

Abstract

The biological treatment of wastewater has evolved significantly from simple single sludge systems practicing organic carbon removal to ones which now include either nitrification/denitrification (N/DN) and / or phosphorus (P) removal. The inclusion of more biological processes have increased the complexity of current wastewater systems which has subsequently led to the development of more complex mathematical models. The operation of plants can be assessed and improved by the use of mathematical modelling tools which require accurate input data. Thus, knowledge of the wastewater characteristics is an important step towards the optimum modelling, design and operation of present and future plants. However, for these tools to be effective, the input data needs to be accurate which is dependent on the current methods used to determine them.

Wastewater is a complex substrate consisting of compounds of differing biodegradability. Biokinetically, these compounds have been divided into readily biodegradable (RBCOD), slowly biodegradable (SBCOD) and unbiodegradable substrate groups. Compounds with intermediate biodegradability i.e. compounds which fall between the RBCOD and SBCOD groups, have been termed readily hydrolyzable organic substrates (RHCOD). The organic matter is discussed in terms of chemical oxygen demand (COD). The readily biodegradable and readily hydrolyzable COD fractions of wastewater can be determined by respirometric tests such as the oxygen utilization rate (OUR) and nitrate-N utilization rate (NUR) tests.

The principal aim of this project was to investigate the NUR test as a tool for wastewater characterization and to study denitrification kinetics in batch reactors. In addition, an experimental readily biodegradable substrate, acetate, was used to determine the reliability of the NUR tests. Acetate was also used to ascertain utilization profiles and rates of a typical readily biodegradable substrate during denitrification. Biodegradable COD characterizations with enhanced biological phosphorus removal (EBPR) sludges were also investigated to determine the impact of anoxic phosphorus removal on NUR tests. The results obtained from the numerous NUR tests added to the understanding of the NUR test.

Samples from 22 wastewater treatment plants were tested, most of which were located in France. Four South African plants were also tested. Data obtained from the NUR tests were used to calculate the RBCOD and RHCOD fractions. The SBCOD, however, could not be determined directly from the 6 h NUR batch tests. The readily biodegradable COD (RBCOD)

fractions ranged between 7 and 25 % of the total COD concentration of raw wastewater, with majority of those results falling within the 10-20 % (of the total COD) range. The results also showed that the initial rapid rate associated with readily biodegradable COD utilization was sometimes followed by a short intermediate phase (*i.e.* short duration, 2 to 3 h). The intermediate fraction was found to range between 5 and 29 % of the total COD concentration and was classed as a readily hydrolyzable COD component of raw wastewater since the magnitude of the RHCOD fraction was too small to be classed as slowly biodegradable COD which comprises approximately 30 to 60 % of the total COD found in raw wastewaters. The variability of the RHCOD fractions suggests that this fraction is either very variable or that the NUR test does adequately or accurately characterize it. Another possibility is that the RHCOD (or second biodegradable fraction) calculated from the NUR test is a component of the RBCOD of the influent wastewater. In this case, the bacteria may have used some of the RBCOD directly for energy and accumulated or stored the rest as part of a survival mechanism which allows them to be more competitive under dynamic operating conditions. Once the readily biodegradable COD becomes limiting, the bacteria will use the accumulated or stored compounds. This hypothesis is substantiated by tests done with acetate as substrate.

An intermediate phase was also observed when acetate was the sole substrate. Thus, it was possible with the 3-phase profiles to calculate a second biodegradable fraction. Results suggest that a significant part of the added acetate (as COD) was stored and the second phase is in fact an 'apparent or residual' phase brought about by the consumption of the stored or accumulated acetate products. This is suggested in two ways : (1) the calculation of the yield coefficient is lower and closer to the 0.5 mg/l values, cited in the literature, when the COD calculated from phases 1 and 2 are considered, and (2) the acetate mass balances were found to be approximately 100 % when phases 1 and 2 were used to calculate the amount of acetate utilized under anoxic conditions.

Several of the NO_x profiles revealed either 2 or 3 rates due to the control of the substrate to biomass ratio ($S/X : \leq 0.1 \text{ mgO}_2 / \text{mgO}_2$). Majority of the samples (*i.e.* 85%) tested produced initial maximum specific denitrification rates (k_1) between 3 and 6 mgN/gVSS.h. The intermediate denitrification rate (k_2) was found to vary between 2 and 3 mgN/gVSS.h. Denitrification rates (k_3) obtained from utilization of influent and endogenous slowly biodegradable COD (SBCOD) varied between 1.0 and 1.5 mgN/gVSS.h. This latter rate is significantly higher than the endogenous denitrification rates cited in the literature. One of the reasons for these higher rates could be linked to the reuse of stored or accumulated products by the microorganisms.

An experimental readily biodegradable organic substrate, sodium acetate, was tested under anoxic conditions. The results were used to formulate several conclusions on acetate utilization during denitrification. Firstly, from acetate mass balances it was found that acetate may be used exclusively for denitrification (100 % acetate was accounted for). In this case, the sludge contains a significant proportion of denitrifiers and little or no polyphosphate accumulating organisms. This observation was made only when non-EBPR (enhanced biological phosphorus removal) sludges were used. Secondly, acetate mass balances which were found to be < 100 % suggest that acetate could be used for denitrification and the production of storage products like polyhydroxyalkanoates (PHA's). These sludges probably contained a higher proportion of polyphosphate accumulating organisms which competed for the available acetate in the bulk liquid. This observation was made for both EBPR and non-EBPR sludges. Thirdly, acetate could be used for denitrification by denitrifiers and for polyhydroxyalkanoate synthesis by denitrifying polyphosphate accumulating organisms. The stored PHA's in the denitrifying polyphosphate accumulating organisms are subsequently utilized during denitrification. This secondary utilization is manifested in the second denitrification phase and is supported by the observation of phosphorus uptake. These results showed that wastewaters high in volatile fatty acids (VFA's) were also subject to denitrifying polyphosphate accumulating organism activity even though the sludge was sampled from non enhanced biological phosphorus removal systems (non EBPR).

In addition, a comparative study on RBCOD determination of wastewaters with enhanced biological phosphorus removal and non-EBPR sludges. It was found that the RBCOD values derived by NUR tests with EBPR sludge were consistently lower (4 to 5 %) than those with non-EBPR sludge. Thus, the NUR tests with EBPR sludge resulted in a 4 to 5 % underestimation of the RBCOD fraction of raw wastewaters. This loss in RBCOD to polyphosphate accumulating organisms appears to be linked to the influent raw wastewater acetate concentration.

These tests showed that the RBCOD fraction could be adequately characterized using the NUR method. The accuracy of the tests appears to be compromised when enhanced biological phosphorus removal sludges are used in the NUR tests. Moreover, it was found that non-EBPR sludges can also consume some of the acetate that is present in the system for the production and replenishment of storage compounds. Fortunately, for the wastewaters tested, the acetate component of the RBCOD fraction was small and therefore, did not significantly affect the results. Mechanisms such as substrate accumulation and storage may also impact on substrate removal and hence, the determination of the readily biodegradable COD concentration of

municipal wastewaters. Thus, while the results showed that the NUR is a useful characterization tool for wastewaters, it will continue to be a more tedious characterization tool than the oxygen utilization rate test, until a suitable nitrate/nitrite electrode is developed to automate the test.