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Performance Comparison of a Self-Cleaning and a Conventional pH Electrode in Wastewater Process Monitoring

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Abstract **– Accurate pH measurement is vital in wastewater treatment for effective process control and regulatory compliance. This study compares a self-cleaning pH sensor (HORIBA 6122 series) with a conventional glass electrode, installed in parallel at a wastewater treatment facility in Metro Manila, Philippines. Over a 97-day period, 2,324 paired readings were recorded. Statistical analysis revealed a significant difference ($t(2323) = 56.88$, $p > 0.05$) in mean values (HORIBA = 6.93, conventional = 6.12). The HORIBA sensor exhibited lower variability (HORIBA = 0.2335, conventional = 0.6461) through time, indicating better stability. These results align with the goals of Process Analytical Technology and support the deployment of self-cleaning sensors for real-time wastewater treatment monitoring.**

I. INTRODUCTION

Accurate and stable pH measurement is fundamental to effective wastewater treatment operations, as it directly affects biological process efficiency, chemical dosing, and regulatory compliance [1]. Biological processes such as nitrification, denitrification, and anaerobic digestion are highly sensitive to pH, and deviations can disrupt microbial activity and treatment performance.

Conventional pH electrodes, typically constructed with glass membranes, are prone to signal drift and fouling when deployed in wastewater environments—especially under conditions with high suspended solids or fluctuating loads. This degradation in performance often necessitates frequent manual cleaning and recalibration, which limits their viability in real-time or automated process monitoring [2].

To overcome these challenges, advanced sensors such as the HORIBA Self-cleaning pH Electrode 6122 series employ UV-irradiated porous TiO_2 coatings on the pH-sensitive glass membrane. Upon UV exposure, this layer becomes photocatalytically active, generating a hydrophilic surface that prevents the adhesion of organic matter. Additionally, it facilitates the production of reactive oxygen species (ROS) that disintegrate fouling biofilms, resulting in significantly reduced signal drift and minimal maintenance requirements [3], [4].

This study evaluates the field performance of the HORIBA 6122 sensor in comparison to a conventional pH electrode. Both devices were deployed in parallel at a wastewater treatment facility in Metro Manila, Philippines, and monitored over a 97-day period. The analysis focuses on their statistical behavior, stability, and integration potential into Process Analytical Technology (PAT) frameworks for automated control systems.

II. REVIEW OF RELATED LITERATURE

Self-cleaning sensor technologies have become increasingly important in wastewater treatment due to their ability to reduce manual intervention while maintaining data integrity. Lu et al. (2024) reviewed the development of self-cleaning membranes for oily wastewater and highlighted how photocatalytic coatings, especially TiO_2, enhance anti-fouling behavior and extend operational life [5].

Li et al. (2021) emphasized that catalytic membrane-based oxidation-filtration systems significantly reduce organic fouling, citing TiO_2 as a leading material for self-cleaning and stability in harsh wastewater environments [6].

Photocatalytic and hydrophilic surface modifications were also shown to improve sensitivity and response time in online sensing systems, aiding in the detection of short-lived pH shifts [4]. Nguyen et al. (2022) discussed the integration of such smart sensors into Process Analytical Technology (PAT) frameworks, enabling real-time automation and process feedback in wastewater filtration [7] [8].

III. MATERIALS AND METHODS

A. Sensor Configuration

Two pH sensors were installed in the aeration tank of a wastewater treatment plant in Metro Manila. The HORIBA 6122 self-cleaning pH electrode, equipped with a TiO_2-coated pH glass membrane irradiated internally with UV light, was immersed alongside a conventional pH electrode. Both sensors recorded synchronized readings within 97 days.

B. Data Processing

Data from January 26 to May 3, 2023 yielded 2,324 paired pH readings. Incomplete values were excluded. Mean, standard deviation, skewness, and kurtosis were calculated.

C. Statistical Analysis

Paired t-tests were used to assess mean differences. Pearson correlation was applied to evaluate signal agreement. Histograms and residual plots were used to examine dynamic behavior.

IV. RESULTS

A. Descriptive Statistics

The HORIBA sensor showed consistent readings with low variability, while the conventional sensor produced broader, less stable values.

Table 1. Descriptive statistics of pH readings

Statistic	HORIBA	Conventional
Mean	6.93	6.12
Median	6.9	5.65
Std. Deviation	0.2335	0.6461
Range	6.54	1.92
Minimum	1.99	5.65
Maximum	8.53	7.57
Skewness	-3.07	0.66
Kurtosis	93.08	-1.52

B. Distribution Comparison

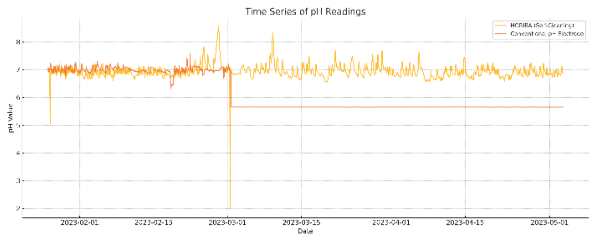

Fig. 1. Time series of pH readings

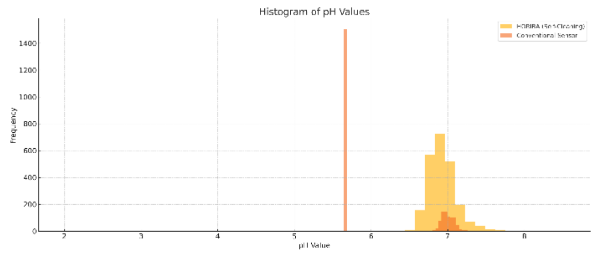

Fig. 2. Histogram of pH readings

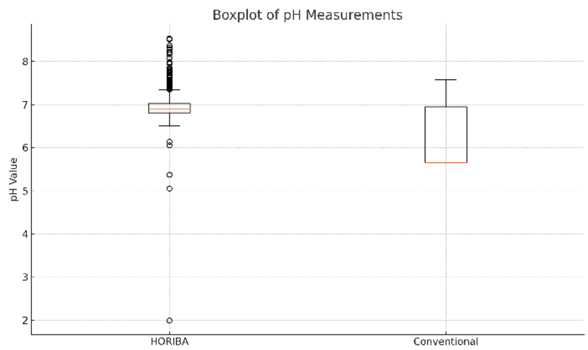

Fig. 3. Boxplot comparison

HORIBA data displayed a high kurtosis value, indicating sharp detection of outliers, including acid shock events. The conventional sensor produced a flatter, more biased distribution.

C. Sensor Agreement and Behavior

The conventional sensor diverged over time, likely due to fouling, while the HORIBA maintained consistent tracking. The Pearson correlation was negligible ($r \approx 0.01$), supporting divergence.

D. Statistical Significance

The difference in means between sensors was statistically significant ($t(2323) = 56.88$, $p < 0.001$), confirming that cleaning mechanisms materially affect measurement output.

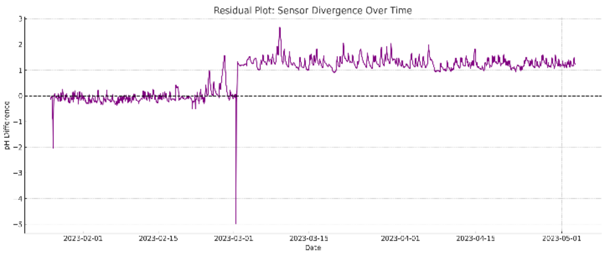

Fig. 4. Residuals between sensors

E. PAT Integration Potential

The HORIBA 6122 sensor aligns with the goals of Process Analytical Technology (PAT) by enabling automated, high-frequency pH monitoring with minimal manual intervention. Its robust photocatalytic coating and chemically stable TiO_2 membrane allow for consistent performance in harsh wastewater environments over extended periods. Studies show that thin-film sensor designs incorporating catalytic surfaces provide signal stability and corrosion resistance, which are critical for long-term unattended applications in real-time water quality control systems [9], [10].

V. DISCUSSION

A. Photocatalytic Self-Cleaning Efficiency

The 6122 sensor's UV-activated TiO_2 coating generates a hydrophilic film that inhibits the adhesion of organic matter on the glass membrane surface. Upon UV irradiation, the TiO_2 layer becomes photocatalytically active, producing reactive oxygen species (ROS), such as hydroxyl radicals, which oxidize and disintegrate biofilms. These photocatalytic effects enable long-term calibration stability in nutrient-rich and alkaline wastewater streams, as demonstrated in TiO_2-enhanced membrane systems and ion-selective electrodes in recent studies [4] [11][12].

B. Operational Advantages

The sensor's long-term signal stability eliminates the need for daily cleaning and recalibration, which in turn minimizes downtime and labor. This operational consistency is especially valuable for automated control architectures. The HORIBA 6122 integrates easily with SCADA (Supervisory Control and Data Acquisition) and PLC (Programmable Logic Controller) systems, enabling closed-loop control and remote performance tracking. Recent studies have emphasized that real-time water quality sensors embedded within distributed monitoring networks and SCADA infrastructures enhance responsiveness and reduce operational uncertainty in wastewater applications [13], [14].

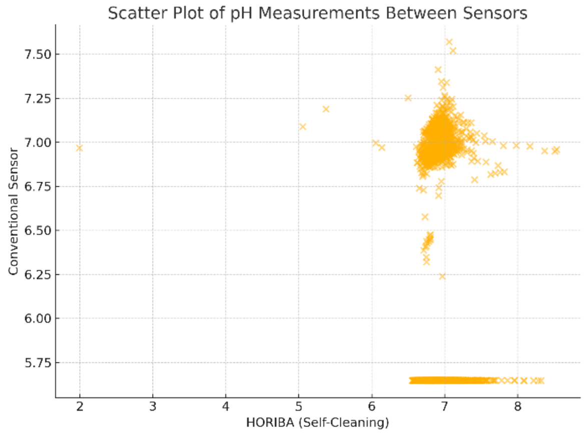

Fig. 5. Scatter plot of paired readings

C. Limitations and Future Work

While the HORIBA 6122 performed reliably under standard treatment conditions, its performance in challenging operational scenarios, such as exposure to chemical surges, elevated total suspended solids (TSS), and extreme temperatures, remains to be comprehensively validated. Several studies emphasize the importance of testing sensors under stressor conditions and cross-validating outputs using established laboratory techniques, such as acid-base titration, to confirm analytical accuracy. Additionally, cost-benefit analyses that account for maintenance savings and automation compatibility are essential to support broader adoption [15], [16].

VI. CONCLUSION

This study demonstrated that the HORIBA 6122 self-cleaning pH electrode offers superior measurement stability, lower variability, and enhanced outlier detection when compared to a conventional glass electrode in wastewater treatment monitoring. Its TiO_2-coated, UV-activated surface successfully resists fouling, preserving calibration integrity and reducing the need for manual cleaning. This not only aligns with the principles of PAT, but also supports its integration in SCADA/PLC-enabled closed-loop control systems.

The sensor's ability to maintain precision under biologically active and organic-rich conditions positions it as a promising technology for continuous, unattended wastewater monitoring. These findings corroborate recent advances in electrochemical self-cleaning platforms, which emphasize reliability and low maintenance in automation-focused water quality systems [17], [18].

However, further validation is recommended under harsher conditions such as chemical dosing surges, elevated TSS, and temperature variability. Additionally, lifecycle cost-benefit modeling and real-time comparison with online titration systems will be valuable to support utility-scale adoption. As wastewater systems move toward Industry 4.0 integration, adaptive and self-sustaining sensors like the 6122 represent a critical component of future-ready water infrastructure [19].

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