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Identification of key chemical species in plasma-treated water for effective and safe disinfection

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For the plasma disinfection of human body for dental and surgical applications, we have developed the reduced-pH method with direct plasma exposure, which brings stronger bactericidal activity in liquid at lower pH, where the threshold is pH 4.8 [1]. Drastic enhancement of bactericidal activity is achieved by controlling the pH of the solution under 4.8, and D value (decimal reduction time) surprisingly became 1/100 when pH is changed from 6.5 to 3.8. D value (*Escherichia coli*) at acidic condition can be controlled to quite small (< 2 sec) under some conditions. In other words, applying an acidic liquid to the target area before irradiating with plasma reduces the time required to achieve the necessary sterilization power to 1/100. We call this technique as "the reduced-pH method".

Considering the plasma treatment of human body, the plasma-induced chemical reactions in the liquid (body fluid) must be worthy of attention. In addition to it, we found that the plasma-treated water (PTW) also has strong bactericidal activity only for a short time under acidic condition. PTW contains many kinds of species, some of which brings bactericidal activity. To understand our PTW experimental results with the reduced-pH method, physicochemical properties are discussed based on chemical kinetics. Lower temperature drastically brings longer half-life, and the bactericidal activity can be kept by cryo-preservation. This means that PTW with higher bactericidal activity could be obtained by longer plasma treatment under enough low temperature. Many researchers are interested in PTW, where the waters are treated / activated by their original devices. For scientific understanding, we should discuss based on chemical species. PTW has many chemical components, and respective components in PTW were isolated by ion chromatography. Result of the analysis (Figure 1) revealed that in addition to peaks of H_2O_2, NO_2^- and NO_3^-, an unknown peak was detected and only this fraction had bactericidal activity. This means that the bactericidal ingredient of PTW was successfully purified. Considering the activation energy for degradation of this species, we assumed that $HOONO_2$ (PNA: peroxynitric acid). is the bactericidal ingredient [2].

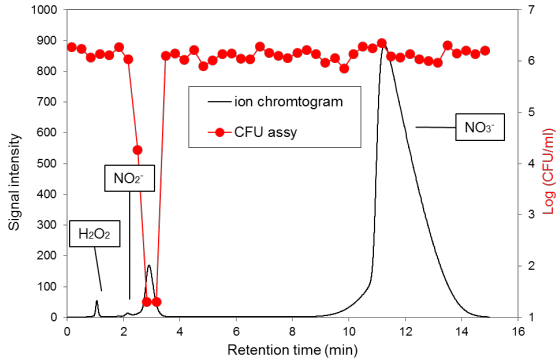

Figure 1. Ion chromatogram of PTW and CFU assay of its each fraction.

Relative bactericidal activity was estimated comparing commercially available bactericides. Serial diluted PTW or commercial bactericides were mixed with bacteria suspension. Bactericidal activity of PTW is calculated to be so high that 22 log reduction (i.e. 10^{-22}) of spore cell (*Bacillus subtilis*) would be achieved with undiluted PTW. This corresponds to 65% hydrogen peroxide (H_2O_2) and 14% sodium hypochlorite (NaClO) respectively, which are deadly poison for human. Unlike such stable chemicals, bactericidal activity of PTW is inactivated quickly by body temperature. Strong oxidative stress by PTW would exert only upon the surface of applied area. This property of short lifetime is expected as a novel disinfectant for human body.

Although the existence of PNA itself including chemical synthesis method has been known since 100 years ago [3], sterilization by PNA has never been reported in past papers. Chemical synthesis is more inexpensive for the practical use of PNA for sterilization [4], but it is just a plasma-inspired new technique.

PNA is known to be chemically synthesized by mixing HNO_2 and H_2O_2 under extremely low pH condition, and simplified chemical reactions are shown as (1) and (2).

$$HNO_2 + H_2O_2 \rightarrow HOONO + H_2O \quad (1)$$
$$HOONO + H_2O_2 \rightarrow HOONO_2 + H_2O \quad (2)$$

These raw chemical materials can be supplied to PTW by plasma exposure. Our chemical synthesis experiments showed that pH should be less than 2 or less, preferably around 0. Just from the fact that pH of the whole PTW is about 2~4, PNA synthesis would not proceed in the PTW. Considering the dynamic supply of chemical species to the water surface, these concentrations around the water surface layer would be very high due to localization during plasma exposure. It is thought that PNA is generated only in the thinner surface of the plasma irradiated solution, where pH is extremely low, and PNA is stored in PTW if the temperature is enough low.

References

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