United States
Environmental Protection
Agency

Risk Reduction
Engineering Laboratory
Cincinnati, OH 45268

Research and Development

EPA/600/S2-88/057 Jan. 1989

EPA

Project Summary

Manganese Dioxide Coated Filters for Removing Radium from Drinking Water

Marc Y. Menetrez, David G. Anderson, and Edward P. Stahel

Research was performed using manganese dioxide (MnO_2) to demonstrate that above pH 3 cations are adsorbed from solution in the order of their affinity, and that the interaction is characterized by the pH dependence of the metal. The relationship of the zero point charge of pH and the solution ionic strength effects on interfacial surface potential and adsorption have been addressed. Characteristics of MnO_2 behavior, structure, and stability found in research investigation were reviewed.

Most of this study was on the use of MnO_2 coated filters for the removal of radium. A few comparison tests on radium removal with ion exchange were also made. Specifically, these tests have shown that acrylic fiber filters coated with MnO_2 will remove radium from water. For a high hardness water with pH = 7.4, total radium removal was 14,200 pCi/g MnO_2 before the MCL of 5 pCi/L was exceeded; and for a low hardness water with pH = 4.5, total radium removal was 5,000 pCi/g MnO_2 before the MCL of 5 pCi/L was exceeded. Hardness passed through the MnO_2 filters with little change; therefore, radium was highly preferred over hardness.

A step-by-step process for the preparation of acrylic fiber filters coated with MnO_2 is included in the full report.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

As of August 1, 1982, a total of 39 public water systems, or 1.9% of the systems tested in North Carolina, were found to be in violation of the 5 pCi/L combined radium limit. When a water system is found to have levels of combined radium activity that exceed the standard, the system owner is responsible for correcting the problem. If utilizing another water source is not realistic, then effective treatment to remove excess radium would be required. Ion exchange, lime-soda softening, and reverse osmosis have been demonstrated to be effective techniques for radium removal.

Adsorption onto MnO_2 coated filters is a treatment alternative that has been tested sparingly but never used to remove radium from drinking water. Extensive testing of MnO_2 filters in the laboratory, in the pilot plant, and in full-scale application is the focus of this report. The use of MnO_2 coated filters has been examined for metal removal and more extensively for radium removal in conjunction with efficiency, cost, safe use of application, and usefulness compared with other forms of treatment.

Flowthrough MnO_2 Filter Preparation System

A system to produce MnO_2 filters with a heavy MnO_2 loading was designed, constructed, and operated successfully. The flowthrough filter preparation system is described in detail in the full report. The system has been successfully used

to generate MnO_2 fiber in both a prewoven filter element form as well as a loose-staple form. The acrylic-based MnO_2 fiber in both forms exceeded the previous limit of 10% to 13% MnO_2 (by weight). Loadings of 20% to 25% MnO_2 (by weight) were consistently produced with the flowthrough filter preparation system. A filter element 10 in. (25.4 cm) long weighing an average of 250 g with an average loading of 22.5% would consist of 56.25 g MnO_2 and 193.75 g acrylic-base fiber. The flowthrough filter preparation system was also used in washing the prepared fiber before packaging. Preparing MnO_2 fiber with the system took less than 1 day/batch to produce the filters. The cost of chemical was less than $2/10-in. filter element, or less than $8/kg of prepared fiber.

The examination of the prepared MnO_2 filter elements revealed that when the MnO_2 filter is installed and rinsed (with 3 to 5 filter volumes), no organic, soluble manganese, insoluble MnO_2, or fiber is released to the effluent stream. This indicates that MnO_2 fiber can be used to treat drinking water without contributing unwanted contaminants. The State of North Carolina, Department of Human Resources, Solid and Hazardous Waste Branch, examined the MnO_2 fiber for leaching under landfill conditions. The results of the (EPA) toxicity test revealed no leaching of any form of manganese or other inorganics at pH 5 conditions. This should allow the disposal of the MnO_2 filters in landfills in North Carolina, pending approval for radium.

Radium Analysis

A modified process for analyzing radium in water was devised and structured, and the results compared with EPA through a quarterly sample analysis and report program. The analysis procedure followed is described in Appendix B of the full report.

Results

Bleed Stream Testing

The bleed stream testing of the MnO_2 filter in the Highland Park water system and the Gateway Mobile Home Park water system revealed that radium was removed and that hardness was passed through the filter relatively unchanged.

The bleed stream results for the Highland Park water system (Table 1) show that total radium removal in excess of 86% can be expected for a treated volume of at least 22,653 L at a flowrate of 11.36 L/m per 25.4-cm filter element. At this level of radium removal, the influent concentration of 36.4 pCi/L total radium is reduced to a maximum effluent concentration of 5 pCi/L total radium, the U.S. EPA Regulation. The single, 25.4-cm filter element consisting of approximately 250 g of MnO_2 fiber removed 0.801 µCi total radium before decreasing to an efficiency of less than 86%. At an MnO_2-to-fiber loading of 22.5% (56.25 g of MnO_2), the total radium-to-MnO_2 ratio of 14,200 pCi/g MnO_2 was demonstrated prior to reaching the 5 pCi/L limit. The halfway point to breakthrough (or the point at which 50% efficiency was reached) occurred after approximately 57,000 L of water was treated, and the total breakthrough of radium occurred after approximately 160,000 L of water was treated.

Bench-top testing of a sample fro the Highland Park water system w performed. The 202.5-L sample w pumped through 15 g of MnO_2 fib containing approximately 3.35 g of MnC at a rate of 0.75 L/min. The resu indicated that the influent concentrati of 36.4 pCi/L was reduced to zero in t effluent. A total of 7,370 pCi of to radium was removed, or 2,180 pCi total radium per gram of MnO_2. Tl removal efficiency never changed fro 100%, therefore, no conclusions can made regarding total uptake of radiu However, a considerable volume of wat was treated while maintaining tot removal.

The bleed stream results for tl Gateway Mobile Home Park wat system (Table 2) show that total radiu removal in excess of 66% can expected for a treated volume of at lea 28,000 L at a flowrate of 11.4 L/m p 25.4-cm filter element. At this level radium removal, the influent conce tration of 13.2 pCi/L total radium reduced to a maximum effluent conce tration of 5 pCi/L total radium, the U. EPA Regulation. The single, 25.4-c filter element consisting of approximate 250 g of MnO_2 fiber removed 0.222 µ total radium before decreasing to efficiency of less than 66%. At a MnO to-fiber loading of 22.5% (56.25 g MnO_2), the total radium-to-MnO_2 rat of 5,000 pCi/g MnO_2 was demonstrate prior to reaching the 5 pCi/L limit. Tl halfway point to breakthrough (or 50 efficiency) occurred after approximate 42,000 L of water was treated, and tl total breakthrough of radium occurre after approximately 85,000 L of wat was treated.

Table 1. *Highland Park Field Study; Bleed Stream Field Test – Total Radium Removal Efficiency and Uptake**

Effluent Radium (pCi/L)	*Total Flow† (ft^3)*	*Removal Efficiency*	*Total Uptake (nCi)*	*Uptake (nCi/g MnO_2)*
2.4	*500*	*0.934*	*481.39*	*8.56*
5.5	*1,000*	*0.849*	*918.89*	*16.34*
14.5	*1,500*	*0.602*	*1,228.96*	*21.85*
17	*2,000*	*0.533*	*1,503.63*	*26.73*
22	*2,500*	*0.396*	*1,707.52*	*30.36*
27.5	*3,000*	*0.245*	*1,833.53*	*32.60*
30	*3,500*	*0.176*	*1,924.14*	*34.21*
31.5	*4,000*	*0.135*	*1,993.52*	*35.44*
32.5	*4,500*	*0.107*	*2,048.73*	*36.42*
34.5	*5,000*	*0.052*	*2,075.64*	*36.90*

** For 25.4-cm long filter element, influent total radium concentration = 36.4 pCi/L, pH = 7.4, and total hardness = 227 mg/L as $CaCO_3$.*

† Multiply by 28.32 to convert ft^3 to liters.

Table 2. *Gateway Field Study; Total Radium Removal Efficiency and Uptake**

Effluent Radium (pCi/L)	Total Flow† (ft^3)	Removal Efficiency	Total Ra Uptake (nCi)	Uptake (nCi/g MnO_2)
2.0	500	0.848	158.58	2.82
4.5	1,000	0.659	281.75	5.01
7.0	1,500	0.470	369.54	6.57
9.0	2,000	0.318	429.00	7.63
12.5	2,500	0.053	438.91	7.80
13.2	3,000	0.000	438.91	7.80

** For 25.4-cm long filter element, influent total radium concentration = 13.2 pCi/L, pH = 4.5, and total hardness = 23 mg/L as $CaCO_3$.*
† Multiply by 28.32 to convert ft^3 to liters.

In-Line Testing

In-line field testing utilized three standard water filtration housings. Each housing held twenty-one 25.4-cm filter elements. The three stainless steel housings were situated in series to extend filter life. The in-line field test results for the Highland Park water system indicated that the removal efficiency of total radium was less than that exhibited with the bleed stream field test. The point halfway to breakthrough of total radium was reached almost immediately for the three-filter housing system containing three canisters of twenty-one 25.4-cm MnO_2 fiber elements. This rapid decrease in filter efficiency was also recorded for the three filter housing systems containing one 20-μm, one 5-μm, and one MnO_2 filter element housing. The decreased capacity of the MnO_2 filters was believed to be caused by a high suspended solids loading on the filters. Large amounts of clay and silt were found coating the filter elements.

This fouling of the MnO_2 sites greatly decreased the ability of the filter to adsorb radium. Even after passing through a 20-μm and a 5-μm pleated paper filter element, significant amounts of fine suspended material were found building on the MnO_2 filter element. The reduced capacity of the in-line field test apparatus is believed to be caused by an improperly drilled and cased well. This problem was not encountered with the bleed stream testing and only became apparent when treating the entire well flow of 125 L/m and 75,700 L/day.

Conclusions

The successful removal of radium with MnO_2 coated filters appears conditional to the lack of fouling agents in the influent stream. Coating of the MnO_2 sites greatly reduces the interfacial ttracting forces. Maximum adsorption efficiency is expected when only the target ion in solution is present. The bleed stream tests resulted in greater amounts of radium loading for the Highland Park water system and lower radium loading for the Gateway water system. This is believed to be caused by the different levels of pH of these two ground water sources. The pH 7.4 of the Highland Park water system allowed for a higher degree of adsorption than did the pH 4.5 of the Gateway water system.

In-lab, bench-top investigation on the removal of dissolved metals has indicated that radium ions as well as interfering ions in solution are adsorbed by MnO_2. The results of metal removal with MnO_2 fiber showed that low concentrations of cadmium, calcium, cobalt, cesium, iron, and manganese can also be removed from solution by adsorption onto MnO_2 fiber.

The ion exchange comparison column bleed stream results were inconclusive in that they lacked actual breakthrough information. A column of MnO_2 fiber 152.4-cm length and 5.08-cm diameter treated approximately 76,000 L of influent water containing 13.2 pCi/L total radium without any variation from an effluent level of 0 pCi/L total radium. A column of ion exchange resin 60.96-cm length and 5.08-cm diameter treated 76,000 L of water containing 13.2 pCi/L total radium, without any significant variation from 0 pCi/L total radium in the effluent. At this point the ion exchange column was regenerated with a 0.85 molar calcium chloride solution because the resin was mistakenly expected to be spent. An additional 78,000 L of water was treated with this column. Again, no variation from zero total radium discharge was observed. No conclusions could therefore be made regarding column life, efficiency, or comparisons of hydrogen ion exchange to calcium ion exchange.

The MnO_2 fiber can be used for treatment of drinking water for the removal of radium. Tests also showed that MnO_2 adsorbs other metals, specifically cadmium, calcium, cesium, cobalt, iron, and manganese. The bleed stream tests showed that radium was highly preferred over calcium and magnesium. A treatment application for radium involving an inability to regenerate resin because of the disposal of regenerant brine or backwash could eliminate the use of ion exchange resin. In these circumstances, MnO_2 coated filters could possibly be used for treatment and the filter disposed of in a sanitary landfill (pending approval by state authorities).

The full report was submitted in partial fulfillment of Cooperative Agreement CR-811119-01 by North Carolina State University under the sponsorship of the U.S. Environmental Protection Agency.

Edward P. Stahel, Marc Y. Menetrez, and David G. Anderson are with the North Carolina State University, Raleigh,NC 27695-7905.
***Richard P. Lauch** is the EPA Project Officer (see below).*
The complete report, entitled "Manganese Dioxide Coated Filters for Removing Radium from Drinking Water," (Order No. PB 89-110 126/AS; Cost: $19.95, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

EPA/600/S2-88/057