were formed and transferred into the compartments containing donor liquid beyond 0.2 m/s, and this provoked phase intermixing and deteriorated the process.

On the basis of the results obtained for phenol concentration changes at various disc rotation speeds and the mass transfer model developed (Eqs. 11 to 14), the film mass transfer coefficients k_W and k_S were evaluated. The identification procedure was performed by using the dynamic simulator TUTSIM (Meerman Automation, The Netherlands) which incorporates the optimization simplex method of Nedler and Mead (*17*).

Based on the experimental data and on the values obtained from the identification procedure used, the adequacy of the model was confirmed within a 95% confidence limit. Figure 5 illustrates the effect of Reynolds number (incorporating the rotation speed) on Sherwood number (incorporating the mass transfer coefficient).

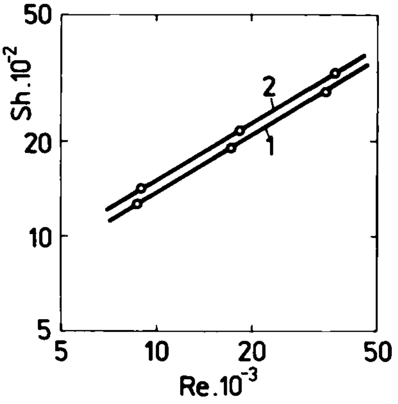

FIG. 5. Effect of disc peripheral velocity (u) on donor side (k_F) and membrane side (k_S) mass transfer coefficients. $Re = ud/\nu_F$; $Sh = k_{F(S)}d/D_{F(S)}$. (1) Aqueous film Sh number. (2) Organic film Sh number.

Equations of the form

$$Sh = ARe^bSc^c \tag{16}$$

were used, where

$$Sh = \frac{kd}{D}; \quad Re = \frac{ud}{\nu}; \quad Sc = \frac{\nu}{D}$$

The exponent c in Eq. (16) was assumed to be 0.33. Regarding the aqueous and the organic phases, the following values for the parameters A and b were found:

For the aqueous phase: $A = 0.648$, $b = 0.60$

For the organic phase: $A = 0.758$, $b = 0.59$

The phenol diffusivities in water and in n-nonane, required in Eq. (16), were calculated according to Wilke and Change method (*16*). Their values for 22°C are $D_W = 1.59 \times 10^{-9}$ m^2/s for the aqueous phase and $D_S = 1.42 \times 10^{-9}$ m^2/s for the organic phase, respectively. The numerical values of k_W and k_S obtained are given in Table 1.

TABLE 1

Rotation speed (m/s)	k_W [(m/s) × 10^6]	k_S [(m/s) × 10^6]
0.0471	11.276	11.235
0.0940	16.889	16.919
0.1885	25.662	25.516

CONCLUSIONS

This study proved that RF pertraction is a stable and effective method for dephenolation of low phenol-containing waters, in particular for cases where untypical solvents like *n*-nonane, with $m = 0.08$, are used. Since the solubility of the membrane liquid is less than 1 ppm, this process completely avoids the additional contamination of treated waters. The rotation of the discs strongly affects the rate of mass transfer. It was found that for the apparatus studied, the optimum peripheral velocity of the discs is 15–20 cm/s.

Acknowledgment

This study has been supported financially by the Ministry of Science and Education under Research Project 0155.

SYMBOLS

a	mass transfer area (m^2)
d	disc diameter (m)
D	diffusivity (m^2/s)
k	film mass transfer coefficient (m/s)
K	overall mass transfer coefficient (m/s)
m	distribution coefficient
t	time (s)
u	peripheral speed (m/s)
V	volume (m^3)
x	concentration (mol/m^3)
ν	kinematic viscosity (m^2/s)

Subscripts

F	refers to donor phase
0	initial
Ph	phenolate
R	refers to acceptor phase

S	refers to membrane phase
W	refers to water phases
SF, FS	denote corresponding side of interface F/S
SR, RS	denote corresponding side of interface S/R

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Received by editor September 11, 1991