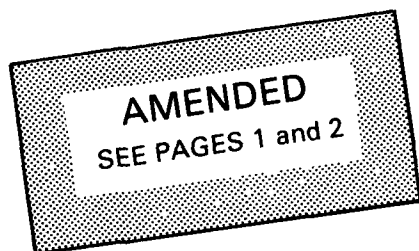




Project Summary

Optimizing Coagulation-Adsorption for Haloform and Total Organic Carbon Reduction

M. J. Semmens, G. Hohenstein, A. Staples, G. Norgaard, K. Ayers, and M. P. Tyson



Coagulation and softening processes were studied for their ability to remove organics from Mississippi River water. The goal was to use these processes to reduce the organic contents of water before expensive treatment with granular activated carbon (GAC) and thereby extend the life of the carbon, improve the product water quality, and reduce the overall cost of water treatment.

Miniature carbon columns were used to evaluate the impact of various pre-treatment strategies on the life and performance of carbon for organics reduction. Assessments were made of (1) removal of specific trace organics from the river water by coagulation, (2) effectiveness of various coagulants, coagulant aids, and lime softening in reducing the organic contents of river water, (3) the nature of the organics removed by coagulation and softening, (4) the effects of these processes on the behavior of miniature carbon columns, and (5) characterization of the organics removed by polarity and molecular weight fractionation studies.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Removal of Specific Trace Organics from Mississippi River Water by Coagulation

Trace organic removal during coagulation was evaluated using a conventional jar test procedure. Four C₁₄-labeled model compounds were studied: phenol, benzoic

acid, salicylic acid, and octanoic acid. These compounds were used to spike river water samples so that removal studies could determine how effective coagulation was in reducing their concentration. Alum and ferric sulfate were tested as primary coagulants, and a study was conducted to identify the value of a cationic polymer (purifloc C31) when used as a coagulant aid. All studies were conducted on the same river water sample so that the relative effectiveness of different operating conditions could be tested.

Alum and ferric sulfate were equally effective as coagulants on a weight basis for the reduction of total organic carbon (TOC) in river water, and the optimum pH for these coagulants was approximately 5.0 and 4.0, respectively. The addition of a polymer enhanced the effectiveness of coagulation for TOC and turbidity removal; it also eliminated the pH dependence of turbidity removal so that good removals were achieved over the entire range studied (pH 4 to 9). The most benefit was gained from a 1-mg/L polymer dose. As polymer doses were raised to 5 mg/L, the benefit of the added polymer diminished. The polymer improved the performance of coagulation more when the primary coagulant was ferric sulfate.

The removals of model organic compounds (100 µg/L initial concentration) were relatively poor and in most cases did not show a strong dependence on coagulant dose. Removals of test compounds were typically < 10%, except for salicylic acid, which was removed slightly better with higher alum dosages.

The influence of pH on the removal of trace organics provided an interesting result. Benzoic acid and octanoic acid

showed either very slight or no pH dependence, whereas phenol and salicylic acid were removed best in the pH range of 5 to 7. Complex formation may best account for the observed removal behavior.

A molecular weight fractionation study indicated that coagulation removed the higher-molecular-weight fractions of the naturally occurring organic matter. Low-molecular-weight (less than 100 nominal molecular weight) organics were only reduced by 10% to 20%, even at high coagulant dosages.

Organics Removal by Coagulant Aids

A variety of jar test studies were conducted on a single water sample to evaluate the relative effectiveness of organics removal during coagulation under various operating conditions. The river water sample tested was freeze concentrated and reconstituted to ensure a constant water quality during the study period. Various coagulants and coagulant aids were studied.

Polymers were studied in detail as primary coagulants and as coagulant aids. Polymers were relatively ineffective coagulants when used alone and were more effective when used with alum or ferric sulfate. Polymers were most beneficial when used with low doses of coagulant, and they improved the performance of ferric sulfate more than that of alum.

Polymers with different charge densities and chemical structures were evaluated. The cationic polymers tested were superior to anionic and nonionic polymers, which caused little or no improvement in organics removal during coagulation. Several cationic polymers were selected for their differences in chemical structure and molecular weight and were tested. Though the improvements in organics removals caused by the use of these polymers were very similar, a slight improvement was noted with increasing molecular weight and increased charge density.

The order of polymer and coagulant addition did not influence organics removal significantly. The slow addition of polymer resulted in slightly better performance than a single, one-shot addition of polymer of equal dose.

Activated silica was tested as a coagulant aid in conjunction with 20 mg/L alum and provided no benefit at pH 5.0.

Multistage coagulation studies were conducted at pH 5, 7, and 9. A marginal benefit was observed for multistage coagulation at the higher pH values, but the extra capital costs required to implement the process would outweigh any benefit

gained in improved organics removal.

Organics removal by alum was a largely reversible process. Coagulant added at pH 9 may remove more organics if the pH is later adjusted toward 5. Conversely, a coagulant used at a low pH may release organics into solution again if the pH is raised.

Softening Studies

Batch softening studies were conducted to identify the impacts of operating conditions on the effectiveness of organics removal from Mississippi River water. In addition, hardness removals were documented, and the relationships between hardness removal objectives and organics removal were identified.

Organics and hardness removals were not influenced by the way in which the lime was added. Lime added as a dry powder gave the same performance as a lime slurry addition.

The rate of organics removal was quite rapid, and more than 95% of the observed removal was complete within 30 minutes. The Ca CO₃ precipitated during recarbonation did not contribute to organics removal.

Alum addition with the lime improved the removals of both hardness and organics, but if too much alum was added, the resulting drop in pH caused a deterioration in performance. The order of alum and lime addition was unimportant.

A cationic polymer, ARCO 6320P, was tested with lime plus alum. The polymer caused a slight deterioration in removal performance for both hardness and organics. Organics removal during softening was most strongly influenced by the operating pH. Softening at a high pH gave better organics removal.

The primary mechanism of organics removal appeared to be precipitation of the organics as calcium and magnesium complexes at high pH. Evidence suggests that adsorption of organics to a Mg (OH)₂ precipitate is not a major mechanism for organics removal.

Nature of Organics Removed by Chemical Pretreatment

A single large water sample was collected from the Mississippi River and subjected to various treatments before application to carbon columns. The pretreatments included alum coagulation, iron and polymer coagulation, and lime softening. Water samples were taken at three stages: (1) the raw river water, (2) following pretreatment, and (3) following carbon adsorption. The samples were analyzed to determine the character of organics removed by each of the processes.

The organic content of each sample was fractionated according to molecular weight and polarity; 40% of the organic content of the river water was hydrophobic and 60% was hydrophilic. In both fractions, the organics were predominately acidic and neutral in character. The molecular weight distribution of the river water for the fractions <1 K, * 1 to 10K, 10 to 100K, and >100K was 23%, 50%, 10%, and 17%, respectively.

Coagulation either with alum or with iron and polymer gave similar performances. Hydrophilic acids were completely removed, and hydrophobic acids were reduced by approximately 60%. The neutral fractions were also reduced. Lime, by comparison, was not as effective in removing the acidic fractions.

Following GAC treatment where the pH was adjusted to favor adsorption, the organic content of the water was essentially independent of the pretreatment provided. Pretreatment reduced the higher-molecular-weight fractions most effectively and did not reduce the <1 K fraction. Indeed, lime addition increased the concentration of organics that were less than 1 K. GAC completely removed the remaining organics in the 1 to 10K fraction and about 60% of the organics in the <1K material.

Trihalomethane (THM) precursors were associated mainly with the acidic and neutral fractions with a molecular weight <10K. The removal of THM precursors bore a strong correlation with the removal of TOC from the different fractions.

A fingerprint of low-molecular-weight, volatile organic compounds was made for each water sample tested following a technique developed by Suffet *et al.* [Environ. Sci. Technol. 12 (12), 1315 (1978)], but no distinctive fingerprints were obtained, probably because the extracts were not methylated. The results show little difference in character for waters receiving different pretreatments, and the analytical methods used were not capable of determining the actual character of the various samples.

Activated Carbon Column Performance Studies

Through the use of miniature carbon columns containing 3 to 7 mL of 50 x 80 mesh GAC (Westvaco WV-G), breakthrough curves were obtained for TOC, ultraviolet absorption (UVA), and THM precursors in 10 to 30 days. By operating four columns in parallel and comparing the column performance for different pretreatment conditions on the same water sample, the

*K = thousand

influence of pretreatment on carbon adsorption was identified. In some studies, the removal behavior of synthetic resins was compared to that of activated carbon for pretreated river water.

The removals of UVA, TOC, and THM precursors by activated carbon all followed the same trends. The relationship between these parameters varied somewhat with different levels of treatment, but each parameter showed the same trends in all the studies. Thus a pretreatment that was best for UVA removal was also the best for TOC and THM precursor removal. This result suggests that simple analysis of UVA removal might be used as an *indicator* of the relative removal of TOC and THM precursors once a detailed correlation is established.

The removal performance of activated carbon was strongly influenced by both solution pH and coagulant dose. Effective carbon adsorption capacity improved as the pH was reduced. At pH 5, the capacity was approximately three to four times greater than that at pH 8 if column operation was terminated at 1 mg/L effluent TOC. If no coagulation was provided, the carbon was unable to reduce the TOC of the raw river water to an acceptable level, and high TOC concentrations broke through immediately. When coagulation was employed as a pretreatment, however, the organic content of the river water was significantly reduced and the carbon columns were able to produce an effluent containing very low concentrations of TOC. In addition, carbon service life increased with increasing coagulant doses, because higher doses caused a greater reduction in the influent organic concentration. A simple cost analysis was conducted and used to illustrate the concept of an optimum pH value and coagulant dose for pretreating Mississippi River water before GAC treatment.

Lime softening improved the carbon adsorption capacity for organics removal from Mississippi River water. As with the coagulation studies, increased levels of organic removals in pretreatment lead to longer carbon service life. Carbon adsorption capacities increased with increasing lime dose during pretreatment, provided the pH was lowered for adsorption.

For Mississippi River water, lime softening was a much less effective pretreatment process for organics removal than coagulation. The data obtained indicate that lime softening with 130 mg/L of high calcium quicklime and 7 mg/L of alum (as practiced at the Minneapolis Water Treatment Plant) produced organics removals roughly com-

parable with those yielded by 20 mg/L of alum at pH 5. A coagulant dose of 80 mg/L of alum gave far superior removal performance and extended the useful life of the GAC columns.

Two weakly basic resins in the free base form were inferior to activated carbon for adsorption of TOC and THM precursors from coagulated river water. These studies were conducted at pH 7, however, and the resins' performance might be improved by operating at different pH values.

A column of strongly basic anion exchange resin (IRA 904 in the chloride form) was as effective as activated carbon for both TOC and THM precursor removal from coagulated river water samples. The resin was also regenerated effectively with sodium chloride, but further studies are needed to identify the best regeneration conditions.

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Leown Moore is the EPA Project Officer (see below).

The complete report, entitled "Optimizing Coagulation-Adsorption for Haloform and TOC Reduction," (Order No. PB 83-210 757; Cost: \$20.50, subject to change) will be available only from:

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