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A new approach to testing the efficacy of drinking water disinfectants

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ABSTRACT

New disinfection procedures are being developed and proposed for use in drinking-water production. Authorising their use requires an effective test strategy that can simulate conditions in practice. For this purpose, we developed a test rig working in a flow-through mode similar to the disinfection procedures in waterworks, but under tightly defined conditions, including very short contact times. To quantify the influence of DOC, temperature and pH on the efficacy of two standard disinfectants, chlorine and chlorine dioxide, simulated use tests were systematically performed. This test rig enabled quantitative comparison of the reduction of four test organisms, two viruses and two bacteria, in response to disinfection. Chlorine was substantially more effective against *Enterococcus faecium* than chlorine dioxide whereas the latter was more effective against the bacteriophage MS2, especially at pH values of > 7.5 at which chlorine efficacies already decline. Contrary to expectation, bacteria were not generally reduced more quickly than viruses. Overall, the results confirm a high efficacy of chlorine and chlorine dioxide, validating them as standard disinfectants for assessing the efficacy of new disinfectants. Furthermore, these data demonstrate that the test rig is an appropriate tool for testing new disinfectants as well as disinfection procedures.

1. Introduction

Disinfection procedures are of widely recognized relevance in ensuring the supply of safe drinking water. Especially if surface waters or groundwater subjected to faecal contamination are used as raw water sources, disinfection should be part of the water treatment train (WHO, 2017). Disinfection is usually the final step during the production of drinking water, acting as an essential barrier against widespread human pathogens. Therefore, active substances for the disinfection of drinking water should be effective against a wide range of bacteria and viruses (while it is generally accepted that only filtration is effective against protozoa). This criterion is met by the standard disinfectants chlorine (as sodium or calcium hypochlorite, chlorine gas), chlorine dioxide and ozone. However, even for these standard disinfectants which have been used for decades, knowledge about their efficacy under the range of water matrices and other conditions still has relevant gaps, and further systematical investigations are needed (Dow et al., 2006; Sigstam et al., 2014).

For drinking water disinfection, chlorination is the oldest and most common procedure. Since toxic chlorination by-products e.g. trihalomethanes may occur, chlorine dioxide may be a suitable alternative, but its use is also limited due to formation of chlorite and chlorate. To prevent infectious diseases, efficacies on one hand and minimization of disinfection by-products on the other have to be balanced to avoid under- or overdosing. Competent authorities need robust quantitative efficacy data to assess microbial safety in relation to the acceptable toxicological burden. In the European Union (EU) only some common active substances are authorized for drinking-water disinfection, but many more are in the pipeline for notification (Grunert and Bartel, 2015). Since not all potential pathogens can be analyzed, indicator organisms are used in the surveillance of raw water and drinking water to indicate faecal contamination. The most common faecal indicators for bacteria are *Escherichia coli* and Enterococci. As indicators for human viruses, somatic and F^+-specific coliphages have been suggested for monitoring as well as for disinfectant tests (Barbeau et al., 2005b; Grabow, 2001; Hornstra et al., 2011; Sobsey, 1989). As the susceptibility to disinfection may vary greatly between bacterial and virus pathogens, it is important to test the efficacy of active substances and biocide products on both – indicator bacteria and surrogates for viruses.

The most widely used parameter for comparative evaluation of the efficacy of various disinfectants is their ct value, i.e. the product of the disinfectant concentration and contact time needed to achieve a defined reduction of target organisms. Inactivation of the organisms is normally assumed to follow first order kinetics. Effects of further parameters such

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as pH value, temperature or disinfectant decay and tailing effects may also be considered (Barbeau et al., 2005b), but for many purposes calculation of simple ct values is sufficient (Clark et al., 2003; Pfeiffer and Barbeau, 2014). For disinfection experiments it is essential to define the water quality. In particular the pH, dissolved organic carbon (DOC) and temperature significantly influence the efficacy and need to be controlled. Depending on their individual composition natural or artificial organic substances show significant impact on the rate of disinfectant decay (Barbeau et al., 2005a, 2005b; Dow et al., 2006; Haas et al., 1996).

So far, due to the lack of standardized tests for determining the efficacy of drinking water disinfection, authorization processes use tests from the food sector. These suspension tests give basic information about efficacy, but are insufficient for evaluating the efficacy of drinking water disinfection in practice: theoretical calculations of the influence of flow behavior on efficacy showed significant deviations between different settings (Pfeiffer and Barbeau, 2014; Smeets et al., 2006). For example, to determine the efficacy of disinfection of *Legionella* sp. in drinking water networks and hot water systems a pilot unit scale 1 “Alphéo II” has been established in Nantes (France) (Farhat et al., 2010), which simulates the drinking water installation of a building. Loret et al. investigated the efficacy of various disinfection methods against biofilms (including *Legionella*) on seven identical test rigs (Loret et al., 2005). Boudaud et al. (2012) investigated the conventional drinking water treatment from river water at pilot scale and the disinfectant efficacy in batch scale. All three approaches show substantial differences in efficacy tests with regard to a practical use.

Only very few experiments on the efficacy against planktonic test organisms and test viruses in continuous flow reactors have been reported so far (Botzenhart et al., 1993; Carlson et al., 1968), but authorities and other users are increasingly requesting simulated use tests that provide a controlled and applied test environment, leading to more realistic data. A further advantage of simulated use tests in continuous flow setups is the option of studying in-situ systems such as units for inline electrolysis and different ozone contactors. We therefore designed a semi-technical scale test rig for simulated use tests working in flow-through mode for evaluating the efficacy of new disinfectants and disinfection procedures. In the following study, we validated this test rig by assessing the efficacy of chlorine and chlorine dioxide against two standard indicator bacteria (*Escherichia coli, Enterococcus feacium*), and applied it to compare the results to those for two virus surrogates – (bacteriophage PRD1, bacteriophage MS2). Furthermore, we derived $ct_{99\%}$-values for these two test bacteria and two test viruses based on numerous experiments at various temperatures, pH and DOC.

2. Materials and methods

2.1. Principle and characteristic properties of the semi-technical test rig

2.1.1. Principle

The designed test rig (photo in abstract and Fig. 1) operates in a flow-through mode, in which microorganisms and disinfectants are dosed continuously into the test water. It consists of a PVC pipe with an inner diameter of 40 mm and small stainless steel sampling taps. After passing the test rig the test water is discarded. Concentrations of test organisms have to be determined at tap 0 (negative control without disinfectant). Subsequently, the disinfectant to be tested is injected into the volume flow. A pipe unit with a small diameter ensures sufficient mixing of test organisms and disinfectant by turbulent flow. Injection of the disinfectant marks the onset of disinfection. During the experiment physico-chemical data (pH *in/out*, conductivity *in/out*, oxidation-reduction potential *in/out*, temperature *in/out*, pressure, total flow-through) are continuously recorded. Concentrations of the test organisms and the disinfectant are both determined at all available taps. Immediately after sampling, the disinfection process in the sample is stopped by neutralization of the disinfectant with sodium thiosulfate in excess. Sampling tubes are filled under shaking, quickly closed, again vigorously shaken two or three times and immediately placed onto a rapid mixer.

After dosing of microorganisms was stopped all bacteria and viruses were flushed out. Analyses had shown that samples between test cycles were always negative.

2.1.2. Dosing and working concentrations of the test organisms

Test organisms (bacteria and viruses) were placed into a storage container of the test rig. Bacterial suspensions (*Escherichia coli*, *Enterococcus faecium*) and the bacteriophage MS2 were tested simultaneously. The analysis of another bacteriophage, phage PRD1, infecting the same host bacteria as phage MS2, was conducted in a separate test. The concentrations of test bacteria in the storage container were between 1×10^8 to 5×10^9 cfu/100 ml and the concentrations of bacteriophages were in the range of 1×10^9 to 1×10^{11} pfu/100 ml. Test organisms were added to the test water at a dilution of 1:1000, resulting in concentrations of bacteria and bacteriophages of 1×10^5 to 5×10^6 cfu/100 ml and 1×10^6 to 1×10^8 pfu/100 ml, respectively.

2.1.3. Test water

Test water is produced in a 20 m^3 storage tank. Depending on the chosen flow rate at the rig between 100 l/h and 1000 l/h, tests can be performed with the same water for at least 10 h up to 4 days. For continuous mixing of the test water a small circulating pump (1.8 m^3/h) and for a fast and complete mixing a circulating pump with a capacity of 125 m^3/h is used. The pH value was regulated through addition of hydrochloric acid (HCl) or sodium hydroxide (NaOH), whereas DOC originated from the source waters. For most experiments, the institute's waterworks (UBA Berlin-Marienfelde) provided groundwater after removal of iron and manganese. In some experiments, the DOC was modified by mixing the groundwater with reverse osmosis water. For experiments with a high DOC of 5 mg/l, treated groundwater from the waterworks Berlin-Stolpe was used, transported in a common tank vessel for emergency drinking water supply. The water temperature was adjusted with a heating-cooling unit (Lauda Integral XT1850W).

2.2. Contact times between organisms, viruses and disinfectants

The contact time is defined as the time from dosing the organisms and disinfectant to the time when the water sample is drawn from the tap. To determine this time span two separate procedures were applied: On the one hand, contact times were calculated theoretically, based on current flow rates, pipe diameters and lengths, thus determining the flow rates at each sampling tap. On the other hand, tracer tests were performed with NaCl (25%) to determine the time from dosing to sampling experimentally from the electrical conductivity peak as 50th percentile. For each test the theoretical contact time was calculated on the basis of current flow rates on every sample tap and adjusted by a correction factor derived from these tracer tests.

2.3. Cl_2 and ClO_2 production and measurement

Chlorine as sodium hypochlorite was applied. The content of free chlorine was measured by the spectrometric method following ISO 7393-2 (ISO, 1985). Chlorine oxidizes N,N-diethyl-1,4-phenylenediamine (DPD) to a purple colored dye that can be analyzed at 510 nm. For better handling the chlorine tests were performed with different volumes but maintaining the proportions of the chemicals (equivalency was verified). Similarly, chlorine dioxide was determined spectrometrically after reacting with DPD according to DIN 38408-5 (DIN, 1990). Chlorine dioxide was freshly produced with a common generator (DIOX-A, Wallace &