Removal of non-ionic organic pollutants from water via liquid–liquid extraction

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Abstract

The removal of model pollutants bromocresol green (BG) and phenol from water is demonstrated via two liquid–liquid extraction methods. Both methods exploit selective interactions established by the pollutant molecule with a surfactant, oil, or alcohol, and are variants of the more general Winsor systems where the phases are in contact along an extremely large interfacial area. In the first method the surfactant and the co-surfactant move from a predominantly oil-in-water microemulsion (Winsor I), to a middle phase microemulsion (Winsor III), and finally to a water-in-oil microemulsion (Winsor II), as the physicochemical conditions of salinity, temperature or hydrophilic–lipophilic balance of the surfactant system are varied. This method achieves better than 99% removal of the pollutant BG from water. It is argued that the removal is produced upon increasing the salinity of the system because the interaction of BG with a medium chain-length alcohol drives it to move along with the alcohol to another phase. The second method, which is scalable to industrial levels, uses a spontaneously produced water-in-oil microemulsion with large interfacial area that appears after bringing in contact water and a pre-formed Winsor II or Winsor III microemulsion system containing different surfactants and oils. The method is applied to the removal of phenol from water, and it is found that systems with polar oils such as ethyl butyrate or with cationic surfactants such as stearyl trimethylammonium chloride are more efficient in removing phenol than systems with normal alkanes or anionic surfactants. It is also shown that a microemulsion formed using a polar oil performs better than using only the polar oil as the extraction solvent. Finally, the efficiency of the second liquid–liquid extraction method can be increased from 69% in a single-stage process to 83% in a two-stage process, using the same total amount of extraction solvent.
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1. Introduction

Because of their extensive use in chemical processing operations, aromatic compounds often appear as undesired pollutants in process water from which they have to be removed before the water can be used again or delivered to the environment. However, separation of aromatics such as phenolic compounds from water is difficult due to their low relative volatilities and their tendency to form azeotropes and eutectics. Hence, distillation cannot be used and alternative techniques such as oxidation in presence of enzymes (Danner et al., 1973) photo catalytic oxidation by TiO_2 particles (Okamoto et al., 1985), separation using liquid

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membranes (Cahn and Li, 1974), and adsorption on activated carbon (Streat et al., 1995; Ehrhardt and Rehm, 1985) and clays are often proposed (Smith and Galan, 1995; Smith et al., 1990; Shen, 2002). Adsorption is the most popular choice among these techniques for water treatment because of the low costs involved.

Adsorption techniques rely on the high interfacial area of the adsorbents. Powdered activated carbon, for instance, shows rapid adsorption kinetics compared to granular activated carbon. However, the recovery of small colloidal powdered activated carbon particles from treated water introduces another separation problem that must be addressed. In this respect, clays are easier to handle because their charged nature allows the use of flocculants, such as surfactants for example.

It has been shown recently that the adsorption of organic cations on the exchange sites of bentonite clays can enhance the uptake of non-ionic organic compounds (NOC) (Smith et al., 1990). That literature suggests that the small organic cations adsorbed on the clays can create a rigid non-polar surface where the NOC can predominantly partition. Such a tendency of an NOC to partition to non-polar regions can possibly be utilized through another major separation process, namely via liquid–liquid extraction (LLE). In a typical LLE operation, two or more immiscible liquid phases that are not in equilibrium are brought in contact to produce an exchange of materials across the interfacial area, where the mass transfer is driven by the chemical potential gradients established between the phases. The transfer process for a compound continues until its chemical potential adopts the same value in each of the different co-existing phases. The separation efficiency of a single-stage LLE operation largely depends on the interfacial area generated through mixing the two phases, i.e., the higher the interfacial area the higher is the separation efficiency. However, systems producing high interfacial area are rarely used in industrial applications because of the very slow separation rate of colloidal droplets (Treybal, 1980). Systems with large droplet sizes are used instead, and the ensuing loss of separation efficiency is compensated by operating in a multistage fashion.

Under certain physicochemical conditions of salinity, temperature or hydrophilic–lipophillic balance (HLB), a surfactant/co-surfactant/oil/brine system easily emulsifies at a low-energy expense to yield extremely large interfacial areas (Salager et al., 1979; Schecter and Bourrel, 1988) i.e., significantly large in comparison to the areas obtained via vigorous mixing of oil and water. A yet more important aspect is that the separation of the phases under the above physicochemical conditions is also extremely rapid (Shah, 1981), making these systems ideal for high-efficiency LLE applications.

This paper examines the feasibility of using spontaneous microemulsification phenomena as the basis for developing LLE methods that are suitable for removing the model pollutants bromocresol green and phenol from water using various oils, surfactants and suitably designed phases that yield high interfacial areas. The envisioned applications where such LLE methods may be highly desirable include situations where there is a need for quickly and effectively removing hazardous pollutants.

For contextual reference it is important to note that the concepts invoked here have relevant links to basic research results realized previously. In particular, researchers in the field of subsurface remediation have applied similar fundamentals to solve the problem of solubilizing/mobilizing non-aqueous phase liquids (West and Harwell, 1992; Shiau et al., 1994; Baran et al., 1994; Doan et al., 2003; Childs et al., 2004). The work presented in this paper differentiates itself from the prior body of literature in at least three aspects. First, the pollutant-extraction methodologies proposed take advantage of the novel observation that Winsor II and Winsor III microemulsions spontaneously break into nanoemulsions of very high interfacial area when brought in contact with water. Second, in contrast with the prior literature, which focused on only non-polar pollutants, the LLE extraction methods proposed include removal of both polar and non-polar species. Third, the extraction method is supplemented with an engineering analysis that shows how to significantly enhance the efficiency through the introduction of a multistage process.

2. Materials and methods

2.1. Materials

Sodium dodecyl sulfate (SDS) (purity 99%), and the water-soluble dye bromocresol green (BG) are supplied by the Sigma Chemical Company (St. Louis, MO). Dodecane, ethyl oleate, ethyl butyrate, n-amyl alcohol, aluminum chloride and phenol are supplied by Fisher Scientific (Fair Lawn, NJ). Stearyl trimethylammonium chloride ($C_{18}TAC$) is obtained as a 50% solution from ICN Pharmaceuticals (Plainview, NY). Ethoxylated nonyl phenols (non-ionic surfactants) of HLB values 9 and 14 with trade names Makon 4 and Makon 12, respectively, are from the Stepan Company (Northfield, IL). All the chemicals are used as-received. Double distilled de-ionized water is used for all the preparations.

2.2. Methods

Two LLE methods are proposed. Both are inspired from the general phase behavior of the (surfactant/ alcohol)/oil/brine system illustrated in Fig. 1. The figure shows that as the salinity or the HLB increases, the

surfactant affinity changes from a hydrophilic to a hydrophobic phase, which makes these systems evolve according to the Winsor rule (Salager et al., 1983): from a two-phase Winsor I system (with an oil in water microemulsion at the bottom in equilibrium with an oil phase at the top) as shown in Fig. 1(a), to a three-phase Winsor III system (with an aqueous phase at the bottom in equilibrium with a bicontinuous microemulsion in the middle which is also in equilibrium with an oil phase at the top) as shown in Fig. 1(b), to a two-phase Winsor II system (with an aqueous phase in equilibrium with a water-in-oil microemulsion at the top) as shown in Fig. 1(c). Most of the surfactant is concentrated in the bottom, middle, or top phase of the Winsor I, III or II system, respectively.

In Method 1, a water source having the hazardous compound BG is formulated with surfactant, co-surfactant, oil and brine to produce compositions,
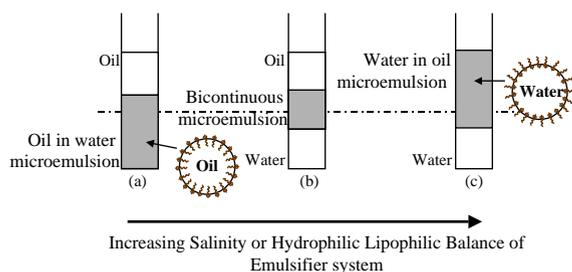

Fig. 1. Schematic of a general (surfactant/alcohol)/oil/brine phase diagram: (a) Winsor I system, (b) Winsor III system and, (c) Winsor II system.

which will ultimately form Winsor II or Winsor III systems. The formulated system is then mixed, creating a nanoemulsion that keeps the water and the oil in close contact along a very large interfacial area that facilitates the mass transfer between the phases as well as among the phases and the interface. The system is then allowed to equilibrate, and the emulsion separates into its constitutive phases. Because of its specific interaction with the chosen surfactant, alcohol, or oil, the pollutant moves along with the surfactant into a bicontinuous microemulsion or into a water-in-oil microemulsion, thus achieving the desired separation of the hazardous molecules from water. Three different microemulsion systems used for evaluating Method 1 are shown in Tables 1–3. The rows in each table represent the compositions used for achieving a particular phase behavior with different surfactants. For example, a typical preparation is given in row 1 of Table 1, which shows that on mixing 2 mL of water containing BG, 1 mL of 10 wt% brine solution, 2 mL of 350 mM SDS surfactant solution, 5 mL of dodecane, and 1 mL of n-amyl alcohol results in a Winsor I system after equilibration.

In Method 2, water containing hazardous components is brought in contact with a preformed bicontinuous or water-in-oil microemulsion. The rationale for this approach is that when water is brought in contact with such a microemulsion, an oil-in-water nanoemulsion with a very large interfacial area is spontaneously produced. As mentioned before, the large interfacial area provides suitable conditions for effective mass transfer among the phases and between the phases and the interface. After

Table 1
Microemulsion system containing SDS, Dodecane, n-amyl alcohol, and brine

Sample	Water (mL)	10 wt% Brine (mL)	350 mM SDS (mL)	Dodecane (mL)	n-amyl alcohol (mL)	Phase behavior
1	2.0	1.0	2.0	5.0	1.0	Winsor I
2	1.8	1.2	2.0	5.0	1.0	Winsor III
3	1.6	1.4	2.0	5.0	1.0	Winsor III
4	1.4	1.6	2.0	5.0	1.0	Winsor III
5	1.2	1.8	2.0	5.0	1.0	Winsor II

Table 2
Microemulsion system containing $C_{12}TAC$, Dodecane, n-amyl alcohol, and brine

Sample	Water (mL)	10 wt% Brine (mL)	350 mM $C_{12}TAC$ (mL)	Dodecane (mL)	n-amyl alcohol (mL)	Phase behavior
1	2.6	0.4	2.0	5.0	1.0	Winsor I
2	2.4	0.6	2.0	5.0	1.0	Winsor III
3	2.2	0.8	2.0	5.0	1.0	Winsor III
4	2.0	1.0	2.0	5.0	1.0	Winsor III
5	1.8	1.2	2.0	5.0	1.0	Winsor III
6	1.6	1.4	2.0	5.0	1.0	Winsor III
7	1.4	1.6	2.0	5.0	1.0	Winsor II

Table 3
Microemulsion system containing Makon 4, Makon 12, Dodecane, *n*-amyl alcohol, and brine

Sample	Water (mL)	350 mM Makon 12 (mL)	350 mM Makon 4 (mL)	Dodecane (mL)	*n*-amyl alcohol (mL)	Phase behavior
1	5.00	0.00	2.00	3.00	1.00	Winsor I
2	4.85	0.15	1.85	3.15	1.00	Winsor III
3	4.80	0.20	1.80	3.20	1.00	Winsor II

the phases have been in contact for a sufficiently long time to reach equilibrium conditions, the nanoemulsion is destabilized by adding an aluminum salt.

The remaining pollutant (BG or phenol) concentration is determined using an HP 8453 UV–visible spectrometer, after filtering the aqueous phase through a 200 nm mesh filter.

It is important to note that even though Method 1 is insightful for laboratory scale separations, only Method 2 is scalable for industrial applications. The reason for this limitation for Method 1 is the requirement of a high and precise salinity control, which will ultimately require an extra unit for desalting, and may considerably increase the equilibration time needed for phase separation (Salager et al., 1979).

3. Results and discussion

To assess the effectiveness of Method 1, water saturated with the pollutant BG was equilibrated with surfactant (anionic, cationic, or mixture of non-ionic), *n*-amyl alcohol, dodecane, and brine, to achieve a Winsor III system. It was noted that all of the Winsor III systems reported in Tables 1–3 removed more than 99% of BG from the original polluted water, irrespective of the nature of the surfactant used. Since the model pollutant has negligible solubility in dodecane, these surfactant-independent results can only be explained by the establishment of a selective interaction of BG with *n*-amyl alcohol. A preferential partitioning of BG into the *n*-amyl alcohol phase was observed after shaking alcohol with BG-polluted water, confirming this hypothesis. It may appear that *n*-amyl alcohol alone is sufficient for the purification of water in such a case. However, it is important to note that polluted water would also contain surfactants, another major class of industrial pollutants. Hence, in practical applications the scenario is more likely to be as shown in Fig. 1(a), i.e., even in the presence of alcohol, the pollutant remains in the aqueous phase. Thus, a proper dosage of salt or of hydrophobic surfactant to change the surfactant affinity of the entire system is the key for the effective removal of pollutants.
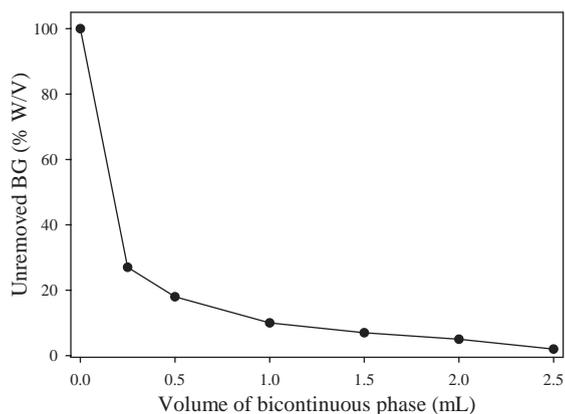

Fig. 2. Effect of the volume of the (SDS/*n*-amyl alcohol)/dodecane/brine middle-phase microemulsion on the removal of Bromocresol green from water using Method 2.

Fig. 2 shows the extent of removal of BG from water obtained using the LLE Method 2. In this test, 25 mL of an aqueous solution containing 1000 ppm of BG are mixed with different volumes (0.25, 0.5, 1, 1.5, 2, and 2.5 mL) of a bicontinuous microemulsion of SDS. Two distinct zones can be clearly identified in the figure. The first zone is characterized by a steep decrease in pollutant concentration, suggesting that small volumes of microemulsion (0–0.5 mL) can remove a large amount (up to 75% w/v) of the pollutant from water. The second zone is depicted by a relatively flat section of the curve, which indicates that the further addition of microemulsion is significantly less efficient in removing the pollutant. Nevertheless, 2.5 mL of the SDS microemulsion is sufficient to remove more than 98% w/v of the pollutant. A probable reason for the large change in the slope of the curve is that the mass transfer obeys a different rate law at low pollutant concentration. More specifically, as the concentration of the pollutant in water decreases, a first-order mass transfer rate may shift to a second-order rate, etc. According to this perspective, a more efficient extraction of pollutant at low concentrations would require the use of a fresh microemulsion. Hence, to maximize the efficiency of the extracting process one should deploy the extraction

method in a multistage manner, perhaps using 0.25 mL of the middle phase for each stage.

The other water pollutant studied, phenol, is recognized by the US Environmental Protection Agency (EPA) as a priority pollutant and is harmful at levels as low as 20 ppm. It is highly soluble in water (1 gm/ 15 mL), which makes it particularly difficult to extract phenol from the water phase using normal LLE solvents. Because of its highly polar nature, the extraction of phenol may require the use of polar oils that can induce a strong driving force for the diffusion of phenol from the aqueous phase to the interface and to the oil phase.

Fig. 3 shows the effect of the nature of the oil phase on the removal of phenol from water using Method 2. It can be seen that a non-polar oil such as dodecane does not remove any phenol. It is only through the use of polar oils such as ethyl oleate and ethyl butyrate as LLE solvents that a significant amount of phenol is extracted. Conceivably, the more effective separation of phenol is achieved due a hydrogen bonding interaction between the carbonyl group on the ethyl ester oils and the alcoholic group in phenol. The amount of phenol removed appears to be dependent on the hydrophilicity of the oil used. Therefore, ethyl butyrate, which is more hydrophilic because of the presence of a short alkyl chain in the structure, removes more phenol than ethyl oleate, which has a long hydrophobic region in its structure. Note that the non-uptake of phenol with non-polar dodecane is in contrast to the hypothesis of a predominant partitioning of an NOC to a non-polar surface created by small organic cations, as suggested in Shen, 2002. The removal of phenol appears to be regulated more by the hydrogen bonding (as shown when using polar oils), by the charge of the cations (as
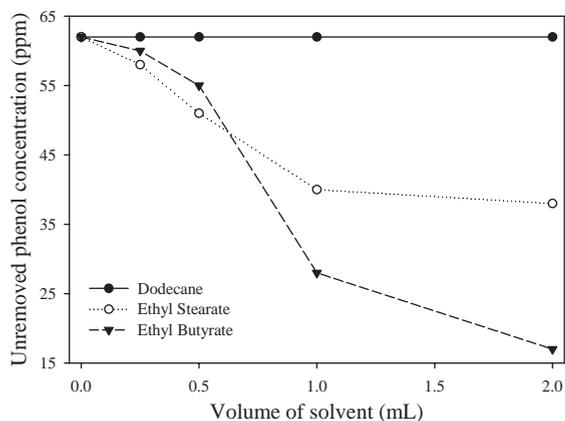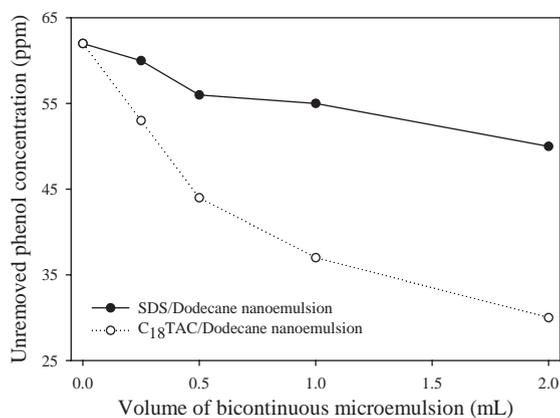

Fig. 4. Effect of the volume and nature of the surfactant in two middle phase microemulsions on the removal of phenol from water using Method 2.

shown below), or by π–π interactions (Shen, 2002), rather than by the presence of a non-polar surface.

The hypothesis that a significant phenol removal is achieved because of a cationic charge is corroborated from the results presented in Fig. 4, which shows the removal of phenol using anionic and cationic nanoemulsions formed using dodecane as the oil phase and amyl alcohol as the cosurfactant. Stearyl trimethylammonium chloride ($C_{18}TAC$), a cationic surfactant, realizes a much better performance than SDS, an anionic surfactant, on the removal of phenol from water, presumably because of a favorable electrostatic interaction with the electron cloud of the aromatic ring.

The results given in Figs. 3 and 4 suggest that a microemulsion system formed by ethyl butyrate and a cationic surfactant should be used to effectively separate phenol from water. However, the precipitation/flocculation of the nano-emulsion is not as easy to achieve in a cationic surfactant system as in an anionic surfactant system. In fact, anionic surfactant coated emulsions can be flocculated easily with multivalent cations such as Al^{3+}. In contrast, for cationic surfactant based emulsions it is necessary to reverse the charge by adding excess anionic surfactant and then using flocculants. To demonstrate the usefulness of the microemulsion route for the separation of phenol, while simultaneously keeping the study simple, in the suite the focus is retained on an (SDS/n-amyl alcohol)/ethyl butyrate/ brine system (see Table 4).

Fig. 5 compares the extraction efficiencies of pure ethyl butyrate oil with that of water in ethyl butyrate microemulsion using Method 2. It can be observed that for small volumes, the microemulsion of ethyl butyrate is more effective than the pure ethyl butyrate oil in the removal of phenol from water. However, for large volumes of extracting phases both systems remove similar amounts of phenol. Apparently, as in the case

Fig. 3. Effect of the volume and nature of three different oils on the removal of phenol from water after shaking the phenol/oil/ water system for 10 min and allowing it to equilibrate for two days.

Table 4
Microemulsion system containing SDS, ethyl butyrate oil, *n*-amyl alcohol, and brine

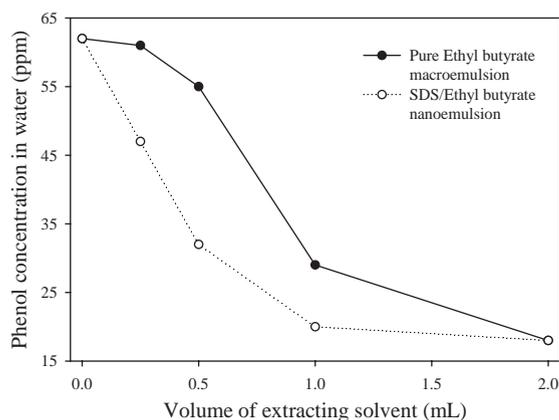| Sample	Water (mL)	10 wt% Brine (mL)	350 mM SDS (mL)	Ethyl Butyrate (mL)	*n*-amyl alcohol (mL)	Phase behavior
1	1.4	1.6	2.0	5.0	1.0	Winsor I
2	1.3	1.7	2.0	5.0	1.0	Winsor III
3	1.2	1.8	2.0	5.0	1.0	Winsor III
4	1.1	1.9	2.0	5.0	1.0	Winsor III
5	1.0	2.0	2.0	5.0	1.0	Winsor II

Fig. 5. Comparison of phenol extraction efficiencies of pure ethyl butyrate oil and water in ethyl butyrate oil microemulsion using SDS surfactant.
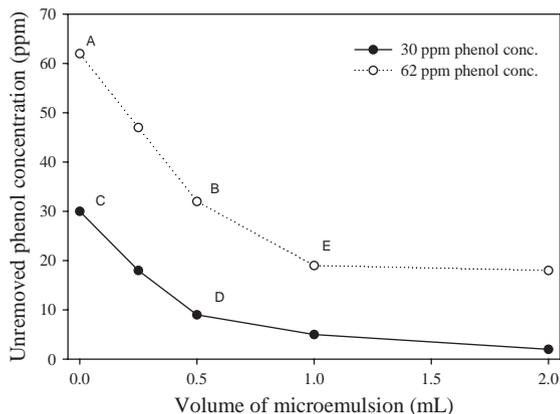

Fig. 6. Effect of the volume of (SDS/*n*-amyl alcohol)/ethyl butyrate/brine water in oil microemulsion on the removal of phenol for two different initial phenol concentrations in water (30 and 62 ppm). A one-stage LLE process reduces the concentration from 62 (point A) to 19 ppm (point E). A two-stage LLE process can reduce the phenol concentration from 62 to 33 ppm in the first stage (A→B), and from 33 to 10 ppm in the second stage (B or C→D).

of the BG pollutant, at low phenol concentrations the extracting process follows a different mass transfer rate law.

To compete favorably with other water purification methods, it is desirable to extract as much phenol as possible using the least microemulsion volume possible. However, the above results show that the smaller driving force available for mass transfer at low phenol concentration limits the maximum amount of phenol that can be extracted. Therefore, a multistage separation process would be desirable to increase the efficiency of removal of phenol from water. The results given in Fig. 6 present a preliminary feasibility study for a two-stage separation process for removal of phenol. Here it can be seen that using 1 mL of extracting phase the phenol concentration can be reduced from 62 (point A) to 19 ppm (point E), amounting to approximately 69% removal via a single-stage LLE operation. However, if the same 1 mL of extracting phase is divided equally in two stages, each of 0.5 mL extractant, the phenol concentration can be reduced to 33 ppm in the first stage (point B or C) and then to 10 ppm in the second stage (point D) amounting to approximately 83% removal of phenol. Hence, when a significant increase

in the extraction efficiency is required by the process specifications, a multistage LLE extraction method can be designed to achieve the required target performance.

4. Conclusions

Two LLE methods have been shown to be effective and efficient for the removal of hazardous pollutants from an aqueous solution. Method 1 is viable for small-scale applications, such as laboratory extraction operations, or for use on the field to purify small amounts of drinking water for humans traveling through a polluted environment. Method 2 is more attractive from an industrial application perspective. The use of specialized solvents (*such as* alcohol for bromocresol green (BG) and ethyl butyrate for phenol) can introduce a significant enhancement in the process of removal of pollutants. Furthermore, a single-stage extraction

efficiency of 69% is realized in the current work for the removal of phenol, and it is shown that the phenol extraction efficiency can be enhanced to 83% by splitting the extraction solvent equally between two stages.

It is worthwhile to mention that the goal of the research documented here is to establish the promise of a microemulsion route for *spontaneously* producing liquid–liquid extraction systems featuring very high interfacial areas for removal of pollutants. Under this perspective, microemulsions with single-stage phenol extraction efficiencies as high as 69%, a value that is comparable to the efficiencies of alternative remediation techniques such as the high-grade activated-carbon method studied by Streat et al. (1995) that realized a 75% efficiency (as can be inferred from the data presented in Figs. 2 and 8 of Streat et al. (1995).

Although the current state of this research succeeds in validating the feasibility and efficiency of spontaneous microemulsion methods for LLE, we have not yet addressed all the issues of interest regarding the residual concentrations of surfactant, co-surfactant, and solvent in the purified water. The next level of engineering research should focus on quantifying the residual concentration of species and assessing the associated level of toxicity. If necessary, FDA-approved surfactants and solvents should be considered as candidates for safe use in the applications envisioned. Note that toxicity concerns are not relevant for the case of the ethyl-butyrate solvent used in our studies, given that it enjoys appropriate FDA approval and is in fact used in many pharmaceutical applications.

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