Development of a $NO_3^- - N$ Analyser for Real-Time Nitrate Control in a Pilot Urban Wastewater Treatment Plant

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***Abstract*— This paper reports on the design and construction of a prototype for the measurement of Nitrate-Nitrogen ($NO_3^- - N$) concentration in urban wastewater for real-time nitrate control in treatment plants. The system acquires the sample in an automatic mode and performs the measurement using an ion selective electrode (ISE). Additionaly the equipment has a friendly user interface and can exchange data with a supervisory system, using the MODBUS protocol over a RS-485 interface.**

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I. Introduction

This paper reports on the development of a $NO_3^- - N$ analyser for real-time control in a pilot urban wastewater treatment plant. The measurement of nitrate is particularly important in wastewater treatment plants. High nutrient concentrations can deliver hard contamination in the receiving water bodies. High nitrate levels in drinking water are also a health hazard, particularly in young children. Nowadays, stringent environmental regulations, particularly in Europe, determine accepted levels of nitrate and total nitrogen concentratios after a wastewater treatment process.

Commonly, urban wastewater treatment is performed using biological means, mainly activated sludge.

II. Generalities of Activated Sludge Wastewater Treatment

Modern activated sludge WWTP are normally composed of the following treatment stages [1],

A. Preliminary treatment

Initially, the waste-water enters the treatment plant and passes through mechanical screens to remove coarse material and solid debris. Grit removal by sedimentation or flocculation reduces potentially damaging large and heavy particles such as sand and gravel, for example. Other preliminary treatment operations include grease removal and flow equalisation. In general, preliminary treatment is a pre-treatment stage that ensures the wastewater passing to the subsequent stages is free from material that could disrupt the plant operation.

B. Primary treatment

Organic material is partially removed by passing the wastewater through primary sedimentation tanks or primary clarifiers. Sedimentation occurs when solids that have a higher specific gravity than the liquid settle to the base of the tank, where the settled solids are removed for sludge treatment. Design of the clarifiers must account for the flow velocity and load. If the velocity of the flow is too high, the solids retention time (SRT) will be less than desirable, resulting in excess solids passing to the secondary treatment phase and exerting an increased demand on the process. Typically, 30-40% of the influent biological oxygen demand (BOD_5) and 60-75% of the influent suspended solids (SS) is removed prior to secondary treatment, [2].

C. Secondary treatment

The driving process of wastewater treatment occurs in the secondary treatment stage. The major biological unit operations are implemented to provide removal of organic waste and nutrients. The three biological processes that can be employed during this phase are:

Aerobic processes*:* Aeration of the wastewater results in oxidation of the carbonaceous and nutrient material (substrate) by chemical reactions initiated when the biomass utilise these components for biological growth. The carbonaceous material is oxidised to CO_2 and the nutrients to more benign forms of the compound. The chemical expressions for oxidisation of organic matter by

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micro-organisms, with (1) and without (2) nitrification, are presented as follows, [3]:

$$C_{18}H_{19}O_9N + 19.5O_2 \rightarrow 18CO_2 + 9H_2O + H^+ + NO_3^- \quad (1)$$

$$C_{18}H_{19}O_9N + 17.5O_2 + H^+ \rightarrow 18CO_2 + 8H_2O + NH_4^+ \quad (2)$$

Anaerobic processes*:* In the absence of free oxygen or nitrate, micro-organisms breakdown the complex organic material by hydrolysis to smaller molecules. Acid-forming bacteria break these fat, protein and carbohydrate molecules into long-chained fatty acids and amino acid, amongst others. The products of this process are acetic acid, formic acid, ethanol and methanol, which are further broken down into hydrogen, carbon dioxide (CO_2) and methane (CH_4). This process requires a number of different types of bacteria to perform the different degradation stages, all of which are sensitive to factors such as pH, temperature, toxicity or even the presence of oxygen. Hence, design of anaerobic treatment processes requires careful selection of conditions to enable the appropriate operational performance. One benefit of anaerobic digestion is the production of biogas (CH_4), which can be used as a source of energy, on-site or supplied to the national electricity grid, if the quantity is large.

Anoxic processes*:* In anoxic conditions, free oxygen is absent, but nitrate is present, providing a source of oxygen for denitrifying bacteria. The process of denitrification may be written as, [1]:

$$6NO_3^- + 5CH_3OH \rightarrow 5CO_2 + 3N_2 + 7H_2O + 6OH^- \quad (3)$$

The principle of the activated sludge plant is that mass flow of wastewater is in kept in continuous motion through the plant by gravity, pumping, mixing and aeration. In this way, treatment is performed in an effective and controllable manner. However, it is necessary to maintain the biology in the secondary phase long enough for biomass growth through contact with the substrate and the subsequent associated reactions. The length of time, or mean cell residence time, that the biomass remains in the secondary treatment stage is known as the sludge age. The hydraulic retention time (HRT) and sludge age must be balanced so that the process kinetics can take place. An internal nitrate recycle may also be used in secondary treatment to supplement the nitrate concentration in the anoxic zone. Typically, the anoxic (denitrification) zone is situated prior to the aeration (nitrification) tank and the internal nitrate recycle is a loop between the end of the aeration tank and the inlet to the anoxic zone. However, it is possible to have different configurations based on the design criteria and treatment objective.

Most of the control priorities are centred in the secondary treatment, which is where most of the biological treatment occurs. The secondary treatment is as well the most sensitive part of the treatment process. As discussed before, the main objective in the secondary treatment is to keep an acceptable concentration of suspended solids in the wastewater, thus controlling nitrification and denitrification, therefore the importance of nitrate measurement.

III. Nitrate Measurement

One of the main limiting factors for the implementation of any control technology is the availability of accurate on-line sensors. Sensor technology for bioprocesses have evolved considerably in the past few years, therefore providing a wider scope of on-line measurements. The instruments employed in wastewater treatment systems are many and varied. Table (I) summarises some of the most useful variables and the type of sensors employed to measure them [1], [4].

Another limiting factor for control implementation is the number of available control handles. Unfortunately, wastewater treatment plants have a very limited number of control handles which are driven by actuators. Figure (1) presents a sensor and actuator distribution in a generalised WWTP, according to the processes and control loops.

As shown in Figure (1), nitrification and denitrifcation processes have time constants in the order of hours. Generally, measurements of ammonia and nitrate have sampling periods or 10 to 15 minutes. Usually there is no need for faster sampling rates. Faster sampling rates would be expensive due to the unnecessary use of consumable chemicals.

A. Analyser Development

The nitrate analyser reported in this paper recovers a sample taken directly from the flow line and performs a nitrate quantification employing an ion-selective method using an electrode. The concentration of nitrate is expressed throughout this paper in units of mg $NO_3^- - N$

TABLE I
SENSORS

Variable	Sensor
Level	Bubblers
	Sonic, ultrasonic and microwave
	Capacitance and impedance probes
	Floar level isntruments
Flow	Weirs
	Parshall flume
	Magnetic meters
	Sonic meters
	Turbine meters
	Venturi tubes and flow tubes
	Vortex shedding
Bio-chemical char.	DO sensors
	pH sensors
	Suspended solids sensors
	Turbidity sensors
	Ammonia analyser $\left(NH_4^- - N\right)$
	Nitrate analyser $\left(NO_3^- - N\right)$
	Phosphate analyser $\left(PO_4^-\right)$
	Chemical Oxygen Demand (COD) sensor

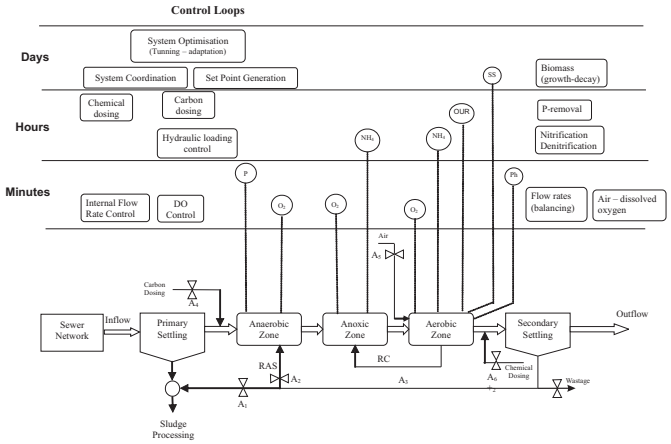

Fig. 1. Sensor and actuator distribution according to processes and control loop.

/L. The unit, $NO_3^- - N$, means nitrogen that is in the form of nitrate. Ion-selective electrodes are a subset of potentiometric methods which respond selectively to a single species. The selective response can be generated by using a membrane which allows the ion of interest to pass through but blocks other ions. In general, activity differences across the membrane of the electrode generate a potential difference across that membrane which can in turn be used to quantify the ion under investigation. Utilising microprocessor-based electronics, advanced features, such as automatic two-point calibration, assessment of the sensor performance have a friendly interface for the user and can exchange data with a supervisory system, using a MODBUS protocol over a RS-485 platform.

B. Ion-Selective-Electrode Method

Determination of nitrate is difficult because of the reactively complex procedures required, the high probability that interfering constituents will be present, and the limited concentration ranges of the various techniques. This section discusses the potentiometric determination of nitrate in aqueous samples with ion-selective electrode.

Many recent developments in analytical measurement are based on methods utilising ion selective electrodes. This method can be used to measure the total solubilised nitrate in drinking waters, natural surface waters, groundwaters, domestic and industrial wastewaters in a fast, simple, accurate, and economical manner.

The electrode has a detection limit from 0.1 to 1,000 mg/L. It is important considerer that ISEs must be used carefully, and results must be interpreted cautiously, since an ISE may be affected by numerous analytical interferences which may either increase or decrease the apparent analyte concentration, or which may damage the ISE. Effects of most interferences can be minimized or eliminated by adding appropriate chemical reagents to the sample (BUFFER). Obtaining the most accurate results, therefore, requires some knowledge of the sample composition. Although the electrodes function satisfactorily in buffers with a pH range from 3 to 9, erratic responses have been noted where pH in not held constant.

The ISE develops a potential across a thin, porous, inert membrane that holds in place a water-immiscible liquid ion exchanger. The electrode responds to Nitrate ($NO_3^- - N$) ion, but it can also respond to numerous interfering anions. The potential developed, is a function of the ionic activity of a species in solution. When the electrode potential of an electrode is measured against a suitable reference electrode, its relationship to ionic activity is logarithmic. The mathematical expression which relates the potential difference across the membrane to the difference in activity is Nernst Equation, which is presented in equation (4) in its reduced form.

$$E = E_o + m\ln(a) \quad (4)$$

Where, E is the measured voltage; E_o is the standard potential for thecombination of the two half cells; m is a constant; and $\ln(a)$ is the natural logarithm of the activity.

IV. Design and Construction

This section presents the design and construction of the Nitrate analyser. The prototype is composed of two parts: hardware and software. Hardware devices are: rollers pumps, mixer, and a microprocessor unit. The software has been programmed using BASCOM AVR.

The prototype turns on pumps, activates the electrode and take measures. The software employs this measures and applies the Nersnt Equation to calculate the actual Nitrate concentration, then match this concentration with a time register and store the complete information in the microprocessor EEPROM Memory.

Communications are performed employing the MODBUS protocol. MODBUS is probably the most widely used serial protocol in industry. Most devices, are capable of communicating serial and talk MODBUS. The embedded communication interface runs in full duplex mode.

Modbus communication is based on a master and a slave arrangement. The master sends a message to one slave at a time and waits for a reply. The slave cannot accept a new message until the existing message is processed and a reply sent to the master (maximum response time 250 milliseconds). The slave monitors the elapsed time between receipt of characters. If the elapsed time without a new character is 31/2 character times, the slave assumes the next character received is the start of a new message. To allow the master to differentiate between more than one slave in a system, each slave is given a unique identity address (between 1 and 99). A broadcast address (address zero) can be used to access all slave devices with one command. This is limited to write messages only and there is no slave acknowledgment.

This prototype supports two functions from the MODBUS protocol: (i) Read Coils; and (ii) Holding Registers.

The systems is also equiped with a Real-Time clock which provides each measurement a Time and Date registry.

V. Experimental results

Several experimental results have been performed over the analyser in order to obtain estimates of repetibility and reproducibility. A total of 30 tests where performed with two operators. Results are presented in Table (II) and Table (III).

TABLE II
STATISTICAL RESULTS

Std. Con. (mg/L)	Mean	Standard Dev.	Precision
1	1.383	0.029	0.018
10	12.993	0.404	0.250
50	48.165	1.151	0.713

TABLE III
REPETIBILITY AND REPRODUCIBILITY

Repetibility	**2.62 %**
Reproducibility	**1.88 %**

VI. Conclusions and Further Work

This paper has presented the development of a nitrate analyser for real-time control for a pilot activated sludge wastwater plant. the nalyser has been implemented using an ion-selective-electrode (ISE), and performs measurements every 15 minutes. The range of the analyser is from 0.2 mg/L to 30 mg/L with acceptable error margins.

The consumption of chemical is of 10 ml per sample. The system is also capable of connecting to a MODBUS industrial network via RS485, and provide time and date stamps of each measurement.

The module provides an alternative for experimental research in pilot wastewater treatment plants, with realiable characteristics for control purposes.

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