Introduction

The kinetics of a process are related to temperature through the Arrhenius relationship (Fogler, 2005). For a given catalytic or microbial system, with given chemical components, this relationship is shown in Eq. (1) with the temperature given in Kelvin:

\[ k(T) = A \cdot \exp\left(\frac{-E}{R \cdot T}\right) \]  

(1)

where:
- \( k(T) \) is the rate constant as a function of temperature
- \( A \) is the pre-exponential factor
- \( E \) is the activation energy in J/mol
- \( R \) is the gas constant = 8.314 J/(mol·K)
- \( T \) is the absolute temperature in K

This relationship is sometimes given in the differential form, as shown in Eq. (2):

\[ \frac{d(\ln k)}{dT} = \frac{E}{RT^2} \]  

(2)

The kinetics of the degradation processes occurring within many reacting biological systems, including municipal wastewater treatment (Benefield and Randall, 1980; Crites and Tchobanoglous, 1998; Nitisoravut and Klonjmec, 2005), anaerobic lagoons (Oleszkiewicz and Koziarzki, 1986), facultative lagoons (Mashauri and Kayombo, 2002) and constructed wetlands (Nitisoravut and Klonjmec, 2005), are described using a modified form of this equation (denoted the Modified Arrhenius Function or MAF) given in Eq. (3), with temperature, \( T \), given in degrees Celcius.

\[ k = k_{20} \cdot \theta^{(T-20)} \]  

(3)

The MAF is attractive as an experimental equation because of its ease of use; the temperature is given in degrees Celcius and the temperature correction factor, \( \theta \), is measurable. The derivation of this form of the Arrhenius Equation is based on the assumption that the operating temperature is close to or below 20°C (Derivation Box 1). In countries with hot climates such as South Africa, and especially those with high humidity, where the effect of evaporative cooling is reduced, the MAF may not be applicable and could result in water treatment and other biological systems that do not perform to design specifications.

For the temperature ranges where this assumption may not hold true, a new form of the Arrhenius Equation is proposed here that will not differ significantly from the current form of the MAF at lower temperatures, yet will follow the exponential form of the Arrhenius equation at higher temperatures.

The primary assumption to be considered when using the MAF is that the temperature is not much greater than 20°C. This assumption allows the conversion of an exponential function into a power function, which has different mathematical properties, which are more pronounced with increasing temperature.

Methods and results of the investigation of the non-applicable temperature range of the MAF

To assess applicable and non-applicable temperature ranges for the MAF, we have used \( \theta \) values related to the design of constructed wetlands. For this assessment \( \theta \) has been assigned.
a value of 1.06 as recommended by the IWA Specialist Group on the Use of Macrophytes in Water Pollution Control (Kadlec et al., 2000) and the value of $k_{293}$ is taken as 1.104/day as specified by the US EPA (US EPA, 2000), since the IWA does not recommend one single value. Using these parameters the rate constant can be calculated for a range of temperatures. If the log of Eq. (1) is taken, the following relation can be obtained:

$$\ln(k) = \left( \frac{-\beta}{T} \right) + \alpha$$  \hspace{1cm} (7)

where:

$$\ln(\alpha)$$ is replaced by $\alpha$ and $\frac{E}{R}$ substituted by $\beta$

The value for $k$ was calculated for the temperature range over which the data were most likely collected; i.e., 0°C to 20°C (273K to 293 K) using the MAF, and a plot of $\ln(k)$ vs. $1/T$ is shown in Fig. 1. The points are essentially reproduced data, and these ‘data’ have been regressed (the line through the points) to determine the constants in Eq. (7).

The y-intercept and the x-intercept of this plot correspond to $\alpha$ and $\beta$ in Eq. (7). The twisting of the data around the regressed line is caused by the conversion of data found from a power function being presented as an exponential function.

These calculated values for $\alpha$ and $\beta$ were then used to fit the Arrhenius function given by Eq. (1), such that $A = 8.83 \times 10^9 \frac{mol}{L \cdot sec}$ and $\frac{E}{R} = 4600$. Using these ‘data’, a comparison of the Arrhenius equation and the MAF was performed and the results are presented in Fig. 2.

This analysis indicates that the difference between the 2 forms of rate constant is 7% at 30°C, 15% at 40°C and 25% at 50°C. This difference would become greater at higher temperatures since the exponential law reaches an asymptote at the value for $A$ at infinite temperature, whilst the MAF increases infinitely with increasing temperature. The analysis was halted at 50°C since there are few reacting biological processes that will operate temperatures higher than this (although some bio-metallurgical operations may occur at temperatures higher than 60°C).

**Discussion of the modified Arrhenius equation**

In hot climes and for certain industries (such as distillery effluents) it is possible that the effluent temperature may rise above 30°C and thus the assumptions upon which the MAF is based may not be valid. It is with this in mind that a new functional dependence of $k$ on temperature, given by Eq. (8), is proposed (Derivation Box 2). In this derivation, the values of $k_{293}$ as measured for the MAF will still be valid (shown as $k(293)$). It is, however, a simple modification to change the temperature to °C.

### Derivation Box 2

**Derivation of an Arrhenius equation for use in biological systems**

Starting with Eq. (1):

$$k(T) = A \cdot e^{\frac{E}{R} \cdot \frac{1}{T}}$$  \hspace{1cm} (1)

The rate constant expression can be solved at 20°C (293 K):

$$k(293) = A \cdot e^{\frac{E}{R} \cdot \frac{1}{293}}$$  \hspace{1cm} (7)

This can be solved for $A$, and substituted back into Eq. (1)

$$k(T) = k(293) \cdot e^{\frac{E}{R} \cdot \frac{1}{T}}$$

which can be solved as:

$$k(T) = k(293) \cdot \exp \left( \beta \frac{T - 293}{293 \cdot T} \right)$$  \hspace{1cm} (8)

**Conclusion**

Whilst the MAF is used substantially for the wastewater and other industries (Benefield and Randall, 1980; Haug, 1993;...
Kadlec et al., 2000), and is undoubtedly applicable to cooler and temperate climates, it should be used with caution at higher ambient or reaction temperatures since it may lead to the use of a rate constant which is greater than that which is occurring. At temperatures lower than 20°C it is not important which equation is used, because the rate constants are small and the difference between the 2 functions is negligible. In countries with hot climates, and especially those with high humidity, where the effect of evaporative cooling is reduced, the MAF may not be applicable and could result in systems that do not perform to design specifications. The MAF may also overestimate the rate constant required for designing systems to treat warm effluents, such as distilleries or for use in hot biological reacting systems such as composting or heap leaching. It should also be relatively easy to reassess existing literature to calculate the values for $A$ and $\beta$ and these could be used, with the published values for $k_{20}$ to find the rate constant at any temperature.

References


