Keeping track of pH sensors in biological wastewater treatment systems

Kito Ohmura1,2, Christian Thürlimann1, Marco Kipf1, Kris Villez1,*
1 Eawag, Department Process Engineering, Dübendorf, Switzerland
2 Toshiba Corporation, Tokyo, Japan
* Corresponding author, email: kris.villez@eawag.ch

ABSTRACT
In the wastewater sector, water quality sensors constitute the most sensitive component to online monitoring and control systems. Consequently, the purported benefits of automation remain an elusive goal in many situations. This is especially true for decentralized wastewater resource recovery facilities (WRRFs) as studied in this work. Indeed, the use of frequent on-site sensor inspection and maintenance is typically economically prohibitive. For this reason, a tremendous amount of research has focused on the development of specialized algorithms for fault detection, isolation, and diagnosis. Such algorithms typically assume (i) that some historical normal data are available for algorithm tuning and (ii) that faults generally do not appear simultaneously in multiple sensors. In this work, we challenge these assumptions by means of a long-term study of wear-and-tear in pH sensors exposed to nitrified urine, a high-strength anthropogenic wastewater. Our results indicate that both assumptions are invalid, thereby preventing an effective use of the majority of fault detection algorithms available today.

KEYWORDS
Instrumentation, control, Ion-selective sensors, Process monitoring, Resource recovery

INTRODUCTION & BACKGROUND
By several accounts, sensors constitute the most sensitive component in advanced control systems for wastewater resource recovery facilities (WRRFs). For this reason, characterizing typical sources of measurement errors and other sources of uncertainty has been identified as an important and challenging endeavor1–2. To answer this need, a wealth of fault detection, fault isolation, and fault diagnosis methods have been developed to facilitate the identification and possibly even reconcile erroneous data3–4. Most of the methods available today are based on the following two assumptions:

1. Gross errors, i.e. systematic deviations, never appear simultaneously in multiple sensors at once.
2. Upon first-time use, a given sensor will function without any gross error for a while.

These assumptions are indeed very useful. For example, by placing 3 or more redundant sensors in a single location, one can identify the most likely sensor exhibiting a gross error as long as only one sensor becomes faulty at a single point in time. In addition, one can tune fault detection algorithms finely by using normal data, i.e. data that are free of gross errors. In the simplest methods, historical normal data are used to define statistical control limits (e.g., a 99%-confidence interval).

In order to benchmark processing monitoring and control methods, the Benchmark Simulation Model (BSM) series was developed5–6. These models include sensor fault models to test fault detection and identification methods. Importantly, the incorporated sensor models adhere to the above assumptions, i.e. all simulated sensor faults start independently and only after some time. Consequently, any fault
detection and identification method selected or tuned based on this benchmark simulation platform is likely to depend on the validity of the above assumptions.

We study to which extent the above assumptions are valid. We focus on pH sensors as they are the simplest and most widely used ion-selective electrodes on the market. The DEMON process is one example of a process requiring precise pH measurement for control\(^7\). In our case, the pH sensors are used for control of a biological urine nitrification process\(^8\). This process is developed for the decentralized production of a fertilizer from anthropogenic urine and enables (i) reducing wastewater loads to existing WWRFs, (ii) avoiding the use of the energy-intensive Haber-Bosch process for nitrogen fertilizer production, and (iii) avoiding nitrogen pollution of natural water bodies.

**METHODOLOGY**

A set of 10 sensors by Endress+Hauser, consisting of pairs of 5 sensor types (T1 – T5), is used for testing. Each of these is a newly bought ion-selective electrode (ISE) pH sensor. The first 3 pairs of sensors (T1 – T3) are in continuous use since the start of the measurement campaign. The 4th pair (T4) was used during the first 180 days of the campaign and replaced after 180 days with the 5th pair of sensors (T5).

The pH sensors are continuously exposed to the medium of a urine nitrification reactor. This medium consists of nitrified urine with total nitrogen concentrations around 5000 g.N/m\(^3\), which is present as ammonia and nitrate in roughly equal proportions. The treated urine exhibits a high salt concentration and conductivity (e.g., 16 mS cm\(^{-1}\))\(^9\). At regular intervals, the sensors are taken out of the reactor medium for testing. In each test, the sensors are mechanically cleaned with a sponge and then exposed to 5 media in 5-minute phases: (1) tap water, (2) calibration medium A (pH 4.01), (3) calibration medium B (pH 7.00), (4) calibration medium A (pH 4.01), and (5) tap water. During these tests, the raw voltage signal of the electrode is recorded at 1s intervals. The offset is computed as the averaged voltage signal in the last minute of the 3rd phase, at which point a steady-state signal is expected. The sensitivity is computed by computing the difference between the averaged voltage signal in the last minute of the 3rd phase and the 4th phase and dividing by 3. Under standard conditions, an ideal pH sensor is expected to deliver 0 mV for the offset and 59 mV per pH unit for the sensitivity.

**RESULTS**

We first discuss the results of the monitored offset. In Figure 1, one can see the recorded offset values as a function of time for all studied sensors. It is quite easy to see that the offset changes over time for every sensor. Moreover, the drifts appear largely unidirectional in the sense that the offset values decrease with time. For the 2\(^{nd}\), 3\(^{rd}\), and 4\(^{th}\) pair the offset amounts to about -59 mV in a year or less. This means that after a year – and without any calibration – one can expect to measure a pH of 6 or lower when the true pH is 7. Important with respect to the assumptions mentioned above are the next observations. First, all sensors produce a non-zero offset immediately or shortly after their initial exposure. This is most dramatic for 4\(^{th}\) pair of sensors. Consequently, it is difficult to find a period of time within which the produced data are free of gross errors. In addition, one can see that the offset and its rate of change is non-zero for all sensors at any given time. This means that placing redundant sensors as a way to find a single, faulty sensor is unlikely to work well in any realistic situation.
Figure 1. Sensor offset as a function of time. Exposure of the sensor to nitrified urine induces a drift in the sensor, which is visible in the computed offset. By the end of the studied time window of approximately 400 days, the pH drift can be as large as 59mV or larger for certain sensor types.

Figure 2 shows the computed sensitivities with scales matching the scales of Figure 1. This means that the figures scales are set so that a given change of the sensitivity in Figure 2 has a similar effect to the same change in Figure 1 when the true pH equals 6. The first observation is therefore that the observed changes in sensitivity have a marginal effect on the pH sensor signal compared to the changes of the offset. The highest (lowest) recorded sensitivity is 61 (54) mV/pH, which corresponds to measuring a pH of 5.97 (6.08) when the true pH is 6 (and the offset zero). Consequently, pH sensor calibration is only beneficial as a way to account for slow changes in the offset. Furthermore, this means that the classical two-point calibration could be replaced with a one-point calibration.

DISCUSSION & CONCLUSIONS
With this work, we have studied the real-world behavior of pH sensors in a biological decentralized process for recovery of fertilizer from human urine. The produced data indicate that the main cause of systematic measurement errors in a pH sensor can be attributed to changes in the sensor’s offset. Quite naturally, such changes are compensated in practice by sensor calibration. It was also shown that drift occurs at all times in all sensors. This has important consequences for the application and study of fault detection and identification methods. Since one cannot record a drift-free reference data set, it follows that significant updates to the application, study, and fine-tuning of fault detection and identification methods are necessary.
Figure 2. Sensor sensitivity as a function of time. For comparison, the scale of all axes match the scale lengths in Figure 1. All recorded sensitivity value stay close to the ideal value of 59 mV/pH, meaning that the exposure to the treated urine medium has little to no effect on the sensitivity.

REFERENCES


