Denitrification Process in Wastewater Effluent to Seawater

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Abstract

Denitrification, the reduction of nitrate ($N03^-$) to nitrite ($N02^-$), and subsequently, to di-nitrogen gas are typically carried out in wastewater treatment processes.

The treatment process can be done in a sequencing batch reactors utilizing a primary wastewater sludge. Process performance kinetic data were analyzed to determine the parameters affecting nitrate removal rates and to apply a kinetic model of the process. three denitrification rates were observed depending on the amount of the organic carbon readily a available for denitrification. The denitrification rates observed were significantly higher than expected than under the low organic carbon concentrations due to the utilization of hydrolyzed particulate carbon and/ or stored carbon.

However, the denitrification rate was not affected by solids retention time (SRT) for high and intermediate organic carbon concentrations.

Introduction

Water is the source of life, and it plays an important role in supporting the life system. Due to increase of industrialization and agricultural activities the overall quality of water is in wane. The water is gradually being contaminated with various pollutants such as inorganic as well as organic nitrogenous compounds originating from agricultural and human activities. The wastewater containing nitrogenous and organic compounds results in eutrophication, biochemical oxygen demand increase and thereby decreases the existence of water bodies.

Due to high solubility of nitrogen compounds in water, it cannot be removed chemically by precipitation. Wastewaters containing nitrogenous compounds are habitually treated bio-chemically by nitrifying as well as denitrifying bacteria [1].

Water consumption and water demand for domestic and industrial needs is constantly increasing. Fresh water is now extensively consumed around the world and people tend to reuse the fresh water from wastewater in order to protect the environment. The waste water emerging out of domestic, food processing, fermentation including sugar mills and poultry usually contaminated with nitrate as well as organic pollutants. These pollutants need to be removed before disposal order to keep ecological equilibrium. Pre-treatment is the treatment of wastewater by commercial and industrial facilities to remove some pollutants before being fed to another system. The system can be as simple as chemical addition or as complex as the integration of multiple unit processes for a complete water treatment system. Normally, pre-treatment of wastewater is used to control and limit the level of certain pollutants in the wastewater. [2].

Biological treatment can be used as pretreatment followed by a physio-chemical process and membrane filtration. Approximately 67% removal of COD was achieved by biological pre-treatment , while the removal of refractory organic compounds was obtained completely by the membrane system [3].

The COD content of some industrial wastewater is very huge, so it should be treated before dumping it to avoid its dangerous impact on the environment. For example, the concentration of organic matter in tannery wastewater is very high with a significant content of ammonium substances, salts as well as Sulphur. Some of the impurities found in the alkaline industrial wastewater can be degraded due to the microbial actions. However, the number of the microbial cells and their growth determine the kinetics and yields of such degradation [4].

Domestic wastewater treatment plants have been traditionally designed to remove suspended solids and to reduce the carbonaceous and nitrogenous materials demand on receiving water bodies. The discharge of oxidized nitrogen (nitrite and nitrate) can, however, have serious public health and ecological problems. High nitrate concentrations in drinking water can cause infant cyanosis, while, nitrosamines, a byproduct of reactions between nitrites and amines, are known to be carcinogenic. Nitrates and nitrites can promote eutrophication of lakes and streams because nitrogen is an essential growth nutrient. To minimize these adverse effects, effluent quality standards have been promulgated necessitating a high degree of oxidized nitrogen removal. Several processes have been developed for oxidized nitrogen removal. The major processes in use on a commercial scale presently are biological denitrification and ion exchange, although reverse osmosis and electrodialysis appear promising especially in the area of drinking water treatment of these processes, biological denitrification has been shown to be the most reliable and cost-effective. Reliability and cost-effectiveness depend mostly on the reactor system selected and the cost and type of the organic carbon source utilized to drive the denitrification reactions. Primary wastewater sludge is an endogenous source of organic carbon that is especially suited for denitrification [5].

The objectives of the present study were to investigate the kinetics of biological elimination of nitrate and nitrite by a pure culture under no carbon source limitation, also to apply a kinetic model that employing data obtained from a lab-scale SBR/denitrification system utilizing primary wastewater sludge. The model can then be used to design SBR/denitrification system and to define the operational characteristics of these systems.

Denitrification by Sequencing Batch Reactors (SBR)

Denitrification kinetics data for this case study are based on the results of important study on sequencing batch reactor that described in more detail elsewhere [5, 6]. There are many treatment systems use sequencing batch reactors (SBRs) that especially suited for carrying out primary sludge hydrolysis and denitrification reactions. SBRs are a modification of the original fill- and- draw activated sludge process. The distinguishing feature of these reactors is the discontinuous (periodic) nature of operation. A treatment sequence consists basically of five operational cycles, namely; fill, react, settle, decant, and idle. This sequential mode of operation makes it possible to regulate all cycles to produce the desired effluent quality; plug or continuous flow regimes can be approximated by adjusting the length of the fill cycle; substrate concentration and sludge characteristics are controlled through adjusting the length of fill, react, mix, and aerate cycles; complete removals can be realized by holding the reactants as long as necessary prior to effluent discharge and through proper adjustment of the degree of mixing, rate of organism wasting, air supply rate, and the length of the fill cycle; substrate concentration and sludge characteristics are controlled through adjusting the length of fill, react, mix, and aerate cycles; complete removals can be realized by holding the reactions as long as necessary prior to effluent discharge and through proper adjustment of the degree of mixing, rate of organism wasting, air supply rate, and the length of each of the operating cycles. Because of this unparalleled flexibility SBR systems have proven superior to traditional systems in many wastewater treatment applications.

Most of the research in this area has been directed toward internal carbon source. SBR operating in mode that will promote carbon storage and subsequent denitrification were studied by Hoepker and Schroeder [6]. The SBR operation by obtaining high nitrate removal efficiencies (90%) using both soluble and particulate wastewater fractions. The applied organic loading and that the denitrification rates obtained using particulate matter were about three times greater than endogenous respiration rates were presented by Miller [7]. Storage product formation (glycogen) accumulation and subsequent utilization for denitrification was demonstrated by alleman [8]. The operational sequence, which consisted of anoxic fill, aerated react for carbon and ammonia oxidation, and anoxic(denitrification) cycles, resulted in nitrogen removal efficiencies greater than 92% with stored carbon. Based on the operational efficiency of denitrification process, organic carbon source, Dissolved Oxygen (DO), hydrogen ion concentration (PH), Temperature, and the presence of promotors or inhibitor substances are the major factors affecting the process.

Denitrification Kinetics

Denitrification process is a complicated one, therefore, an in-depth analysis is required to study the denitrification as well as gas emission rates vis-a`-vis the various parameters. However, this process of denitrification involves emission of N2O which in turn depends on the concentration of nutrients like COD and nitrogen source along with microbial concentration. Denitrification plays an important role in various ecosystems such as wastewater and agricultural activities. Various factors such as oxygen, organic matter, nitrate redox-potential, temperature, and pH plays an important role in determining the denitrification kinetics [1].

For a constant temperature Hoepker et Shroeder . [6] proposed a model to describe the relationship between denitrification rate (r_d) and the limiting substrates (nitrate and organic carbon):

$$r_d = r_{d\,max} * \frac{C_{NO_3^-}}{K_n + C_{NO_3^-}} * \frac{C}{K_C + C} \ldots\ldots\ldots\ldots(1)$$

where:

r_d : rate of denitrification (1/time),

$r_{d\,max}$: maximum rate of denitrification(1/time),

$\boldsymbol{C_{NO_3^-}}$: $Nitrate\ concentration, \left(\frac{mass}{volume}\right),$

K_n : Nitrate half-saturation constant, (mass/volume),

K_C : Organic carbon half-saturation constant, (mass/volume),

C : organic carbon concentration (mass/volume).

For model simplification, zero order of reaction rate was assumed, thus, the mass balance equations for a nitrate-limiting substrate may be stated as follows:

i- Fill cycle:

$$\frac{d(C*V)}{dt} = Q*(C_i - C) + rV \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where:

C : Nitrate concentration, (mass/volume),

C_i : Initial (idle) nitrate concentration, (mass/volume),

Q : Feed flowrate (volume/ time),

V : SBR volume = V_i + Q * t

V_i : Initial (idle) reactor volume,

r : Nitrate conversion rate, (mass/volume-time),

t : Elapsed time.

For a zero order reaction, the conversation rate is proportional to the average organism concentration (X).

The reaction rate :

r = - K * X

where:

K :Reaction Rate constant.

Equation(1) may be reduced to:

$$\frac{dC}{dt} + \frac{Q*C}{V} - \frac{Q*C_i}{V} + K*X = 0 \ldots\ldots\ldots\ldots..(3)$$

ii- React cycle :

during this cycle there is no flow into the reactor (Q=0) and equation (3) reduced to :

$$\frac{dC}{dt} = -K*X \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots\ldots.(4)$$

A general solution for nitrate concentration in SBR during both fill/react and react cycle may be found by solving equation (3) (assuming that organism mass remains relatively constant throughout an operation cycle):

$$C = \frac{(QC_i - KX\ \ V_i)*t}{V_i + Q*t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(5)$$

Reaction kinetics

Kinetic study program consisted of monitoring the variation in concentrations of selected variablesover an operational sequence, namely pH, filterabletotal organic carbon (fTOC), ammonia, nitrate, nitrite, nitrate-nitrogen, mixed liquor suspened ssolids(MLSS), effluent suspended solids. According to the proposed assumptions, the basic operational and kinetic data of the model are shown in Table. 1 and Table. 2.

Table 1. Operational data [5].

Property	Value	Unit
Nitrate feed	2	L/hr
SRT 1	6	Day
SRT 2	12	Day
SRT 3	24	Day
Nitrate feed bottle	4	Litre
Cylindrical reactor	6	Litre
Effluent collection bottle	4	Litre

Table 2. Kinetic constants [5]. .

SRT (day)	**fTOC (mg/L)**	**kinetic constants (day^{-1})**		
		K1	**K2**	**K3**
6	29.6	0.0225	0.0155	0.0017
6	42.3	0.0385	0.0225	0.0017
6	10.7	0.0285	0.0180	0.0011
12	10.6	0.0170	0.0170	0.0008
12	9.7	0.0285	0.0185	0.0012
12	16.2	0.0285	0.0185	0.0017
24	15.4	0.0360	0.0285	0.0010
24	41.8	0.0240	0.0140	0.0010
24	31.9	0.0230	0.0155	0.0009

Analysis of reactor performance data were conducted based on two assumptions nitrate removal rate is zero order with respect to nitrate under the operational condition. The reaction rate id dependent on the organic load (fTOC).

MATLAB program:

MATLAB means a Matrix Laboratory which a generalized mathematical software program with many features such as numerical computations, analysis, visualization a available from Mathworks [9]. As with any software program, there are few ' rules' and 'codes' which must be followed. The structure of MATLAB consists of M-file or command file type, M-file, there are few general statements to be made about M-file or MATLAB code, is a collection of commands that are executed sequentially, commands can be mathematical operation, function call, flow control statement, and calls to the functions or scripts, the execution of m-file program can be controlled from command file windows or other m-file code. There are two types of m-files, functions and scripts. Function has variables that can passed into and out of the function. Any other variables used inside the function are not saved in memory when the execution of function is finished. Scripts on the other hand, save all their variables in the MATLAB work space. Functions and scripts should be nominated. The first line of a function must contain a function declaration, using a following format:

Function [output 1, output 2, ...]= function name(input 1, input 2, ...)

Commented lines immediately following the function declaration and variables nomenclature [10]

Due to the high performance and flexibility of MATLAB program. The developed model was implemented and solved using MATLAB program that constructed based on object oriented programming. The MATLAB code was developed by using scripts and built in functions.

Results and Discussion

In the literature, The organic carbon content of primary sludge is approximately 90 times that of raw wastewater. The organic carbon to nitrogenous matter ratio of primary sludge is very high(approximately 16). Because most of the carbon and nitrogenous matter is in the particulate form, and because the organic carbon release rate from sludge particulate matter is significantly higher than that of nitrogenous matter, less ammonia nitrogen will be introduced into the denitrification system.

The reaction is favored at low O2 concentration as at higher concentration the denitrifies enzymes were deactivated but some of the denitrifies can use $NO3^-$ as well as O2 as electron acceptor [1]. The denitrification process can be considered as a redox reaction. The process forms various intermediates such as nitrite (NO2-), nitric oxide (NO), N2O, and finally N2. In the first step, the NO3- is reduced to NO- by nitrate reductase enzyme (Nar). The NO2- is further reduced to NO by nitrite reductase, followed by further reduction to N2O by nitric oxide reductase. The final conversion of N2O to nitrogen gas is carried out by nitrous oxide reductase. The microbiological species involved in the total process are termed as denitrifies. The notable denitrifies are Pseudomonas, Bacillus, Propionibacterium, etc. The biological species are facultative heterotrophs which utilize nitrate (NO3-) as an electron acceptor instead of oxygen (O2) during respiration [1, 2].

In this work, A typical trend in the time of concentration of Total Organic Carbon, nitrate , and nitrite are shown in figure 1.

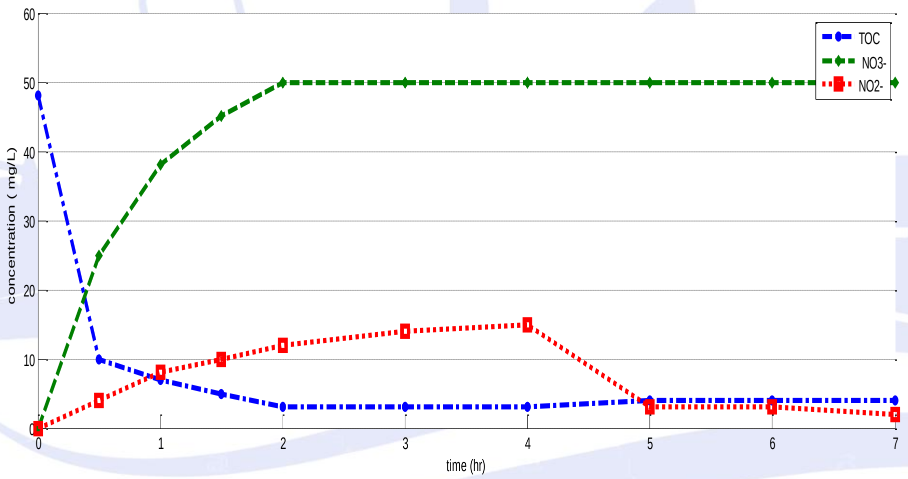

Figure. 1 Concentrations of SBR operational cycles.

it can be seen in figure 1, that the soluble organic carbon concentration decrease rapidly during the fill/ react cycle due to the dilution effects and to the up take by denitrify organisms. However, a minimum level is reached which persists through he react cycle . this concentration may even increase slightly following the disappearance of oxidized nitrogen due to hydrolysis. The persistence is brobably due to the refactory nature of the residual organic carbon and thus its unability for degradation by the organisms. It can be seen also that nitrate is converted to dinitrogen gas. Nitrite accumulate following nitrate conversion, but disappears rapidily after nitrate removal. Nitrate reduction appears to proceed at relatively constant rate during the react cycle.

Conclusions:

primary sewage sludge is an excellent source of organic carbon for denitrification in SBR. High denitrification rates can be obtained with a minimum of ammonia and organic carbon released to the SBR system. The reaction kinetics is zero order for high nitrate concentration and first order for nitrate concentration below 5 mg/L. the denitrification rate is independent of SRT between 6 and 24 daysfor non-carbon limiting condition. Denitrification performance of SBR/primary sludge systems can be reliably predicted using a simple kinetic model adopted to SBR conditions.

Acknowledgment

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