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Fabrication of nitrate ion sensor based on conductive polyaniline doped with nitrate using thick film technology

Abstract

Nitrate is one of the nutrients that can give an effect on the environment if it is applied in excess. It is also easily soluble in water and it has the potential to be a pollutant in groundwater by the over-process of fertilizer. Therefore, it needs a detected component to give the right measure for nitrate in the soil, called a nitrate ion sensor. It consists of three electrodes configuration, namely, working, counter, and reference electrodes with conductive polyaniline doped with Nitrate (NO_3^-) which is fabricated by thick film technology. In previous research, acidic media was used as a solvent for polyaniline, while this research used water (H_2O) solvent. The result of characterization showed that particles were distributed evenly on the sample with the form of particles being small balls with a dimension of $0.18 \mu\text{m}$ and the percentage of atomic elements being: 91.96 % carbon, 3.14 % nitrogen, and 4.9 % oxygen. The performance of sensors was investigated using potentiostat with four concentrations of nitrate standard solution. The result showed good response with a voltage range in each concentration of nitrate standard solution being 0.5002 Volt (10 mg/l), 1.3552 Volt (20 mg/l), 1.1208 Volt (50 mg/l), and 0.8963 Volt (100 mg/l). It was found that nitrate sensors with nitrate-doped conductive polymer, polyaniline, as the sensitive membrane responded well to detecting nitrate elements in precision farming and the sensitivity showed that for every 1 mg/l concentration in nitrate standard solution, the voltage increases by 0.0007.

Keywords: electropolymerization process; performance of nitrate sensor; the polyaniline; thick-film technology.

I. Introduction

This Indonesia as an agrarian country has quite extensive agricultural land and most of its people work in this sector. Based on Statistics Indonesia (BPS), non-ministerial government, which contains the Indonesian labor situation as of February 2018, it is stated that the percentage of Indonesian workers working in agriculture is 30.46 % [1].

One of the factors supporting the production of the agricultural sector is the fulfillment of macronutrients consisting of nitrogen (N), phosphor (P), and kalium (K). Nitrogen is an element that is needed in large quantities and is often found in soil in the chemical bonds of nitrates (NO_3^-) or ammonium (NH_4^+). Nitrate is one of the macronutrients which is easily evaporated and easily absorbed by water

so that the availability of nitrate in the soil can be limited and it takes the addition of nitrate by nitrogen, phosphorus, and potassium (NPK) fertilizer. However, fertilizer application must also follow the rules and must know the condition of the land to be used and this is rarely applied so that if there is an excess of nitrate due to excess fertilizer then this can cause water pollution to the soil [2][3][4].

The list of chemical parameters for environmental health purposes, which are contained in table 3 Chapter II in the Republic of Indonesia Minister of Health Regulation Number 32 of 2017 concerning environmental health quality standards and water health requirements for sanitary hygiene, swimming pools, solus per aqua (SPA), and public baths, explained that Nitrates are included in the mandatory chemical parameters among the ten other mandatory chemical parameters (including: pH, iron, fluoride, manganese, cyanide) and the level of nitrate as N that is allowed in soil and water land is 10 mg/l [5].

Research related to the detection of nitrate levels in soil has been carried out. One of them uses conventional technology, namely, the process of detection by taking soil samples to the laboratory for research (sampling process), but this process takes a long time and costs a lot. This led to the emergence of other methods, namely: a fertilizer detection sensor based on the infrared ray that has been combined into a data acquisition system that can detect levels of NPK fertilization [6][7][8]. The development of fertilizer sensors is also carried out using an optical transducer, LEDs, and photodiodes that can detect NPK fertilizer levels by displaying fertilizer levels, namely low voltage, medium voltage, and high voltage [9][10][11].

Other research that has also been widely developed is detecting of nitrate levels using nitrate-doped conductive polymer of polypyrrole as the sensitive membrane to coat electrodes that have been fabricated using thick-film technology. The results of the study show that these electrodes have good performance and can be used to detect nitrate levels in the soil [12][13][14].

Based on previous research about polyaniline, among the conducting polymers, polyaniline has received much attention and intensive research work has been performed with the polymer in its native state or functionalized form. This is mainly because polyaniline and its derivatives or composites or copolymers with other materials are easy to synthesize chemically or electrochemically by oxidative polymerization [15].

In this study, the fabrication was carried out using conductive polymer polyaniline (PANI) sensitive membrane with water (H₂O) solvent as a substitute for polypyrrole that will be doped with nitrate in the same fabrication method, namely, thick film technology [16][17][18]. In some research, the sensor was fabricated using polyaniline and polypyrrole thin film immobilized glass surfaces. Polyaniline sensor gives a good response at low humidity conditions and saturates at high humidity conditions. The sensitivity of the polypyrrole sensor is higher at high humidity levels. Polypyrrole sensor showed quick response and recovery times compared to polyaniline sensor [19][20][21].

When it is compared with the previous method used in previous research, water (H₂O) solvent is a good solvent for polypyrrole (monomer and polypyrrole) because polypyrrole, which will be the doping material, is easily soluble in water compared with other solvents, and it is easily electro synthesized in aqueous solution [22][23].

II. Materials and Methods

A. Equipments and materials

Manuscript The were some equipments that were used in this research: Beaker, which is used as a container to react materials, a container to contain chemicals in the form of solutions, solids, pastes or flour, a place to dissolve materials and a place to heat materials; digital scale, a measuring device used to measure the weight or mass of an object or substance; potentiostat, an electronic device used to measure the concentration of a substance resulting from a reduction-oxidation reaction; digital multimeter, which is an electronic device that is used to measure electric current, which has two kinds of currents that are direct current (DC) and alternating current (AC); nitrogen gas cylinders, which are used to transfer the pressure, at the beginning of the electropolymerization process; power supply, which is used to increase or decrease the voltage, in every process of electrical circuit; computer, which is used to processing data and; to give an output result; screen maker model 3000TT, which is used to screen print the sensor design that has been made with smoother and better results; furnace infrared/infrared heater (radiant technology), which is to produce heat energy and burn the sensor that has been printed with a screen maker, with the appropriate temperature measurement to produce a good sensor.

Some materials that were used were: alumina, which was the material that was

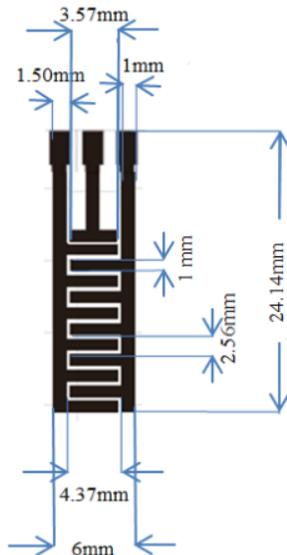


Figure 1. The electrode design

used as a substrate; platinized carbon paste (ferro), and Ag|AgCl (ferro) which were used for making an electrode design (working electrode, counter electrode, and reference electrode); conductive polymer polyaniline (PANI/C₆H₇N) (Sigma-Aldrich) and nitrate/NO₃⁻ (from sodium nitrate/NaNO₃) (Sigma-Aldrich) that were used as a dopant for sensitive membrane; Al₂O₃ (Merck) that was used for the purification process of PANi; nitrate standard solution in 1.000 mg/l NO₃⁻ (Merck) that was used for sensor performance testing.

B. Design of nitrate sensors

In this research, the design of working electrodes, reference electrodes, and counter/auxiliary electrodes were made with Corel Draw software to determine the design and layout of the three electrodes. The design and layout of the electrodes were chosen based on several things, including the area and the connectivity of each electrode. In addition, several experiments have been done regarding the design and layout of the electrodes. The electrode design is

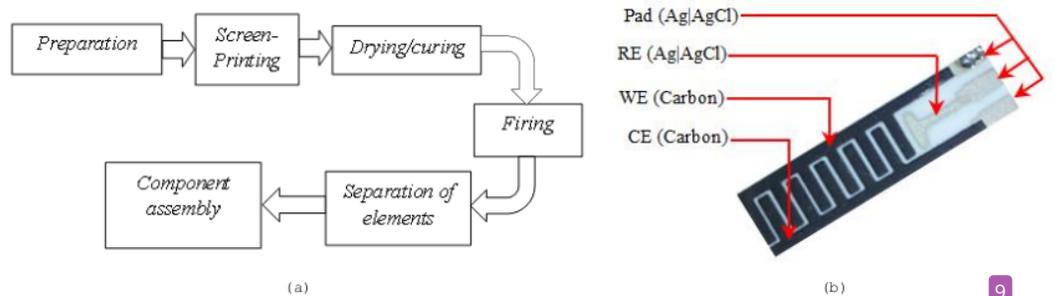


Figure 2. (a) The process of thick film technology; (b) The fabricated electrode, which contains: working electrode (WE), counter electrode (CE), reference electrode (RE), and pad

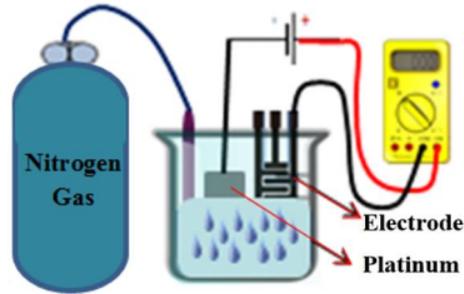


Figure 3. The electro polymerization process uses a potentiostatic method, using nitrogen gas that induces deoxygenated in a beaker which contains electrode and platinum that are connected to a digital multimeter

shown in Figure 1.

C. Sensitive membrane

The first process to produce a sensitive membrane is the purification process of polyaniline using Al₂O₃ for the preparation of a sensitive membrane doped with nitrate (NO₃⁻). The second process is the dissolution of liquid polyaniline (C₆H₇N) with water (H₂O) as a solvent, while previous studies used acid media as a solvent [15]. The last process is the dissolution of solid/crystal (granular) sodium nitrate (NaNO₃) with water (H₂O) as a solvent in a correct measurement to get a nitrate concentration and to get sensitive membrane consisting of Polyaniline (PANI) 1 M and nitrate (NO₃⁻) 0.1 M.

D. The fabrication process with thick film technology

Thick film technology is a 'printing' and 'firing' technology that uses conductive, capacitive, and insulation paste which is deposited on a pattern with screen printing method and then processed at the temperature that is according to a substrate and pastes to be used [24] [25] [26].

The electrode fabrication started with the printing, drying, firing, and packaging process (Figure 2a). The working electrode (WE) and counter/auxiliary electrodes (CE) are worked on simultaneously because both of

them use platinized carbon paste and will be heated at a temperature 120 °C for 15 minutes. The reference electrode (RE) and pad use silver|silver chloride (Ag|AgCl) and are heated in a firing machine (furnace infrared/infrared heater) at a temperature of 800 °C for 30 minutes. The fabricated electrode is shown in Figure 2b.

E. The electro polymerization/electroplating process

The electro polymerization/electroplating process is a process of deposition/coating of sensitive membrane on the working electrode by using a potentiostatic method (measurement with fixed potential) (Figure 3). The process is as follows, a solution of 0,1 M nitrate (NO_3^-) is mixed with a solution of 1 M polyaniline ($\text{C}_6\text{H}_7\text{N}$) in a beaker glass with the same ratio (50:50). The electro polymerization process lasts 30 minutes with a potentiostatic method (fixed potential value) of 1V. During the electro polymerization process, nitrate and polyaniline solution are de-oxygenated through the purging process 10 h nitrogen gas, and the positive voltage source (+) is connected to the working electrode and the negative voltage source (-) is connected to

platinum (Pt). In 30 minutes of the electro polymerization process, an electron transfer reaction will occur and the resulting current will be recorded and observed.

F. Electrode examination (nitrate sensor)

Sensor testing will be done 5 three steps. The first step was scanning electron microscopy (SEM)-energy dispersive x-ray spectroscopy (EDS), which is a characterization test of the electrodes to get the information about the morphology of the sample surface and to analyze quantitatively the percentage of each element. The characterization testing used the instrument with type SU3500 10 kV with a magnification 20k secondary electron (SE). After that reference voltage testing and characterizing process, which means the examination process that has done by comparing the reference voltage of the electrode that has been made, with the factory reference electrode/commercial Ag|AgCl reference electrode obtained from Acumet in 3 M KCL electrolyte solution (Figure 4). The characterization graph will show the comparison of the two and the deviations that occurred will be observable.

G. The testing and characterizing of nitrate sensor performance

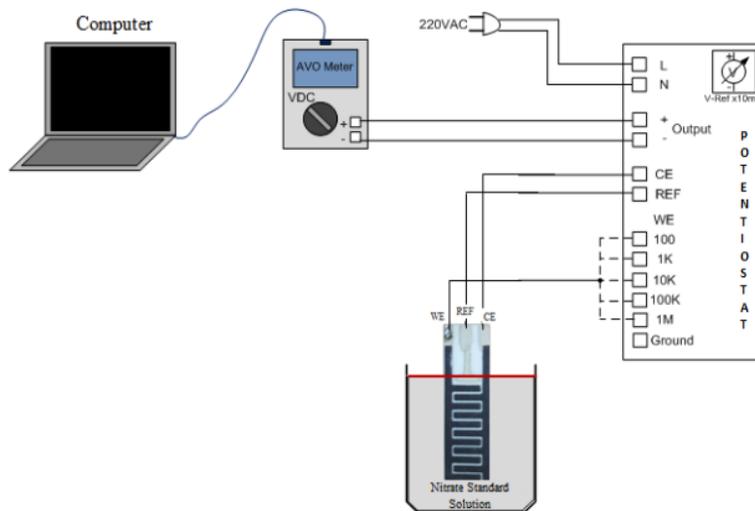


Figure 5. Sensor performance testing

Tabel 1. Percentage of sample elements before and after the electro polymerization process

Element	Weight %		Atomic %		Error %		K Ratio		Z		A		Befc
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	
C K	90.09	90.03	92.38	91.96	2.7	2.5	0.8013	0.8184	1.0048	1.004	0.8851	0.9053	1
N K	0	3.59	0	3.14	0	40.72	0	0.0027	0	0.977	0	0.0762	0
O K	9.91	6.38	7.62	4.9	14.82	19.27	0.0111	0.0066	0.9545	0.9537	0.1176	0.1078	1

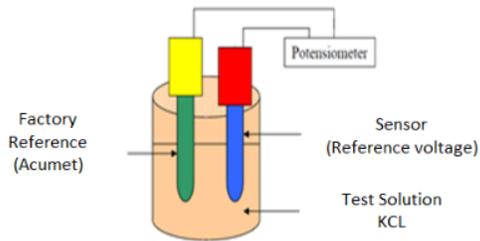


Figure 4. The reference voltage examination

Performance testing of nitrate ion sensors used a potentiostat and nitrate standards solution with four concentrations, which were: 10 mg/l, 20 mg/l, 50 mg/l, 100 mg/l (Figure 5). The result showed the generated current.

III. Results and Discussions

A. The result of scanning electron microscopy (SEM)- energy dispersive x-ray spectorscopy (EDS)

In SEM-EDS characterized testing, polyaniline (C_6H_7N) and nitrate (NO_3^-) as a sensitive membrane will be tested to get the morphology and percentage of each atomic element. The first testing showed the morphology of sample elements before electro polymerization (Figure 6(a)), while the second testing showed a sample with a particle size that is evenly distributed on the surface of the sample after the electro polymerization process and obtained a shape obtained that formed small balls with the size ranging from 0.18 μm (Figure 6(b)).

The differences in the percentage of sample elements before and after the electro polymerization process are shown in the tables below (Tabel 1). Before the electro polymerization process the percentage of atomic elements: 92.38 % carbon and 7.62 % oxygen, while after the electro polymerization process

showed the percentage of atomic elements from each element obtained: 91.96 % carbon, 3.14 % nitrogen, and 4.9 % oxygen. It also showed that the carbon element contained in the working electrode material and one of the polyaniline elements (C_6H_7N) had a large percentage value, which represents that polyaniline evenly coated the sample. On the other hand, nitrogen and oxygen elements have a better percentage value, which indicates that nitrate (NO_3^-) has been doped properly.

B. The electro polymerization process examinations

The graph of the electro polymerization process indicates the appearance of electron transfer reactions with a peak current value of 0.223 mA in the first process, which, however, declines and tends to be stable in the current of 0.01 mA for the last 30 minutes. The Current resulted from the electro polymerization process that is shown in Figure 7.

C. The result of reference voltage testing

Results The obtained reference voltage was measured by potentiometric process between platinized carbon paste that has been coated with sensitive membrane polyaniline (PANI) which is doped nitrate (NO_3^-) with the commercial Ag|AgCl reference electrode from Acumet to a KCL electrolyte solution with a concentration of 3 M. 12

This testing has an important role which aims in monitoring the stability of the voltage produced by the electrode and determining whether the electrode can be used in the process of detecting nitrate ions. The graph in Figure 8 shows the reference voltage that resulted from this testing. The graph shows that the peak voltage occurs in the first process with a voltage value

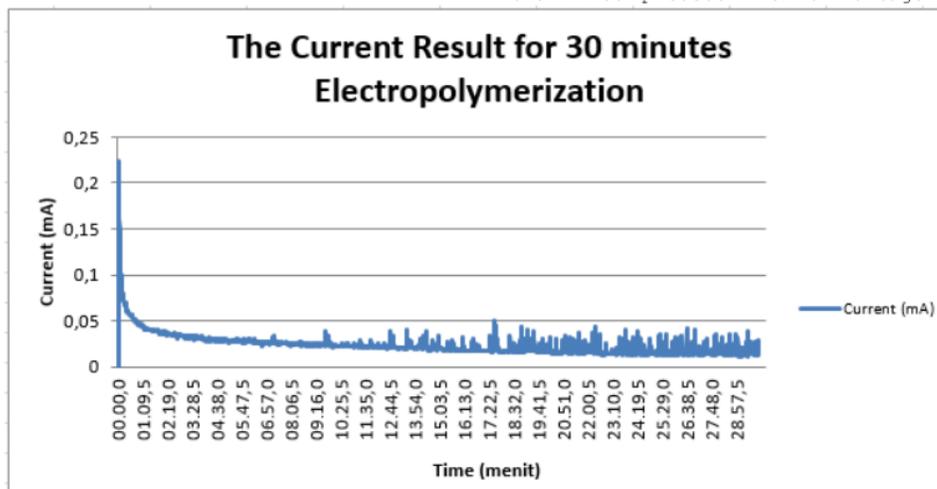


Figure 7. Current result from the electro polymerization process

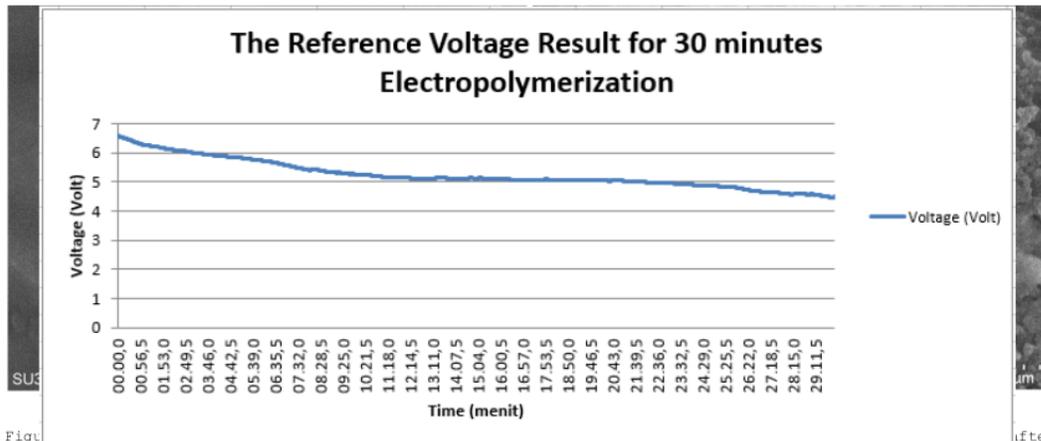


Figure 8. The reference voltage result

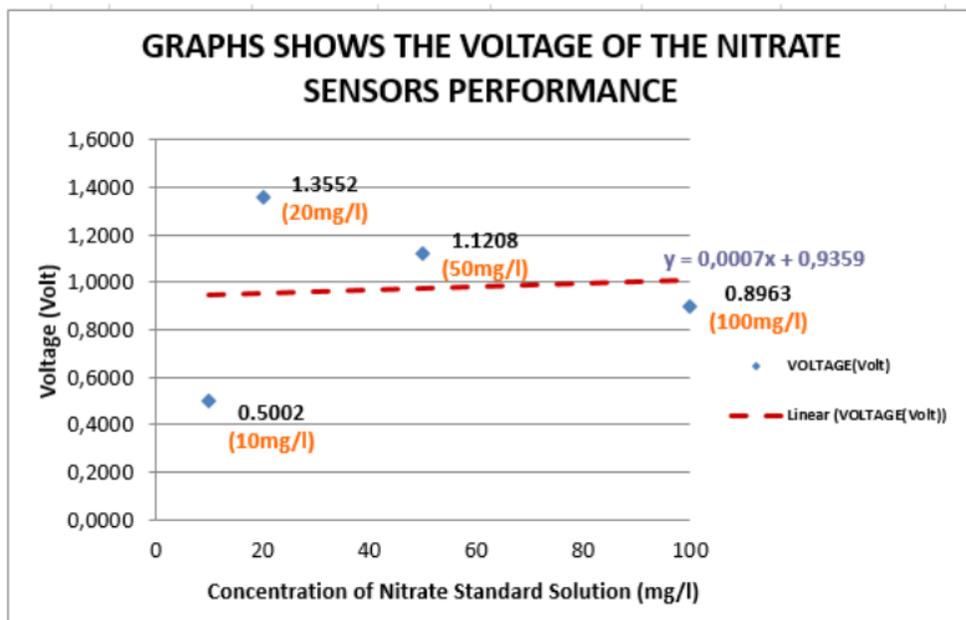


Figure 9. The voltage result from sensor performance testing

of 6.58 mV, and is stable at a voltage of about 5 mV, but tends to decrease to 4.41 mV in 30 minutes. It shows that it can be used in the detection process.

D. The result of sensor performance testing

The performance sensor was tested using potentiostat (resistance of 10 k Ω) and nitrate standard solutions with 4c and for each concentration, 5 tests were carried out. The voltage result showed good response with voltage output 7 each concentration being 0.5002 Volt (10 mg/l), 1.3552 Volt (20 mg/l), 1.1208 Volt (50 mg/l), and 0.8963 Volt (100 mg/l) (Figure 9).

The graph shows two output responses that occur at four concentrations of nitrate standard nitrate. The first

output voltage response occurred at a concentration of 10 mg/l - 20 mg/l, which displays a voltage that tends to rise linearly proportional to the concentration of the standard nitrate solution, with a voltage of 1.3552 Volt.

The output voltage response that occurs afterward tends to decrease, which is at a concentration of 20 mg/l - 100 mg/l with a decreasing trend that was linear too with a voltage of 0.8963 Volt. In Figure 9, the sensitivity shows that for every 1 mg/l concentration in standard nitrate solution, then the voltage increases by 0.0007

IV. Conclusion

This research proposes several conclusions. SEM-EDS testing showed the

particles of sensitive membrane morphology that were evenly distributed on the surface of the sample and formed small balls with a size ranging from 0.18 μm and EDS results indicate atomic element percentage: 91.96 % carbon, 3.14 % nitrogen, and 4.9 % oxygen. In the electro polymerization process, the output currents indicate the electron transfer reaction, with a positive current value indicating that the sensitive membrane coating process on the electrode is successful. The reference voltage testing has an essential role in the testing process which shows that the electrode can be used in the detection process of nitrate ions, with output voltage being around 4.41 mV - 6.58 mV. The first output voltage response linearly increased (10 mg/l - 20 mg/l), but then it decreased when the concentration of nitrate standard solution was increased to 50 mg/l - 100 mg/l. It can be concluded that nitrate sensors with 1 M polyaniline and 0.1 M NO_3^- have good performance, especially at a concentration of 20 mg/l. Ion sensors with polyaniline sensitive membranes doped with nitrate (NO) that have been designed and made can detect nitrate ions with a sensitivity of 0.0007.

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