COR'S ACCEPTANCE REPORT

DATE OF REQUEST: August 21, 2001
AWARD NUMBER: DE-FG26-99FT40618

FROM: Joseph S. Maury
TO: Paula B. Flenory

NAME OF AWARDEE: Hampton University

PROJECT TITLE: Removal of Organic Chemicals from Wastewater
by Surfactant Separation

Overall Rating of Awardee's Performance (Check one):
Satisfactory [X]

[ ] Unsatisfactory, please explain on separate sheet (attached).

Overall rating should be determined by, but not necessarily limited to, the following:
evaluation of technical adherence to scope of work; evaluation of technical performance and technical approach to project; evaluation of report submission, and whether Awardee overran or underran award.

FINAL ACCEPTANCE: This is to certify that all Goods/Services required under the referenced award as amended, has been completed and finally accepted; that the Goods/Services has been inspected/evaluated by me or my duly authorized representative and has been found to comply with the terms and conditions of the award instrument and the specifications governing same. Therefore, all Goods/Services under this award are accepted as of this date on behalf of the United States Department of Energy, National Energy Technology Laboratory.

[Signature]
Paula B. Flenory
NAME OF C.O.R.

[Date]
12/5/01

COR's Comments:
REMOVAL OF ORGANIC CHEMICALS FROM WASTEWATER
BY SURFACTANT SEPARATION

Liang Hu*, Adeyinka A. Adeyiga and Effie Miamee
School of Engineering and Technology, Hampton University
Hampton, Va 23668

ABSTRACT

This research presents a novel hybrid process for removing organic chemicals from contaminated water. The process uses surfactant to carry out two unit operations (1) Extraction; (2) Foam flotation. In the first step, surfactant is used to extract most of the amounts of organic contaminants in the stream. In the second step, foam flotation is used to further reduce organic contaminants and recover surfactant from the stream. The process combines the advantages of extraction and foam flotation, which allows the process not only to handle a wide range of organic contaminants, but also to effectively treat a wide range of the concentration of organic contaminants in the stream and reduce it to a very low level. Surfactant regeneration can be done by conventional methods. This process is simple and low cost. The wastes are recoverable.

The objective of this research is to develop an environmentally innocuous process for the wastewater or reclaimed water treatment with the ability to handle a wide range of organic contaminants, also to effectively treat a wide range of the concentration of organic contaminants in contaminated water and reduce it to a very low level, finally, provides simpler, less energy cost and economically-practical process design. Another purpose is to promote the environmental concern in minority students and encourage minority students to become more involve in environmental engineering research.

Because of the limitation of funding availability, our research only focus on the feasibility study of the proposed process. The research activities include analytical method development, extraction separation and flotation. A simulated wastewater containing 10 ppm phenol was tested. By using non ionic surfactant Triton X-100, the concentration of phenol in wastewater was reduced by more than half after one stage of extraction. After extraction, the simulated surfactant lean phase was tested with flotation for surfactant recovery and further removal of phenol. The experimental results showed that Triton X-100 was able to be recovered completely. At experimental conditions, the concentration of phenol in collected foam was five time higher than that in surfactant lean phase.

Feasibility study proved that proposed hybrid process is able to remove organic chemicals from wastewater, and to recover surfactant Triton X-100 completely.

Keywords: Surfactant, extraction, flotation, wastewater, organic contaminates.

*Author to whom all correspondence should be addressed. Phone, 757/727-5530; e-mail: lianghu59@yahoo.com
I. Introduction

Wastewater often contained many kinds of organic compounds like PCBs, pesticides, herbicides, phenols, polycyclic aromatic hydrocarbons, aliphatic and heterocyclic compounds, etc. Removal and recovery of the above chemicals from contaminated water and recycle of wastewater will be beneficial to the environment. An overview of various physicochemical process used to treat wastewaters has been provided by Mark R. Matsumoto et. al. The methods in the review included precipitation, coagulation, flocculation, sedimentation, flotation, filtration, membrane processes, sorption, oxidation/reduction, air stripping, extraction etc.[1-5] Among those traditional methods, solvent extraction is of great interest because it is flexible for a wide range of waste contaminants. The contaminants removed from wastewater can be recovered. However, the drawbacks are (1)solvent loss, (2) contamination from solvent occurs if solvent used with toxicity, (3) inefficiency in reducing contaminant concentration to a relative low level. By using membrane solvent extraction, which employs a microporous polymeric membrane as the interface while two phases flow on two sides of the membrane, some of the disadvantages can be overcome. As reported, this method is successful in removal of organic pollutants like phenols [6,7], but it is easy to cause fouling if proper pretreatment is not applied. In the past several years, a rapid expansion of surfactant use into a number of new, important area of technology has been seen, especially in the area of wastewater treatment process. These technologies includes froth flotation, absorptive bubble separations, surfactant-based liquid membranes, micellar-enhanced ultrafiltration, coacervate-based separation, micellar chromatography. Surfactant-based separations have a number of potential advantages over traditional methods. They often are low-energy processes because large temperature variation or endothermic phase changes are not being used to effect separations. Surfactants are often environmentally innocuous and of low toxicity in contrast to toxic solvents from traditional liquid-liquid extraction. However current use of surfactant-based wastewater treatment processes has some limitation, either the loss of the surfactant in the process of wastewater treatment or the limited or narrow concentration range for the treatment of the contaminated water.

Early work reported by G. A. Nyssen, etc. [12] has shown that trace levels of pentachlorophenol and other acidic phenols (which exist in aqueous solution as anions) can be
removed from water by foam flotation with cationic surfactant, cetyltrimethylammonium bromide. From their results, the residual PCP concentrations of less than 0.05 ppm were obtained after 5 minutes flotation with initial PCP concentrations of 20 ppm or less. Grieves and coworkers [13] studied the removal of phenols by adsorptive bubble separation techniques. Valsaraj and Springer [14] investigated the removal of pentachlorophenol by solvent sublation. According to the report by Gerard A. Nyssen, Jonathan S. White, etc. [15], they utilized the foam flotation technology to remove trace levels of aromatic amine from aqueous solution. With initial amine concentrations of 10 mg/L or less, residual amine concentrations of less than 0.1mg/L were obtained after 10 - 30 minutes of flotation. Aromatic amines included 4 - aminobiphenyl, 1 - and 2 - aminonaphthalene, and 2, 6 - xylidine. The surfactant which was used in the process was sodium dodecylsulfate (SDS).

Surfactant extraction process has found application in some areas, such as bioseparation process[5], environmental remediation process etc. Wayt, Clarke, Wilson and Gannon reported the processes using surfactant extraction for soil washwater recycle [8-11]. In those process, surfactant lean phase was directly fed back into the system without any further treatment. The disadvantage was obvious. The contaminates in the surfactant lean phase reduced the efficiency of the soil wash and left high contaminates in the soil.

This research presents a process for treatment of water which is contaminated by organic chemicals, such as, phenols, polycyclic aromatic hydrocarbons, aliphatic and heterocyclic compounds etc. The process consists of two steps (1) Extraction; (2) Foam flotation. In the first step, a surfactant is used to extract most of the amount of organic contaminants in the stream. In the second step, foam flotation is used to further reduce organic contaminant concentration and recover the dissolved surfactant. The process combines the advantages of extraction and foam flotation, which allows the process not only to handle a wide range of organic contaminants but also to effectively treat a wide range of the concentration of organic contaminants in contaminated water and reduce it to a very low level. Surfactant regeneration can be achieved by many conventional methods.

II. OBJECTIVE

The objective of this proposed research is to develop an environmentally innocuous process
for the wastewater or reclaimed water treatment with the ability to handle a wide range of organic contaminants, also to effectively treat a wide range of the concentration of organic contaminants in contaminated water and reduce it to a very low level, finally, provides simpler, less energy cost and economically-practical process design. Another important purpose for this proposed research is to promote the environmental concern in minority students and encourage them to become involved in environmental engineering research.

III. WORKING PRINCIPLE & PROCESS DESCRIPTION

The proposed process for removing organic contaminants from waste stream consists of two major steps (1) extraction by surfactant; and (2) foam flotation.

(1) Surfactant extraction

The principle of the surfactant extraction is based on a surfactant phenomenon, cloud point. Cloud point is the temperature above which all but very dilute aqueous solutions become turbid and eventually form two phases, surfactant-lean and surfactant-rich.

Surfactant has hydrophilic and lipophilic properties. Their lipophilic ends aggregate and hydrophilic ends associate with water when they are solubilized in water, forming micelles. As temperature increases, the hydration forces of hydrophilic ends is reduced. The surfactant then becomes less soluble in water. The separation of aqueous solution of non-ionic surfactant into surfactant-rich and surfactant-lean phases occur when the temperature of aqueous solutions is over cloud point.

In application, surfactant is added into organic contaminated water at the temperature below cloud point. With temperature increasing to above cloud point, two phases appear. The dissolved organics will tend to be much more soluble in the surfactant-rich phase. The organics in contaminated water can be concentrated into surfactant-rich phases by using a multistage operation.

(2) Foam flotation

The basic principle of using foam flotation for removing organics from contaminated water is simple. When surfactant exists in water phase, micelles are formed. Organic compounds are solubilized into micelles. When gas bubbles passes through aqueous phase, the micelles are adsorbed on the gas/liquid interface to reduce Gibbs Energy and emerge
from water phase as foam.

In application, the surfactant is chosen so that its adsorption at the air/water interface creates an environment that is favorable to the adsorption of the organic contaminants to be removed from solution. The air bubbles sparged into a column of water rise to the top of the column. Surfactant which solubilizes the organic contaminants in its micella adsorbed on the air/water interface and rise to the surface of water as foam. The foam can then simply be skimmed off.

(3) Removal of organic impurities from contaminated water by surfactant extraction-flotation

In the proposed process (see Figure 1) the contaminated stream flows into extraction column 1. In the extraction column 1, the stream is extracted by nonionic surfactant at a temperature above cloud point to remove most of the amount of organic impurities. After extraction, the surfactant rich phase which contains organic impurities is forwarded to regeneration unit 3 for regeneration of surfactant. This is where organic impurities in the surfactant-rich phase are separated from surfactant-rich phase. After regeneration, the surfactant-rich phase is fed back into extraction column 1 for recycling. The surfactant-lean phase from extraction column 1 is forwarded to foam flotation column 2. The foam flotation column 2 is operated below cloud point. This means temperature of surfactant lean phase from extraction tank 1 has been cooled down to below cloud point by the heat exchanger before entering into foam flotation column 2. In the column, gas bubbles pass through surfactant lean phase. The organic impurities and surfactant come out of surfactant-lean phase in the form of foam. The foam is removed from the top of the column and forwarded to regeneration unit 3 for further separation of the organic impurities and the surfactant. The surfactant lean phase (treated wastewater) can then be released or recycled.

The advantages of combining extraction and foam flotation are that the system is able (1) to effectively treat a wide range of organic contaminant concentrations in wastewater and reduce it to low levels without high cost; (2) to treat a wide range of organic contaminants without toxicity; and (3) to recover organic contaminants.
IV. EXPERIMENT & RESULTS

The research was focused on feasibility study. The experiments were divided by three parts: analytical method development, extraction separation, and flotation separation. The objective of the experiments are to provide the information on the feasibility of proposed research.

ANALYTICAL METHOD

1. Instrument and operation conditions

The simulated wastewater contained Phenol or Acenaphthylene (one of the components of PAH) and non ionic surfactant Triton X-100. The high pressure liquid chromatography (HPLC, HP Series 1100 with HP 1046A Programmable Fluorescence Detector) was used to perform quantitative analysis of above compounds. The operation conditions were as follows:
Column: HP ODS Hypersil  
5 um, 250 x 4.6 mm  
P/N 79916 18-584

Mobile phase: Acetonitrile / Water = 60 % / 40.0 %

Flow rate: 1.5 ml/min

With above HPLC column and operation conditions, the instrument is able to separate and identify all of the compounds.

2. Calibration curve for Phenol and Acenaphthylene.

Calibration curve for Phenol and Acenaphthylene was carried out by the method of internal standards with five different concentrations. The concentrations of five standard solution for calibration were 1 ppm, 5 ppm, 10 ppm, 30 ppm, 50 ppm. The liner relationship of concentration (ppm) and the signal area (mAU*s) of HPLC spectrum for both Phenol and Acenaphthylene were obtained. The correlation and residual standard deviation for phenol were 0.9916 and 33.56. The correlation and residual standard deviation for acenaphthylene were 0.9944 and 24.00.
3. Influence of Triton X-100 on the quantity analysis of Phenol

Different amount of Triton X-100 surfactant was added into 10 ppm Phenol solution to study the influence of Triton X-100 on the quantitative analysis of Phenol. Experimental results showed that analytical results for the concentration of Phenol would not be influenced by Triton X-100 concentration.

<table>
<thead>
<tr>
<th>Conc. of Phenol (ppm)</th>
<th>Conc. of Triton X-100 (%wt)</th>
<th>Area (mAU*s) (Phenol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.1</td>
<td>87.17</td>
</tr>
<tr>
<td>10</td>
<td>0.2</td>
<td>87.08</td>
</tr>
<tr>
<td>10</td>
<td>0.5</td>
<td>86.90</td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
<td>87.58</td>
</tr>
</tbody>
</table>

4. Quantitative analysis of Triton X-100 surfactant by HPLC

Quantitative analysis of Triton X-100 surfactant also can be conducted by HPLC. Calibration curve for Triton X-100 was carried out with four different concentrations. The concentrations of...
four standard solution for calibration were 0.1 %, 0.2 %, 0.5 %, and 1.0 %, all in weight %. As seen, a liner relationship between area (mAU’s) and concentration was obtained.

![Calibration curve of Triton X-100](image)

5. Quantitative analysis of Triton X-100 surfactant by weight analysis

Based on the difference of vapor pressure, weight analysis was applied to quantify the surfactant, Triton X-100, in the aqueous solution. The experimental results showed that analytical error for Triton X-100 by weight analysis was in 2 %.

<table>
<thead>
<tr>
<th>Initial weight (g)</th>
<th>40.7319 (DI water) + 0.3949 (Triton X-100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight after dry in oven</td>
<td>0.4020</td>
</tr>
</tbody>
</table>

*Oven temperature set to 110 °C. Dry period was 24 hours.
EXTRACTION SEPARATION

1. Surfactant selection

Surfactants play the most important role in the separation process. First, they solubilize organic contaminants into micelles, and second, they form micelles into which organic solubilized contaminants attach on the gas/liquid interface. The proper surfactant(s) should at least have the following characteristics: (1) high solubilization capacity for organic contaminants, and (2) hydrophobic characteristics of the formed micelle, which means the formed micelle will adsorb on the gas/liquid interface firmly.

Nonionic surfactants have been proven to have better solubilizing power for organic compounds like hydrocarbons and long chain polar compounds [16][17], and they are commonly used as frothers in the froth flotation process. It is for these properties that we selected a nonionic surfactant in our research system. Another important reason is that nonionic surfactants have a lower cloud point than other types of surfactants.

For our feasibility study, we used Triton X-100 (Octylphenoxypolyethoxyethanol nonionic surfactant). This viscous liquid is a nontoxic, widely-used nonionic surfactant with a pale yellow color, 1.06 g/cm density, and molecular weight of 624. Other physical properties as follows:

- Boiling point, 760 mm Hg: $> 200 \, ^\circ C$
- Freezing point: 6 °C
- Vapor pressure at 20 °C: $< 0.01 \, \text{mmHg}$

It is miscible with water, alcohol and acetone. It is soluble in benzene and toluene but insoluble in petroleum ether. Research from W.N.J. Maclay [18], A.S. Sadaghania and A. Khan [36] showed that the cloud point in Triton X-100 and water systems changed with the concentration of Triton X-100 by wt%. The cloud point is about 66 °C when the concentration of Triton X-100 is below 6 % by weight. As Triton X-100 concentration increases, temperature of cloud point increases. At about 60 % by weight of Triton X-100, the cloud point is about 88 °C. Influence from inorganic and organic chemicals as solubilizates is sometimes significant and complicated. They can either increase or decrease cloud point. Some results can be taken from references [18][19].

2. Experimental procedure

In the primary extraction study, 50 ml Phenol solution with the concentration of 10 ppm was
placed into 200 ml volume flask (at room temperature, 21 °C). Two grams of triton X-100 surfactant was added into volume flask, which made the concentration of Triton X-100 equal to 3.85 %wt. The solution was stirred to fully dissolved with a stir bar. After then, the volume flask was placed into 80 °C water bath. There are two phases appears in the solution, one was surfactant rich phase, another was surfactant lean phase. About 2 ml surfactant rich phase was formed in the bottom of the volume flask, separated and sampled. Samples were analyzed by HPLC. Analytical results showed that Phenol concentration in surfactant lean phase (water phase) was reduced to 4.1 ppm. The residue of Triton X-100 in surfactant lean phase was 0.079 % wt.

**FLOTATION**

The purpose of foam flotation was to recover the surfactant Triton X-100 and further remove Phenol from wastewater. The apparatus used for flotation was a 250 ml glass bottle with a side tube for collecting foam. A fritted glass gas sparger was inserted into the bottle. Compressed air flowed through the fritted glass gas sparger and bubbled through wastewater (surfactant lean phase). In our experiment, 150 ml of simulated surfactant lean phase with 5 ppm phenol and 0.1 % (wt) Triton X-100 was placed into glass bottle. During flotation, samples were taken from surfactant lean phase for HPLC to determine the concentration of Phenol and Triton X-100. The experimental results as follows:

<table>
<thead>
<tr>
<th>flotation time (minutes)</th>
<th>concentration of phenol in surfactant lean phase (ppm)</th>
<th>concentration of Triton X-100 in surfactant lean phase (% wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.07</td>
<td>0.11</td>
</tr>
<tr>
<td>11</td>
<td>5.10</td>
<td>0.11</td>
</tr>
<tr>
<td>21</td>
<td>5.17</td>
<td>0.10</td>
</tr>
<tr>
<td>31</td>
<td>5.01</td>
<td>0.09</td>
</tr>
<tr>
<td>41</td>
<td>5.04</td>
<td>0.09</td>
</tr>
<tr>
<td>401</td>
<td>4.93</td>
<td>0.01</td>
</tr>
<tr>
<td>821</td>
<td>4.52</td>
<td>0.00</td>
</tr>
</tbody>
</table>

After flotation, the liquid volume of collected foam was about 1.5 ml. The solution was analyzed by
The concentration of phenol in foam was 25.23 ppm and Triton X-100 was 6.65 % (wt).

The experimental results showed that non ionic surfactant Triton X-100 was totally recovered after flotation. Phenol concentration in surfactant lean phase was reduced to 4.5 ppm from 5 ppm. However, the concentration of phenol in foam was 5 times higher than that in aqueous phase.

V. CONCLUSION

As we expected, non ionic surfactant Triton X-100 is able to effectively extract phenol from its aqueous solution. Experimental results showed that phenol concentration was reduced by more than half after 50 ml, 10 ppm phenol aqueous solution extracted by 2 g of Triton X-100.

A simulated surfactant lean phase was tested with flotation for surfactant recovery and further removal of phenol. Experimental results showed that non ionic surfactant Triton X-100 was able to be recovered completely. At the experimental conditions, partial phenol was removed from surfactant lean phase. However, the concentration of phenol in foam was five times higher than that in its aqueous solution. In our experimental conditions, collected foam contain phenol about 25 ppm, Triton X-100 6.65 % (wt).

Feasibility study proved that proposed hybrid process is able to remove organic chemicals from wastewater, but to recover surfactant Triton X-100 completely. The experimental data showed that the future for the proposed hybrid process seems great. As we proposed, it is possible for this process to provide a new method for the wastewater treatment which effectively treat a wide range of organic contaminants without loss of surfactant.

Further study of the process should be focused on following area:

1. More types of contaminants should be tested.
2. Study phase equilibrium for the basic information of extraction process.
3. Study multistage extraction for further reducing the concentration of contaminants in surfactant lean phase, at the same time, obtaining more concentrated surfactant rich phase for more efficiency process.
4. Further improvement of the separation efficiency of flotation. To reach this goal, first to select more effective surfactant. Second, to search optimized operation conditions.
V. REFERENCE