OFFICE OF NAVAL RESEARCH
END-OF-THE-YEAR REPORT
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N00014-93-1-0780

PR Number 98PR03897-00

Title of GRANT or CONTRACT
RESPONSIVE AMPHIPHILIC POLYMERS AND MEMBRANES FOR WATER REMEDIATION

Name of Principal Investigator
Charles L. McCormick

Name of Organization
The University of Southern Mississippi

Address of Organization
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Date Submitted
July 10, 1998

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Contract/Grant Number: N00014-93-1-0780
Contract/Grant Title: Responsive Amphiphilic Polymers and Membranes for Water Remediation
Principal Investigator: Charles L. McCormick
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a. Number of papers submitted to refereed journals, but not published: 2
b. + Number of papers published in refereed journals (for each, provide a complete citation): 7
c. + Number of books or chapters submitted, but not yet published: 0
d. + Number of books or chapters published (for each, provide a complete citation): 0
e. + Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 6
f. Number of patents filed: 0
g. + Number of patents granted (for each, provide a complete citation): 0
h. + Number of invited presentations (for each, provide a complete citation): 7
i. + Number of submitted presentations (for each, provide a complete citation): 4
j. + Honors/Awards/Prizes for contract/grant employees (list attached): 1
   (This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this PR number: 7
   Graduate Students: 6
   Post-Doctoral Associates: 1
   including the number of,
   Female Graduate Students: 1
   Female Post-Doctoral Associates: 0
   the number of
   Minority* Graduate Students: 0
   Minority* Post-Doctoral Associates: 0
   and, the number of
   Asian Graduate Students: 0
   Asian Post-Doctoral Associates: 1
l. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)
   Gillette Research Foundation ($80,000/year)
   Nalco Corporation ($30,000/year)
   Calgon Corporation ($10,000/year)
B. Published Papers in Refereed Journals


E. Published Papers in Non-Refereed Journals


H. Invited Presentations


Polymers for Application in Petroleum Oil Recovery. Caracas, Venezuela (July 9-19, 1997).

Polyampholyte and other Zwitterionic Systems. BASF, Germany (August 1, 1997).

Zwitterionic Cyclocopolymers: A New Class of Polyampholytes Containing Sulfbetaine and Carboxybeteaine Moieties. R. Scott Armentrout, Yuxin Hu, Michael F. Richardson, and Charles L. McCormick, Fifth Chemical Congress of North America, Cancun, Mexico (November 11-15, 1997).


I. Submitted Presentations


J. Honors

EOY Report-Part II

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e. Significant results during the last year:

During the past year our group has demonstrated that polymer enhanced ultrafiltration may be utilized to effectively remove organic foulants from a wastewater stream. This technology is an advancement of micellar enhanced ultrafiltration that is commonly found in many remediation efforts. Micellar enhanced ultrafiltration is characterized by the addition of a small molecule surfactant to the aqueous stream containing an organic foulant. The foulant is solubilized within the micellar hydrophobic core and the stream is then passed through a microporous membrane, such that most of the organic solute and surfactant remain in the retentate. Although this method often achieves high efficiencies of removing a foulant, monomeric surfactant continuously crosses the membrane into the permeate. Therefore, added surfactant is required as time progresses to maintain a critical micelle concentration. In order to circumvent this problem, we have utilized a commercially available polymeric surfactant (Pluronic F127) as the solubilization agent. In this case, the size of the surfactant is sufficiently large to prevent passage through the membrane into the permeate and the addition of surfactant to the retentate is unnecessary. We have shown that the PEO-PPO-PEO triblock copolymer will associate with model water foulants in an ultrafiltration application such that this technology may be utilized in a closed system such as that would be required on a naval vessel.

f. Summary of plans for next year's work

To date, we have demonstrated that the utilization of polymeric surfactants may replace small molecule surfactants in micellar enhanced ultrafiltration applications. However, our ultimate goal is to develop environmentally responsive polymeric surfactants such that the binding of the foulant to the polymer may be controlled by changes in temperature, pH, ionic strength, etc. These systems would allow for an in situ mechanism of removing the foulant from the polymeric surfactant. We are currently involved in the synthesis and characterization of novel polymeric surfactants based on cyclopolyomers of diallyl methyl amine. These polymers show pH dependent aggregation behavior in aqueous media. It is our plan to investigate the efficiency of these novel polymers in the polymer enhanced ultrafiltration application as discussed above.
Graduate Student Investigators
R. Scott Armentrout
Martin E. Cowan
Kathy M. Johnson
Garrett Poe
Geoffrey L. Smith
David Thomas

Post-Doctoral Associate
Yuxin Hu
Micellar Enhanced Ultrafiltration
University of Southern Mississippi, Hattiesburg, Mississippi

Technology Issues: Greywater remediation, design and synthesis of environmentally responsive polymeric surfactants, controlled binding of water foulants within polymeric associates

Objective: Develop new technologies to remove foulants from a wastewater stream.

Approach:
• Develop structure-property relationships in the development of environmentally responsive polymeric surfactants
• Utilize polymeric surfactants in micellar enhanced ultrafiltration applications

Accomplishment:
• Demonstrated the use of commercially available polymeric surfactants in an ultrafiltration application for the removal of model water foulants

Impact:
• Polymeric surfactants utilized in an ultrafiltration application are quantitatively retained within the retentate thereby circumventing the addition of small molecule surfactants throughout the process. (A major problem in conventional micellar enhanced ultrafiltration.)
Ultrafiltration via Responsive Polymeric Surfactants

Goal: Enhanced Water Remediation
- Efficient Foulant Rejection
- High Permeate Flux
- Stimuli Reversible Sequestration

![Graph showing concentration of residue over time](#)

Figure 1. Plot illustrating capture and concentration of foulant, p-cresol, with time allowing passage of cleaned water. (Retentate flow rates are shown in legend.)
Hollow Fiber Remediation Filter

Retentate (Filled Polymer)

Clean Permeate