CHAPTER IV

CONTINUOUS CLOUD POINT EXTRACTION OF VOLATILE ORGANIC CONTAMINANTS FROM WASTEWATER IN A MULTI-STAGE ROTATING DISC CONTACTOR: EFFECT OF STRUCTURE AND CONCENTRATION OF SOLUTES*

4.1 Abstract

Cloud point extraction (CPE) has been successfully scaled up to continuously remove aromatic contaminants from wastewater in a multi-stage rotating disc contactor (RDC) using t-octylphenolpolyethoxylate. The extraction performances for removal of organic solutes with difference structures and degrees of hydrophobicity were compared here for both batch and continuous CPE. Included are the volatile aromatics benzene, toluene, and ethylbenzene; volatile chlorinated compounds dichloroethane, trichloroethylene, and tetrachloroethylene; and non-volatile phenolics phenol, o-cresol, and catechol. The higher the K_{ow} (octanol-water partition coefficient) or hydrophobicity of solutes, the better the extraction due to the greater affinity of solutes to solubilize into micelles. The empirical linear correlations between log K_{ow}, log (solute partition ratio), and log (height of transfer unit or HTU) were developed. Toluene is used as a model solute for the study of effect of initial solute concentrations in the continuous RDC. The extraction ability decreases as the concentration of toluene in the wastewater increases mainly due to coacervate entrainment into the overhead effluent.

Keywords: cloud point extraction, nonionic surfactant, volatile organics, continuous, octanol-water partition coefficient

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4.2 Introduction

The environmental remediation of wastewater from industrial sources prior to discharging to public reservoirs is a critical concern today. Aromatic compounds and their derivatives are a major class of toxic chemicals contained in wastewater, leading to severe harm for humans because of their carcinogenic and mutagenic properties, even at extremely low concentrations at the ppm and sub-ppm level. Without using an organic solvent, which is often toxic, surfactant-based separations are an alternative to traditional separation processes because they utilize a relatively benign surfactant as the separating agent (1-4). Our present research focuses on cloud point extraction (CPE), a surfactant-based separation technique, which utilizes a nonionic surfactant as the separating agent and is recognized as an effective technique for removing dissolved organic contaminants from wastewater (5-15). When an aqueous nonionic surfactant solution at concentrations at least 3 to 20 times of its CMC is at a temperature above its cloud point (CP), it will undergo a phase separation resulting in a micellar rich phase or coacervate phase and a micellar dilute phase, which have a large difference in surfactant concentration. The organic solutes contained in the solution tend to incorporate or solubilize into surfactant micelles and concentrate into the micellar rich phase after the phases have separated so that the dilute phase containing a lower concentration of solutes can be released to the environment if the concentration is below the regulated level as treated water.

Many studies have been made over the years on the CPE of organic compounds as well as biomaterials in batch experiments (7-10, 13). However, in order for this technology to become commercially viable for treatment of large volume wastewater streams, scale-up to continuous, multi-stage units is necessary. Recently, the CPE technique was successfully scaled-up to remove aromatic contaminants from a wastewater stream continuously in a multi-stage rotating disc contactor (RDC) by our research group (11, 12). The efficient recovery and reuse of the surfactant is also a major concern for economical operation of the CPE process. Hence, we have chosen volatile organic compounds (VOCs) as the target contaminant in our studies since VOCs can be vacuum-stripped from the micellar rich phase after the CPE, permitting recycle of this stream containing the separation agent (surfactant) in high concentrations. Many researchers have studied the CPE of organic contaminants in batch experiments, but little work has been done with VOCs except for our studies, despite their great environmental concern in industrial wastewater or polluted groundwater. It is believed that this is due to the experimental difficulty of making accurate measurements on these systems due to leakage of these compounds because of volatilization. In 2002, the batch CPE study of the removal of aromatic VOCs, (benzene, toluene, and ethylbenzene) from wastewater used octylphenolpolyethoxylate as a nonionic surfactant (13). The influences of temperature, concentration of total surfactant, added electrolyte, and degree of alkylation of aromatic solutes on the extraction efficiency were investigated. Subsequently, toluene and ethylbenzene were selected as toxic compounds when the CPE was scaled up using RDC for removal of volatile aromatic contaminants from wastewater (11, 12). In that work, the concentration of solutes in the coacervate phase increased as agitator speed, wastewater/surfactant solution flow rate ratio, degree of alkylation of the aromatic solutes, operating temperature, and electrolyte concentration increased. Vacuum stripping in continuous bench-scale unit was reported to successfully strip the VOCs (toluene) from a concentrated surfactant solution (14). Detailed studies in our laboratory are further demonstrating the feasibility of vacuum stripping the micellar rich phase from CPE in a continuous, packed bed stripper (15) so that the solute-free micellar rich stream can be recycled for reuse in the CPE unit.

This present work has two focuses: firstly to investigate the effect of degree of hydrophobicity and molecular structure of three classes of organic solutes; and secondly to study the effect of inlet toluene concentration on the performance of the continuous RDC extractor and to compare the obtained results with ones from batch experiments. The volatile alkylbenzenes are benzene, toluene, and ethylbenzene. The volatile chlorinated hydrocarbons are 1,2-dichloroethane (DCE), trichloroethylene (TCE), and tetrachloroethylene (PCE). A series of non-volatile phenolics are also investigated for an understanding of solute structural effects on CPE using phenol, 1,2-methylphenol (o-cresol), and 1,2-benzenediol (catechol).

4.3 Experimental

4.3.1 Materials

A polydisperse commercial branched t-octylphenolpolyethoxylate, $OP(OE)_7$, with an average of 7 moles of ethylene oxide per mole of octylphenol (trade name Triton X-114) contributed by Dow Chemical Inc. (South Charleston, USA) was used as the nonionic surfactant in this study. The CMC of the surfactant is reported by the supplier as 100 ppm or 0.186 mM at 25°C. Reagent grade 99.8% pure toluene, benzene, ethylbenzene, trichloroethylene (TCE), tetrachloroethylene (PCE), phenol, and o-cresol were purchased from Carlo Erba Inc. (Italy). The 1,2-dichloroethane (DCE) was purchased from Labscan Inc. (Ireland) and catechol was purchased from Aldrich chemical company, Inc (USA). All chemicals were used as received. Distilled water was used for solution preparation. Some of the physical and chemical properties of solutes were summarized in Table 4.1.

4.3.2 Apparatus: Rotating Disc Contactor (RDC)

Figure 4.1 is a schematic of the cloud point extraction pilot unit used in this work. The CPE apparatus consisted of a pyrex glass cylindrical column with a 1000 mm height, covered by an acrylic water jacket with a 149.2 mm inside diameter through which temperature controlled water was circulated. The extractor column had a mixing zone (29.2 mm ID) in the middle and settling or empty zones (100 mm ID) at either end of the column. The empty zones were included in order to lengthen the residence time of the dilute and the coacervate stream before leaving at the top and bottom of the column. The heights of the mixing zone and empty zone were 700 mm and 150 mm, respectively. The rotor discs, stators, and shafts made of 316-stainless steel, were assembled and welded as a complete set before installation in the column, and fixed by the teflon-supporter and screws at the either neck of the column. The agitator speed of the rotating discs was regulated by a speed adjustable motor. More details about the apparatus were described in our previous work (11,12).

4.3.3 Procedures

For continuous experiments, as detailed in our previous study (11, 12), the contaminated feed water containing individual solute as the trace pollutant, and the

Table 4.1 Physical and chemical properties of all solutes at 25 °C (16-18)

Solutes	M.W.	Density (g/cm^3)*	Water solubility (mg/L)	Log octanol-water partition coefficient, Log K_{ow}
Benzene	78.11	0.8786	1770	2.13
Toluene	92.14	0.8669	533	2.69
Ethylbenzene	106.17	0.8670	169	3.15
DCE	98.96	1.2351	8700	1.48
TCE	131.39	1.4642	1370	2.29
PCE	165.83	1.6227	151	3.40
Catechol	110.11	1.1493	636190	0.88
Phenol	94.11	1.0576	86600	1.46
σ-cresol	108.14	1.0273	26000	1.96

*observed at 20 °C

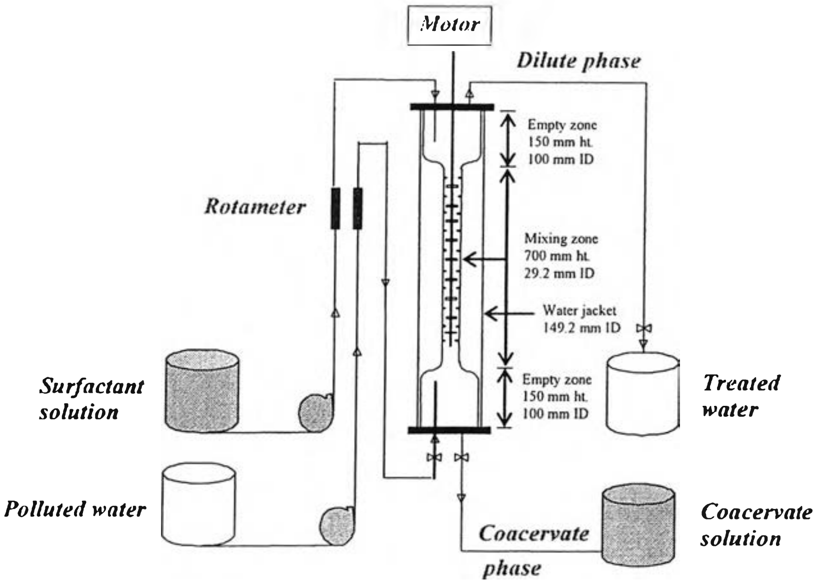


Figure 4.1 Schematic of the cloud point extraction pilot unit.

surfactant solution were fed into the extractor countercurrently at defined flow rates regulated by rotameters. Based on the density difference, the heavy surfactant solution was fed into the top, while the light wastewater was fed into the bottom of the extractor. In the column, the coacervate phase was beaten into tiny drops as rotating discs induced shear and these drops settled down to the bottom of the column; while the dilute phase or the treated water was ejected at the top of the column. In all experimental runs, triplicates of the feed wastewater and the dilute phase samples were carefully collected, by transferred them to the vials and sealing them with aluminum caps and rubber septa coated with polytetrafluoroethylene (PTFE), to avoid a leakage of solutes, at 45 minute intervals for analysis of the solute concentration. Due to the high volatility of the solute, the solute concentration of the inlet wastewater was closely monitored to ensure that it was unchanged for the entire operating time and that there was no significant loss of the solute by volatilization before feeding into the column. When the system reached steady state, as indicated by the absence of change in solute concentration in the dilute phase with time, triplicate samples were carefully collected from the effluent dilute phase and the coacervate phase (see Figure 4.1). To analyze the VOC concentrations, 1 mL of dilute phase and wastewater feed sample, and 0.1 mL of coacervate phase sample was collected. The volume of sample used to analyze surfactant and phenol concentrations were varied depending on dilution needs in order to fit the calibration curve range. The concentrations of nonionic surfactant and solute were measured in order to evaluate the extraction performance of the column. Moreover, the flow rate of the dilute phase stream and the coacervate phase stream were determined by measuring the volume of the dilute phase and coacervate phase collected over a measured time interval.

The operating conditions and variables were as follows: operating temperature: 40 °C; concentration of surfactant in surfactant feed solution: 350 mM; concentration of solute in wastewater feed: 100 to 430 ppm; rotating disc speed: 60 to 150 rpm; wastewater/surfactant solution flowrate ratio: 12.65 to 15.53 where the flow rate of wastewater was fixed at 18.6 mL/min.

For batch experiments, homogeneous aqueous solutions containing nonionic surfactant and individual solute were prepared and then transferred into several identical vials where experiments were conducted at the following conditions: 70 mM surfactant concentration, 100 ppm solute concentration (for studies of the effect of solute structure), 100 to 4000 ppm toluene concentration (for studies of the effect of solute concentration) and 40 °C operating temperature. To prevent headspace loss, especially for the volatile solute samples, the solution must occupy almost all of the vial volume to avoid overhead vapor volume. Rubber septa coated with PTFE were used to seal these vials to make sure that no leakage occurred. The vials were placed in an isothermal water bath and phase separation occurred very rapidly because of the density difference between two phases. When equilibrium was reached in about 2 days, which is defined as the time where no further change in coacervate volume is observed, the relative phase volumes of each phase were measured by the solution height. Both coacervate phase and dilute phase were carefully collected and the concentrations of nonionic surfactant and solute in each phase were analyzed.

The concentrations of $OP(EO)_7$ and the volatile solutes were measured by using a CE 2000 series UV-spectrophotometer (Cecil Instrument Limited, Cambridge, England) at 224 nm and a gas chromatograph with a flame ionization detector (Agilent Technology, USA), respectively. Due to the high volatility of some solutes, a static headspace autosampler was used for sample injection. The conditions of the gas chromatograph for VOCs determination were as follows: capillary column: HP-5; carrier gas: helium with a flow rate of 15 mL/min; make up gas: ultra pure nitrogen with a flow rate of 30 mL/min; oven temperature: 120 °C isothermal for benzene, toluene, and ethylbenzene and 80 °C isothermal for the chlorinated solutes; injector temperature: 200 °C; and detector temperature: 300 °C. The external standard quantitative calibrations were obtained for the analysis of surfactant and organic solutes in both phases. Closure of the material balance was taken as evidence that leakage of the volatile solute was negligible.

The concentration of phenols was analyzed by the 4-aminoantipyrine colorimetric method with a UV-spectrophotometer at 510 nm. Phenols combine in alkaline solution with 4-aminoantipyrine to produce a stable reddish-brown colored antipyrine dye. The amount of color (absorbance) produced is a function of the concentration of the phenolic material.

The external standard quantitative calibrations were measured for the analysis of surfactant and solute concentrations in both phases. Closure of the material balance (error of less than 10 percent) was taken as evidence that leakage of the volatile solute was negligible. For any particular studied conditions, the experiments were performed at least two times to ensure reproducibility, and the experimental data were averaged to yield the reported values. The standard deviation is less than ±5%.

4.4 Results and Discussion

4.4.1 Preliminary Studies

Variables investigated in the RDC pilot unit were the wastewater and surfactant feed flow rates, rotating disc speed and operating temperature. In this work, the efficiency of this RDC is quantified in terms of the treated wastewater throughput, the fraction of solute extracted, the amount of surfactant used, and the surfactant loss due to coacervate entrainment.

Figure 4.2 shows the toluene concentration in the feed and the dilute phase as a function of operation time for the base condition: 350 mM surfactant feed solution, 100 ppm toluene in wastewater, 100 rpm rotating disc speed, 40 °C operating temperature, and wastewater/surfactant solution flow rate ratio of 12.65, where the flow rate of wastewater was fixed at 18.6 mL/min. The toluene feed concentration remained constant (about 100 ppm in this run), indicating loss of toluene in the wastewater feed solution reservoir by volatilization was not significant. The toluene concentration in the dilute phase became constant after approximately 4 hours, indicating an attainment of the steady state condition. This defines the minimum column operation time before samples were taken for analysis. The fraction of toluene extracted was 99.3% at this base condition and the final toluene concentration in the dilute phase was lower than 1 ppm. Even though the base condition of this study was different from our previous study (11, 12); the same minimum time to attain steady state was observed.

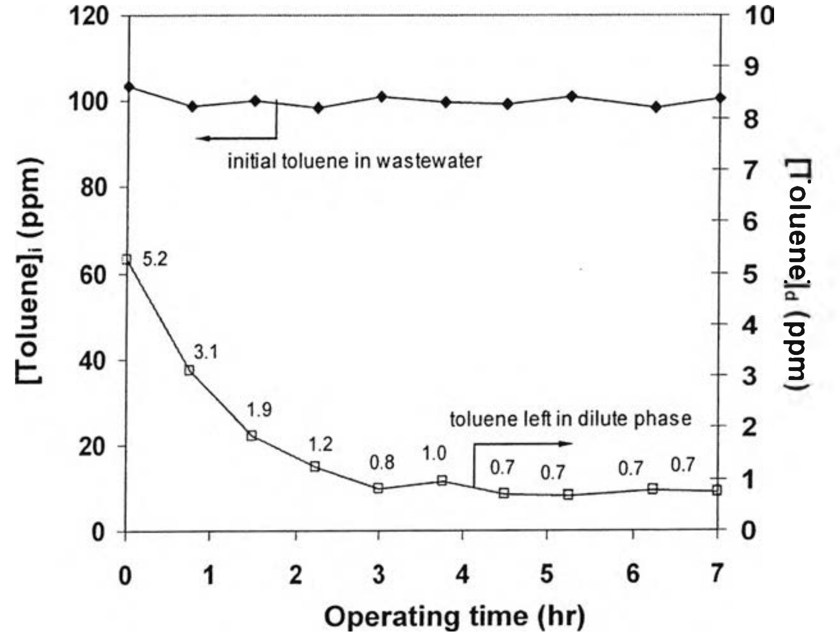


Figure 4.2 Toluene concentration as a function of operation time. Condition: 350 mM surfactant feed solution, 100 ppm toluene in wastewater, 100 rpm rotating disc speed, 40 °C operating temperature and wastewater/surfactant solution flowrate ratio 12.65.

4.4.2 Effect of Structure and Hydrophobicity of Various Solutes

In this work the octanol-water partition coefficient (K_{ow}) is used to represent the degree of hydrophobicity of the solutes. Generally, the octanol-water partition coefficient is the ratio of the equilibrium concentration of solute in an octanol phase to that in a water phase at a specified temperature. Octanol is an organic solvent that is used as a surrogate for natural organic matter. This parameter is used in many environmental studies to help determine the fate and transport of chemicals in the environment and has been correlated to water solubility of organic solutes. The lower the water solubility of the solute, the more hydrophobic it tends to be and the greater its tendency to solubilize in micelles rather than dissolve in water (19, 20). The correlation between K_{ow} and solubilization in micelles can be poor, particularly for ionic surfactants and polar solutes where ion/dipole interactions between the charged surfactant head groups and the polar moiety of a solute (e.g. a hydroxyl group) can be very strong and is not reflected by the solubility of the solute in octanol (21). However, with the nonionic surfactants and uncharged solutes used in this study, the van der Waals forces are expected to dominate in both octanol and micellar solubilization, so the K_{ow} is expected to reflect the solubilization of solute into micelles in the coacervate phase. The extraction conditions of this study were as follows: 350 mM surfactant feed solution, 100 ppm initial solute concentration in wastewater, 60 rpm rotating disc speed, 40 °C operating temperature, and wastewater/surfactant solution flow rate ratio of 15.53. The solute partition ratio, surfactant partition ratio, the fraction of solutes extracted in the coacervate solution for both batch and continuous CPE, and the value of K_{ow} are shown in Table 4.2 for the nine solutes studied here. The partition ratio is defined as the ratio of concentration in the coacervate phase to that of in the dilute phase. The higher the partition ratio, the better the separation. As degrees of alkylation and chlorination of the solute increases and degree of hydroxylation decreases, the partition ratios of solute and the fraction of solute extracted in the coavervate phase increase due to an increase in the degree of hydrophobicity (higher K_{ow}) or the lower the water solubility of the solute. The greater extraction efficiency with increasing K_{ow} of the solute was achieved in both batch and continuous extractions. These results agree well with our previous CPE studies (13, 22, 23), which investigated the effect of

Table 4.2 The comparisons of solute partition ratios, surfactant partition ratios, and the fraction of solute extracted in the coacervate solution among three classes of solute with different degree of octanol-water partition coefficient (K_{ow}) in batch and continuous operation. Condition: Batch: 70 mM surfactant in initial solution, 100 ppm solute in initial solution and 40 °C operating temperature, Continuous: 350 mM surfactant feed solution, 100 ppm solute in wastewater, 60 rpm rotating disc speed, 40 °C operating temperature and wastewater/surfactant solution flow rate ratio of 15.53

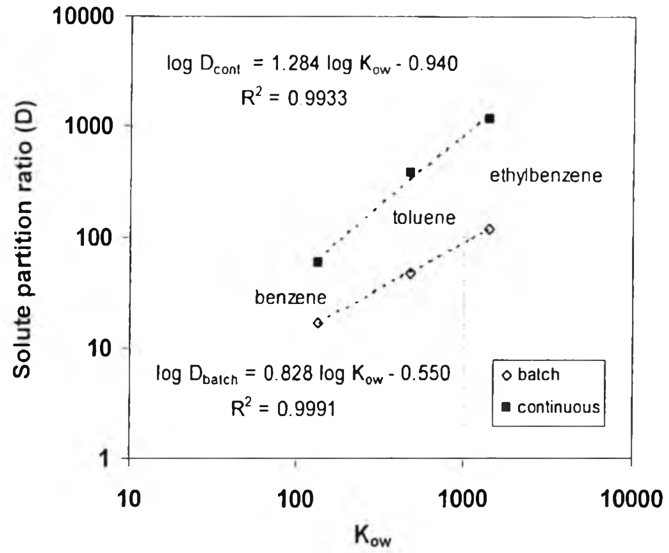
	Batch			Continuous		
Solutes	Surfactant partition ratio	Solute partition ratio	Fraction of solute extracted (%)	Surfactant partition ratio	Solute partition ratio	Fraction of solute extracted (%)
Volatile alkylbenzenes:						
Benzene	1329.1	16.6	76.4	279.0	58.5	72.8
Toluene	1343.8	46.0	89.9	287.5	376.8	94.6
Ethylbenzene	1367.0	116.8	95.8	300.9	1176.3	98.2
Volatile chlorinated:						
DCE	1310.0	11.6	69.2	263.9	25.1	57.2
TCE	1220.8	48.8	90.5	294.3	220.5	91.3
PCE	1223.6	126.8	96.1	284.9	605.1	96.9
Non-volatile phenolics:						
Catechol	1245.2	4.19	44.9	274.9	6.42	26.1
Phenol	1314.4	10.7	67.6	279.0	24.8	55.6
σ-cresol	1326.0	25.5	83.2	309.9	170.5	89.9

hydrophobicity of volatile aromatic and chlorinated compounds on extraction efficiency at equilibrium in batch experiments.

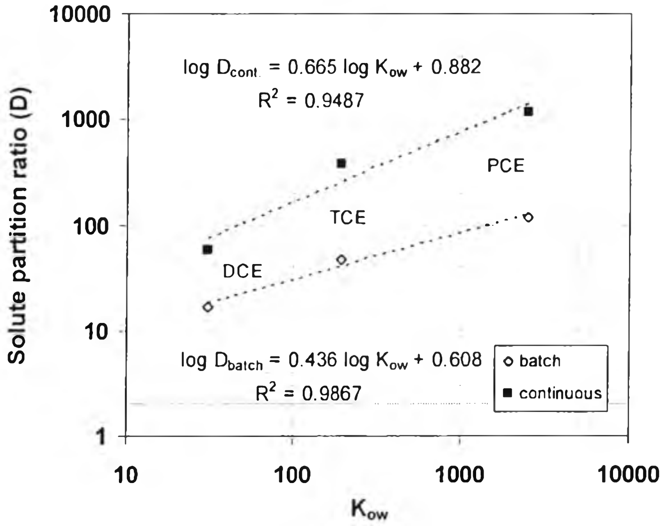
The effect of the structure and degree of hydrophobicity or K_{ow} of various solutes on the surfactant partition ratios in batch (equilibrium) and continuous operation is reported in Table 4.2. The surfactant partition ratio remains almost constant regardless of solutes used in this study at 1297.8 ± 54.0 mM for batch experiments and 286.0 ± 14.0 mM for continuous operation. The surfactant partition ratios for the continuous RDC was about a factor of 5 lower than those for batch operation due to the entrainment of coacervate droplets in the dilute phase under continuous countercurrent operation. As discussed in our previous study (11), the addition of nonpolar solutes can depress the cloud point, resulting in a greater temperature difference between the operating temperature and the cloud point, which leads to an increase in the surfactant partition ratio. However, it was observed that the cloud point of this surfactant solution at 70 mM is 25 ^{o}C and the addition of all nine solutes used in this study at a low concentration of 100 ppm only slightly depresses the cloud point to 24 ^{o}C, irrespective to the degree of hydrophobicity of the solutes. This level of cloud point depression is too small to significantly affect the surfactant partition ratios at the 40 ^{o}C used here.

The solute partition ratios, on the other hand, increase substantially (over two orders of magnitude for the compounds studied here) as the degree of hydrophobicity of solutes increases both in continuous and batch experiments as shown in Figure 4.3 and 4.4. Therefore, the tendency for the solutes to be extracted is mainly determined by the solubilization tendency of the solutes, rather than the lowering of cloud point of the system. The increase in solute partition ratios with the degree of hydrophobicity of solutes obtained from continuous extractions is greater than that obtained from batch extractions, as the slope obtained from continuous operation is steeper compared to that of the batch experiments. It should be noted that it is difficult to design experiments which permit an exact comparison of batch and continuous extractor performance. For batch experiments, the total surfactant concentration used was 3.75 weight percent, while that of continuous experiments was 1.12 weight percent. Even more important is that the height of the column is

(a) aromatic VOCs



(b) chlorinated VOCs



(c) phenolics

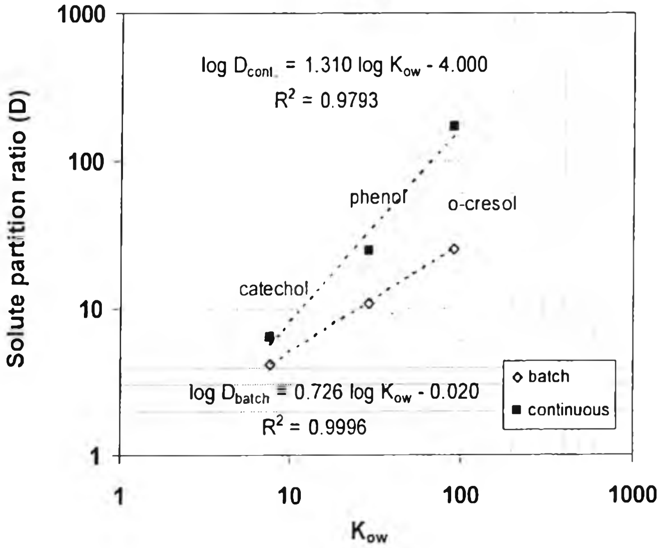


Figure 4.3 The correlation of solute partition ratios (D) and octanol-water partition coefficient (K_{ow}) of aromatic VOCs (a), chlorinated VOCs (b), and phenolics (c), respectively in batch and continuous operation.

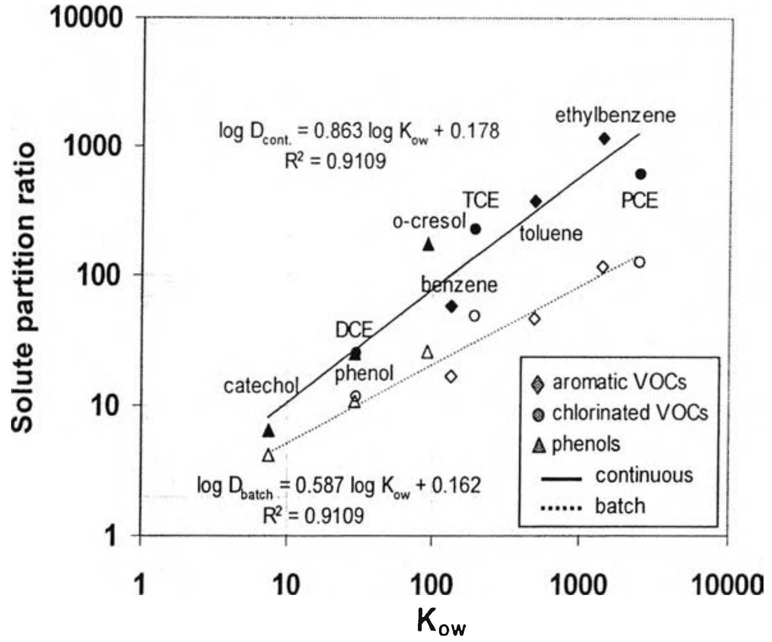


Figure 4.4 Comparisons of solute partition ratios in batch (open symbols) and continuous operation (closed symbols) as a function of octanol-water partition coefficient (K_{ow}) of the various solutes.

constant. Since the number of transfer units (NTU) varies with solute structure, from 0.81 to 4.45 transfer units for the solutes used here (Table 4.3). This will be examined in detail when discussing Figure 4.5 later.

The strong linear correlation between log of solute partition ratios (D) and log K_{ow} of aromatic VOCs, chlorinated VOCs, and phenolics in batch and continuous operation are illustrated in Figure 4.3. Traditionally, these values are presented as log (base 10), so this is how we present numerical correlations of our data. As degrees of alkylation or chlorination increases or degree of hydroxylation decreases, the value of K_{ow} increases. For example, log of K_{ow} of benzene, toluene and ethylbenzene are 2.13, 2.69 and 3.15, respectively. The solute partition ratio should be approximately proportional to the partition coefficients of solute between micellar phase and water phase or solubilization equilibrium constant (K_m) (23) at the high and constant coacervate surfactant concentrations observed here. The CPE of PAHs-naphthalene, fluorene, phenanthrene, and pyrene with Tergitol 15-S-7 nonionic surfactant was studied by Li et al. (10). They also reported a strong linear correlation of the K_{ow} and solute partition ratios or partition coefficients of these 4 compounds with R^2 equal to 0.9998. As a theoretical basis for log correlations, basically free energies are linear function of number of CH_2 or CH_3 groups and free energy is a log function of concentration. Therefore, the log-log plots of partition ratios versus K_{ow} is linear for the aromatic solutes but the slope of the curve gives insight into the relative affinity of a CH_2 or CH_3 group for octanol versus micelle interaction. Previous researchers have found linear relationship exist between log K_m and log K_{ow} of nonionic solutes for an individual surfactant, and the meaning of the slope and intercept of log K_m and log K_{ow} of various solutes was also reported (24-27). The magnitude of the intercept indicates the solubilization site of a molecule; the closer the value to zero, the more the similarity of micellar environment to octanol. The slope of greater than unity indicates that it is thermodynamically more favorable for the solute to partition from the aqueous phase to the micellar phase than to the octanol phase. In this work, only batch (equilibrium) data can be applied since surfactant entrainment strongly affects the continuous data. The similar slopes of less than unity of aromatics, chlorinated and phenolics compounds indicate that there is a lesser tendency of the incremental methyl, methylene, chlorine, a reduced hydroxyl groups to solubilize in micelles than to dissolve in octanol, although this is complicated in the case of DCE by added -H and replacement of double by single bonds.

Szymanowski et al. (28) tried to correlate the distribution or partition coefficient and log K_m of organic solutes in cloud point extraction using the linear solvation free energy of the Abraham model (29,30). The study demonstrated that the most important parameter for the distribution of organic solute between the coacervate and dilute phase are the hydrophobicity of the compound, represented by the intrinsic McGowan characteristic volume or McGowan molar volume of the solute, and also the hydrogen-bond acidity and basicity or the hydrogen-bond donating and accepting abilities of the solute. The stronger the interaction between water, as the hydrogen-bond acceptor, and solutes, the lower the partition ratio, and vice versa. For solutes with the same homologous structure, the value of their hydrogen bonds acidity and basicity are reported to be only slightly different and that does not affect the partition coefficient. Therefore, the partition coefficient is solely depended on the degree of hydrophobicity of solutes (10,28,31), which corresponds well with our results (linear correlation) as shown in Figure 4.3.

Figure 4.4 plots the logarithm of the solute partition ratio versus logarithm of K_{ow} for all nine studied solutes altogether. It is remarkable how well this correlation holds over such a wide range of solute types for both the batch and continuous operation. Since the slopes of the three series of compounds in Figure 4.3 are different, the correlation in Figure 4.4 is not as good as each of those (lower R^2 for Figure 4.4). It is interesting and fortuitous that those compounds which represent the hydrophobicities which are of the most environmental concern happen to fall on about the same curve in Figure 4.4 for all three series studied here. So, one could predict the performance of CPE for this surfactant for a solute of known K_{ow} from Figure 4.4 as a first approximation without any experimental data. It should be noted that the high extents of solute incorporation into micelle can induce changes in micellar structure and intramicellar solute-solute interaction so that the nature of the solubilization site can be changed and the correlation may not work well (30). The conditions used here correspond to fairly low micellar loadings in the coacervate phase (maximum of 0.05 molecules solute/molecule surfactant). In the next section of this paper, we will discuss other operational problems with a continuous CPE operation at high toluene/surfactant feed ratios, so solute partition ratios under these high micellar loading conditions may not be of much interest practically.

The height of transfer unit (HTU), the number of transfer unit (NTU), and the overall volumetric mass transfer coefficient (K_a) were determined to evaluate the performance of the multi-stage RDC column (Table 4.3). The definitions of these variables and calculation procedures for NTU and HTU have been described in previous work (11). The HTU is the column height required to attain the separation which is equivalent to one equilibrium stage batch extraction and the NTU is the number of these single stage, batch extraction equivalents in the experimental column used (32, 33). A knowledge of HTU combined with staging calculations permits estimation of the required height of a RDC column to achieve a specified fractional removal of the solute. The higher the solute partition ratio, the lower the HTU is and the shorter the column can be. The HTU multiplied by the NTU equals the height of our experimental column (70 cm). The K_a describes the rate of mass of the solute transferred from the wastewater effluent stream to the coacervate stream per unit cross sectional area. It is a standard parameter used in mass transfer

Table 4.3 The determination of the number of transfer unit (NTU), height of transfer unit (HTU) and overall volumetric mass transfer coefficient (K_a) of various solutes. Condition: 350 mM surfactant feed solution, 100 ppm solute in wastewater, 60 rpm rotating disc speed, 40 °C operating temperature and wastewater/surfactant solution flow rate ratio of 15.53

		Continuous		
Solutes	Log K_{ow}	NTU	HTU (cm)	K_a (S^{-1})
Volatile alkylbenzenes:				
Benzene	2.13	2.38	29.4	1.57E-03
Toluene	2.69	3.81	18.4	2.52 E-03
Ethylbenzene	3.15	4.45	15.7	2.94 E-03
Volatile chlorinated:				
DCE	1.48	1.62	43.3	1.07 E-03
TCE	2.29	3.09	22.7	2.04 E-03
PCE	3.40	3.83	18.3	2.53 E-03
Non-volatile phenolics:				
Catechol	0.88	1.102	63.50	7.29 E-04
Phenol	1.46	1.98	35.4	1.31 E-03
O-cresol	1.96	3.78	18.5	2.50 E-03

operations and its value is to permit a relative comparison of CPE operations to other extractions for investigators reviewing efficiency of different liquid/liquid extractions. The value of K_a was calculated by the mass velocity based on tower cross sectional area divided by the density of the effluent stream and the HTU. As HTU decreases, more solute is transferred between phases in a given length of column, so K_a increases as seen in Table 4.3. The HTU decreases when K_{ow} increases as shown in Figure 4.5, from 86.19 cm to 15.74 cm per transfer unit. This result confirmed that the greater the hydrophobicity of the solute, the better the separation in a continuous unit or the shorter the required column height. As a result, for our experimental column, the NTU increases with increasing K_{ow}, from 0.81 transfer units with log K_{ow} of 0.88 (catechol) to 4.45 transfer units with log K_{ow} of 3.15 (ethylbenzene). From Figure 4.4, in our study, the continuous RDC unit always had a higher solute partition ratio than the batch system, but this would not be true if the RDC column were shorter or if a solute less hydrophobic were used. Therefore, a continuous unit does not necessarily produce a better separation than a single stage batch unit. Of course, economically and operationally, a continuous system is generally much better than a batch system for large flow rate feed streams requiring multiple stages and NTU can be increased by increasing the column length.

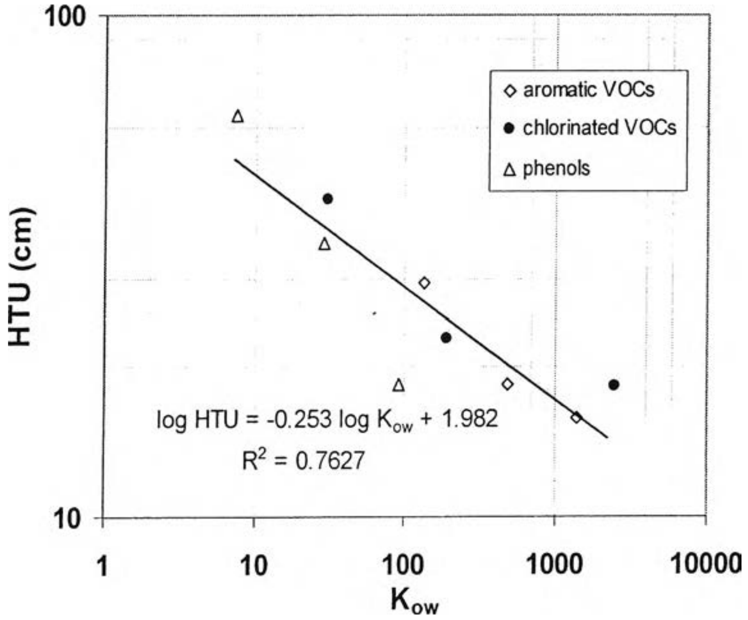


Figure 4.5 Height of transfer unit (HTU) as a function of octanol-water partition coefficient (K_{ow}) of the various solutes in continuous operation.

4.4.3 Effect of Concentration of Toluene in Wastewater Feed

From Figure 4.2, 99.3% of toluene is extracted at the condition: wastewater/surfactant solution flow rate ratio of 12.65, 100 rpm rotating disc speed, 40 °C operating temperature, and 100 ppm toluene concentration in the wastewater feed. In this work, the concentration of toluene in wastewater feed was varied from 100 ppm to 430 ppm. Solubilization of toluene in the micellar solution of polyethoxylated nonionic surfactant can reduce the cloud point (13). The cloud point depression is greater as the initial toluene concentration increases. In this work, the cloud point of this surfactant solution at 70 mM of 25 °C, was lowered to 24 °C with an addition of 100 ppm toluene concentration, and consecutively decreased to 20 °C as the toluene concentration increased to 500 ppm. As shown in Figure 4.6(a) and 4.6(b), the concentrations of surfactant and toluene in the coacervate phase increase with increasing initial toluene concentration, respectively. The surfactant concentration in the coacervate was more than 20,000 times that of the CMC and its concentration in the dilute phase was ranged from 9 to 18 times that of the CMC. Although, the TCE concentration in CPE with t-octylphenolethoxylated in our previous batch study showed an insignificant effect on the extraction efficiency, it should be noted that a low concentration range of TCE: surfactant ratios (< 0.04 M/M ratio) was covered in that study (22).

On the other hand, an increase in the initial concentration of toluene in wastewater in continuous operation results in a higher toluene concentration in the dilute phase effluent as shown in Figure 4.6(b). In addition, the fraction of toluene extracted and fraction of surfactant present in the coacervate phase is reduced with increasing feed toluene concentration as shown in Figure 4.7. The fraction of toluene extracted is 99.3% at 100 ppm of initial toluene concentration, but is reduced to about 95% when the initial concentration of toluene was higher than 300 ppm. When the toluene concentration in the coacervate was higher than 3000 ppm, the coacervate phase seemed to change its appearance from transparent to a milky or opaque state, and the stability of the coacervate droplets were reduced as evidenced by easier breaking up of coacervate droplets due to the shear induced by the rotating discs.

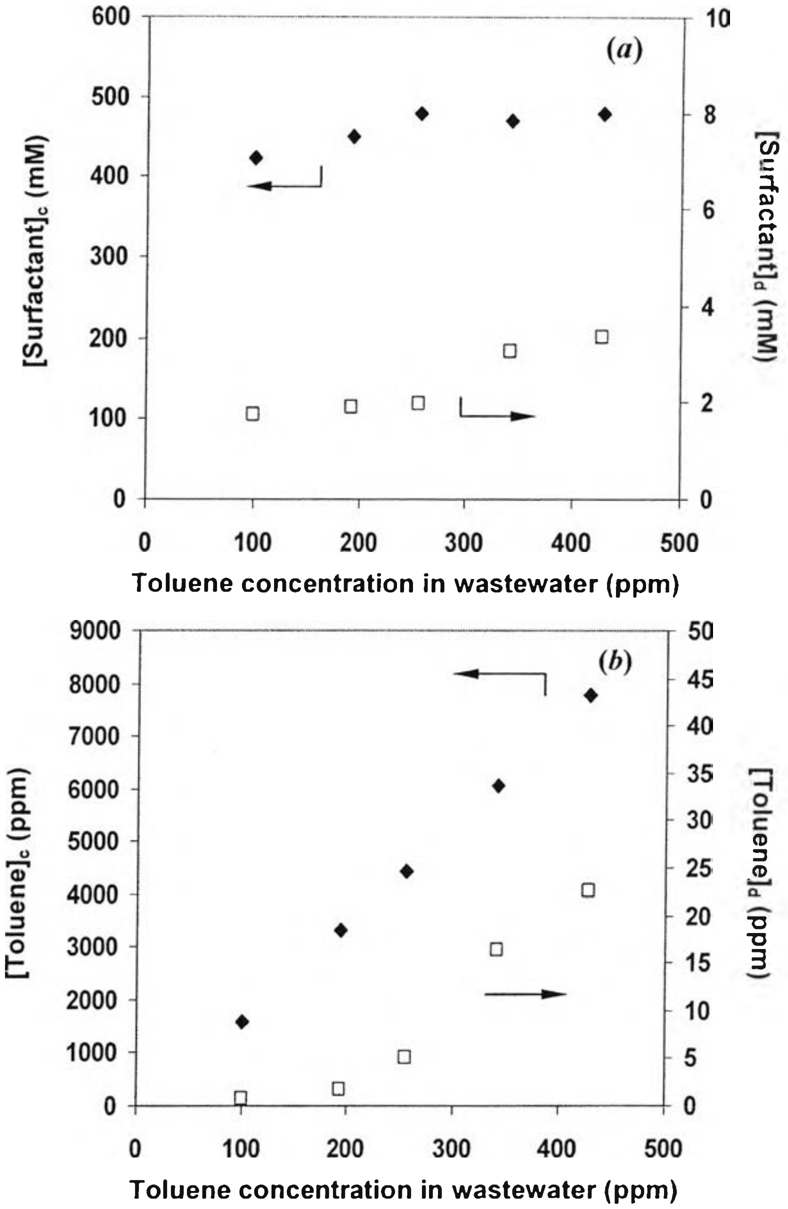


Figure 4.6 Surfactant (a) and toluene (b) concentration in coacervate (c) and dilute phase (d) as a function of toluene concentration in wastewater in continuous operation, respectively.

This resulted in a higher amount of small and low-density coacervate droplets entrained to the top of the column by the dilute effluent, causing higher concentrations of toluene and surfactant in the dilute phase. The poor phase separation was also confirmed by the CPE of toluene in batch experiments at high initial toluene concentrations. It was found that when the toluene concentration was more than 1,500 ppm or the toluene: surfactant in the system is more than 0.23 M/M ratio, the entire solution appeared to be opaque and milk-like; and a phase separation was hard to achieve. The milky solution without clean phase separation probably indicates that a stable macroemulsion of the coacervate droplets in the dilute phase is forming (Figure 4.8).

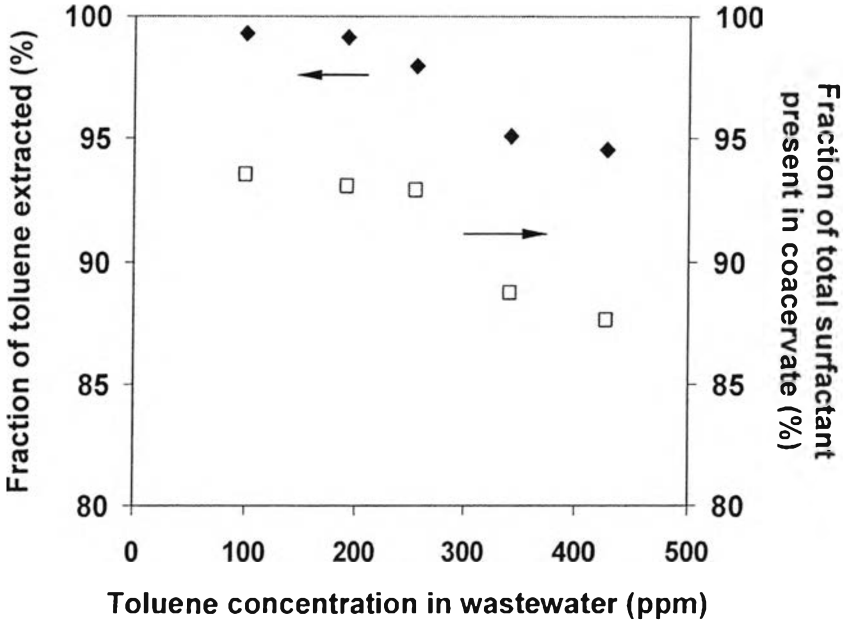


Figure 4.7 Fraction of toluene extracted and fraction of total surfactant present in coacervate as a function of toluene concentration in wastewater in continuous operation.

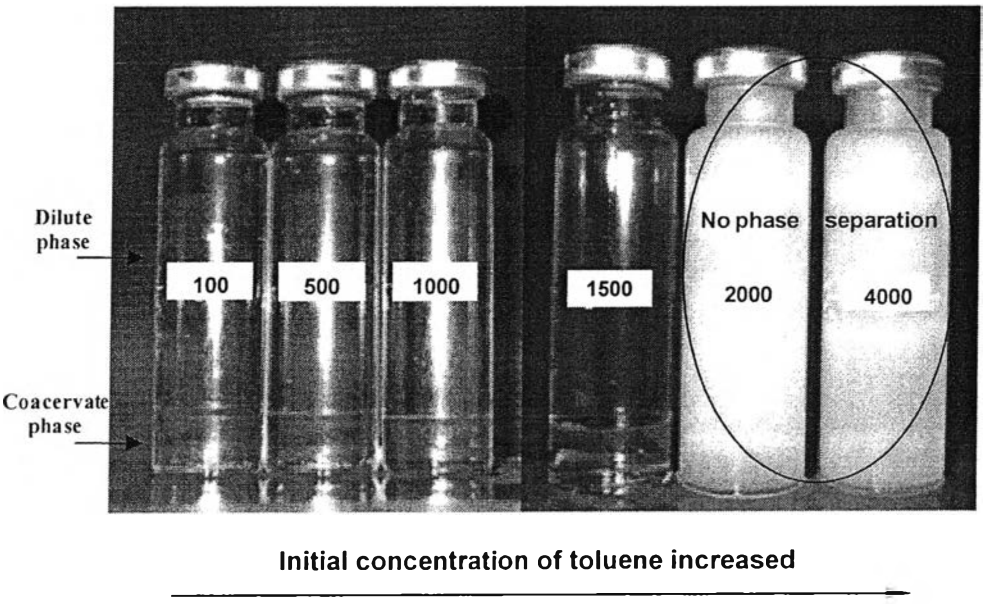


Figure 4.8 Pictures of phase separation of nonionic surfactant solution at various initial concentrations of toluene (ppm). Condition: 70 mM surfactant in initial solution and 40 °C operating temperature.

Surfactant and toluene partition ratios from batch and continuous operation as a function of toluene concentration in wastewater were compared in Figure 4.9(a) and 4.9(b), respectively. Toluene partition ratios obtained from continuous extractions were 1 to 2 orders of magnitude higher than those from batch extractions; in contrast, the surfactant partition ratios from continuous extractions were about 1 order of magnitude lower than that from batch experiments.

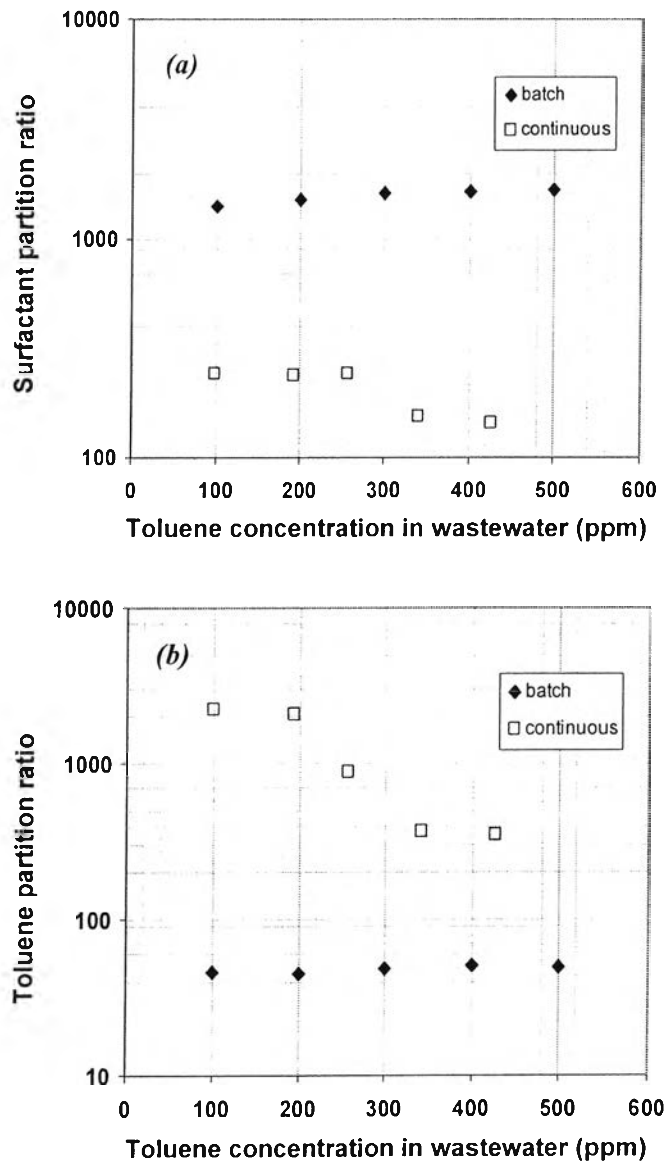


Figure 4.9 Surfactant and toluene partition ratios of batch and continuous operation as a function of toluene concentration in wastewater respectively.

The effect of toluene concentration in the low concentration range was very small in batch extractions with surfactant and toluene partition ratios being almost constant as toluene concentration changed as shown in Figure 4.9. At very high concentrations of toluene (e.g., 2000 ppm), phase separation does not occur. In continuous operation, dramatic decreases in surfactant and toluene partition ratios were observed at a high toluene concentration. The decreases in surfactant and toluene partition ratios as toluene concentration increases in the RDC was mainly due to the entrainment of coacervate droplets, not due to a thermodynamic effect. From the batch results, if phase separation is clean and equilibrium is attained, there should be a negligible effect of toluene feed concentration on either surfactant or toluene partition ratio for the RDC. The problem of surfactant loss by the entrainment of coacervate droplets to the dilute phase from the continuous RDC needs to be mitigated in future work. Figure 4.10 shows that the HTU increases when the toluene concentration increases, from 11.0 cm to 41.8 cm per transfer unit. Consequently, the NTU decreases as the toluene concentration in wastewater increases, from 6.3 transfer units with 100 ppm toluene to 1.7 transfer units at 430 ppm toluene. The overall volumetric mass transfer coefficient or K_a also declines with increasing toluene feed concentration as shown in Figure 4.11.

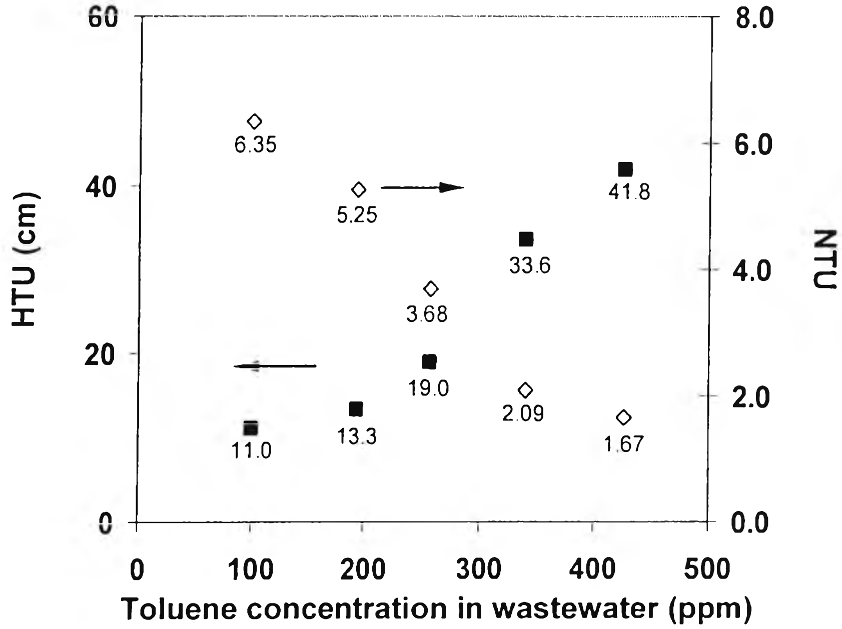


Figure 4.10 Height of transfer unit (HTU) and number of transfer unit (NTU) and as a function of toluene concentration in wastewater feed.

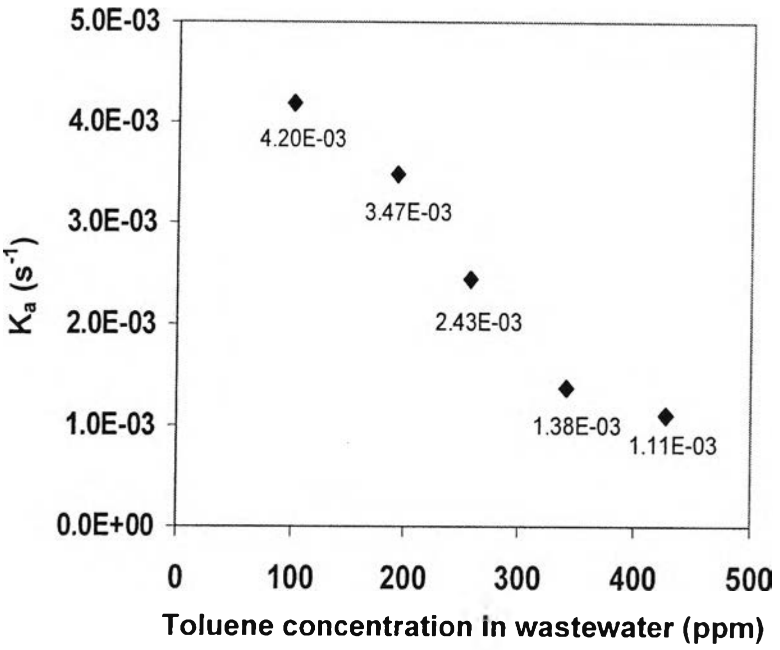


Figure 4.11 Overall volumetric mass transfer coefficient (K_a) as a function of toluene concentration in wastewater feed.

4.5 Conclusions

Cloud point extraction of various organic compounds from aqueous solutions using t-octylphenolpolyethoxylate nonionic surfactant in continuous operation were studied and compared with batch experiments. The CPE performance increased as the degree of hydrophobicity of solutes or K_{ow} increased; and logarithm of CPE partition ratio and logarithm of HTU are linear functions of the logarithm of K_{ow} for various types of solutes. Therefore, the K_{ow} can be used as a parameter to predict the extraction and partition performance of the solute system in the CPE process, especially for the solutes with same homologous structure. In addition, the CPE performance in continuous operation decreased as the concentrations of toluene in wastewater feed were in a higher range, due to the poor phase separation in the extraction column. In contrast, the solute concentration doesn't significantly affect the solute partition ratio for batch experiments. The CPE process can be applied in many applications, for example by purifying wastewater streams from the petroleum or petrochemical industries, where there are some leakages of gasoline tank or industrial effluents. Not only a wide variety of VOCs, but also any other organic compounds in wastewater can be extracted by this RDC due to the ubiquitous nature of the solubilization process responsible for the separation. Moreover, it can be applied to removal of inorganic metals in wastewater by adding some ligands. Much more environmentally benign ethoxylated alcohol (AE) which properly similar in the physical properties to the alkylphenolpolyethoxylate surfactant would be likely to be applicable to cloud point extractions to be used in real wastewater treatment applications.

4.6 Acknowledgements

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