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Real-time control strategy for nitrogen removal via nitrite in a SHARON reactor using pH and ORP sensors

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Abstract

This paper presents a real-time control strategy for nitrogen removal via nitrite in a continuous flow SHARON reactor using on-line available and industrially feasible sensors (pH and ORP). The developed control strategy optimizes the length of aerobic and anoxic phases as well as the external carbon source addition. This strategy, implemented in a laboratory-scale SHARON reactor fed with synthetic wastewater and real dewatering sludge supernatant, was able to cope with step variations in influent flow rate and ammonium concentration. The main advantages of this control strategy over the traditional operation mode with fixed carbon source dosification and fixed length cycle operation were: better effluent quality (ammonia concentration decreased from 12 to 2 mg NH_4-N L^{-1} and nitrogen removal efficiency raised from 95% to 98%) as result of the shorter cycle length: 2.9 hours versus 4.0 hours, and savings in external carbon addition: 1332 mg COD L^{-1} versus 2100 mg COD L^{-1}.

Keywords fuzzy logic; nitrogen removal via nitrite; ORP; pH; SHARON.

1. INTRODUCTION

Biological nitrogen removal via nitrite has become an attractive and suitable alternative to treat wastewater streams with high ammonium concentration since aeration costs and organic carbon demand are reduced in comparison with nitrogen removal via nitrate [1]. The nitrite route is accomplished when the ammonium oxidizing bacteria (AOB) are maintained in the activated sludge, while the nitrite oxidizing bacteria (NOB) are washed out. Therefore, ammonium is oxidized to nitrite by nitritation process, and subsequently it is reduced to nitrogen gas by denitritation process. The SHARON process (Single reactor High Activity ammonium Removal over Nitrite) is a well-known industrial application of this technology [2]. This process is usually operated in a continuous stirred tank reactor (CSTR) without biomass retention [3], where aerated and non-aerated periods are alternated to reach nitritation and denitritation processes, respectively. In aerobic conditions, the pH undergoes variations as a consequence of nitritation and dioxide carbon stripping processes. During nitritation, the pH decreases as two moles of protons ($2H^+$) are produced per mole of ammonium converted (Eq. 1). In anoxic conditions pH increases due to the denitritation process, where 1 mole of H^+ is neutralized per mole of NO_2^- reduced (Eq. 2).

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+ \qquad \text{Eq. 1}$$

$$NO_2^- + 0.5CH_3OH + H^+ \rightarrow 0.5N_2 + 0.5CO_2 + 1.5H_2O \qquad \text{Eq. 2}$$

The SHARON process is usually applied to the supernatant from anaerobically digested sludge. Due to the low organic matter concentration in this stream, an external organic carbon source must be supplied during the anoxic phases for the denitritation process, avoiding low pH values as a result of alkalinity recovery. Methanol is the organic carbon source most frequently used.

On-line nitrogen analysers could be used for process control and optimization. However, practical experience using nitrogen analysers in full-scale applications has shown that their maintenance, calibration and operation are time-consuming and require considerable economic resources [4]. In contrast, other on-line available and industrially feasible but low-cost sensors, like pH and ORP offer an attractive alternative to nutrient analysers for process control and optimization. The pH and ORP measurements could be related to biological processes such as organic matter degradation, nitrification and denitrification [5,6]. Real-time control strategies for biological nitrogen removal processes using pH and ORP sensors have been developed and tested in sequential batch reactors, where the changes in the pH and ORP profiles are more evident than in continuous flow reactors [7-10]. However, there are only a few practical experiences on the development, application and validation of this sort of controllers on continuous processes [11,12]. In this study, a real-time control strategy based on pH and ORP sensors has been developed and validated for the biological nitrogen removal via nitrite in a laboratory scale continuous flow SHARON reactor. The length of the aerobic and anoxic phases was automatically adjusted and the external carbon source addition was optimized by means of a fuzzy logic-based controller.

2. MATERIALS AND METHODS

2.1 Experimental set-up and process operation

A laboratory-scale reactor with a working volume of 7 L has been operated as a continuous stirred tank reactor (CSTR), under aerobic and anoxic conditions. The system was equipped with a mechanical stirrer set to ensure good sludge mixing and the temperature was controlled at 35 ºC by means of a thermostated water bath. Air supply was provided by an air sparge system. An on-off controller was installed to keep the dissolved oxygen (DO) concentration at 3.5 mg O_2 L^{-1}. Methanol was added as an external carbon source at the beginning of each anoxic phase. High precision dosification unit (Liquino 711, Metrohm) was used for methanol dosage. The pH (SP10B, Consort), temperature (ST10N, Consort), ORP (SP50X, Consort), conductivity (SK10B, Consort) and DO (CellOx 325, WTW) probes were connected to a multi-channel analyser (Consort C832) and an oxymeter (Oxi340 WTW), respectively. These devices were in turn connected via RS232 to a PC with Visual Basic 6.0 software for data monitoring and storage (every 30 seconds).

2.2. Influent wastewater composition

The reactor was initially fed with synthetic wastewater whose composition emulated the reject water from the dewatering facilities of anaerobically digested sludge. The concentrations of ammonium and alkalinity were modified according to each experimental stage, maintaining the molar alkalinity/ammonium ratio close to 1 (typical ratio in supernatant liquors from anaerobically digested sludges). Finally, in order to assess the performance of the real-time control strategy proposed, the SHARON reactor was fed with supernatant from the dewatering facilities of anaerobically digested sludge from the Carraixet urban WWTP (Valencia, Spain). The composition of the synthetic influent wastewater and real supernatant are listed in Table 1.

2.3 Analytical Methods

Process performance was characterized by measurements of ammonium, nitrite, nitrate and alkalinity at the end of aerobic and anoxic phases and in daily composite samples collected and preserved at 4 ºC. Twice a week total suspended solids (TSS), volatile suspended solids (VSS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were determined. Nitrogen compounds were analysed by colorimetric methods and TSS, VSS, COD, BOD were determined according to Standard Methods [13]. Alkalinity was measured following the method proposed by Moosbrugger *et al.* [14].

3. REAL-TIME CONTROL STRATEGY

The proposed real-time control strategy was designed using the information provided by previous operation and monitoring results [15]. The aims of this control strategy were: the automatic adjustment of the length of aerobic and anoxic phases and the optimization of external carbon source dosage at the beginning of anoxic phases.

3.1 Optimization of the length of aerobic and anoxic phases

Aerobic phase: The control strategy finishes the aerobic phase when at least one of the following conditions are accomplished: a) pH value is lower than 6, b) the length of the phase is longer than 4 hours, c) smoothed moving pH slope is higher than -0.5. During aerobic phases the oxidation of both ammonium accumulated in the previous anoxic phase and ammonium continuously entering with the influent takes place. When the accumulated ammonium is consumed the nitritation rate decreased significantly and the aerobic phase should finish. The pH decrease rate is used to decide the end of the aerobic phase since a similar trend is followed by both pH and ammonium concentration (Figure 1a). The pH decrease rate has been calculated by means of a smoothed moving pH slope using a sample size of 15 consecutive data since noticeable oscillations were observed in the non-smoothed moving pH slope (Figure 1b).

Anoxic phase: The control strategy finishes the anoxic phase when at least one of the following conditions are accomplished: a) pH value is higher than 8.5, b) the length of the phase is longer than 4 hours, c) moving pH slope reaches zero. During anoxic phase denitritation process takes place while ammonium present in the influent wastewater accumulates in the reactor since it cannot be oxidized to nitrite. Denitritation process ends when either organic carbon or nitrite is exhausted and anoxic phase should be stopped at this moment avoiding unnecessary ammonium accumulation. Note in Figure 1a that nitrite was exhausted around minute 150 while ammonium concentration continues rising until the end of the phase. Figure 1a also shows that pH increases during the denitritation process; afterwards, pH remains constant. Therefore, when pH gets constant anoxic phase should finish. The end of the anoxic phase is determined when pH_{MS} is zero (Figure 1b).

3.2 Optimization of organic matter dosage

The control strategy optimizes the methanol dosage by adding the amount required to remove the nitrite produced in the previous aerobic phase. Excessive carbon source addition can be detected by the presence of bending points in the ORP profile at the beginning of the following aerobic phase [15] (Figure 1c). Deficient carbon source addition leads to incomplete denitritation that can be detected by: a) ΔpH aerobic higher than ΔpH anoxic [15] b) the ORP value at the end of the anoxic stage [11, 16,17].

A fuzzy logic controller has been developed using the following four input variables (Figure 1c):

- *tbpORP*: The time when the bending point in the ORP profile occurs. The latter the bending point occurs the more methanol has been added in excess in the previous anoxic phase. The tbpORP is established at the time when the ratio between the current moving ORP slope (ORP_{MS}) and the prior ORP_{MS} is higher than 1.05.
- $\Delta tbpORP$: the difference between the tbpORP in the current cycle and the tbpORP in the previous cycle.
- ΔpH: the difference between $\Delta pH_{aerobic}$ and ΔpH_{anoxic}. As it was previously commented, when ΔpH is positive incomplete denitritation takes place due to organic matter shortage.
- ORP_{endAX}: the ORP value recorded at the end of the anoxic phase.

In the fuzzification step Gaussian-type membership functions were used to convert the aforementioned input variables into linguistic variables. Figure 2a shows the membership function for the *tbpORP* variable. The fuzzy inference engine was applied using the max-prod method [18]. Thus, for each one of the 16 rules defined in Figure 2b, the following operator was applied: ($\mu_{rule,i} = \Pi_i^j \mu_j$) where μ_j represents the membership degree to each of the input fuzzy sets involved in the rule i. To establish only one output linguistic value when the consequences of different rules are the same, the following operator was applied: ($\mu_{ki} = Max(\mu_{rule,i})$) where μ_{ki} represents the membership degree to each of the output fuzzy sets. To convert the linguistic variables in the corresponding numerical control actions, the mean defuzzifier method was employed applying the following equation: $\left(\Delta Vd = \frac{\sum_{i=1}^{n} c_i \cdot \mu(ki)}{\sum_{i=1}^{n} \mu(ki)}\right)$ where c_i are the singletons. The output variable (ΔVd) is the increment of the methanol dosage respect to the previous cycle dosage.

4. RESULTS AND DISCUSSION

The lab-scale SHARON reactor operation was divided into nine stages (Table 2) in order to evaluate the developed control strategy under different operating conditions. Figure 3a shows the evolution of nitrogen compounds along the whole experimental period. As can be seen in this figure, nitrogen removal via nitrite was successfully and stably achieved in all the stages. Effluent nitrate concentrations were usually below 1 mg NO_3-N L^{-1}. Higher nitrate concentrations were transiently observed in stages VII and IX when influent nitrogen load was purposely increased. As it will be described later, the control system quickly reduced nitrate production.

4.1 Control system start-up (stages I and II)

During stage I, the SHARON process was operated with fixed phase length: 2 hours in aerobic conditions and 2 hours in anoxic conditions (4 hours per cycle). Along this stage the effluent ammonium concentrations were relatively stable below 15 mg N L^{-1} (Figure 3a). The average nitrogen removal efficiency was close to 95%. After implementing the control strategy (stage II), the effluent ammonium concentration slightly increased while nitrite concentration rose notably, even nitrate concentration reached a value close to 10 mg NO_3-N L^{-1}. To reduce the amount of nitrite and nitrate accumulated, the ORP_{endAX} was included as a controller input variable (day 56) and the set of rules was modified, leading to a reduction in effluent nitrite and nitrate concentrations. The control system optimized the length of the aerobic and anoxic phases. The average cycle length was shortened from 4 hours to 2.9 hours: 2 hours in aerobic conditions (69%) and 0.9 hours in anoxic conditions (31%), effluent ammonium concentrations decreased (from 12 to 2 mg NH_4-N L^{-1}) and nitrogen removal efficiency increased (from 95% to over 98%). Moreover, savings in organic matter supplies close to 36% were achieved (from 2100 mg COD d^{-1} in stage I to 1332 mg COD d^{-1} in stage II).

4.2. Control system performance under variable influent flow rate (stages III-IV)

In stage III the control system was evaluated under variable influent flow rate (Table 2). In stage IV the control system was switched off, and the process was operated with fixed-length phases and constant methanol dosage using the average values obtained in stage III. As can be seen in Figure 3a, ammonium and nitrite concentrations rose at the beginning of stage III as a consequence of the influent flow dynamic pattern. After a few days, low ammonium concentrations were reached due to the control system performance. The defuzzification parameters were modified in order to get a faster nitrite concentration decrease. After this control system fine-tuning, nitrogen removal efficiency was close to 98%. The length of the phases followed a similar pattern to the influent load variation, the higher the influent load the longer the length of both aerobic and anoxic phases (data not shown). Likewise, methanol dosage was automatically modified according to nitrite production.

Nitrogen removal efficiency in stage IV was similar to that obtained in stage III (around 98%). The main difference between the results obtained in both stages was the increase observed in nitrate concentration from day 134, reaching a nitrite:nitrate ratio close to 1. This nitrate accumulation can be attributed to excessive aerobic phase duration during the low loading periods. Excessive aeration must be avoided in order to prevent nitrite oxidation [10].

4.3 Control system performance under step variations of influent ammonium concentrations (stages V-VIII)

In stage V the control system was switched on again, and the effluent nitrate concentrations decreased to negligible values (Figure 3a). In stage VI, the influent ammonium concentration was increased from 400 to 450 mg NH_4-N L^{-1}, and the control system performance allowed maintaining similar nitrogen removal efficiencies (around 98%). The biomass concentration in stage VI was not able to remove the high influent ammonium concentration tested in stage VII (550 mg NH_4^+-N L^{-1}), leading to an ammonium accumulation in the SHARON reactor (up to 14 mg NH_4-N L^{-1}). The control system increased the duration of aerobic phases to enhance the growth of AOB. This increase in the length of aerobic phases resulted in an accumulation of nitrite and nitrate (up to 32 mg NO_2-N $L^{-1}$and 15 mg NO_3-N L^{-1}, respectively). The methanol dosage increase together with the reduction of aerobic phases commanded by the control system when microorganism population in the reactor was enough to cope with the influent nitrogen load, led to an improvement in nitrogen removal efficiency (close to 98%) and negligible nitrate production. Finally, in stage VIII the influent ammonium concentration was decreased to 350 mg NH_4^+-N L^{-1}, and the control system shortened the aerobic phases and decreased the methanol dosage. As can be seen in Figure 3a, the removal efficiency along the whole stage VIII was around 98%. During these stages the control system actions resulted in the following relationship: the higher the influent nitrogen load the longer the aerobic and anoxic phase lengths and the more methanol was dosed (data not shown).

4.4. Control system performance using supernatant from a full-scale WWTP (stage IX)

From the beginning of this stage, the flow rate was increased from 1 L d^{-1} to 2 L d^{-1}. This flow rate increase jointly with the sudden increase in the supernatant ammonium concentration (up to 700 mg NH_4- N L^{-1}around day 245) led to an ammonium accumulation in the reactor up to 87 mg NH_4- N $L^{-1.}$ The control system performance was similar to that observed in stage VII. The duration of aerobic phases was enlarged to enhance the growth of AOB resulting in an accumulation of nitrite and nitrate (up to 32 mg NO_2-N L^{-1} and 30 mg NO_3-N L^{-1}, respectively). As complete nitrite removal was not achieved, the methanol dosage was increased. When accumulated ammonium and nitrite were removed, methanol dosage as well as aerobic and anoxic phase lengths were sharply reduced. As can be seen in Figure 3b, complete nitrite removal was achieved at the end of the anoxic phase of cycle 4, since the ORP value at the end of the anoxic phase of this cycle was quite lower than in the previous cycles (from -105mV to -160mV). From cycle 4 to 13, a series of bending points can be observed in the ORP profile indicating that organic matter was added in excess. These bending points are progressively less pronounced because the control system reduced the methanol dosage from 160 mg COD L^{-1} to 60 mg COD L^{-1}.

5. CONCLUSIONS

The main conclusions drawn from this study are:

- pH and ORP on-line measurements have proven to be very useful tools for real-time process control in a continuous flow SHARON reactor.
- The implementation of the developed real-time control system, allowed optimizing the length of aerobic and anoxic phases as well as the methanol added in each cycle.
- Compared with the traditional operation with fixed carbon source dosification and fixed length cycle operation, the developed control system exhibited the following advantages: better effluent quality (ammonia concentration decreased from 12 to 2 mg NH4-N L^{-1} and nitrogen removal efficiency raised from 95% to 98%) as result of the shorter cycle length (2.9 versus 4.0 hours), up to 36% savings in external carbon addition (1332 mg COD L^{-1} versus 2100 mg COD L^{-1}), and flexibility to automatically adapt the operational conditions to the typical fluctuations of flow rate and composition in the supernatant of the anaerobically digested sludge.
- The control system performance was able to cope with step-variations in flow-rate and ammonium concentration, and the variations observed in supernatant from the full-scale Carraixet WWTP dewatering facilities.

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Figure 1. a) pH profile evolution and nitrogen compounds concentrations along one cycle of operation with fixed phase length (stage I) .b) Evolution of the pH moving slope (pH_{MS}) and the average value of pH moving slope (pH_{AMS}) in the same cycle of operation. c) Illustration of how the input variables to the fuzzy logic controller are calculated from pH and ORP profiles during two consecutive cycles.

Figure 2. a) Membership functions for the tbpORP, b) Fuzzy control rules for the methanol addition controller.

Figure 3. a) Evolution of nitrogen compounds during the whole experimental period. b) pH and ORP profiles, and methanol dosed throughout days 264 and 265 of operation (cycles 1 to 17) when accumulated ammonium and nitrite were completely removed. Arrows indicate bending points in the ORP profile.