Operational Paper

Water disinfection using electrolytically generated silver, copper and gold ions

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ABSTRACT

The investigation described in this article examined an oligodynamic water disinfection method employing metal ions (Ag^+, Cu^{2+}, Au) generated by an electrolytic process. The efficacy of using different silver/copper/gold combinations (within the limits of current drinking water regulations) for killing *E. coli*, *Legionella pneumophila*, *Salmonella* and other pathogens was examined. The study investigated the dependence of bacterial killing time against metal ion concentration, different initial bacteria concentrations (from 10^3 to 10^{12} CFU l^{-1}), and the influence of different ion (Cl^-, SO_4^{2-}, S^{2-}, Fe^{2+}, Fe^{3+}) concentrations on the disinfection process.

Key words | disinfection, oligodynamic method, pathogen, water

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INTRODUCTION

Water supply systems, water storage systems, cooling water in air-conditioners, and swimming pools are some of the most attractive and vulnerable targets for bioterrorism. Moreover, in many developing countries, fresh water resources are limited and unevenly distributed, and even drinking water often contains extraordinarily large quantities of bacteria.

One of the water disinfection methods used to mitigate those potential threats is the oligodynamic method. And one of its modifications is based on using electrochemical processes: electrolytically introducing into the water reactive metal ions from an electrode (Kulsky 1982). Electrodes are placed into the water stream and a current is applied to the electrode to cause the controlled release of metal ions. Metal ions bind to the bacterial cell wall, causing cell-wall disruption and lysis during the disinfection process, although studies have shown that bacteria have many means to defend against heavy metal intrusion (Silver & Phung 1996).

Different materials are used as the electrodes: silver (Kulsky 1982), copper (Munson 2000), and alloys of silver and copper in varying proportions (generally ranging from 10% silver/90% copper to 30% silver/70% copper (Silver Institute 1999; Munson 2000)). For example, more than 125 leading hospitals in the United States have installed silver/copper ionization systems to eradicate *Legionella pneumophila* from their hot water systems (Silver Institute 1999).

The concentration of electrolytically introduced metals in the disinfected water is of significant concern, particularly for potable applications. Maximum concentrations of metals in drinking water are regulated at various levels in different countries. For example, copper is regulated in the United States at a concentration of 1.3 mg l^{-1} (which is an *action level*, not a maximum contaminant level); silver is regulated at a concentration of 0.1 mg l^{-1} as a secondary (i.e. non-enforceable) constituent because of its aesthetic effect, the discoloration of

plumbing fixtures. The German and Russian drinking water regulation limit is 0.1 mg l^{-1} for Cu, and 0.01 mg l^{-1} and 0.05 mg l^{-1} for Ag, respectively. The concentration of metal ions required for disinfection is sometimes greater than the regulatory limits and, as a result, the oligodynamic method cannot be used (Rohr *et al.* 2000). Moreover, the concentration and relation of metal ions in water (i.e. its disinfecting efficacy) strongly depend on factors such as the composition of electrodes, the water flow rate near the electrode surface (to eliminate the gradient of ion concentrations in the layer of water near the electrode surface), and the concentration of cations and anions in the water.

The objective of this investigation was to find the optimal alloy for different bacteria, and to improve existing oligodynamic methods.

MATERIALS AND METHODS

Experiments were conducted with the following bacterial cultures: *E. coli* (272), (Strain 33218), (NCTC 10538), *Salmonella typhimurium* (251), fecal coliforms, typhoid – paratyphoid, *L. pneumophila*, *Salmonella* and *Vibrio cholera* in the temperature range 18–36°C. The cultivation, culture enrichment and the testing bacteria were performed following the Standard Methods (USSR, Russia) for Testing Chemical Procedures (Drinking Water. Hygiene requirements and quality control 1982) for the evaluation of disinfection.

Electrodes with different alloy compositions (Ag 39–100%, Cu 0–60%, Au 0–0.2%) were tested. The electrodes had various shapes: a ball with diameter of 5 mm, a disc with diameter of 20 mm and a rectangle 20 mm × 30 mm. Alloy electrodes were placed into the water pipe and a current was applied to the electrode to cause the release of Ag and Cu as ions, and Au as a colloidal element. The distance between electrodes was varied from 8 mm to 20 mm. The test water was recirculated through the test apparatus. A control valve regulated the flow rate across the electrodes. A constant-current generator established a stable electric current between the electrodes, independent of water conductivity.

A portable experimental water-disinfecting device was constructed. It consists of a 12 V battery, the constant-current generator and electrodes with the alloy composition Ag/Cu/Au in the ratio 79.9%/20%/0.1% (Khaydarov *et al.* 1997; Khaydarov and Mayshev 2001).

The influence of Cl^-, SO_4^{2-}, S^{2-}, Fe^{2+}, Fe^{3+} ions on the efficacy of the disinfecting process was investigated at different concentrations. Stock solutions containing 1,000 mg of ions per litre were prepared by dissolving appropriate amounts of NaCl, Na_2SO_4, Na_2S, $Fe(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ in deionized water and transferred to test solutions by using a dilution scheme. The water conductivity in the tests was not less than 10 μS cm^{-1}. In the experiments with low ion concentrations the conductivity was adjusted by adding the necessary amount of Na_2SO_4 stock solution.

Deluxe Meter with Ion Measurements (Cole-Parmer Benchtop pH Meter) and Cole-Parmer Combination Ion Selective Electrodes were used to determine concentrations of Ag and Cu ions in the water. Concentrations of Cu and Au were determined by neutron activation analysis. Water samples were irradiated at the nuclear reactor of the Institute of Nuclear Physics (Tashkent, Uzbekistan). A Ge(Li) detector with a resolution of about 1.9 keV at 1.33 MeV and a 6144-channel multichannel analyser were used. The areas under the γ-peaks of the radionuclides ^{64}Cu (half-life of 12.8 h, energy of the γ-peak is 0.511 MeV) and ^{198}Au (half-life of 64.8 h, energy of the γ-peak is 0.412 MeV) were measured to calculate the concentrations of Cu and Au, respectively. Sensitivities of determination of Cu and Au (irradiation in a reactor neutron flux of 1×10^{13} n cm^{-2} s^{-1}) are 10^{-9} g g^{-1} and 10^{-10} g g^{-1} (or 10^{-12} g g^{-1} and 10^{-13} g g^{-1} after preconcentration), respectively, and limits of standard deviation are 10% (De Soete *et al.* 1972; Alfassi 1990). This method was used in experiments when Cu concentration was less than 0.1 ppm.

RESULTS AND DISCUSSION

Natural waters typically contain chloride (Cl$^-$) ions. During the electrolytic process, the concentration of Ag$^+$ ions

in the thin water layer near the surface of the anode increases considerably and AgCl is formed (solubility product of 1.8×10^{-10}), controlling the concentration of Ag^+ to low levels. Similarly, metal hydroxides (e.g. $Cu(OH)_2$) are formed near the cathode. Thus, the concentrations of metal ions (Ag^+, Cu^{2+}) in solution and their relation usually differ from their relation in the electrode alloy and from the value calculated by Faraday's laws of electrolysis.

The concentration of metal ions (C_i) in water can be increased up to the value corresponding to the complete dissolved mass of the electrodes (Δm_e) by using the water flow between electrodes. The minimum value of the water flow rate V_{min} (when the concentration C_i is not less than the value corresponding to the dissolved mass of the electrodes $0.9\,\Delta m_e$) can be described by the empirical formula:

$$V_{min} = a\ i \tag{1}$$

Where i is the electric current density, in amp m^{-2}. The factor $a = 0.06 \pm 0.02$, and the confidence limit corresponds to the level of significance of 99%. The standard deviation of a is large here because of influence of the flow turbulence.

Disinfection can be described by the following empirical formula:

$$N(t) = N_0 \exp\ (-Ct/K) \tag{2}$$

or $Ct = -K \ln(N/N_0)$

Where N_0 is the initial concentration of bacteria; N is the final concentration of bacteria; C is the effective concentration of metal ions in the water for a given ion collection, in mg l^{-1}; K is the coefficient of resistance for a given ion collection, depending on bacteria types and the concentrations of cations and anions in the water (that can react with disinfecting metal ions); t is the time after introducing the metal ions into the water, i.e. disinfecting time, in seconds. This formula shows that the concentration of metal ions C and time t necessary for water disinfection depend logarithmically on the initial concentration of bacteria, N_0.

Experimental results presented in Table 1 demonstrate the synergistic disinfecting effects obtained by using alloys with various silver/copper/gold combinations. In this table, the coefficient K is given for each composition of electrodes. Standard deviations of the coefficient K are given for $p = 0.68$. Concentrations of disinfecting ions in the water can be recalculated by using the value of concentration of Ag ions for each composition of electrodes.

Table 1 shows that the best disinfection is obtained by using an alloy of silver/copper/gold composition with concentrations of metals in the ratio 70–90%/10–30%/0.1–0.2%, respectively. These particular compositions allow reaching the minimum value of the coefficient K, and provide considerable reduction of metal ion concentrations in the water in comparison with other combinations.

Table 2 summarizes coefficients K for different pathogens and disinfecting times when employing the electrodes described above. These data correspond to concentrations of silver, copper and gold of 30 µg l^{-1}, 7.5 µg l^{-1} and 0.075 µg l^{-1}, respectively.

The influence of different cations and anions (e.g. Cl^-, SO_4^{2-}, S^{2-}, Fe^{2+}, Fe^{3+}) in the water on the disinfecting process was investigated. Test results using the electrodes described above are given in Table 3. Initial concentration of *E. coli* in these experiments was 10^7 CFU l^{-1}, and the concentration of Ag^+ ions in the water was 0.1 mg l^{-1} (the corresponding concentrations of Cu^{2+} and gold were 0.025 mg l^{-1} and 0.00025 mg l^{-1}, respectively), that is, greater than drinking water regulation limits. These results show that Cl^- and Fe^{2+} ions have the most impact on the disinfecting process: they react with disinfecting metal ions with formation of AgCl and reduction of ions, decrease the concentration C of disinfecting metal ions and increase the disinfecting time t in Equation (2). The influence of other ions is not significant in comparison with the influence of Cl^- and Fe^{2+} ions and can also be estimated by Equation (2).

The portable experimental device with the electrode alloy described above has been tested within the last 5-year period in different laboratories and universities. The study investigated the dependence of disinfecting time against effective concentration C, initial bacteria concentration N_0 (from 10^3 to 10^{12} CFU l^{-1}) and organism type.

Table 1 | Minimal concentration of disinfecting metal ions for killing *E. coli* with initial concentration 1,000 CFU l^{-1} (final concentration ≤1 CFU l^{-1}) within 30 minutes

Composition of electrodes (%)			Concentration of Ag ions (mg l^{-1})	
Ag	Cu	Au	K (mg s l^{-1})	
100.0	0.0	0.0	1.5	390 ± 120
99.9	0.0	0.1	1.5	390 ± 120
99.8	0.0	0.2	1.5	390 ± 120
90.0	10.0	0.0	0.1	26 ± 8
89.9	10.0	0.1	0.05	13 ± 4
89.8	10.0	0.2	0.05	13 ± 4
80.0	20.0	0.0	0.05	13 ± 4
79.9	20.0	0.1	0.03	8 ± 3
79.8	20.0	0.2	0.03	8 ± 3
70.0	30.0	0.0	0.05	13 ± 4
69.9	30.0	0.1	0.04	10 ± 3
69.8	30.0	0.2	0.04	10 ± 3
50.0	50.0	0.0	0.5	130 ± 40
49.9	50.0	0.1	0.3	80 ± 25
49.8	50.0	0.2	0.3	80 ± 25
40.0	60.0	0.0	1.0	261 ± 80
39.9	60.0	0.1	0.8	210 ± 60
39.8	60.0	0.2	0.8	210 ± 60

In the Central Sanitary and Epidemiological Laboratory of the Ministry of Defence of Uzbekistan, this device was tested on two contaminated water samples containing 10^8 and 10^9 CFU l^{-1} *E. coli*. River water with conductivity of 900 µS cm^{-1} and concentration of Cl$^-$ ions of 120 mg l^{-1} was used as the initial water. The electrode insertion times t were 3, 5 and 10 minutes (the corresponding concentrations of Ag$^+$ and Cu^{2+} ions were 50 and 12.5 µg

Table 2 | Coefficient K and disinfecting time (initial concentration 1,000 CFU l^{-1})

Pathogen	K (mg s l^{-1})	t (min)
Typhoid–Paratyphoid	15–30	60
Legionella pneumophila		
Salmonella	8–15	30
Vibrio cholerae	8–15	30

Table 3 | Influence of cations and anions on disinfecting time of *E. coli* (10^7 CFU l^{-1} initial concentration)

		Disinfecting time					
Ions	Concentration of ions (mg l^{-1})	15 min	30 min	60 min	90 min	2 hours	24 hours
Cl^-	2	300	3	< 1	< 1	<	
	6	1200	23	3	< 1	< 1	< 1
	20	2400	220	4	< 1	< 1	
	60	5000	28000	170	10	< 1	
	350	10^4	5000	890	70	12	
SO_4^{2-}	1.5		230	< 1	< 1		
	25	290	< 1	< 1			
	250	250	< 1	< 1			
S^{2-}	0.01	1000	120	< 1	< 1		
	0.05	1200	120	< 1	< 1		
	0.15	1600	140	< 1	< 1		
	0.30	1800	150	< 1	< 1		
Fe^{2+}	1.5	5700	2700	1600			
	15	10^4	7900	3800			
Fe^{3+}	1.2	2000	40	20	< 1		
	11.12	2200	110	9	< 1		

l^{-1}, 80 and 20 µg l^{-1}, 160 and 40 µg l^{-1}, respectively); the water samples were tested over a 20-day period following treatment by the device to determine the rate of bacterial regrowth. There was no detectable decrease of the disinfecting ion concentrations during 20 days. The electric current between electrodes was set at 5 mA. Some of the test results are given in Table 4. In accordance with Equation (2) the electrode insertion times, the corresponding concentration of ions C and disinfecting times *t* in these experiments are greater than in the laboratory tests described above because of extremely high bacteria concentrations.

Similar tests of the experimental device with alloy electrodes were performed by the Department of Pathology of the University Sains of Malaysia in 1999. Pond water samples (5 l) were each contaminated with 5 grams of fecal matter. Initial bacteriological quality was estimated at 5×10^{12} CFU l^{-1} coliforms. The electrode insertion time was 30 minutes and concentrations of Ag^+, Cu^{2+} and gold were 0.08 mg l^{-1}, 0.02 mg l^{-1} and 0.0008 mg l^{-1} (i.e. above regulated concentration for silver). Samples were evaluated 1 hour, 3 hours, 1 day and 1 week following treatment. No growth was reported for each of these samples, compared with mixed coliform

Table 4 | Test results of the portable experimental device

Disinfecting time	Initial concentration 10^9 CFU l^{-1} *E. coli*			Initial concentration 10^8 CFU l^{-1} *E. coli*		
	3 min insertion	5 min insertion	10 min insertion	3 min insertion	5 min insertion	10 min insertion
30 min	100–150	100–150	100–150	90–100	50	45
2 hours	100–120	30	3	70	6	5
2 days	15	< 1	< 1	2	< 1	< 1
3–20 days	< 1	< 1	< 1	< 1	< 1	< 1

growth in the control (i.e. undisinfected) samples. There was no detectable decrease of the disinfecting ion concentrations during 7 days. Tests of the portable experimental device conducted by Moscow Medical Academy (Russia) and EN Technology, Inc. (Korea) have confirmed the results described above.

One of the prospective uses of the method described here is its application to air purification in building heating, ventilating and air-conditioning (HVAC) systems by disinfecting the water used in recirculating systems. The method described in this report has been tested in air-conditioners and the equipment for treatment of potable water. Experimental devices (Khaydarov *et al.* 1997, 2001) with a capacity of 5 m^3 h^{-1} (voltage 12 V DC, power 5 Wh) were installed at water pumps in the Aral Sea region of Uzbekistan and swimming pools and have been tested during the course of 1 year.

CONCLUSION

The test results of these investigations demonstrate the efficacy of the oligodynamic method using a suitable alloy mixture (silver/copper/gold composition) for non-potable water disinfection. The method can be used for preventing bacterial contamination in water storage systems and cooling water in air-conditioners.

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