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C. Zhang[a]; K. T. Valsaraj[b]; W. D. Constant[a]; D. Roy[c]
[a] DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING, LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISIANA, USA [b] DEPARTMENT OF CHEMICAL ENGINEERING, LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISIANA, USA [c] DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING, POLYTECHNIC UNIVERSITY, BROOKLYN, NEW YORK, USA

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Studies in Solvent Extraction Using Polyaphrons. II. Semibatch and Continuous Countercurrent Extraction/Flotation of a Hydrophobic Organic Dye from Water

C. ZHANG
DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

K. T. VALSARAJ*
DEPARTMENT OF CHEMICAL ENGINEERING

W. D. CONSTANT
DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

LOUISIANA STATE UNIVERSITY
BATON ROUGE, LOUISIANA 70803, USA

D. ROY
DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING
POLYTECHNIC UNIVERSITY
6 METROTECH CENTER, BROOKLYN, NEW YORK 11201, USA

ABSTRACT

Transport mechanisms and a mathematical model for a continuous countercurrent predispersed solvent extraction (PDSE) process are proposed in this paper. Solvent extraction using polyaphrons provides enhanced mass transfer (extraction) of solute through larger interfacial areas of micron-sized predispersed solvent. Increased rise velocity is needed for subsequent phase separation (flotation) of dispersed polyaphrons through attachment onto micron-sized gas dispersions called colloidal gas aphrons (CGAs). PDSE experiments were conducted in both batch and continuous countercurrent modes to remove a hydrophobic organic dye (Solvent Red 27) from water into kerosene. Sodium dodecylbenzenesulfonate was used as the water-soluble surfactant and Tergitol-15-S-3 as the kerosene-soluble surfactant to form polyaphrons. The CGAs were prepared using hexadecyltrimethyl ammonium bromide in water. Results from batch experiments showed that

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* To whom correspondence should be addressed.

the efficiency of dye removal depended not only on the duration of flotation but also on the settling time after flotation. Longer settling times increased the process efficiency, indicating gradual removal of the smaller polyaphrons. In the continuous countercurrent mode, the mathematical model predicts that the process efficiency is a function of the flow rates of CGA and polyaphrons relative to feed water flow rate, the partition coefficient of the solute, relative sizes of polyaphrons to CGAs, and the attachment efficiency of polyaphrons to CGAs. Experimental results in the continuous countercurrent mode are tested against the proposed model.

INTRODUCTION

In a recent article, solvent extraction was identified as an applicable technology for Superfund site remediation (1). When a broad class of less volatile, toxic, and/or hydrophobic organic compounds with large equilibrium distribution coefficients are considered for removal from the aqueous phase, solvent extraction is an attractive method as compared to steam stripping, activated carbon, or even biological treatment. The major problems which limit the wide application of conventional solvent extraction are twofold: 1) the requirement of an expensive and energy-consuming mixer-settler, and 2) the high solvent consumption due to a large volume ratio of the extracting solvent to contaminated water, which requires a secondary treatment process.

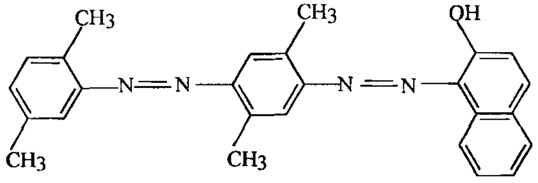
Recent advances have improved upon the conventional process of solvent extraction. Predispersed solvent extraction (PDSE), first proposed by Sebba (2), is one such innovation. This process involves precomminuting organic solvent into micron-sized polyaphrons, which are used to extract solutes from the aqueous phase. The dispersed solvent is then separated by flotation using microgas dispersions called colloidal gas aphrons (CGAs). The advantage of this process is that polyaphrons can be uniformly dispersed with a minimum of energy input, and thus the solvent/aqueous phase interfacial area for mass transfer can be maximized. The principles and applications of this separation process for waste treatment have not been fully explored, although a few lab-scale experiments have been reported. These include oil recovery from tar sands and oil removal from drilling mud during oil exploration (3), recovery of metals from wastewater (4, 5), and recovery of ethanol from a fermentation broth (6). Michelsen and coworkers (7) tested the removal of an organic compound (*o*-dichlorobenzene) from water using decane as the solvent in a PDSE process conducted in a small lab-scale batch mode and showed that it was about 5 to 10 times more effective than straight solvent extraction using a similar quantity of solvent. More recently, Save et al. (8) reported bench-scale column studies of the extraction of Cu from aqueous acidic solutions using kerosene polyaphrons, and observed that PDSE is far superior to conventional spray columns. For the same value of the percent solute extracted, the spray column required a 300% larger solvent flow rate. PDSE was observed to enhance mass transfer and also reduce the solvent consumption.

In Part I of this series, the size distribution and flotation of different polyaphrons were discussed as a prelude to use in laboratory- and pilot-scale demonstrations of PDSE for removing hydrophobic organic compounds from wastewaters (10). To test the feasibility and performance of PDSE for large-scale applications, experiments were performed on both batch and continuous countercurrent experiments in laboratory pilot-scale setups. In this paper we present the theory and a mathematical model for this separation process. The experimental data obtained on the removal of a hydrophobic dye (Solvent Red 27) into kerosene polyaphrons are tested using the proposed model.

EXPERIMENTAL

Kerosene was chosen as the organic solvent for producing polyaphrons. It has been suggested as a potentially useful solvent for extraction of a variety of chlorinated organics from a wastewater stream due to highly favorable partition constants and low costs associated with its disposal (13). Kerosene (Curtin Matheson Scientific, Inc.) polyaphrons were generated using the procedure described in detail in previous work (10). An oil-soluble surfactant (Tergitol-15-S-3 supplied by Sigma Chemical Co.) was used in kerosene, and a water-soluble surfactant (sodium dodecylbenzenesulfonate, SDBS, manufactured by Aldrich Chemical Co.) was used in the production of polyaphrons with a phase volume ratio (PVR) of 19 (10). The CGA dispersion was prepared using hexadecyl trimethyl ammonium bromide (HTAB manufactured by Sigma Chemical Co.) (100 $mg \cdot L^{-1}$) as the surfactant in the aqueous phase using a generator originally described by Chaphalkar (11). The choice of the type of polyaphron and CGA dispersion was dictated by our earlier work (10).

An oil (kerosene) soluble dye (Solvent Red 27) was chosen as a surrogate to test the performance of PDSE for the removal of a hydrophobic organic compound. The dye was used because of the ease of analysis and ability to visually follow the extraction and flotation process in progress. The dye was supplied by Aldrich Chemical Company. The dye had two peak maxima in its absorption spectrum (359 and 518 nm). The absorption spectrum of the dye dissolved in methanolic water or kerosene showed little or no variation in peak maxima. Figure 1 shows the structure and molecular formula of the dye.



Common Name: Solvent Red - 27 (Oil Red O)

Chemical name: 1-((4-(xylylazo)xylyl)azo)-2-naphthol

Formula weight: 408.5

Melting point : 120°C

FIG. 1 Structure and properties of the hydrophobic organic dye, Solvent Red 27.

PDSE experiments were conducted in an apparatus designed for both batch and continuous countercurrent modes of operation as shown in Fig. 2. The glass column had dimensions of 8 cm ID and 100 cm height, with provision for solvent overflow at the top. In the batch mode of operation, 3500 mL of aqueous solution containing the dye was placed in the column. The initial concentration of the dye in the aqueous phase was 0.5 ppm. A given volume (10 mL) of diluted polyaphrons was introduced into the column. The CGA dispersion was pumped into the base of the column from the generator using a peristaltic pump (Cole Parmer Inc.) at a flow rate of 19.5 ± 2.5 mL/min for 1, 5, and 10 minutes of flotation time. Thus both CGA and polyaphron were introduced as pulse inputs, and samples were taken at different settling times after flotation. As settling time increased, a thin layer of solvent phase appeared at the top of the aqueous phase, increasing with time. Since the analysis of either phase would give identical results, and since the volume of the solvent phase was very small, only the aqueous phase sample was considered for analysis.

For continuous countercurrent experiments, both CGA dispersion and diluted polyaphrons were pumped continuously into the base of the column with the polyaphron inlet 10 cm above the CGA inlet. The total CGA dispersion flow rate varied from 11 to 51 mL/min, while the flow rate of the aqueous portion of the CGA dispersion excluding the air phase varied from 6.3 to 21.7 mL/min. In other words, the quality of the CGA dispersion, *f*, varied from 0.34 to 0.67. The quality factor (*f*) was determined by a drainage test as described by Chaphalkar (11). The original polyaphron

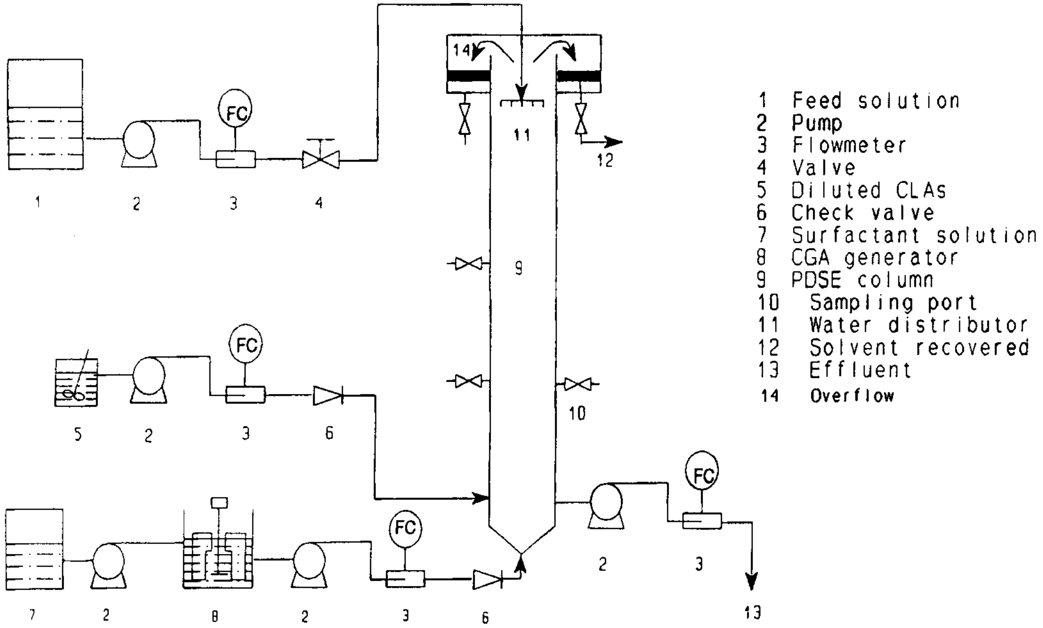


FIG. 2 Schematic of the experimental setup for continuous countercurrent and semibatch predispersed solvent extraction.

suspension prepared was diluted either 1:1 or 1:3 (v/v) before being fed into the column. The total flow rate of the diluted polyaphron suspension ranged from 1 to 2.3 mL/min, which is equivalent to a solvent flow rate of approximately 0.5 mL/min. Feed solution containing the dye was continuously pumped at either 25 or 50 mL/min and introduced through a distributor at the top of the column just below the solvent/water interface. The flow rate of the solvent layer in the overflow was approximately 0.10 to 0.34 mL/min. The effluent was sampled periodically and analyzed for the dye concentration. For the analysis of the dye, 100 mL of the aqueous phase was sequentially extracted into three 5 mL portions of kerosene and the kerosene phase combined.

The concentrated sample of kerosene was analyzed for Solvent Red 27 on an HP 8542A diode array spectrophotometer with an HP 89531 and MS-DOS UV/VIS operating software. A calibration curve was prepared for the dye in kerosene. In addition to the dye concentrations, the aqueous phase was also analyzed for the residual concentration of the anionic water-soluble surfactant SDBS used in preparing the polyaphrons. This was done using Standard Method 5540 (12).

RESULTS AND DISCUSSION

The process of PDSE involves two steps: (1) solute mass transfer (extraction) from the aqueous phase of the organic solvent phase of the polyaphron, and (2) attachment of the polyaphrons to CGAs and subsequent flotation of the oil core polyaphron by CGAs.

Mass Transfer Mechanism in PDSE

The rate of solute mass transfer from the aqueous to the solvent phase is given by $N_A = k_w a \Delta C$, where k_w is the solute mass transfer coefficient (cm/s), a is area of a polyaphron in the aqueous phase (cm^2), and ΔC is the concentration driving force for mass transfer (mol/cm^3). Save et al. (8) indicated that the enhanced mass transfer rate in PDSE was due to the greater interfacial area of stable micron-sized polyaphrons. The interfacial area provided by polyaphrons is enormous. For example, 1 L of kerosene polyaphrons of PVR 19, of average diameter 10 μm, would have a total oil/water interfacial area of 570 m^2. The mass transfer coefficient can, however, be effectively reduced owing to the resistance afforded by the soapy shell of the polyaphron. However, results so far have shown that this additional resistance has minimal impact on mass transfer rate and is overwhelmed by the positive effects of the vastly increased interfacial area (6). This is due to the small concentration of a surfactant necessary to stabilize the film at the oil/water interface of a polyaphron. At these low concentrations the surfactant is oriented parallel to the surface, with the total area occupied by the surfactant being very small. Thus the film encapsulating the polyphron is largely water, and hence the diffusion of the solute across the shell is not hindered.

CGA-Assisted Flotation of Polyaphrons

The advantage of high interfacial area is, however, lost due to the small rise velocities of polyaphrons. Their rise velocity is enhanced by a flotation using CGAs, an essential step in the PDSE process. Based on earlier experiments on flotation of polyaphrons using various types of CGAs (anionic, cationic, and nonionic surfactants), we deduced that the major mechanism of flotation is the coulombic attraction between the polyaphron and the CGA (10). The maximum number of polyaphrons that a CGA can attach is proportional to the available surface area of a CGA. Based on geometry, we can deduce that this number is given by

$$n = 3.8\left(\frac{R}{r}\right)^2 \qquad (1)$$

Assuming Stokes' law for the rise velocity of a single polyaphron and a single CGA, and using Eq. (1) along with a force balance on a polyaphron-loaded CGA, we can obtain the following equation for its rise velocity:

$$V = \sqrt{\frac{8g\left(1 - \frac{\rho_a}{\rho_w}\right)R^3 + 30.4g\left(1 - \frac{\rho_s}{\rho_w}\right)R^2 r}{3(R + 2r)^2 C_D}} \qquad (2)$$

where $C_D = 24/\mathrm{Re}$ is the drag coefficient. Utilizing the expression for $\mathrm{Re} = 2V(R + 2r)/v$ and assuming that $\rho_a \ll \rho_w$, we have the following equation for the rise velocity of a single CGA with n polyaphrons attached to it:

$$V = \frac{\left(2 + 7.6\left(1 - \frac{\rho_s}{\rho_w}\right)\frac{r}{R}\right)}{9\left(1 + \frac{2r}{R}\right)\nu} gR^2 \qquad (3)$$

The above equation states that the rise velocity is related to the ratio of the radius of the polyaphron to that of a CGA. For a CGA of diameter 100 μm that attracts a number of polyaphrons of average diameter 10 μm, the rise velocity is 0.5 cm/s, whereas that of the single polyaphron is

0.0011 cm/s. Thus the residence time of a polyaphron in the presence of an oppositely charged CGA is decreased by a factor of 454. Figure 3, obtained using Eq. (3), gives the rise velocity of a single CGA when it is attached to polyaphrons of different diameters. These values encompass the range of diameters of CGA and polyaphrons used in the present experiments. With increasing diameter of the CGA, the rise velocity of the CGA/polayphron complex is also increased. However, for a given CGA size the rise velocity of the CGA/polyaphron complex is only minimally affected by the different sizes of polyaphrons attached to it.

Batch Experiments

Figure 4 illustrates the results of the batch experiments. For the batch process a constant volume of the aqueous phase is treated with a short duration pulse of polyaphrons and CGA. Results of three different experiments are shown for different durations of flotation, namely, 1, 5, and 10 minutes. Following flotation, the aqueous phase was sampled after different settling times of 15 minutes to 100 hours. Figure 4 shows that higher

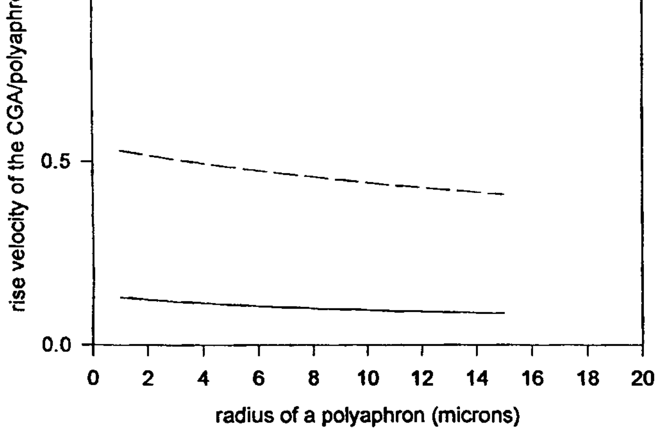


FIG. 3 Rise velocity of a CGA when attached to polyaphrons of various sizes.

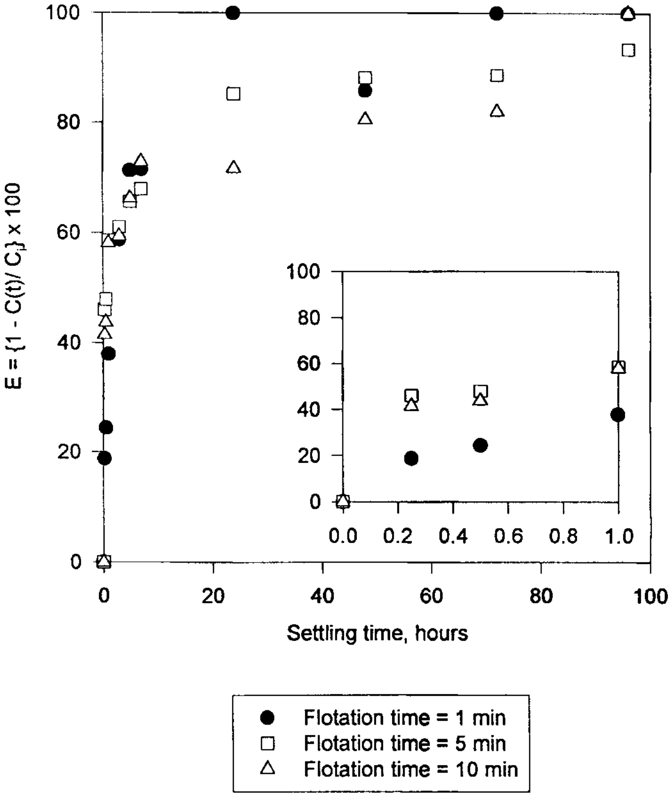


FIG. 4 Removal of the dye in a batch PDSE process.

process efficiencies were observed for the 5 and 10 minutes flotation times than for the 1 minute flotation time during the first hour of settling time following flotation, as shown in the inset in Fig. 4. Increasing the flow rate of CGAs will decrease the residence time of the polyaphron/CGA complex and hence will improve the removal rate. Increasing the flotation time will also increase the removal from the aqueous phase. Once the flotation process is terminated, further separation occurs by the free rise of polyaphrons unassisted by CGAs. Because of the slow rise velocities of polyaphrons, extended settling times are required in this phase of the process. Settling times beyond 1 hour had significant effects on the percent removal as shown in Fig. 4. The ultimate dye removal after several hours of settling time approached 100%. Based on earlier work (10), the recovery efficiency can be explained as follows. In Part I (10) we reported that the average size distribution of polyaphrons changed from 30 μm before flotation to 10 μm after flotation and 10 minutes of settling time and to 5 μm after 2 hours of settling time. We attributed this to the very slow rise velocities of the smaller polyaphrons, whereas large aphrons are efficiently removed by flotation. The amount of total solvent recovered at the top of the aqueous column even after these long settling times ranged from 58 to 63%. The solvent recovery showed no dependence on the duration of flotation, but showed an increase with settling time. The generally small solvent recovery can be attributed to the adhesion of some portion of the 4.6 mL of kerosene in the form of charged polyaphrons to the walls of the extraction column. We can summarize these observations on the dye removal in the batch process by stating that the settling time played an important part in addition to the duration of flotation. However, long settling times such as those used in these experiments are unrealistic in practical applications. More rapid and efficient methods of recovering residual solvent in the form of smaller polyaphrons from the aqueous phase have to be considered for implementation.

The ultimate percent of dye removal (~100%) should be contrasted with the maximum extraction efficiency of 75% calculated for a single-stage conventional extraction process using the measured partition constant of 1310 for the dye between kerosene and water. The efficiency in the batch PDSE is dependent not only on the duration of flotation but also on the number of residual polyaphrons bouyed up to the surface of the aqueous phase during the settling stage. In a conventional batch extraction process using a straight solvent, the transfer of solute from water to the organic solvent will cease as soon as equilibrium is established between the two phases. However, in a batch PDSE process, equilibrium is established only between the polyaphron and the water immediately surrounding it. With each polyaphron leaving the aqueous phase, the concentration of solute in water decreases and the succession of polyaphrons that comes after each one continually adjusts to a new equilibrium state and removes more of the solute species from the aqueous phase. Thus the process is rate controlled, dependent on the number of polyaphrons that leave the aqueous phase during the settling stage, and the solute removal can be virtually complete. The conventional extraction process requires intense mixing of the solvent and water in a mixer vessel followed by an extended settling time for phase separation. On the other hand, the batch PDSE process requires only a gentle flow of the predispersed solvent (polyaphrons) in a column reactor, and phase separation can be achieved faster. In large-scale processes the benefits in terms of energy savings and capital equipment may be considerable in a PDSE process.

The residual anionic surfactant (SDBS) in the aqueous phase resulting from the polyaphrons introduced into the column was measured after flotation. Two sets of results are presented (Fig. 5), one in which the concentration of HTAB for CGA production was 100 ppm in water and another one for which the concentration was 500 ppm in water. For the former case, a 5-minute flotation time showed a lower residual SDBS than that for a 1-minute flotation time. When the CGAs were generated with higher HTAB concentration, the effect of flotation time was not significant. We conclude that the residual SDBS in the aqueous phase can be controlled by the type of surfactant used to produce the CGAs. This is expected since we demonstrated earlier that the flotation process is one in which coulombic forces between oppositely charged polyaphrons and CGA play the dominant role in separation (10).

Continuous Countercurrent Experiments

In these experiments the water containing dye was in continuous countercurrent contact with both the CGA dispersion flow and the diluted

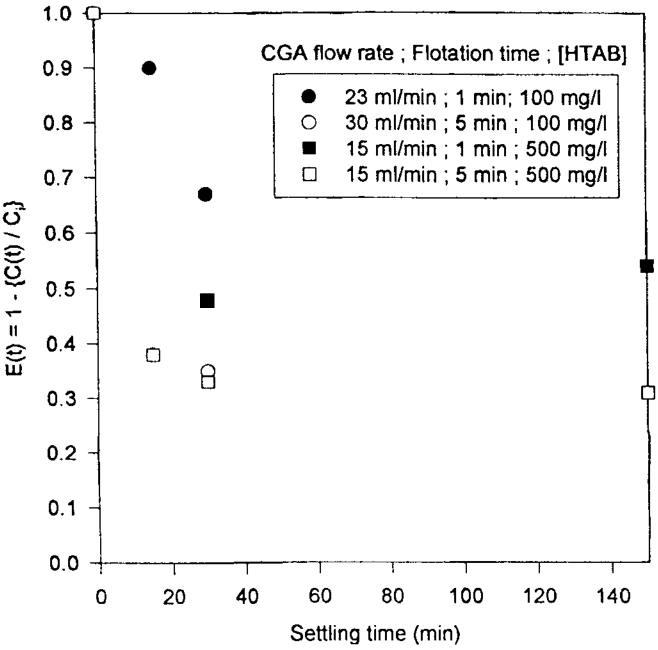


FIG. 5 Residual concentration of SDBS after semibatch PDSE using different concentrations of HTAB for CGA production.

polyaphron flow. The solvent layer formed at the top of the aqueous phase continuously overflowed along with some water resulting from the foam at the top. A simplified model for the continuous countercurrent PDSE process will be derived first to ascertain the parameters that affect the process efficiency. Let us assume that the aqueous phase is completely mixed. The flow rate of feedwater and the dimensions of the column are assumed such that the residence time of the aqueous influent exceeds the time needed for solute partition equilibrium between the solvent and water. Also, assume that the attachment of polyaphrons to a CGA is instantaneous, and that the solvent introduced in the form of polyaphrons is recovered in the overflow at the top of the aqueous section. Let us finally assume that solute diffusion from the overlying organic solvent layer to the aqueous phase is negligible. We can then write the following mass balance for the contaminant in the aqueous phase as illustrated in Fig. 6: (Mass accumulated in the aqueous phase) = (Mass in the aqueous influent) − (Mass in the aqueous effluent) − (Mass in the overflow organic

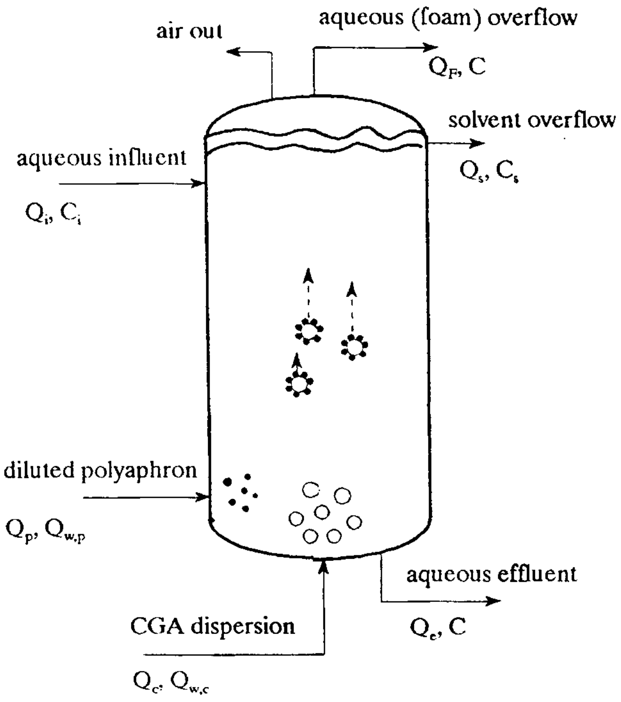


FIG. 6 Mass balance for the contaminant in the aqueous column.

solvent) − (Mass in the aqueous phase of the foam overflow). This gives

$$V_w \frac{dC}{dt} = Q_i C_i - Q_e C - Q_s C_s - Q_F C \tag{4}$$

The concentration of the solute in a polyaphron (solvent) is controlled by the mass transfer of solute between the aqueous phase and the polyaphron through the following equation:

$$\frac{dC_s}{dt} = k_w a(C - C^*) \tag{5}$$

where C_s is the concentration of the solute (mol·cm^{-3}) in the solvent (polyaphron), $(C - C^*)$ is the concentration gradient (mol·cm^{-3}), k_w is the mass transfer coefficient (cm/s), and a is the surface area per unit volume of a polyaphron (cm^2·cm^{-3}). The equilibrium concentration C^* is given by $C^* = C_s/K_{ow}$. Hence we have

$$\frac{dC_s}{dt} + \alpha C_s = \beta C \tag{6}$$

where $\alpha = ak_w/K_{ow}$ and $\beta = ak_w$. Assuming that the value of C does not change appreciably during the rise time (τ) of a single polyaphron that is attached to a CGA, we can arrive at the following equation for the concentration of solute in a polyaphron (i.e., the concentration in the solvent) by integrating the above equation:

$$C_s = K_{ow}C(1 - e^{-\alpha\tau}) \tag{7}$$

The approximation used above for integrating the equation has been used successfully for modeling bubble aeration and solvent sublation in glass columns, activated carbon adsorption columns, and solvent extraction columns (9). For a typical case of a 100-μm CGA collecting a 10-μm radius polyaphron, the velocity of rise is 0.5 cm/s from Fig. 3. In a 100-cm tall aqueous column the rise time will then be 200 seconds. For the dye considered here, K_{ow} is 1310. For a typical value of k_w = 0.1 cm/s (8) and a 10-μm polyaphron, $k_w a$ is 600 s^{-1}. Therefore the term $(1 - e^{-\alpha\tau})$ approximates to 1. Thus, if the rise time of the CGA/polyaphron complex is large and the mass transfer coefficient and interfacial area per unit volume of the aphron are large, equilibrium is established between the aqueous phase and the polyaphrons. Therefore, we have

$$C_s = K_{ow}C \tag{8}$$

As the CGA dispersion and the diluted polyaphron stream are introduced into the column, they contribute to some dilution of the aqueous phase because of their water content. An overall mass balance on the aqueous phase over the entire column gives

$$Q_i + Q_{w,c} + Q_{w,p} = Q_e + Q_F \tag{9}$$

where $Q_{w,c}$ and $Q_{w,p}$ are respectively the flow rates of the aqueous phase resulting from the CGA dispersion and the diluted polyaphron stream. For all practical purposes, $Q_{w,p} \ll Q_{w,c}$. Using the above equation in Eq. (4), we obtain the following expression for the contaminant mass balance in the aqueous phase:

$$V_w \frac{dC}{dt} = Q_iC_i - (Q_i + Q_{w,c} + Q_{w,p} + Q_sK_{ow})C \tag{10}$$

Since we have established earlier (10) that the mechanism of flotation is via coulombic attraction between CGA and polyaphrons, an expression for Q_s can be derived in terms of their radii and the impact efficiency, η. The total number of CGAs introduced at the base of the column is given by

$$N_{\mathrm{CGA}} = \frac{fQ_c}{(4/3)\pi R^3} \tag{11}$$

where f is the fraction of air content in a CGA dispersion (typically varies from 0.3 to 0.65). Note also that $Q_{w,c} = (1 - f)Q_c$. The quality parameter, f, can be determined using a simple drainage test (11). Using Eq. (1) and (11) and defining an impaction factor, η, for the polyaphrons on a CGA, we obtain the solvent flow rate as

$$Q_s = 3.8(\eta f)\frac{r}{R}Q_c \tag{12}$$

Using the above in Eq. (10) and integrating using the initial condition ($t = 0$), $C = C_1$, we obtain the efficiency of removal, $E(t) = 1 - C/C_1$, as follows:

$$E(t) = \frac{\left[\dfrac{(1 - f)Q_c + Q_{w,p}}{Q_i} + 3.8\eta fK_{ow}\dfrac{r}{R}\dfrac{Q_c}{Q_i}\right](1 - e^{-\zeta t})}{1 + \dfrac{(1 - f)Q_c + Q_{w,p}}{Q_i} + 3.8\eta fK_{ow}\dfrac{r}{R}\dfrac{Q_c}{Q_i}} \tag{13}$$

where

$$\zeta = \frac{1}{V_w}\left(Q_i + (1 - f)Q_c + Q_{w,p} + 3.8\eta fK_{ow}\frac{r}{R}Q_c\right)$$

We can now simplify the above equation to obtain the steady-state removal as follows:

$$E_{ss} = \frac{\left((1 - f) + 3.8\eta f K_{ow} \frac{r}{R}\right) \frac{Q_c}{Q_i} + \frac{Q_{w,p}}{Q_i}}{1 + \left((1 - f) + 3.8\eta f K_{ow} \frac{r}{R}\right) \frac{Q_c}{Q_i} + \frac{Q_{w,p}}{Q_i}} \tag{14}$$

The steady-state efficiency is a function of Q_c/Q_i, r/R, η, and K_{ow}. For a given type of CGA and polyaphron, r/R and f are constants. K_{ow} is characteristic of the solute. η is a variable dependent on the fluid dynamics in the column. The process variable is Q_c/Q_i. For a given influent feed rate, Q_i, increased process efficiency can be realized for larger Q_c values. Noting that $Q_s = N_{CGA} n V_p \eta$, it is clear that the larger the number of polyaphrons attached to a CGA, the greater is the efficiency of removal. Obviously, the higher the attachment efficiency, η, and higher the solvent–water partition constant, K_{ow}, the greater is the process efficiency. From Eq. (13) it is clear that the approach to steady state is dependent on the magnitude of ζ which has units of inverse time. It is dependent on the aqueous phase detention time Q_i/V_w and the residence time of the CGA, Q_c/V_w. The larger the value of ζ, the faster is the approach to steady state.

Figure 7 shows the results from the continuous countercurrent experiments on the removal of the dye. The process was run continuously with respect to both the influent feed and the polyaphron and CGA feeds. The initial rate is fast, which then leads to a slow approach to steady state. A steady state is reached in about 200 minutes of operation for an influent feed rate of 25 mL/min and a total CGA flow rate of 19 mL/min. The quality of the CGA dispersion used in this experiment was good (f = 0.67) and hence the air flow rate in the form of CGAs (given by fQ_c) was 13 mL/min, and the flow rate of water resulting from the CGA dispersion was 6 mL/min. The original polyaphron sample was diluted 1:1 (v/v) before being introduced into the column, giving a $Q_{w,p}$ of 0.5 mL/min. The steady-state removal efficiency under these conditions ($fQ_c/Q_i = 0.52$) is 0.64. Also shown is an experiment at a total Q_c of 51 mL/min and at the same Q_i of 25 mL/min. The quality factor for the CGA dispersion was 0.58 and the actual flow rate of air is therefore fQ_c = 29.5 mL/min whereas the flow rate of water resulting from the CGA was 21.5 mL/min. The value of $Q_{w,p}$ in this case was 1.6 mL/min and the original polyaphron sample was diluted 1:3 (v/v) before introduction into the column. The value of

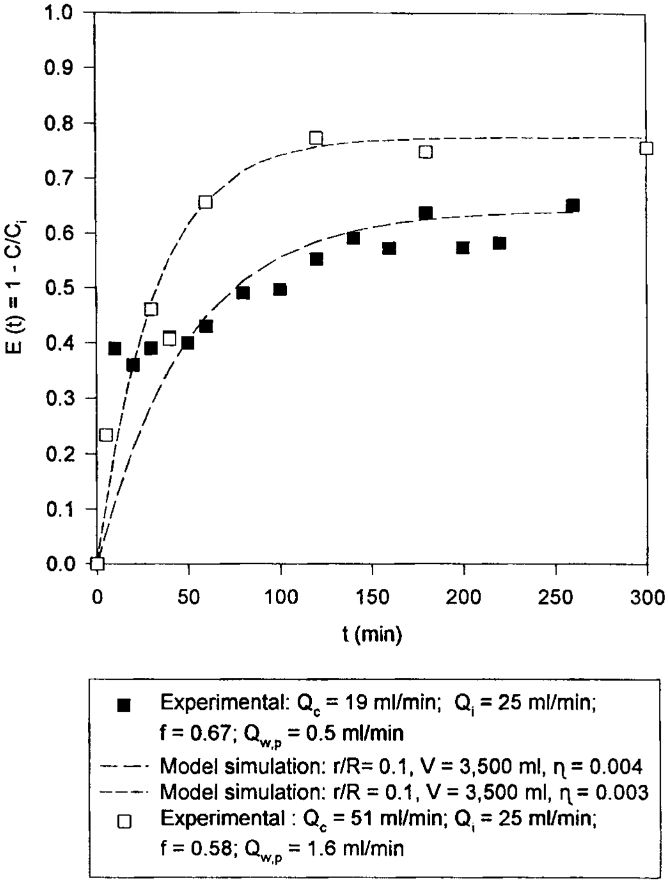


FIG. 7 Removal of the dye in a continuous countercurrent PDSE. Q_i = 25 mL/min.

fQ_c/Q_i was 1.18 in this case and the steady-state efficiency increased to 0.78.

Figure 8 shows the effects of increasing CGA dispersion flow rate at a different influent feed rate (50 mL/min) on the removal efficiency. At a given influent feed rate the amount of polyaphrons attached to a CGA is proportional to the total surface area of the CGA, which in turn is proportional to the gas (CGA) settling time in the column. The CGA settling time is determined by its flow rate. Hence the limiting factor can be expected to be the CGA flow rate. Whereas an efficiency of 0.38 was noted at a CGA flow rate of 11.7 mL/min, a further increase to 41.2 mL/min gave

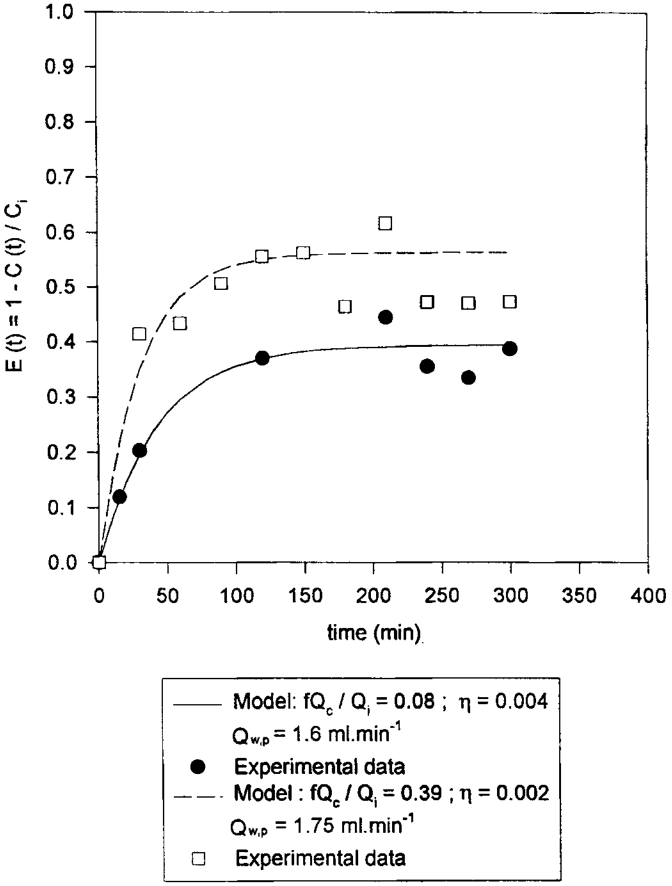


FIG. 8 Removal of the dye in a continuous countercurrent PDSE. Q_i = 50 mL/min.

only an efficiency of 0.56. In the first case the CGA quality was poor (f = 0.34) while in the second case the quality was marginally better (f = 0.47). Therefore the actual air flow rate was 3.9 mL/min in the first case and 19.3 mL/min in the second case. The original polyaphron sample was diluted 1:3 (v/v) before introduction into the column. The values of $Q_{w,p}$ were 1.6 mL/min in the first case and 1.7 mL/min in the second case. A steady state is reached in about 120 minutes of operation. The value of fQ_c/Q_i was 0.08 for the first case and 0.39 for the second case. The fact that the efficiency only increased from 0.38 to 0.56 with a fivefold increase in the ratio of air to aqueous flow rates may be due to excessive dilution of the aqueous phase by CGAs in the second case and a consequent decrease in the mass transfer driving force.

Utilizing the impaction factor (η) as the only variable and using Eq. (13), the experimental curves were simulated. These are shown in Figs. 7 and 8. The total volume of the aqueous column was 3500 mL in these experiments. Typical values of $r = 10\ \mu m$ and $R = 100\ \mu m$ were used (10). An experimentally determined value of the partition constant, $K_{ow} = 1310$, was used in the model. Reasonable predictions of the observed concentration variation with time were obtained. The model satisfactorily predicts the final steady-state efficiency. The value of η used for obtaining approximations to the experimental data varied from 0.002 to 0.004. It is encouraging to note that the assumption of equilibrium mass transfer between the polyaphrons and water holds in these simulations. Overall, we conclude that the model is quite satisfactory in predicting PDSE performance. The model described herein is simplified, but it is instructive in providing a better understanding of the PDSE process.

CONCLUSIONS

The proposed model appears to adequately describe the continuous countercurrent PDSE process. The increased surface area of the predispersed solvent combined with the flotation of polyaphrons afford good separation efficiencies for a hydrophobic organic dye (Solvent Red 27) from the aqueous phase into kerosene. Provided effective attachment is attained through coulombic forces, CGAs greatly enhance the rise velocity of dispersed polyaphrons. Results from batch experiments showed that the duration of flotation as well as the increased aqueous phase settling time had a significant effect on the separation. This indicated the gradual removal of submicron-sized polyaphrons by bouyancy, which was in agreement with the model that indicated a proportional increase in rise velocity with the square of the radius of the polyaphron. The continuous countercurrent process was found to depend on the ratio of the CGA flow rate (Q_c) to the influent feed rate (Q_i). The process efficiency increased with an increase in the ratio, in agreement with the model. Excessive dilution of the aqueous phase and poor mass transfer efficiency appeared to adversely affect the process efficiency at high CGA flow rates. The proposed model also predicted that small values of the relative sizes (r/R) and the partition constant will delay the approach to steady state.

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SYMBOLS

a	surface area of a polyaphron (cm^2)
C	solute concentration in the aqueous phase at time t ($mol \cdot cm^{-3}$)
C_i	solute concentration in the aqueous influent feed ($mol \cdot cm^{-3}$)
C_e	solute concentration in the aqueous effluent ($mol \cdot cm^{-3}$)
C_s	solute concentration in the organic solvent outflow ($mol \cdot cm^{-3}$)
C_F	solute concentration in the aqueous overflow ($mol \cdot cm^{-3}$)
C_D	drag coefficient
$E(t)$	percent solute removal from the aqueous phase at time t
E_{ss}	percent solute removal from the aqueous phase at steady-state
f	fractional air content of a CGA dispersion (quality parameter)
g	gravitational constant (980 $cm \cdot s^{-2}$)
k_w	mass transfer coefficient for the solute between water and organic solvent ($cm \cdot s^{-1}$)
K_{ow}	partition constant for the solute between solvent and water
n	maximum number of polyaphrons that can attach to a CGA
N	flux of solute from water to polyaphron ($mol \cdot s^{-1}$)
N_{CGA}	total number of CGAs introduced into the column at time t
Q_i	aqueous influent feed rate ($cm^3 \cdot s^{-1}$)
Q_e	aqueous effluent flow rate ($cm^3 \cdot s^{-1}$)
Q_c	total flow rate of the CGA dispersion ($cm^3 \cdot s^{-1}$)
$Q_{w,c}$	flow rate of water from CGA dispersion ($cm^3 \cdot s^{-1}$)
$Q_{w,p}$	flow rate of water from diluted polyaphron ($cm^3 \cdot s^{-1}$)
Q_s	organic solvent overflow rate ($cm^3 \cdot s^{-1}$)
Q_F	aqueous foam overflow rate ($cm^3 \cdot s^{-1}$)
r	average radius of a polyaphron (cm)
R	average radius of a CGA (cm)
Re	Reynolds number
t	time (s)
V_w	total volume of water in the flotation column (cm^3)
v	rise velocity of a polyaphron ($cm \cdot s^{-1}$)
V	rise velocity of a polyaphron-loaded CGA ($cm \cdot s\mathscr{S}H^1$)
V_p	volume of a polyaphron (cm^3)
η	impaction factor of polyaphrons to a CGA
ρ_a	density of air ($g \cdot cm^{-3}$)
ρ_w	density of water ($g \cdot cm^{-3}$)
ρ_s	density of organic solvent kerosene ($g \cdot cm^{-3}$)

ζ time constant for the PDSE process (s^{-1})
ν kinematic viscosity of water ($m^2 \cdot s^{-1}$)

REFERENCES

1. J. B. Berkowitz and A. L. Farkas, *Environ. Sci. Technol.*, *26*, 247 (1992).
2. F. Sebba, *J. Colloid Interface Sci.*, *40*, 468 (1972).
3. F. Sebba, *Foams and Biliquid Foams*: *Aphrons*, Wiley, New York, 1987.
4. G. H. Beyer, A. Rodarte, and F. Sebba, *Waste Manage.*, *1*, 297 (1986).
5. A. J. Aggarwal, Thesis submitted to the Virginia Polytechnic Institute and State University, Blacksburg, VA, 1986.
6. D. A. Wallis, D. L. Michelsen, F. Sebba, J. K. Carpenter, and D. Houle, *Biotech. Bioeng. Symp.*, *15*, 399 (1985).
7. D. L. Michelsen, K. W. Ruettimann, K. R. Hunter, and F. Sebba, *Chem. Eng. Commun.*, *48*, 155 (1988).
8. S. V. Save, V. G. Pangarkar and S. K. Vasant, *Sep. Technol.*, *4*, 104 (1994).
9. A. N. Clarke and D. J. Wilson, *Foam Flotation*: *Theory and Applications*, Dekker, New York, 1983.
10. C. Zhang, K. T. Valsaraj, W. D. Constant, and D. Roy, *Sep. Sci. Technol.*, *31*, 1059 (1996).
11. P. G. Chaphalkar, Ph.D. Dissertation submitted to Louisiana State University, Baton Rouge, LA, 1994.
12. A. E. Greenberg, L. S. Clesceri, and A. D. Eaton (Eds.), *Standard Methods for the Examination of Water and Wastewater, APHA/AWWA/WEF*, 18th ed., American Public Health Association, Washington, D.C., 1992.
13. T. A. Barbari and C. J. King, *Environ. Sci. Technol.*, *16*, 624 (1982).

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