Water Research Institute

Annual Technical Report

FY 1998

Introduction

Research Program

Basic Project Information

Basic Project Information	
Category	**Data**
Title	Evaluation of Biocidal Polymers for the Treatment of Domestic Water Supplies: Application of Polymers to the Surface of Carrier Particles
Project Number	WRI18
Start Date	09/01/1997
End Date	08/31/1999
Research Category	Water Quality
Focus Category #1	Water Quality
Focus Category #2	None
Focus Category #3	None
Lead Institution	West Virginia University

Principal Investigators

Principal Investigators			
Name	**Title During Project Period**	**Affiliated Organization**	**Order**
Richard Turton	Professor	West Virginia University	01

Problem and Research Objectives

The focus of the proposed research was to demonstrate that fine powders of the N-halamine class of biocidal polymers can be coated onto carrier particles and to evaluate the efficacy of the coated particles. The coating process was to be carried out using a fluidized bed coating apparatus that had been modified for powder coating. It was proposed that batches of coated particles would be produced in this work. The mechanical integrity and biocidal effectiveness of these coated particles would also be evaluated using a packed bed flow cell.

Methodology

The mechancial integrity of the particles was to be tested by exposing the coated particles to high velocity water flows for extended periods of times. The loss of weight of coating was to be checked and used to compare the long-term effectiveness of different binder solutions. The biocidal effect of the coated particles was tested by flowing distilled water seeded with a non-pathogenic from of bacteria (Escherichia coli) through a packed bed cell containing batches of coated particles. The feed and effluent concentrations of bacteria were measured under varying conditions of flowrate and feed concentration of bacteria.

Principal Findings and Significance

During this research, the determination of a suitable binder to adhere the polymer to the carrier was made. A number of binders were investigated but emphasis was focused on the Aquacoat and Eudragrit lines, manufactured by FMC and Rohm, respectively. These binders are pharmaceutical grade and have received approval by the Food and Drug Administration of the United States government. Both binders are commonly employed for producing sustained release medications. The additions of appropriate plasticizers, such as dibutyl sebecate (DBS), can procide water-insoluble coatings that were thought to be appropriate for this research. Coating tests demonstrated encouraging results. The combination of Aquacoat and DBS produced the most stable and suitable water-insoluble binder coating. Aquacoat is an aqueous ethyl cellulose dispersion that consists of 30% by weight solids. DBS plasticizer is added at a level of 24% by total-solids weight in order to lower the glass transition temperature of the ethylcellulose to approximately 40 degrees celsius. Coating in a Wurster fluidized bed process, at temperatures above the glass transition temperature, results in stable uniform coatings. Because the prepared solution of Aquacoat and DBS has a viscosity similar to water, it can be pumped into the fluidized bed at relatively high flow rates. Coating experiments were conducted successfully with spray flow rates as high as 15 milliliters per minute. This results in faster coating. High binder coating levels are required to form more uniform coatings on the surface of the large (~lmm) carrier particles. Binder addition levels of 30% and 50% by weight of the initial carrier particles have demonstrated strong, stable, and uniform coatings. Additional coating levels such as 15% and 25% have also been tested with positive results. After a suitable coating material (Aquacoat and DBS) had been found, the application of powder coating ina fluidized bed was investigated. The equipment used to coat powder on the surface of the polystyrene beads was a modified fluidized bed apparatus. The main difference between this equipment and the standard apparatus used for liquid coatings was the addition of a separate powder feeding device located on the side of the main fluidizing column. This device allowed fine particle to be "blown" into the dense phase region (annular, downward moving packed bed). This caused the powder (n-halamine) to adhere to the particles (polystyrene beads) prior to the subsequent over-coating with Aquacoat and DBS Solution that was sprayed into the upward moving core region. Due to the limited supply of n-halamine powder preliminary runs were conducted with a model powder with the same average particle size as the n-halamine. The results with the model powder were encouraging and showed that between 60-80% of the powder added to the bed adhered to the surface

of the beads. The final step in this research was to determine the biocidal efficacy of the n-halamine coated beads. An extensive program of testing was initiated with the help of Dr. Gary Bissonnette from the Department of Plant and Soil Sciences at West Virginia University. Biocidal activity of our n-halamine sample was tested in both a small-scale and a large-scale flow unit. After extensive testing of different batches of n-halamine polymer obtained from NewChem, Inc., New Cumberland, WV, it was found that the chemical composition of this polymer did not correspond to that of n-halamine. This result was determined from IR spectrophotometry carried out in the Department of Chemistry at WVU. Specifically, the IR scan for n-halamine should possess peaks at approximate wavenumbers of 1805 and 1750 cm-1. The scan for the polymer used in this work gave peaks at 1774 and 1723 cm-1. These peaks corresponded to those for the unchlorinated precursor molecule. An effort was made to chlorinate this polymer using a concentrated bleach solution for a period of 24 hrs. This resulted in shifting the IR peaks by only about 10 wavenumbers. Finally, a small sample showed excellent biocidal activity in our small-scale flow cell. Using this small sample of active polymer (approx. 20g) a coating run was performed by which this polymer was bound onto the surface of 500g of polystyrene beads using 125 g of Aquacoat and DBS coating solution. Initial results for these coated beads in the small-scale flow unit were very promising, with essential total kill recorded for initial bacterial concentrations of 10 6 - 10 8 CFU/ml (Colony Forming Units/ml). Prior to each experiment, a concentrated bleach solution was allowed to flow through a bed of beads for a period of 20 hrs in order to regenerate particles. After this, they were flushed with a relatively high flow of water (>1 1/min) for a short period of time. However, in the course of doing these experiments it was noted that different results were obtained depending on whether or not the beds were subsequently flushed for an extensive period of time with distilled water prior to exposing them to the bacteria laden water. In a seperate set of experiments, it was found that the beads coated only with the Aquacoat and DBS (no n-halamine) retained a significant amount of chlorine and that this was most likely responsible for the high bacteria kill. By flushing with distilled water for a period of time the bound chlorine was removed from the surface of the beads. After flushing these beads (with and without n-halamine) showed essentially zero kill rates in the small-scale flow unit. In summary, the results of this research are inconclusive. Biocidal efficacy was demonstrated for the polymer coated beads but there is evidence that a substantial amount of residual chlorine absorbs on the surface of the beads after regeneration that makes determination of the cause of the biocidal activity difficult. The biocidal (n-halamine) having the correct chemical structure show excellent biocidal activity. This activity is probably still present when it is coated onto the surface of the polystyrene beads, however, due to the low loading of polymer-to-beads; this biocidal effect is masked by the ability of the coating material to absorb significant levels of chlorine.

Descriptors

Biocidal Polymer, Fluidized Beds, Biological Treatment, Water Quality Control, and Drinking Water Supply

Articles in Refereed Scientific Journals

Book Chapters

Dissertations

Evaluation of Biolocidal Polymers for the Treatment of Domestic Water Supplies: Application of Polymers to the Surface of Carrier Particles, Robert M. Taylor, M.S. Thesis, Department of Chemical Engineering, West Virginia University, 1999

Water Resources Research Institute Reports

Conference Proceedings

Other Publications

Information Transfer Program

West Virginia Water Resources Research Institute Information Transfer Report FY1999 P.F. Ziemkiewicz, Director 7 Jul 1998 Meet with Patriot Mining to discuss water treatment options. 7 Jul 1998 Meet with Deputy Commissioner of WV Dept. of Agriculture to give status report on WRI projects 22 and 23: Poultry Wastes in the Potomac Headwaters. 8 Jul 1998 Chair meeting of Potomac Headwaters Steering Committee. 14 Jul 1998 Meet with Canaan Valley Institute to discuss WVWRI capabilities and potential for technical support for CVI's citizen outreach program. 24 Jul 1998 Tour Arch Coal Mountaintop Removal/Valley Fill sites in Logan County. 30 Jul 1998 Take OSM/PRC delegation on tour of mine sites. 31 Jul 1998 Meet with WV Department of Agriculture analytical lab staff to discuss QA/QC program for poultry waste program. 5 Aug 1998 Assist Hiser/Manilla Creek Watershed Association in identifying mine drainage sources and treatment options for preparation of EPA 319 grant application. 6 Aug 1998 Host meeting of the Eastern Mine Drainage Federal Consortium: six subsequent meetings. 7 Aug 1998 Meet with USDOE/FETC to develop program to address flooding of underground mines in the Pittsburgh Coal Basin. 15,16 Sep 1998 Resource Recovery Conference: sit on panel to discuss acid mine drainage (AMD) treatment technology. 17 Sep 1998 Meet with WV DEP to provide technical assistance in court case involving Valley Mining Co. 21-23 Sep 1998 Present Pittsburgh Coal Basin Mine Flooding project to EPA/EMPACT conference. 6 Oct 1998 Presentation to Ohio Mining and Reclamation Association on restoration of AMD affected watersheds. 13 Oct 1998 Speak to WV Acid Mine Drainage Task Force Meeting regarding new AMD treatment methods. 28 Oct 1998 As a member of WV DEP T&T task force, meet to develop remediation strategy in the Coastal Corp./USEPA/WV DEP settlement for the T&T mine: four subsequent meetings. 13 Jan 1999 Presentation to annual meeting of the WV Mining and Reclamation Association regarding reforestation of mountain top removal sites. 16 Mar 1999 Presentation to the Dunkard Creek Watershed Association (WV) regarding impact of flooding underground coal mines on the Dunkard Creek basin. 29 Mar 1999 Kingwood WV. Presentation to the Cheat River Watershed Association regarding the TMDL process. 19 Jun 1999 Presentation to PA Environmental Council workshop on watershed restoration on AMD remediation practices and sit on panel to discuss opportunities for cost offsets through resource recovery.

USGS Internship Program

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	2	N/A	N/A	N/A	2
Masters	1	N/A	N/A	N/A	1
Ph.D.	N/A	N/A	N/A	N/A	N/A

Post-Doc.	N/A	N/A	N/A	N/A	N/A
Total	N/A	N/A	N/A	N/A	N/A

Awards & Achievements

Publications from Prior Projects

Articles in Refereed Scientific Journals

Carpenter, M..W. and D.J. Gardner. 1993. Fixation/leaching of CCA in selected hardwoods at two temperatures. In: Chromium-containing waterborne wood preservatives: Fixation and Environmental Issues. J. Lang, Production Coordinator pp. 52-55. Kuhlman, John M. and Lyell, M.J. "The Development of a User-Friendly Planning Software Planning Tool to Assess the Effect of Biofilm Activity on Contaminant Reduction in Streams" Network and Computer Applications, Vol. 19, 1996, pp. 249-64.

Book Chapters

Dissertations

Mullenbach, R.A. 1995. M.S. Thesis. Evaluation of methods for detection of coliforms in rural groundwater supplies. West Virginia University, Division of Plant and Soil Sciences, Morgantown, WV. Field of Study: Environmental Microbiology Carpenter, Deborah. MA Department of Geology and Geography, West Virginia University. "Exploring the River Continuum Concept: General Theory vs. Context Variation". Strager, Michael P. 1995. Prioritizing Acid Mine Drainage Affected Watersheds: A Compromise Programming Approach, unpublished MS thesis, West Virginia University, Division of Resource Management, Morgantown, WV. 119 pages. Brian E. Mace, 1998, "Emissions Testing of Two Recreational Marine Engines with Water Contact in the Exhaust Stream", West Virginia University, Department of Mechanical and Aerospace Engineering, Morgantown, WV. 51 pages. Todd J. Vanyo, 1997, "Determination of Airborne and Waterborne Marine Engine Exhaust Contaminant using Chromatographic Methods of Analysis", West Virginia University, Department of Chemistry, Morgantown, WV. 81 pages.

Water Resources Research Institute Reports

Lyell, M.J. and Kuhlman, J.M. "Development of Planning Tools for River/Stream Bioremediation" Final Report. Submitted to the WV WRRI.

Conference Proceedings

Gardner, D.J. and J. Slahor. 1994. Fixation of chromated cooper arsenate (CCA) in selected Appalachian Hardwoods. In: 1994 Hardwood Research Council Annual Meeting Proceedings Vanyo, T.J., Morrison, R.W., Remcho, V.T., Mace, B.E., Nine, R.D. and Clark, N.N., "Development of Analytical Tools for the Determination of Airborne and Waterborne Marine Engine Exhaust Contaminants", 19th International Symposium on Capillary Chromatography and Electrophoresis, Wintergreen, VA. 1997. Mace, B.E., Nine, R.D., Clark, N.N., Vanyo, T.J., Remcho, V.T., Morrison, R.W., and McLaughlin, L.W., "Emissions from Marine Engines with Water Contact in the Exhaust

Stream", SAE International Congress, Detroit, Feb. 1998, SAE Paper 980681. Nine, R.D., Clark, N.N., Mace, B.E., Morrison, R.W., Remcho, V.T., Lowe, P.C., and McLaughlin, L.W., "Use of Soy-Derived Fuel for Environmental Impact Reduction in Marine Engine Applications", American Society of Agricultural Engineers Meeting, Orlando, Fl., July 1998. ASAE Paper 986083

Other Publications