Back to pre-disinfection of highly polluted waters

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Abstract The initial pre-disinfection was one of the stages that most contributed to the formation of a large number of halogenated disinfection by-products (DBPs). The threat and awareness to the formation of chlorine disinfection by-products, refrained from using pre-disinfection with chlorine in the treatment of contaminated raw waters, to be used as drinking water. The main purpose of this research was to study whether chlorine dioxide can be used for pre-disinfection in the treatment of highly polluted wastewaters and surface waters. Chlorine dioxide was found suitable, as a replacement for chlorine, for disinfection of water containing natural organic substances, effluents' organic materials and ammonium ions, due to its advantages, and especially because it is an effective disinfectant for killing pathogenic microorganisms and destroying viruses. Chlorine dioxide does not form THMs and barely creates chloroorganic compounds. However, the main disadvantage of the chlorine dioxide is the creation of undesirable chlorite and chlorate ions, which are suspected of being toxic. This research showed that the undesirable chlorite ions can be removed completely by adding Fe^{+2}, which reduces ClO_2^- to the harmless Cl^-, and is oxidized to Fe^{+3}, to form the ferric polyhydroxo complexes, that can be used as the flocculant, in the next flocculation step, for the achievement of safer drinking water.

Keywords Chloride dioxide; chlorite ions; DBPs; ferrous ions; flocculation; pre-disinfection

Introduction

In the past pre-chlorination was used in the conventional treatment of contaminated raw waters in order to decrease the microbial pollution load in the following treatment facilities, which led to the formation of a large number of halogenated disinfection by-products (DBPs). During recent decades, chlorine has been the most generally accepted disinfectant and its wide use has dramatically improved the health of people throughout the world. Rook (1974) found that the interaction of chlorine with natural organic materials, such as humic substances, produced disinfection by-products, among which are the trihalomethanes (THMs), presumed to be carcinogenic. In addition to the THMs, other chloroorganic compounds, such as haloacetic acids (HAAs), haloacetonitriles, haloketones, and haloaldehydes were identified, and suspected of being hazardous to public health (Symons *et al*., 1975; Lykins *et al*., 1994; Heller-Grossman *et al*., 1999). The chloroorganics pollute the environment. They are not easily biodegradable, persist, and accumulate in aquatic and soil systems. There is also a danger of their possible penetration and accumulation in aquifers, resulting from the reuse of chlorinated wastewaters for irrigation and groundwater recharge. This problem triggered the search for an alternative disinfectant such as ozone, UV radiation or chlorine dioxide.

Chlorine dioxide as a disinfectant

For several years the Narkis group studied the use of chlorine dioxide in the disinfection of wastewaters (Narkis, 1998; Narkis and Kott, 1992; Narkis *et al*., 1988, 1990, 1992, 1995, 1998; Katz *et al*., 1994; Katz and Narkis, 2001). The chlorine dioxide was found to be suitable, as a replacement to chlorine, for the purpose of disinfection of water containing natural organic substances, effluents' organic materials and ammonium ions, due to its advantages, and especially because it is an effective disinfectant for killing pathogenic

microorganisms and destroying viruses. The ClO_2 is a powerful and active disinfectant at a wide range of pH values. Chlorine dioxide does not form THMs. It is a strong oxidizing agent, which oxidizes the organic compounds and barely creates chloroorganic compounds (Weinberg and Narkis, 1992). It does not react with the ammonium ions and organic amines. Chlorine dioxide is cheaper than ozone, but more expensive than chlorine. It has a stable residue that can be measured for control purposes.

Chlorite ion toxicity

In spite of the advantages, there is a serious problem when using chlorine dioxide. During the treatment of water and wastewater, part of the chlorine dioxide is reduced to undesired chlorite and chlorate ions, which are suspected of being toxic and creating health hazards (Werdehoff and Singer, 1987; Gordon *et al.*, 1990). Chlorite ion caused hemolytic anemia when fed in very high concentration (500 mg/L), to rats and mice via drinking water (Gates, 1991; Gates and Harrington, 1992, 1995). Similar to other oxidants, it can damage the membranes during dialysis and, as a result, chlorite ions will reach the blood cells and cause hemolysis. When there is a deficiency, due to an hereditary disturbance of the G-6PD enzyme (Glucose-6-phosphate dehydrogenaze), the body's defensive mechanism malfunctions and does not prevent interaction between oxidant agents and sensitive biological macromolecules. Therefore, a state of G-6PD deficiency causes hemolysis and the destruction of the red blood cells. The degree of toxicity of chlorite and chlorate ions is not yet completely proved and is still under investigation. The EPA's concern regarding residual chlorine dioxide, chlorite and chlorate ions has led to limiting their concentrations in drinking water by regulation. The US EPA (Fed. Reg., 1994) proposed the limiting maximum concentration of residual chlorine dioxide to 0.8 mg/L, on the basis of daily sampling, and a maximum concentration of residual chlorite ions of 1.0 mg/L, on a basis of monthly average. The implementation of this proposal commenced in June 1998.

In considering the advantages of using chlorine dioxide as a disinfectant it is desirable to find ways of reducing the unwanted by-products of chlorine dioxide. Elimination of these reaction by-products could greatly enhance the potential for chlorine dioxide usage in drinking water and effluents treatment, and lower the limitations imposed by the regulations.

Pre-disinfection

In the past, pre-chlorination was used in the conventional treatment of contaminated raw waters in order to decrease the microbial pollution load in the following treatment facilities. The initial pre-disinfection was one of the stages that most contributed to the formation of a large number of halogenated disinfection by-products, DBPs. The threat and awareness of the formation of chlorine disinfection by-products, refrained from using pre-disinfection with chlorine in treatment of contaminated raw waters, to be used as drinking water. As a result of the recognition of THMs and other chlorine disinfection by-product formation threats in many water treatment plants, the pre-disinfection was avoided.

The main purpose of this research was to study and evaluate whether chlorine dioxide could be used for pre-disinfection in treatment of highly polluted wastewaters and surface waters, containing natural organics, such as humic and fulvic acids, turbidity caused by colloidal and suspended solids, pathogenic microorganisms and viruses.

Experimental

Analytical procedures

The concentration of chlorine dioxide, chlorite and chlorate ions, stock solutions were determined by the amperometric titration method as described by Aieta and Roberts

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(1981). The concentrations of ClO_2^- and ClO_3^- ions in the working solutions, and in the solutions after the reaction with the ferrous ions, were analyzed by using an ion chromatograph. The ion chromatograph DIONEX AL 450 is equipped with AS9 column for anions, especially developed for ClO_2^- and ClO_3^- ion determination. The eluent solution is a mixture of Na_2CO_3 1.8 mmole/L and $NaHCO_3$ 1.7 mmole/L. Initial and final concentrations of ferrous and ferric ions, as well as the COD and $PO_4^{\equiv}$ concentrations, were determined colorimetrically by the phenanthroline method, as described in the Standard Methods for the Examination of Water and Wastewater (1995).

Methods

Two sets of experiments were carried out to study the redox reactions of ferrous ions with ClO_2^- and ClO_3^- and the flocculation process in the presence and in the absence of atmospheric oxygen. The experiments were carried out in especially developed reactors, in order to drive off the oxygen and keep it as a closed system, as described by Katz and Narkis (2001).

The flocculation tests were carried out in a jar test system, manufactured by Phipps and Bird, Richmond VA, USA. The flocculation tests in the absence of oxygen were carried out in specially designed clogged beakers. The cover had three openings: the central opening was used for the stirrer; the second opening for purging nitrogen; and the third opening was used for introducing the chemicals such as the flocculants, ClO_2 and acid or base for pH corrections.
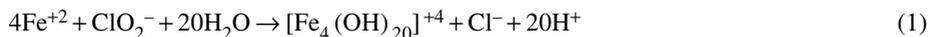
The flocculation of 25 mg/L Ca-Montmorillonite mineral clay suspensions was carried out at a constant pH values in the following conditions: 5 minutes of rapid mixing at 100 rpms, followed by 25 minutes of slow mixing at 25 rpms, and 30 minutes of settling. The samples were taken from 4 cm below the water surface to determine the residual apparent and true turbidities, true color, ClO_2, ClO_2^-, ClO_3^-, Fe^{+2} and Fe^{+3}, total and soluble COD and phosphate concentrations. Spectrophotometer Spectronic 601, manufactured by Milton Roy, was used for optical densities determination; for the turbidity at $\lambda = 405$ nm, and for true color at $\lambda = 254$ nm in a quartz cell.

Results and discussion

The chlorine dioxide was found to be suitable as a replacement to chlorine, for the purpose of disinfection of water containing natural organic substances, effluents' organic materials and ammonium ions, due to its advantages, and especially because it is an effective disinfectant for killing pathogenic microorganisms and destroying viruses (Narkis *et al*., 1988, 1990, 1995a,b; Narkis and Kott, 1992). However, the main disadvantage of the chlorine dioxide is the creation of the undesirable chlorite ClO_2^- and chlorate ClO_3^- ions. Narkis *et al*. (1988, 1990, 1998) showed that the higher the organic load in the contaminated waters, the more ClO_2^- ions are formed as DBPs; or vice versa, the better the treated water quality, the less ClO_2^- ions are formed (Narkis, 1998).

Aieta and Roberts (1986) proposed the use of ferrous ions as a means for chlorite ion removal from water treated with chlorine dioxide. Griese *et al*. (1991, 1992) and Iatrou and Knocke (1992) reported on efficient reduction of residual chlorite ions and chlorine dioxide to chloride ions by ferrous ions, while the concentration of the chlorate ions was almost unaffected. Traquin *et al*. (1995) reported on the effective elimination of excess chlorite ions by using ferrous chloride in El Paso full-scale water treatment plants.

This research showed that the undesirable chlorite ions can be removed completely by adding ferrous ions Fe^{+2}, as shown in Eq. (1).

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$$4Fe^{+2} + ClO_2^- + 20H_2O \rightarrow [Fe_4(OH)_{20}]^{+4} + Cl^- + 20H^+ \qquad (1)$$

At the redox reaction, Fe^{+2} reduces ClO_2^- to the harmless Cl^- ions, and is oxidized to Fe^{+3}, which reacts with water to form the ferric polyhydroxo complexes that can be used as the flocculant, in the next flocculation step, in the sequence of the conventional water treatment, for removal of colloidal and suspended solids, organic materials and color. Ferrous ions efficiently lowered chlorite ion concentration by reducing them to chlorides and a very small part by oxidizing them to chlorate ions (Katz, 1999; Katz and Narkis, 2001). The chlorite ion concentration decreases as the ferrous ions dose increased until they were entirely removed. For example, Figure 1 shows that when an aqueous solution of a mixture with an initial concentration of 3.03 mg/L ClO_2^- and 4.90 mg/L ClO_3^- was exposed to a dose of 12.08 mg/L Fe^{+2} and above, chlorite ions were completely removed, with a zero mg/L residual. At the same time the Fe^{+2} was consumed and was oxidized to Fe^{+3}.

The stoichiometry and kinetics of the reaction between the chlorite ions and Fe^{+2} were studied in the presence and absence of oxygen (Katz and Narkis, 2001). The theoretical ratio, calculated from Eq. (1), of 3.31 mg Fe^{++} required for complete reduction of 1.0 mg ClO_2^-, matched the experimental results. The kinetics experiments showed that the reaction rate was very fast. At initial pH values from 5.1–7.9, all the chlorite ions were removed within 30 seconds and the consumed ferrous ions were oxidized to ferric ions. In all pH values, the rate of Fe^{+2} oxidation by chlorite ions was much faster than the oxidation by the atmospheric oxygen, which required at least 15 minutes. Hence, the atmospheric oxygen does not compete with the chlorite ions for ferrous ion oxidation. Only after the complete removal of the chlorite ions, the atmospheric oxygen oxidizes the ferrous ions residuals to ferric ions, which further act as a flocculant. The following figures summarize the flocculation curves of M-20 Montmorillonite mineral clay suspensions, in concentration of 25 mg/L clay, by using Fe^{+2} ions alone (Figure 2), and Fe^{+3} alone (Figure 3). All the flocculation tests were carried out in nitrogen atmosphere, in the absence of oxygen. The flocculation curves show the effect of various doses of flocculants on optical densities of the apparent and true turbidities and color. Ferrous ions are not effective at all as a flocculant (as shown in Figure 2); while ferric ions are very effective flocculant (as shown in Figure 3) with a good clarification at doses range between 2.3–4.7 mgL. The minimum dose, 2.3 mg/L, that gave good clarification is called the optimal flocculant dose. Figures 3 to 5 show the effect of Fe^{+2} addition to the same M-20 montmorillonite mineral clay suspension into which 1.0 mg/L chlorine dioxide and 0.36 mg/L chlorite ions were added at pH 7.9. Figure
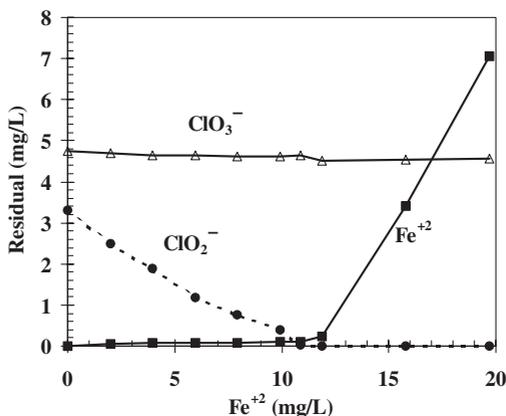

Figure 1 Effect of various doses of ferrous ions on the removal of chlorite and chlorate ions from an aqueous solution, containing a constant initial concentration of chlorite and chlorate ions, in an atmospheric open system
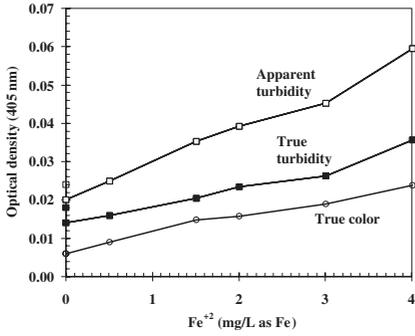
Figure 2 Flocculation of M-20 Montmorillonite mineral clay suspension by Fe^{+2} in the absence of oxygen
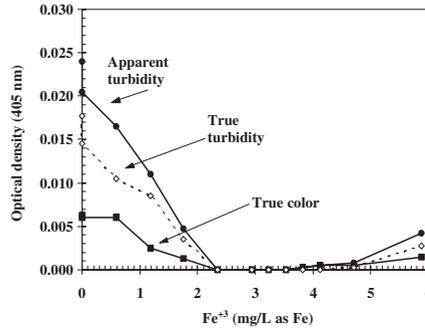

Figure 3 Flocculation of M-20 Montmorillonite mineral clay suspension by Fe^{+3} in the absence of oxygen. Initial pH = 7.5

4 shows that the Fe^{+2} reduced chlorite ions concentration up to zero, i.e. complete removal, at a dose of 2.15 mg/L Fe^{+2}. Chlorine dioxide was less affected by Fe^{+2}, leaving a desirable residual of 0.4 mg/L as ClO_2, even at a dose of 4.0 mg/L Fe^{+2}. As a result of the redox reaction, the ferrous ions concentration decreased, and the generated Fe^{+3} ions concentration increased.

Figure 5 shows the effect of addition of various doses of Fe^{+2} to this mineral clay suspension, which contained ClO_2 and ClO_2^- ions, on residual Fe^{+2}, generated Fe^{+3} ions and total iron concentration. The generated Fe^{+3} ions hydrolyzed to ferric polyhydroxo complexes, which served as an effective flocculant, for efficient removal of turbidity and good clarification, as shown in Figure 6, which gives the flocculation curves in this experiment.

Similar behavior was obtained in the study of chlorite ions removal from the same M-20 Montmorillonite mineral clay suspension, in the presence of 10 mg/L humic acids, into which 3.13 mg/L chlorine dioxide and 1.32 mg/L chlorite ions, were added, at initial pH = 6.2. Figures 7 to 9 summarize the effect of Fe^{+2} addition on removal of chlorite ions and chlorine dioxide, as shown in Figure 7, on residual Fe^{+2} and Fe^{+3} concentration, as shown in Figure 8, and the flocculation curves by the generated Fe^{+3} ions acting as an effective flocculant, in the mineral clay suspension in the presence of 10 mg/L humic acids, as shown in Figure 9.
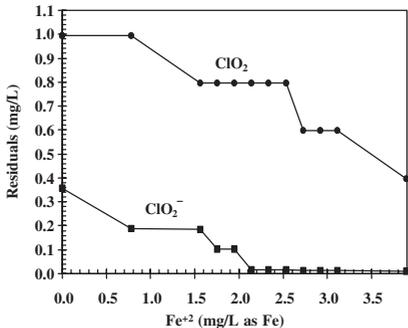

Figure 4 Effect of flocculation of M-20 Montmorillonite mineral clay suspension by Fe^{+2}, in the presence of 1.0 mg/L chlorine dioxide and 0.36 mg/L chlorite ion, at initial pH = 7.9, in nitrogen atmospheric condition, on the residual concentrations of chlorine dioxide and chlorite ion
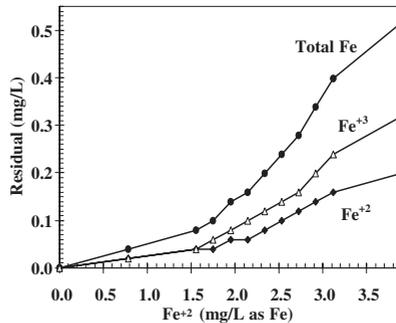

Figure 5 Effect of flocculation of M-20 suspension by Fe^{+2}, in the presence of 1.0 mg/L chlorine dioxide and 0.36 mg/L chlorite ion, at initial pH = 7.9, in nitrogen atmospheric condition, on the residual concentrations of ferrous ions, ferric ions, and total iron
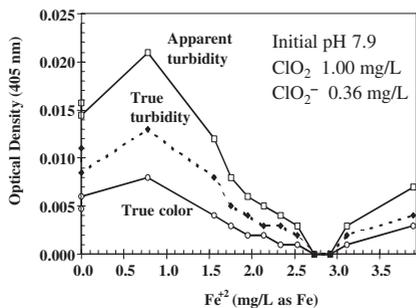
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Figure 6 Effect of Fe^{+2} on flocculation of M-20 Montmorillonite mineral clay suspension in the presence of 1.0 mg/L chlorine dioxide and 0.36 mg/L chlorite ion, at initial pH = 7.9, in nitrogen atmospheric condition
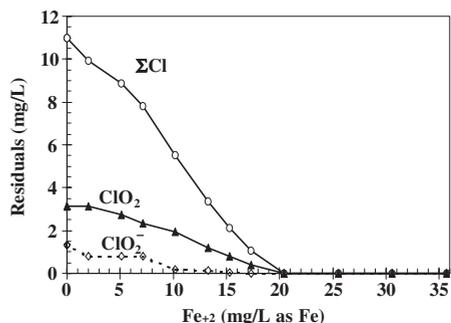

Figure 7 Effect of flocculation of M-20 Montmorillonite mineral clay suspension by Fe^{+2}, in the presence of 10 mg/L humic acids, 3.13 mg/L chlorine dioxide and 1.3 mg/L chlorite ion, at initial pH = 6.2, in nitrogen atmospheric condition, on the residual concentrations chlorine dioxide, chlorite ion and ΣCl
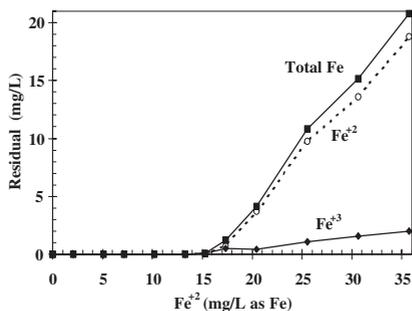

Figure 8 Effect of flocculation of M-20 Montmorillonite mineral clay suspension by Fe^{+2}, in the presence of 10.0 mg/L humic acids, 3.13 mg/L chlorine dioxide and 1.32 mg/L chlorite ion, at initial pH = 6.2, in nitrogen atmospheric condition, on the residual concentrations of ferrous ions, ferric ions, and total iron
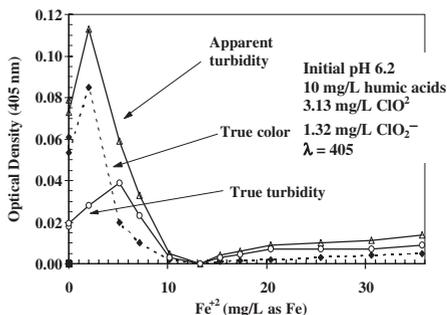

Figure 9 Effect of flocculation of M-20 Montmorillonite mineral clay suspension by Fe^{+2}, in the presence of 10.0 mg/L humic acids, 3.13 mg/L chlorine dioxide and 1.32 mg/L chlorite ion, at initial pH = 6.2, in nitrogen atmospheric condition, on the apparent and true turbidities and color, measured as optical density (O.D.) at $\lambda = 405$ nm, 1 cm cell

The concentration of the ferric ions, generated from the reduction of the chlorite ions or the chlorine dioxide, by the ferrous ions, depends on the Fe^{+2} dose, on the ClO_2 and ClO_2^- concentrations, and on the quality of the water or the effluents. The generated ferric ions hydrolyze to ferric poly-hydroxo complexes, which can serve as an effective flocculant, for efficient removal of the turbidity and the natural color. It was proved that the ferrous ions remove the chlorite ions and the chlorine dioxide effectively from the Ca-montmorillonite clay minerals suspensions, in the presence and absence of organic material as humic acids, and oxidized to ferric ions, which act as a flocculant.

Although ferrous ions by themselves are not suitable to serve as a flocculant, and in their presence, there is an increase in the color and turbidity level, as shown in the increased optical density in Figure 2, the ferric ions, generated by the redox reaction with ClO_2^- and ClO_3^-, and their hydrolysis products can serve as an effective flocculant for removal of the turbidity and natural color.

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Effluents

In the case of the Haifa Municipal Sewage Treatment Plant effluents, 9 mg/L ClO_2 were required for disinfection. It was proved that Fe^{+2} effectively removed the ClO_2^- formed and residual ClO_2, from the pre-disinfection stage, and was oxidized to ferric ions, although the amount of Fe^{+3} produced was insufficient. It was in the underdose range of the flocculation curve by ferric ions alone. Therefore, in the case of effluents' disinfection, followed by Fe^{+2} treatment for removal of ClO_2^-, an additional dose of flocculant was needed in order to complete the flocculant demand for effective flocculation and clarification. Thus, a significant part of the flocculant dose requirement is spared by the ferric ions generated from the reaction of Fe^{+2} for the removal of ClO_2^-, formed in the pre-disinfection of highly contaminated waters.

Conclusions

The results of this work show that pre-disinfection by ClO_2, of highly polluted waters is feasible. The DBPs, mainly chlorite ions, can be removed and reduced to harmless chloride ions by ferrous ions, which oxidize to Fe^{+3}, that further serve as an effective flocculant, for the achievement of a better quality and safer waters.

Acknowledgements

References

Aieta, E.M. and Roberts, P.V. (1981). Chlorine dioxide chemistry: generation and residual analysis. In: *Chemistry in Water Re-Use*, W.J. Cooper (ed.), Vol. 1, Ann-Arbor Science, Ann Arbor, Michigan, USA.

Aieta, E.M. and Roberts, P.V. (1986). A review of chlorine dioxide in drinking water treatment. *J. AWWA*, **78**(6), 62–72.

Armenter, J., Cristia, J. and Matia, L. (1998). Pretreatment options for water with high disinfection by-products formation potential. *J. Water Supply*, **16**, 543–550.

Dixon, K.L. and Lee, R.G. (1991). The effect of sulfur-based reducing agents and GAC filtration on chlorine dioxide by-products. *J. AWWA*, **83**(5), 48–55.

Fed. Reg. (1994). Disinfectants/disinfection By-products. *Proposed Rule. Fed. Reg.*, 59:145:38668, July 29, 1994.

Gates, D. (1991). *Chlorine Dioxide in Drinking Water: Practical Applications versus Potential Health Effects*. Report Rio Linda Chemical Co., Sacramento, CA, USA.

Gates, D. and Harrington, R.M. (1992). Drinking water disinfection practices: chlorine dioxide for the nineties. Presented at the 5th National Conference on Drinking Water: *Disinfection Dilemma: Microbiological Control Versus By-products*, 13–15 September, Manitoba, Canada.

Gates, D. and Harrington, R.M. (1995). Neuro-reproductive toxicity issues concerning chlorine dioxide and the chlorite ion in public drinking water supplies. *Amer. Water Works Assoc. Water Quality Technical Conference*, New Orleans, LA, 813–830.

Gordon, G., Slootmaekers, B., Tachiyashiki, S. and Wood, D.W. (1990). Minimizing chlorite ion and chlorate ion in water treated with chlorine dioxide. *J. AWWA*, **82**(4), 160–165.

Griese, M.H., Hauser, K., Berkemeier, M. and Gordon, G. (1991). Using reducing agents to eliminate chlorine dioxide and chlorite ion residuals in drinking water. *J. AWWA*, **83**(5), 56–61.

Griese, M.H., Kaczur, J.J. and Gordon, G. (1992). Combining methods for the reduction of oxychlorine residuals in drinking water. *J. AWWA*, **84**(11), 69–77.

Heller-Grossman, L., Idin, A., Limoni-Relis, B. and Rebhun, M. (1999). Formation of cyanogen bromide and other volatile DBPs in the disinfection of bromide-rich lake water. *J. Environ. Sci. Technol.*, **33**, 932–937.

Iatrou, A. and Knocke, W.R. (1992). Removing chlorite by the addition of ferrous iron. *J. AWWA*, **84**(11), 63–68.

Katz, A. (1999). *Removal of Chlorine Dioxide Disinfection By-products*. D.Sc. thesis, Department of

Environmental and Water Resources Engineering, Technion–Israel Institute of Technology, Haifa, Israel.

Katz, A. and Narkis, N. (2001). Removal of chlorine dioxide disinfection by-products by ferrous salts. *Wat. Res.*, **35**(1), 101–108.

Katz, A., Narkis, N., Orshansky, F., Friedland, E. and Kott, Y. (1994). Disinfection of effluent by combinations of equal doses of chlorine dioxide and chlorine added simultaneously over varying contact times. *Wat. Res.*, **28**(10), 2133–2138.

Lykins, B., Koffskey, W. and Patterson, K. (1994). Alternative disinfectants for drinking water treatment. *J. Environ. Eng.*, **120**, 745–758.

Narkis, N. (1998). *Chlorine Dioxide at Each Step of Advanced Physico-Chemical Treatment of Effluents*. Chemical Oxidation Technology for the Nineties. 8th Chemical Oxidation Symposium. Nashville, Tennessee, USA., April 1–3.

Narkis, N. and Kott, Y. (1992). Comparison between chlorine dioxide and chlorine for use as a disinfectant of wastewater effluents. *Wat. Sci. Tech.*, **26**(7–8), 1483–1492.

Narkis, N., Offer, R. and Betzer, N. (1988). The use of chlorine dioxide in disinfection of advanced treated effluents. In: *Proceedings of the 19th Annual Conference of the Israel Society for Ecology and Environmental Quality Sciences*, June, Tel-Aviv, Israel.

Narkis, N., Offer, R., Linenberg, E. and Betzer, N. (1990). The use of chlorine dioxide in disinfection of wastewater. In: *Water Chlorination–Chemistry, Environmental Impact and Health Effects*, R.E. Jolley (ed.), Vol. 6, Lewis Publ. Inc., Chelsa, Michigan, USA, 955–966.

Narkis, N., Armon, R., Offer, R., Orshansky, F., Friedland, E. and Kott, Y. (1995a). Effect of suspended solids on chlorine dioxide disinfection efficiency. *Wat. Res.*, **29**(1), 227–236.

Narkis, N., Katz, A., Orshansky, F., Kott, Y. and Friedland, E. (1995b). Disinfection of effluents by combinations of chlorine dioxide and chlorine. *Wat. Sci. Tech.*, **31**(5–6), 105–114.

Pomes, M.L. *et al*. (1999). DBP formation potential of aquatic humic substances. *J. AWWA*, **91**, 103–115.

Rook, J.J. (1974). Formation of haloforms during chlorination of natural waters. *J. Water Treatment Exam.*, **23**, 234–243.

Standard Methods for the Examination of Water and Wastewater (1995). 19th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

Symons, J.M. *et al*. (1975). National organic reconnaissance survey for halogenated organics. *J. AWWA*, **67**, 634–647.

Traquin, A., Hansel, G. and Rittman, D. (1995). Reduction of chlorite concentrations in potable water with ferrous chloride. *Water Engineering and Management*, February, 35–37.

Venosa, A.D. and Isaac, R.A. (1988). Disinfection. *J. Wat. Pollut. Contrl. Fed.*, **60**, 845–852.

Weinberg, H. and Narkis, N. (1992). Oxidation by-products resulting from the interaction of chlorine dioxide with nonionic surfactants. *Chemical Oxidation. Technology for the Nineties, Proceedings of the Second International Symposium*, 19–21 February, Vanderbilt University, Nashville, Tennessee.

Werdehoff, K.S. and Singer, P.C. (1987). Chlorine dioxide effects on THMFP, TOXFP, and the formation of inorganic by-products. *J. AWWA*, **79**(9), 107–113.