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Monitoring off-gas O_2/CO_2 to predict nitrification performance in activated sludge processes

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ABSTRACT

Nitrification/denitrification (NDN) processes are the most widely used technique to remove nitrogenous pollutants from municipal wastewater. The performance of nitrogen removal in the NDN process depends on the metabolism of nitrifying bacteria, and is dependent on adequate oxygen supply. Off-gas testing is a convenient and popular method for measuring oxygen transfer efficiency (OTE) under process conditions and can be performed in real-time. Since carbon dioxide is produced by carbonaceous oxidizing organism and not by nitrifiers, it should be possible to use the off-gas carbon dioxide mole fraction to estimate nitrification performance independently of the oxygen uptake rate (OUR) or OTE. This paper used off-gas data with a dynamic model to estimate nitrifying efficiency for various activated sludge process conditions. The relationship among nitrification, oxygen transfer, carbon dioxide production, and pH change was investigated. Experimental results of an online off-gas monitoring for a full-scale treatment plant were used to validate the model. The results showed measurable differences in OUR and carbon dioxide transfer rate (CTR) and the simulations successfully predicted the effluent ammonia by using the measured CO_2 and O_2 contents in off-gas as input signal. Carbon dioxide in the off-gas could be a useful technique to control aeration and to monitor nitrification rate.

1. Introduction

Nitrification/denitrification (NDN) in the activated sludge process (ASP) is the state of the art technique to remove nitrogenous pollutants in municipal wastewater. The activated sludge process consists of many different types of active bacteria, often called "active mass" in structured ASP models (Clifft and Andrews, 1986), which can have a wide range of biodegradation mechanisms for different types of pollutants. Consumption of carbonaceous compounds and denitrification are generally performed by heterotrophic bacteria, and nitrification is performed by autotrophic bacteria. The performance of an ASP is highly dependent on the operating conditions. In aeration basins, many criteria must be carefully maintained to provide a suitable habitat for microorganisms, especially for nitrifiers, such as proper pH, temperature, (Painter, 1970; Painter and Loveless, 1983), adequate solids retention time (SRT, Poduska and Andrews, 1975), and sufficient dissolved oxygen (DO) concentration (Stenstrom and Poduska, 1980).

Nitrification failure can easily occur under low DO conditions, which are controlled by a number of factors, such as oxygen transfer efficiency (OTE) and the overall oxygen uptake rate (OUR, Stenstrom and Song, 1991). The off-gas test described by Redmon et al. (1983) can be used to estimate process water oxygen transfer status for aeration systems

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Nomenclature

CH_xO_y	empirical formula of carbonaceous substrate
CO_2	CO_2 mole fraction in off-gas (mole/L)
CTR	CO_2 transfer rate (kg/day)
CUR	CO_2 uptake rate (kg/day)
H_{CO2}	Henry's constant (mole CO_2/mg $H_2CO_3^*$)
S	carbonaceous substrate (mg/L)
S^∞	saturated dissolved gas concentration (mg/L)
S_O	dissolved oxygen concentration (mg/L)
S_{NH}	ammonia (mg-N/L)
K_1, K_2	CO_2 dissociation constants
K_D	decay coefficient (1/day)
K_S	half-velocity coefficient of substrate (mg/L)
K_N	half-velocity coefficient of nitrification (mg/L)
K_O	half-velocity coefficient of DO (mg/L)
O_2	O_2 mole fraction in off-gas (mole/L)
OTR	oxygen transfer rate (kg/day)
OUR	oxygen uptake rate (kg/day)
Q_g	air flow rate (m^3/day)
Q_l	volumetric flow rate (m^3/day)
V	volume (m^3)
X_H	concentration of heterotrophic bacteria (mg COD/L)
X_I	concentration of inert biomass (mg COD/L)
X_N	concentration of autotrophic bacteria (mg COD/L)
X_{STO}	concentration of stored mass (mg COD/L)
Y	yield coefficient (g COD biomass/g COD substrate)
$\overline{Y}$	molar yield (mole biomass/mole substrate)
$\alpha K_L a$	oxygen transfer coefficient under processing conditions (1/day)
$\alpha K_L a_{CO2}$	CO_2 transfer coefficient under processing conditions (1/day)
δ	storage coefficient
μ_{max}	maximum specific heterotrophic growth rate (g COD/g COD-day)
μ_N	maximum specific autotrophic growth rate (g COD/g N-day)
f_{XI}	fraction inert biomass from decayed cells (g COD/g COD)
$f_{H_2CO_3}$	fraction bicarbonate over total dissolved CO_2
$r_{HCO_3^-}$	transfer rate to bicarbonate (kg/hour)
k_1, k_2	CO_2 transformation kinetics
k_{sto}	specific reaction rate of substrate stored reaction (g COD/g COD-day)

Subscripts or superscripts

C	carbonaceous oxidation reaction
D	cell decay reaction
$H_2CO_3^*$	dissolved carbon dioxide
HCO_3^-	bicarbonate
H,S	direct synthesis of heterotrophic biomass
H,STO	heterotrophic growth on stored mass
IN	influent conditions
O	for dissolved oxygen
N	ammonia oxidation reaction, nitrification
NH	for ammonia
STO	stored mass

(Rosso et al., 2005), and has been widely used to test aeration basins under process conditions (American Society of Civil Engineering, ASCE, 1997). The off-gas analyzer and testing procedure can also be used to measure other gas fractions (nitrogen, carbon dioxide, water vapor, volatile organic chemicals), but it is commonly used to measure only oxygen mole fraction. The CO_2 mole fraction can be easily measured if an additional analyzer, such as a CO_2 absorption tube or infrared sensor is used.

Because the reaction by-products of carbonaceous and nitrogenous compounds are different, the relative amounts of CO_2 produced and oxygen consumed can become the basis for a new method of analyzing nitrification rate: the molar fraction of carbon dioxide in the off-gas should be greater if nitrification is limited, or the fraction of nitrogenous compounds of the total oxygen demand is less.

The main problem of the proposed method is the "supersaturatation" of dissolved carbon dioxide due to change of pH. At normal pH, carbon dioxide concentration in gas phase is a function of dissolved CO_2 concentration, influent alkalinity, and pH. When pH changes, dissolved carbon dioxide acts as a buffer and shifts the fraction between carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-) to consume or release hydrogen ions. Since CO_2 transfer relates to the concentration of carbonic acid, increasing the fraction of bicarbonate creates a supersaturated condition until the dissolved CO_2 can be stripped. Stripping of CO_2 also leads to an increase in pH, which shifts the equilibrium towards bicarbonate and similar to the response of receiving high alkalinity influents. Hellinga et al. (1996) calculated the ratio of carbon dioxide production rate (CPR) and oxygen uptake rate (OUR) for different wastewater compositions. The authors demonstrated that off-gas measurements are useful for evaluating the reactivity of carbonaceous substrate (i.e. COD/TOC ratio), because the changes of CPR are small due the buffering capacity of bicarbonate equilibrium. Similar discussions were also presented by others (Nogita et al., 1982; Minkevich and Neubert, 1985; Spérandio and Paul, 1997).

Experimental and modeling studies have evaluated or simulated the supersaturated conditions of dissolved CO_2 in bioreactors. Pratt et al. (2003, 2004) used a titrimetric technique with off-gas analysis, called on-line titrimetric and off-gas analysis (TOGA), to calculate the effect of changing pH in batch systems. Hydrogen ion production rate (HPR) was measured by monitoring the shift of pH due to *in-situ* titration, and CPR was monitored in the off-gas using a mass spectrometer. By knowing HPR and CPR, the transfer rates of oxygen, nitrogen and carbon dioxide were calculated from stoichiometry. Weissenbacher et al. (2006) proposed a simplified model to take account the effect of pH shift or change in alkalinity to off-gas CO_2 mole fraction. Instead of simulating alkalinity and pH shift, the authors used on-line pH measurements as input signals to experimentally evaluate CPR. This modeling approach is similar to what is used in this paper.

Goals of this paper are to understand the relationships of CO_2 and O_2 in off-gas emissions and to develop a method for estimating nitrification efficiency of a full-scale ASP bioreactor