REACTOR KINETICS 6

6.1 INTRODUCTION

Of primary consideration in stormwater treatment is how quickly a pollutant is removed. The change in the concentration of a pollutant depends on four factors: the reaction rate, the hydraulic regime, and time. The reaction rate is a function of temperature and the nature of the biotic or abiotic process that drives the reaction.

6.2 REACTION ORDER

What is a reaction order

The reaction order defines the relationship between the rate of reaction and the concentration of the pollutant, given by the equation:[1060]

$$-\frac{\partial C}{\partial t} = kC_o^{\,n} \qquad (6.1)$$

Where: C = concentration at time *t*
C_o = initial concentration at $t = 0$
k = reaction or removal rate (1/day)
n = reaction order
t = time

The equation states that the rate of change in the concentration is a function of the reaction rate, *k*, and the initial concentration of the pollutant to an exponential power called the reaction order, *n*. The simplest form of the reaction order is as whole numbers: 0, 1, and 2. However, it need not be a whole number. Presented below are modifications of Equation 6.1 for three reaction orders.

If $n = 0$:

$$C = C_o - kt \qquad (6.2)$$

The equation states that the amount of reduction remains the same irrespective of the influent concentration for the same *kt*. For the same *kt*, efficiency decreases with increasing influent concentration. Negative effluent values occur mathematically but not in reality. For the desired effluent concentration, *C*, the detention or hydraulic residence time (HRT) to achieve a given efficiency is:

$$H_{RT} = (C_o - C)/k \quad (6.3)$$

If n = 1:

$$C = C_o e^{-kt} \quad (6.4)$$

Where: H_{RT} = hydraulic residence time

The equation states that the efficiency is independent of the initial influent concentration of a pollutant. For a given *kt* the efficiency is the same irrespective of the influent concentration. If several samples were taken along the length of a wet pond or grass swale the concentration would be found to decrease exponentially through the facility, dropping quickly in the front of the facility and decreasing gradually towards the outlet. According to Equation 6.4 the effluent value can never reach zero, which more correctly represents the real world than a zero order reaction. Most mathematical formulations of pollutant reduction in stormwater and wastewater treatment presume a first order reaction. The hydraulic residence time to achieve a given efficiency is:

$$H_{RT} = (\ln C_o/C)/k \quad (6.5)$$

If n = 2:

$$C = C_o(1 - Ckt) \quad (6.6)$$

A reaction order can be greater than one, in which case the mathematical form is complicated by concentration appearing in the reaction rate constant. Equation 6.6 states that reduction is a function of the initial concentration, as well as the final concentration. The hydraulic residence time to achieve a given efficiency is:

$$H_{RT} = \frac{C_o - C}{kCC_o} \quad (6.7)$$

To clarify the different definitions and symbols of time: *t* refers to any point in time through the treatment system; T_n (introduced in Chapter 5) refers to the nominal or theoretical detention without consideration for dead zones and short-circuiting (basin volume/flow rate). Detention time is the same as the hydraulic residence time (HRT), as H_{RT} in the equations. As the latter terminology is the modern form, it is used through the remainder of the book.

The three general reaction orders are represented in Figure 6.1. Removal occurs most rapidly with $n = 0$, and it is possible for the concentration to reach zero. It is possible to reach zero concentration for any value of *n* less than 1. At values of *n* equal to or greater than 1, the removal tapers exponentially, and slows in comparison to the zero order reaction. Theoretically, 100 percent removal or conversion of a constituent never occurs in a finite time.

The order of a reaction may differ depending upon the initial concentration. Most reactions are zero order only when the initial concentration of the pollutant is very high. The reaction order becomes positive ($n \neq 0$) as the concentration is reduced by the reaction. As the concentrations of pollutants in stormwater are commonly low, reactions in stormwater treatment are not likely to be zero order.

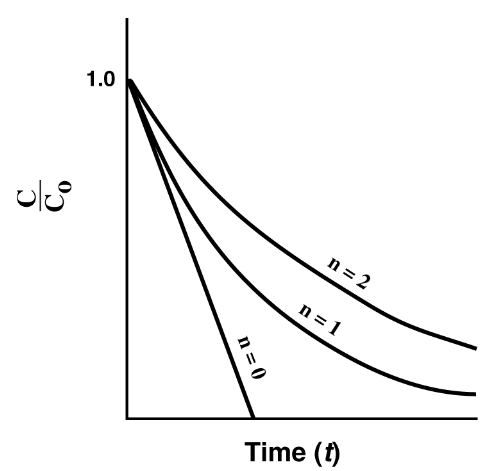

FIGURE 6.1
Reaction order