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# Title: Evaluation of Self-Cleaning pH Electrodes in Factories

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**Abstract:** We developed a self-cleaning pH electrode with a durable antifouling protection by photocatalytic effect. Our goal with this project was to solve common problems in electrode maintenance such as personnel shortages, electrode cleaning costs, periodic calibrations, on-site movements, and risk on worker safety. The self-cleaning pH electrode was evaluated over several months at sites heavily polluted by various organic and inorganic species. We have extended the maintenance cycles of wastewater treatment tanks in machine factories and returned sludge tanks in chemical factories by about 120 times and 60 times, respectively. This paper highlights the structure，features of the newly developed electrode. We also discuss results of measurements from wastewater treatment tanks using inorganic flocculants and wastewater influent tanks containing a lot of protein.

**Keywords**: Water quality measurement, pH electrode, Wastewater treatment

## 1. Introduction

More than 100 years have passed since the use of thin-film glass as a principle for pH (hydrogen ion concentration) measurement (glass electrode method) was first reported in 1906[1]). The pH electrode has been improved in terms of stability and performance according to the purpose and application [2]-[10]). Among these, since the electrode is immersed in the sample for a long period of time in industrial applications, contamination over time is still an issue, and various measures have been taken. Typical measures include mechanical cleaning such as automatic washers that use a stream of water, brushes, or chemicals, and manual cleaning such as wiping the electrode directly. In addition to these cleaning procedures, electrode maintenance requires a large amount of cost (work time), such as moving the electrodes to the installation site, calibration work, and use of chemicals. In addition, the problem is that it is hazardous to workers at sites where 24-hour operation requires nighttime work, in hazardous installation environments such as industrial plants, and at sites where work must be performed at heights. Although cleaning machines and devices with automatic calibration functions are available on the market, they require a large investment in terms of securing an installation site and installation costs.

In response to these problems, we have developed a maintenance-free pH electrode (hereafter referred to as “self-cleaning pH electrode”) that is capable of self-cleaning and preventing contamination over a long period of time [11]-[15]).

This paper describes the structure and features of the electrode and its antifouling effects in heavily contaminated sites such as wastewater treatment tanks in machine shops and wastewater treatment tanks in chemical plants.

## 2. Experimental method

Fig. 1 shows a photograph of the self-cleaning pH electrode developed in this study. The total length of the electrode is about 20 cm, the outer diameter of the glass support tube is 17.5 mm, and the TiO2 coating is 40 mm from the tip of the response glass. The coating was applied using a dip coater. After coating, the coating was sintered at 500°C for 10 minutes. A UV-LED was built into the inner tube of the support tube, and UV light penetrated through the glass tube from the inside of the electrode and irradiated onto the TiO2. The inside of the support tube was filled with a gel containing granular KCl, as in the previous report [15]. The outer tube has a single through-hole less than 1 mm in diameter.

The basic performance of the self-cleaning pH electrode used in this study was measured in advance with a pH standard solution and showed pH sensitivity and asymmetric potential equivalent to those previously reported [15], confirming that it has the necessary performance as a pH electrode. In this study, mounting tests were conducted at four sites with different sample conditions. This abstract shows results from wastewater treatment tank as an example.

**3. Result and Discussion**

Figs. 2(a)~(e) show the condition of the electrodes at 2-week intervals after the start of the test. After 2 months, the pH value was measured using a pH7 standard solution, and the pH value was 6.82. Fig. 3 shows the pH value of the self-cleaning pH electrode over time. pH value shifted from pH 6.5 around 12/8 to pH 7 around 1/26, about 0.5 pH to the positive side. The response curve shows a shift from 12/8 to 12/26. The response curve shows a periodic pH shift to pH 8 once every 7 days between 12/8 and 12/29, and once a day between 1/12 and 1/26, which is assumed to be due to the addition of alkali. Occasionally, the pH value was below pH 6, but this was since the electrode was pulled out of the wastewater treatment tank to photograph the condition of the electrode. The results of Fig. 3 confirm that continuous measurement is possible, as these phenomena are not observed in similar samples such as the present site.

**4. Summary**

Based on these results, the self-cleaning electrode is an electrode that can realize a reduction in the maintenance load for users. The electrode is also designed to ensure worker safety and reduce the amount of reagents used. The items are itemized below.

- The electrode can greatly reduce man-hours at sites where frequent maintenance is required, such as those where manual cleaning is performed every day (the maintenance cycle can be extended three times or more). The same is true for sites with multiple installations, remote locations, etc., where travel time is required.
- The calibration cycle can be extended and the amount of reagents used, such as standard solutions, can be reduced. Also, cleaning solutions such as hydrochloric acid and surfactants are not required.
- The time and frequency of the work can be shortened to reduce exposure at the site. Accurate measurement is possible due to the antifouling effect of dirt, which reduces the frequency of error reporting and provides peace of mind.
- The non-replenishing type of internal liquid does not require pressurization (no air piping for pressurization is needed) because it is a gel type, even at pressurized sites. In addition, KCl solution does not need to be replenished, so there is no need to worry about forgetting to replenish the KCl solution.

No on-site installation work is required, as is the case with water jet washers and air jet washers.

The system is useful at sites where brackish water or other cleaning equipment rusts, or where there is no space to install a cleaning equipment.

There are very few examples of photocatalyst coating such as $TiO_2$ on the sensor part, and we believe that we can develop a new market for the detection part of other analysis (UV meter, turbidimeter, colorimeter, etc.). We will continue to develop products that are environmentally friendly (performance improvement and maintenance) and human-friendly (less burden on users).

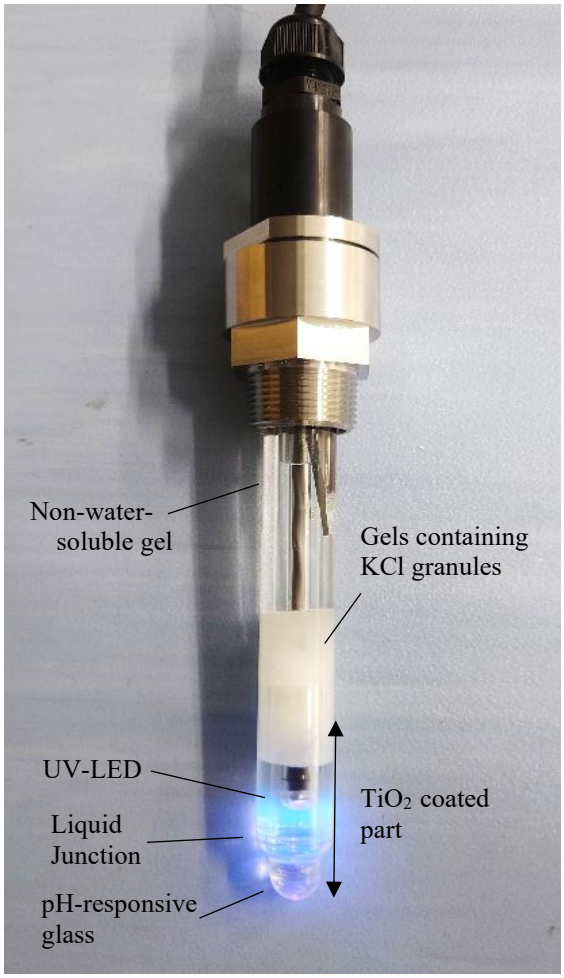


**Figure 1** Fig. 1 Picture of assembled Self-Cleaning pH electrode

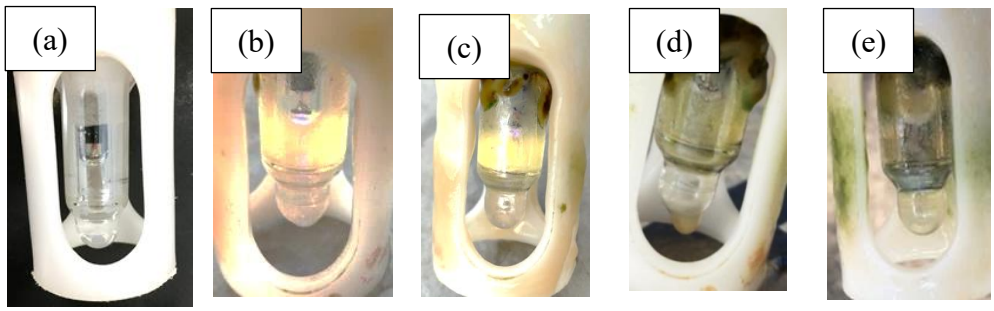


**Figure 2** Pictures of Self-Cleaning pH electrode (a) before experiments: (b) after 2 weeks: (c) after 4 weeks: (d) after 6 weeks: (e) after 8 weeks

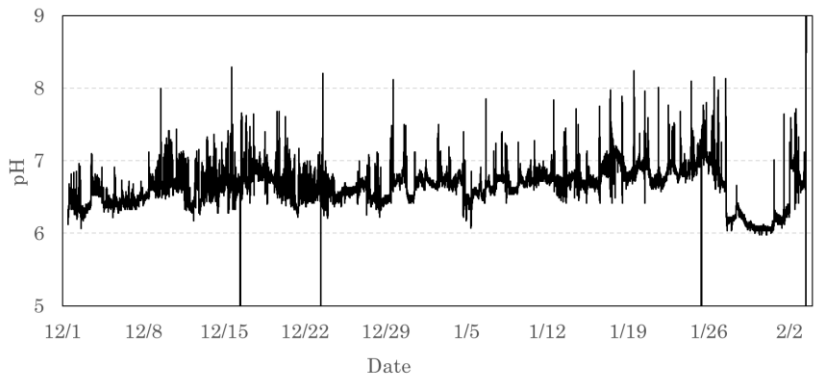


**Figure 3** Results of continuous pH measurement at wastewater treatment tanks in chemical factories

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