RADIONUCLIDES REMOVAL
WITH
OPTIMIZED IRON / MANGANESE FILTRATION

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INTRODUCTION

The proposed revision to the Radionuclides Rule will require drinking water supplies throughout the Midwest to add treatment to remove radium, as well as several other radionuclides. In an effort to find a low cost treatment alternative, the Minnesota Department of Health has investigated the possibility of optimization of existing iron/manganese filtration to remove radionuclides.

The study involves five iron/manganese filtration plants in Minnesota which utilize potassium permanganate, and that have had exceedences or detects of radium 226, radium 228 and uranium. The Minnesota Department of Health also reviewed the removal efficiencies at treatment plants in Knoxville, Iowa and Menomonie, Wisconsin.

According to previous research, it had been observed that the use of manganese oxides proved to be effective in the removal of radium 226[1-3]. The Minnesota Department of Health used the existing research to further investigate the capabilities of potassium permanganate, anthracite/greensand media and anthracite/sand media in the removal of radium 226, radium 228 and uranium.

DISCUSSION

The five treatment plants were asked to follow normal operating procedures during the study, i.e. filter run length, chemical feed rates, and backwash rate; as the study was designed to be a snapshot of existing treatment. The raw water and filter effluent was sampled for iron, manganese, competing cations, pH, gross alpha, gross beta, radium 226, radium 228, and uranium. Filter effluent samples were taken at the beginning, midpoint and end of each filter run; and a grab sample was taken from the backwash waste.

Several research projects have focused on the removal of radium 226 using a variety of processes available to iron/manganese filtration plants. The results from previous research was applied when investigating the optimization of existing treatment plants.

Dr. Valentine et al studied the use of hydrous manganese oxides as an adsorption site for radium, allowing radium to be removed in the filtration process[1,2]. While Dr. Mott et al researched the effect of mixed iron/manganese oxides with soluble iron and manganese in the removal of radium 226[3]. None of the supplies in Minnesota utilize hydrous manganese oxides or manganese sulphate, therefore optimization criteria is based on prior research and results from the treatment plants in Knoxville, Iowa[4] and Menomonie, Wisconsin.

RESULTS

Several variables were taken into consideration when reviewing the data from each of the five treatment plants. These included the filter media used, the amount of potassium permanganate fed, the presence of competing cations, iron and manganese, and the use of air/water backwash.

Removal Efficiencies
The treatment plants were studied under normal operating conditions with none of the supplies optimizing treatment to specifically remove radium. It is expected that the removal rates would improve if the supplies were to optimize treatment by improving pre-oxidation, adding manganese sulfate, adding detention time, or changing filter media. Each supply should conduct a pilot study to evaluate removal before any improvements are made.

Overall efficiencies fell between 19 and 63% for removal of radium 226, and between 23 and 82% for removal of radium 228 as shown in the figure below.

Removal Efficiencies (%)

Radium 226 (light gray)
Radium 228 (dark gray)

Treatm
e
nt
Plant
1
2
3
4
5

Below is the sequence of processes used in treatment plants one through five.
1) chlorination, potassium permanganate, anthracite/sand, water backwash
2) aeration, chlorination, potassium permanganate, anthracite/greensand, air/water backwash
3) aeration, chlorination, detention, potassium permanganate, anthracite/sand, water backwash
4) chlorination, potassium permanganate, anthracite/sand, air/water backwash

5) aeration, chlorination, potassium permanganate, anthracite/greensand, air/water backwash

In addition to the removal efficiencies shown, the study found that iron/manganese filtration has a radium removal threshold and can not completely remove radium. The study found that radium 226 was reduced to 0.65 pCi/L while radium 228 removal stopped at 0.77 pCi/L.

Filter Media

It was determined that effective removal was found using continuous potassium permanganate feed with both anthracite/greensand filter media and anthracite/sand filter media. The anthracite/greensand media did have better radium 226 and radium 228 removal rates, since the greensand media is more porous thereby creating more adsorption sites and making removal more effective. Although due to that same porosity the greensand may retain more radium over time, making disposal of spent media more difficult.

Pre-Oxidation

At the start of the study, it was assumed that increasing the amount of potassium permanganate fed would improve removal rates. However increasing the feed rate is not a feasible option for several of the supplies as it would create pink water in the distribution. Optimization then requires using pre-chlorination or adding aeration, or perhaps adding detention time to allow for the formation of manganese dioxide.

Competing Cations

The presence of calcium, magnesium, beryllium, sodium, strontium and barium as competing cations seem to have little effect at the concentrations found in the study. Although if there were significant levels of these cations, interference may occur in the adsorption process.

Iron and Manganese

The presence of iron and manganese in the raw water plays a significant role in radium removal. The manganese should aid in the adsorption of radium, while iron in the ferric state (II) utilizes the existing adsorption sites on the filter media. To compensate for inadequate manganese in the raw water, manganese sulphate or hydrous manganese oxides may be added.

Inadequate pre-oxidation may be a factor when observing the effect of iron and manganese in the raw water. This may explain why treatment plant 4, which had relatively low iron and high manganese, had less effective removal rates (19% for radium 226 and 23% for radium 228).

Air/Water Backwash

The use of air and water in the backwashing process seemed to only slightly improve radium removal efficiencies. This was observed at treatment plant 2 which used anthracite/greensand, but it may apply to anthracite/sand media as well. By scouring the media with air, more surface area should be available for adsorption, thereby improving removal. In reality, radium 226 removal improved by only 15%, while radium 228 removal stayed the same.

Uranium Removal

The study found that the use of iron/manganese filtration did not remove uranium, although there may not have been enough uranium in the raw water to determine treatment effectiveness. For those supplies that have an occurrence of radium 226, radium 228, and uranium, a more effective treatment may include lime softening.

CONCLUSION

Supplies with existing iron/manganese filtration should investigate several areas of optimization before making any significant infrastructure improvements. Each supply needs to understand the chemical processes taking place during treatment in order to improve removal efficiencies. The supply also needs to take into consideration the existing infrastructure and raw water quality. Some options, such as the addition of chemical feed, require minimal changes and would be the first step in improving removal.

Optimization with Pre-Oxidation

This is the one of the least expensive infrastructure modifications, and the addition of or the increased use of pre-oxidation is very simple to try in a pilot study. Currently, many supplies rely heavily on potassium permanganate to oxidize iron and manganese. By using pre-chlorination or aeration to more completely oxidize the iron and manganese, the potassium permanganate could be used more effectively to remove radium.

In addition, some supplies may want to consider increasing the potassium permanganate fed to possibly enhance removal. Many supplies tend to be conservative when adding potassium permanganate for fear of feeding pink water into the distribution system.

Optimization with Manganese Sulfate or Hydrous Manganese Oxides

The addition of manganese sulfate and hydrous manganese oxides have proven to be effective in reducing radium levels. This is another low cost infrastructure modification, and is very simple to use in a pilot study.

Both of these must be fed after either aeration or pre-chlorination to insure that the iron has been oxidized. If the iron is not oxidized and remains in the two valence state, it takes up potential adsorption sites on the manganese dioxide. Radium has the same valence state as ferric iron, but due to electron potential the iron (II) molecule is more likely to take available space.

The city of Knoxville, Iowa currently uses this optimized treatment process to remove radium 226 from 3.7 to 2.2 pCi/L and radium 228 from 4.7 to 2.5 pCi/L.

Optimization with Detention Time

The addition of detention time has proven to be effective in the removal of radium. For those supplies using potassium permanganate, adequate time must be given to allow potassium permanganate to become manganese dioxide. Once this has occurred, radium will adsorb onto manganese dioxide, allowing it to be removed in the filtration process.

The city of Menomonie, Wisconsin has three treatment plants using optimized treatment with a minimum detention time of 30 minutes. This provides them with radium removal rates of 43% for radium 226 and 45% for radium 228.

Optimization with Filter Media

The use of anthracite/greensand has proven to be more effective than anthracite/sand in removing radium. The greensand has the advantage of being more porous than anthracite/sand, thereby providing more media surface area. It has been shown that anthracite/greensand, when used with potassium permanganate, removes radium 226 by 56 to 63% and radium 228 by 46 to 57%. Whereas, anthracite/sand media and potassium permanganate had removal rates of 19 to 59% for radium 226 and 23 to 71% for radium 228.

Since greensand is more efficient and retains more radium, it is more likely to be considered a hazardous waste when the filter media is disposed of.

SUMMARY

The Minnesota Department of Health has determined that the optimization of existing iron/manganese filtration may be the low cost alternative in removing radium 226 and radium 228. The four treatment alternatives listed above should be considered in the optimization of existing treatment before investing in other treatment technologies.

ACKNOWLEDGMENTS

Minnesota Department of Health
    Bassam Banat, Richard Clark, Lih-in Rezania, David Schultz, Mark Sweers
Hinckley, MN Water Utility
    Jerry Williams
Inver Grove Heights, MN Water Utility
    Jim Sweeney, Larry Blurton
Knoxville, IA Water Utility
    Steve Inskeep
Madelia, MN Water Utility
    Doug Fredrickson
Menomonie, WI Water Utility
    Ron Koenig
Sandstone (MN) Federal Correctional Facility
    Ken Faulkner
Savage, MN Water Utility
    Terry Thene, Allen Gansen

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