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Iodine based water disinfection: A review

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Often bacteriological quality of ground water or surface water does not meet the prescribed standards. Iodine has been known for its germicidal action and has been used since 1920 for water disinfection. NASA, USA has used iodine-based disinfection in its space flights. In this review, water disinfection by different formulations incorporating iodine and the mechanisms of germicidal action are discussed.

Keywords: Antimicrobial polymers, Iodine, Water disinfections, Water supply

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Introduction

Majority of municipal water treatment facilities in India employ chlorine for disinfection of raw water. However, water distribution systems are seldom available in rural areas and urban slums. Use of hand pumps lifted ground water is common. Ground water from shallow hand pumps and insane surroundings get contaminated by microorganisms. Hence an alternate method of disinfection easily accessible to this section of the population has become important.

Disinfection methods include: i) Physical disinfection methods like boiling, pasteurization, UV, ultrasound and solar disinfection (SODIS); and ii) Chemical disinfection methods using strong oxidizing agents like chloride, chlorine dioxide, ozone, bromine and iodine (Table 1). These methods annihilate pathogenic organisms by causing irreversible destruction of cells, disruption of metabolic processes, disruption of biosynthesis and development[1]. The actual mechanism depends on the kind of organism and disinfection factor used.

Iodine-based Disinfection

Iodine in Aqueous Solution

Iodine is an effective, simple and cost efficient means of water disinfection. However, there is considerable controversy about the maximum safe iodine dose and duration of use when iodine is ingested in excess of the recommended daily dietary amount[2]. Impetus to the use of iodine for water treatment came in early 1920 when it was added to water to prevent goiter[3]. Iodine was used to disinfect drinking water for troops in France during First World War[4]. Subsequently, US army during Second World War used Globalin (tetraglycine hydroperiodide) tablets. Since 1950, numerous reports have been published on disinfection efficiencies of various forms of iodine[5-8]. More recently, iodine based disinfection has been in use by NASA in space flights[9]. Ellis *et al*[10] carried out a study on iodine disinfection with three sets of poor quality water with different turbidity ranges (5-7, 50-54 & 93-97 NTU), which were prepared by adding stream sediments, digested sludge and raw sludge to stream water. Different concentrations of iodine (1-10 mg/l) were employed to inactivate *Escherichia coli* in these samples at three different pH (6, 7.5 & 9.0) and temperatures (5, 20 & 35°C). Under all conditions, when 3.0 mg/l iodine dosage was used for the first set, virtually no *E. coli* was detected beyond 30 min. For digested sludge, 8.0 mg/l iodine was required to achieve the same quality water, whereas samples containing raw sludge required 10 mg/l iodine. Disinfection of potable water and swimming pool water[11] by iodine has been studied against many microorganisms. It was found to be a good disinfectant except against few microorganisms like *Legionella* bacteria and some fungi[12].

Iodine has following advantages: i) It is effective against many varieties of pathogenic organisms including spores, cysts, viruses etc. in a short time, at

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Table 1—Various disinfection methods with their mode of action

Disinfection methods	Mechanism of action	Comments
Boiling	Disruption of plasma membrane, denaturation, inactivation of enzyme	If temperature and time of boiling is suitable, annihilation of all the pathogenic organisms can be obtained
Pasteurization	Disruption of metabolic processes	It has application only in households and some branches of food industry
UV light	Lethal UV wavelength corresponds to absorption peaks of nucleic acid and leads to inactivation of microorganism	There is a danger from under-dosing or using incorrect wavelength due to stimulative effect on the microorganisms
Ultrasounds	Destruction of cellular structures and the change of functional properties of bacteria mechanically by vibrations of waves	It does not protect against re-growth of microorganisms in water works and must be applied together with other chemical disinfectant
Chlorination	Chlorine forms the strong oxidizing agent hypochlorous acid, which alters cellular components	Chlorine derivatives formed are toxic in nature
Iodination	Iodine inhibits protein function and is strong oxidizing agent	Iodine alone or as component of inorganic and organic compounds
Ozonation	Oxidation	Ozone is gaining attention as a potential replacement for chlorination

relatively short dosages; ii) Ammonia and organic nitrogenous impurities have no pronounced effect on germicidal efficiency; and iii) Iodinated drinking water eliminates chances of disease caused due to deficiency of iodine[12]. Some disadvantages of using iodine are: i) Higher concentration of iodine (in ppm) is required as compared to chlorine; ii) It is 20 times more costly than chlorine per unit of germicidal effectiveness; iii) Taste and slight color produced can affect palatability and aesthetic quality; and iv) Physiological effect of prolonged use by children remains to be ascertained although no ill effects were seen in normal people over prolonged use (up to 20 ppm) as pure crystallized iodine for water disinfection[13].

Iodine-based Formulations

Compounds of iodine tried for more regulated release of iodine include the following: (a) Organic iodide compounds (bisglycine hydroiodide, potassium tetraglycinetriodide etc.); (b) Iodophors, a combination of iodine with solubilising compounds (non-ionic surfactants)[14]; and (c) Other iodine release systems[15-19] such as iodine incorporated resins, which release disinfecting levels of iodine. The triodide form of quaternary ammonium polymer (cross linked copolymer of styrene and divinylbenzene) containing quaternary ammonium active sites to which I_3^- ions are attached, has been shown to be effective. This combination is insoluble but provides lethal quantities of iodine on demand[18]. Use of sorbents like rice husk, charcoalised coconut shell in addition to ion exchange resins to absorb iodine for release have also been tried[20]. NASA has used iodine -polyvinyl pyrrolidone complex for controlled release of iodine on its flights at the level of 2-3 μg/ml of molecular iodine I_2 and 0.5-1.5 μg of iodide[21]. Another system developed by NASA[9] for controlled release of iodine is the Microbial check valve (MCV), which is a flow through device containing an iodinated polymer, which imparts a bacteriostatic residual concentration (approx 2 mg/l) to the aqueous stream. Under MCV, dissolved iodine undergoes a series of hydrolytic disproportionation and related reactions, which result in the formation of an array of inorganic species like I^-, I_3^-, HOI and OI^-. Solution studies[21] of iodine by UV-Vis spectrophotomety showed four distinct peaks (in the volumetric iodine spectrum), which are indicative of three different iodine species formed after hydrolytic disproportionation in solution. The highest energy peak (226 nm) is from I^-, the two intermediate peaks (290 & 350 nm) are from I_3^-, and the lowest energy and weakest peak (460 nm) reveals the presence[20] of I_2. High Performance Liquid Chromatography and spectrophotometric detection method was used to determine different iodine species including organoiodine for fresh water and seawater samples[22]. Dissolved iodine species that dominate natural water system are iodide, iodate, and organic iodine. This method can be successfully applied to determine iodide, iodate as the difference of total inorganic iodide and iodide after reduction of the sample and organic iodine as the difference of total iodide (after organic decomposition and reduction) and total inorganic iodide.

An enzyme based iodine (EBI) disinfectant system[23] continuously generates free molecular iodine in a controlled fashion and evaluates for use in disinfecting flexible fibreotic endoscopes. Kawai *et al*[24] developed iodine containing articles for controlled release of iodine gas for disinfection. A triodide polymer membrane based on a blend of polystyrene and polyethylene has also been evaluated against *E. coli* for disinfection of water. It was seen that release of iodine (in ppm) from the membrane did not exceed the experimentally determined oral and intravenous doses of iodine from the membrane and was sustained for a long period[25].

Many other systems have been tried for enhanced iodine treatment of drinking water. Shanbrom Technologies[26] claimed to have developed a mixed bed of iodine source/iodine capture resin, which provides high flow rates that are useful for treatment of water which significantly increases the amount of iodine released into aqueous solution and enhances the disinfecting power. Another work[27] is reported on manufacturing of low iodine release polyiodide resin prepared by mixing of KI and I_2. On the passage of water containing *E. coli* through the quaternary ammonium triodide resin, triocide, the bacterium was inactivated by iodine attached to the cytoplasmic membrane[28]. Currently, a variety of devices like tap attachable water filter, candle filters, electrolytic purifiers etc. are in use. One such purifier, consisting of polyiodide resin granules, is available in the market but these granules are found to disintegrate slowly with time. Granules then pass through the filter and contaminate water; or simply clog the filter causing back flow. At such a situation, a safe, economical, stable over long time duration, and effective antimicrobial polymeric system for water treatment is needed.

A new concept was reported[29] on contact type of disinfection by iodine-based resin formed by adsorption of iodine on a strong alkaline anion-exchange resin. In this system, iodine resin could remove and kill (>99.9%) of *E. coli*, *Staphylococcus aureus* and *Candida albicans* in water at 25°C and pH 6.5 after contact for 1.07, 1.71 and 6.37 sec respectively. Another quaternary ammonium exchange resin binding tri-iodide or penta iodide, used to disinfect water containing *Legionella pneumophile*[30] indicated that iodinated resins are stable demand release disinfectants. There was no residual iodine detected by amperometric titration. When an aqueous suspension of *L. pneumophile* (2.7×10^9 cfu/ml) was passed through tri-iodinated resins, less than 0.004 percent of *L. pneumophile* was recovered. No viable cells were detected by direct plating from a suspension (2.3×10^9 cfu/ml) eluted through penta-iodinated resins (>99.99% viability reduced).

Chemistry of Germicidal Actions of Iodine

Out of the 4 species (I_2, I^-, I_3^- and HOI obtained in aqueous iodine), I_2 and HOI are essentially responsible for biocidal action of Iodine solutions[31]. I_2 is reported[7] more cysticidal than HOI and I_3^-. Cysticidal efficiency of HOI is half of I_2 and that of I_3^- is 1/8th of I_2. Pronounced[8] reduction was found in the effect of iodine at pH 9. Biocidal activity correlates with oxidizing capability of the species[31], concentrations of which are determined by the following equilibria:

$$I_2 + H_2O \Longleftrightarrow HOI + I^- + H^+;\ K = 5.44 \times 10^{-3}\ \text{mol}^{-1}$$

$$I_2 + I^- \Longleftrightarrow I_3^-;\ K = 723\ \text{mol}^{-1}$$

In pharmaceutical preparations and controlled release formulations, which generally contain iodine and iodide, free molecular iodine is almost entirely responsible for the actual microbiocidal activity. The primary reactions can be attributed to the iodination of N-H, C-H and S-H compounds in one of the following ways[32]:

(i) With basic–NH functions of amino acids and nucleotides, corresponding N-iodo compounds are formed. In this process, important positions for H-bonds are blocked resulting in a lethal change in protein structure:

$$R\text{-}NH_2 \xrightarrow{I_2} R\text{-}NHI$$

(ii) The –SH groups in the cytoplasm is oxidized which means that the ability to make disulphide bonds, an important factor in protein synthesis, is lost:

$$R\text{-}SH \xrightarrow{I_2} [R\text{-}SI]$$

(iii) The phenol group of the amino acid tyrosine reacts with iodine forming mono and diiodo derivatives. The size of iodine atoms sterically hinders the formation of H-bonds with the phenolic OH groups.

(iv) By addition to olefinic double bonds of unsaturated fatty acids, a change in the physical properties of the lipids takes place which leads to a decrease in fluidity of the cell membrane.

$$R\text{-}CH{=}CH\text{-}R^1 + I_2 \longrightarrow R\text{-}CHI\text{-}CHIR^1$$

(v) In case of cationic polymers with quaternary ammonium groups, bacterial cell wall surface is negatively charged and cationic disinfectants are positively charged. The disinfectants are adsorbed onto the cell surfaces by electrostatic interaction leading to disruption of membrane. The adsorption of polycations onto the negatively charged cell surfaces is expected to take place to greater extent than that of monomeric cations because of higher charge density carried by the polycations[33].

Conclusions

Instead of directly adding iodine or its soluble compounds, it is desirable to have controlled release of active iodine from suitable resins. More work is needed on various iodine species and their bioactivity. Shelf life and other considerations such as devices (or forms) in which iodine based polymers have to be incorporated in a water disinfecting system, require further study. The efficacies of many of the systems are still based on actual release of iodine or its compounds in drinking water. Physiological effects due to long-term ingestion of iodine, even though at ppm levels, could be an issue. Hence, feasibility of incorporating iodine in the system for killing bacteria on contact without actually releasing iodine into water is the best approach. This would result in a break through in iodine-based disinfection, both in terms of cost effectiveness and health consideration.

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