

Cyclic Voltammetry Method for Analysis of Phosphate Concentration in Water

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Abstract: Phosphate is a nontoxic element but a limiting element for productivity. Several methods have been established to analyze the phosphate concentration in water. This study aims to analyze phosphate concentration in water using the voltammetry method using cyclic voltammetry. Cyclic voltammetry is an electroanalytical method that measures the current outcome of oxidation-reduction reactions in response to the potential. The current outcome is directly proportional to the phosphate concentration in the solution. The calibration curve was formed from the KH_2PO_4 standard solution using concentrations of 0.1 mg/L, 0.2 mg/L, 0.4 mg/L, 0.8 mg/L, and 1.6 mg/L. The voltammogram showed that the analyte does not have an anode peak current (I_{pa}), which means that the analyte solution did not have an oxidation reaction, so the cathode peak current (I_{pc}) value was used. Based on the calibration curve, the linear regression graph with a straight-line equation is $y = -0,00000645632x - 0,000208737$ with R^2 of 0,99737. Meanwhile, this cyclic voltammetry method was validated by calculating the LOD and LOQ values; the results are 0.1034 mg/L and 0.3134 mg/L, respectively. Hence, based on the analysis of phosphate concentration in water samples, this method works satisfactorily and is suitable for routine analysis because of its advantages.

Keywords: Analysis; Cyclic Voltammetry; Method; Phosphate; Water.

Introduction

Phosphorous (P) is the eleventh most abundant element in the earth's crust. It is an essential nutrient widely present in the environment and plays a critical role in the growth of all living things [1]. Naturally, various forms of phosphorous are present in the water environment. These phosphorous forms can be analyzed as phosphate because this is most commonly found [2]. Although phosphate is a nontoxic element, it is a limiting element for productivity. An excess phosphate concentration in the water environment promotes the proliferation of algae and aquatic plants, reducing the light intensity and dissolved oxygen level. This condition is known as eutrophication. Eutrophication has a detrimental effect on aquatic life [1–3]. Phosphate constantly accumulates in the water environment due to the discharge from various sources of phosphate, such as industrial uses, domestic sewage of households, and agriculture, with excessive use of fertilizers and animal wastes [4]. Thus, it is necessary to discover user-friendly and cost-effective analytical methods to analyze phosphate concentration in water.

Several methods have been established to analyze the phosphate concentration in the water environment. Currently, a widely used method is spectrophotometry [1–3]. However, this method requires precise control of reagents and takes time for the reagents to react. The commonest spectrophotometry includes ammonium molybdate as a reagent and using a reducing agent, ascorbic acid. Some earlier papers reported that the usage of ascorbic acid in the spectrophotometry method has limitations due to its stability [1,2]. Therefore, exploring alternative methods is needed.

Voltammetry methods are also suitable for these purposes. Voltammetry is a commonly applied

electrochemical method for determining dissolved substances in aqueous solutions or organic solvents [5]. Voltammetry is an electroanalytical method that measures the current outcome resulting from oxidation-reduction reactions occurring on the electrode surface in response to the potential given at the working electrode. The current outcome from the reduction reaction is a cathodic current, and the current from the oxidation reaction is anodic. The current outcome is directly proportional to the analyte concentration in the solution [6]. All elements that can undergo oxidation-reduction reactions on the electrode surface can be analyzed by voltammetry [7]. In this method, ions are separated according to their oxidation-reduction potential, so the analysis of significant elements does not interfere with minor elements [8]. The voltammetry method can be an alternative because of its analysis speed, high selectivity, and low detection limit [9].

One of the most commonly practiced methods in voltammetry is cyclic voltammetry. In cyclic voltammetry, the current outcome is measured as a function of potential in two sweeps so that the oxidation-reduction reaction information of the analyte can be appropriately observed [10]. The parameters in cyclic voltammograms are potential peaks (E_{pc} , E_{pa}) and current peaks (I_{pc} , I_{pa}) at the cathode and anode [7]. The advantages of cyclic voltammetry are easy usage, fast time analysis, high sensitivity and selectivity, low detection limit, and reversibility to maintain the sample's concentration unchanged. Moreover, the electrode can be utilized repeated times [11]. Due to the advantages of this method, the phosphate concentration in water was analyzed in this study using the voltammetric method using cyclic voltammetry.

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Research Methods

Materials

The materials used in this study were potassium dihydrogen phosphate KH_2PO_4 (Merck), potassium chloride KCl (Merck), filter paper Whatman No. 42, and distilled water.

Instrumentation

The tools used in this study were a watch glass, beaker glass (Iwaki Pyrex), measuring cylinder (Iwaki Pyrex), volumetric flask (Iwaki Pyrex), Erlenmeyer flask (Iwaki Pyrex), volumetric pipette (Iwaki Pyrex), analytical balance (OHAUS), and voltammeter (797 VA Computrace).

Preparation of phosphate stock solution

A phosphate stock solution with a concentration of 100 mg/L was prepared by dissolving 0.0100 g of potassium dihydrogen phosphate (KH_2PO_4) in distilled water. The resulting solution was then brought to a final volume of 100 mL using a volumetric flask.

Preparation of phosphate standard solution

Subsequently, the series of phosphate standard solutions was prepared with various concentrations of 0.1 mg/L, 0.2 mg/L, 0.4 mg/L, 0.8 mg/L, and 1.6 mg/L. The phosphate standard solution of varying concentrations was made by serial dilution using the stock solution. The stock solution was pipetted into a 100 mL volumetric flask and diluted with distilled water to the limit mark. Then, it was homogenized.

Calibration curve of phosphate standard solution

The calibration curve results in the linear regression graph with a straight-line equation based on Equations (1) [12].

$$y = ax + b \quad (1)$$

With the description: y is peak current outcome; x is a concentration of analyte; a is slope, and b is intercepted.

Limit of Detection (LOD) and Limit of Quantification (LOQ)

Limit of Detection (LOD) and Limit of Quantification (LOQ) values are determined according to Equations (2) and (3) respectively [13].

$$\text{LOD} = \frac{3.3 \times \text{standard deviation}}{\text{calibration curve slope}} \quad (2)$$

$$\text{LOQ} = \frac{10 \times \text{standard deviation}}{\text{calibration curve slope}} \quad (3)$$

Preparation of sample

The samples are water for aquaculture containing phosphate, which is collected after the adsorption process. A volume of 100 mL of samples was subjected to filtration using Whatman No. 42 filter paper. Then, each sample was ready to analyze the phosphate concentration by a voltammeter [1].

Analysis of sample phosphate

About 10 mL of analyte was put into the chamber of a voltammeter and added with 10 mL of 100 mg/L KCl solution. The current value was analyzed using a voltammeter with a potential value of -2 V to 1 V, a scan rate of 200 mV/sec, and a deposition time of 10 seconds [14].

Results and Discussion

In this work, the phosphate concentrations in water are analyzed by a voltammeter using cyclic voltammetry method. The phosphate concentrations can be determined by a voltammeter due to the polarization of electrodes in an electrochemical cell at a specific potential range, causing changes in the current by the cell as the result of the oxidation-reduction reaction of an analyte. This method involves an oxidation-reduction reaction at the anode and cathode, so the current outcome at both was observed [6].

The voltammetry equipment uses three electrodes: a working electrode, an auxiliary electrode, and a reference electrode [15]. This work used CuSAE as the working electrode, Pt as the auxiliary electrode, and Ag/AgCl as the reference electrode. The working electrode is a place for oxidation-reduction reactions [16]. CuSAE is a copper solid amalgam electrode. The amalgam electrode exhibits high sensitivity, low toxicity, and ease of manipulation as it can be utilized repeatedly and has the potential for miniaturization.

Furthermore, the benefit of using a copper amalgam electrode lies in its affordability and widespread availability. Occasionally, the Cu/Hg electrodes may exhibit better electrode characteristics than the Ag/Hg and Au/Hg electrodes [5]. The auxiliary electrode, along with the working electrode. This electrode is used to conduct the current so that the current can be analyzed. The material usually used as an auxiliary electrode is inert. Platinum (Pt) is an electrochemical electrode material widely used due to the optimal benchmark system [17].

Furthermore, Pt has high electrical conductivity and catalytic activity [18]. Meanwhile, the reference electrode has a significant feature of the potential energy being fixed and stable, unaffected by variations in the type and composition of the samples. This electrode determines the potential energy of an electrochemical cell by comparing it to a working electrode. The reference electrode commonly used is Ag/AgCl [19].

Calibration curve of phosphate standard solution

Before analyzing the phosphate concentration in water, the first step was to create the calibration curve of the KH_2PO_4 standard solution. The calibration curve indicates the correlation between the standard phosphate solution concentration and the peak current outcome. The standard phosphate solution was determined with concentrations of 0.1 mg/L, 0.2 mg/L, 0.4 mg/L, 0.8 mg/L and 1.6 mg/L, respectively. Phosphate analysis was conducted by putting the analyte into the chamber of a voltammeter and adding it to the KCl solution. KCl acts as a salt bridge between the working and reference electrodes. Also, it acts as a supporting electrolyte to maintain ions and minimize migration so that oxidation-reduction reactions occur. According to Rofiansyah & Setiarso [9], the concentration of KCl used in voltammetry is 50-100 times higher than that of the primary analyte. In voltammetry, the potential given and the current outcome were presented in a voltammogram. The voltammogram of the KH_2PO_4 standard solution was processed using OriginPro software, as shown in Figure 1.

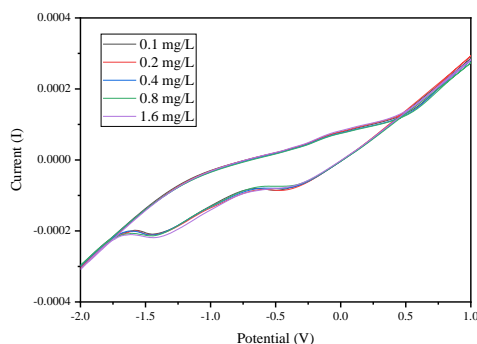


Figure 1. The voltammogram of the KH_2PO_4 standard solution

Figure 1 shows that the voltammogram does not have an anode peak current (I_{pa}), so the cathode peak current (I_{pc}) value was determined to create a calibration curve. The absence of an anode peak current indicates that the KH_2PO_4 standard solution had no oxidation reaction. The cathode peak current of the KH_2PO_4 standard solution is presented in Table 1.

Table 1. The cathode peak current of KH_2PO_4 standard solution

Standard concentration (mg/L)	Cathode peak current (I)
0.1	-0.00020907
0.2	-0.00021019
0.4	-0.00021151
0.8	-0.00021392
1.6	-0.00021901

The results of the cathode peak current of the KH_2PO_4 standard solution were processed with OriginPro software to create a calibration curve, as shown in Figure 2.

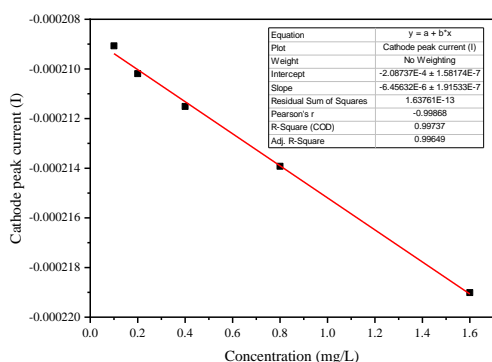


Figure 2. The calibration curve of phosphate

Based on the calibration curve in Figure 2, the linear regression graph with a straight-line equation is $y = -0,00000645632x - 0,000208737$ with R^2 of 0,99737. The value of the straight-line equation can be used to determine the phosphate concentrations using the cyclic voltammetry method. Meanwhile, R^2 is termed the coefficient of determination. This value can be interpreted as the proportion of variance in one variable that is accounted for by the other. In this study, the R^2 value is close to 1, indicating an excellent proportion of correlation between cathode peak current and phosphate concentration in the measured solution [20]. Subsequently, the cyclic

voltammetry method could applied to analyze phosphate concentration in water.

Limit of Detection (LOD) and Limit of Quantification (LOQ)

As a follow-up, a validation was performed by calculating the LOD and LOQ values for the cyclic voltammetry method. Limit of Detection (LOD) refers to the minimum concentration of an analyte that may be accurately detected and quantified by an analytical method. Meanwhile, the Limit of Quantification (LOQ) refers to the minimum concentration at which the analyte may be identified with a high level of reliability while also meeting specific criteria for bias and imprecision [21]. LOD and LOQ are typical examples of validation parameters whose values must be verified and defined in every construction and application of the calibration line. The use of calibration line models is the most frequent case in analytical practice, and most analytical techniques deal with these models [13].

The LOD and LOQ values can be determined based on the standard deviation and the calibration curve slope values according to Equations (1) and (2) [13]. Based on the calculations, the LOD value of this cyclic voltammetry method is 0.1034 mg/L. Instead, the LOQ value of this method is 0.3134 mg/L. LOD and LOQ values are used to determine the sensitivity of a method. The sensitivity of the method improves as the LOD or LOQ value decreases.

In contrast, as the LOD or LOQ value of the method increases, the sensitivity of the method decreases. According to Uhrovčík [13] states that there is no universal model with satisfactory suitability for all cases of trace analysis. The correct choice of a valid model for calculating LOD and LOQ values since LOD and LOQ values depend on the requirements for reliable detection or quantification of analytes in different types of samples; for example, spectrometric techniques are compared with other techniques by different principles. Hence, they have different assumptions regarding the validity of the observed values and data.

Analysis of sample phosphate

Furthermore, the samples' phosphate was analyzed using a standard solution method. The samples used in this study are water for aquaculture containing phosphate, collected after adsorption. Thus, the remaining phosphate concentration after the adsorption process of each sample needs to be analyzed. The results of the sample voltammogram are presented in Figure 3.

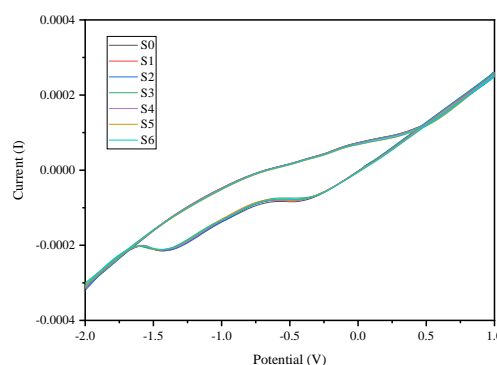


Figure 3. The voltammogram of the samples

Based on Figure 3, the cathode peak current was determined to obtain the phosphate concentration of samples. The cathode peak current and the phosphate concentration of samples are presented in Table 2.

Table 2. The cathode peak current and phosphate concentration of samples

Sample	Cathode peak current (I)	Phosphate concentration (mg/L)
S0	-0.00021514	0.9917
S1	-0.00021426	0.8554
S2	-0.00021385	0.7919
S3	-0.00021318	0.6882
S4	-0.00021233	0.5565
S5	-0.00021170	0.4589
S6	-0.00021117	0.3768

The results showed that the phosphate concentration in water was successfully analyzed using the cyclic voltammetry method. The samples contain phosphate with a relatively high concentration. This condition can occur due to the accumulation of various phosphate sources, especially from feed and aquatic waste [4]. Excessive phosphate concentration in the water environment can lead to the proliferation of algae and aquatic plants, reducing light intensity and dissolved oxygen levels, which can impact detrimental aquatic life [1–3].

Halim et al. [22] stated that based on standard operating procedures at CV. Lancar Sejahtera Abadi, the optimal phosphate concentration for aquaculture water is 0.5-1 mg/L. The highest phosphate concentration of the samples was 0.9917 mg/L by sample S0, indicating a concentration close to the phosphate threshold in aquaculture water. On the other hand, samples S1-S6 had lower phosphate concentrations because the adsorbent had adsorbed the phosphate in the water samples, indicating an optimal phosphate concentration in aquaculture.

Based on the results of phosphate concentration in water samples, it is shown that routine analysis of phosphate concentration in the water environment is essential. Therefore, a user-friendly and cost-effective method is required for routine analysis. Hence, cyclic voltammetry can be used as an alternative method due to several advantages such as easy usage, fast time analysis, low detection limit, high sensitivity, and selectivity [11].

Conclusion

The cyclic voltammetry method for analysis of phosphate concentration in water was studied. Based on the calibration curve, the linear regression graph with a straight-line equation is $y = -0,00000645632x - 0,000208737$ with R^2 of 0,99737. The R^2 value is close to 1, indicating an excellent proportion of correlation between cathode peak current and phosphate concentration in the measured solution. Subsequently, the value of the straight-line equation can be used to determine the phosphate concentrations in the water using the cyclic voltammetry method. As a follow-up to this method, validation was performed by calculating the LOD and LOQ values, and the results are 0.1034 mg/L and 0.3134 mg/L, respectively. Hence, based on the results of the analysis of phosphate concentration in water samples, this method works satisfactorily and is suitable for routine

analysis because of some advantages such as easy usage, fast time analysis, low detection limit, high sensitivity, and selectivity.

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