Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A FEASIBILITY STUDY OF USING HEMATITE TO REMOVE DISSOLVED ORGANIC CARBON IN WATER TREATMENT

P. Hagare[a]; R. Thiruvenkatachari[a]; H. H. Ngo[a]
[a] Environmental Engineering Group, Faculty of Engineering, University of Technology, Sydney, Australia

To cite this Article Hagare, P. , Thiruvenkatachari, R. and Ngo, H. H.(2001) 'A FEASIBILITY STUDY OF USING HEMATITE TO REMOVE DISSOLVED ORGANIC CARBON IN WATER TREATMENT', Separation Science and Technology, 36: 11, 2547 — 2559

To link to this Article: DOI: 10.1081/SS-100106109

URL: http://dx.doi.org/10.1081/SS-100106109

SEPARATION SCIENCE AND TECHNOLOGY, 36(11), 2547–2559 (2001)

A FEASIBILITY STUDY OF USING HEMATITE TO REMOVE DISSOLVED ORGANIC CARBON IN WATER TREATMENT

P. Hagare,* R. Thiruvenkatachari, and H. H. Ngo

Environmental Engineering Group, Faculty of Engineering,
University of Technology, Sydney, Australia

ABSTRACT

An experimental investigation of using hematite to remove natural organic substances from water was carried out. Hematite sols (iron oxide, α-Fe_2O_3) prepared in the laboratory were found to form flocs with natural organic substances. Jar tests revealed that when a 85 mg/L hematite concentration (as Fe) was used, natural organic substances in the form of fulvic acid (4 mg/L) were totally removed. Direct filtration experiments using hematite were effective in removing dissolved organic carbon (DOC) from water; however the large hematite-organic flocs clogged the filter and reduced the filter run.

A conventional filtration system, which included flocculation and sedimentation prior to filtration, was found to be very effective at removing total DOC from water. An 86 mg/L hematite concentration (as Fe) was found to effectively remove 4 mg/L of fulvic acid from Milli-Q water. A residual iron concentration in the final effluent from the filtration unit was well below the allowable

---

*Corresponding author. Fax: +61-2-95142633; E-mail: Prasanthi.Hagare@uts.edu.au

Australian drinking water guideline. Further research is warranted to optimize hematite concentration, pH, and ionic strength for application of this process in conventional water treatment plants.

Key Words: Dissolved organic carbon (DOC); Fulvic acid; Hematite; Coagulation; Sedimentation; Filtration

INTRODUCTION

Humic substances, the major organic component of soil and organic sediments, are widely distributed over the earth's surface and occur in almost all terrestrial and aquatic environments. Aquatic humic substances constitute 40 to 60% of dissolved organic carbon (DOC) and are the largest fraction of natural organic matter in water. Organic concentrations in Australian waters follow seasonal variations. In a 1987 study conducted by Hine and Bursell (1), the DOC varied from 1.6 mg/L to 20.2 mg/L. The recorded high values were associated with winter rainfall. Natural organic matter in water forms highly carcinogenic disinfection by-products (DBPs) when it combines with disinfectants such as chlorine in water treatment plants (2). Natural organic substances also contribute to taste and odor in water, increase the demand for coagulants and disinfectants, increase the potential to transport metals and hydrophobic organic chemicals, increase the potential of corrosion and bacterial growth in distribution systems, increase membrane fouling that limits equipment efficiency and lifetime, and interact with activated carbon, which reduces its pollution-removal capacity (3–5).

In a water treatment plant, the effectiveness of chemical coagulation for DBP-precursor removal strongly depends on the type and concentration of the natural organic material present in the raw water, the coagulant type, the coagulant dose, and the coagulation pH (5–10). Researchers have used different coagulants/flocculants, such as alum, ferric chloride, polyaluminum chloride, polymers, or even soda ash to remove organic and inorganic pollutants from water (11–13). Enhanced coagulation with alum and $FeCl_3$ removed most of the inorganic pollutants and some of the organic pollutants (5,14). Natural water consists of particles that may include clay, aluminum, iron oxides, hydroxides, and silica among other components. Studies conducted by several researchers showed that natural organic substances adsorb to some of these particles, thus changing their chemical characteristics (15,16). Due to this tendency, researchers have used iron oxide particles to model these particles to study the effect of natural organic substances on processes such as aggregation, coagulation, in-line flocculation-filtration, and filtration (17,18). Many researchers have found that iron oxide in its various forms is an effective coagulant. Fine magnetite particles, a form of iron oxide (commercially known as SIROFLOC), were found to effectively remove particles from both water and wastewater (19). Iron oxide, when used as a coating on sand, was found to remove significant concentrations of natural organic substances (32–53%) from water during slow sand filtration (20).

This paper presents the results of a feasibility study in which hematite particles, a form of iron oxide (α-Fe_2O_3), were used as coagulants in water treatment. Hematite, prepared in the laboratory, was found to attract natural organic substances. Because hematite is inexpensive, it can be used as either a coagulant or a coagulant aid in existing water treatment plants. In this paper, the details of experiments conducted to study the removal of natural organic substances from water using coagulation, sedimentation, filtration and in-line flocculation-filtration will be described, and the results obtained will be discussed in detail.

EXPERIMENTAL MATERIALS

Hematite (α-Fe_2O_3) particles prepared in the laboratory as a coagulant were used in this study. Hematite was prepared by a process developed and modified by Penners and Koopal (21). The procedure consists of forced hydrolysis of an homogenous ferric chloride solution. Hematite sols of 1.7 g/L (as Fe) were prepared, rinsed in potassium chloride solution, and stored in a suspension of 10^{-3} mol/L $HClO_3$ solution in a dark place.

Suwannee River fulvic acid extracted and distributed by the International Humic Substances Society at the Colorado School of Mines, Golden, Colorado, USA was used to simulate the natural organic fraction present in fresh waters. The concentration of fulvic acid in water samples was measured as DOC by a Dorhmann TOC (Phoenix 8000) analyzer. For this purpose, samples were passed through a 45-μm filter before they were tested for DOC.

EXPERIMENTAL METHOD

A systematic approach was adopted to test the feasibility of using hematite to remove fulvic acid from water. Initial jar test experiments were carried out to find the optimum operating conditions, such as hematite concentration, ionic strength, and pH. Using these conditions, in-line flocculation-filtration experiments were conducted to test the applicability of using hematite in direct filtration plants. This was followed by tests for the applicability of using hematite in a conventional treatment process in which the experimental setup consisted of a sedimentation tank and a filtration unit. The following section describes the experimental plan adopted.

Jar Test Experiments

A series of jar test experiments were conducted to optimize the chemical and operating conditions to remove 4 mg/L of fulvic acid from suspensions prepared in Milli-Q water. For these tests, suspensions were rapidly mixed with chemicals for 60 s at 100 rpm. This was followed by a slow mixing at 40 rpm for 30 min, and the suspensions were allowed to settle for 60 min (22). Hematite concentrations varying from 0 to 175 mg/L (as Fe) were used. Ionic strength of the suspensions throughout the study was maintained at 120 mmol/L of $CaCl_2$. This ionic strength value was determined by conducting a separate set of jar test experiments and simultaneously determining the zeta potential using a Zetasizer (Zeta 4000). For this feasibility study, the pH of the suspensions was maintained at 3 because hematite sols are stable at this pH. The performance of these tests was assessed in terms of turbidity and DOC.

Direct Filtration Experiments

Under the optimum conditions as obtained during jar tests, a series of inline flocculation-filtration experiments were conducted. The experimental setup consisted of a 200-mm filter column with a filter bed depth of 50 mm. The filter column diameter was 30 mm. Glass beads of 0.175 mm were used as filter grains. Suspensions prepared with Milli-Q water dosed with 4 mg/L of fulvic acid were corrected for ionic strength and allowed to pass through the filter at a constant filtration rate of 1.5 m/h. Hematite solution of concentrations varying from 0 to 172 mg/L (as Fe) were used as coagulants. The filter column was fitted with a manometer, which measured head loss development. Filtered samples were collected every 5 min for the first 30 min and then every 15 min thereafter until the end of the experiment. The filtrate quality was evaluated in terms of turbidity and DOC. Head loss was also recorded at every collection.

Conventional Filtration System

A series of experiments were conducted with a setup in which flocculation and sedimentation processes were included prior to filtration. An artificial organic suspension was prepared by dissolving 4 mg/L of fulvic acid in Milli-Q water at optimum pH and ionic strengths. A Perspex tank was used for flocculation and sedimentation processes. A predetermined concentration of hematite was added to the organic suspension and rapidly mixed at a velocity gradient (G) of 250 s^{-1} followed by slow mixing ($G_f t_f = 90{,}000$). This process involved the formation of hematite-organic flocs that were then allowed to settle for 1 h. The supernatant, which consisted of microflocs, was then pumped to a filtration unit where it was allowed to pass through a 5-cm filter bed at a filtration rate of 1.5 m/h. The performances of both sedimentation and filtration processes were monitored by turbidity and DOC removals. Head loss development was used as an additional performance indicator of the filtration process. The residual iron concentration was also monitored at various stages of this experiment.

RESULTS AND DISCUSSION

Hematite Jar Test Results

Jar test experiments revealed that hematite is effective in removing fulvic acid from water. Under optimum conditions of pH and ionic strength, hematite concentrations of 86 mg/L and above were effective in the complete removal of fulvic acid as measured by DOC. Hematite particles, owing to their submicron size of 50 nm, increased the initial turbidity of the suspension. The initial turbidity of suspension prepared with Milli-Q water and fulvic acid was less than 5 NTU (nephelometric turbidity units). As can be seen from Table 1, the turbidity of the suspension increased to more than 1100 NTU when the hematite concentration was increased to 172 mg/L. However, after rapid mixing and settling, the amount of hematite suspended was reduced, thus the turbidity levels were also reduced (Table 1). Fulvic acid molecules, being polymeric and negatively charged, bind to several particles of hematite, forming small and large dense flocs. This led to the destabilization of organic molecules, which resulted in the removal of DOC from the suspension (Fig. 1). This process of destabilization was enhanced due to the added $CaCl_2$. However, when the number of hematite particles exceeded the number of fulvic acid molecules, some hematite particles remained suspended. This led to residual turbidity in the settled suspension (Table 1).

Table 1. Effect of Hematite on Turbidity and DOC Removal

Hematite as Fe (mg/L)	Influent Turbidity (NTU)	Effluent Turbidity (NTU)	Influent DOC (mg/L)	Effluent DOC (mg/L)	DOC Removal %
43	320	42.1	0.2951	0.0318	89
86	629	59.4	0.2771	0	100
129	908	35.4	0.2803	0	100
172	1145	47.7	0.2795	0	100

pH = 3; fulvic acid concentration = 4 mg/L; $CaCl_2$ concentration = 120 mmol/L.

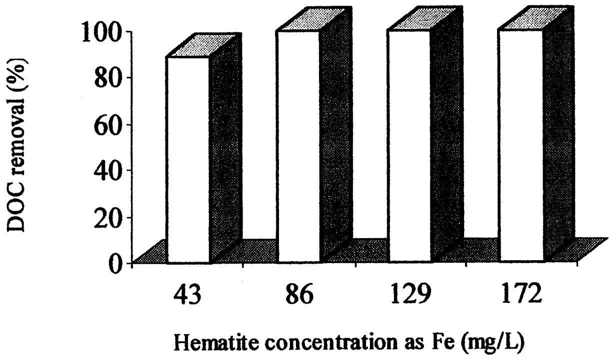

Figure 1. DOC removal at different hematite concentrations (pH = 3; ionic strength = 120 mmol/L of $CaCl_2$; fulvic acid concentration = 4 mg/L).

Direct Filtration Experiments

As the results obtained from the jar tests were encouraging, direct filtration studies were conducted to investigate the performance of hematite to remove DOC. The aim of these studies was also to reduce the residual turbidity in the effluent. A series of experiments were conducted using hematite concentra-

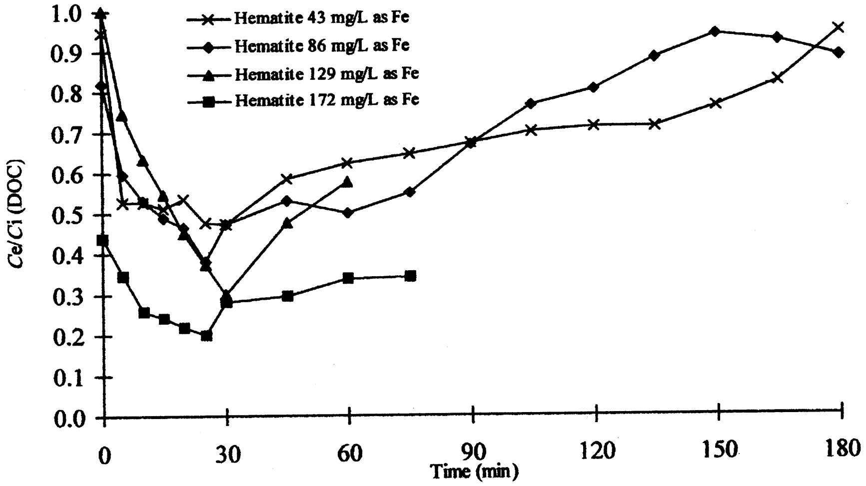

Figure 2. DOC removal in direct filtration with hematite (pH = 3; fulvic acid = 4 mg/L; filtration velocity = 1.5 m/h; filter media = glass beads; filter media size = 0.175 mm; filter column diameter = 30 mm; filter bed depth = 50 mm).

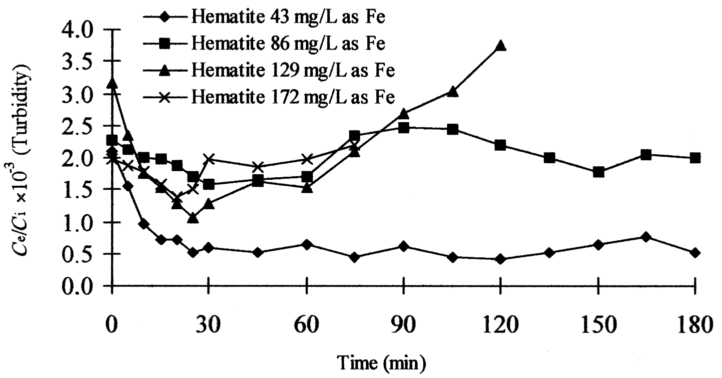

Figure 3. Turbidity removals in direct filtration with hematite (pH = 3; fulvic acid = 4 mg/L; filtration velocity = 1.5 m/h; filter media = glass beads; filter media size = 0.175 mm; filter diameter = 30 mm; filter bed depth = 50 mm).

tions (as Fe) varying from 43 mg/L to 172 mg/L. The performance of direct filtration was monitored in terms of DOC and turbidity removal as well as head loss development.

Figure 2 shows the variation of DOC removal in terms of C_e/C_i with filtration time. DOC removal increased with an increase in hematite concentration. However, in the experiment in which hematite concentrations were higher than 86 mg/L, the filter bed clogged rapidly. The filtration rate reduced within 80 min of filter run for a hematite concentration of 129 mg/L and within 60 min of filter run for a hematite concentration of 172 mg/L. During this series of experiments, a maximum DOC removal of 62% was achieved after 25 min of filter run with a hematite concentration of 86 mg/L (as Fe). As can be seen in Fig. 3, the turbidity removal was also very high at this concentration.

The flocs formed during these direct filtration experiments were very large (20–30 μm), and they clogged the filter bed, which was composed of 0.175-mm glass beads. Most of the clogging was observed forming a thin layer on the top of the filter bed. This clogging was reflected in head loss development that is shown in Fig. 4.

Conventional Filtration System

In direct filtration experiments, operational problems of filter bed clogging and high head- loss development were observed. To overcome these drawbacks, a conventional filtration system was used. The quality of filtrate in terms of DOC and turbidity was superior. Figures 5 and 6 show the performance of the overall

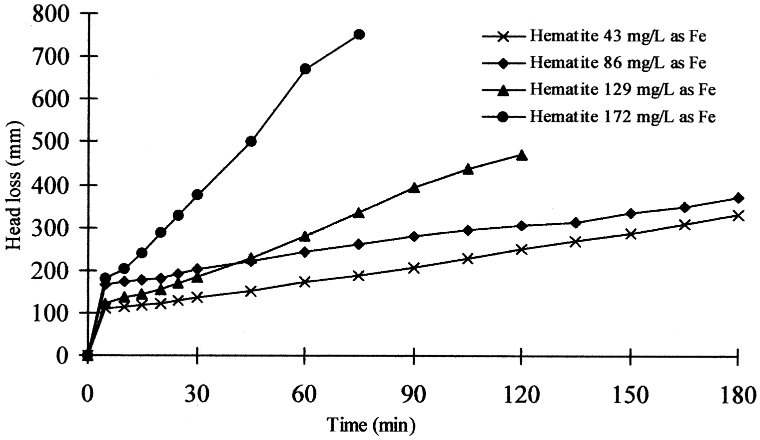

Figure 4. Head Loss in a direct filtration system with hematite (pH = 3; fulvic acid = 4 mg/L; filtration velocity = 1.5 m/h; filter media = glass beads; filter media size = 0.175 mm; filter diameter = 30 mm; filter bed depth = 50 mm).

system in terms of C_e/C_i of DOC and turbidity. Here the C_i is the concentration of DOC or turbidity in the influent to the system and C_e is the concentration in the filtrate. The figures show that the higher the hematite concentration, the higher is the removal of DOC and turbidity. For hematite concentrations of 86 and 129 mg/L (as Fe), the effluent DOC and turbidity values remained 0 mg/L and less

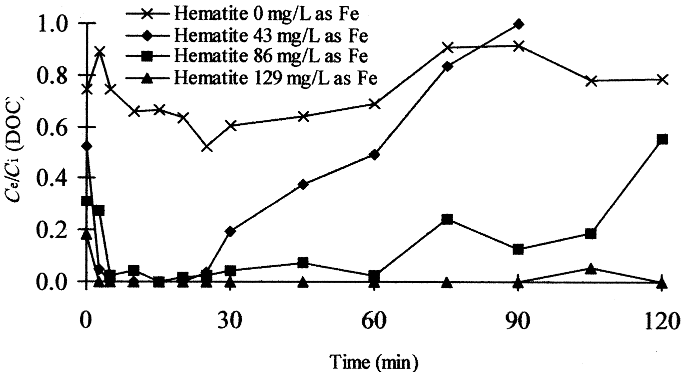

Figure 5. The performance of conventional filtration system with hematite in terms of DOC (pH = 3; fulvic acid = 4 mg/L; filtration velocity = 1.5 m/h; filter media = glass beads; filter media size = 0.175 mm; filter column diameter = 30 mm; filter bed depth = 50 mm).

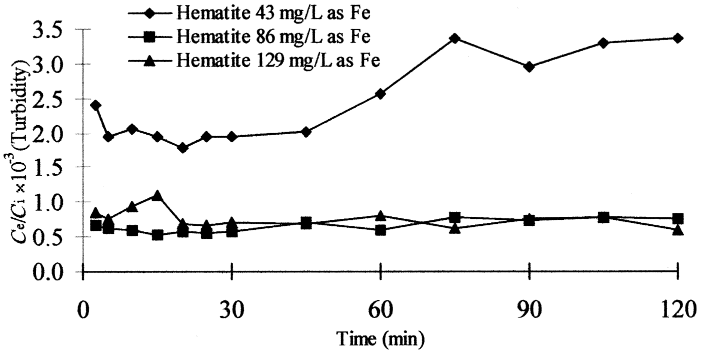

Figure 6. The performance of a conventional filtration system with hematite in terms of turbidity (pH = 3; fulvic acid = 4 mg/L; filtration velocity = 1.5 m/h; filter media = glass beads; filter media size = 0.175 mm; filter column diameter = 30 mm; filter bed depth = 50 mm).

than 1 NTU, respectively, for most of the filtration times. As can be observed from Fig. 7, the head loss development was minimal for all concentrations of hematite used.

In this conventional filtration system, the large and dense hematite-organic flocs that are formed were removed during the sedimentation process. Table 2

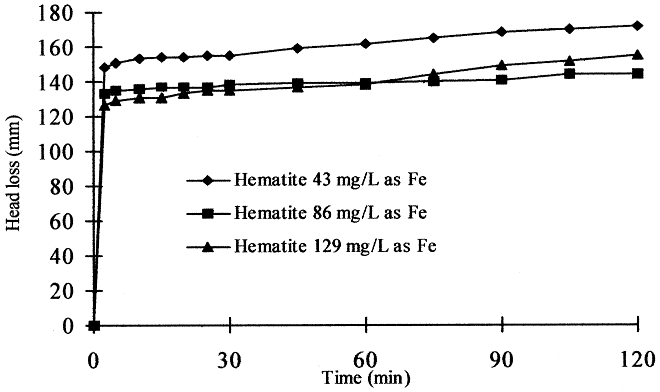

Figure 7. Head loss development in a conventional filtration system with hematite (pH = 3; fulvic acid = 4 mg/L; filtration velocity = 1.5 m/h; filter media = glass beads; filter media size = 0.175 mm; filter column diameter = 30 mm; filter bed depth = 50 mm).

Table 2. Turbidity at Different Hematite Concentrations in a Conventional Filtration System

	Flocculation-Sedimentation Stage		Filtration Stage
Hematite as Fe (mg/L)	Influent Turbidity (NTU)	Effluent Turbidity (NTU)	Effluent Turbidity at 60 min Filtration (NTU)
43	320	104.6	0.46
86	629	73.8	0.41
129	908	162.8	0.59

pH = 3; fulvic acid concentration = 4 mg/L; ionic strength = 120 mmol/L of $CaCl_2$; filtration velocity = 1.5 m/h; filter media = glass beads; filter media size = 0.175 mm; filter column diameter = 30 mm; filter bed depth = 50 mm.

gives the influent and effluent turbidity values for the flocculation-sedimentation process as well as the effluent turbidity values for filtration. Table 2 shows that the turbidity of effluent from the sedimentation processes dropped from 320–908 NTU to 105–163 NTU when hematite concentrations varied from 43 mg/L to 129 mg/L (as Fe), respectively. The remaining filterable flocs (15–30 μm) were then easily removed during filtration.

Table 3 gives the residual iron concentration at the end of the sedimentation process and in the effluent from the filtration unit measured at 60 min of filtration time. The final treated water had 0.168 mg/L of residual iron, which is well below the allowable Australian drinking water guideline value of 0.3 mg/L (23). The overall performance of the conventional filtration system was found to be remarkable.

Table 3. Residual Iron in a Conventional Filtration System

	Flocculation-Sedimentation	Filtration Stage
Hematite as Fe (mg/L)	Residual Iron (mg/L)	Effluent Residual Iron at 60 min (mg/L)
86	71	0.168

pH = 3; fulvic acid concentration = 4 mg/L; ionic strength = 120 mmol/L of $CaCl_2$;, filtration velocity = 1.5 m/h; filter media = glass beads; filter media size = 0.175 mm; filter column diameter = 30 mm; filter bed depth = 50 mm.

CONCLUSIONS

Better understanding of the nature and the reactive mechanisms of the humic substances, which are major constituents of natural organic matter (NOM), can help in selecting better treatment technologies for NOM removal. Even though various processes are currently adopted in NOM removal, a simple and a more cost-effective method is needed. This paper presents the results obtained from the experiments conducted to test the feasibility of using hematite (α-Fe_2O_3) to remove organic substances from water. Initial jar tests proved that under optimum conditions of pH 3 and ionic strength of 120 mmol of $CaCl_2$, hematite was found to be effective in complete removal of 4 mg/L of fulvic acid measured as DOC. Direct filtration experiments showed that, though a high removal of DOC (62%) can be expected through the use of hematite, this process may not be suitable due to short filter runs, which was caused by rapid clogging of the filter bed. Further experiments conducted using a conventional filtration system showed that hematite (86 mg/L or more as Fe) can be effective in complete removal of DOC from water. Though the turbidity of influent increased due to the addition of hematite particles, the performance of the conventional filtration system in terms of effluent quality and head loss development was superior to the direct filtration system. The filter run time was extended as the practical head loss development was minimal. The results also showed that a very small amount of iron residual was present in the final treated water (0.168 mg/L).

This feasibility study shows that hematite can be used to remove natural organic substances from water. The concentration of hematite can be reduced if it is used to aid other coagulants. Further research is required to assess the feasibility of hematite as a coagulant aid and to optimize the operating conditions, such as pH and ionic strength, for their applications to existing water treatment plants.

ACKNOWLEDGMENTS

The authors acknowledge the support received from Internal Research Grants from the University of Technology, Sydney, and from the Key Research Strength Project in Water and Waste Management.

REFERENCES

1. Hine, P.T.; Bursell, D.B. *Seasonal Trends of Natural Organics in South Australian Waters and Their Effects on Water Treatment*; AWRC Research Report, Department of Resources and Energy, SA, 1987.

2. Rook, J.J. Formation of Haloforms During Chlorination of Natural Water. Water Treat. Exam. **1974,** *23,* 234.
3. Jacangelo, J.G.; DeMarco, J.; Owen, D.M.; Randtke, S.J. Selected Processes for Removing NOM: An Overview. J. AWWA **1995,** *87* (1), 64–76.
4. Drikas, M. NOM the Curse of the Water Industry. Water **1997,** *24* (5), 29–32.
5. Vrijenhock, E.M.; Childress, A.E.; Elimelech, M.; Tanaka, T.S.; Beauhler, M.D. Removing Particles and THM Precursors by Enhanced Coagulation. J. AWWA **1998,** *90* (4), 139–150.
6. Kavanaugh, M.C. Modified Coagulation for Improved Removal of Trihalomethane Precursors. J. AWWA **1978,** *70* (11), 613–620.
7. Chadik, P.A.; Amy, G.L. Coagulation and Adsorption of Aquatic Organic Matter and Humic Substances: An Analysis of Surrogate Parameters for Predicting Effects on Trihalomethane Formation Potential. Environ. Tech. Letters **1987,** *8,* 261.
8. Semmens, M.J.; Field, T.K. Coagulation: Experiences in Organic Removal. J. AWWA **1980,** *72* (8), 476.
9. Najm, I.N.; Patania, N.L.; Jacangelo, J.G.; Krasner, S.W. Evaluating Surrogates for Disinfection By-products. J. AWWA **1994,** *86* (6), 98–106.
10. Crozes, G.; White, P.; Marshall, M. Enhanced Coagulation: Its Effect on NOM Removal and Chemical Costs. J. AWWA **1995,** *87* (1), 78–89.
11. Amirharajah, A.; Dennett, K.E.; Studstill, A. Ferric Chloride Coagulation for Removal of Dissolved Organic Matter and Trihalomethane Precursors. Wat. Sci. Tech. **1993,** *27* (11), 113–121.
12. Lind, C. Reducing Total and Dissolved Organic Carbon: Comparing Coagulants. Environmental Technology **1996,** *6* (3), 54–58.
13. Edward, M. Predicting DOC Removal During Enhanced Coagulation. J. AWWA **1997,** *89* (5), 78–89.
14. Randtke, S.J. Organic Contaminant Removal by Coagulation and Related Process Combinations. J. AWWA **1988,** *80* (5), 40.
15. Stumm, W.; Morgan, J.J. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Water*, 2nd ed.; Wiley-Interscience Publications: New York, 1981.
16. Tiller, C.L.; O'Melia, C.R. *Natural Organic Matter and Colloidal Stability: Models and Measurements*, Research Report 1292 ENV 7; The Johns Hopkins University: Baltimore, Md, 1993.
17. Waite, D.; Amal, R.; Ngo, H.H.; Vigneswaran, S. Effect of Adsorbed Organic Matter on Size, Structure and Filterability. Wat. Sci. Tech. **1993,** *27* (1), 171–178.
18. Prasanthi, H.; Vigneswaran, S.; Waite, D.; Ben Aim, R. Filtration of Submicron Particles: Effect of Ionic Strength and Organic Substances. Wat. Sci. Tech. **1994,** *30* (9), 149–158.

19. Storm, A.G. Aspects of Water and Sewage Treatment in Australia. J. Inst. Wat. Eng. Sci. **1984,** *38* (6), 493–510.
20. McMeen, C.R.; Benjamin, M.M. NOM Removal by Slow Sand Filtration Through Iron Oxide-Coated Olivine. J. AWWA **1997,** *89* (2), 57–71.
21. Penners, N.H.G.; Koopal, L.K. Preparation and Optical Properties of Homodisperse Haematite Hydrosols. Colloids Surfaces **1986,** *19,* 337–349.
22. *Standard Methods for the Examination of Water and Waste Water,* 17th Ed.; APHA, AWWA, WEF: Washington, DC, 1989.
23. NHMRC/ARMCANZ. Australian Drinking Water Guidelines. August 1996.

Received December 1999
Revised November 2000

Downloaded At: 10:45 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS100106109