

# Modification of Screen-Printed Carbon Electrode (SPCE) by Magnetic Fe<sub>3</sub>O<sub>4</sub>-Chitosan for Detection of Hexavalent Chromium

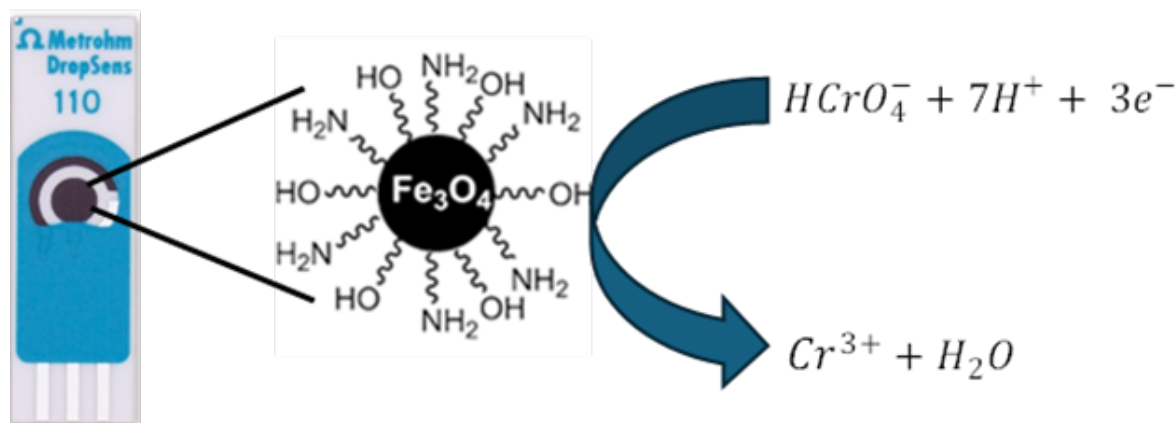
Ani Mulyasuryani\*, Yuniar Ponco Prananto

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Brawijaya University, Malang, Indonesia

 \*corresponding author: [mulyasuryani@ub.ac.id](mailto:mulyasuryani@ub.ac.id)

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## GRAPHICAL ABSTRACT



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## ABSTRACT

A new modification of screen-printed carbon electrode (SPCE) with magnetic Fe<sub>3</sub>O<sub>4</sub>-chitosan has been developed. Magnetic Fe<sub>3</sub>O<sub>4</sub>-chitosan was made from a mixture of Fe<sup>2+</sup>/Fe<sup>3+</sup> (1:2) with 1% chitosan. Sodium tripolyphosphate was used as a crosslinking reagent for chitosan under alkaline conditions using NH<sub>3</sub>. SPCE modification with Fe<sub>3</sub>O<sub>4</sub> can increase the sensitivity of Cr(VI) detection by differential pulse voltammetry (DPV). This method resulted in a sensitivity of 21.9 ppm/μA in the 0.1 - 1 ppm Cr(VI) concentration range in a 0.005 M KCl-HCl electrolyte mixture. The detection limit (LoD) is 0.2 ppm with an average accuracy of 94%.

## 1. INTRODUCTION

Chromium ion has both positive and negative effects on human health depending on absorption, exposure time, and degree of oxidation. The Cr(III) form is an essential nutrient for humans, and according to the World Health Organization [1], the ideal daily intake is between 50 and 200 g per day for carbohydrate, protein, and fatty acid metabolism. However, its excess in the body causes serious health problems. In contrast, Cr(VI) ion is 10-100 times more dangerous than Cr(III) because when it is accumulated in the human body, it leads to cancer, liver, and kidney damage. The Cr(VI) may also cause skin irritation and be considerably toxic to the protoplasm of living things [2].

Determination of chromium content is generally expressed in terms of total chromium, although chromium ions have different toxicity levels. Several methods for determining the concentration of chromium are atomic absorption spectrometry (AAS), atomic emission spectrometry (AES), X-ray spectroscopy, inductively coupled plasma mass spectrometry (ICP-MS), high-pressure liquid chromatography (HPLC) [3–7]. The determination of chromium as Cr(VI) can be done using a diphenyl carbazide reagent. However, oxidation must be carried out to determine Cr(III) [8–10]. Meanwhile, the electrochemical method of Cr(VI) can be detected specifically and, in potentiometry, has a higher detection limit than the threshold value [11–14]. Voltammetrically, Cr(VI) can be reduced to Cr(III) in acidic conditions, so it is not determined as total chromium. Therefore, the proposed method for determining hexavalent chromium ions in this study uses an electrochemical voltammetric sensor.

Hexavalent chromium electrochemical sensors have been developed using the voltammetric stripping technique with various working electrodes, either with or without modification of other materials [15–21]. Several voltammetric methods of determining both Cr(III) and Cr(VI) species have been developed, and stripping voltammetry is generally used. The Au-Ag-Pt electrode was used as the working electrode for the determination of Cr(VI) by differential pulse cathodic stripping voltammetry (DPCSV) [15]. An electrochemical sensor for determining Cr(VI) using SPE surface-modified gold nanoparticles (AuNPs). SPE modification by casting pure AuNPs increased the sensitivity to detect Cr(VI) ions using anodic stripping voltammetry. The Cr(VI) ion was reduced to metal chromium on SPE-AuNPs by applying a precipitation potential of  $-1.1$  Volt for 180 seconds. After that, the peak chromium oxidation current was obtained by linear sweep voltammetry in the range of  $-1.0$  to  $0.2$  Volt [16, 17]. Moreover, AuNPs/rGO Nanocomposite [18], a nanocomposite of gold nanoparticles deposited on the sidewall of a carbon nanotube, Ox-MWCNT-Au, was reported and prepared using simple chemical reduction. Carbon nanotube-gold was used by cyclic voltammetry, and Cr(VI) reduction was observed at a peak potential of  $0.52$  V compared to SCE in acidified  $\text{H}_2\text{SO}_4$  solution, pH 2.0 [19]. Iron-based materials have increased the sensitivity of detecting hexavalent chromium ions, including nickel hexacyanoferrate, as a modifier for glassy carbon electrodes [20].  $\text{Cr}^{3+}$  ions can be reduced to  $\text{Cr}^{2+}$  at a potential of  $-0.408$  volts, and  $\text{Cr}_2\text{O}_7^{2-}$  ions are reduced to  $\text{Cr}^{3+}$  at a potential of  $+1.33$  volts under acidic conditions. Determination of hexavalent chromium by voltammetry has also been carried out with a modified glassy carbon electrode of  $\text{Fe}_3\text{O}_4$ -starch composite as the working electrode. The Cr(VI) is reduced to Cr(III) at a potential of  $0.99$  volts under acidic conditions with a supporting electrolyte of  $0.05$  M  $\text{H}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$ . The electrode detection limit is  $3$  ppm, less sensitive, and disposable [21]. The two reduction potentials are so far apart that trivalent and hexavalent chromium ions can be determined simultaneously [22].

Therefore, in this study, a modification of the screen-printed carbon electrode with  $\text{Fe}_3\text{O}_4$ -chitosan composite was carried out. Magnetite ( $\text{Fe}_3\text{O}_4$ ) is a superparamagnetic metal oxide that can increase electron transfer. Modifying carbon electrodes with magnetite has been studied to determine paracetamol voltammetrically [23]. Meanwhile, chitosan can adsorb Cr(VI), with an adsorption capacity of  $212.8$  mg/g chitosan [24]. Chitosan is a natural polymer that can form nanoparticles with sodium tripolyphosphate (Na-TTP). Chitosan dissolved in acid was reacted with Na-TTP in an alkaline solution [25, 26]. Chitosan nanoparticles were made within 2 hours using the ionic gelation method. Chitosan molecules in the form of gel contact with poly-anions due to the formation of inter- and intramolecular cross-links mediated by poly anions. Chitosan nanoparticles were made by adding a negatively charged Na-TTP solution with a positively charged chitosan solution while stirring at room temperature. The ratio of chitosan to Na-TTP will determine the size of the resulting nanoparticles [27].

## 2. EXPERIMENTAL

### 2.1 Reagents and apparatus

The reagents used were of high purity and used as received. Double-distilled water was used for all tests. Chemicals used include: KCl (Merck), HCl (Merck, 32%;  $1.18$  g/mL),  $\text{NH}_4\text{OH}$  (Merck, 25%;  $0.9$  g/mL),  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , chitosan powder (Merck, DAC Degree  $\geq 80\%$ ),  $\text{CH}_3\text{COOH}$  (Merck, 99.5–100%;  $1.05$  g/mL), Na-tripolyphosphate (Merck). General standard laboratory glassware, Dropsens  $\mu\text{Stat}200$  (Metrohm), and SPCE (Metrohm) were used for preparation and apparatus.

## 2.2. Modification of Screen-Printed Carbon Electrode

A 5.40 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 2.78 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  each were dissolved in 25 mL of distilled water. The two solutions were mixed and added to 100 mL of 1% chitosan solution while stirred at 1000 rpm for 20 minutes at 40 °C. After 20 minutes, the reaction was heated to 60 °C, and then 6 mL of Na-TPP solution was added while continuously stirred at 1000 rpm for 3 hours. 40 mL of 25%  $\text{NH}_4\text{OH}$  was then added dropwise into the solutions. The  $\text{Fe}_3\text{O}_4$ -chitosan was washed 3 times with distillate water and then separated by a magnetic field. The SPCE was coated with  $\text{Fe}_3\text{O}_4$ -chitosan and then heated at 30 °C for 5 minutes to form a thin film.

## 3. RESULTS AND DISCUSSION

### 3.1. Screen-Printed Carbon Electrode Modification

The sensor was made by modifying the screen-printed electrode using synthetic  $\text{Fe}_3\text{O}_4$ -chitosan. Figure 1a shows the SEM image of  $\text{Fe}_3\text{O}_4$ -chitosan; the particles appear to form aggregates. This is due to its in-situ synthesis. Based on the EDX spectrum (Figure 1 – b), it is confirmed that the primary component is iron, which is 70.58%. Thus,  $\text{Fe}_3\text{O}_4$  is confirmed to be in the  $\text{Fe}_3\text{O}_4$ -chitosan modifier. Modified SPCE can be evaluated by cyclic voltammetry (CV) compared with SPCE without modification, in which both for the blank solution are a mixture of electrolytes KCl and HCl, each 0.05 M.

Figure 2 presents the voltammogram of blank solutions (a) and (b) 2 ppm Cr(VI) solution. The peak of the CV wave in unmodified SPCE is estimated to be an oxidation of  $\text{Cl}^-$  to  $\text{Cl}_2$ , while in the modified SPCE, it is the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  ( $E^\circ = 0.77$  Volt vs SHE). The 2 ppm Cr(VI) solution did not significantly affect the peak potential ( $E_p$ ) shift, but there was an increase in the peak current ( $I_p$ ) in the unmodified SPCE. The  $E_p$  shift and  $I_p$  increase in the modified SPCE is probably due to 2 ppm Cr(VI) (Table 1).

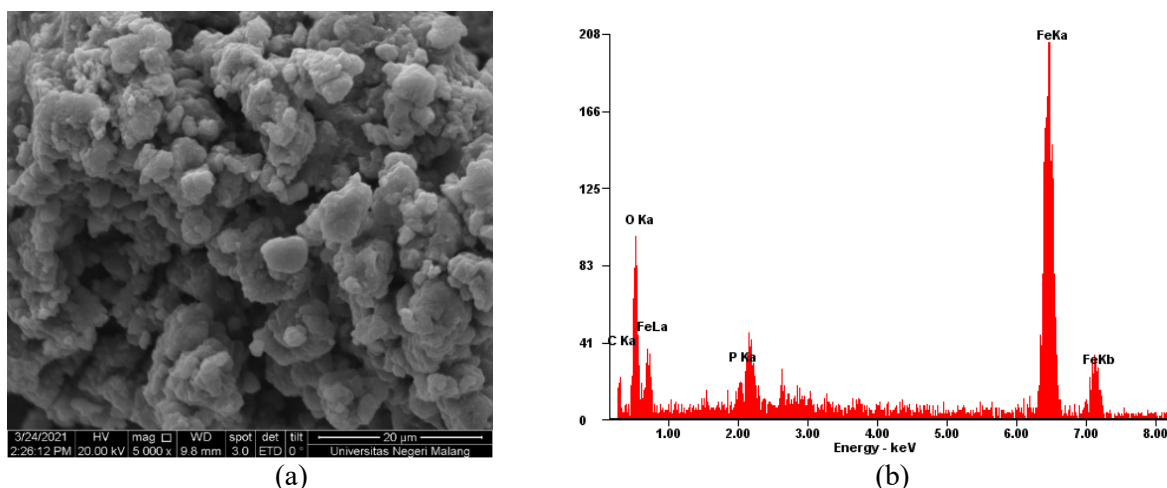


Figure 1. SEM image of  $\text{Fe}_3\text{O}_4$ -Chitosan surface (a); EDX spectrum of the elements in the sample (b).

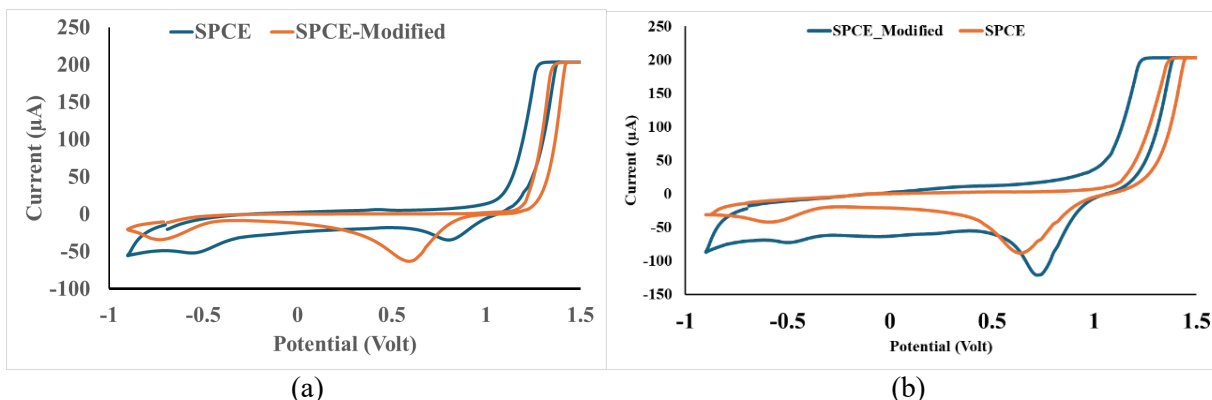


Figure 2. CV voltammogram of 0.05 M KCl-HCl solution (a) 2 ppm of Cr(VI) solution in 0.05 M KCl-HCl (b), in unmodified and modified SPCE, respectively.

TABLE I. Effect of SPCE modification by  $\text{Fe}_3\text{O}_4$ -chitosan on  $E_p$  shift and  $I_p$  increase in cyclic voltammetry.

Electrode	$E_p$ (Volt)			$I_p$ ( $\mu\text{A}$ )		
	Blank	Cr(VI) 20 ppm	$\Delta E_p$	Blank	Cr(VI) 20 ppm	$\Delta I_p$
Unmodified SPCE	0.61	0.63	0.02	52.79	73.40	20.62
Modified SPCE	0.85	0.74	-0.11	25.43	94.05	68.62

Hexavalent chromium, in acidic media such as  $\text{HCrO}_4^-$ , can be reduced to Cr(III) and involves three electrons ( $E^\circ = 1.35$  volts vs SHE). In this study, the supporting electrolyte was a mixture of KCl and HCl. Electrolyte concentration greatly influences the peak potential and peak current of the voltammogram. As shown in Figure 3, the peak that appears on the cyclic voltammetry for the blank is the peak of the oxidation of  $\text{Cl}^-$  to  $\text{Cl}_2$  ( $E^\circ = 1.36$  volts vs. SHE). There was a shift in peak potential and an increase in current in the 2 ppm Cr(VI) solution compared to the blank, but in 0.05 M KCl-HCl, it was more significant than that of 0.01 M KCl-HCl (Table 2).

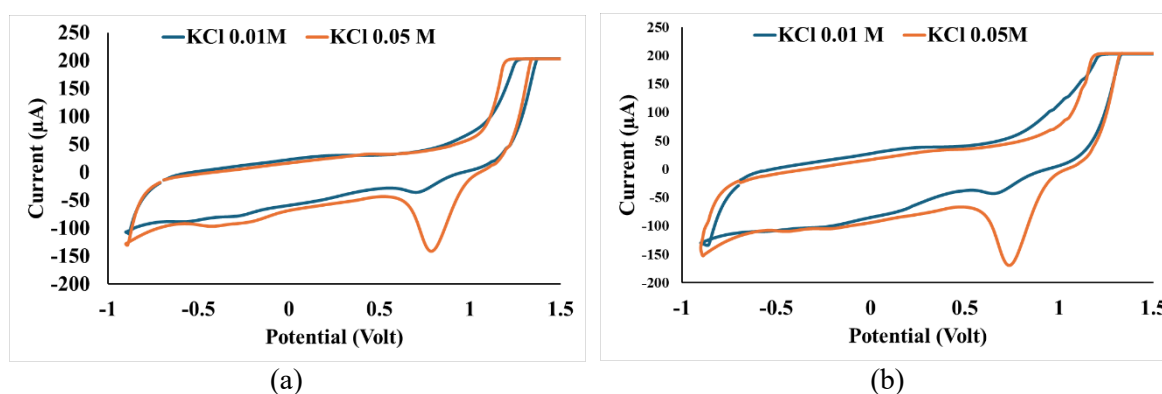
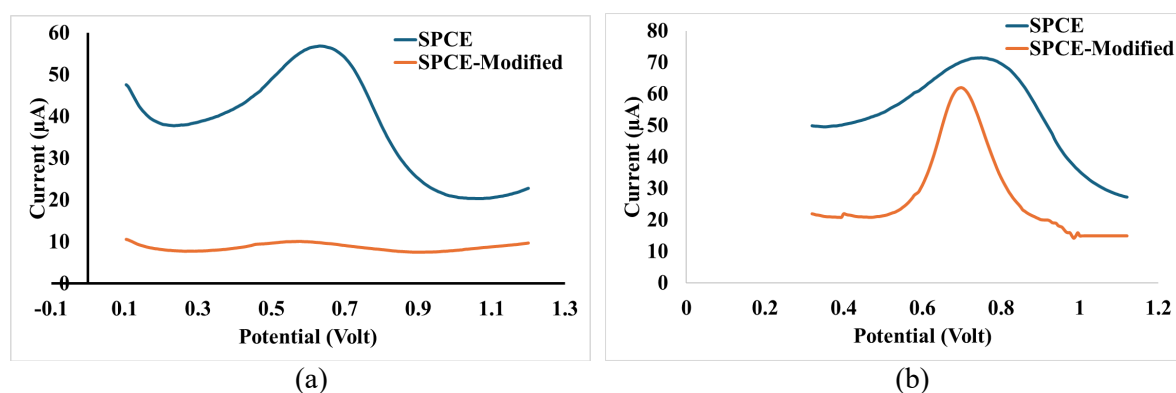


Figure 3. CV voltammogram of blank solution (a) and 2 ppm Cr(VI) solution (b) in 0.01 and 0.05 M KCl-HCl measured by the modified-SPCE.

TABLE II. Effect of electrolyte concentration on  $E_p$  shift and  $I_p$  increase in the cyclic voltammetry.

[KCl-HCl] (M)	E <sub>p</sub>			I <sub>p</sub>		
	Blank	2 ppm	ΔE <sub>p</sub>	Blank	2 ppm	ΔI <sub>p</sub>
0.01	0.76	0.7	-0.06	13.97	22.08	8.10
0.05	0.86	0.77	-0.09	108.81	136.30	27.49

Differential pulse voltammetry (DPV) measurements were also carried out for analysis purposes. The DPV voltammogram is shown in Figure 4 for both the blank and the 2 ppm Cr(VI) solutions, compared between the unmodified and modified SPCE. In Figure 4, the voltammogram of the blank solution in unmodified SPCE has a higher peak current than the modified SPCE. Thus, the presence of Fe<sub>3</sub>O<sub>4</sub>-chitosan can decrease the background current (Figure 4a). In Figure 4b, it can be seen that the voltammogram in the modified SPCE is more perfect for Cr(VI) 2 ppm in KCl-HCl 0.05 M. This shows that Fe<sub>3</sub>O<sub>4</sub>-chitosan can increase the peak current, kinetics Fe<sub>3</sub>O<sub>4</sub>-chitosan in SPCE can accelerate the mass transport of Cr(VI) from the bulk solution to the electrode surface. Chitosan in an acidic environment will be positively charged on its amine group, so it can adsorb Cr(VI), which is negatively charged, so it is estimated that there are two mechanisms of Cr(VI) transport: adsorption and diffusion. But this needs to be proven further. The difference in E<sub>p</sub> of blank solution with 2 ppm Cr(VI) solution is higher in unmodified SPCE than in modified SPCE, likewise with each difference in peak current (Table 3).



**Figure 4.** DPV voltammogram of 0.05 M KCl-HCl solution (a) and 2 ppm of Cr(VI) solution in 0.05 M KCl-HCl (b), in unmodified and modified SPCE, respectively.

TABLE III. Effect of SPCE modification by Fe<sub>3</sub>O<sub>4</sub>-chitosan on E<sub>p</sub> shift and I<sub>p</sub> increase in differential pulse voltammetry.

Electrode	E <sub>p</sub> (Volt)			I <sub>p</sub> (μA)		
	Blank	2 ppm	ΔE <sub>p</sub>	Blank	2 ppm	ΔI <sub>p</sub>
Unmodified SPCE	0.620	0.765	0.145	18.83	31.18	12.35
Modified SPCE	0.626	0.715	0.089	9.50	42.39	32.89

Based on the CV and DPV voltammograms, it is suggested that the voltammetric determination of Cr(VI) can be carried out indirectly using an electrolyte or ion easily oxidized by Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> in an acidic environment. The results showed that Cl<sup>-</sup> was more easily oxidized by the dichromate, but the system was easier to reduce the ions in the working electrode (SPCE). In this case, the E<sub>p</sub> is present at 0.7 volts, which is the reduction potential from Fe<sup>3+</sup> to Fe<sup>2+</sup>. Therefore, it is most likely that Fe<sup>3+</sup> is reduced by the system and then re-oxidized by dichromate. Hence, the increase in dichromate concentration is directly proportional to the peak current. It is also noticed that the baseline current of the voltammogram increases proportionally with the dichromate concentration (Figure 5 and Figure 6). Based on EDX measurement,

the modifier contains 70% iron, of which 2/3 of it is  $\text{Fe}^{3+}$ . Due to only a few  $\text{Fe}_3\text{O}_4$  on the SPCE surface, the concentration of dichromate that can be determined is limited to low concentrations.

### 3.2. Analytical Parameters

As shown in Figure 4, the better concentration of supporting electrolyte is KCl-HCl 0.05 M, although the background current is considerably high, a normalization can be done. The concentrations of Cr(VI) are varies from 1 to 9 ppm, the sensitivity is 7.3 uA/ppm (Figure 5), which may be due to the limitations of the apparatus. Therefore, to increase the sensitivity, both the Cr(VI) and the electrolyte concentration were reduced by 10 times (Figure 6).

As shown in Figure 6, the sensitivity increases three times in the Cr(VI) concentration range of 0-1 ppm in 0.005 M KCl-HCl supporting electrolyte. The SPCE- $\text{Fe}_3\text{O}_4$ -Chitosan sensitivity in the Cr(VI) concentration is 21.86 uA/ppm, with a detection limit of 0.2 ppm. This result was obtained in measurement conditions: pulse amplitude is 0.1 volts with an amplitude time of 20 msec, and scan rate is 0.1 mV/sec.

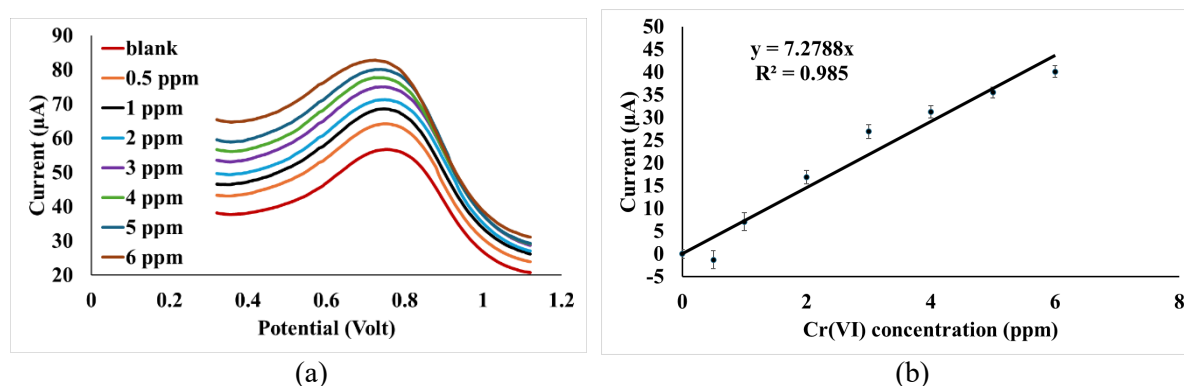


Figure 5. DPV voltammogram of Cr(VI) in 0.05 M KCl-HCl solution (a) and standard curve of Cr(VI) (b), measured by SPCE- $\text{Fe}_3\text{O}_4$ -Chitosan.

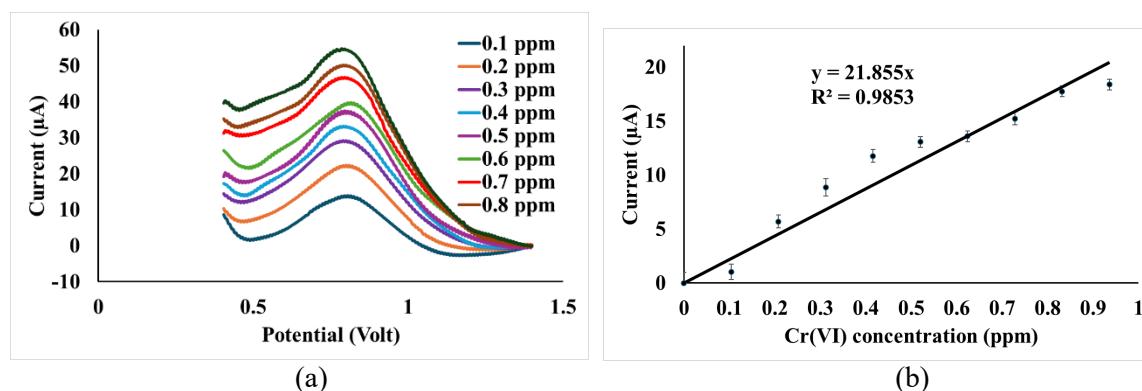


Figure 6. DPV voltammogram of Cr(VI) in 0.005 M KCl-HCl solution (a) and standard curve of Cr(VI) (b), measured by SPCE- $\text{Fe}_3\text{O}_4$ -Chitosan.

TABLE IV. Concentration of Cr(VI) of the sample, standard addition sample (A) compared with the Cr(VI) concentration of standard plus sample (B).

Sample	Standard concentration (ppm)	Current (uA)		Concentration of Cr(VI) (ppm)		Recovery (%)	
		Sample	Sample + Standard	Sample	Sample + Standard		
					A		B



1	0.8	4.33	19.69	0.20	0.9	1.0	90.28
2	0.8	12.69	27.06	0.58	1.2	1.4	89.68
3	0.8	4.49	22.26	0.21	1.0	1.0	101.29
4	0.8	1.09	16.56	0.05	0.8	0.8	89.17
5	0.8	7.90	23.53	0.36	1.1	1.2	92.71
6	1.2	13.54	37.27	0.62	1.7	1.8	93.73
7	1.2	1.09	25.92	0.05	1.2	1.2	94.90
8	1.2	0.88	26.44	0.04	1.2	1.2	97.56
9	1.2	8.73	33.54	0.40	1.5	1.6	95.95
10	1.2	3.37	28.70	0.15	1.3	1.4	96.98

Validation was carried out on ten aqueous sample solutions and addition standard solutions of Cr(VI) 0.8 and 1.2 ppm, in which each measurement was repeated 5 times. Calculation of the Cr(VI) concentrations was based on the standard curve in Figure 6(b). Using the same standard curve in Figure 6(b), the limit of detection (LoD) of the DPV method can also be calculated for the measurement of Cr(VI) in 0.005 M KCl-HCl. The LoD is calculated based on the assumption of a normal distribution where  $y = y_B + 3SD$ . The result of the LoD calculation is 0.2 ppm. Table 4 also reported that the recovery or accuracy ranges from (89 – 101) %, averaging 94%.

#### 4. CONCLUSION

Screen-printed carbon electrodes can be modified by Fe<sub>3</sub>O<sub>4</sub>-chitosan for voltammetric determination of Cr(VI). The Fe<sub>3</sub>O<sub>4</sub>-chitosan contains 70% iron, which is dominated by Fe(III). Voltammetry modification of SPCE with Fe<sub>3</sub>O<sub>4</sub>-chitosan can shift the potential and current increase its peak. The average reduction peak potential of the modified SPCE is 0.825 volts in the concentration range of 0.1 – 1.0 ppm Cr(VI) in 0.005 M KCl-HCl solutions. The operating conditions of the instrument were at 0.1 volts pulse amplitude with an amplitude time of 20 msec and a scan rate of 0.1 mV/sec. This method has a sensitivity of 21.86 ppm/ $\mu$ A, a detection limit of 0.2 ppm, and an average accuracy of 94%.

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