Modification of Glassy Carbon Electrodes on Starch-Based for Detection of Chromium Hexavalent

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Abstract

This study aimed to investigate the effect of the percentage addition of conductivity material on phosphorylated starch to modify a Glassy Carbon Electrode (GCE) for detecting Cr(VI). The conductivity materials used are activated carbon from rice husk and Fe_3O_4 nanoparticles. Phosphorylated starch was prepared by adding STPP as a cross-linker to starch. The method used for optimising the conductivity material in the phosphorylated starch. The sensor performance was determined by the limit of detection, sensitivity, and range of linear concentration. Data were collected by measuring Cr(VI) in the electrolyte H_2SO_4: K_2SO_4 using Differential Pulse Voltammetry (DPV). As a result, adding conductivity material increases the Cr(VI) current and shifts the peak potential to the left. The amorphous form of activated carbon and trigonal Fe_3O_4 nanoparticles affect the measured Cr(VI) current on the percentage of conductivity material in the phosphorylated starch matrix. The percentage of optimum conductivity of activated carbon and Fe_3O_4 nanoparticles in the phosphorylated starch matrix is 5%. The phosphorylated starch composition with Fe_3O_4 nanoparticles obtained the best sensor performance. The sensor performance obtained is the limit of detection 3.48 ppm; sensitivity 0.2120 ppm/µA in a linear concentration range of 2.6 – 18.2 ppm.

Keywords: Activated carbon, chromium hexavalent, Fe_3O_4, glassy carbon electrode, nanoparticles, phosphorylation starch.

1. INTRODUCTION

The development of electrode modification refers to the use of renewable natural materials. Modification electrodes can be reached by renewable natural materials such as starch (Mulyasuryani *et al.,* 2019). Starch has the limitations, such as forming unstable paste at low or high temperatures, low resistance to mechanical treatment, and low viscosity under acidic conditions (Herawati, 2016). The phosphorylation process can increase the ability of starch with the insertion of a phosphate group. Phosphorylation of starch increase material properties such as thermal resistance properties, acid stability, paste stability, and improves starch's texture properties (Sechi *et al.,* 2017). However, applying phosphorylation starch in the electrochemical method still has limitations. The phosphorylation of starch leads to a decrease in the conductivity of starch (Dong *et al.,* 2020). As a result, the modifier has good electrical conductivity is needed.

Activated carbon from rice husk and Fe_3O_4 nanoparticles are modifiers that have good conductivity to increase the electrical conductivity of the polymer. Both materials have a specific surface area, a microporous structure, good conductance, and a high value of specific capacity (Yi *et al.,* 2016). Some research to synthesize activated carbon from rice husks was carried out. Yi *et al.,* (2016) got activated carbon with a specific capacitance of 147 F g^{-1} and a high specific surface area of 2696 m^2 g^{-1}. Xu *et al.,* (2014) obtained activated carbon with a specific capacity of 250 Fg^{-1} and a high specific surface area of 2523.4 m^2 g^{-1}. In another research, Le Van *et al.,* (2014) received activated carbon from rice husk with a specific surface area is 2681 m^2 g^{-1}

and a specific capacitance of 198.4 F g^{-1}. In another way, Fe_3O_4 nanoparticles have a specific surface area of 165.05 m^2 g^{-1}, and a specific capacitance is 207.7 F g^{-1} (Wang *et al*, 2013). Some research on adding Fe_3O_4 nanoparticles for modifier electrodes has been done. Andawiyah *et al.,* (2020) show that adding Fe_3O_4 nanoparticles to PVA for paracetamol detection increases the sensors' sensitivity and decreases LOD. Mulyasuryani *et al.,* (2019) show adding Fe_3O_4 nanoparticles on cassava starch membrane to detect acetaminophen and caffeine. The obtained sensor has an accurate measurement of 96–99%. It shows that activated carbon and Fe_3O_4 nanoparticles can be used as conductive materials to improve electrical conductivity.

Chromium (Cr) is one of the most earth elements with numerous 100 mg/kg crust of the earth. Chromium is present in a stable form as trivalent and hexavalent. Furthermore, Cr(VI) has a robust oxidizing ability. This character makes Cr(VI) have toxic, mutagenic, and carcinogenic effects (Xu *et al*, 2019)(Tu *et al*, 2018). The toxicity of Cr(VI) is 100 times higher than Cr(III) (Filik *et al*, 2019). WHO (World Health Organization) assign limited quality standard Cr(VI) in groundwater is 50 ppb (Cuéllar *et al*, 2016). Standard Nasional Indonesia (SNI) standardized analysis for Cr(VI) is spectrophotometry (with diphenylcarbazide agent) and Atomic Absorption Spectroscopy (AAS). They have limitations. There is an analysis for total Cr (Wiryawan *et al*, 2018). This is causing a high selectivity detection for analysis Cr(VI) was needed.

Voltammetry is an ion-specific method that measures the current at the reduction potential of the analyte. Measurement of Cr(VI) with the existence of Cr(III) will not be disturbed. It is because they have different reduction potentials. The reduction potential of Cr(VI) is at 1.33 V, while the reduction potential of Cr(III) is at -0.74 V. The specific Cr(VI) measurement can be conducted by arranging the potential used (Tu *et al.,* 2018).

The development of voltammetric measurements is carried out by modifying the electrodes to increase sensitivity and selectivity. Several studies of electrode modification to detect Cr(VI) have been carried out using gold nanoparticles and bismuth. For example, modification of the SPCE (Screen-Printed Carbon Electrode) using gold nanoparticles showed a high increase in sensitivity, namely LOD (Limit Of Detection) 5.4 g/L and a concentration range of 20–200 g/L (Tu *et al.,* 2018). While the modification of the GCE with bismuth also obtained high sensitivity with a LOD of 0.6 ppb, LOQ (Limit Of Quantitative) 2 ppb, and a concentration range of 2–12 ppb (Th Hue *et al.,* 2020). However, modification using gold nanoparticles has a weakness, whereas the synthesis of gold nanoparticles takes much time, effort, and cost with not environmentally friendly (Yasser *et al.,* 2019). In comparison, using bismuth is expensive and susceptible to temperature instability (Rossel *et al*, 2010). In this study, modification of GCE was carried out with starch as a renewable material.

This research aimed to investigate the influence of adding mass conductive material on a phosphorylated starch to modifier GCE and determine quantitative analysis from obtained sensors. In this research, the conductive material used was Fe_3O_4 nanoparticles and activated carbon.

2. MATERIALS AND METHODS
Materials and Tools

The materials used in this study were cassava starch, sodium tripolyphosphate (Sigma Aldrich), hydrocloric acid (Chemicals SAP), potassium dichromate (Pudak Scientific), activated carbon from rice husk, Fe_3O_4 nanoparticle (Sigma Aldrich), sodium hydroxide (Merck), sulfate acid (Smartlab), potassium sulfate (Ensure), and aquades.

The tools used in this study were glassy carbon electrode with a disk (Methrohm) as work electrode, platinum electrode (Methrohm) as a counter electrode, Ag/AgCl electrode (Methrohm) as reference electrode, galvanostat potentiostat (Autolab PGSTAT204), oven (Yenaco YNC-OV), analytical balance, scanning electron microscopy (SEM) FEI Inspect S50, and glassware.

Prepared of Phosporylation Starch (PS)

Preparing phosphorylation starch (PS) was adapted from Mulyasuryani's experiment (Mulyasuryani *et al.,* 2019). 2 g of cassava starch was added to 50 mL of boiling water and stirred until homogeneous. Next, 50 mL water and 8 drops of 2 M HCl were added and kept the solution at 90 °C for one hour, then add 2 M NaOH until pH 8. Next, a 70 mL

solution of starch was put into another beaker glass and added 20 mL 2% STPP. Stir this mix solution at 90 °C overnight. Finally, the solution was placed in a petri dish and dried at 60 °C for 4 hours.

Modified of Glassy Carbon Electrode (GCE)

The modification of GCE was carried out by 0.1 g of PS, and 1 mL of hot water was mixed and stirred for 5 min to form a homogenous solution. Next, activated carbon and Fe_3O_4 nanoparticles were added to the solution and stirred. Finally, the GCE surface was lubricated with a solution and dried for 4 min at 50 °C. The composition of modifier GCE (activated carbon and Fe_3O_4 nanoparticles) is shown in **Table 1**.

Table 1. Composition of modifier GCE

Electrode	Activated Carbon (%)	Fe_3O_4 Nanoparticles (%)
GCE/PS	-	-
PSC1	5	-
PSC2	10	-
PSC3	20	-
PSC4	50	-
PSN1	-	5
PSN2	-	10
PSN3	-	20
PSN4	-	50

Differential Pulse Voltammetry (DPV) Measurement

Quantitatively measured Cr(VI) in mixed solution 0.05 M H_2SO_4 and 0.05 M K_2SO_4 using differential pulse voltammetry (DPV). The setting were potential range 0.6–1.4 V (vs Ag/AgCl), potential step 0.01 V, modulation amplitude 0.1 V; modulation time 0.05 V, interval time 0.5 V and scan rate 0.02 V/s.

3. RESULTS AND DISCUSSION
Influence Mass Ratio Membran and Conductive Material

The percentage of activated carbon in the PS matrix produces the highest current on the PSC1 sensor, shown in **Figure 1a-b**. Furthermore, an increased percentage of activated carbon in the PS matrix indicates a

decrease in Cr(VI) measurement current. According to Koncar (2019), decreasing peak current occurs due to the addition of conductive material in the polymer matrix being elongated and breaking some conductivity paths. That causes an increase in the electrical resistivity of the polymer matrix. Consequently, the current decreases as the mass of activated carbon increases.

The increase in the percentage of Fe_3O_4 nanoparticles in the PS matrix shows the best current peak of Cr(VI) by the PSN1 sensor (**Figure 2a–b**). Therefore, adding Fe_3O_4 nanoparticles reduces the current, then increasing current from PSN2 to PSN4. The result occurred because, on PSN1, numerous Fe_3O_4 nanoparticles and PS matrix were proportional electrically. Then, the decrease of current at PSN2 occurs because adding Fe_3O_4 nanoparticles came down the cross-section of PS (membrane matrix) while conductivity paths were still low. Then, intensifying of current occurs because adding material conductive like Fe_3O_4 nanoparticles create more conductivity paths. Therefore, it caused an increase in the current (Koncar, 2019).

Activated carbon and Fe_3O_4 nanoparticles were analyzed with XRD. The XRD pattern of activated carbon used in this research shows two peaks at 23° dan 44°. This result shows that activated carbon was amorphous (Riyanto *et al*., 2020). In contrast, the XRD pattern of Fe_3O_4 nanoparticles used in this research shows seven peaks at 18.3°; 30.1°; 35.5°; 37.1°; 43.1°; 53.5°; and 57°. According to Inorganic Crystal Structure Data (ICSD): 196988, this peak was Fe_3O_4 with crystal system trigonal. Therefore, the results obtained differ based on the structure difference between activated carbon and Fe_3O_4 nanoparticles.

Comparison of GCE/PS, PSC1, and PSN1

Figure 3 shows that modifying GCE with PS can increase the measurement current of Cr(VI). Moreover, this result proves that adding mass of the conductivity material like activated carbon and Fe_3O_4 nanoparticle in PS can increase the analysis current of Cr(VI). Rising the current of Cr(VI) can be explained because activated carbon and Fe_3O_4 nanoparticle, as conductivity properties, has high specific capacitance (Le *et al*., 2014; Pai *et al*., 2021).

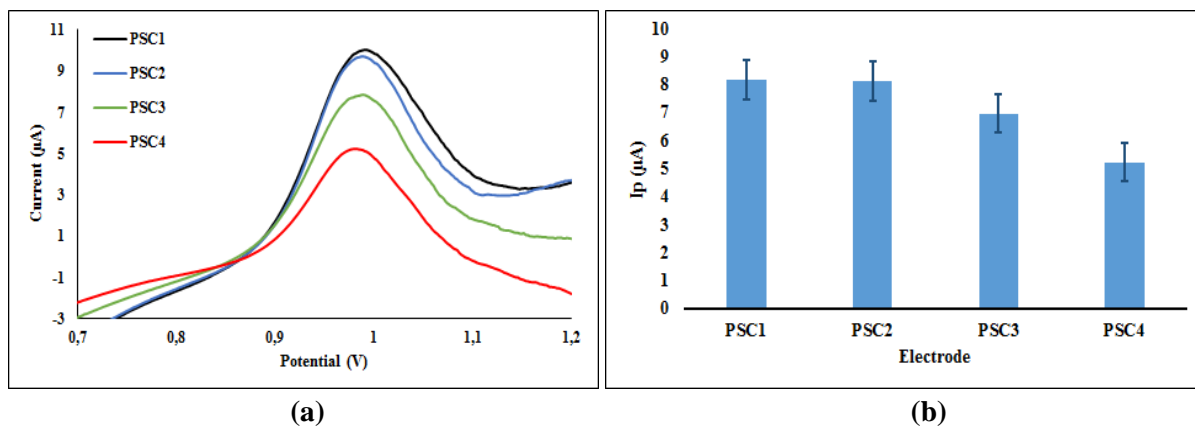**(a)**   **(b)**

Figure 1. (a) Voltamogram influence percentage of activated carbon in the PS matrix ; (b) Observed peak currents for Cr(VI) 31.2 ppm; in 0.05 M H_2SO_4 and 0.05 M K_2SO_4
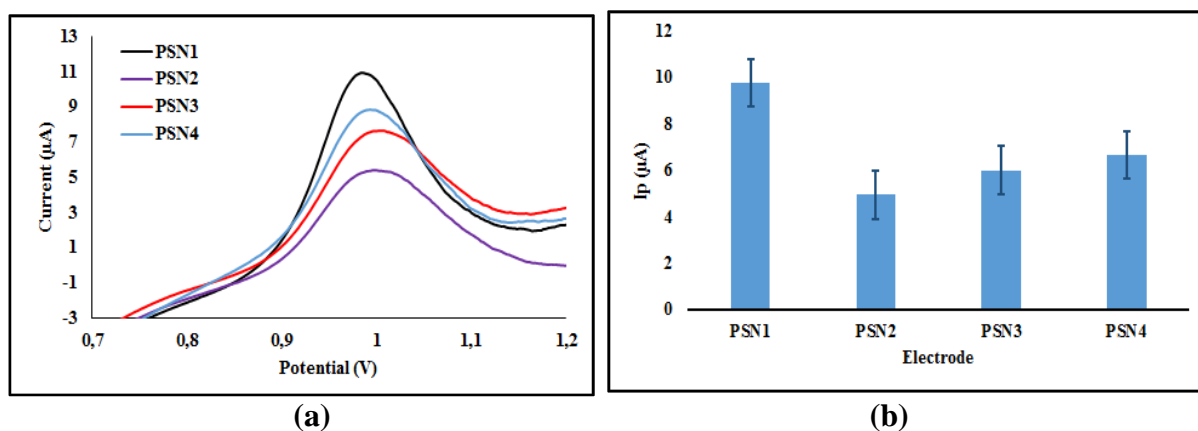

(a)   **(b)**

Figure 2. (a) Voltamogram influence percentage of Fe_3O_4 nanoparticles in the PS matrix ; (b) Observed peak currents for Cr(VI) 31.2 ppm; in 0.05 M H_2SO_4 and 0.05 M K_2SO_4

Table 2. Potential peak (Ep) and current peak (Ip) sensors of Cr(VI)

Electrode	Ep (V) vs Ag/AgCl	Ip (µA)
GCE	1.00067	2.7258
GCE/PS	0.99075	6.0734
PSC1	0.98679	7.6515
PSN1	0.98679	9.2231

SEM characterization of PSC1 and PSN1 is shown in **Figure 4**, which shows that adding conducting material in the PS. The addition of activated carbon to the PS revealed that the arrangement of activated carbon was dispersed irregularly due to differences in the size and shape of the activated carbon. Meanwhile, adding Fe_3O_4 nanoparticles to the PS showed that Fe_3O_4 nanoparticles were regularly dispersed on the PS.

Table 3 shows that modification with PS can sift the peak of potential to the left. It occurs because the starch membrane has some carboxyl groups. This group can to reduced Cr(VI) at measurement. In addition, adding activated carbon and Fe_3O_4 nanoparticles can swipe the peak potential to the left and plays a role in increasing the conductivity. Besides that, adding conductive material will facilitate electrons to move in the modifier film (Koncar, 2019).
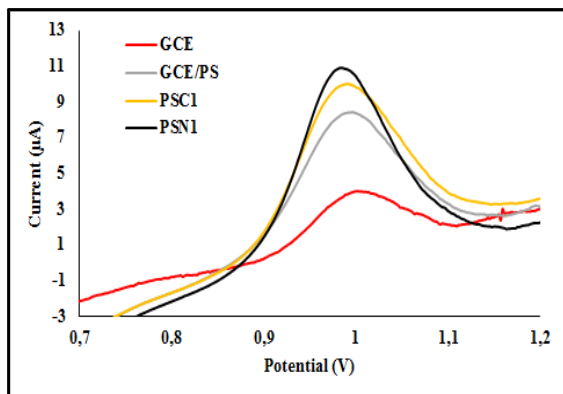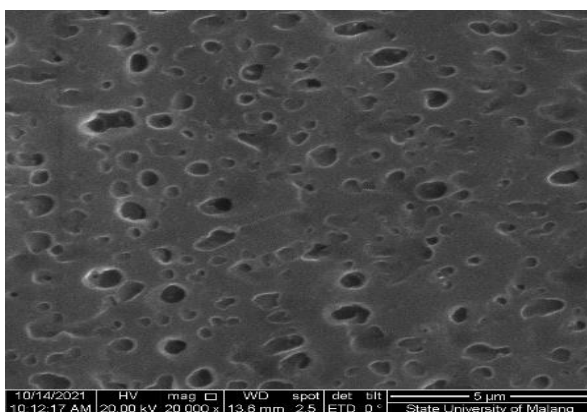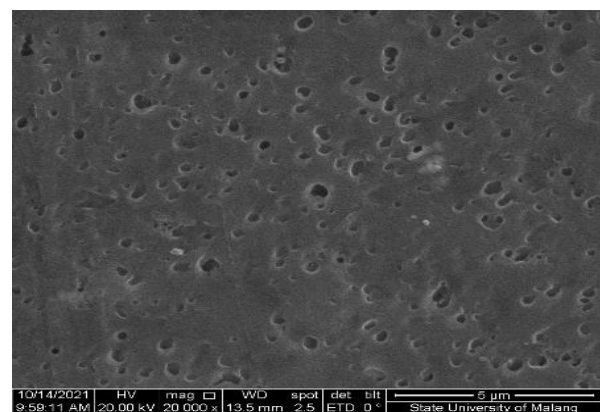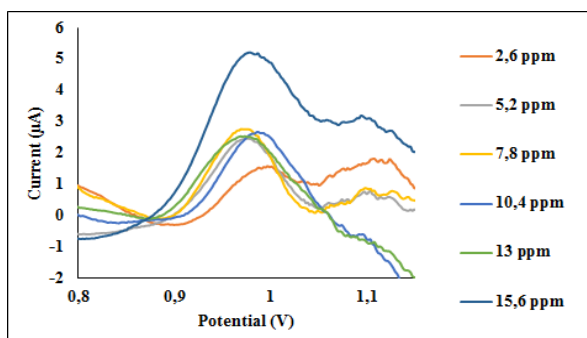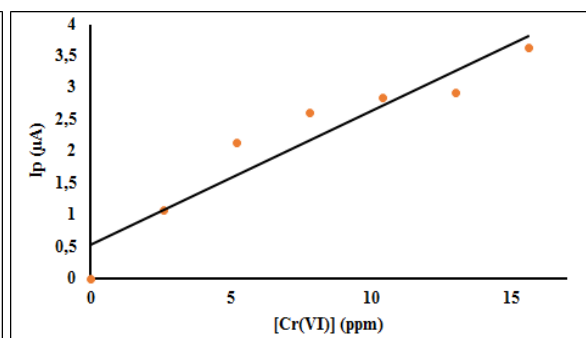
Figure 3. Voltamogram Cr(VI) at GCE, GCE/PS, PSC1, and PSN1

Performance of Sensor

The performance of PSC1 and PSN1 was determined to understand the relationship between the concentration of Cr(VI) and the current peak using the DPV technique. The result of this experiment is a voltammogram and standard curve shown in **Figure 5**. The parameters of analysis Cr(VI) are shown in **Table 4**. Results show that adding Fe_3O_4 nanoparticles in the PS has better parameter analysis of Cr(VI) than adding activated carbon.

(a)   (b)

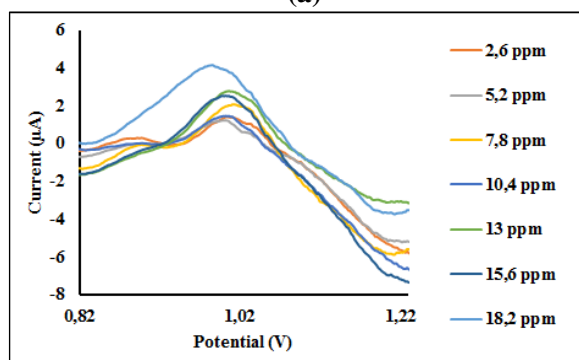**Figure 4.** Characterization SEM of (a) PSC1 and (b) PSN1

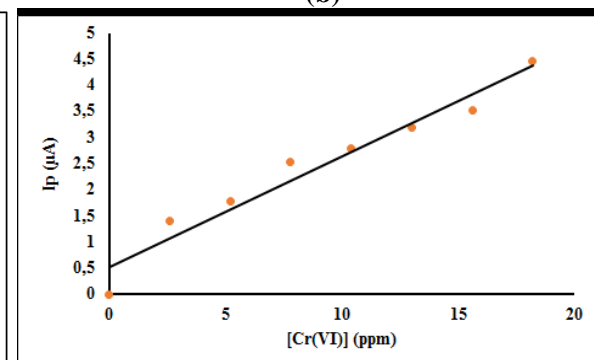**Figure 5.** (a) Voltammogram and (b) Standard Curve of PSC1; (c) Voltammogram and (d) Standard Curve of PSN1

Table 3. Performance of sensors

Electrode	LOD(ppm)	Sensitivity (ppm/µA)	Range of Concentration (ppm)
PSC1	5.09	0.2098	2.6–15.6
PSN1	3.48	0.2120	2.6–18.2

4.   CONCLUSIONS

The addition of activated carbon and Fe_3O_4 nanoparticles in the PS matrix has increased the sensor's performance. The optimum percentage of both activated carbon and Fe_3O_4 nanoparticles is 5%. Different kind of conductive material causes different impact increase percentage in the PS matrix for the current peak of Cr(VI). Enhancing activated carbon with amorphous shapes causes decreasing Cr(VI) current. While increasing Fe_3O_4 nanoparticles with trigonal structure increase the current of Cr(VI). The obtained sensor shows that the best conductive material for sensor Cr(VI) is Fe_3O_4 nanoparticles. To improve the performance of the sensor, further study needs to experiment with optimum electrolyte concentration.

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