



## Enhanced Organic Precursor Removals Using “Aged” Filter Media

### Objectives

The main goals of this project was to evaluate the dissolved organic carbon (DOC) removal potential of “aged” sand filter media. This refers to filter media of conventional Drinking Water Treatment Facilities (DWTF) on which metal oxides which were formed from coagulant floc carryover have deposited on the surface of the sand media.

The scope of this bench study was limited to:

- Assess coating characteristics of “aged” rapid sand filter media
- Evaluate optimum initial cleaning/backwashing conditions
- Quantify natural organic matter (NOM) removals using Al or Fe oxide coatings on rapid sand filter media.

### Methodology

#### A. Characterization of coated sand media

The sand media was collected from the rapid sand filters of the Baxter WTP in Philadelphia, PA. The main coagulant in use for at least the last ten years has been ferric chloride.

The media coating which depends essentially on the type and quantity of coagulant used and the length of exposure was characterized by digested metal content. A small amount of sand was acid digested and the digestate analyzed with an Ion-coupled-plasma spectrophotometer. In order to normalize the available surface area of the sand grains the media was sieved to a grain diameter size between 0.595 and 0.833 mm. This equates to an available surface area per unit volume of roughly 9000 to 6500 m<sup>2</sup>/m<sup>3</sup>.

#### B. Synthetic organic carbon challenge solution

A concentrated, purified, and desalted humic acid stock solution was prepared using Aldrich humic acid that was dissolved in laboratory grade water (Milli-Q system, Bedford, MA). This solution was stored at 4°C and used in all synthetic organic carbon challenge solutions.

The UV absorbance for the synthetic challenge solution ranged from 0.405 to 0.425 cm<sup>-1</sup> which equals a total organic carbon concentration of approximately 5.4 – 5.7 mg/l. The dilution water was buffered with 168 mg/l of NaHCO<sub>3</sub> (Alk = 100 mg/l as CaCO<sub>3</sub>) and 40 mg/l of NaCl in laboratory grade water. The pH was adjusted to the target pH using 0.1 N HCl and 0.1 N NaOH. Fresh buffered water and influent solution were prepared prior to each filter challenge.

#### C. Coagulated raw water challenge solution

In addition, coagulated raw water samples from the Baxter WTP were used to challenge the columns. The remaining particulate matter in the water was removed in a sequential filtration using Whatman glass fiber filters with a pore size of 1.6 μm and 0.7 μm. The North Sedimentation Effluent had a UV absorbance of 0.034 cm<sup>-1</sup> and a TOC concentration of 2.0 mg/l. The South Sedimentation Effluent had a UV absorbance of 0.023 cm<sup>-1</sup> and a TOC concentration of 1.6 mg/l.

## D. Experimental Setup and Procedures

### 1. Regeneration procedure

Fifty ml of sand were placed in a 1000 ml glass beaker with 500 ml of buffered water. The BW regeneration pH was adjusted utilizing a Cole-Palmer pH controller with 0.6 N NaOH and 0.1 N HCl. The water was stirred gently with a Teflon coated paddle and held at the target pH for one hour. (Figure 1).

### 2. Equilibration procedure

The same experimental setup was used for the equilibration and challenge procedure. It consisted of a Cole-Palmer pH controller, a solution reservoir, a peristaltic pump with four parallel pumpheads, four glass columns, and an autosampler (Figure 2). After the BW regeneration 20 ml of sand were put into each column. A reservoir was filled with buffered water at the target pH and pumped through the columns in a down flow mode. The flow rate was maintained at 4 ml/min, i.e. an empty bed contact time (EBCT) of 5 minutes. This procedure lasted a minimum of 60 minutes and up to 90 minutes depending on the effluent pH which was measured periodically.

### 3. NOM challenge procedure

In this procedure a reservoir was filled with the respective challenge solution which was pumped through the columns immediately following the equilibration procedure. The flowrate was reduced to 2 ml/min, i.e. an EBCT of 10 minutes. All challenge runs were conducted in duplicate to quantify reproducibility.

Effluent samples were collected after every 20 ml by an autosampler and analyzed for UV absorbance, pH, and total organic carbon (TOC).

## E. Analytical Procedures

### 1. pH measurement

The pH was measured using a Corning pH meter. The calibration of the pH meter was checked daily using pH 4.0, pH 7.0 and/or pH 10.0 standard buffers. The pH controllers were calibrated with the respective standard buffers before each run.

### 2. Ultraviolet absorbance

UV absorbance at a wavelength of 254 nm was used as a surrogate to measure the presence of humic material (Hitachi UV spectrophotometer, S2000). Blanks were checked every 10 samples to check for instrument drift and readings were duplicated on every sample. The samples did not have to be buffered as the pH was between 4 and 10 (Eaton, 1995).

### 3. Organic carbon analysis

The TOC concentration of samples was analyzed using an automated TOC analyzer (Sievers Instruments). The principle of this analysis is the oxidization of the organic carbon to carbon dioxide by persulfate in the presence of

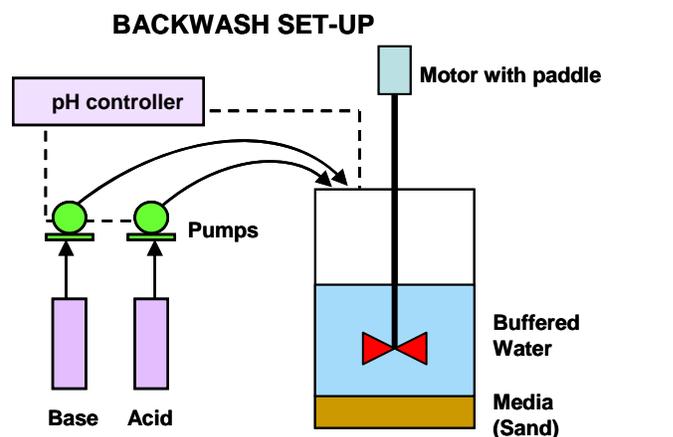


Figure 1. Schematic of Backwash Set-up for Initial cleaning of filter Media

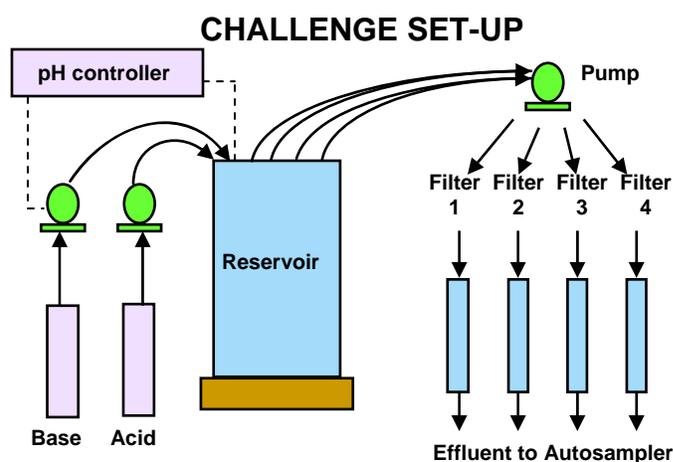


Figure 2. Schematic of Equilibration and Challenge Set-up

ultraviolet light. All samples were analyzed as duplicates if possible. A correlation between UV absorbance and TOC content of the challenge solution influent and effluent was established (Figure 4.3). The correlation showed an excellent fit of  $r^2 = 0.996$  and the relation of TOC [mg/l] =  $12.454 * UV_{254} \text{ abs. [1/cm]} + 0.44$ .

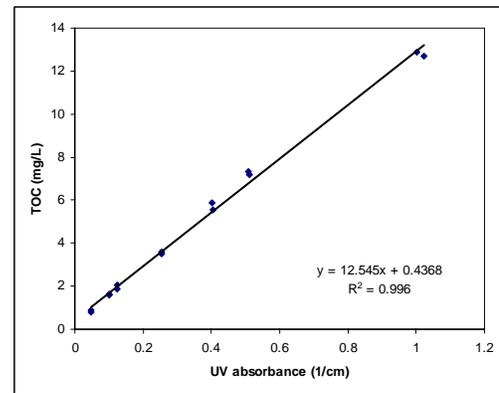


Figure 3. Correlation Between TOC vs. UV Absorbance of the Synthetic Challenge Solution

## Results

### A. Characterization of the sand media coating

The ICP analysis of the acid digested media samples showed a significant metal coating of the media (Figure 4). The main metal in the Baxter WTP media coating was iron at just under 4000 mg/kg dry wt. of media. Manganese and aluminum were the other significant metals in the coating at approximately half the iron concentration.

### B. Effect of initial backwashing pH

Five sand cleanings were conducted to investigate the effect of BW pH on sand regeneration and the subsequent organics removal by the iron coated sand. The BW regeneration pH varied between 9 and 13 and the influent solution pH was 6 for all challenges. A pH 6 was chosen as a reference for the influent solution because the studied media came from WTPs that operate in that pH range.

The pH of the BW solution for initial sand regeneration had no significant impact on organic carbon removal for the iron coated sand at a challenge solution influent pH of 6 as noted in Figures 5 and 6.

During the BW regeneration the pH had to be periodically readjusted indicating that the hydroxides were being consumed. The color of the backwashing solution changed from a light yellow (pH 9) to a brown (pH 13) as the BW pH increased. This indicated that the sand released more and more organic molecules with increasing BW pH which was later confirmed by TOC analysis.

The amount of NaOH required to adjust the BW regeneration pH for each run are indicated in Table 1. The values shown are only relative quantities. The amount of NaOH added would have to be higher if the sand was exhausted or would be lower if the sand was regenerated previously. For the other media tested in the study, a BW pH of 12 required a volume of NaOH that was four times higher than for a BW pH of 11, with a comparable amount

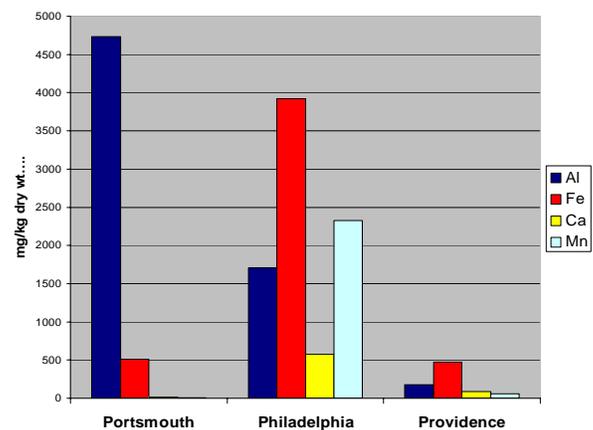


Figure 4. Metal Content of Sand Filter Media Coating

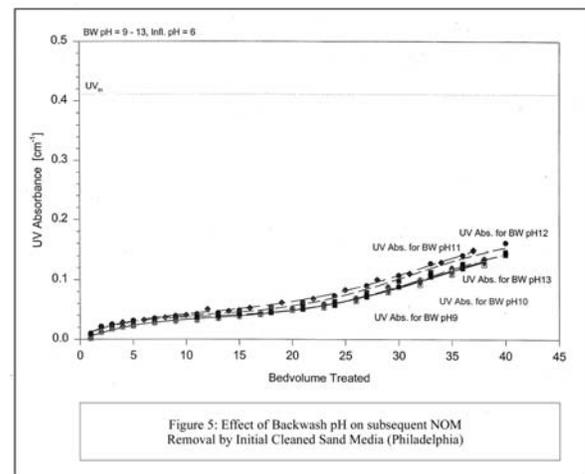


Figure 5: Effect of Backwash pH on subsequent NOM Removal by Initial Cleaned Sand Media (Philadelphia)

of subsequent carbon removal. Consequently, a backwash at a pH of 11 was chosen to achieve efficient regeneration.

Table 1: Amount of NaOH Required to Adjust BW Regeneration pH (in 500 ml of Buffered Water, Alk = 100 mg/l as CaCO<sub>3</sub>) FOR Baxter WTP (Philadelphia)

BW pH	10	11	12	13
NaOH added (meq/50 ml sand)	0.7	1.8	6.0	53

### C. Effect of influent challenge pH

The influent solution pH had a significant impact on the organic carbon removal efficiency, as can be seen in Figure 6. The backwash regeneration pH was 11 for all experiments and influent solution pH was adjusted to 6, 5 or 4. The quantity of HCl required to adjust the influent solution pH to the target pH would depend on the initial alkalinity of the raw water.

The removal remained constant at about 90% for up to 60 bed volumes at an influent pH of 4. The removal started to decrease steadily from 90% after about 20 bed volumes to about 70% at 60 bed volumes for an influent pH of 5. For an influent pH of 6, the removal started to decrease at almost three times the rate (12% over 10 bed volumes) after bed volume 20 as for an influent pH of 5. The total mass of organic carbon removed was about 280 mg TOC/L of sand for pH 5 and 300 mg TOC/L of sand for pH 4 after 60 bed volumes.

The experimental setup and time constraints did not allow the runs to reach exhaustion of the metal oxide coated sands. Nevertheless, the results for lower influent pH's appear to be very promising for the enhancement of organic carbon removal.

### D. Raw water challenge runs

The raw water challenge solutions were coagulated raw waters collected at the Baxter WTP. Organic carbon removal for the challenge runs leveled out at about 60% for the north sedimentation effluent (NSE) after about 10 bed volumes and remained relatively constant up to bed volume 60. For the south sedimentation effluent (SSE) the organic carbon removal also leveled out after about 10 bed volumes but at a level between 30 and 40% (Figure 7).

The backwash regeneration pH for the experiments was 11 and the influent pH of the coagulated raw waters was adjusted to a pH of 5. The amounts of base and acid needed to reach the respective pH's are indicated in Table 1 and Table 2. The difference in organic carbon removal between NSE and SSE challenge solutions might be explained by the TOC concentration and ionic strength of the influent. The TOC concentration and ionic strength of the NSE was slightly higher than that of the SSE. This should decrease the removal efficiency compared to the SSE but exactly the opposite occurred. This might suggest that the removal efficiency of metal oxide coated media is also dependent on a minimum NOM concentration of the challenge solution not just the ionic strength of the influent.

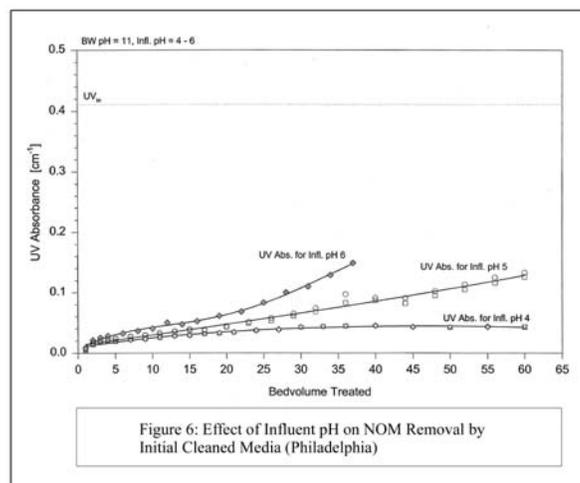


Figure 6: Effect of Influent pH on NOM Removal by Initial Cleaned Media (Philadelphia)

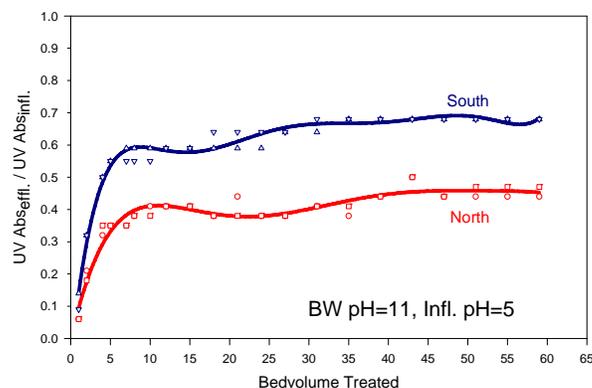


Figure 7. Influence of Philadelphia settled water sources on organic carbon removal by cleaned Philadelphia sand filter media

Table 2: Amount of HCl Required to Adjust Baxter WTP (Philadelphia) sedimentation effluent to the target influent pH

HCl	Influent pH	Target pH		
HCl added (meq/500 ml sample)		6	5	4
HCl added to North Sed. Eff. (meq/500 ml sample)	pH = 6.8	0.6	0.95	1.35
HCl added to South Sed. Eff. (meq/500 ml sample)	pH = 8.4	0.7	0.95	1.35

## Conclusions

The Baxter WTP filter media in Philadelphia appeared to be an effective adsorbent for NOM after a regeneration procedure. The sand media had a significant iron oxide coating and could be easily regenerated with buffered water at an alkaline pH.

The removal of previously deposited organic matter from the media surface was more efficient with higher pH's. An optimum BW regeneration was determined to occur at pH 11.

The TOC removal efficiency for the synthetic challenge solution increased significantly as the operational influent solution pH decreased. At an influent pH of 4 the maximum TOC removal of about 90% was maintained for up to 60 bed volumes treated. The TOC removal at pH 5 decreased from 90% up to 20 bed volumes and about 70% at 60 bed volumes. Removal of influent TOC at influent pH 6 decreased at approximately twice the rate of removal at pH 5 after 20 bed volumes.

A maximum amount of organic matter removal could not be determined because the sand could not be exhausted at lower pHs due to setup and time constraints.

## Recommendations

The results of this limited study appear to be very promising for water treatment facilities that operate in the sweep-floc mode. A metal oxide coating develops naturally on the filter media after years of exposure of sweep floc coagulation. These coating can be utilized to increase the TOC removal with minimal changes to the existing process.

Due to the limited scope of this research some questions remain to be answered and also some issues arose during the study that could not be investigated.

- Additional experiments to determine the physical stability of the media coatings should be conducted.
- The BW procedure was performed in a beaker in order to have control of the solution pH. This may not be achieved in a full scale filter and should be studied under more realistic conditions.
- Additionally, only an initial BW procedure was performed to keep the initial conditions between the runs the same. Preliminary results indicate that the amount of base that has to be added for the increase in BW pH is lower for subsequent regenerations. This should be investigated further.
- Other possible treatment properties such as metal adsorption and particle filtration should be investigated.
- Interference of competing anions.

A pilot or full scale study could supply answers to most of the questions that are mentioned above and should also be possible with a relatively small investment in new equipment to upgrade an existing rapid sand filter.

## Principle Investigators

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## Disclaimer

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