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Equilibrium and mass transfer characteristics of 2-chlorophenol removal from aqueous solution by liquid membrane

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Abstract

Experiments were conducted to investigate the extraction of 2-chlorophenol (2-CP) from aqueous solution by liquid membrane. Main research efforts were focused on the identification of the optimal operating conditions for the liquid membrane system. An equilibrium equation of the Langmuir-type was proposed for describing the equilibrium 2-CP distribution between the external aqueous phase and the internal water-in-oil (W/O) emulsion phase. The proposed model predicts reasonably well the 2-CP phase equilibrium relation. Furthermore, a mass transfer model based on the linear driving force principle was also adopted in this work for representing 2-CP mass transfer from the external aqueous phase to the W/O emulsion. The simplified mass transfer model involved only a single parameter, i.e. the empirical mass transfer coefficient, which was easily established using observed data generated under various operating conditions. The mass transfer model considerably facilitates estimation of the 2-CP mass transfer rate in the liquid membrane system.

Keywords: Liquid membrane; 2-Chlorophenol; W/O emulsion; Equilibrium relation; Mass transfer model

1. Introduction

Phenol and phenolic derivatives appear in wastewaters from many chemical, petrochemical and oil refining industries. Because of their toxicity to human and marine life, increasingly stringent restrictions have been imposed on the concentrations of these compounds in the wastewater for safe discharge [1]. In Taiwan, for instance, the phenol concentration in the industrial wastewater for safe discharge has been reduced from 2 to 1 mg/l primarily due to health consideration. Hence, treatment of industrial wastewater containing phenolic compounds is mandatory.

Traditionally, activated sludge process has been the most widely used method to treat phenolic wastewater because of its simplicity and relatively low cost [2]. However, the microorganisms in an activated sludge system, even well acclimated, can only deal with chemical wastewater containing relatively low concentration of phenolic compounds, usually less than 100 mg/l, due to low biodegradability and inhibitory effects of these compounds [3]. Unfortunately, the chemical wastewaters from many chemical and petrochemical industries contain phenolic compounds far exceeding this concentration level. Hence, efficient treatment of high concentration phenolic wastewaters by chemical or physical alternatives is necessary.

There are various chemical or physical methods for dealing with industrial wastewaters containing high concentration phenolic compounds. These methods included extraction by liquid membrane [4], adsorption by activated carbon [5], macroreticular resin [6] and organoclays [7], chemical decomposition by Fenton's reagent [8], wet air oxidation [9,10] and ozonation [11]. Among the various methods, extraction by emulsion liquid membrane is a good attractive alternative because of its high efficiency and recovery of phenolic compounds for reuse as raw materials [12].

Since its initial work by Li [13], liquid membranes have demonstrated considerable potential as effective tools for an increasing variety of separation applications [4]. Among the various previous investigations, an aspect that received much attention is mathematical modeling of the liquid membrane extraction process. Mathematical modeling of the liquid membrane process not only helps us to elucidate the extraction mechanism, but also provides a good tool for process design. Many mass transfer models have been considered by investigators for describing the various liquid membrane extraction processes [4,14–19]. Those models were mathematically rather complex and involved

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many model parameters, identifications of which were not really easy. To enhance the values of those models, proper simplification would be needed.

The objective of this study is first to identify the optimum operating conditions of liquid membrane extraction of 2-chlorophenol (2-CP) from aqueous solution. The model compound (2-CP) was chosen because of its importance as a solvent or raw material in the many industrial processes. Second, a simplified mass transfer model was adopted for describing the liquid membrane extraction process. In contrast to the complex mass transfer models proposed by many previous investigators which involve many model parameters, the present simplified model contains only an empirical mass transfer coefficient. As demonstrated in this work, the empirical model coefficient can be easily evaluated using the experimental mass transfer data obtained under various operating conditions. Finally, a Langmuir-type equilibrium model is also proposed to represent the equilibrium extraction of 2-CP by liquid membrane. The proposed correlation offers a better alternative than the previous one in establishing the equilibrium relation between the external aqueous phase and the water-in-oil (W/O) emulsion [20]. Test data were gathered to verify the equilibrium model and to estimate the model parameters.

2. Materials and methods

The composition of the W/O emulsion consisted of surfactant Span-80 (sorbitan monoleate) obtained from Aldrich Chemical (Milwaukee, Wisconsin), kerosene (solvent) obtained from China Petroleum (Taiwan) and sodium hydroxide and 2-CP obtained from Aldrich Chemical (Milwaukee, Wisconsin). According to the manufacturer, Span-80 had a relatively low HLB (hydrophile–lipophile balance) value of 4.3 which renders it appropriate for hydrophobic W/O emulsion preparation. The W/O emulsion was prepared by putting appropriate amounts of kerosene, Span-80 and NaOH in a 2 l container in the homogenizing apparatus that was manufactured by Fu Chang Chemicals (Taoyuan, Taiwan). The apparatus was equipped with a mixer that had four 30° downward facing turbine blades. Driven by a high speed motor, the mixing speed could reach as high as 6000 rpm. In the present W/O emulsion preparation, a constant speed of 4000 rpm was maintained for 20 min. After homogenization was completed, the W/O emulsion was left still for 30 min to insure emulsion stability.

The batch extraction tests were conducted in an extraction cell. The Pyrex cell had a diameter of 6.5 cm and was 13.3 cm high. It was equipped with a cooling jacket for temperature control. The extraction cell had four pieces of baffles attached to the cell wall 90° apart and each baffle was 10 cm and extended 1 cm from the wall. A four-blade impeller stirrer, located 3 cm from the cell bottom was provided so that the W/O emulsion in the phenolic wastewater could be maintained well mixed. The W/O emulsion was expected to have a wide range of globule sizes. At least microscopic pictures were taken by a microscope at different cylindrical locations of the extraction cell and the average W/O emulsion globule size was estimated from these microscopic pictures to be 2 ± 0.14 mm that was in line with those observed by other investigators [4]. An extraction run was started by putting a desired amount of 2-CP wastewater (with 1000 mg/l initial 2-CP concentration) in the extraction cell which was kept at a constant temperature (25 °C). The stirrer was turned on and maintained at a constant speed of 100 rpm. A desired amount of prepared W/O emulsion was added to the 2-CP wastewater. Then small samples of the continuous phase were taken periodically and the 2-CP concentration was determined by a HP gas chromatograph (Model HP 5890, Hewlett Packard Instrument, Colorado, USA) equipped with an FID detector and a GP80/100 Carbopack capillary column.

3. Results and discussion

3.1. Effect of operating variables

In the extraction test runs, both baffled and non-baffled cells were employed. The effect of baffle on the 2-CP extraction is demonstrated in Fig. 1. Significant difference in the liquid phase 2-CP reduction (C/C_0) for baffled and non-baffled extraction cells is obvious in this figure for the first 20 min of the extraction operation. The improvement in extraction efficiency for the baffled cell over the non-baffled one is apparently due to better mixing and suspension of W/O emulsion globules in the aqueous solution. However, after 20 min of extraction, a slight decrease in the 2-CP extraction rate was observed for the baffled case and the two extraction efficiencies became rather close to each other at around 30 min. The decrease in the extraction efficiency is attributable presumably to swelling and break-up of some

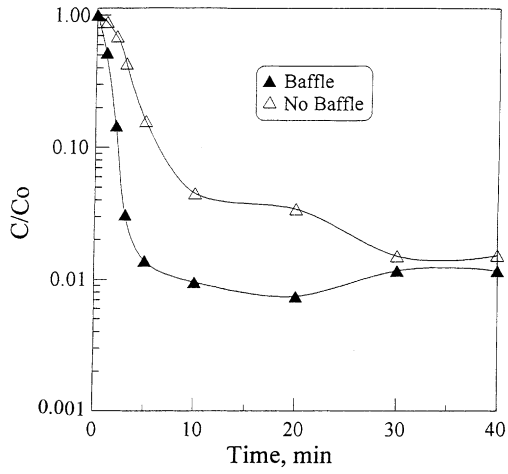

Fig. 1. Effect of baffles on the 2-CP reduction with 1000 mg/l initial 2-CP concentration, 5% Span-80, 1% NaOH, 0.1 V_e/V_w (emulsion to liquid volume ratio).

W/O emulsion globules in the baffled cell. This time frame of 30 min serves as the upper limit of the 2-CP extraction by liquid membrane. Such a short extraction time was made possible because of very large surface area of the W/O emulsion globules. Hence, for efficient extraction operation, baffled extraction cell is definitely a good choice and was adopted for the rest of all experimental investigations.

The effect of the amount of surfactant (Span-80) on 2-CP extraction is twofold. More surfactant in the W/O emulsion tends to reduce the surface tension of the W/O emulsion leading to smaller and more stable emulsion globules and much larger surface area for the same amount of W/O emulsion. This in turn enhances the extraction efficiency. However, as more surfactant is added, the liquid membrane thickness of the W/O emulsion globule is expected to increase, leading to an increase in the 2-CP mass transfer resistance which adversely influences the 2-CP extraction rate. The combined effect of these two conflicting factors is shown in Fig. 2. As the initial surfactant concentration of W/O emulsion increases from 1 to 5%, the efficiency of 2-CP extraction improves steadily. The improvement in the extraction efficiency, however, is drastically reversed as the surfactant concentration is further elevated from 5 to 11%. In this case, the reduced mass transfer of 2-CP due to thicker emulsion layer apparently more than offsets the beneficial effect of reduced surface tension. Hence, 5% surfactant concentration offers the optimum choice for the present liquid membrane system. It is further noticed in Fig. 2 that 10–15 min appear to be a better time duration for the 2-CP extraction which is in line with that observed in Fig. 1.

The sodium hydroxide (NaOH) inside the W/O emulsion globules has two major effects on the liquid membrane extraction process. First, it serves to convert 2-CP that has diffused through the liquid membrane, into sodium 2-chlorophenolate. The chlorophenolate is retained within the emulsion globules without back-diffusion [19]. Hence,

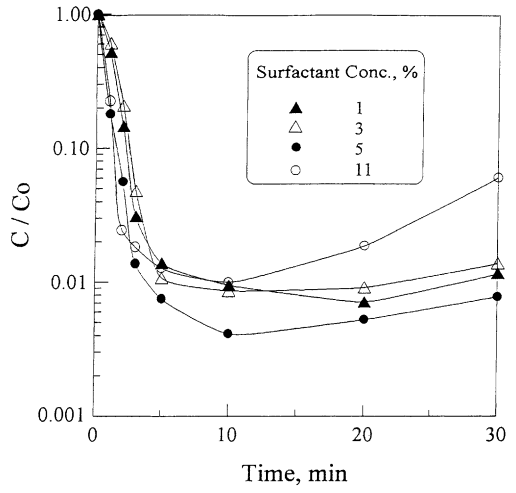

Fig. 2. Effect of surfactant (Span-80) concentration on the 2-CP reduction with 1000 mg/l initial 2-CP concentration, 1% NaOH, 0.1 V_e/V_w ratio.

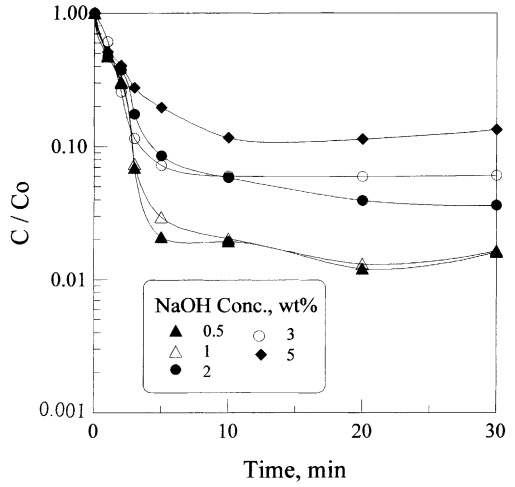

Fig. 3. Effect of NaOH concentration on the 2-CP reduction with 1000 mg/l initial 2-CP concentration, 5% Span-80 and 0.1 V_e/V_w ratio.

an increase in the NaOH concentration would be beneficial to the liquid membrane extraction. However, existence of the NaOH concentration difference between the external liquid phase and the W/O emulsion phase creates an osmotic pressure between these two phases [4], which causes water in the external liquid phase to diffuse through the liquid membrane into the small W/O emulsion globules. Accumulation of water inside the W/O emulsion globules will cause globule swelling and eventually break-up, leading to a loss in the liquid membrane extraction efficiency. Furthermore, an increase in NaOH can cause hydrolysis of the ester bonds of Span-80 [4], leading to a decrease in the W/O emulsion stability. Hence, an increase in NaOH concentration will adversely affect the extraction efficiency. The interplay of these conflicting effects will strongly influences the 2-CP extraction efficiency. This overall NaOH effect is revealed in Fig. 3. The adverse effect of NaOH is apparent for a NaOH concentration above 1%. In fact, with a 0.1 emulsion/liquid volume ratio, 1000 mg/l 2-CP concentration in the liquid phase and 0.5% NaOH concentration in the emulsion phase, the total NaOH in the emulsion globules is approximately the stoichiometric amount required for complete reaction with 2-CP. A NaOH concentration above 0.5% is theoretically in excess. This figure reveals that a NaOH concentration above the stoichiometric one does not appear to yield any benefit at all and for the case shown here 0.5% NaOH concentration is optimum.

Another factor that deserves some attention is the relative amounts of W/O emulsion and wastewater to realize the best 2-CP extraction. Fig. 4 shows the 2-CP removal as a function of the volume ratio of W/O emulsion to wastewater containing 1000 mg/l initial 2-CP concentration. As the volume ratio increases, the 2-CP removal increases rapidly until it reaches 0.1 beyond which extraction efficiency essentially remains constant. Such an optimal volume ratio is certainly related to the 1000 mg/l initial 2-CP concentration.

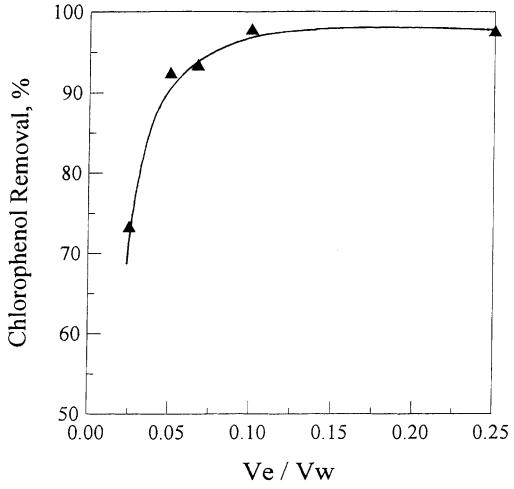

Fig. 4. 2-CP removal as a function of the volume ratio of W/O emulsion to aqueous solution with 1000 mg/l initial 2-CP concentration, 5% Span-80 and 1% NaOH.

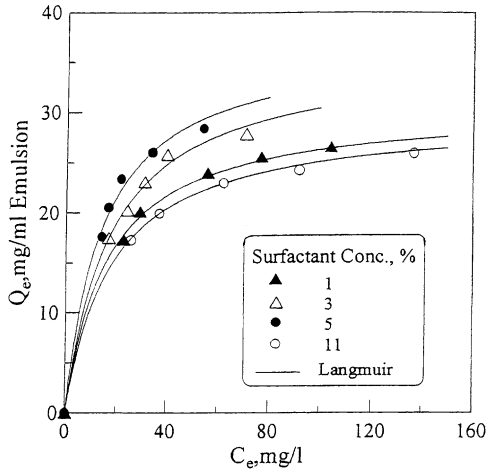

Fig. 5. Effect of surfactant concentration on the equilibrium 2-CP relation with 1000 mg/l initial 2-CP concentration, 1% NaOH and 0.1 V_e/V_w ratio.

As the initial 2-CP concentration varies, the optimal volume ratio is bound to change.

3.2. Equilibrium extraction correlation

Depending on the pH of the aqueous solution, molecular 2-CP and its ionic form are known to exist in equilibrium according to the following equation:

$$\mathrm{PhClOH} \Leftrightarrow \mathrm{PhClO^-} + \mathrm{H^+}$$

Based on the above equilibrium, an equation was established to relate the 2-CP concentration in the external aqueous phase to that in the W/O emulsion [4,14–19]. This equilibrium equation correlates well the 2-CP concentrations in different phases only under well-defined conditions and a mechanism was proposed by Cahn and Li [19] to explain the equilibrium of 2-CP between the external and internal phases. Adoption of this type of equilibrium relation to a wide variety of practical situations is much hampered because of shortage of experimental data for establishing the parameters in the equilibrium correlation [4,14–19]. To overcome this difficulty, an empirical equilibrium equation is proposed here.

Dispersion of W/O emulsion in the extraction cell under well-mixed conditions results in suspension of emulsion globules in the 2-CP wastewater [4,14,15]. This phenomenon is in fact not much different from suspension of adsorbent in an aqueous solution. By visualizing the W/O emulsion globule as an adsorbent particle, 2-CP extraction by liquid membrane from the wastewater is functionally equivalent to an adsorption process. Hence, an adsorption equilibrium isotherm could be adopted for describing the 2-CP equilibrium between the external aqueous phase and the internal W/O emulsion. The empirical Langmuir isotherm is first adopted for this purpose. This isotherm is represented by [20]

$$Q_e = \frac{abC_e}{1 + bC_e} \tag{1}$$

in which Q_e is the equilibrium extraction capacity of W/O emulsion (in mg 2-CP removed per ml emulsion), C_e the 2-CP equilibrium concentration in the aqueous phase (mg/l), and a and b are the constant parameters. To determine the two parameters, Eq. (1) is rewritten as

$$\frac{1}{Q_e} = \frac{1}{a} + \frac{1}{abC_e} \tag{2}$$

The 2-CP equilibrium concentration (C_e) in the aqueous phase was measured in a test run and the equilibrium extraction capacity (Q_e) was readily calculated using the measured data and the known initial conditions. According to Eq. (2), a plot of $1/Q_e$ vs. $1/C_e$ would yield a straight line and the model parameters (a and b) are obtained from the slope and intercept. In fact, the isotherm parameters in Eq. (1) could also be obtained using non-linear regression. For the present study, both methods yield essentially the same results. Fig. 5 reveals that the equilibrium Langmuir extraction model, represented by the solid lines, describes reasonably well the 2-CP equilibrium relation in the liquid membrane extraction system. The constant parameters for this extraction system obtained from the model fit are listed in Table 1. This table

Table 1
Model parameters of 2-CP extraction by liquid membrane

Surfactant concentration (%)	Langmuir parameter	
	a	*b*
1	30.46	0.06
3	35.90	0.06
5	37.26	0.07
11	29.63	0.06

reveals that the parameter a is strongly influenced by the surfactant concentration, while the second parameter b remains constant. The proposed equilibrium correlation offers significant advantages over the previous one [19] in that the model parameters are much easier to establish from the experimental equilibrium data. Such an equilibrium correlation can be adopted for use in stagewise liquid membrane extraction of phenolic compounds from aqueous solution [19].

3.3. Extraction mass transfer model

2-CP transfer from the external aqueous phase through the liquid membrane to the emulsion droplets could be governed by several potential mass transfer resistance between the two phases. Different models of varying complexity have been proposed for describing the mass transfer process [14–18,21,22]. Those models are not easy to use because of the difficulty in obtaining the solution and the many parameters involved which are not easy to evaluate either. To overcome this difficulty, a simplified version based on the principle of linear driving force principle [23] is employed here. The simplified model assumes that the 2-CP concentrations in the external aqueous phase and the internal W/O emulsion are uniform. The model can be represented by the following equation [23]:

$$\frac{d\bar{C}}{dt} = k_L a(\bar{C}^* - \bar{C}) \tag{3}$$

where $\bar{C}$ is the 2-CP concentration (mg/l) in the W/O emulsion droplet, $\bar{C}^*$ is that under equilibrium condition (mg/l) and $k_L a$ the capacity coefficient (min^{-1}). Integration of the above equation yields

$$\ln\left(\frac{\bar{C}^*}{\bar{C}^* - \bar{C}}\right) = (k_L a)t \tag{4}$$

Note that the 2-CP concentration in the W/O emulsion droplet ($\bar{C}$) is related to that in the external aqueous solution (C) by the following material balance:

$$V_L(C_0 - C) = V_R\bar{C} \tag{5}$$

in which V_L and V_R are the volumes of the external aqueous phase and the W/O emulsion (ml), respectively, and C_0 is the initial 2-CP concentration in the external aqueous phase (mg/l). The equilibrium concentration of 2-CP ($\bar{C}^*$) in the W/O emulsion was determined using Eq. (5) when C is equal to C_e. In the test runs of liquid membrane extraction, the 2-CP concentration in the external aqueous phase (C) was measured as a function of time. Hence, $\bar{C}$ was calculated using Eq. (5). The quantity (Y) on the left-hand side of Eq. (4) was thus obtained. Plot of Y vs. t would yield a straight line with a slope of k. Figs. 6 and 7 demonstrate the line plots of Y vs. t as a function of the emulsion to liquid volume ratio (V_e/V_w) and NaOH concentration, respectively. The model (straight lines) is seen to fit the experimental data reasonably well in both figures. The slopes of the straight lines obtained

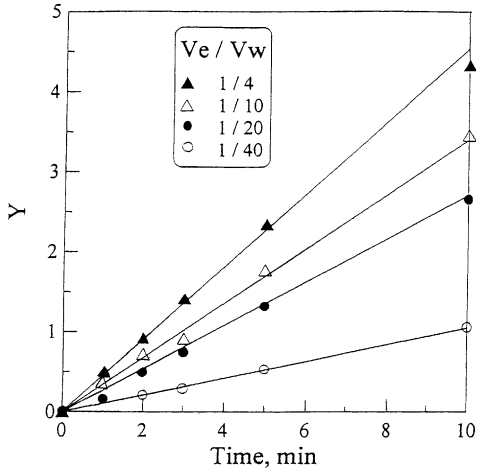

Fig. 6. Comparison of the theoretical predictions by the adopted mass transfer model to the experimental data for various volume ratios (V_e/V_w) with 1000 mg/l initial 2-CP concentration, 5% Span-80 and 1% NaOH.

from Figs. 6 and 7 are the overall mass transfer coefficients (k) which are shown in Figs. 8 and 9 as a function of the emulsion to liquid volume ratio and the NaOH concentration, respectively. The overall mass transfer coefficient in Fig. 8 increases with an increase in the volume ratio. This may be attributable to an increase in the number of emulsion globules when higher emulsion volume is used. However, an excessive amount of the emulsion is not beneficial and hence the overall mass transfer approaches a constant value at high V_e/V_w ratio. In Fig. 9, however, a distinct maximum value around 3% NaOH concentration is apparent. Occurrence of maximum mass transfer at this NaOH concentration does not agree with the corresponding one (0.5% NaOH concentration) based on the maximum 2-CP reduction observed in Fig. 3. The difference in the optimum NaOH concentration could be due to the fact that the properties of W/O emulsion

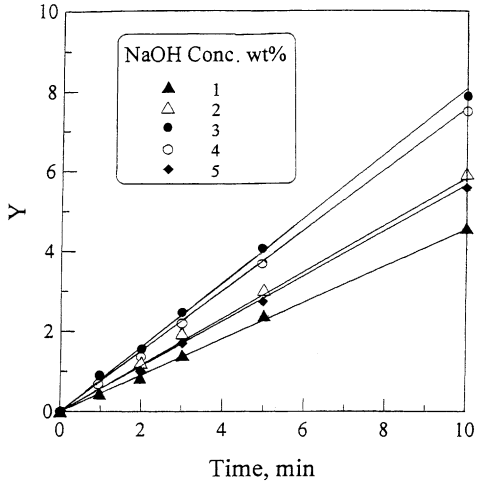

Fig. 7. Comparison of the theoretical predictions by the adopted mass transfer model to the experimental data for various NaOH concentrations with 1000 mg/l initial 2-CP concentration, 5% Span-80 and 0.1 V_e/V_w ratio.

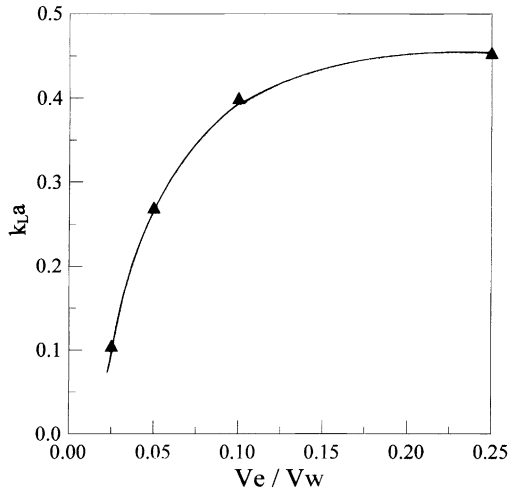

Fig. 8. Empirical capacity coefficient (k_La) as a function of the volume ratio (V_e/V_w) with 1000 mg/l initial 2-CP concentration, 5% Span-80 and 1% NaOH.

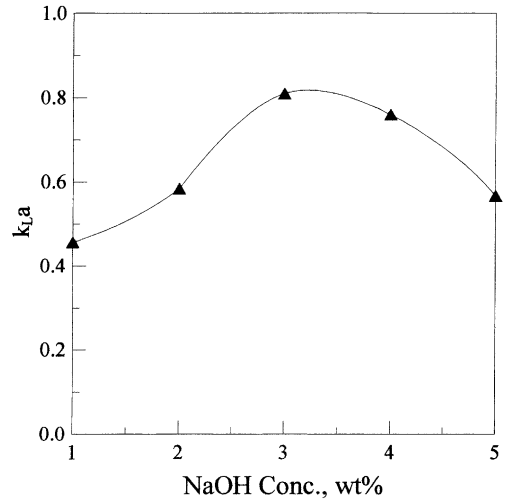

Fig. 9. Empirical capacity coefficient (k_La) as a function of the NaOH concentration with 1000 mg/l initial 2-CP concentration, 5% Span-80 and 0.1 V_e/V_w ratio.

are altered by the NaOH in the system and such a property change were not considered in the mathematical modeling.

4. Conclusions

Investigations on 2-CP removal from aqueous solution by liquid membrane were conducted in this work. Experimental runs were performed under various operating conditions in order to identify the optimal operating ranges of those variables. From the test results, the following conclusions can be drawn:

1. Extraction cell with baffles was found to perform significantly better than that without. Hence, baffled extraction cell is recommended for practical purposes.
2. Five percent surfactant and 0.5% NaOH concentrations in the preparation of W/O emulsion were observed to yield the very good extraction results for all the cases tested here. Also, an optimal 0.1 emulsion to liquid volume ratio existed in the present liquid membrane system.
3. A proposed equilibrium correlation of the Langmuir-type described well the 2-CP equilibrium between the external aqueous phase and the W/O emulsion. The model parameters are easy to estimate from the experimental data.
4. A simplified mass transfer model based on linear driving force principle was adopted in this study and was found to represent quite well the observed data. The model involved only single empirical parameter which is easy to establish from the experimental data.

Acknowledgements

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