Wireless, Accurate and Long-term Nitrogen Monitoring in Wastewater by Solid-State Ion-Selective Membrane (S-ISM) Sensors

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ABSTRACT

In the 21st century, a pivotal requirement for treating wastewater is the availability of low-cost, real-time in situ, accurate and long-term water quality monitoring. This study develops state-of-the-art wireless solid-state, ion-selective membrane (WS-ISM) sensors targeting nitrogen contaminants including ammonium and nitrate in wastewater. The mm-sized S-ISM sensors were made by precisely embedding liquid-state ionophore in a well-crafted matrix consisting of Polyvinyl chloride (PVC) and plasticizers for enhanced adhesion to the electrode surface. The S-ISM sensors were then couple to a wireless gateway as a WS-ISM prototype and examined in continuous-flow rigorous field tests using municipal wastewater for 7 days. Test results indicated that the WS-ISM nitrogen sensors possessed excellent accuracy and precision, high selectivity, and multi-day stability. In summary, the compact mm-sized WS-ISM nitrogen sensing technology developed in this study enables an unprecedented accuracy and durability for continuous wastewater monitoring, and thus pose a great potential toward data-driven wastewater infrastructure.

KEYWORDS

Ion-selective membrane (ISM) sensors, Wireless monitoring, Nitrogen contaminants, Municipal wastewater, Polyvinyl chloride (PVC).

INTRODUCTION & BACKGROUND

Biological nutrient removal (BNR) has been widely used for wastewater treatment. However, BNR has suffered from high chemical dosage, intensive energy consumption (e.g. pumping, aeration), large space occupation and low stability.[1] In order to reduce energy consumption and enhance treatment efficiency, cost-effective sensing technology should be developed to decode the “black box” of BNR systems and obtain a complete picture of physio-bio-chemical status. However, most of the commercial sensors are made of fragile ion-selective membranes (ISM) that can only last couple hours to couple days in wastewater and require frequent replacement.[2]

We report here the development of a new generation of mechanically stable solid-state ISM (S-ISM) for accurate monitoring of ammonium (NH_4^+) and nitrate (NO_3^-) in wastewater over long-term period. Linear models between the concentrations of NH_4^+ and NO_3^- in wastewater and the potential signal output (mV) of sensors were developed. We demonstrate the major features of accuracy, precision, selectivity and resolution of S-ISM nitrogen sensors. Wireless nitrogen S-ISM sensor prototypes were assembled and installed in a continuous flow chamber fed with real municipal wastewater for 7-day tests, through which real-time remote data access of nitrogen concentration in wastewater is achieved, and real-time temperature auto-correction features on the cloud were validated. The energy-savings and pollution alleviation of the wireless nitrogen monitoring system developed at steady operations as well as under transient shock conditions were estimated.

METHODOLOGY

Fabrication of solid-state ion selective membrane (S-ISM) NH_4^+ and NO_3^- sensors

The mm-sized solid-state sensors were fabricated by printing gold and silver inks onto a polyimide film (thickness: 127 µm, American Durafilm Co.) (Figure 1a). Details about the gold ink and silver ink components, fabrication protocols and sensor printing procedures were described previously.[3-5] The S-ISM sensors for NH_4^+ and NO_3^- was individually prepared by drop coating of specific ionophore polymer cocktail selective to NH_4^+ and NO_3^- onto the mm-sized sensor surface. The cocktails contain NH_4^+ or NO_3^- ionophore (liquid-state ISM), plasticizer and Polyvinyl chloride (PVC). The S-ISM$_{CNT}$ sensors were prepared as described above for the ion-selective S-ISMs, but with the addition of 2% (w/w) multi-walled carbon nanotubes (CNT; 10 µm average length, 12 nm average diameter, Sigma Aldrich). The modified S-ISM$_{CNT}$ sensors were compared side-by-side with the corresponding S-ISM nitrogen sensors by running an open circuit potential-time (OCP-T) program during a 7-day lab test.

Characterization of S-ISM nitrogen sensors

Calibration, temperature compensation, precision, accuracy, resolution, sensitivity and selectivity of S-ISM nitrogen sensors were conducted in lab tests using simulated wastewater and compared side-by-side with commercial nitrogen sensors (YSI). Afterwards, the NH_4^+ and NO_3^- S-ISM sensors were assembled with a circuit board and a wireless gateway for the real-time continuous monitoring of nitrogen concentrations in real wastewater. The sensors were examined a continuous flow chamber (diameter: 59.1 cm, water volume: ~10 gallon) holding wastewater during the 7-day test period (Figure 1b). The readings (mV) of NH_4^+ and NO_3^- S-ISM sensors were real-time accessed on the cloud for remote monitoring.

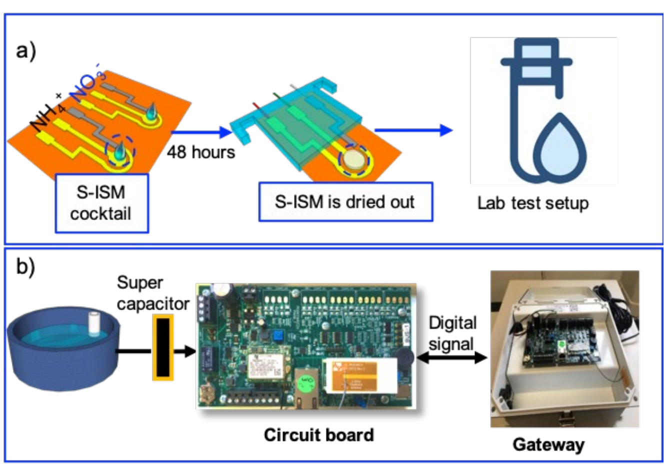

Figure 1 The diagram of the nitrogen S-ISM sensors for the lab test and field test. a) The fabrication process and the lab test setup of S-ISM sensors; b) The field tests of wireless nitrogen S-ISM sensors in a continuous flow chamber.

RESULTS

S-ISM nitrogen sensors performance in lab tests

Both of NH_4^+ and NO_3^- S-ISM sensors exhibited a near-Nernstian slope of 53.3 mV and 48.9 mV per decade of nitrogen concentration, with excellent linear regressions ($R^2 > 0.99$ Figure 2a). Importantly, the sensors exhibited a prompt electrode potential (mV) response to changes of the concentrations of NH_4^+ and NO_3^- by reaching steady conditions within 10 sec. With the temperature compensation equation, we were able to accurately measure nitrogen concentration in wastewater without the temperature interference (Figure 2b and 2c). Furthermore, there was no statistical difference between the readings of multiple pieces of S-ISM sensors, and there was no statistical difference between nitrogen S-ISM sensors and commercial sensors (Figure 3). Both of the NH_4^+ and NO_3^- S-ISM sensors were able to detect increment changes of 0.1 mg N/L at low nitrogen concentration (5 mg N/L) (Figure 4).

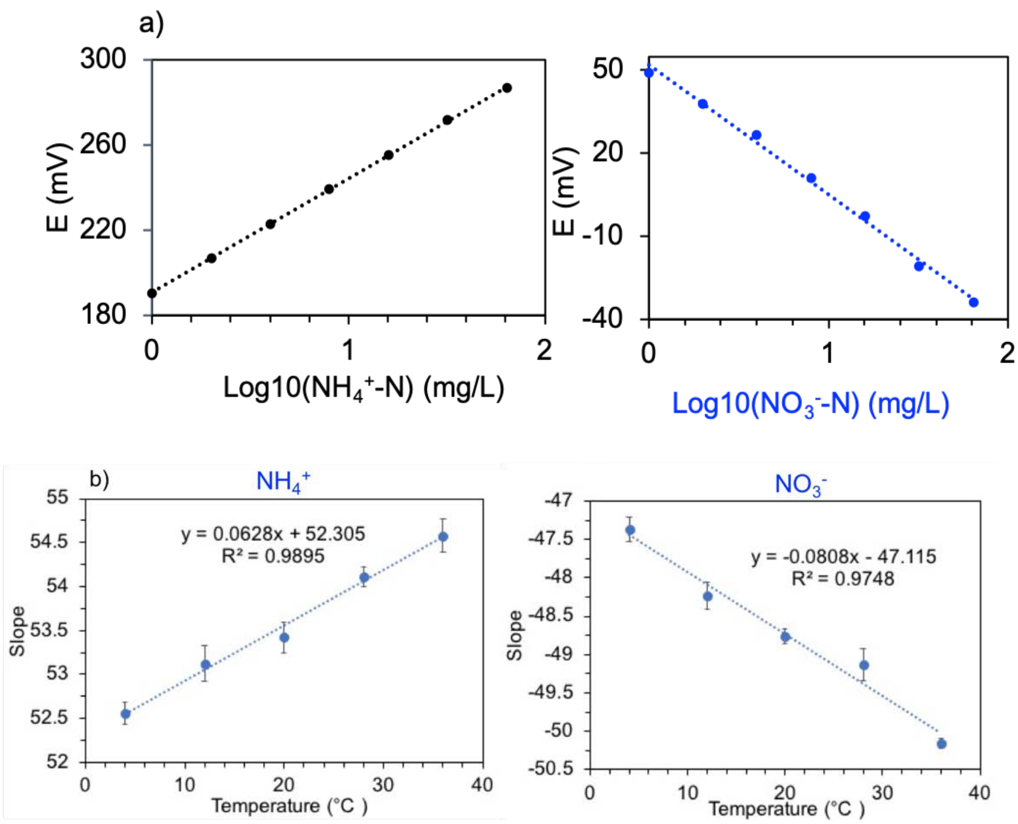

Figure 2 Characterizations tests of the nitrogen S-ISM sensors. a): The calibration curve of the NH_4^+ S-ISM sensor and NO_3^- S-ISM sensor; b): The influence of temperature on the slope of the calibration curves.

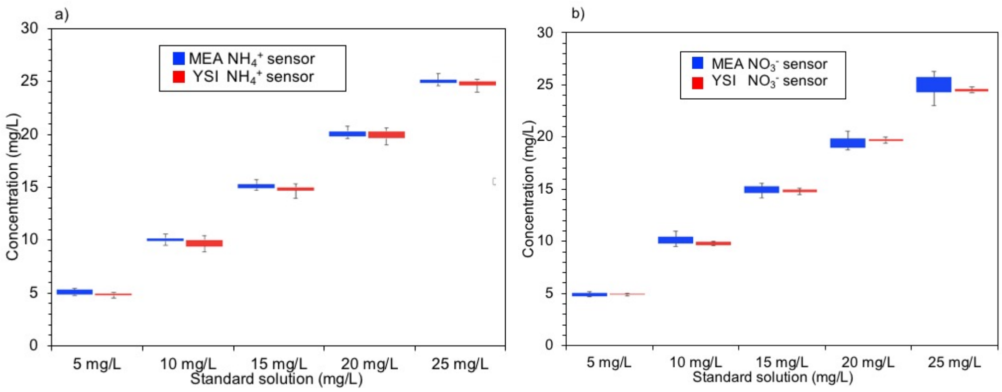

Figure 3 The comparison of nitrogen S-ISM sensors with the commercial sensors at five different concentrations (5, 10, 15, 20 and 25 mg-N/L). a) NH_4^+ S-ISM sensor (Two-way analysis P value: 0.133, 0.125, 0.145, 0.451 and 0.265 for five pieces of S-ISM sensors. T-test P value: 0.134, 0.163, 0.0354, 0.150 and 0.0836 between S-ISM sensors and commercial sensors); b) NO_3^- S-ISM sensor (Two-way analysis P value: 0.125, 0.103, 0.590, 0.385 and 0.409 for five pieces of S-ISM sensors. T-test P value: 0.291, 0.101, 0.147, 0.294 and 0.070 between S-ISM sensors and commercial sensors).

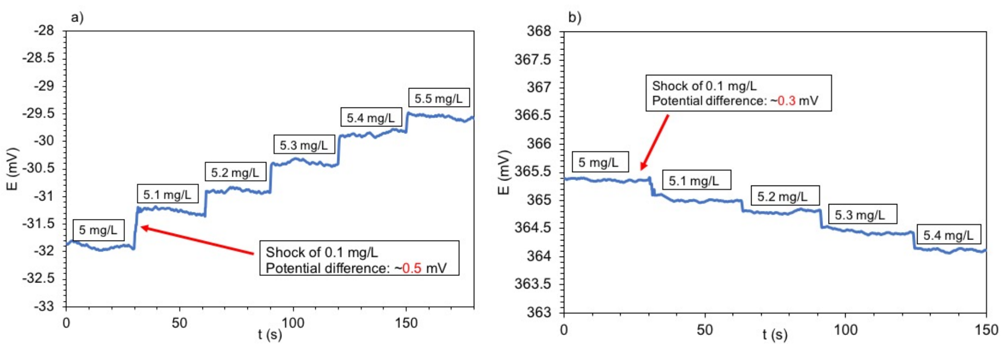

Figure 4 The resolution test of the nitrogen S-ISM sensors at low (5 mg-N/L) concentrations.

In selectivity test, non-target ions caused nearly negligible interference to the readings of both NH_4^+ and NO_3^- S-ISM sensors. In contrast, when the targeted electrolytes (NH_4^+ and NO_3^-) were added into the solution, the sensor signals changed promptly and became stable within 15 s (Figure 5). This excellent selectivity over other potentially interfering ions recommended our nitrogen S-ISM sensors for the real-time, *in situ* monitoring of nitrogen concentrations in real wastewater.

Before the field test, the potential signals captured by circuit board and gateway were processed by signal filter. The signal noise in the real municipal wastewater was alleviate after data processing (Figure 6).

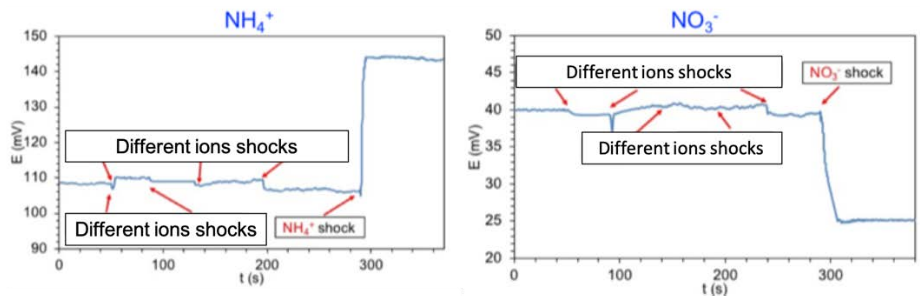

Figure 5 The selectivity tests of the nitrogen S-ISM sensors.

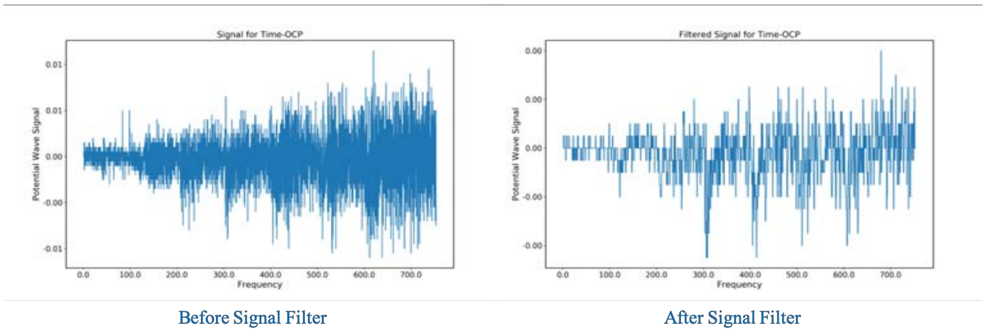

Figure 6 The signal noise before and after data processing.

Field tests of wireless continuous real-time monitoring in real wastewater

During the 7-day continuous flow field tests, indeed, the nitrogen sensors promptly captured two low concentration shocks and two high concentration shocks (Figure 7), with a discrepancy of less than 2 mg/L from the lab validation test results. The good sensitivity of the nitrogen S-ISM sensors was attributed to the effective prevention of NH_4^+ and NO_3^- ionophore leakage from the PVC-based membrane.[6] Furthermore, the nitrogen S-ISM sensors also promptly captured the shock incurred by nitrified wastewater starting on the 47th hour and the shock incurred by raw wastewater on the 66th hour. The sensor readings on the cloud provided the alarm within 5 seconds after the wastewater shocks (Figure 6), demonstrating the capability of nitrogen S-SIM sensors for accurate monitoring of nitrogen fluctuations in wastewater in a real time mode.

The resistance-type "interdigitated" temperature sensor was used to capture the temperature variation in wastewater (16.4 °C to 32.5 °C), which was accommodated into the sensor algorithm on the cloud to assure the accuracy of sensor readings under different temperatures (Figure 7). The NO_3^- concentration readings showed a more stable distribution with temperature compensation (RSD: 7.7% compared to 7.91%), indicating the effect of temperature on the NO_3^- S-SIM sensors was diminished using the correction at relatively high nitrate concentrations (> 7 mg-N/L).

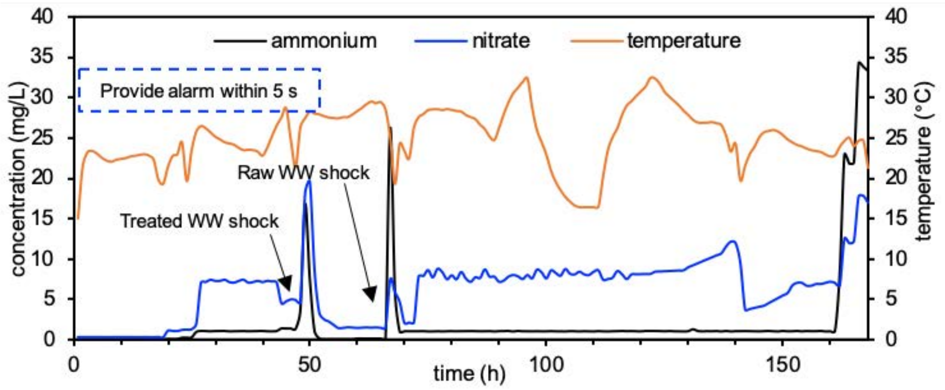

Figure 7 The readings of the nitrogen S-ISM sensors on the cloud during the 7-day continuous flow field test using real wastewater.

DISCUSSION

By incorporating highly selective ionophores in a thin polymer membrane on an mm-sized electrode, we pioneeringly explored the distinct solutions for nitrogen sensors: maintain high accuracy as well as prolong lifespan. The compact mm-sized S-ISM nitrogen sensors developed possessed excellent sensing capability. Coupled to wireless data transmission enabled remote data access in real time mode. A temperature compensation algorism on the cloud minimized temperature effects and enhanced measurement accuracy. We thus were able to monitor NH_4^+ and NO_3^- in wastewater with high accuracy, precision, sensitivity, resolution, and stability. It was estimated that real-time, *in situ* monitoring using wireless S-ISM nitrogen sensors could save 25% of electric energy under normal operational conditions and reduce 22% of nitrogen discharge under shock conditions. The technology has a great potential to improve wastewater monitoring for energy-saving BNR processes, enable the early warning of malfunction, and ultimately enhance system efficiency and resilience.

CONCLUSIONS

Accurate real-time *in situ* monitoring of contaminants in wastewater is vital for energy saving and pollutant control. By incorporating known ionophores in a thin polymer membrane on an electrode, we developed solid-state S-ISM nitrogen sensors with excellent sensing profiles. Coupled to wireless data transmission enabled remote data access in a real-time mode. A temperature compensation algorism on the cloud minimized temperature effects and enhanced measurement accuracy. We thus were able to monitor with high accuracy, precision, sensitivity, resolution, and stability NH_4^+ and NO_3^- in wastewater remotely in real-time. This compact wireless mm-sized nitrogen S-ISM sensor enables to an unprecedented degree the monitoring of nitrogen in WWTP waste streams. The technology has a great potential to improve wastewater monitoring for energy-saving operation, enable the early warning of malfunction, and ultimately enhance the efficiency and resilience of wastewater treatment processes.

It should be noted that the WS-ISM sensors suffer from the ISM-peeling off and data drifting for long-term monitoring. ISM mixed with poly(acrylate) of a low water diffusion coefficient and silicone rubber could reduce the water uptake in ISM[7] and might alleviate data drifting. Thereby, a S-ISM membrane with a higher hydrophobicity (e.g. poly(methyl methacrylate)–poly(decyl methacrylate) ISE membrane,[8] colloid-imprinted mesoporous carbon membrane[9]) will be the next step to enhance the sensors' accuracy and precision.

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