Comparison and combination of titrimetric and respirometric techniques to estimate nitrification kinetics parameters

Elena Ficara, Andrea Musumeci and Alberto Rozzi*
DIIAR, Department of Hydraulic Environmental Engineering and Survey – Environmental Section
Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milan, Italy

Abstract

A respirometric technique (open respirometry) and a titrimetric technique (pH-stat) were compared to monitor the first nitrification step (ammonia oxidation to nitrite) by providing a titrimetric biosensor (ANITA), previously developed to measure ammonia oxidation kinetics, with an oxygen electrode. Then, a new procedure for the simultaneous estimation of kinetic constants related to both ammonia and nitrite oxidisers which couples both open respiration and titration, is presented. This procedure allows for the complete characterisation of the nitrifying biomass kinetics with simple and short (1 to 1.5 h) tests without any analytical substrate determination. All data handling was implemented on Excel data sheets in order to be able to follow data interpolation step by step instead of using software packages which automatically perform data processing.

Introduction

In order to increase the performance and reliability of biological wastewater treatment plants, effective and fast on-line monitoring is required to promptly identify malfunctioning factors and to upgrade the control level of the overall biodegradation process (Nielsen and Onnerth, 1994). New control technologies, such as biosensors, which enable us to obtain more complete information than conventional physico-chemical sensors, such as DO (dissolved oxygen), pH, ORP meters etc., are being developed in order to attain this goal.

Nitrifying bacteria are considered to be, among the aerobic microbial populations, the most sensitive to inhibition and toxicity effects, especially in activated sludge processes (Dutka et al., 1983; Beg and Hassan, 1987; Blum and Speece, 1991; Kroiss et al., 1992). Nitrification requires the simultaneous presence of two bacterial groups which perform two reactions in series: the oxidation of ammonia to nitrite (brought about by ammonia oxidisers, hereafter referred to as AO) and, subsequently, the oxidation of nitrite to nitrate (carried out by nitrite oxidisers, referred to as NO). Usually, nitrite is overlooked as an intermediate reaction product, and the overall nitrification kinetics are more simply described as the direct oxidation of ammonia to nitrate, using the kinetics parameters of the first reaction. This procedure is followed by several authors, e.g. Henze et al. (1995) in defining the IAWQ model No. 2. This approximation is acceptable if, as it occurs in most practical applications, the rate-limiting step is the first reaction, i.e. the oxidation of ammonia is appreciably slower than the oxidation of nitrite, thus making accumulation of nitrite negligible. However, there are cases in which the kinetics related to the second step are slower than those related to ammonia oxidation and appreciable nitrite concentrations build up (Alleman, 1985; Holiencin and Gujer, 1996; Nowak et al., 1995). Environmental conditions which slow down nitrite oxidation rate include: high temperature levels (Randall and Buth, 1984; Nowak et al., 1995), low DO concentrations associated with high pH values (Yang and Alleman, 1992), high free ammonia concentrations (Suthersan and Ganczarczyk, 1986; Balmelle et al., 1992) and the presence of specific inhibitors to nitrite oxidisers (Hynes and Knowles, 1993). On account of the very low nitrites concentration in final effluents imposed by national regulations (e.g. 0.6 $mg \cdot \ell^{-1}$ NO_2-N in Italy, 1 $mg \cdot \ell^{-1}$ NO_2-N in Switzerland and Austria), it is crucial to detect incoming conditions unfavourable to nitrite oxidation. A model describing the two steps separately was proposed by Nowak et al. (1994). In order to calibrate this model it is necessary to evaluate the kinetic parameters of the two oxidation reactions but, according to the authors' knowledge, this separate determination is seldom carried out.

Biosensors for the estimation of the kinetics of autotrophic bacteria may be classified into two main categories: respirometers and titrimetric systems. Respirometers allow for the measurement of kinetic parameters of heterotrophic and autotrophic populations by processing DO concentration data. These instruments may be further subdivided into closed and open respirometers. Among the former, the NITROX respirometer (Surmacz-Gorska et al. 1995, 1996; Gernaey et al., 1997) was proposed to evaluate the maximum nitrification rate based on the difference between the oxygen uptake rate (OUR) due to the overall heterotrophic and autotrophic populations and the OUR obtained after selective inhibition of ammonia (AO) or nitrite (NO) oxidisers through addition of specific inhibitors (allylthiourea or sodium chlorate respectively). Through this method, the separate determination of the activity related to the two groups of nitrifying bacteria is attained (see also Nowak et al. 1994; Andrews et al., 1980). However, the inhibition step in this procedure requires biomass inactivation and, therefore, a new sludge sample for each test, which may be a drawback in laboratory-scale investigations. Moreover, this method uses inhibitors whose specificity has been questioned (Hynes and Knowles, 1983). Vanrolleghem and Verstraete (1993) have proposed the evaluation of the kinetic constants of both heterotrophic and autotrophic populations in a single test by simultaneously dosing carbonaceous and nitrogenous substrates in the RODTOX apparatus which is an open respirometer (Vandebroek, 1986; Vanrolleghem et al., 1990). From the resulting oxygen profile, which depends on the oxygen diffusing through aeration into the mixed liquor and on

* To whom all correspondence should be addressed.
☎0039–02–23996407; fax 0039–02–23996499;
e-mail: rozzi@amb1.amb.polimi.it
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