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INCORPORATION OF SUBMICRON COLLOIDS INTO LARGER FLOC IN WATER TREATMENT

By Zaid K. Chowdhury, Gary L. Amy, Member, ASCE, and Roger C. Bales, Member, ASCE

INTRODUCTION

Relatively few studies (Bales et al. 1984; McGuire et al. 1982) have addressed the presence of submicron (<1 μm) colloids in potable-water supplies and their removal by water treatment. The potential importance of this issue is severalfold: (1) Sorption of metal and organic contaminants onto colloids; (2) the occurrence of biocolloids such as viruses; (3) the incidence of naturally occurring asbestos fibers; and (4) the anticipated promotion of a more restrictive turbidity standard.

The primary objective of the research reported herein was to determine submicron colloid numbers, fluxes, and removals in two conventional water-treatment plants. A secondary objective was to gain an understanding of the associated behavior of supramicron (>1 μm) particles.

METHODS

Samples were collected from two water-treatment plants operated by the Metropolitan Water District of Southern California (MWD); the Mills filtration plant, located in Riverside County, and the Weymouth filtration plant located in La Verne, Calif. Six sampling locations were chosen for both plants (Fig. 1), to examine particle fluxes between unit processes. In addition, thickener-pond samples were taken only at the Weymouth plant; thickener-pond supernatant is recycled into the source water. The Mills plant was sampled on September 4 and November 9, 1987; the Weymouth plant was sampled only on the second date. The two plants are of similar design but receive different source waters and use different coagulant chemicals.

The Mills plant, which receives Sacramento River Delta (California State Project) water from the California aqueduct, was sampled twice in 1987. First it was operating at 13,000 m³/h [81 MGD (million gallons per day)] during the high-demand summer period (September 4) and second during the low-demand winter period (November 9), when the flow was 3,600 m³/h (23 MGD). The plant used alum as the primary coagulant (3.9 mg/L on September 4 and 2.5 mg/L on November 9), with small doses of a cationic polymer aid (Cat-Floc-T) added (1.9 mg/L on September 4 and 1.2 mg/L on November 9). A filter aid (0.01 mg/L) was added before the filters. Caustic soda (6.4 mg/L on September 4 and 4.5 mg/L on 9) was added to finished water for pH buffering.

The Weymouth plant, sampled on November 9, was receiving River water from Lake Havasu through the Colorado River aqueduct, 36,000 m³/h (227 MGD), and 0.25 mg/L of a cationic poly- plus was added as the primary coagulant. No coagulant aids, filter aid soda were used.

Total particle number (TPN) concentrations were measured by particle counting (OPC) for particle diameters, dₚ > 2 μm, and electron microscopy (SEM) for dₚ < 1 μm. Details of the methods appear in Chowdhury et al. (1991). Volume-average diameter calculated from the measured number concentrations, represent size distributions. In this work, the TPN and dₚ, parameters represent descriptions of particle-size distribution (PSD) data. Supra- particle determinations were made on-site with a 12-channel analyzer automatic-bottle sampler with a 2-150-μm sensor. Other on-site methods included pH and turbidity, as well as average surface area estimated by electrophoretic mobility (Rank Brother Mark II microphor, 5.0 μm phoresis unit, capable of evaluating both submicron and supramicron samples for SEM counting were prefilted through 5.0 μm pore membrane (Nuclepore) filters to separate large particles an remaining particles in the 5.0 μm filtrate were then collected for Nuclepore filters. The prefiltro step provided an operation of floc versus Itrate nanoparticles. SEM specimens were prepared for the time of sampling and subsequently analyzed, with submersion enumeration accomplished by visual examination of SEM graphs; PSD's over the 0.1 μm to 1.0 μm range were obtained in μm filtration, dissolved aluminum [Al by atomic absorption] and dissolved organic carbon (DOC) were measured. The Mills raw and finished water samples on September 4 were duplicate.

RESULTS

Particle number concentrations (Table 1) in the Mills raw water were very similar during September (submicron = 43 × 10⁴ L⁻¹; microns = 9.7 × 10⁴ L⁻¹) versus November (submicron = 24 × 10⁴ microns = 5.3 × 10⁴ L⁻¹). The average raw water electrophoretic mobility were approximately the same for particles/collids in both sets: -1.3(μm s⁻¹)/(V cm⁻¹) versus -1.2(μm s⁻¹)/(V cm⁻¹). The water had a 100-fold fewer submicron colloids (0.3 ×
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THEORY

Very few studies (Bales et al. 1984; McGuire et al. 1982) have addressed the presence of submicron (<1 μm) colloids in potable-water plants and their removal by water treatment. The potential importance of these colloids is severalfold: (1) sorption of metal and organic contaminants on colloids; (2) the occurrence of biocolloids such as viruses; (3) the potential for naturally occurring asbestos fibers; and (4) the anticipated formation of a more restrictive turbidity standard.

The primary objective of the research reported herein was to determine colloid numbers, fluxes, and removals in two conventional water-treatment plants. A secondary objective was to gain an understanding of the behavior of submicron particles (>1 μm).

SAMPLING

Samples were collected from two water-treatment plants operated by the Metropolitan Water District of Southern California (MWD): the Mills plant, located in Riverside County, and the Weymouth filtration plant in La Verne, Calif. Six sampling locations were chosen for each plant (Fig. 1), to examine particle fluxes between unit processes. In the Weymouth plant, two supernatants were collected at the source water. The Mills plant was sampled on September 4 and November 9, 1987; the Weymouth plant was sampled only on the second date. The two plants are of similar design and collect different source waters and use different coagulants chemistry.

The Mills plant, which receives Sacramento River Delta water from the California aqueduct, was sampled twice in 1987. The first sampling was in March, when the plant was operating at 13,000 m³/h (11 MGD) million gallons per day) during the high-demand summer period (September 4) and second the low-demand winter period (November 9), the flow was 38 MGD. The plant used alum as the primary coagulant (3.9 mg/L on September 4 and 2.5 mg/L on November 9), with small doses of polymer aid (Cat-Floc-T). A filter aid (0.01 mg/L) was added before the filters. Caustic soda (6.4 mg/L on September 4 and 4.5 mg/L on November 9) was added to finished water for pH buffering.

The Weymouth plant was receiving Colorado River water from Lake Havasu through the Colorado River aqueduct. Flow was 36,000 m³/h (227 MGD), and 0.25 mg/L of cationic polymer (WT20) was added as the primary coagulant. No coagulant aids, filter aids or caustic soda were used.

Total particle number (TPN) concentrations were measured by optical particle counting (OPC) for particle diameters, d_p, > 2 μm, and by scanning electron microscopy (SEM) for d_p < 1 μm. Details of the methodology appear in Chowdhury et al. (1991). Volume-average diameters (d_v) were calculated from the measured number concentrations, representing particle-size distributions. In the Weymouth plant, d_v parameters represent summary descriptions of particle-size distribution (PSD) data. Supramicron particle determinations were made on-site with a 12-channel analyzer (a HIAC automatic-bottle sampler with a 2-150 μm sensor). Other on-site measurements included pH and turbidity, as well as surface area measurements, as estimated by electrophoretic mobility (Rank Brothers Mark II microelectrophoresis cell). Samples for SEM counting were prefiltered through 5.0 μm polycarbonate membrane (Nucleopore) filters to separate large particles and flocs; the remaining particles in the 5.0 μm filter were then collected on 0.1 μm Nucleopore filters. The prefiltration step provided an operational definition of floc versus discrete particles. SEM specimens were prepared on-site at the time of sampling and subsequently analyzed with submicron colloid enumeration accomplished by visual examination of SEM photomicrographs; PSDs over the 0.1 μm to 1.0 μm range were obtained. After 0.45 μm filtration, diluted aluminum (Al by atomic absorption spectroscopy (AAS)) and dissolved organic carbon (DOC) were measured. Analyses of the raw and finished water samples on September 4 were run in duplicate.

RESULTS

Particle number concentrations (Table 1) in the Mills raw water were slightly higher during September (submicron = 43 × 10^6 L^-1; supramicron = 9.7 × 10^4 L^-1) versus November (submicron = 24 × 10^6 L^-1; supramicron = 5.3 × 10^4 L^-1). The average raw water electrophoretic mobilities were approximately the same for particles in both sets of samples: -1.3(μm s^-1)(V cm^-1) versus -1.2(μm s^-1)(V cm^-1). Weymouth raw water had about a 100-fold fewer submicron colloids (0.3 × 10^6 L^-1) but...
<table>
<thead>
<tr>
<th>Sample point</th>
<th>pH</th>
<th>DOC (mg/L)</th>
<th>Al (µg/L)</th>
<th>Turbidity (NTU)</th>
<th>Supramicron TPN (L⁻¹ × 10⁶)</th>
<th>d₄ (µm)</th>
<th>Submicron TPN (L⁻¹ × 10⁶)</th>
<th>d₄ (µm)</th>
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<td>(a) Mills Filtration Plant (9/4/87)</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Raw</td>
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<td>3.25 (\pm 6)%</td>
<td>15 (\pm 52)%</td>
<td>2.25 (\pm 16)%</td>
<td>9.67 (\pm 4)%</td>
<td>42.6 (\pm 9)%</td>
<td>0.45 (\pm 5)%</td>
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<tr>
<td>Finished</td>
<td>8.46 (\pm 1)%</td>
<td>2.92 (\pm 6)%</td>
<td>108 (\pm 11)%</td>
<td>0.13 (\pm 58)%</td>
<td>7.34 (\pm 4)%</td>
<td>1.97 (\pm 14)%</td>
<td>0.48 (\pm 3)%</td>
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<td>(b) Mills Filtration Plant (11/9/87)</td>
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<tr>
<td>Raw</td>
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<td>25</td>
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<td>0.08</td>
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<td>(c) Weymouth Filtration Plant (11/9/87)</td>
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<tr>
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<td>0.80</td>
<td>11.5</td>
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*Coefficient of variation.
about the same concentration of supramicron particles (8.6 × 10⁶ L⁻¹) compared to Mills. The average electrophoretic mobility of raw water colloids/particles at Weymouth was -0.9 (μm s⁻¹)/(V cm⁻¹). Although significant TPN reductions were found, little overall change in volume-average diameter dₐ was observed for either submicron or supramicron particles in raw versus finished waters. Whereas dₐ is an index of the overall PSD, it can be disproportionately affected by larger particles.

Total particle numbers were significantly lower in finished waters than in raw water. Submicron particle concentrations in finished water at Mills were 4.6% and 1.4% of raw water levels for the September and November sampling dates, respectively (Table 1). The finished-water TPN concentration at Weymouth was 43% of the raw-water level (Table 1). Similar changes in concentration were observed for supramicron particles: finished water levels were 2.3%, 1.5%, and 9.3% of raw-water levels for the three samples, respectively (Table 1).

Within a treatment plant, chemical addition in the rapid-mix unit initially adds colloids/particles to the water. After chemical addition, significant changes in submicron colloids begin in rapid mixing (Fig. 2); the observed decrease in concentration in flocculation is due to incorporation of the submicron particles present in the raw water plus those created in the rapid-mixing unit into larger floc. The gradual change throughout the plant reflects the contribution of detention time in all of the unit processes to particle aggregation and eventual solid-liquid separation. Most removal at Mills occurred through the flocculator and filter; Weymouth exhibited little change in submicron colloid concentration. The volume-average diameter (dₐ) for submicron particles (≤0.5 μm) changed little through either plant (Fig. 2). It is reasonable to expect filter performance to be influenced by the status of the filter run.

Supramicron particle removal was greatest across the filtration unit, with little change in concentration across other units (Fig. 2). Turbidity also decreased from >1.0 NTU (nephelometric turbidity units) to about 0.1 NTU through the plants. Corresponding changes in volume-average diameters show the extent of particle growth through the process train. The effectiveness of coagulation of supramicron particles is indicated by the increase in volume-average diameter dₐ from about 7 μm to about 12 μm for the Mills September 4 sample. The lack of decrease in volume-average diameter after sedimentation likely reflects the relatively small total particle concentrations, small volume-average diameter (indicating low settling velocities), and the relatively short detention time associated with the sedimentation step.

While significant reductions were achieved for supramicron TPNs with some reduction in submicron TPNs, averages and ranges of sizes remained somewhat constant. In other words, particle-size distributions in raw versus finished water were found to be somewhat similar, as shown for the Mills September data in Fig. 3 (it should be noted that the 50% values shown in Fig. 3 reflect number-average as opposed to volume-average diameters). This trend suggests that TPN reductions were accomplished by aggregation of colloids/particles from the entire range of sizes into floc, with subsequent solid-liquid separation.

On September 4, the recovery of backwash water at the Mills plant by sedimentation in an open pond was only moderately effective, reducing the submicron particle concentration from 4.0 × 10⁴ L⁻¹ to 5.0 × 10³ L⁻¹ and the supramicron particle concentration from 7.0 × 10⁴ L⁻¹ to 5.0 × 10³ L⁻¹.
FIG. 2. Total Particle Number and Volume Average Diameter Profiles for the Mills and Weymouth Plants

L⁻¹. On November 9, the backwash flow was very small and the pond was not effective in removing submicron particles (~12 × 10⁶ L⁻¹), although there was a significant reduction in supramicron particle concentration (2 × 10⁶ L⁻¹ to 1 × 10⁶ L⁻¹). The concentration of submicron particles in the pond influent water was significantly higher than in the pond return water (40 × 10⁵ L⁻¹ versus 5 × 10⁵ L⁻¹). During the September sampling at the Mills plant the flow through the thickener pond was continuous, providing slow agitation that would enhance removal of particulates; the water also contained coagulant chemicals. As noted before, pond effluent is recycled at this plant. Our results suggest that, on a mass basis, there is little recycling of submicron particles in association with the thickener-pond supernatant.

Residual Al concentrations were near the equilibrium concentration (Chowdhury 1988) in all the samples analyzed (Table 1). Both source waters were moderate in dissolved organic carbon (DOC) concentration (~3.0 mg/L); about a 30% reduction in DOC was achieved in treatment plant. Water at the Mills plant had a slightly lower pH than the Weymouth plant (~8.3). It is noteworthy that turbidity is a parameter, which indirectly measures the collective properties of micron particles and submicron colloids.

**Comment**

The Mills plant was more effective in particle removal than the Weymouth plant. The difference is attributed to source-water differences and/or coagulant dosages. The two plants are otherwise quite similar. The coagulant employed are based on turbidity compliance. The Mills plant showed two log reductions in both supramicron and submicron particle concentrations. The Weymouth plant only provided about a one log reduction in supramicron particles, and little reduction in submicron colloids. Laboratory experiments (Chowdhury et al. 1991), have observed greater than 99.9% removal (>2 log units), performance that can be achieved by water treatment plants through optimum operational conditions of pH and coagulant dose.

In a previous study it was reported that 99% or greater removal of supramicron asbestos fibers occurs in MWD's plants 50% of the time. 99.9% removal occurs about 10% of the time (Bales et al. 1984). Other instances of mean fiber removals on the order of 99% have been reported (Logsdon et al. 1981).

Conventional water treatment plants in California's Central Valley reported even higher mean removals. Eighteen sets of samples from Kern County Water Agency's 1D-4 plant, which receives high-turbidity water from the California Aqueduct, showed that a 99% or better removal occurred 90% of the time (Bales 1986). Raw water levels avera...
were moderate in dissolved organic carbon (DOC) concentration (approximately 3.0 mg/L); about a 30% reduction in DOC was achieved at either treatment plant. Water at the Mills plant had a slightly lower pH (~8.0) than the Weymouth plant (~8.3). It is noteworthy that turbidity is an optical parameter, which indirectly measures the collective properties of supramicron particles and submicron colloids.

**COMMENT**

The Mills plant was more effective in particle removal than the Weymouth plant, a result attributable to source-water differences and/or coagulant type; designs of the two plants are otherwise quite similar. The coagulant doses employed are based on turbidity compliance. The Mills plant showed almost two log reductions in both supramicron and submicron particle concentrations. The Weymouth plant only provided about a one log reduction in supramicron particles, and little reduction in submicron colloids. In related laboratory experiments (Chowdhury et al. 1991), we have observed reductions of >99.9% (>3 log units), performance that can be brought about in water treatment plants through optimum operational conditions involving pH and alum dose.

In a previous study it was reported that 99% or greater removal of submicron asbestos fibers occurs in MWD's plants 50% of the time and that 99.9% removal occurs about 10% of the time (Bales et al. 1984). Several other instances of mean fiber removals on the order of 99% have been reported (Logsdon et al. 1981).

Conventional water treatment plants in California's Central Valley have reported even higher mean removals. Eighteen sets of samples from the Kern County Water Agency's ID-4 plant, which receives high-turbidity raw water from the California aqueduct, showed that a 99% or better removal occurred 90% of the time (Bales 1986). Raw water levels averaged 1,250
× 10⁶ L⁻¹, while finished-water levels averaged 2.5 × 10⁶ L⁻¹. Alum coagulant dose averaged about 25 mg/L, and the monthly average turbidity of finished water ranged from 0.05 NTU to 0.17 NTU (Bales 1986). The major difference between Central Valley plants and MWD plants that is thought to be responsible for better removals is the higher raw water turbidity and coagulant doses in the Central Valley, which provide more contact opportunities for coagulation of submicron colloids.

Submicron asbestos fiber removals of over 99.9% were also achieved in a series of pilot-scale studies carried out at MWD's Jensen filtration plant (Bales 1984). Equivalent asbestos fiber removals were observed with both 5 mg/L and 30 mg/L of alum, but turbidity deteriorated early in the filter runs with the higher dose. Fiber removal was good for both dual media and sand filters, further suggesting that the important step in fiber removal is incorporation of the submicron colloids into larger floc. There was little difference in 6- versus 30-min flocculation times, consistent with observations of Chowdhury et al. (1991) that control of chemical conditions in rapid mixing is a key to good submicron colloid removal.

CONCLUSION

Removals of submicron colloids ranged from 57% to 99%, while removals for supramicron particles ranged from 91% to 99% for two conventional water treatment plants processing two source waters. These submicron colloid removals are lower than other values reported in the literature involving higher coagulant doses. Particle aggregation during rapid mixing and flocculation provided the greatest reduction in submicron colloid numbers, whereas the largest removal of supramicron particles was achieved by the filtration process.

ACKNOWLEDGMENT

Financial support for this research was provided by the U.S. Environmental Protection Agency (Grant #R812235). The contents of this technical note do not necessarily reflect the views and policies of the EPA. The cooperation of the Metropolitan Water District of Southern California (MWD) is gratefully acknowledged.

APPENDIX. REFERENCES


while finished-water levels averaged $2.5 \times 10^6$ L$^{-1}$. Alum dose averaged about 25 mg/L, and the monthly average turbidities ranged from 0.05 NTU to 0.17 NTU (Bales 1986). The difference between Central Valley plants and MWD plants that is responsible for better removals is the higher raw water turbidant doses in the Central Valley, which provide more contact time for coagulation of submicron colloids.

Asbestos fiber removals of over 99.9% were also achieved in pilot-scale studies carried out at MWD’s Jensen filtration plant. Equivalent asbestos fiber removals were observed with both 30 mg/L of alum, but turbidity deteriorated early in the filter at the higher dose. Fiber removal was good for both dual media and further suggesting that the important step in fiber removal is the aggregation of the submicron colloids into larger floc. There was little difference in 6- versus 30-min flocculation times, consistent with observations by others (1991) that control of chemical conditions in rapid mix is key to good submicron colloid removal.

Portions of submicron colloids ranged from 57% to 99%, while removals of supramicron particles ranged from 91% to 99% for two conventional treatment plants processing two source waters. These submicron colloids are lower than other values reported in the literature involving dual media dosing. Particle aggregation during rapid mixing and flocculation the greatest reduction in submicron colloid numbers, whereas removal of supramicron particles was achieved by the filtration stage.

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REFERENCES


