Performance and Cost-Effectiveness of Ferric and Aluminum Hydrous Metal Oxide Coating on Filter Media to Enhance Virus Removal

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Abstract

Coating sand and granular activated carbon with iron aluminum hydroxides changed the zeta potential of these filtration media from negative to positive at pH 6-9, while also significantly improving removal of viruses (MS2, PRD1, Polio1). A quaternary ammonium based coating on sand also increased zeta potential, but led to limited improvement in virus removal. The coated activated carbon was effective in both columns and faucet filters. Performance of faucet filters decreased slightly (e.g., 98% removal initially vs. 89% removal after 1 month) with time. The chemical costs of coating would add approximately 10% to the cost of water delivered by large-scale municipal systems, whereas coating chemical costs would add less than 1% to the cost of water treated by point-of-use faucet filters. The improvement in virus removal performance gained by use of coated filter media provides a significant benefit to the consumer in terms of increased microbiological quality at a modest-to-negligible increase in cost.

1. Introduction

Chemicals such as aluminum sulfate or ferric chloride are traditionally added to water to reverse the surface charge on microbes, promoting their coagulation and flocculation with other particulate matter in the water. An alternate approach is to modify the surface properties of the filter media, e.g., by coating with an electropositive material. The first investigators of this approach (Brown et al., 1974a, Brown et al., 1974b; Farrah et al., 1988; Farrah et al., 1991) found that iron aluminum hydroxide coating increased removal of viruses by diatomaceous earth from less than 30% to greater than 80%. Subsequently, Lukasik et al. (1996, 1999) tested removal of viruses by columns filled with fine sand (less than 0.3 mm) coated with iron aluminum hydroxide. They reported that virus removal by uncoated sand was typically less than 30% whereas coated sand gave removals of greater than 99%

One objective of the present work was to extend the evaluation of the use of coated granular media for virus removal. We chose a media size range (0.6-0.7 mm) for sand that lies within that used in large-scale municipal and industrial water filters (J.M. Montgomery, Inc., 1985). We also evaluated granular activated carbon as a filtration medium, because it is a common component of point-of-use filtration systems, e.g., faucet filters. Such systems are becoming increasingly popular in households because of concern over microbiological quality of water delivered by municipal utilities.

A second objective was to evaluate a coating with antibacterial activity. This is desirable to limit bacterial growth in point-of-use water filters. The coating chosen for this purpose (AEM 5700; Aegis, Midland, MI) consists of a positively-charged quaternary ammonium linked to a carbon chain. It is widely used as a bactericidal agent in consumer products.
The final objective of this work was to determine the costs of chemicals used in the coating process and compare them, expressed on a unit volume basis, to the typical costs of water from municipal supply systems and point-of-use systems.

2. Materials And Methods

2.1 Chemicals
Aluminum chloride (AlCl₃·6H₂O), ferric chloride (FeCl₃·6H₂O), and ammonium hydroxide (28-30% as NH₃) were obtained from Fisher Scientific. AEM 5700 antimicrobial agent, consisting of 42% 3-(trimethoxysilyl) propyldimethyl-octadecyl ammonium chloride, with the balance of the solution consisting of methanol and inerts, was obtained from Aegis Environmental Management (Midland, MI).

2.2 Viruses and Viral Assays
The following phages and their hosts were used: MS-2 (ATCC 15597-B1) was assayed using Escherichia coli C-3000 (ATCC 15597) as a host. Bacteriophage PRD-1 was assayed using Salmonella typhimurium (ATCC 19585) as a host. These phages are commonly used models of enteric viruses (Gerba, 1984). Phages were assayed as plaque-forming units (PFU) using agar overlay procedure (Snustead and Dean, 1971). Poliovirus was proliferated and assayed as PFU on Buffalo Green Monkey (BGM) cells using an agar overlay method (Smith and Gerba, 1982).

2.3 Coating Procedure
2.3.1 Modification of Filter Media by In Situ Precipitation of Metallic Hydroxides
Activated carbon (20×40 mesh) was obtained from Aldrich Chemical Company. Ottawa sand (25×30 mesh after sieving) was obtained from Fisher Scientific. The media were first rinsed with deionized water, then soaked to saturation in a solution of 0.25M ferric chloride and 0.5M aluminum chloride, and finally heated at 60°C until dry. The media was then mixed to saturation with 3N ammonium hydroxide and heated at 60°C until dry. A second precipitation with ammonium hydroxide was performed to precipitate any un-reacted chlorides.

2.3.2 Modification of Ottawa Sand with AEM5700
Ottawa sand (25×30 mesh) was washed three times in deionized water then soaked to saturation in a 1% aqueous solution of AEM 5700. The solution was agitated for ten minutes at room temperature. The media was then filtered from the solution using Whatman paper, rinsed 5 times, and dried overnight.

2.3.3 Faucet Filter Modification
Faucet filters (Ameritech Co.) were cut open and the activated carbon removed. The carbon was then coated with iron aluminum hydroxide as described previously. The modified carbon was placed back into the shell and the shell was sealed with epoxy. Unmodified filters were also cut open and resealed to act as controls.

2.4 Characterization of Filter Media
The zeta potential of the filtration media was determined using an Anton Paar Electro Kinetic Analyzer (EKA, Anton Paar, Graz, Austria). The cylindrical flow cell had an I.D. of 2.0 cm and a packed length of 4.0 cm. The electrolyte was 1.0×10⁻³ M KCl. Zeta potential (ζ) was computed according to the Fairbrother and Mastin (1924) equation:

$$\zeta = \left( \frac{\Delta U}{\Delta P} \right) \frac{\eta k}{\epsilon} \tag{1}$$

where η is the viscosity of water and k is conductivity. The parameter ε in SI units is found from:

$$\epsilon = \epsilon_r \epsilon_0 \tag{2}$$

where \( \epsilon_r = 78.54 \) at 25°C and \( \epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/(\text{J} \cdot \text{m}) \).

2.5 Experimental Protocols
2.5.1 Comparison of Coated and Uncoated Media in Columns
Four identical filtration columns, each 1.9 cm in diameter and 50 cm long, were filled with either Ottawa sand, AEM 5700 coated Ottawa sand, or metal hydroxide coated Ottawa sand. The filter media was added incrementally through the top of the columns, which were partially charged with water from the bottom. After the addition of sand, the column was thoroughly tapped to pack the media and to remove any trapped air bubbles. Wire mesh was placed at the ends of the column to prevent loss of media. Acrylic plastic caps were secured to the columns to hold the mesh and to provide connections for the PVC tubing (1/8 in. ID) used in the experiments. Once packed and assembled, water was passed through the columns to further rinse the media. The columns were operated in parallel using two multi-head peristaltic pumps, which were calibrated prior to the experiments.

Viral suspensions were passed top-to-bottom through the columns at a superficial velocity of about
which is typical of industrial and other water treatment processes. The same suspension was fed to all four columns. Samples were taken for assay from the inlet and from the exit of each column periodically for about two hours or about 70 pore volumes, ensuring steady-state conditions.

### 2.5.2 Comparison of Coated and Uncoated Granular Activated Carbon in Columns

Activated carbon (Aldrich Chemical Co.) was freshly prepared and coated with iron aluminum hydroxide as previously described. Modified carbon was packed into one column while unmodified carbon was packed into another column (30 cm long, 5 cm diameter). Four liters of deionized water, containing bacteriophage MS2, were then pumped through each of the columns at a rate of 40 mL/sec. After initial passage of the water through the columns, the effluent was recirculated through the columns to assess second-pass removals. Triplicate samples of column influent and effluent were collected and assayed for virus removal.

### 2.5.3 Comparison of Point-of-Use Filters containing Coated and Uncoated Media

Faucet filters containing either coated or uncoated granular activated carbon were attached to a pressure vessel that contained dechlorinated tap water seeded with bacteriophage and poliovirus 1. The test solution was forced through the filters at a rate of 25 mL/s using nitrogen gas. Multiple influent and effluent samples were collected and assayed to determine percent removal of viruses. For long term coating stability and performance studies, the filters were rinsed daily with at least 8 L of tap water. Samples were collected and assayed weekly for a period of one month.

### 3. Results

#### 3.1 Surface Characteristics of Filter Media

The coating of Ottawa sand with iron aluminum hydroxide increased the zeta potential from $-40 \pm 6.6$ mV to $+45 \pm 9.8$ mV at pH 7.0. The zeta potential of the uncoated activated carbon used in the column experiments (Aldrich) was $-2.6 \pm 3.0$ mV. After coating, the Aldrich carbon had a zeta potential of $+24.8 \pm 8.2$ mV. The activated carbon used in the faucet filter experiments had a measured zeta potential of $-1.2 \pm 5.1$ mV before coating. After coating, the zeta potential measured $+27.2 \pm 10.2$ mV (Table 1). Coating sand with AEM 5700 also resulted in a change in zeta potential from negative to positive (data not shown).

#### 3.2 Effect of Coating on Virus Removal by Sand in Columns

Filtration columns packed with Ottawa sand, iron and aluminum coated Ottawa sand, and AEM 5700 coated Ottawa sand were charged with suspensions of MS-2 and PRD-1. Virus removals for each column and organism are reported in Figure 1. Metal hydroxide coated sand removed 52% and 46% of MS-2 and PRD-1, respectively, whereas viral reductions for unmodified sand were 16% and $-3 \pm 4%$ respectively. A two-factor analysis of variance revealed a significant difference ($\alpha = 0.05$) in percent removals between different sand columns. Tukey’s test was performed with $\alpha = 0.05$ to directly compare the percent removals of pairs of columns. Metal hydroxide coated Ottawa sand removed more MS-2 and PRD-1 than uncoated Ottawa sand and more PRD-1 than AEM 5700 coated Ottawa sand. AEM 5700 coated sand removed significantly more MS-2 than unmodified sand but not significantly more PRD-1.

| Filter media                  | Zeta potential (mV) |
|-------------------------------|---------------------|
| Sand (uncoated)               | $-40.0 \pm 6.6$     |
| Sand (coated)                 | $+45.0 \pm 9.8$     |
| Faucet Filter carbon (uncoated)| $-1.2 \pm 5.1$     |
| Faucet Filter carbon (coated) | $+27.2 \pm 10.2$    |
| Aldrich carbon (uncoated)     | $-2.6 \pm 3.0$      |
| Aldrich carbon (coated)       | $+24.8 \pm 8.2$     |

*Values represent the mean $\pm 1.0$ S.D. (N = 10)*
3.3 Effect of Coating on Virus Removal by Granular Activated Carbon in Columns

Columns containing modified activated carbon outperformed columns containing unmodified activated carbon in the removal of viruses from aqueous solutions. The first pass of water seeded with bacteriophage MS2 through the columns resulted in an average 92% reduction of MS2 by the coated carbon, compared to an average 32% reduction by unmodified carbon (Table 2). Passage of column effluents back through the respective columns resulted in a cumulative 99% reduction of bacteriophage MS2 by the coated carbon and a cumulative 54% reduction by the unmodified carbon.

| Pass | % Cumulative removal Coated | % Cumulative removal Uncoated |
|------|-----------------------------|-----------------------------|
| 1    | 92±5                        | 32±4                        |
| 2    | 99.6±0.5                   | 54±7                        |

Values are the means ±1.0 S.D. (N=3)

| Significantly greater than control (uncoated) at α=0.01 |

3.4 Effect of Coating on Virus Removal by Activated Carbon in Faucet Filters

Faucet filters containing activated carbon coated with ferric and aluminum hydroxide removed more microorganisms from water than all unmodified filters. The modified filters removed >99% of MS2 and 84±8% of poliovirus 1 while the unmodified filters removed 34±11% of MS2 and 35±4% of poliovirus (Table 3). Long-term evaluation indicated that the coatings are stable and capable of maintaining their effectiveness for several weeks. Each filter tested removed greater than 85% of all organisms used to challenge the system after 30 days of use (Fig. 2).

Table 3: Effect of Coating on Granular Activated Carbon in Faucet Filters

| Virus | % Removal Coated | % Removal Uncoated |
|-------|------------------|--------------------|
| MS2   | 99.7±0.4         | 34±11              |
| Polio 1 | 84±8             | 35±5               |

Values are the means ±1.0 S.D. (N=5)

| Significantly greater than control (uncoated) at α=0.01 |

3.5 Economic Comparison

The chemical costs of coating filter media with iron and aluminum hydroxides were estimated based on observed chemical requirements for coating media in the laboratory, together with costs of chemicals in bulk quantities (Table 4). The total coating cost for sand was 7.0 cents per kg, whereas the coating cost for activated carbon was 55 cents per kg. These costs were used in determining the added price to the consumer of water treated by coated filter media.

The lower of the mean percent removals (46% achieved with PRD1) was chosen to be representative of virus removals obtained by coated sand. Given this level of performance in a 0.5 m deep column, a corresponding removal of 70% may be expected in a 1.0 m deep column based on first-order removal (Tien, 1989). The cost of coating filter media to achieve this removal can be based on a unit cross-sectional area of 1.0 m² (normal to the downward flow direction of the water being treated). The chemical cost to coat the media contained in this unit area would be $120.57 (Table 5). The volume of water treated in 1 month by this unit area, based on a superficial velocity of 1.4 mm/s [2 gal/(ft² min)] and a 5% loss for backwashing, would be 3498 m³. The unit chemical cost for
water treatment with coated media is thus computed to be 3.4 cents per cubic meter. This compares to a typical delivered water price in U.S. municipal systems of 40 cents per cubic meter.

The cost of water treatment by a conventional household faucet filter as compared to the chemical cost of coating the activated carbon in such a filter is determined in Table 6. Based on a retail cost of $10 per filter, a lifetime of 1 month, and a daily throughput of 8 L, the unit cost of water treated by a faucet filter was estimated to be 4.1 cents per liter. Coating the activated carbon contained in one faucet filter would require 2.9 cents worth of chemicals, amounting to an additional cost of 0.01 cents per liter.

### Table 5  Cost of using coated sand for municipal/industrial filtration

| Filter coefficient | 1.2 m⁻¹ |
|--------------------|---------|
| Bed depth          | 1.0 m   |
| Initial virus removal | 70%   |
| Porosity           | 0.35    |
| Bed cross-sectional area | 1.0 m²   |
| Bed depth          | 1.0 m   |
| Bed volume         | 1.0 m³  |
| Media weight       | 1722.5 kg |
| Unit coating cost  | $0.07/kg |
| Coating cost for 1.0 m³ bed | $120.57 |
| Superficial velocity | 1.4 mm/s |
| Volume treated in 1 month | 3498 m³ |
| Unit cost          | 3.4 cents/m³ |
| Typical U.S. delivered municipal water cost (conventional filter media) | 40 cents/m³ |

| Media weight per filter | 52 g |
| Initial virus removal   | 98%  |
| Unit coating cost       | $0.55/kg |
| Coating cost for 1 filter | 2.9 cents |
| Daily water consumption | 8 L |
| Volume treated in 1 month | 243.5 L |
| Typical retail cost of conventional faucet filter | $10 |
| Water cost for conventional faucet filter (assuming change-out after 1 month) | 4.1 cents/L |
| Additional chemical cost for using coated media in faucet filter | 0.01 cents/L |

### Table 6  Cost of using coated activated carbon in faucet filters

| Media weight per filter | 52 g |
| Initial virus removal   | 98%  |
| Unit coating cost       | $0.55/kg |
| Coating cost for 1 filter | 2.9 cents |
| Daily water consumption | 8 L |
| Volume treated in 1 month | 243.5 L |
| Typical retail cost of conventional faucet filter | $10 |
| Water cost for conventional faucet filter (assuming change-out after 1 month) | 4.1 cents/L |
| Additional chemical cost for using coated media in faucet filter | 0.01 cents/L |

### 4. Discussion

Coating of sand and granular activated carbon with iron aluminum hydroxide made the zeta potential more electropositive, while also significantly improving virus removal. This effect on sand has been observed by several other investigators (Lukasik et al., 1999; Chen et al., 1998; Truesdail, 1999; Shaw et al., 2000), who attributed increased removals of viruses, bacteria and protozoa to the change in filter media potential from negative to near-zero or positive. A similar effect on zeta potential of sand was achieved by the AEM 5700. Although AEM 5700 is a popular antimicrobial agent for consumer products, use of this material for coating water filter media is novel. However, the AEM 5700-coated sand showed a limited capacity to remove viruses.

Use of iron aluminum hydroxide coating to increase the zeta potential of granular activated carbon from negative to positive values was reported for the first time in this work. Uncoated granular activated carbon, which is a standard component in point-of-use fil-
ters, was a moderate to poor collector of viruses. After coating, the activated carbon achieved very high virus removals in both columns and faucet filters.

An important issue in the application of coated filter media is the lifetime of the coating. The performance of faucet filters decreased slightly (e.g., 98% removal of PRD1 initially vs. 89% removal after 1 month) with time. Previous studies using coated sand in columns indicated that little of the coating was lost over time. Chen et al. (1998), in a study of aluminum hydroxide coated sand for bacterial removal from wastewater, found that three-fourths of the aluminum originally coated on the sand was still present after 3 months of continuous flushing. Lukasik et al. (1999) reported that iron and aluminum concentrations in the effluents of filtration columns containing coated media were below the detection limit (0.1 ppm for Fe; 0.01 ppm for Al) of ICP.

The estimated chemical costs for coating sand and activated carbon, when expressed relative to the volume of water treated, are low relative to typical consumer costs for water. The chemical costs of coating would add approximately 10% to the cost of water delivered by municipal systems, whereas coating chemical costs would add less than 1% to the cost of water treated by faucet filters. Improvement in virus removal performance gained by use of coated filter media thus provides a significant benefit to the consumer in terms of increased microbiological quality at a negligible-to-modest increase in cost.

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References

1) Brown, T.S., J.F. Malina, Jr., and B.D. Moore. Virus removal by diatomaceous earth filtration, part 1. J. Am. Water Works Assoc. 66: 98-102 (1974a).
2) Brown, T.S., J.F. Malina, Jr., and B.D. Moore. Virus removal by diatomaceous earth filtration, part 2. J. Am. Water Works Assoc. 66: 735-738 (1974b).
3) Chemical Market Reporter. Inorganic chemicals. Vol. 257, No. 1, pp 18-25 (2001).
4) Chen, J., Truesdail, S., Lu, F., Zhan, G., Belvin, C., Koopman, B., Farrah, S., and Shah, D. Long-term evaluation of aluminum hydroxide-coated sand for removal of bacteria from wastewater. Water Research 32, 2171-2179 (1998).
5) Farrah, S.R., M.A. Girard, G.A. Toranzos, and D.R. Preston. Adsorption of viruses to diatomaceous earth modified by in situ precipitation of metallic salts. Z. Gesante Hyg. 34, 520-521 (1988).
6) Fairbrother, F. and Mastin, H. Studies in Electro-endosmosis. Part I. J. Chem. Soc. 125, 2319-2330 (1924).
7) Farrah, S.R., D.R. Preston, G.A. Toranzos, M. Girard, G.A. Erdos, and V. Vasuhdivan. Use of Modified Diatomaceous Earth for Removal and Recovery of Viruses in Water. Appl. Environ. Microbiol. 57(9): 2502-2506 (1991).
8) Gerba, C.P. Applied and theoretical aspects of virus adsorption to surfaces. Advances in Applied Microbiology. 30: 133-167 (1984).
9) J.M. Montgomery, Inc. Water Treatment Principles & Design. John Wiley & Sons, New York (1985).
10) Lukasik, J., Y.F. Cheng, F. Lu, M. Tamplin, and S.R. Farrah. Removal of microorganisms from water by columns containing sand coated with ferric and aluminum hydroxide. Wat. Res. 33(3): 769-777 (1999).
11) Lukasik, J., S. Truesdail, D.O. Shah, and S.R. Farrah. Adsorption of microorganisms to sand and diatomaceous earth particles coated with metallic hydroxides. Kona Particle and Powder. 14: 87-91 (1996).
12) Shaw, K., Walker, S., and Koopman, B. Effect of Hydrous Iron Aluminum Oxide Coating on Sand in the Filtration of Cryptosporidium Oocysts. Journal American Water Works Association. 92, 103-111 (2000).
13) Smith, E.M. and C.P. Gerba. Laboratory methods for the growth and detection of animal viruses. In C.P. Gerba and S.M. Goyal, ed. Methods in environmental virology. Marcel Dekker, Inc. New York (1982).
14) Snustad, S.A. and D.S. Dean. Genetic experiments with bacterial viruses. W.H. Freeman and Co., San Francisco (1971).
15) Tien, C. Granular filtration of aerosols and hydrosols. Butterworths, Boston (1989).
16) Truesdail, S. Fundamental forces important to the enhancement of biological colloidal removal. Ph.D. Dissertation, University of Florida, Gainesville, FL USA (1999).
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