

Full Paper

Electro-determination of Chromium Ions based on Carbon Paste Electrode Decorated with Highly Nitrogen-Sulfur-Doped Graphene Oxide

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Received: 15 May 2023 / Received in revised form: 17 June 2023 /

Accepted: 21 June 2023 / Published online: 30 June 2023

Abstract- This research has successfully created a carbon paste electrode that has been modified with nitrogen-sulfur-doped graphene oxide, allowing for the accurate detection of chromium ions in aqueous solutions. The surface morphology of the modifier was investigated by FT-IR and SEM. Through the use of anodic stripping differential pulse voltammetry, the electrochemical response of the modified carbon paste electrode to chromium ions has been analyzed and shown to exhibit an excellent electro-oxidation response when exposed to chromium ions. The linear dynamic range of chromium analysis produced a remarkable sensitivity of 0.1986 between 0.01 and 10 nM, with a sensitivity of 0.2048 between 10 and 125 nM. The detection limit was found to be 4.58 pico-molar. In a real sample, the electrode was able to measure chrome (VI) with results comparable to other techniques used in measuring chrome (VI). This achievement highlights the possibilities of utilizing innovative technology to create solutions that can address real-world problems.

Keywords- Doped Graphene Oxide; Electrochemical sensor; Modified Electrode; Anodic Stripping Voltammetry; Trace determination

1. INTRODUCTION

The chromium element is a metal that has been extensively used in various industries, including steel, coatings, alloy manufacturing, tanneries, galvanoplasty, wood treatment, and dyeing. It is a metal that has multiple applications [1]. The current situation can result in a

significant amount of diverse chromium compounds being discharged into the surroundings, causing harm to the flora and fauna on Earth. There are different oxidation states that chromium can exist in, ranging from Cr (0) to Cr (VI) in its most oxidized state. As a result of their stability, only the oxidation states (III) and (VI) are usually found in the environment [2]. It is known that hexavalent chromium (Cr(VI)) is highly toxic and is capable of easily entering the cell and causing damage [3]. Hexavalent Chromium exposure can cause a number of diseases, including ulcers, contact dermatitis, chronic bronchitis, gastrointestinal and hepatic disease, emphysema and pneumonia, hemorrhage, liver damage and cancer [2,4,5]. There are many organs in the body that can be affected by this condition that may result in death. For Cr (VI) in groundwater, the World Health Organization (WHO) has published a guideline concentration of 50 micro grams per liter [6]. For total chromium in drinking water, the Environmental Protection Agency (EPA) regulated a level of 100 μg per liter [7].

It is important to remember that the toxicity of chromium depends on the state of its oxidation, particularly when it is in its hexavalent form. It is therefore highly desirable that a method be developed in order to determine the specific amount of hexavalent chromium [1]. Several methods have been used to determine chromium (III) and chromium (VI) including fluorescence [3], atomic absorption [4], colorimetry [5], flame atomic absorption spectroscopy [6], solid phase extraction and HPLC-UV detection [7], but solid phase spectrophotometry has also been employed to determine chromium (III) and chromium (VI) [8]. Nevertheless, these techniques present several disadvantages, such as the high cost, the need for a qualified individual, the complexity of the materials, and the numerous steps required for the analysis. It is important to note that most existing analytical techniques are not flexible and cannot be used to analyze compounds simultaneously. This has led to the development of electrochemical techniques that offer a low-cost, sensitivity, and selectivity alternative [1]. It is known that electrochemistry provides the most informative and sensitive electro-analytical techniques, such as voltammetric techniques, as it is not only efficient in analyzing small quantities of electroactive analytes but also provides ample and characteristic information regarding the chemical nature of the analyte [9]. As the name implies, an electrochemical sensor is a method by which electrochemical interactions between an analyte and an electrode are transformed into an analytically useful signal. A carbon paste electrode (CPE) is one of the most common types of working electrodes and a promising electrochemical sensor with a wide range of applications [10]. In various electrochemical applications, carbon paste electrodes can be considered a reliable non-expensive method for screening potential candidates [11]. CMEs were first studied by Murray and Coworkers in the middle of the 1970s. Different approaches can be used to modify the electrode surface chemically. The enhancement of electrochemical properties is the result of such an interest [12]. Over the last few years, a significant amount of attention has been given to the examination of modified electrodes and their potential for measuring ions and pharmaceutical compounds. This area of research has garnered interest due

to its potential impact on various fields, including medicine, environmental science, and chemistry [13-23]. Carbon paste electrode modified by graphene-oxide have widely been used in aqueous solution. Based on other literature when Nitrogen(N) and Sulfur (S) functionalized nanomaterials they have been shown a high affinity to hexavalent chromium ions [24]. Our team has developed a practical and cost-effective method for accurately measuring hexavalent chromium ions. This approach is both fast and dependable, allowing us to precisely determine the level of these ions in any sample. This measurement technique is crucial in ensuring the utmost precision and accuracy in determining the amount of hexavalent chromium ions present.

2. EXPERIMENTAL

2.1. Materials

Graphite powder, thiourea, potassium dichromate ($K_2Cr_2O_7$) and all solvent and salt were purchased from Merck Company (Darmstadt, Germany). Ultrapure water was used in all experiment to preparation the solution. The wastewater real sample was obtained from Kavir Tire Company (Birjand, Iran) and stored in a polyethylene bottle and kept in the dark. All the solutions were prepared on the same day.

2.2. Apparatus

Electrochemical measurements were carried out with a three-electrode system including carbon paste electrode modified (MCPE) with nitrogen-sulfur doped graphene oxide (NSD-GO) as a working electrode, saturated calomel electrode (SCE) as reference electrode and platinum wire as an auxiliary electrode (Azar Electrode Co, Iran), using Ivium galvanostat/potentiostat (CompactStat, Switzerland). Fourier transforms infrared spectra (FT-IR) was recorded using a (Shimadzu 1650) spectrometer. Scanning electron microscope images were obtained using (KYKY-EM3200) instrument. The pH was measured with a model (TaT-PVT515) pH meter. Heidolph heater stirrer model MR Hei-Standard (Germany) was used for heating and stirring of the solutions. Zolalan device (ZP101-C, Iran) was used to prepare Ultrapure water.

2.3. Synthesis of nitrogen-sulfur doped with graphene oxide (NSD-GO)

Graphene oxide was synthesized by the Hammers method [25]. NSD-GO was synthesized according to the below steps. 60 mg of graphene oxide powder was dipped in 80 ml ultrapure water under ultrasonic conditions, then 6 mmol of thiourea was added to the solution and kept in an autoclave at 180 °C for 12 h. The product of the previous step should be cooled to room temperature and then washed with ultrapure water several times and finally dried in an oven at 60 °C for 24 h.

2.4. Fabrication of the unmodified and modified CPEs

In order to prepare unmodified carbon paste electrodes (u-CPEs), a mixture of graphite powder and paraffin oil 75/25% (W/W) ratio. The paste was kept overnight. The resulting paste was used to fill the cavity (2 mm in diameter and 5 mm deep) at the polyethylene rod. An electrical connection was established by a copper wire. Then the surface of the electrode was polished. The modified carbon paste electrodes (CPE) were obtained from a mixture of NSD-GO 5% (W/W) graphite powder and paraffin oil 70/20 % (W/W) ratio the electrode was prepared as u-CPEs and polished before use.

2.5. Real sample

The real sample was wastewater it was taken from Kavir Tire Company (Birjand-Iran), which was analyzed without preparation. The water sample was collected in a polyethylene bottle and kept in the dark. After filtration, Hydrochloric acid (HCl) 0.10 M was added, according to the optimized condition, wastewater adjust pH at 1.0.

2.6. Determination procedure

The prepared modified electrode was placed in Chromium ion (Cr(VI)) solution for 10 min. After rinsing, the electrode was placed in an electrochemical cell containing HCl 0.10M solution in order to reduce Chromium ion on the surface of the electrode, a -1.0 V prepotential was applied for 30 seconds. Finally, differential pulse voltammetry analysis (DPV) was performed in the potential range of +0.75 to +1/25.

3. RESULTS AND DISCUSSION

3.1. Characterization of synthesized modifier

According to the NSD-GO infrared spectrum, the peak observed at 3421cm^{-1} is caused by the OH and NH functional groups. An observed vibration at 1718cm^{-1} can be attributed to the C=O functional group. The peak due to the C=C bond is located in the region of 1633cm^{-1} . Two weak peaks in the range of 1455 and 1500cm^{-1} can be attributed to COO^- and CN, while a broad peak in the area of 11168cm^{-1} indicates the presence of C-O, C-N, and C-S groups. Based on this spectrum, we can conclude that nitrogen atoms (C-N) and sulfur atoms (C-S) are present in the sample. There is a good agreement between the spectrum obtained and the previous one Figure 1(a). We used SEM analysis as a method of determining the size of the particles of NSD-GO in order to analyze their composition. Quality was determined randomly from SEM images of the sample. Figure 1(b) shows the SEM image of the NSD-GO pieces and layers.

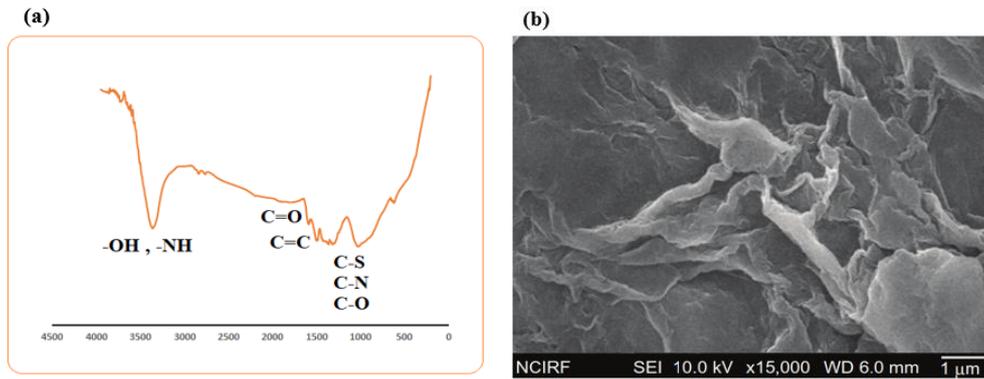


Figure 1. The FT-IR image of NSD-GO (a). The SEM image of NSD-GO (b)

3.2. Performance improvement of CPE with the modification by NSD-GO

As part of the study to evaluate the performance of the MCPE, DPV responses were measured in a 10.0 nM Cr(VI) solution in 0.10 M HCl with pH 1.0 under the following conditions: a pre-potential of -1.0 V was applied for 35 seconds in order to compare its performance with the u-CPE. As shown in the figure below, it is evident that electrodes modified with NSD-GO Figure 2(a) respond strongly compared with u-CPE Figure 2(b).

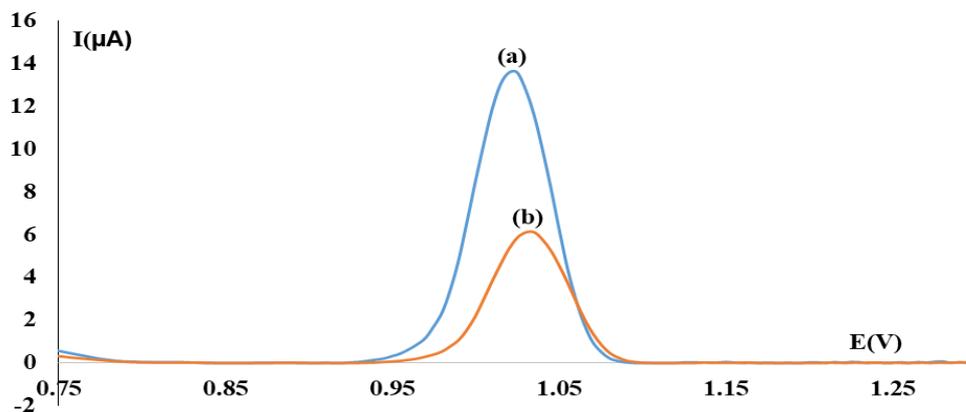


Figure 2. Differential pulse voltammograms of the 10 nM Cr(VI) solution at pH 1.0 on the surface of electrodes modified with graphene oxide doped with nitrogen-sulfur (NSD-GO) (a) and unmodified carbon paste electrode (u-CPE) (b)

3.3. Optimization of experimental variables

3.3.1. Effect of pH

As mentioned earlier, the pH of the solution plays a crucial role in the process of measuring Cr(VI). Due to the fact that Cr(VI) has greater solubility in an acidic solution than in the neutralized version. A differential pulse voltammetry technique was used to study the effect of different pH values from 1.0 to 5.0 on Cr (VI) solution using different pH values. The following figure illustrates the peak current diagram according to the pH value as shown in Figure 3. It

was decided that pH 1.0 was the most optimal condition for future analysis, and this is what was chosen.

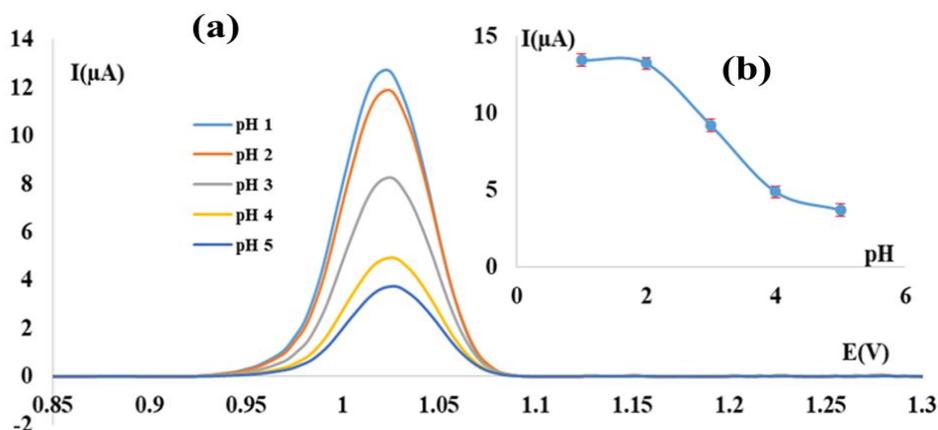


Figure 3. Differential pulse voltammograms of 10 nm Cr(VI) solution at various pHs from 1.0 to 5.0, on the surface of the NSD-GO electrode (a). A platinum electrode was used as an auxiliary electrode and a SCE electrode was used as a reference electrode at room temperature. pH effect diagram on current intensity (b)

3.3.2. Effect of accumulation time

As a part of this study, the effect of accumulation time on the response of the proposed sensor was investigated between the periods of 1 minute and 15 minutes in order to examine how it affects the response of the sensor. The results are shown in Figure 4(a). As shown in Figure 4(a), the current increased as the accumulation time increased. This is probably a result of the accumulation of chromium ions on the electrode surface as shown in Figure 4(a). Even though the accumulation time increased by a certain amount after 10 minutes, the current resulting from accumulation remained almost constant. Therefore, the time of 10 minutes was chosen as the optimal accumulation time for further study in order to reduce test time.

3.3.3. Optimization of the amount of modifier in the electrode

According to the results, using NSD-GO modifier in mixture of CPE was increased the current. In order to optimize the modifier percentage in the carbon paste, different ratios (w/w) were tested. It was observed that by increasing the modifier percentage up to 5%, the current increased, and after that a decrease in the current was observed. Due to the non-conductivity of the modifier, it probably caused the insulation of the electrode surface Figure 4(b).

3.3.4. Pre-potential optimization

A -1.0 V potential was applied to the electrode in order to be more efficient and obtain a lower detection limit. The chromium ions were reduced to metal form at surface of electrode (plating step), after that the analysis was done with DPV technique (stripping step) Figure 4(c).

3.3.5. Optimization of pre-potential time

Pre-potential time is one of the most critical factors contributing to the electrode's efficiency. During time period of 10-45 S, a potential of -1.0 V was applied. When the time is increased to the 35 s, the current also increase, and after that, it remains unchanged. To achieve maximum results, 35 s was selected as the ideal time to apply the pre-potential Figure 4(d).

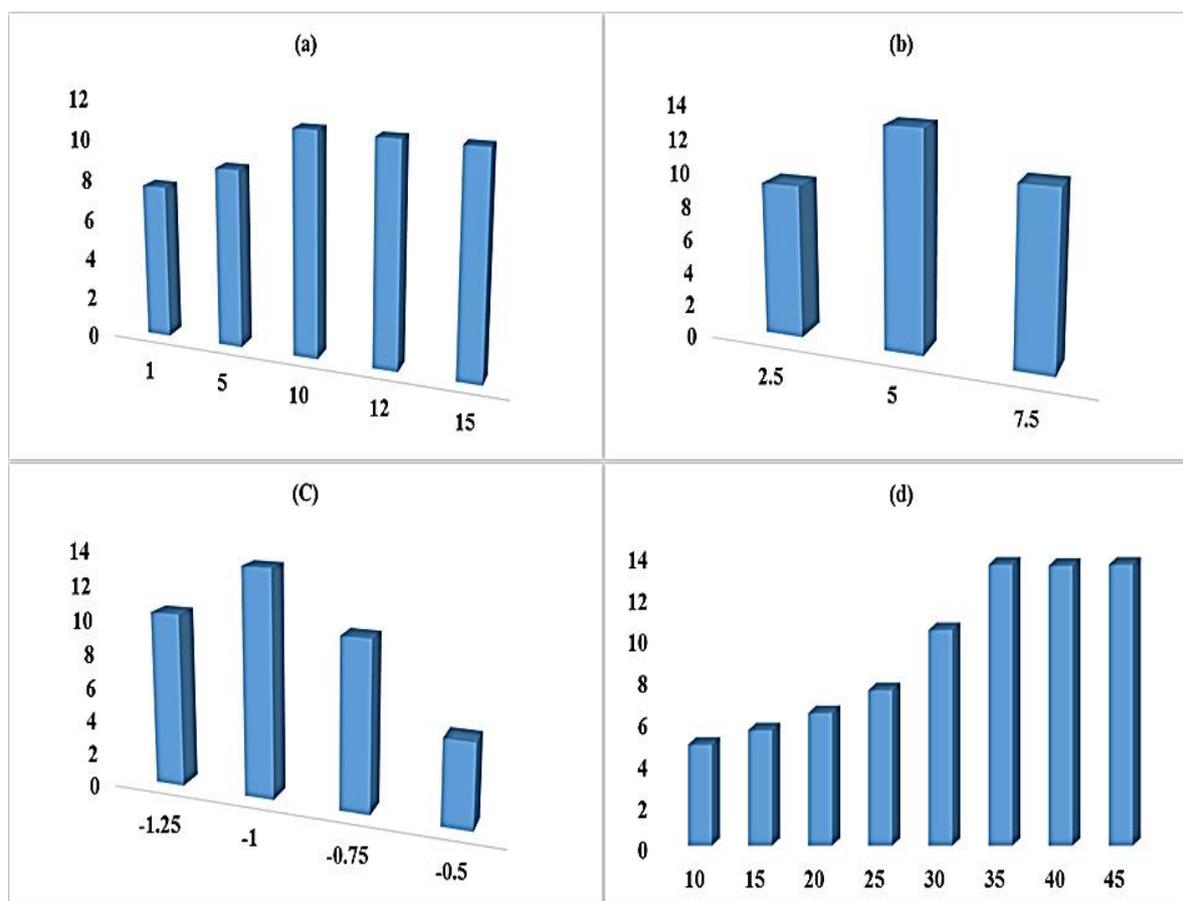


Figure 4. Effect of accumulation time (a), amount of modifier (w/w%) (b), the value of applying pre-potential(c), and pre-potential applying time on the electrochemical response of 10.0 nM of chromium ions solution at pH 1.0

3.3.6. Effect of sample volume

The amount of sample volume plays a very important role when it comes to determining the actual sample volume. Therefore, the volume of chromium (VI) samples was measured between 5.0 and 30.0 ml. An increase of over 20.0 ml in sample volume does not produce a significant change in peak current, because the adsorption sites on the electrode surface are saturated. On the basis of the differential pulse voltammetry results, it was decided to take a sample volume of 20.0 ml.

3.3.7. Repeatability, reproducibility and stability

MCPE was also subjected to a study in order to determine the reproducibility, reproducibility, and stability of the electrode. After carrying out three consecutive experiments, the repeatability of NSD-GO electrodes in 10 nM Cr(VI) solution at pH1.0 has been investigated, and the relative standard deviation has been calculated to be 0.25%. In order to verify the reproducibility of electrode preparation, three electrodes were prepared under completely similar conditions. The relative standard deviation was 0.167. To determine the stability value of an electrode, it was necessary to take the DPV value from an electrode manufactured under completely identical conditions within a 30-day period. It was found that after 30 days, the current reached a value of 90.98% of its original value.

3.3.8. Measuring the electrode surface

To measure the surface of the modified electrode, a CV analysis was performed with a scan rate of 20 to 60 mV/s. This was in order to measure the surface of the electrode. This was done with 0.1 mM {Fe(CN)₆}^{-3,-4} solution as a probe. A measurement of the electrode surface was performed using Randles-Sevcik equation (Eq. 1).

$$I_p = (2.69 \times 10^5) n^{\frac{3}{2}} \times v^{\frac{1}{2}} \times D^{\frac{1}{2}} \times C_o^* \times A \quad \text{Equation. 1}$$

Herein, I_p represents the anodic current, while n represents the number of electrons that have been transferred during the process. It is appropriate to refer to A as the surface of the electrode, D as the diffusion coefficient of (5.8), U as the scan rate, and C_o as the concentration of the {Fe(CN)₆}^{-3,-4}. According to the equation above, a surface area of 0.324 cm² was found to be obtained.

3.3.9. Analytical applications

A differential pulse voltammogram can be seen in Figure 5 due to optimal conditions for obtaining Cr(VI) figures of merit. A dynamic range of 0.010 to 10.0 nM was measured with a sensitivity of 0.9186 with a correlation coefficient of 0.9827. Furthermore, the sensitivity is 0.2048 with the correlation coefficient is 0.9954 for 10.0 to 125 nM. The method detection limit was 4.58 pM, based on S/N=3. A comparison was made between the prepared electrode and other previously measured electrodes. According to Table 1, this sensor demonstrates a high level of efficiency. For each concentration range, (Equations 2 and 3) provide a relationship between current and concentration.

$$I (\mu A) = 2.4254C (nM) + 0.9186 \quad R^2 = 0.9827 \quad \text{Equation 2}$$

$$I (\mu A) = 9.4776C (nM) + 0.2048 \quad R^2 = 0.9952 \quad \text{Equation 3}$$

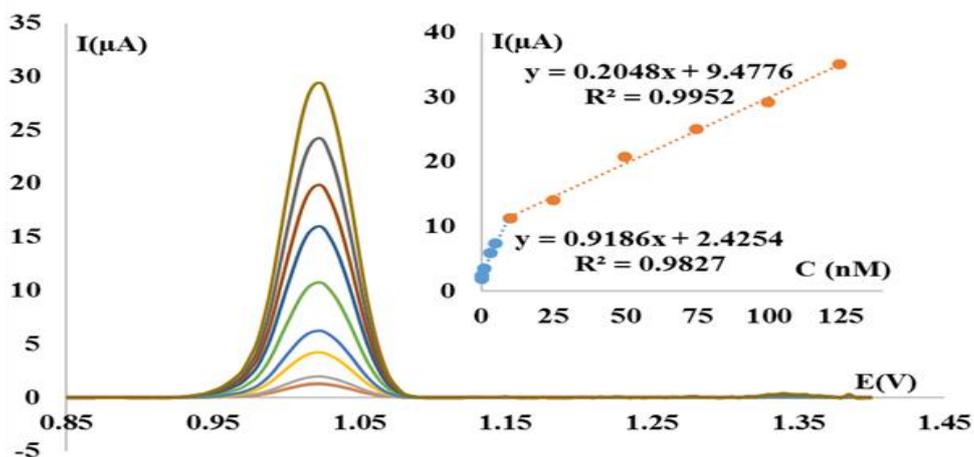


Figure 5. Plots of the peak current as a function of Cr(VI) ions concentration; inset: Linear calibration graphs of NSD-GO under optimal experimental conditions in the range of 0.01-200 nM chromium ions concentrations

3.3.10. Interference studies

Figure 6 shows the result of an investigation into the selectivity of the electrode, which has been modified with NSD-GO, by immersing it in different solutions containing 10 nM Cr (VI), as well as some ions that may cause interference at different concentrations. In accordance with Table 1, the level of interference caused by a number of interferers does not have a significant effect on the proposed sensor for detecting Cr(VI). Maximum disturbances are acceptable when the analytical response is within 10% of the true value.

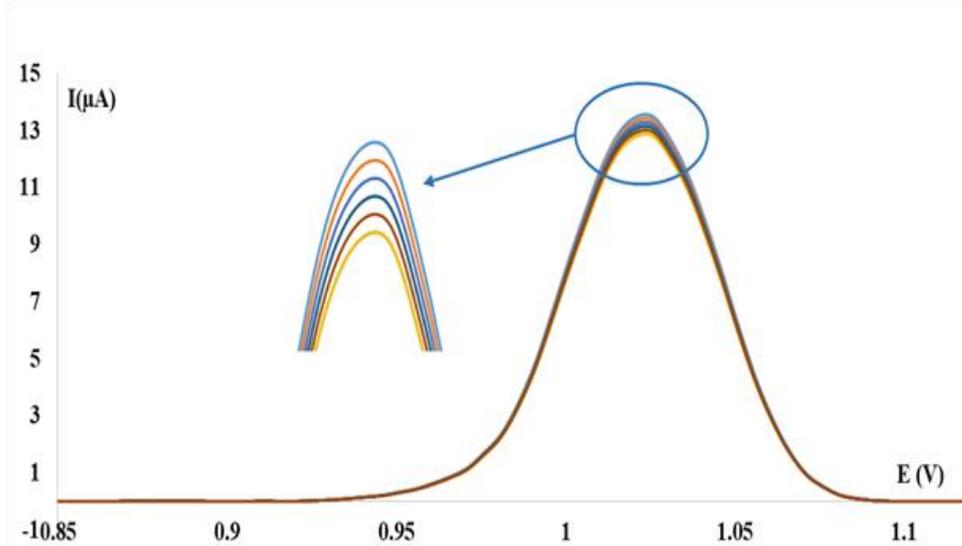


Figure 6. Investigation of NSD-GO electrode selectivity by differential pulse voltammograms of 10 nM Cr(VI) solution at various concentrations of interfering ions, on the surface of the NSD-GO electrode. A platinum electrode was used as an auxiliary electrode and a SCE electrode was used as a reference electrode at room temperature.

Table 1. Interference level of some interferers in chromium ion measurement with the proposed electrode

Interference level	Species
170	Cl ⁻ , NO ³⁻
150	Fe ²⁺ , Mn ²⁺ , Co ²⁺ , Ni ²⁺
120	Cd ²⁺ , Cu ²⁺ , Zn ²⁺
250	Hg ²⁺

3.3.11. Using the prepared sensor to analyze a real sample

Testing of the sensor on real samples was conducted using a sample of municipal wastewater Figure 7. Chromium ions were not detected in this sample. Different amounts of chromium standard solution were applied to the sample matrix, and the results were measured. Chromium (VI) was recovered from the real sample at a level between 99.5 and 102.5. Based on the results, it can be concluded that the NSD-GO sensor is capable of measuring low levels of chromium (VI) in real samples with sufficient accuracy.

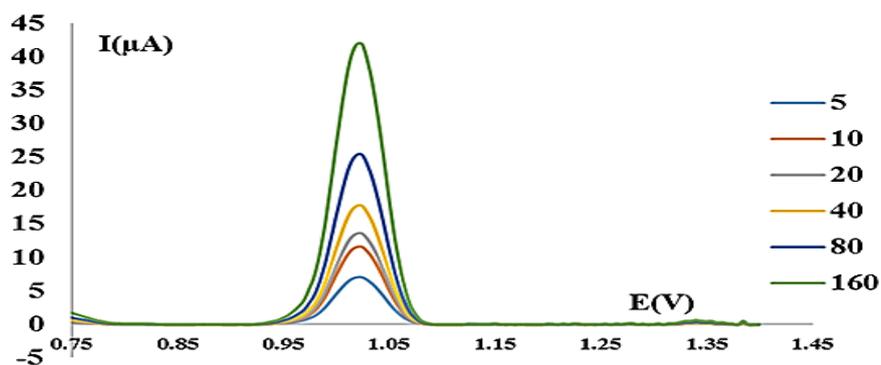


Figure 7. Efficiency of NSD-GO electrode in real sample measurement of chromium ion containing different concentrations of chromium ions solutions of: 5.0; 10.0; 20.0, 40.0; 80.0, and 160.0 nmol L⁻¹ Cr(VI), respectively

4. CONCLUSION

The purpose of this research was to study and investigate the measurement of chromium (VI). As a first step, NSD-GO was synthesized as a modifier, and the surface morphology of the modifier was investigated by FT-IR and SEM. Differential pulse voltammetry was used to study the electrochemical behavior of ions on electrode surfaces. A determination of the ion detection limit was made following optimization of the device and concentration parameters. Table 2 displays a comparison of figures of merit for the proposed method and other electrochemical procedures. It can be observed from the table that the proposed method offers

a wider linearity range and lower detection limit. It was found that the proposed sensor for measuring chromium (VI) ions performed well and was able to measure the ions at very small levels. It is much more economical than other methods due to its suitable detection limit and wide linear range.

Table 2. Comparison of the performance of NSD-GO-CPE with other electrodes reported in the literature for the electrochemical measurement of chromium ions

Electrode	LOD (pM)	Linear Range (nM)	Ref.
Graphite screen-printed electrodes (SPEs)	1000000	3×10^6 - 10×10^6	[26]
Carbonscreen-printedelectrodes (CSPEs) modified with silver nanoparticles	850000	5×10^2 - 3.8×10^4	[27]
C. freundii-modified CPE (Cp-CPE)	1000	1×10^5 - 1×10^5	[28]
Tandem electromembrane extraction	600	0.2-100	[29]
Nitrogen-sulfur doped graphene oxide (NSD-GO)	5.21	0.01-200	Present work

Acknowledgements

The authors express their gratitude to the University of Birjand for providing financial support towards this work.

Declarations of interest

Conflicts of interest are not declared by the authors.

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