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WHITE'S HANDBOOK OF CHLORINATION AND ALTERNATIVE DISINFECTANTS

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Hypochlorous Acid

HOCl is overall the most effective disinfectant of the chlorine species present in dilute solution at the pH values associated with water and wastewater treatment. Because HOCl- is uncharged and has a relatively low molecular weight, it is better able than other chlorine species to penetrate cells walls; and it reacts more rapidly than other chlorine species, in both oxidative and substitution reactions, with organic matter, including critical components of cells.
Since the dissociation of HOCl- to form OCl- is strongly dependent on pH, and since OCl- is a much weaker disinfectant than HOCl-, the germicidal efficiency free chlorine depends very strongly on pH. Table 2.3 shows the percentage of undissociated HOCl- in a chlorine solution as a function of pH values and temperature. Lowering the pH increases the percentage of HOCl-, generally enhancing disinfection. Lowering the temperature suppresses dissociation, which would suppress disinfection if this were the only consideration; however, an increase in temperature will also increase the rate of diffusion of chlorine into cells, increase the rate of reaction of chlorine with vital cell components, and increase metabolic activity (accelerating the toxic effects of chlorine on cells), so an increase in temperature actually increases the rate of inactivation rather than decreases it.
As HOCl- is consumed at constant pH, OCl- ions will combine with H^+ ions to form more HOCl-, so the percentage of free chlorine present as HOCl- will remain unchanged. This is commonly referred to as the "reservoir effect." This effect occurs because both dissociation of HOCl- to OCl- and the reverse reaction (Eq. 2.9) are extremely rapid (virtually instantaneous), and the balance between HOCl- and OCl- (embodied in Eq. 2.10) depends only on pH if the temperature and other conditions (such as ionic strength) remain constant.
The chlorine dosages employed for water and wastewater disinfection are typically small compared with the alkalinity of the water, so changes in pH due to chlorine consumption are usually negligible. However, if high dosages of chlorine are employed, or if it reacts to produce or consume a significant amount of alkalinity, a significant pH change may occur.

Hypochlorite Ion

The OCl- ion is a relatively poor disinfectant because of its inability to diffuse through the cell walls of microorganisms. Since it is negatively charged, it is electrostatically repelled from cell walls, which are also negatively charged. Since it is ionic, it is strongly hydrated and effectively much larger in size than an unhydrated molecule having a similar molecular weight (such as HOCl-), so it also diffuses into cells more slowly than HOCl- due to its larger size. Furthermore, chlorine substitution reactions, which presumably play a key role in disrupting the functions of enzymes and nucleic acids, are enhanced by a low pH and the presence of HOCl-, whereas oxidative reactions involving chlorine, which typically proceed much more slowly than substitution reactions, are favored by a high pH and the presence of OCl-. This is consistent with the observations of Fair et al.[43]. Based on the earlier work of Butterfield et al.,[188] they computed the activation energies associated with disinfection using free and combined chlorine as a function of pH. They noted that the activation energy associated with HOCl- (7000 cal/mol) was in the range associated with diffusion, whereas the activation energy for OCl- (15,000 cal/mol) was characteristic of chemical reactions.

Fair et al.[43] concluded that HOCl- is 80 times more effective than OCl- for inactivation of *Escherichia coli*. They based this estimate on the assumption that the effects of HOCl- and OCl- are additive and on calculations involving the equilibrium expression for dissociation of HOCl- (Eq. 2.10) and an equation fitted to inactivation data (chlorine concentration to achieve 99% inactivation vs. pH). According to White,[110] Selleck (R.E. Selleck, pers. comm.) found HOCl- to be only 20 times more effective than OCl- for inactivating an unspecified organism, while another study found that the relative effectiveness of HOCl- to OCl- increased from 150 to 300 over a temperature range of 3 – 23 ° C for inactivation of *Entamoeba histolytica* cysts.

Given the complexity of the reactions involved in chlorine disinfection and differences among organisms, even those of the same species grown under different conditions, it is not surprising that estimates of the relative effectiveness of HOCl- and OCl- vary from one study to another. Although most studies have found that HOCl- is far superior OCl- as a disinfectant, Scarpino et al.[189,190] found that although this was true for bacteria, OCl- is superior to HOCl- for inactivation of poliovirus type 1, and this finding was later confirmed by other investigators.[13] One factor that has been shown to influence the effectiveness of OCl- as a disinfectant, and that may therefore explain at least some of the variability in the results are various investigators, is the ion pair formation between OCl- and cations such as sodium or calcium.[13,136-139,191,192] Neutral or positively charged ion pairs should be able to diffuse into cells much more readily than OCl-.

Footnotes

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