

Quantification of the effect of CO₂ transfer on titrimetric techniques used for the study of biological wastewater treatment processes

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Abstract

Titrimetric methods are considered to be useful for the study of biological wastewater treatment processes, particularly those processes that have negligible influence on the dissolved inorganic carbon pool. However, the application of titrimetric methods for studying biological processes that produce/consume carbon dioxide is not straightforward as microbial activity affects the total amount of dissolved inorganic carbon with a proportioned change (determined by pH) in the concentration of every species of inorganic carbon. In this work, the impact of adjustments to the inorganic carbon pool on titrimetric data was assessed by considering a pH-stat titration of heterotrophic carbon oxidation. It was confirmed that at typical operating conditions (pH 7.5 and $K_L a_{CO_2} \approx 22.5 \text{ h}^{-1}$) carbon oxidation causes a marked increase in the rate of carbon dioxide transfer and consequently has impact on titrimetric data. Model simulation was used to quantify the impact for a wide range of operating conditions. It was found that only when a titration is operated at pH > 8 with a $K_L a_{CO_2} < 10 \text{ h}^{-1}$ can the interference that results from action of the bicarbonate system be neglected (< 5% error induced). Outside these operating conditions it is suggested that the interference be accounted for by either measurement or modelling of carbon dioxide transfer.

Keywords: bioprocess monitoring, sensors, titration, gas-liquid mass transfer, hydrogen ion production, aerobic processes

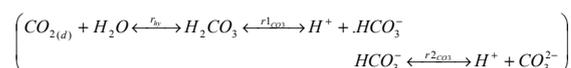
Nomenclature

APE	average percentage error
$K_L a$	mass transfer coefficient
m	fraction of dissociated acid A ⁻ in the liquid phase for a monoprotic acid HA
n	number of protons produced by the carbonate and bicarbonate systems per CO ₂ molecule dissolved
p	fraction of NH ₄ ⁺ among NH ₃ + NH ₄ ⁺ in liquid phase
pK	acid-base dissociation constant; general (pK_a), ammonium (pK_{NH_4}), carbonic acid ($pK_{H_2CO_3}$), bicarbonate (pK_{HCO_3}).
CTR	carbon dioxide transfer rate
CPR	carbon dioxide production rate
HPR	hydrogen ion production rate
Hp	cumulative net hydrogen ion production
H_{CO_2}	Henry's constant for carbon dioxide
OUR	oxygen uptake rate
pHsp	pH set point
r_{NH_4}	rate of dissociation of ammonium
r_{HA}	rate of dissociation of acid
r_{hy}	rate of hydration of carbon dioxide
$r_{CO_3}^1$	rate of dissociation of carbonic acid
$r_{CO_3}^2$	rate of dissociation of bicarbonate
r_{Ac}	rate of removal of acetic acid
r_{NH_3}	rate of removal of NH ₃
R	ideal gas constant

T	temperature
$Y_{H,c}$	biomass yield based on carbon
γ_s	degree of reduction of substrate $CH_f O_z$
γ_x	degree of reduction of biomass $CH_a O_b N_c$

Introduction

Microbial activity has a wide-ranging effect on pH. Invariably, the effect is a consequence of the action of acid-base buffering systems, whereby the biological consumption or production of components of these systems results in a change in hydrogen ion concentration (Pratt et al., 2003). For instance, when ammonia is consumed for biomass growth or oxidised during nitrification then dissociation of ammonium ions occurs, the result being an increase in hydrogen ion concentration; ($NH_4^+ \xrightarrow{r_{NH_4}} NH_3 + H^+$) when volatile fatty acids (VFA) are produced/consumed during anaerobic digestion then acid dissociation/formation results in a change in hydrogen ion concentration ($HA \xrightarrow{r_{HA}} A^- + H^+$); and even when carbon dioxide is produced/consumed during biological activity the carbonic acid concentration is altered, which again results in a change to the hydrogen ion concentration:



The examination of biological processes by the measurement of addition of titrant to counter the aforementioned effects on pH, formally referred to as pH-stat titration (Jacobsen et al., 1957), has been widely reported. A necessary aspect of pH-stat titration is eliminating the contribution to titrimetric data of background physico-chemical processes (Ficara et al., 2003), in particular the contribution, via action of the bicarbonate system,

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Received 21 July 2006; accepted in revised form 10 October 2006.