Fabrication of Multifunctional Nano Sensor System to Monitor Quality of Aquacultural Water Applied in Mekong Delta Area

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Abstract – In this study, the fabrication of the nano sensor systems to assess quality of aquaculture water was reported. These sensor systems had some advantages in comparison with the commercial ones. They were the multifunctional system with ability to measure maximum 8 parameters of aquacultural farming water including pH, dissolved oxygen (DO), oxidation/reduction potential (ORP), salinity, NH₄⁺, NO₃⁻ and Cl⁻ concentrations. There were two system configurations for the users’ choice: a full option with a turtle-shaped sensor version with independent operation and remote control. It could measure 8 parameters of water and long-time working thanks to the high capacity battery. Another version of the sensor system was a compact portable version. It could measure 5 parameters of water including DO, pH, temperature, NH₄⁺ and NO₃⁻ concentrations and had visual display of LCD. Both two systems could transmit and store data to the web server and send a warning message if the measurement parameters exceed the threshold which could be set by the users. These products are specially designed to meet demands of monitoring continuously and online the aquacultural farming water. They are expected to monitor the aquaculture water quality with a high accuracy, help the farmers to control the aquacultural farming water and contribute to the development of agriculture in the Mekong Delta, Vietnam.

Keywords – Nano Sensor Systems, Aquaculture Water, Multifunctional System.

I. INTRODUCTION

For many years, the strong development of aquaculture has helped the Mekong Delta area become one of the key areas of aquaculture in our country. This is also a special economic strength of this area. However, due to the strong development, the environmental fluctuations happened with a diverse scale [1].

The aquaculture industry plays an important role in the economy of the Mekong Delta. Environment of soil, water and ecosystems in aquaculture development has been changed, causing environmental degradation and pollution. The Mekong Delta is a region with a lot of potential and active alkaline soils. When digging and cultivating aquatic ponds, digging canals for supplying and draining water, cleaning ponds make the potential active alkaline soil layers affected by the oxidation process then spreading alkaline process happened strongly causing to reduction of water pH, environmental pollution and disease of shrimp as well as fish. The sources of waste water into rivers and canals have caused changes in the water environment. Water quality in aquaculture ponds including freshwater fish and coastal shrimp farming, especially in industrial farming models, has shown signs of organic pollution (BOD, COD, nitrogen, higher phosphorus), the occurrence of toxic components such as H₂S, NH₄⁺, and Coliforms microbiological index, indicating that this waste water source needs to be thoroughly treated before being flowed into rivers and canals. Waste in aquaculture is sludge containing faeces of fish and shrimp species, sources of excess food decomposing, residues of materials used in farming such as chemicals, lime and other minerals such as Diatomite, Dolomite, sulfur deposition, toxic substances in alkaline soil Fe²⁺.
Fe\(^{3+}\), Al\(^{3+}\), SO\(_4^{2-}\), components containing H\(_2\)S, NH\(_3\). Especially, with the high technology and density of farming such as intensive farming, industrial farming, the waste source and the environmental pollution were become larger [1].

The authorities should strongly focus on regional environmental planning and specific environmental protection plans in the zoning planning for aquaculture such as freshwater aquaculture, coastal aquaculture. At the same time, the state needs to pay more attention to investment to meet the requirements of water supply for farming, water drainage and water purification after the breeding process to protect the environment in the whole area planned for aquaculture. It should strengthen water quality monitoring to forecast environmental developments as well as diseases that may arise. Since then, there are solutions to timely handle when incidents occur.

Traditional water quality test methods involve sampling and laboratory techniques [2, 3]. However, these methods are time consuming (causing to delayed detection of and response to actions) and the cost of these methods are very high in comparison with the standard level, which the farmer could pay. Water quality monitoring could also be achieved through bio measurements as well as physical measurements [4]. However, these commercially products are usually complex and expensive. Monitoring with sensor technology become a very effective method. It is more affordable than the traditional methods. The equipment cost, reliability and maintenance are acceptable but data handling and management still need to be improved.

Different sensors, both at prototype scale and already in the market have been developed during recent years to monitor water quality. Fluorescence-based optical technology is now the forefront technology for emerging water quality sensors. The United States Geological Survey (USGS) has already been using this technology to detect the dissolved organic carbon (DOC) concentrations and in some cases, other related biogeochemical variables such as trihalomethane (THM) precursors and methyl mercury (MeHg) concentrations [5].

In 2007, the Secur Eau project developed a sensor to monitor water quality. The Kapta TM 3000 OT3 sensor equipped with 40 sensors could measure water quality online and send the results to operational centers every 2 hours but it has not been popular on the market until now [6].

Some of commercial sensor systems are existing on the market today such as the Kapta TM 3000 AC4 [7], the Spectro: :lyser™ [8], the :i: :scan [9], The Event Lab [10], The Lab-on-Chip [11], the TOX control [12], the Algae Toximeter [13], the COLIGUARD® [14] are all modern systems. They can measure several tens to several hundred water parameters. However, they also have some disadvantages. They need strictly requirements for operating conditions and they are not suitable for field conditions in agriculture. Another problem is that the price of these sensor systems is too high; from thousands to tens of thousands US dollars, making it difficult for users' approach [7-14].

Some of handheld sensor systems [15] (for example, YSI 5200A Multiparameter Monitoring and Control Instrument, Pro DSS Multi parameter Water Quality Meter, Multi Lab 4010-3W) also have similar problems in price and popularity. In addition, due to the size requirements, these portable systems sometimes do not integrate real-time or cloud storage features [16].

Following this trend, the sensor research group at Institute for Nanotechnology (INT), Vietnam National University-Ho Chi Minh City (VNU-HCM) has been developing a multifunctional nano sensor system to monitor the quality of aquaculture water. This system could measure pH, dissolved oxygen (DO), oxidation/reduction
potential (ORP), salinity, NH$_4^+$ and NO$_3^-$ and Cl$^-$ concentrations. The measurement results were real-time uploaded to the web server or visual display on an LCD. Shrimp farm owners could get these results by their mobile phone or tablet and make the adjustment to create the comfortable environment for shrimp growth in their ponds.

II. Experiments

The sensor system fabricated at INT-VNUHCM consisted of 3 main parts: the mechanical part (protective plastic case as well as the frame for mounting sensors and control printed circuit board- PCB), the electronic control board (includes the power supply controller, the sensors data collector and the data uploaded controller) and the sensor part (includes 8 sensor probes for the measured parameters).

The mechanical part of the sensor system had two configurations: one had the turtle-shaped with full options of 8 parameter sensors and a portable version with 5 parameter sensors. The shapes of the sensor cases were individually designed for the first time on the market and INT owned the industrial design protection patent. The turtle-shaped system was designed with high capacity of power supplier to ensure it could work continuously for a long time. The portable system had the build-in LCD which helped users could receive the measurement results immediately.

The PCB was fabricated on the manufacturing line of Bungard Elektronik, Germany. Arduino Mega 2560 processor was used to control multi-tasks such as received digital signals from the sensors, converted the signals to the readable data. Module SIM800A and Atenna 2.4 Ghz 4dbi were used for the wireless data transfer and uploaded data to the webserver. For the power supply, undervolt module LM2576 and volt-booster module DC XL6009 were used to adjust the input and output voltage of PCB. MCP601 operational amplifier was used to provide low bias current, high-speed operation, high open-loop gain, and rail-to-rail output swing. The MCP601 is available in standard 8-lead PDIP, SOIC, TSSOP and 5-lead SOT-23A packages.
A combination of 8 sensor probes were used for the sensor component. The chloride ion-selective electrode ELIT 8261, ammonium ion-selective electrode ELIT 8051 and the nitrate ion-selective electrode ELIT 8021 from Nico 2000 Ltd., UK were used to measure the ion concentrations. The pH, ORP, DO, conductivity and temperature were measures by Industrial pH Probe ENV-50-pH, ORP Probe ENV-50-ORP, Dissolved Oxygen Probe ENV-40-DO, Conductivity Probe K 1.0 ENV-50-EC-1 and Temperature Probe PT-1000, respectively from Atlas Scientific LLC., N.Y., US.

These sensor probes were linked with the corresponding signal amplifiers then connected to the control PCB and covered by the special design plastic cases. The completed products were showed in Figure 3 below.

![Fig. 3. The completed a) turtle-shaped and b) portable nano sensor products of INT.](image)

**III. RESULTS AND DISCUSSION**

After the fabrication process, the completed sensor system was tested with some standard solutions from the sensor probe manufacturers to assess the accuracy of this system. Some comparison results between fabricated sensor system and the reference commercial sensor system were also performed.

3.1. *Testing the Accuracy of pH Measurement*

An ideal electrode at 25°C will create a 0 mV signal when put in a standard solution with pH = 7. The sensitivity of the ideal electrode at 25°C is 59.16 mV per pH unit [17].

![Fig. 4. Voltage distribution as a function of pH level](image)

The pH electrode would create a linear voltage signal with pH value as in the above function. The voltage signal generated from the pH electrode was very small, so it had to go through the amplifier. The processor would read the signal after amplification and the pH value was automatically calculated.

In this test, two standard pH solutions from Atlas Scientific LLC., N.Y., US were used to assess the pH measurement accuracy. Figure 6 and Table 1 below showed the testing results of the fabricated nano sensor. The error of 5% was acceptable in the pH measurements.
Testing the Accuracy of DO Measurement

The dissolved oxygen detector used in this research was a passive device that created a low voltage from 0 mV to ~40 mV depending on the oxygen saturation of the Teflon film. After passing the amplifier, this signal was changed from 0-5 V corresponding to 0-20 mg/l dissolved oxygen. The processor read this signal and automatically calculated the dissolved oxygen value.

In this test, a standard solution with a fixed DO concentration of 6.3 by changing its temperature to room temperature of 29ºC, atmospheric pressure at 760 mmHg and solution salinity of 40 ppt. The fabricated sensor system and a reference one from Sensorex, Inc., CA, USA were used to make a comparison result.
Table 2. Comparison DO measurement results by INT and Sensorex sensor systems.

<table>
<thead>
<tr>
<th>DO con. (ppm)</th>
<th>INT sensor results</th>
<th>INT sensor error (%)</th>
<th>Sensorex sensor result</th>
<th>Sensorex sensor error (%)</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>6.25</td>
<td>-0.8</td>
<td>6.27</td>
<td>-0.48</td>
<td>-0.32</td>
</tr>
</tbody>
</table>

The result in Figure 7 and Table 2 showed that the measurement results of INT sensor system was quite good with the error was under 1%. In comparison with the reference commercial sensor system from Sensorex, the relative error was -0.32%. This error value was negative so the INT sensor was less sensitive than the reference sensor but this value was acceptable in DO measurements.

3.3. Testing the Accuracy of Salinity Measurement

In this test, a standard solution with salinity of 12880 μS was used to make the comparison measurement results between the INT sensor system and the reference one from Sensorex, Inc., CA, USA.

![Fig. 8. Comparison salinity measurements by a) INT and b) Sensorex sensor system](image)

Table 3. Comparison salinity measurement results by INT and Sensorex sensor system.

<table>
<thead>
<tr>
<th>Salinity (μS)</th>
<th>INT sensor results</th>
<th>INT sensor error (%)</th>
<th>Sensorex sensor result</th>
<th>Sensorex sensor error (%)</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12880</td>
<td>12740</td>
<td>-1.1</td>
<td>12400</td>
<td>-3.7</td>
<td>+2.6</td>
</tr>
</tbody>
</table>

The result in Figure 8 and Table 3 showed that the measurement results of INT sensor system was quite good with the error was only nearly 1%. In comparison with the reference commercial sensor system from Sensorex, the relative error was +2.6%. This error value was positive so the INT sensor was more sensitive than the reference sensor.

3.4. Testing the Accuracy of NH₄⁺, NO₃⁻ and Cl⁻ ion Concentration Measurement

In the ion concentration measurements, an ion selective sensor (ISE) was used with a reference electrode to build up the correlation between voltage and ion concentration which is given by the NERNST equation.

Two standard solutions of NH₄⁺ ion with concentration of 1 and 10 ppm were used to test the accuracy of INT sensor system in the ion concentration measurement. The other measurement with NO₃⁻ and Cl⁻ had the same processes.
The result in Figure 9 and Table 4 showed that the measurement results with the high ion concentration standard solution were better than with the low one. This could be explained by the mobility of these ions in the solution was too high causing the concentration of ions in solution changing quickly over the feedback time of the sensor probes. This would need an improvement in the near future.

Table 4. Ion concentration measurement results by INT sensor system.

<table>
<thead>
<tr>
<th>Ion concentration (ppm)</th>
<th>INT sensor results (ppm)</th>
<th>INT sensor error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4^+$ ion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.3</td>
<td>+30</td>
</tr>
<tr>
<td>10</td>
<td>10.86</td>
<td>+8.6</td>
</tr>
<tr>
<td>NO$_3^-$ ion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.04</td>
<td>+4</td>
</tr>
<tr>
<td>10</td>
<td>10.32</td>
<td>+3.2</td>
</tr>
<tr>
<td>Cl$^-$ ion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.13</td>
<td>+13</td>
</tr>
<tr>
<td>10</td>
<td>10.67</td>
<td>+6.7</td>
</tr>
</tbody>
</table>

3.5. Testing the Operation of Sensor System in Real Conditions

The fabricated sensor system was put into the aquaculture ponds, then measured parameters and continuously transmitted the measurement data by the wireless connection. The system could instantly send converted data to the users on smartphones, laptops and tablets via internet or sending alert SMS via telecommunication networks. The data were also sent and stored on the web server then the user could login with an account and password provided by INT (Figure 10) to view them later.
After logging successful, the users would go to the data statistic interface as showed in Figure 11 below.

Fig. 11. The data statistic interface on web server.

On the statistic data interface, the measurement parameters of the nano sensor systems such as ORP, pH, DO, conductivity, salinity, ions concentration, were arranged in columns named “RUA_01”.

The users could review the measurement log of the sensor system (the measurement data of the previous days) by entering values in the "start date" and "end date" boxes then click the "Find" button. Measurement results can be exported as excel tables and saved easily (Figure 12).

Fig. 12. Measurement log review interface.

In addition, the sensor system had an attached GPS navigation system, so the users could locate the various systems at different places by selecting the search button 📍. The users would then get the location of the available system (Figure 13).

Fig. 13. The available sensor system was located by GPS.
IV. CONCLUSIONS

In this study, a multifunctional nano sensor system for monitoring the quality of aquaculture water was design and fabricated. This configuration of the nano sensor have some advantages such as: multi parameters could be monitored (8 parameters), real-time measurement results, immediately displayed by LCD, online data storage, easy access with the friendly interface web server. With these features, this nano sensor system was expected to make a big contribution to the development of agriculture in Mekong Delta region of Vietnam.

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