

Summary: Microorganisms like Giardia and Cryptosporidium have captured media attention lately, bringing new focus on the water treatment industry and its abilities to prevent outbreaks of these diseases. However, they are not the only potentially dangerous microbes out there, handicapping many water treatment methods don't have what it takes to destroy them in all cases. A herbicidal water treatment method developed by Auburn University may offer one solution.

Disinfections of Water by N-Hal amine Biocide Polymers

By S.D. Worley, Ph.D., and J.F. Williams, Ph.D.

The resurgence of infectious diseases in the United States and internationally has created an unprecedented level of awareness of the hazards of bacteria and viral microbes.

Although this newfound awareness of infectious disease is being fomented by media attention, its root causes are real enough. These diseases derive from the declining effectiveness of antibiotics; the appearance and rapid spread of entirely new pathogens, such as HIV and Hantaviruses; the Legionnaires' disease bacillus; and other contributing factors such as the speed and scale of international travel, which enables intercontinental transport of pathogens in hours. All of these developments have created an enormous increase in the demand for environmental control of microbes, especially in potable water supplies. Unfortunately, there have been very few advances in the development of new and better means of sanitization of potable water over the past 20 years.

In a perfect world

The ideal potable water biocide should possess the following characteristics, not necessarily presented in the order of importance:

For ease and safety of handling in water treatment facilities, it should be a stable solid at ambient temperatures;

It should be insoluble in waters so that it is not consumed by those drinking the treated water (i.e., it should be packed in a filter);

- It should be biocidal to a broad spectrum of pathogenic microorganisms and viruses in brief contact times;

- It should not leach potentially toxic chemical decomposition products into the water;

- Any free halogen (e.g., chlorine) leached into the water should be at low concentration levels so as not to impart color, odor, taste, or subsequent reaction products such as trihalomethanes (THMs) into the water;

- It should be effective in broad pH and temperature ranges for all qualities of water;

- It should be stable for long periods of use and regenerative upon exhaustion of its biocidal properties, and

- It should be inexpensive to produce and competitive in price with other potable water biocides currently in use.

- A biocide that meets this criteria mentioned has been developed recently in laboratories at Auburn University in Auburn, Ala.

A new polymer

The new biocidal material is a chlorinated or brominated polystyrene hydration (e.g., $C_pH_{10}N_1O_2CU$) may be inexpensively produced in a three-step chemical process starting from commercial polystyrene and simply modifying the polystyrene chain by introducing chloral- and bromo-hydantoin moieties—groups or substituents—in repeating units of the polymer. Chloral- and bromo-hydantoin monomer units are soluble in water and are in heavy use today

in the United States and elsewhere in the disinfections of recreational water supplies such as swimming pools or spas.⁸ Although the new biocidal polymer materials have not yet been tested for toxicity or gained U.S. Environmental Protection Agency (USEPA) approval, the two component parts—the polystyrene and the hydration moieties—are certainly approved for human contact. The polymers will be submitted in the near future to the agency for its evaluation.

We believe the new biocidal polymers will find use in a variety of filter applications. Obvious applications for potable water include: hand-held filter units such as those employed by backpackers and the military; filter units mounted in the water-inlet lines of the home; filters in water storage units in Third World nations where disinfections technology is lacking, and possibly even for small city water treatment plants. Other applications will include filters for swimming pools and spas, particularly for storage and demand release of free-bromine.

In any case, the polystyrene chloral- and bromo-hydantoin are completely insoluble in water, such that they can be employed in filter applications with no chance for consumption by those drinking water treated by them. Further more, the chlorinated polymer leaches less than 0.1 parts per million (ppm) of free chlorine

into flowing water; the brominates analog leaches out about 2.5 ppm free bromine. These quantities of free halogen are insufficient to impart significant taste, odor or color to the effluent water, which is a definite advantage when compared to commercial iodinated resins that leach out greater quantities of free iodine, especially at alkaline pHs. Upon exhaustion of chlorine or bromine by the new biocidal polymers, simply exposing them to free chlorine or free bromine in flowing water can regenerate them. Analyses of effluent water samples passed through filters containing the chlorinated polymer have shown no appreciable amounts of decomposition products present; for example, the concentration level of THMs is well below the maximum 100 ppb level allowed by the USEPA for potable water. The brominates polymer has not yet been tested in this regard.

Effectiveness

The biocidal efficacies of the new polymers are outstanding. The chlorinated polymer has been tested against aqueous solutions of 10 different species of bacteria, including *Klebsiella terrigena*, the fungus *Candida albicans*, the protozoan *Giardia lamblia* cysts, and rotavirus in a filter application. For example, a filter tube containing only 6.3 grams of this polymer was challenged with one-liter aqueous solutions of the Gram-positive bacterium *Staphylococcus aureus* and the Gram-negative bacterium *Escherichia coli* at microorganism concentrations of 4.9×10^7 and 3.1×10^8 colony forming units (CFU)/ml, respectively, and at a flow rate of 1.4 milliliters per second (mL/s). No viable bacteria were isolated from the effluents. The material worked well in the pH range 4.5-9.5 and at temperatures from 4-to-37°C. Typical contact times in the experiments range from only about 1-to-20 seconds, depending upon the resistance of the organism to disinfections by combined chlorine. Of particular interest has been the recent

finding of high efficacy against *Legionella pneumophila*, the bacterium that causes Legionnaires' Disease (7 log reduction by the bromo-polymer). The polymer works well for inactivating organisms in water containing salts, turbidity and heavy chlorine demand, as well as for pure chlorine demand-free water. The polymers in-activate rotavirus effectively (4 log reduction for chloro-polymer in a contact time of 10 seconds), which is significant in that virus particles are too small to be trapped by current commercial ceramic water filters. The brominates polymer is more effective at inactivation of microorganisms than the chlorinated one; the necessary contact times for inactivation by a similar amount of brominates polymer are shorter than those for the chlorinated polymer for all organisms tested thus far. It has been observed previously that N-bromamines are generally more toxic to organisms than are corresponding N-chloramines.⁸

The mechanisms of inactivation of the microorganisms by the polymers have not yet been determined. However, we believe that the most likely mechanism should be direct contact of the cell wall of the organism with the chlorine or bromine atoms on the hydration moieties of the polymer. As the organisms collide with the halogen atoms, the halogen atoms are transferred to the cell wall where they penetrate and eventually kill

the cell by an oxidation process. The reason why contact times necessary for inactivation are so short for the biocidal polymers is that numerous collisions between the microorganisms and the polymer particles occur during passage through the filter.

Essentially the polymer can be viewed as being a biocide of infinite concentration since it is completely insoluble in water. Water-soluble biocides require contact times of several minutes at concentrations of several parts per million to achieve

Polystyrenehydantoin

