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ORIGINAL STUDY

Development of a Chromium (VI) Biosensor Using Silver-modified Milkfish (*Chanos chanos*) Gelatin and Carbon Electrodes

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Abstract

Detection of chromium (VI) metal ions using fish gelatin-based electrodes and silver-modified carbon electrodes (FGC-AgE) has been successfully developed. Chromium (VI) is a toxic heavy metal commonly found in contaminated water sources and poses significant risks to human health and the environment. Therefore, monitoring and control of Cr (VI) are very important. The purpose of this study was to develop a sensitive and selective electrochemical sensor for detecting Cr (VI) in water. The research stages include: (1) extraction of fish gelatin, (2) fabrication of FGC-AgE working electrodes, and (3) analysis of electrode performance. The tests include optimization of pH, concentration effects, selectivity to other ions, and repeatability tests. All analyses were carried out using the cyclic voltammetry method in the potential range of −1000 mV to +1000 mV with a scanning rate of 100 mV/s. The results showed that FGC-AgE worked optimally under alkaline conditions, with the highest current response at a potential of −0.249 V. This electrode has a measuring range of 1−7 μM, a detection limit of 0.295 μM and a sensitivity of 14.32 μA. $\mu M^{-1}.mm^{-2}$. In addition, FGC-AgE showed high selectivity towards Cr (VI) and was not affected by the presence of other metal ions such as iron, cadmium, lead, copper, and chromium (III). Repeated tests showed consistent electrode performance. In summary, FGC-AgE electrode has the potential to be an effective and reliable alternative for detecting Cr (VI) ions in the future.

Keywords: Chromium (VI), Fish gelatin, Carbon, Cyclic voltammetry

1. Introduction

Gelatin is a natural protein derived from collagen found in animal body parts such as bones and skin. One possible source of gelatin is fish, which is called fish gelatin [1,2]. An example of fish that can be used as a gelatin source is milkfish (*Chanos chanos*) [3,4]. As a biopolymer, gelatin finds various applications in the food, pharmaceutical, cosmetic, and photographic industries [5]. In addition, gelatin is also specifically used as a multifunctional support material in biosensors. This is due to its ability to dissolve electrode material, its high adhesive force in binding small particles, and its biocompatibility properties that support electrode activity [6].

The use of fish gelatin in biosensors is evolving to create sensors that are sensitive, selective, and stable. Hutapea et al. (2018) reported the successful use of milkfish gelatin as biosensor active materials for the determination of chromium (III) [7]. Another study showed that fish gelatin could be used as a long-lasting biosensor to detect hydrogen peroxide [6]. These

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advantages make fish gelatin a promising material for the development of biosensors, including for the detection of chromium (VI).

Chromium is a toxic heavy metal with multiple oxidation states. The most stable forms in nature are Cr (III) and Cr (VI). Cr (VI) comes from the compound CrO_3 and exists in the form of yellow chromate (CrO_4^{2-}) or orange-red dichromate ($Cr_2O_7^{2-}$). Cr (VI) is considered very dangerous because it is easily absorbed by the body and can cause various health problems such as skin and eye irritation, impaired liver and kidney function, and epigenetic effects on DNA [8]. In addition, the presence of Cr (VI) in the environment can damage soil and water quality, thus negatively affecting ecosystem health [9]. Therefore, monitoring Cr (VI) content is very important to prevent negative impacts on humans and the environment [10,11].

Various analytical methods have been used to detect Cr (VI), including spectrophotometric, adsorption, neutron activation, and electrochemical methods [12−15]. Among these methods, electrochemistry offers several advantages such as easy operation, short analysis time, and relatively low cost. The development of electrochemical methods is ongoing with various modifications of working electrodes, including carbon-based electrodes [16]. Carbon electrodes work well due to their large electroactive surface area and are used for various applications such as the detection of levofloxacin [17], Hydroxychloroquine [18] and catechol in water samples [19]. The use of carbon is advantageous because it has a high electroactive surface area [20].

In this study, fish gelatin was combined with carbon as a modification material for silver electrodes to detect Cr (VI) using an electrochemical method [21]. This combination is expected to provide an effective and innovative new alternative for Cr (VI) analysis in the future.

2. Materials and methods

2.1. Materials

The materials used in this research were milkfish bones taken from home industry in Tarakan City, North Borneo, aqua DM (Brataco), potassium chromate (K_2CrO_4), sodium hydroxide (NaOH), Lead Nitrate $Pb(NO_3)_2$, Chromium Nitrate ($Cr(NO_3)_3 \cdot 9H_2O$), Copper Sulfate ($CuSO_4$), Cadmium Chloride ($CdCl_2 \cdot H_2O$) purchased from Merck.

2.2. Fish gelatin extraction

Fish gelatin extraction follows the procedure that Hutapea et al. (2020) have carried out. Gelatin is extracted from the bones of milkfish (*Chanos chanos*), which is the industrial waste of Milkfish without thorns in Tarakan City, North Kalimantan. The fish bones are cleaned of meat residues and dried. The dried fish bones are then soaked in a 0.1 M NaOH solution for 48 hours. After that, it is washed until the pH is neutral. Next, it was soaked in 0.1 M HCl solution for 72 hours. After that, it is washed to neutral pH. Furthermore, the extraction process uses water solvent with a ratio of milkfish bones and water of 1:3. The extraction process is carried out in stages at a temperature of 55 °C for 4 hours using a water bath. After that, the filtrate is dried using an oven at a temperature of 50 °C [22].

2.3. Preparation of milkfish and carbon gelatin modified silver electrode (FGC-AgE)

The Fabrication of FGC-AgE was carried out by mixing gelatin and carbon with a mass ratio of 1:1 on the watch glass. Next, it is heated using *a hotplate* until it forms a paste. Then, the paste is manually inserted into the electrode body, which has been filled with silver wire with a diameter of 1 mm and a length of 5 cm. The paste should touch the end of the silver wire.

2.4. Electrochemical characterization of FGC-AgE to Cr (VI) determination

All FGC-AgE performance for Cr (VI) detection uses cyclic voltammetry (CV) techniques; if there is a test without CV, it will be described. Testing uses an AUT84948 *type* Metrohm Autolab tool with a 3-electrode system. The three-electrode cells used are FGC-AgE as a working electrode, Ag/AgCl (KCl 3 M) as a comparison electrode, and platinum wire as an auxiliary electrode. Measurement was performed at −1 V to +1 V potential with a scan rate of 100 mV/sec. The effect of electrode modification using Fish Gelatin was studied by measuring 7 μM Cr (VI) in 0.1 N NaOH using silver electrode (AgE), Carbon electrode (CE), and FGC-AgE. The influence of pH in measurements was studied by measuring the same solution at pH 1.7 and 13. The effect of concentration was also studied by measuring various concentrations of Cr (VI) solutions (1, 2, 3, 4, 5, 6, and 7 μM) to obtain detection limits and sensitivity. FGC-AgE selectivity was studied by measuring copper (Cu), iron (Fe), lead (Pb), and cadmium (Cd) solutions, each with a concentration of 7 μM in NaOH 0.1 N. Repeated electrode testing was carried out by measuring 7 μM Cr (VI) 5 times using a single electrode.

3. Result and discussion

3.1. Fish gelatin extraction

Gelatin extracted from Tarakan City, North Kalimantan, Indonesia *Chanos chanos* produce yellow

crystals and soluble in water. The gelatin obtained has moisture content of 6.39 %; ash content of 1.92 %; pH of 6.1 and viscosity of 5.39 cP. All gelatin characteristics have been reported in Hutapea et al. (2020) [22].

3.2. Electrochemical characterization of FGC-AgE to Cr (VI) determination

The FGC-AgE showed a positive response to the determination of Cr (VI). Fig. 1 showed a significant difference in the current response between the blank solution and the Cr (VI) solution at a potential of −0.249 V for FGC-AgE. This difference shows that the electrode can work well on the target compound [23]. The difference in current response between the blank solution and the Cr (VI) solution was not found in the silver and carbon electrodes. It means that when the gelatin and carbon material is removed from the electrode, there is no response to the Cr (VI) solution. We thought that Cr (VI) ions undergo reduction to Cr (III) due to interactions with atoms such as nitrogen and oxygen present in gelatin [24] and supported by carbon which has a high conductivity value.

3.2.1. Determination of optimum pH

FGC-AgE was tested on three different solution conditions, namely acidic, alkaline, and neutral conditions, to determine the optimal pH condition of the test. The results are shown in Fig. 2. Voltammograms show that FGC-AgE can work optimally in alkaline conditions to detect chromium (VI). It can be seen from the significantly different current response between the blank and Cr (VI) solution. The blank does not show the current response, while the Cr (VI) solution shows the peak current response. In contrast to the alkaline condition, in the acidic and neutral conditions, the gap between the blank and the Cr (VI) solution did not show a significant difference in the current response. Although Cr (VI) reduction often occurs in acidic condition, but in an alkaline condition, Cr (VI) can also be reduced to Cr (III) [25−27]. So that the next test is carried out under basic conditions.

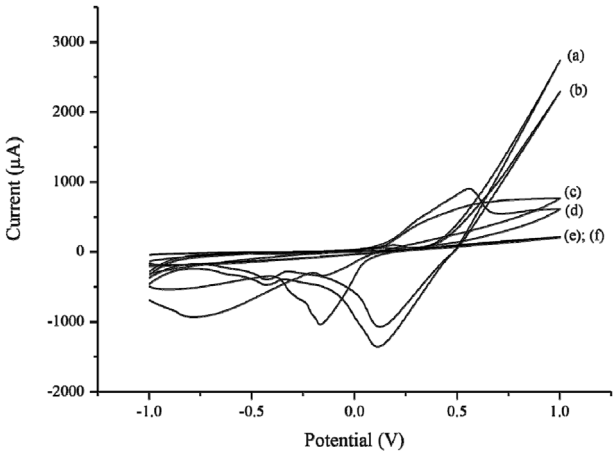

Fig. 2. Voltammogram response FGC-AgE in acid conditions to (a) blank, (b) Cr (VI); alkaline conditions (c) blank, (d) Cr (VI); neutral conditions (e) blank, (f) Cr (VI).

3.2.2. Determination of detection limits and sensitivity

Fig. 3 is a voltammogram from FGC-AgE measurements of Cr (VI) solutions from concentrations 1−7 μM. The reduction peak in −0.249 V, the current value

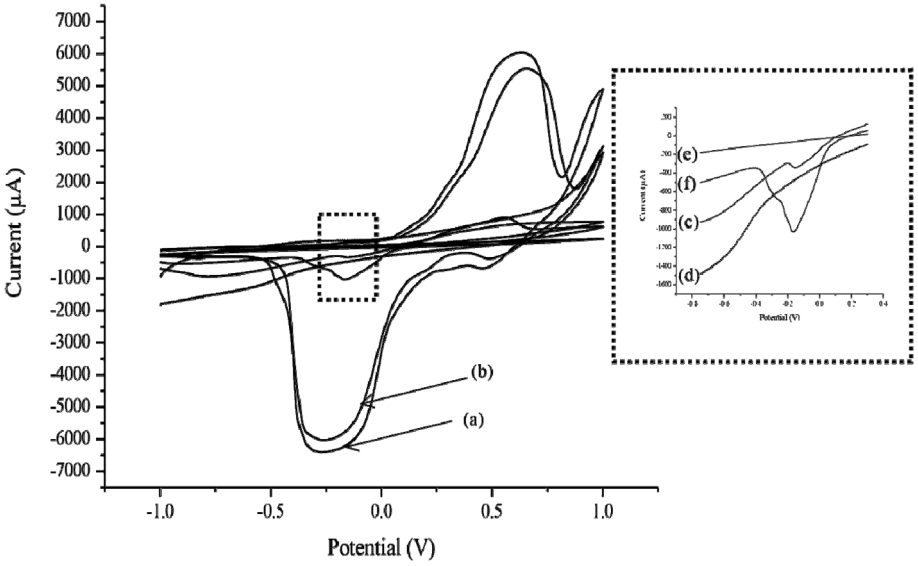

Fig. 1. Voltammogram response electrode Ag to (a) blank, (b) Cr (VI); Carbon electrode to (c) blank, (d) Cr (VI); Ag modified gelatin and car-bon (e) blank, (f) Cr (VI).

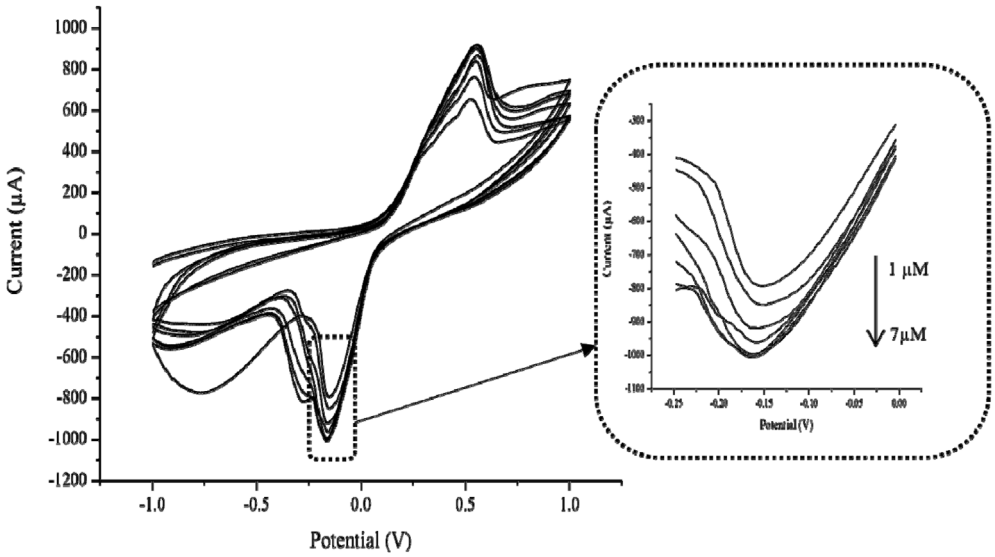

Fig. 3. Voltammogram response electrode to Cr (VI) with concentration 1–7 μM.

increases as the concentration of the test solution increases. These results confirm that FGC-AgE has a good sensitivity to Cr (VI).

Fig. 4 is a linear curve between the peak anodic current value and the Cr (VI) concentration. The linear regression equation and the correlation coefficient (R^2) is i_{pa} (μA) = −754.1−49.6 c (μmolL^{-1}) and 0.9823. The detection limit calculation uses formula 3 σ/m, where m is the slope of the line and σ is the standard deviation of the blank [28]. The detection limit value is 0.295 μM. While the sensitivity value obtained is 14.32 μA. μM^{-1} .mm^{-2}. The detection limit value generated by FGC-AgE against Cr (VI) is better than that of other electrodes. A comparison of chromium (VI) determination detection limit values with various electrodes is listed in Table 1.

The reaction that occurs on the electrode surface is confirmed through Electrochemical impedance spectroscopy (EIS) measurements. The resistance value generated by measuring EIS on the electrode (Fig. 5) shows that there is a difference in resistance between the blank and the Cr (VI) solution; every second, the measurement is different. Table 2 shows the difference in resistance that occurs between the blank and the test solution up to the 20th second. This shows that there are obstacles at the time of measurement. This obstacle occurs due to the presence of elements or compounds that undergo a reaction. It is suspected that the reaction is a reduction-oxidation reaction (redox) that occurs on the surface of the electrode. The possibility of this reaction is the reaction of the reduction of Cr (VI) ions to Cr (III) ions (Fig. 6). In an alkaline condition, gelatin will undergo structural changes and become more electronegative. The electronegativity of gelatin will be a reducing agent with carbon to reduce the Cr (VI) ion in the compound CrO_4^{2-} into a Cr^{3+} ion.

Table 1. LOD value from other research.

Electrode	Range Concentration (μM)	Limit of Detection (μM)	Ref.
Gold nanoparticle-modified screen-printed	—	0.4	[29]
Silver nanoparticle modified screen printed	—	0.85	[29]
Gold macro	20 to 2000	4.5	[30]
Gold macro modified screen printed	10 to 1600	4.4	[31]
Gold nanoparticle-modified indium-tin oxide	5 to 100	2	[32]
FGC-AgE	1 to 7	0.295	This work

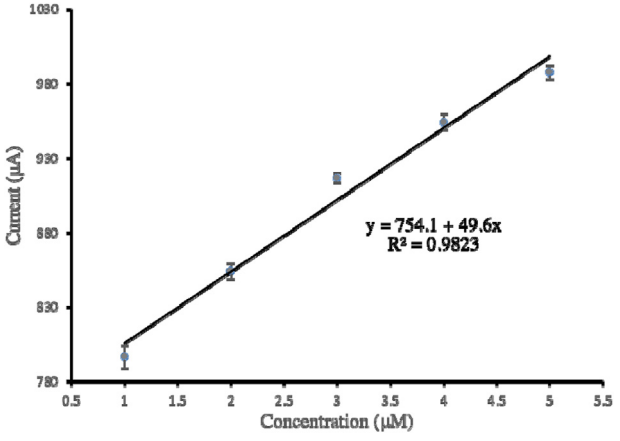

Fig. 4. Linear curve current response vs concentration.

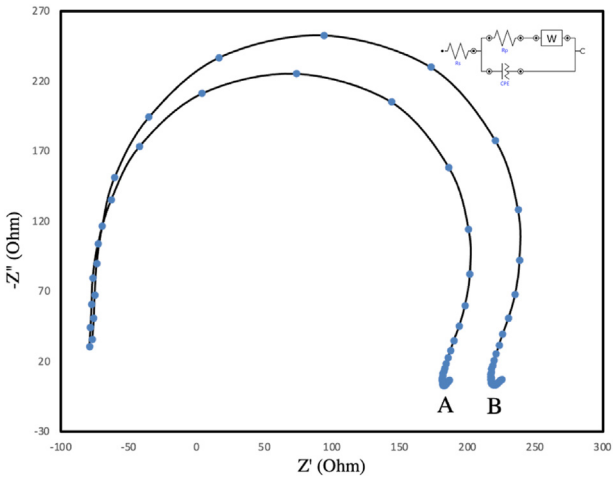

Fig. 5. Nyquist plots of FGC-AgE before (A) and after (B) Cr (VI) measurement.

3.2.3. Selectivity analysis

The electrode selectivity test for Cr (VI) ions is carried out by testing the electrode on other metal ions. This study conducted tests on ferrous metal ions, cadmium, lead, copper, and chromium (III). From the resulting voltammogram (Fig. 7), there is a significant difference between the current response of chromium (VI) metal ions and other metal ions. At a potential of −0.249 V, other metal ions have no peak current response. These results confirm that FGC-AgE has good selectivity for Cr (VI) metal ions. Selectivity testing is an important test in the field of sensors. Sensors that have high selectivity in certain compounds are sensors that have good quality.

3.2.4. Repeatability testing

The repeatability test was carried out by measuring one FGC-AgE against the Cr (VI) solution twice with 5 cycles per measurement. The results are shown in Fig. 8. The data taken was the peak value of anodic current at a potential of −0.249 V. Next, a significance test (*t*-test) was carried out on the data generated using the Mc. Excel program. The results are shown in Table 3.

After a *t*-test on the current data generated on the electrode in the first measurement against the second

Table 2. Resistance value from EIS.

Index	Frequency (Hz)	Z' (Z)		-Z'' (Z)		Time (s)
		Blank	Test solution	Blank	Test solution	
1	1.00E+06	−78.9675	−76.8888	30.509	35.8381	8.97826
2	828,629	−78.1069	−75.7247	44.1222	50.733	12.3316
3	686,646	−77.3576	−75.1167	60.5408	67.1876	13.6991
4	568,985	−76.5483	−73.6849	79.3883	89.5301	15.9923
5	471,489	−72.6832	−69.4144	103.739	116.603	18.3089
6	390,686	−62.9822	−60.4211	134.969	151.03	20.5552

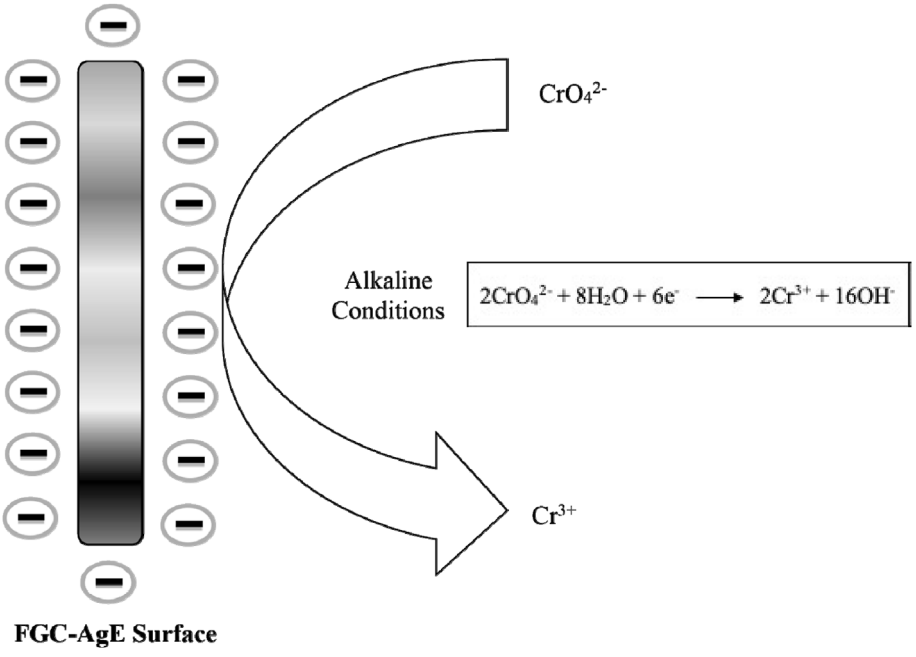

Fig. 6. The possible reaction mechanism of Cr at FGC-AgE surface.

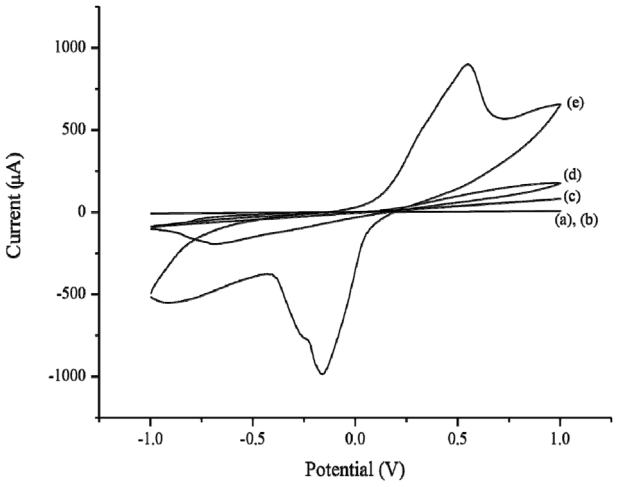

Fig. 7. Voltammogram response FGC-AgE to (a)cadmium, (b) copper, (c) lead; (d) chromium (III) and (e) chromium (VI).

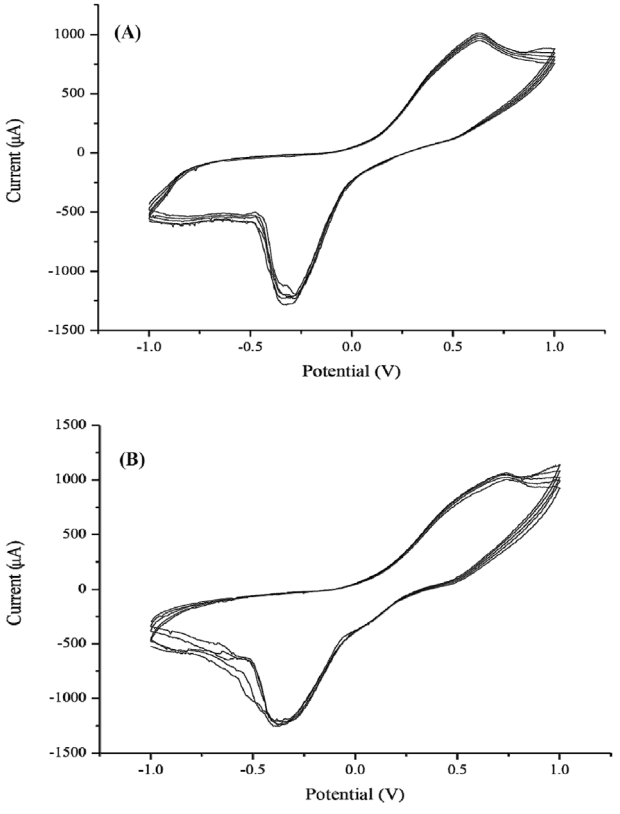

Fig. 8. Voltammogram response electrodes (A) 1 and (B) 2.

measurement, it was shown that the calculated t-value was less than the critical t-value. It can be concluded that at the 95 % confidence level, the first and second measurements have no significant difference at the 95 % confidence level. This means that the use of FGC-AgE on Cr (VI) solution can be repeated with stable results. Electrodes that can be used repeatedly are

Table 3. t-Test value for repeatability test.

	Measurement 1	Measurement 2
Mean	−1186	−1220
Variance	3580	250
Observations	5	5
Hypothesized mean difference	0	
df	5	
t stat	1.22847	
P (T ≤ t) one-tail	0.136968	
t critical one-tail	2.015048	
P (T ≤ t) two-tail	0.273935	
t critical two-tail	2.570582	

electrodes with high economic value and good prospects for future development.

4. Conclusions

FGC-AgE can detect chromium (VI) metal ions at a potential of −0.249 V in an alkaline condition. The resulting detection limit is 0.295, and the sensitivity is 14.32 μA μM^{-1} mm^{-2}. Electrodes also have good selectivity against other metals. Based on the repeatability test, the electrode performed well and could be used repeatedly. These results show that FGC-AgE can be utilized in Cr (VI) metal ion sensor applications. In conclusion, the additions of *Chanos chanos* gelatin increases the sensitivity and lower the detection limit of the Cr (VI) ion selective electrode.

Conflicts of interest

The authors declare that they have no competing interest.

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