



Project Summary

Radium Removal from Water by Manganese Dioxide Adsorption and Diatomaceous Earth Filtration

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This study reveals that radium adsorption onto precipitated MnO_2 , followed by diatomaceous earth (DE) filtration is a very effective treatment process for radium-contaminated water. Radium removals in the range of 80% to 97% were observed for preformed MnO_2 feed concentrations of 0.63 and 1.26 mg/L as Mn in groundwaters with hardness in the range of 100 to 245 mg/L as CaCO_3 . Radium removal increased slightly with increasing pH whereas it decreased slightly with increasing hardness and iron (II) concentrations.

Pilot studies were performed in Lemont, IL, using DE filtration and multimedia filtration on a groundwater containing 12 pCi/L ^{226}Ra and 6 pCi/L ^{228}Ra . Radium removals for both pilot plants ranged from 90% to 97% at a MnO_2 feed concentration of 1.26 mg/L as Mn, a total hardness of 245 mg/L as CaCO_3 , and a pH of 6.5. The costs of water treatment by MnO_2 adsorption and DE filtration were estimated at \$0.71 per 1000 gal for 280,000 gpd plants and \$0.47 for 1 Mgd plants. These costs are competitive with ion exchange softening for similar plant capacities.

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

Radium is an alkaline-earth metal with chemical and physical properties similar to the other elements in this group—calcium, magnesium, barium, and strontium. Radium, found primarily in groundwater supplies, has three naturally occurring isotopes, ^{226}Ra , ^{228}Ra , and ^{224}Ra . ^{228}Ra , a member of thorium series, is a weak beta emitter with a half life of 5.7 yr. ^{226}Ra , a member of uranium series, is a long-lived alpha emitter with a half life of 1620 yr. ^{224}Ra , the second generation progeny of ^{228}Ra , is a short-lived alpha emitter with a half life of 3.64 days. All radium isotopes are bone seekers; ^{226}Ra is considered to be the most detrimental radium isotope because it is so long-lived, and it has five alpha-emitting progeny including its immediate daughter ^{222}Rn , the inert gas radon.

Based upon the potential health hazards of radium, the maximum contaminant level (MCL) of total radium ($^{226}\text{Ra} + ^{228}\text{Ra}$) is currently 5 pCi/L. Analysis of ^{228}Ra is, however, only required if activity of ^{226}Ra exceeds 3 pCi/L. Using the compliance data from 50,000 public water systems, the U.S. Environmental Protection Agency (EPA) estimated that 500 systems exceed the radium MCL of 5 pCi/L. The highest ^{226}Ra concentration reported was approximately 200 pCi/L. Few supplies exceed 50 pCi/L, however, and about two-thirds of the supplies exceeding 5 pCi/L are below 10 pCi/L.

Several radium removal technologies, including reverse osmosis, sodium ion-exchange softening, and lime-soda softening, have been applied for small community



water supply treatment but not widely used because of cost and complexity. This has led to the search for simpler methods of radium removal. Some new technologies now in the experimental stage involve adsorption onto one of the following adsorbents: a BaSO₄-impregnated cation resin called the DOW radium selective complexer (RSC); microbial biomass; BaSO₄-impregnated and plain activated alumina; manganese-impregnated acrylic fibers; filter sand; and iron and manganese precipitates. This report on removing radium deals with adsorbing radium onto MnO₂ and then removing the manganese precipitate by filtration.

Manganese dioxide (MnO₂ or MnO₂(s)), often called hydrous manganese oxide (HMO), was chosen as the radium adsorbent because it had been used in several previous studies to abstract radium from both seawater and groundwater. DE was chosen as the filter media for most of the experiments because it is effective in removing fine particulates like MnO₂ from water.

The major objective of this study was to determine the feasibility of MnO₂ adsorption followed by DE filtration for removing radium from water. Additional objectives were to:

- determine the effects of pH, MnO₂ concentration, total hardness, iron and manganese concentration, and the method of iron and manganese oxide formation on radium removal,
- determine radium loadings on the MnO₂ surface as a function of radium concentration in the water,
- determine the magnitude of MnO₂ leakage into the filter effluent,
- compare multimedia depth filtration to DE filtration for MnO₂ and radium removal on a pilot scale, and finally,
- estimate the cost of the MnO₂ adsorption/DE filtration process for small community water supply treatment.

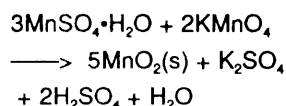
Materials and Methods

The bench- and pilot-scale experimental work was done in several stages. Preliminary screening experiments were performed by precipitating MnO₂ in ²²⁶Ra-spiked Houston groundwater and then filtering the suspension with a paper filter in a Buchner funnel or a DE-coated filter to determine the feasibility of MnO₂ adsorption followed by DE filtration as a treatment process. In these bench-scale tests, the pH, hardness, radium, and MnO₂ concentrations were varied to determine their effect on radium removal. Then, a 0.3 gpm bench-scale DE filtration system was tested

with ²²⁶Ra-spiked Houston tap water to determine radium removal efficiency in a continuous process. Finally, two pilot plants (DE filtration and multimedia filtration) were run in Lemont, IL, to establish the performance of each process with actual radium-contaminated groundwater.

Preparation of Manganese Dioxide Stock Solution

MnO₂ stock solution was prepared using MnSO₄·H₂O and KMnO₄. Reagent grade chemicals were used in bench- and pilot-scale experiments performed at the University of Houston. Food-grade MnSO₄ and water treatment grade KMnO₄ were used in the Lemont pilot studies. The precipitation of MnO₂ is an oxidation/reduction reaction in which MnSO₄ (Mn(II)) is oxidized and KMnO₄ (Mn(VII)) is reduced to Mn(IV). The precipitation reaction is:



First, the predetermined amount of MnSO₄·H₂O was added to water and mixed thoroughly before adjusting the pH into the 8 to 9 range by adding NaOH. KMnO₄ was then added gradually while NaOH was added periodically to maintain the pH between 8 and 9. A 5% stoichiometric excess of KMnO₄ was added to achieve complete oxidation of manganous ion and to oxidize iron in the water. To make a stock solution of 1000 mg/L MnO₂, 1166 mg MnSO₄·H₂O and 738 mg KMnO₄ were added to a liter of water. This preformed MnO₂ slurry was kept in suspension by continuous mixing and was normally used within 24 hr. This suspension was fed to the raw water to achieve the desired MnO₂ concentration in the feedwater.

Bench-Scale Experiments with Houston Groundwater

²²⁶Ra-spiked Houston groundwater was adjusted to a pH of 7.5 (except in pH studies), and then placed into a 2-L polypropylene beaker where preformed MnO₂ was added. For the MnO₂ to adsorb the radium, this water was then magnetically stirred for 1 hr to equilibrate radium with MnO₂. To prepare a DE filter, a slurry containing 3.11 g of DE was distributed onto a 90-mm filter placed into a Buchner funnel where a 0.1 lb/ft² DE coating on the filter paper was formed by vacuum filtration. The feedwater, containing radium equilibrated with MnO₂, was then vacuum filtered through this DE-coated filter. In the screening experiments,

the filtrate was collected and passed through the same DE filter a second time to ensure equilibration and good filtration. The filtrate was then analyzed for radium and manganese concentrations. All the experiments were carried out in duplicate, and a new filter was used for each experiment. Controls were also run in which MnO₂-free feedwater was filtered through a DE-coated filter.

Radium activity and MnO₂ concentration were varied to determine their effects on radium removal. In these experiments, Houston groundwater was spiked with either 13 or 25 pCi/L of ²²⁶Ra, and the preformed MnO₂ concentrations were maintained at 0.05, 0.15, 0.35, 0.63, or 1.26 mg/L as Mn.

To determine the effect of pH on radium removal, the raw water pH was adjusted to 6.5, 7.5, 8.5, or 9.5 with the use of 1N NaOH or concentrated HCl. Total hardness values of 60, 120, 250, and 500 mg/L as CaCO₃ were used to establish the effect of hardness on radium removal. Because Houston groundwater had a total hardness of 120 mg/L as CaCO₃, the 60-mg/L total hardness sample was prepared by adding equal amounts of deionized (DI) water and Houston groundwater. The 250 and 500 mg/L total hardness samples were prepared by adding CaCl₂·2H₂O and MgCl₂·6H₂O salts in the 3:1 Ca:Mg ratio existing in the groundwater.

Experiments were also done to compare the addition of preformed MnO₂ with the simultaneous, in-situ oxidation of iron and manganese to Fe(OH)₃ and MnO₂, respectively. The in-situ preparation of MnO₂ was carried out by adding MnSO₄ to the feedwater. Then, KMnO₄ was gradually added to oxidize MnSO₄ to MnO₂. In another experiment, manganese and iron were simultaneously oxidized in the feedwater to establish the influence of iron on radium removal by MnO₂ adsorption. Experiments were also done to compare the addition of preformed Fe(OH)₃ with in-situ oxidation/hydrolysis of ferrous ion to Fe(OH)₃ with the use of Cl₂.

Continuous Bench-Scale Experiments with Houston Tap Water

A laboratory apparatus was assembled for the purpose of running continuous radium removal experiments with MnO₂ adsorption followed by DE filtration. Two 55-gal tanks were used for radium-spiked feedwater. ²²⁶Ra-spiked Houston tap water (pH = 7.5 and radium concentration = 25 pCi/L) was pumped at a rate of 0.3 gpm (0.1 gpm/ft² of surface area) and preformed MnO₂ was blended in-line to achieve a

MnO₂ concentration in the feedwater at 0.63 mg/L as Mn. The water was then passed through an Everpure* point-of-use DE filter and subsequent radium removals were measured. The DE filter surface area was about 3 ft² with 100 g of DE filter media impregnated on it. The water/MnO₂ contact time ahead of the filter was only 10 sec, so another experiment was done to determine the effect of mixing and MnO₂ contact time on radium removal. In this "greater mixing" case, the water was recycled, after MnO₂ addition, at three times the flow through the filter, i.e., a quarter of the flow was passed through the filter while three quarters was recycled. A long tubing of small diameter was added in-line to increase the turbulence and mixing of MnO₂ with the feedwater. With recycle, the contact time was increased to about 60 sec. A control run was also done to determine radium removal by the DE filter when no MnO₂ was added to the feed.

Pilot-Plant Studies with Lemont Groundwater

We found results of the bench-scale experiments sufficiently encouraging to further pursue radium removal studies in Lemont. There, two pilot plants were run in parallel using MnO₂ as an adsorbent. One pilot plant was a DE filtration system with a 1-ft² filter, and the other was a multimedia filter consisting of coal, sand, and ilmenite (10-in. height of each) packed in an 8-in. diameter column. A flow schematic of the pilot plants is depicted in Figure 1.

Diatomaceous Earth Pilot Plants

Two DE pilot plants were obtained from Manville Company. One was a 3.14-in.²-filter pilot plant, and the other was a 1-ft²-filter pilot plant. The smaller pilot plant was used to optimize process parameters for DE filtration. The 1-ft² pilot plant was then used to perform the actual runs.

Optimization of Process Parameters for DE Filtration

To optimize process parameters, effluent manganese concentrations were determined for three commercially available grades of DE: Celite 560, Celite 545, and Hyflo Super-Cel. Hyflo Super-Cel was the finest of the three, whereas Celite 560 was the coarsest. Penetration of black colloidal particles of MnO₂ into the filter cake was

also checked. To determine the optimum body feed ratio, differential pressure and run time were recorded and plotted for body feed ratios of 2:1, 5:1, 10:1, and 15:1. One experiment was also run with no body feed, i.e., with precoat only. The optimum body-feed ratio was determined from the differential pressure versus run time curves by calculating total water throughput per gram of DE.

The DE pilot runs were made with the 1-ft²-filter pilot plant. The previously optimized body feed ratio of 10:1 (20 mg/L DE body feed) was used for all the runs. MnO₂ stock solutions were made in a 30-gal (114-L) tank using raw water. Stock solution was prepared every 12 hr and continuously mixed. Another 30-gal tank, also equipped with a propeller mixer, was used as a feed tank in which MnO₂/radium equilibrium was achieved. Preformed MnO₂ was pumped into this tank to achieve a MnO₂ concentration of 1.26 mg/L as Mn, and a conservative residence time of 10 to 25 min was allowed for radium to adsorb onto MnO₂ surface. DE body-feed solution was prepared in a 15-gal (57-L) tank, and this solution was pumped in-line with feedwater to achieve a feedwater DE concentration of 20 mg/L. Both the precoating and filtration rates were 1 gpm/ft². The effluents were sampled every 4 hr, and the run ended after about 20 hr, at which time the pressure differential had reached 30 psi.

In one DE pilot run, there were two deliberate stagnation periods of 8 and 16 hr. During each stagnation period, the flow through the filter was stopped. Extreme caution was used when closing and opening the valves to the filter so as to minimize cake dislodging. Nevertheless, some cake was dislodged when restarting the run after the stagnation period. Hence, the effluent was sampled only after the water had cleared up (about 10 to 15 min after the start of the run). Another run was done to determine the radium adsorption capacity or desorption potential of radium-loaded MnO₂ already on the filter. In this run, the feedwater containing MnO₂, radium, and DE body feed was passed for 20 hr, and then only the radium-contaminated raw water (MnO₂-free) was passed through the filter cake for an additional 24 hr.

Multimedia Filter Pilot Plant

The multimedia and DE pilot plant feedwaters were taken from the same tank to compare the two means of post-filtration. The feedwater containing MnO₂ passed at the rate of 1.75 gpm (5 gpm/ft²) to the multimedia filter. The filter continuously operated for 84 hr before a deliberate 8-hr stagnation period was observed.

The filter was then restarted without backwashing and operated for 12 more hours before another 16-hr stagnation period. Finally, the filter was restarted and operated for 12 more hours before terminating the run. The effluents were sampled every 12 hr for the normal run. Following the stagnation periods, the effluent was sampled immediately on the restart and every 6 hr thereafter.

Analysis Methods

The Quality Assurance/Quality Control (QA/QC) procedures incorporated into the daily operation of the research included good laboratory practices regarding sampling, sample labeling, preservation, and glassware washing. To guarantee confidence in the experimental outcomes, all important experiments were duplicated. All the data and observations were promptly written in log books with carbon copies sent to the principal investigator. The quality assurance and radium analysis procedures passed the scrutiny of an EPA radioanalytical chemist and an EPA quality assurance contract auditor.

Radium Analyses

Radium analysis procedures were calibrated with ²²⁶Ra standards obtained from EPA's Environmental Monitoring and Support Laboratory (EMSL) in Las Vegas, NV. All ²²⁶Ra activity measurements in this study followed a modified EPA Method 900.1—the gross radium alpha screening procedure for drinking water with a carefully controlled aging time to minimize interference from ²²⁴Ra. This procedure with modified holding time had been used to analyze more than 2,000 radium-contaminated water samples in Lemont before the MnO₂/DE pilot study.

During MnO₂/DE research, approximately 200 water samples were analyzed for ²²⁶Ra with the use of EPA Method 900.1. In preparation for the research, the laboratory researcher performed and interpreted approximately 100 analyses of standard solutions to develop the calibration curve and to achieve a high degree of analytical competence.

Other Analyses

All the cation analyses in this study were done with a Perkin-Elmer ICP 5500, inductively coupled plasma spectrometer. Standards run at the beginning and at the end of every set of analyses determined deviation of the standard curve during the course of the analyses.

The miscellaneous analyses included pH, temperature, and flow rates. The pH meter was calibrated regularly using stan-

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

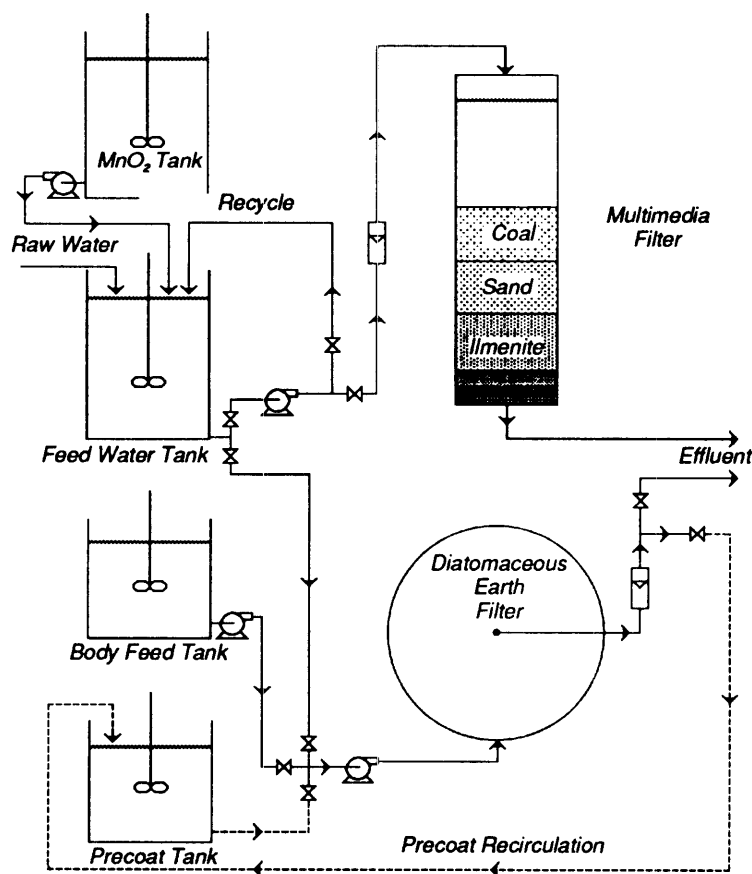


Figure 1. Flow schematic of parallel-operated diatomaceous earth and multimedia pilot plants.

standard buffers. The flow rates were measured using a 1-L graduated cylinder and stop watch. Proper care was observed during all the measurements to ensure reliability.

Results and Discussion

Bench-Scale Experiments with Houston Groundwater

Effect of MnO_2 Concentration and Feed Radium Activity

Figure 2 shows the effect of MnO_2 concentration on radium removal when filtering out the MnO_2 with a DE-coated filter in a Buchner funnel. The removal increased from 30% to about 90% when MnO_2 concentration was increased from 0.05 to 1.26 mg/L as Mn. The effluent radium activity ranged from about 2 to 17 pCi/L for a radium feed activity of 25 pCi/L. Thus, for a radium feed activity of 25 pCi/L, a MnO_2 concentration of 0.63 mg/L as Mn or greater

would be adequate to reduce the effluent radium activity to less than 5 pCi/L. No difference in percent removal was observed for the two different radium feed activities used—13 and 25 pCi/L. Thus, it was concluded that (a) percent removals can be estimated from Figure 2 as a function of MnO_2 concentration irrespective of radium feed activity and (b) an equilibrium isotherm plot of solid-phase radium loading versus liquid-phase concentration would be linear. A control run to determine radium removal by DE showed that, as expected, no significant radium removal was observed with DE alone.

Effect of pH

pH showed little influence on the radium removal, which only increased from 80% to about 95% as the pH increased from 6.5 to 9.5 at a MnO_2 concentration of 1.26 mg/L as Mn. Some improvement was expected because increasing the pH increases the negative charge on the MnO_2 particle, thus increasing its capacity to ad-

sorb radium—a divalent, hydrophobic cation. The magnitude of the increased radium removal was not great, however, because the point of zero charge (ZPC) for MnO_2 occurs at low pH, 2.8 to 4.5, which is far from the 6.5 to 9.5 range tested. Although slightly better radium removals were achieved with increasing pH, the higher pHs may not be practical for full-scale treatment.

Effect of Total Hardness

Figure 3 shows the effect of total hardness on radium removal. The removal decreased from 95% to about 70% as the total hardness increased from 60 to 500 mg/L as $CaCO_3$ at an MnO_2 concentration of 1.26 mg/L as Mn. This trend was expected because increasing the total hardness level increases the divalent cations, viz, calcium and magnesium, which increases competition for adsorption sites on MnO_2 . The decrease in percent removal in this study was not linear, i.e., at low hardness, the decrease in percent radium removal was more dramatic than at higher hardness. Beyond a certain hardness, about 250 to 300 mg/L as $CaCO_3$ in this case, the increase in hardness caused little further decrease in percent radium removal. We caution, however, that the hardness effect shown in Figure 3 cannot be extrapolated to brine concentrations such as 0.5 M calcium concentration and beyond.

Effect of Iron and Manganese

Experiments were done to determine the effect of iron and manganese on radium removal and to compare the addition of preformed MnO_2 and ferric ion with the simultaneous oxidation of manganous ion to MnO_2 , and oxidation of ferrous ion to ferric ion. The results are shown in Figure 4. About 90% was removed when preformed MnO_2 was added at 1.26 mg/L as Mn; slightly less (85%) was removed when 2.5 mg/L Fe was added as a ferric ion along with preformed MnO_2 . Although a 5% decrease in removal was observed, the results are statistically inconclusive because the relative standard deviation for radium analyses was also 5%. Only 70% was removed, however, when these same concentrations of Fe and Mn were simultaneously oxidized by $KMnO_4$. The reduction in radium sorption in the latter case is thought to be due to the influence of positively charged oligomers of hydrous iron (III) oxide that adsorb to the negatively-charged surface of preformed MnO_2 . These oligomers are short-lived and can only influence the MnO_2 surface when $Fe(OH)_3$ is precipitated in-situ. Opposite behavior was

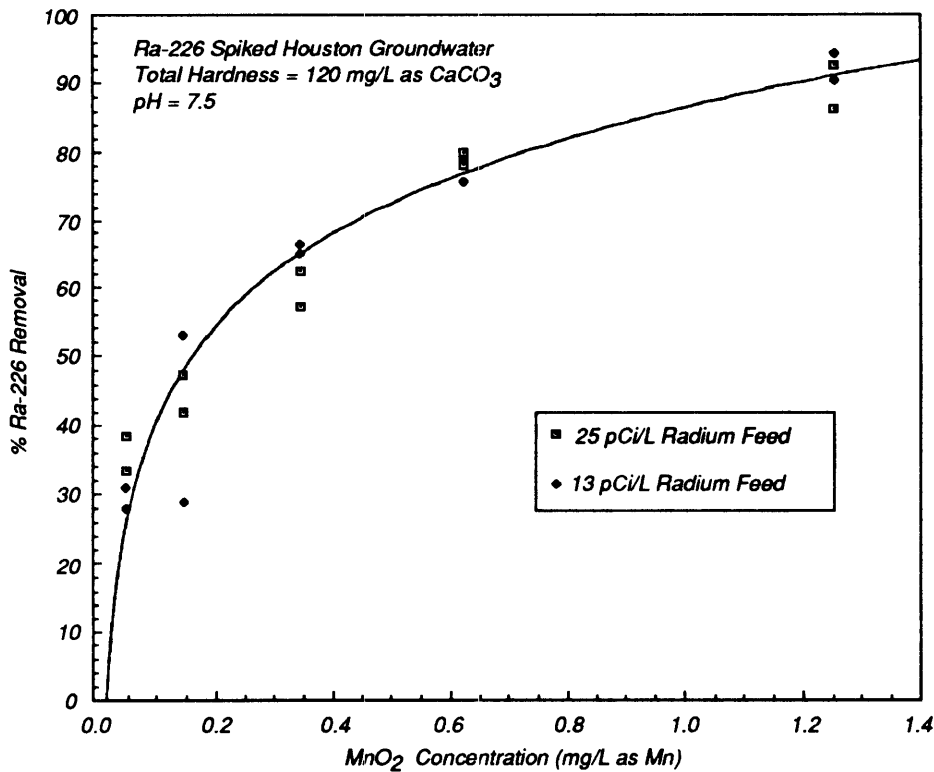


Figure 2. Effect of MnO_2 concentration and feed radium activity on radium removal during screening tests with the use of DE and a Buchner funnel.

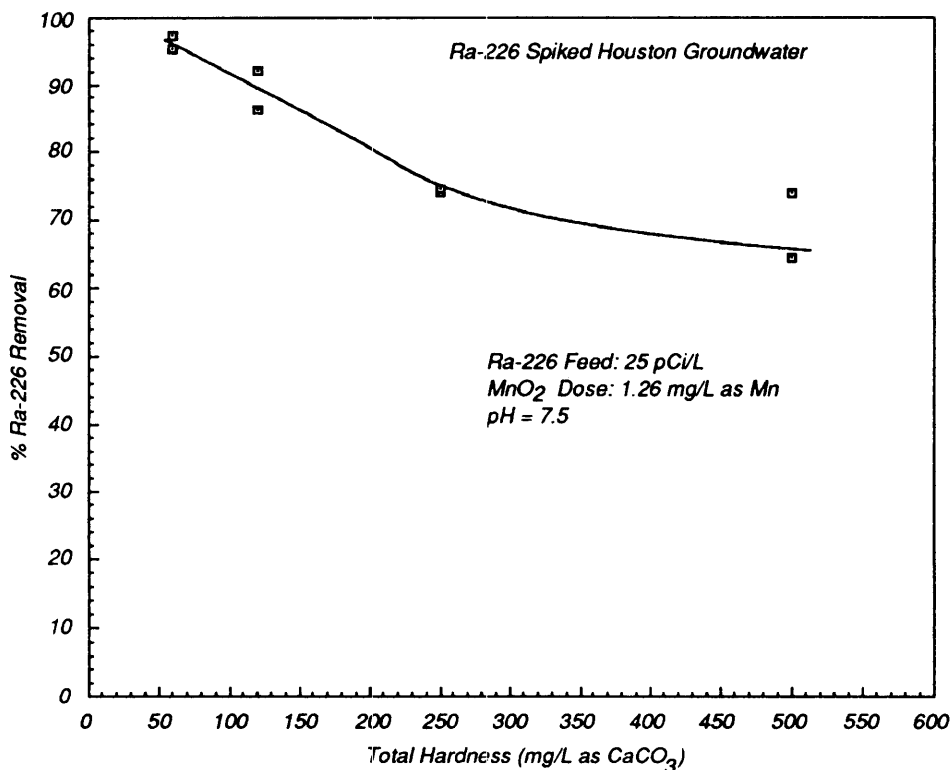


Figure 3. Effect of total hardness on radium removal during MnO_2 /DE screening tests.

observed between preformed $Fe(OH)_3$ and oxidation of ferrous ion to $Fe(OH)_3$ by Cl_2 in the absence of MnO_2 . In this experiment, oxidation to $Fe(OH)_3$ resulted in more removal as compared with preformed $Fe(OH)_3$. This agrees with the typical behavior of $Fe(OH)_3$ during conventional coagulation where in-situ precipitation is best. Radium removal by Fe alone was observed in the range of 5% to 30%, which agrees with the published literature values for iron-removal plants.

Continuous Bench-Scale Experiments with Houston Tap Water

The pilot-scale results from experiments done to evaluate continuous radium removal by MnO_2 adsorption followed by DE filtration were very encouraging. As a control, ^{226}Ra -spiked Houston tap water was passed through a DE-coated filter without any MnO_2 being added or present on the filter. This resulted in 15% radium removal, which was comparable with the removal of radium by pure DE filtration during the batch bench-scale experiments.

When MnO_2 was fed at 0.63 mg/L as Mn to the bench-scale continuous filter, about 80% of the radium was removed, which was similar to that observed in batch experiments. The radium loading on MnO_2 was about 20 pCi/mg MnO_2 when the equilibrium effluent radium activity was 4.6 pCi/L, i.e., a radium loading similar to that observed in batch experiments. The radium/ MnO_2 contact time in the system was about 10 sec. This contact occurred following in-line mixing at 0.3 gpm in 3/8-in. ID tubing after adding MnO_2 to the feedwater. The value of velocity gradient, G , for this system was estimated to be 1150 sec^{-1} using Camps' equation. Thus, the Gt value for this system was approximated at 11,500, which falls in the 10,000 to 100,000 range recommended for conventional mixing in water treatment.

After 6 hr (108 gal throughput), in-line MnO_2 feed to the filter was stopped and only ^{226}Ra spiked Houston tap water (MnO_2 -free) was passed through the filter. At this point, the filter had about 400 mg of MnO_2 accumulated on it. An immediate increase in effluent radium activity was observed as soon as the MnO_2 feed was stopped. Results suggest that MnO_2 , when fed along with radium-contaminated raw water, quickly comes to equilibrium with the effluent radium activity. When the MnO_2 feed was stopped, radium removal gradually decreased as the DE filter came to equilibrium with the feed radium activity in about 72 hr.

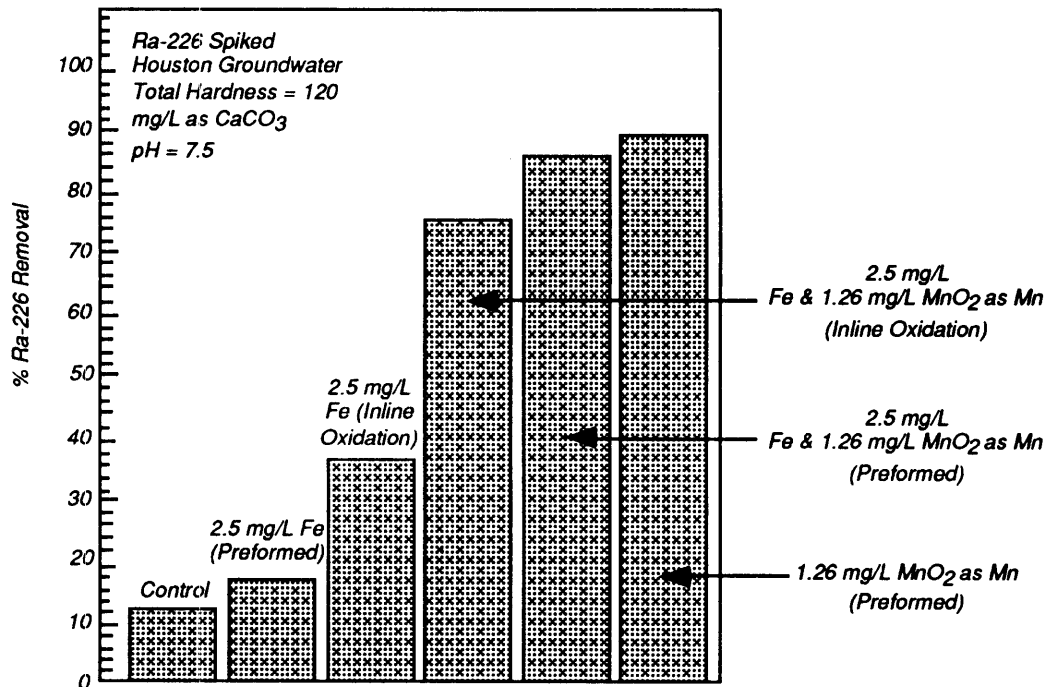


Figure 4. Effect of iron and manganese on radium removal during MnO₂/DE screening tests.

During a second experiment with the bench-scale filter, the contact time was increased to about 60 sec by adding a loop in the line and recycling part of the flow. The turbulence was increased by the loop, which was a 1/8-in. ID tubing with diameter contraction and expansion where it was connected to the 3/8-in. OD feedwater tubing. The Gt value for this system was 77,400. No significant difference in radium activity of the effluent was observed as a result of increasing Gt from 11,500 to 77,400. The radium removals for both were near 80%. Thus, initial mixing (Gt = 11,500) and 10-sec contact time were sufficient for near-equilibrium radium adsorption onto MnO₂ with this continuous 0.3 gpm DE filter unit.

Throughout the experimental program, contact times from 10 sec to 2 hr were used to equilibrate MnO₂ with radium in bench- and pilot-scale experiments. The similar removals in all these experiments indicate the lack of kinetic effects within this contact-time range for radium adsorption onto MnO₂. It was thus concluded that a very short contact time, e.g., 10 sec, is sufficient for good radium removal.

Pilot Plant Studies with Lemont Groundwater

Further pilot-scale radium removal studies were carried out in Lemont, where radium removal by resins, membranes, and adsorbents was being studied in the UH/EPA Mobile Drinking Water Treatment Research Facility. To determine the best DE grade to use, the small pilot-plant filter cake was visually inspected after the run was terminated. Hyflo Super-Cel, with the least MnO₂ penetration into the DE cake, was chosen as the optimum DE grade. It was then used to optimize the body feed rate, which was subsequently used for all the runs with the 1-ft² pilot plant. An optimum filtered product water yield of 29 L throughput/g DE occurred at a body feed ratio of 10:1 (20 mg DE/L).

The radium removals observed during three runs with the 1-ft² DE pilot plant operated at a MnO₂ feed of 1.26 mg/L as Mn were excellent—90% to 97%. Again, these removals were comparable to the removals observed in the bench-scale experiments with Houston groundwater. At an average influent activity of 11.4 pCi/L, the effluent ²²⁶Ra activity ranged from about 0.5 to 1.2 pCi/L during the 20-hr run. The ²²⁶Ra loading on the MnO₂ surface was about 6.7 pCi/mg MnO₂. Table 1 summa-

rizes the radium loadings observed in this study. Theoretically, they represent individual points on a linear equilibrium isotherm in which radium on the solid MnO₂ (pCi/mg) is in equilibrium with the effluent radium activity (pCi/L).

The Lemont pilot-scale run was ended after 20 hr when the differential pressure across the filter reached 30 psi. The dry weight of the filter cake was 168 g, and its radium activity was 565 pCi/g. In actual practice, the filter septum could be cleaned by spray washing the filter with an estimated 20 gal (75.7 L) of water, which would result in a radium activity in the filter spray wastewater of about 1250 pCi/L in the form of radium on particulate MnO₂.

After shutting down the filter without spray washing and then restarting, radium removal decreased for a brief period. Decreases of 3% and 8%, respectively, were observed after 8- and 16-hr stagnation periods. When resuming DE filtration immediately after a stagnation period, the product water was cloudy and had to be directed to waste for about 15 min until it became clear. The higher radium activity after the stagnation surely resulted from cake dislodging, which, in turn, leaked radium-contaminated MnO₂ into the effluent. Because cake dislodging will always be a

Table 1. Summary of Radium Loadings on MnO₂ Surface

Experiment	MnO ₂ Dose (mg/L)	Radium Loading (pCi/mg MnO ₂)	Equilibrium Radium Activity (pCi/L)
Batch bench-scale with Houston groundwater	1	20	5.2
Batch bench-scale with Houston groundwater	2	12	2.7
Continuous bench-scale with Houston tap water	1	20	4.6
Pilot plant with Lemont groundwater	2	10.4	1

problem after stagnation, a run should not be interrupted once it begins. On the positive side, in spite of cake dislodging, the ²²⁶Ra activity in the effluent after the stagnation was never greater than 2 pCi/L, which is well below the 5 pCi/L MCL.

A pilot-scale radium breakthrough curve (Figure 5) very similar to the continuous bench-scale results was observed in Lemont when the MnO₂ feed was stopped after 20 hr of effective radium removal. As can be seen in Figure 5, it took only 24 hr for the effluent radium activity to level off at about 15% below the influent radium activity. This radium breakthrough is much faster than that occurring in deep-bed sand filters being fed MnO₂. In this latter case, in-depth filtration occurs, the sand grains become coated with MnO₂, and the bed behaves like a packed-bed adsorber with a radium concentration gradient from inlet to outlet. Also, the sand itself adsorbs and desorbs radium in response to radium concentration variations in the feed. The result of these phenomena is a much slower sand-filter response to changes in MnO₂ addition such as Valentine observed in his MnO₂ radium removal studies in Forest City and in West Liberty, IA. In his studies, radium removal continued for as long as 30 days after stopping MnO₂ addition. Similarly, effective radium removal did not begin until many days after starting MnO₂ addition to a sand bed already in equilibrium with radium contaminated waters.

Results from the multimedia-filter pilot plant operated to compare its performance with that of the DE pilot plant were also encouraging. Excellent radium removals (> 96%) were observed throughout its 108 hr of operation, including the periods immediately following 8- and 16-hr flow interruptions. The effluent ²²⁶Ra activity ranged from 0.2 to 0.5 pCi/L for an average feed radium activity of 14 pCi/L and a feed MnO₂ concentration of 1.26 mg/L as Mn. The multimedia pilot plant performed slightly better than did the DE pilot plant during both continuous and interrupted flow tests.

Manganese Leakage

Fortunately, no significant manganese leakage was observed during this entire study, in which manganese effluent concentrations ranged from 0.01 to 0.03 mg/L. The only exception to this immediately followed the stagnation period for DE filtration when higher manganese concentrations were observed due to cake dislodging. Multimedia filtration also showed no manganese leakage into the effluent. It should be noted that the filter had a new filter media (coal, sand, and ilmenite). The performance of the multimedia filter after backwashing is yet to be studied, however.

Conclusions

1. Adsorbing radium onto MnO₂ followed by DE filtration is very effective for treating radium-contaminated water. Radium removals in the range of 80% to 97% were achieved at MnO₂ concentrations of 0.63 and 1.26 mg/L as Mn in waters with hardness in the range of 100 to 245 mg/L as CaCO₃.
2. Radium adsorption onto MnO₂ appeared to follow a linear isotherm because percent radium removal was not dependent on feed radium activity in the range of 13 to 25 pCi/L.
3. Radium removal by MnO₂ was not very sensitive to pH in the 6.5 to 9.5 range.
4. Radium removal decreased asymptotically from 95% to about 70% as the total hardness increased from 60 to 500 mg/L as CaCO₃. In-situ oxidation of iron (II) reduced the percent removal of radium by preformed MnO₂.
5. The radium loading on the MnO₂ surface was in the range of 10 to 20 pCi/mg MnO₂ with equilibrium radium activities in the range of 1 to 5 pCi/L.

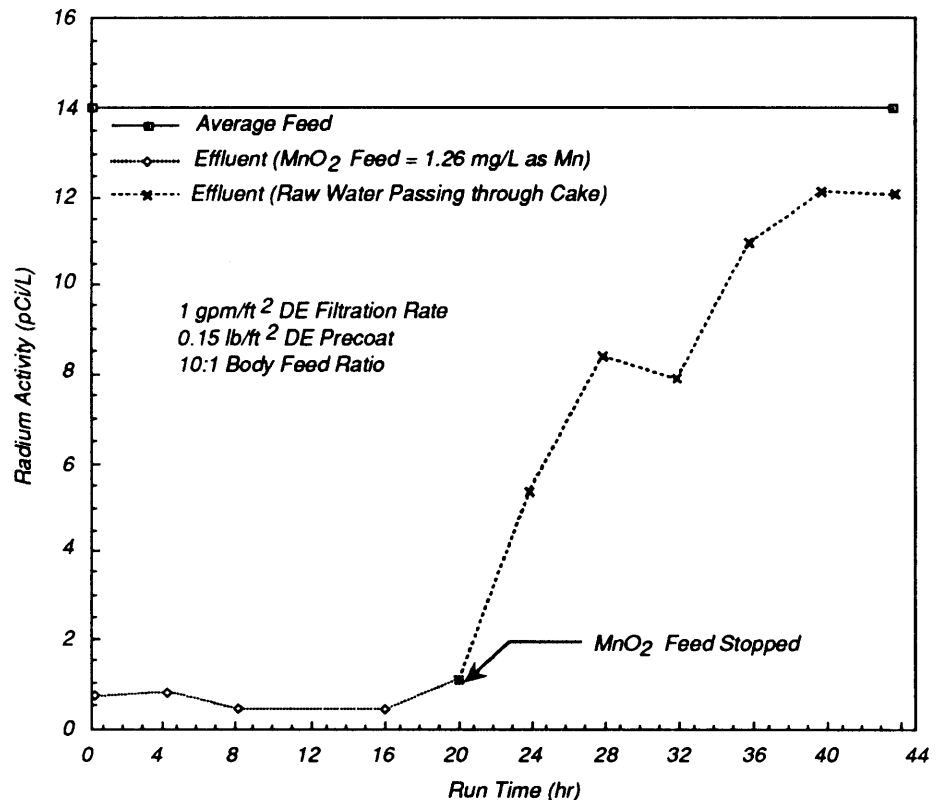


Figure 5. Effect of MnO₂ feed on radium removal by MnO₂ adsorption and DE filtration during pilot-plant studies at Lemont, IL.

-
6. Manganese concentrations in the DE filter effluent ranged from < 0.01 to 0.03 mg/L for the entire study, which is below its secondary MCL of 0.05 mg/L.
 7. The Lemont pilot-scale studies showed that following MnO₂ addition multimedia filtration was as effective

- for radium removal as was DE filtration.
8. The costs of water treatment by MnO₂ adsorption and DE filtration were estimated at \$0.71 and \$ 0.47 per 1000 gal for 280,000 gpd and 1 mgd plants, respectively. These costs are competitive with ion exchange for similar

plant capacities and much less than MnO₂ adsorption and multimedia filtration for smaller plant capacity.

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The complete report, entitled "Radium Removal from Water by Manganese Dioxide Adsorption and Diatomaceous Earth Filtration," (Order No. PB92-115260/AS; Cost: \$19.00, subject to change) will be available only from:

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