

Voltammetric Nanostructure Based Sensor for Determination of Sudan I in Food Samples

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Ionic liquid/CdO/NPs carbon paste electrode (IL/CdO/NPs/CPE) has been used as a high sensitive sensor for the professional quantitative determination of sudan I in food samples in aqueous solution. In the first step, CdO/NPs synthesis using chemical precipitation method and characterized with different methods such as transmission electron microscopy (TEM) and X-ray diffraction (XRD). The propose sensor shows a better electrochemical response with lower over-potential and high sensitivity for sudan I compared with unmodified carbon paste electrode using linear sweep voltammetry (LSV). The electro-oxidation of sudan I occurred in a pH-dependent e⁻ and H⁺ process, and the electrode reaction followed a diffusion-controlled pathway. Under the optimum conditions in square wave voltammetry (SWV), the voltammetric oxidation peak current of sudan I showed linear dynamic ranges with a detection limit of 0.05 μM for sudan I. The modified electrode was successfully used for the determination of the analytes in real samples with satisfactory result.

Keywords: Sudan I analysis, CdO nanoparticle, Ionic liquids, Modified electrode, Sensor

1. INTRODUCTION

Sudan dyes belong to a family of industrial dyes normally used for colouring plastics and other synthetic materials. Up to now four Sudan dyes have been detected in certain food products, in particular Sudan I and Sudan IV (or Scarlet Red) [1]. Sudan I has also been adopted for colouring

various foodstuffs, especially curry powder and chili powder, although the use of Sudan I in foods is now banned in many countries, because Sudan I, Sudan III, and Sudan IV have been classified as category 3 carcinogens (not classifiable as to its carcinogenicity to humans) [2] by the International Agency for Research on Cancer.[3] Sudan I is still used in some orange-coloured smoke formulations and as a colouring for cotton refuse used in chemistry experiments [4]. Therefore, determination of sudan I is very important in food samples.

Modified carbon electrodes and especially carbon paste electrodes are becoming increasingly useful, and application in surface composition enhances the sensing capability [5-15]. In the two decade, the electrochemical based sensor was developed based on carbon paste electrode modified with multiwall carbon nanotubes, electroactive mediator, nanomaterials and/or other nanocompounds for drug, food, pharmaceutical, environmental and other important biological compounds analysis [16–30]. In continuous of modification of carbon paste electrode, room temperature ionic liquids (RTIL), was used as a binder instead of the usually used paraffin oil and other compounds used for pasting [31-40]. According to the published papers and obtained results from them, carbon paste electrode modified with nanomaterials in the presence of RTILs, was used due to its strong capacity for improving all operational metrics such as the limit of detection and sensitivity, making these voltammetric sensor responses better than currently used sensors [41–47].

Nanoscience has become one of the most interesting disciplines in basic science today. The intense interest in nanoscience is being driven by various interesting fields and is leading to a new industrial revolution [48-60]. Electrochemical analysis is taking advantages from all the possibilities offered by nano-based materials easy to be detected by electrochemical methods [61–70].

Therefore, in continuation of our studies concerning the preparation of chemically modified electrodes for electroactive compounds analysis [71–90], in the present work, we describe preparation of a new IL/CdO/NPs/CPE and investigate its performance for the electro-oxidation determination of sudan I in aqueous solutions. We also evaluate the analytical performance of the modified electrode for determination of sudan I in food samples.

2. EXPERIMENTAL

2.1. Chemicals

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout.

Sudan I stock solution, 1×10^{-3} mol L⁻¹, was prepared by dissolving 0.03 g of the reagent in a 100-mL volumetric flask (ethanol–water (1:1) solution).

Phosphate buffer (sodium dihydrogen phosphate and disodium monohydrogen phosphate plus sodium hydroxide, 0.1 mol L⁻¹) solutions (PBS) with different pH values were used.

High viscosity paraffin ($d = 0.88$ kg L⁻¹) from Merck was used as the pasting liquid for the preparation of the carbon paste electrodes.

2.2. Apparatus

Cyclic voltammetry, chronoamperometry, and square wave voltammetry were performed in an analytical system, μ -Autolab with (μ 3AUT 71226) PGSTAT (Eco Chemie, the Netherlands). The system was run on a PC using NOVA software. A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an Ag/AgCl/KCl_{sat} electrode as a reference electrode was used. The working electrode was either an unmodified carbon paste electrode (CPE), CdO/NPs/CPE, IL//CPE or a IL/CdO/NPs/CPE. X-ray powder diffraction studies were carried out using a STOE diffractometer with Cu-K α radiation ($k = 1.54 \text{ \AA}$).

2.3. Synthesis of CdO/NPs

To prepare the CdO/NPs, in a typical experiment, a 0.25 M aqueous solution of Cd(NO₃)₂ and a 0.5 M aqueous solution of sodium hydroxide (NaOH) were prepared in distilled water. Then, the beaker containing NaOH solution was heated at the temperature of about 70 °C. The Cd(NO₃)₂ solutions were added drop wise (slowly for 2.0 h) to the above heated solution under high-speed stirring. The beaker was sealed at this condition for 2 h. The precipitated Cd(OH)₂ was cleaned with deionized water and ethanol then calcined at 400 °C for 3.0 h for synthesis of CdO/NPs.

2.4. Preparation of the modified electrode

CdO/NPs/CPE was prepared by hand-mixing of 0.90 g of graphite powder and 0.10 g CdO/NPs plus paraffin at a ratio of 70/30 (*w/w*) and mixed well for 40 min until a uniformly wetted paste was obtained. The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper. IL/CdO/NPs/CPE was prepared by mixing of 0.2 g of 1-butyl-3-methylimidazolium hexafluoro phosphate, 0.8 g of the liquid paraffin, 0.20 g of CdO/NPs, and 0.90 g of graphite powder. Then the mixture was mixed well for 40 min until a uniformly wetted paste was obtained. A portion of the paste was filled firmly into one glass tube as described above to prepare IL/CdO/NPs/CPE.

2.5. Preparation of real samples

2.5 g sample was weighed exactly and 100.0 mL ethanol was added. After 30 min ultrasonication, the mixture was filtrated with a 0.25 μ m organic filter membrane and the liquid phase was collected in a 100.0 mL volumetric flask. Then proper amount of the sample solution was transferred to the cell and detected by SWV under the optimal conditions.

3. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) data were recorded using Cu K α radiation (1.5406 Å) (Fig. 1A). The intensity data were collected over a 2 θ range of 10–90°. The average grain size of the samples was estimated with the help of Scherrer equation using the diffraction intensity of (200) peak. XRD studies confirmed that the synthesised materials were CdO, and all the diffraction peaks agreed with the reported Joint Committee on Powder Diffraction Standards (JCPDS) data, and no characteristic peaks were observed other than CdO. The mean grain size ($D = 35$ nm) of the particles was determined from the XRD line broadening measurement using Scherrer equation:

$$D = K\lambda / (\beta \cos\theta) \quad (1)$$

where λ is the wavelength (Cu K α), β is the full width at the half-maximum (FWHM) of the CdO (200) line and θ is the diffraction angle. A definite line broadening of the diffraction peaks is an indication that the synthesised materials are in the nanometre range. The morphology of the as-grown nanostructures was characterized by TEM technique. Figure 2 shows the TEM image of the synthesized product. It is clear that in this case, a CdO nanoparticle was successfully prepared.

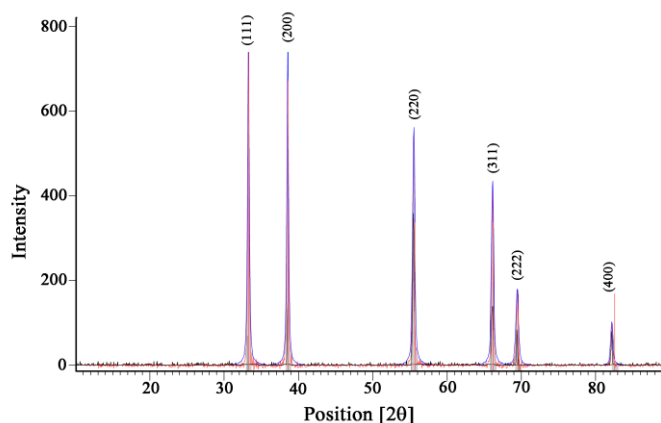


Figure 1. XRD patterns of as-synthesized CdO nanoparticle.

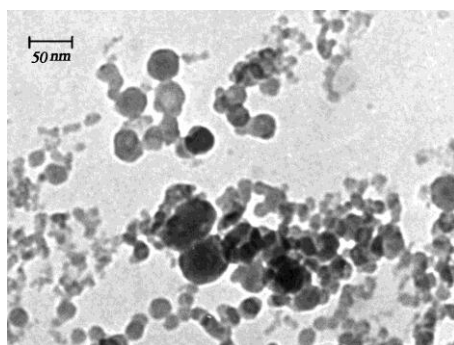
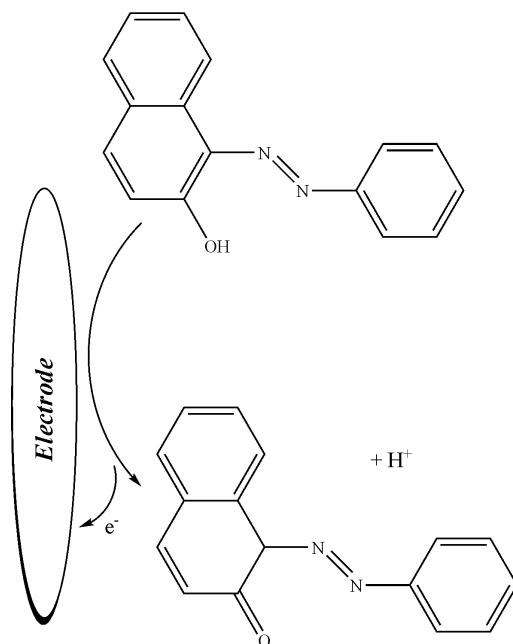


Figure 2. TEM image of CdO/NPs.

According to scheme 1, the oxidation peak current of Sudan I is closely related to the pH value of electrolyte solution. Therefore, the effect of pH was investigated using linear sweep voltammetry technique.



Scheme 1: Electrooxidation mechanism for Sudan I at a surface of modified electrode

Standard solutions of sudan I (120 μM) was used to find the optimum pH of supporting electrolyte which is best suited for determination of sudan I employing modified electrode.

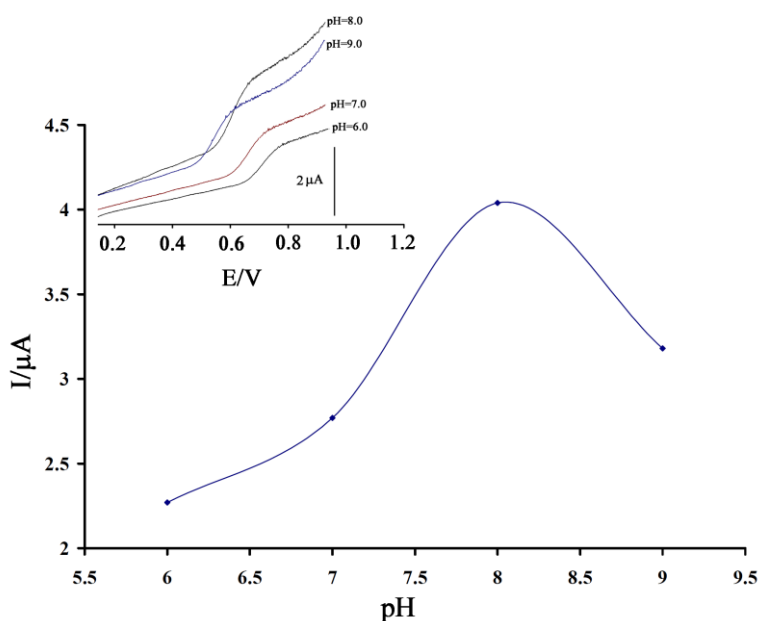


Figure 3. Current–pH curve for electrooxidation of 50 μM sudan I at IL/CdO/NPs/CPE with a scan rate of 100 mV s^{-1} . Inset: influence of pH on cyclic voltammograms of Sudan I at a surface of the modified electrode, (pH 6–9, respectively).

The influence of the pH on the oxidation peak current of sudan I was investigated employing PBS. It was observed that as pH of the medium was gradually increased, the potential kept on shifting towards less positive values, suggesting the involvement of proton in the reaction (Figure 3 insert). Over the pH range 6.0–9.0, the peak potential (E_p) for sudan I oxidation is a linear function of pH. From the plot of E_p vs. pH, slopes of -59.4 mV pH^{-1} was obtained for sudan I in the working pH range. The E_{pa} of sudan I has linear relationship with pH of the buffer solution regarding following equations:

$$E_p = -0.0594 \text{ pH} + 1.1318 \quad (R^2=0.9941) \quad (2)$$

This slope of -59.4 mV pH^{-1} reveal that an equal number of protons and electrons are involved in the oxidation reactions of sudan I. It was observed that the peak current for sudan I was maximum at pH 8.0 (Figure 3). Thus, this pH was employed for further studies. This result is relative to pKa sudan I and better solubility of sudan I in basic condition.

The SW voltammograms of sudan I (500 μM) at IL/CdO/NPs/CPE, IL/CPE, CdO/NPs/CPE and CPE are given in Fig. 4. It can be observed from the figure that moving from CPE to IL/CdO/NPs/CPE, the anodic peak current of sudan I increases and oxidation peak potential shift to negative value simultaneously. It can also be observed that the background current is higher for IL/CdO/NPs/CPE. This is due to the increased surface area of the electrode surface. Thus, the oxidation of sudan I becomes facile on IL/CdO/NPs/CPE.

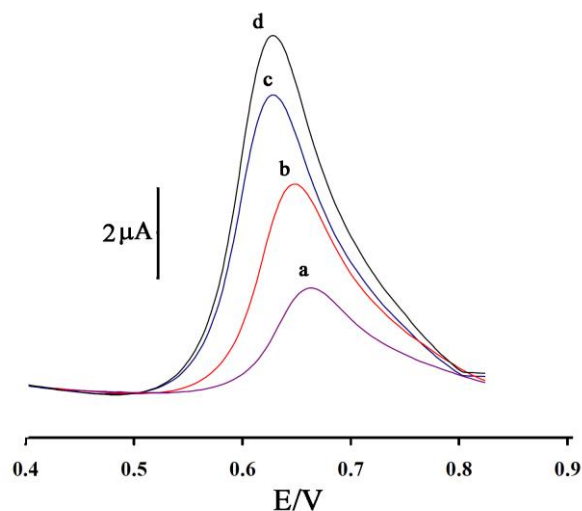


Figure 4. SW voltammograms of a) CPE, b) CdO/NPs/CPE, c) IL/CPE and d) IL/CdO/NPs/CPE in the presence of 500 μM sudan I at a pH 8.0, respectively.

The effect of scan rate (ν) on the oxidation current of sudan I was also examined (Fig. 5 inst). The results showed that the peak current increased linearly with increasing the square root of scan rate that ranged from 30 to 100 mV s^{-1} . The result shows that the electrode process is controlled under the diffusion step [91-100]. On the other hand, the peak potential shifts in negative direction when the scan rate increases, meaning that the electrochemical reaction is quasi-reversible [101-110].

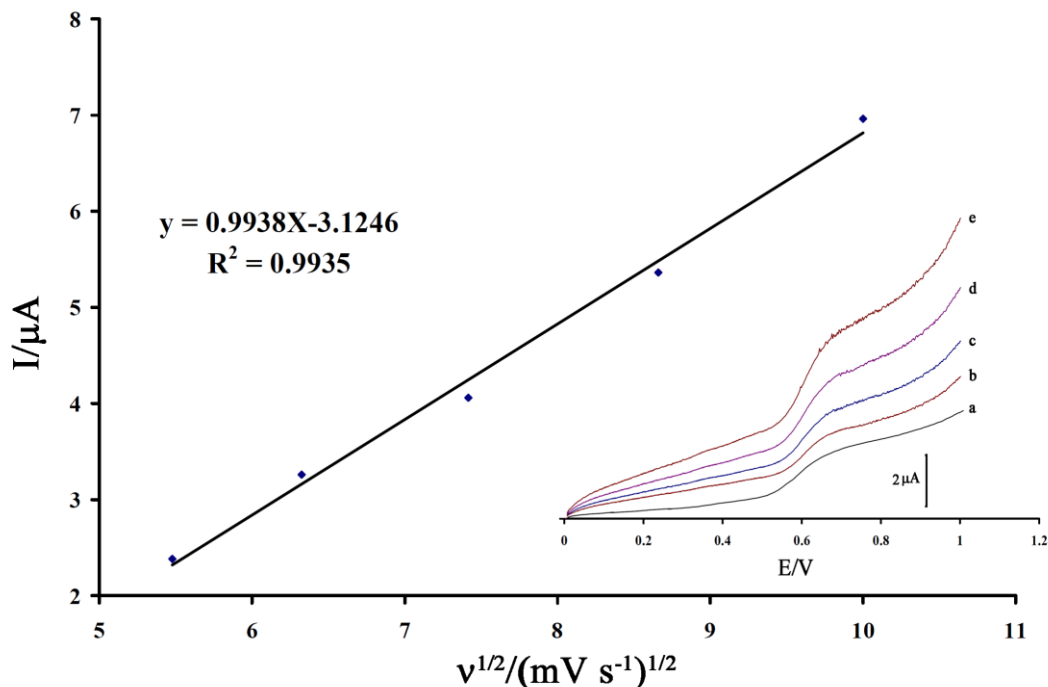


Figure 5. Plot of I_{pa} versus $v^{1/2}$ for the oxidation of sudan I at IL/CdO/NPs/CPE. Inset shows linear sweep voltammograms of sudan I at IL/CdO/NPs/CPE at different scan rates of a) 30, b) 40, c) 55, d) 75, and e) 100 mV s^{-1} in 0.1 M phosphate buffer, pH 8.0.

To obtain further information on the rate determining step, a Tafel plot was developed for the sudan I at a surface of IL/CdO/NPs/CPE using the data derived from the raising part of the current–voltage curve (not shown) [111-118]. The slope of the Tafel plot is equal to $n(1-\alpha)F/2.3RT$ which comes up to $0.303 \text{ V decade}^{-1}$ (Fig. 6). We obtained α as 0.8.

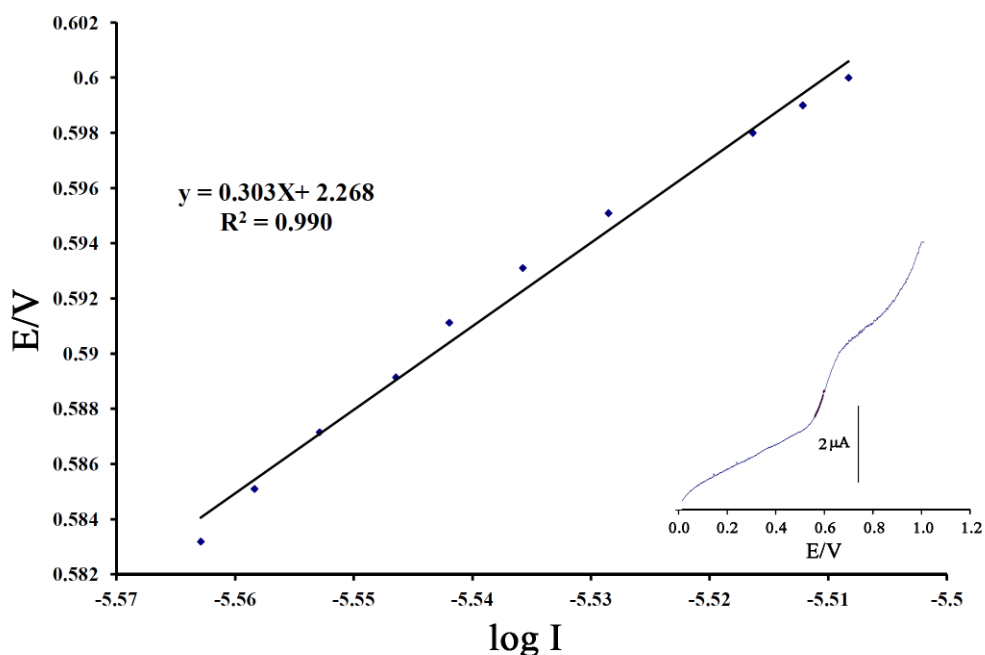


Figure 6. Tafel plot for IL/CdO/NPs/CPE in 0.1 M PBS (pH 8.0) in the presence of L-DOPA.

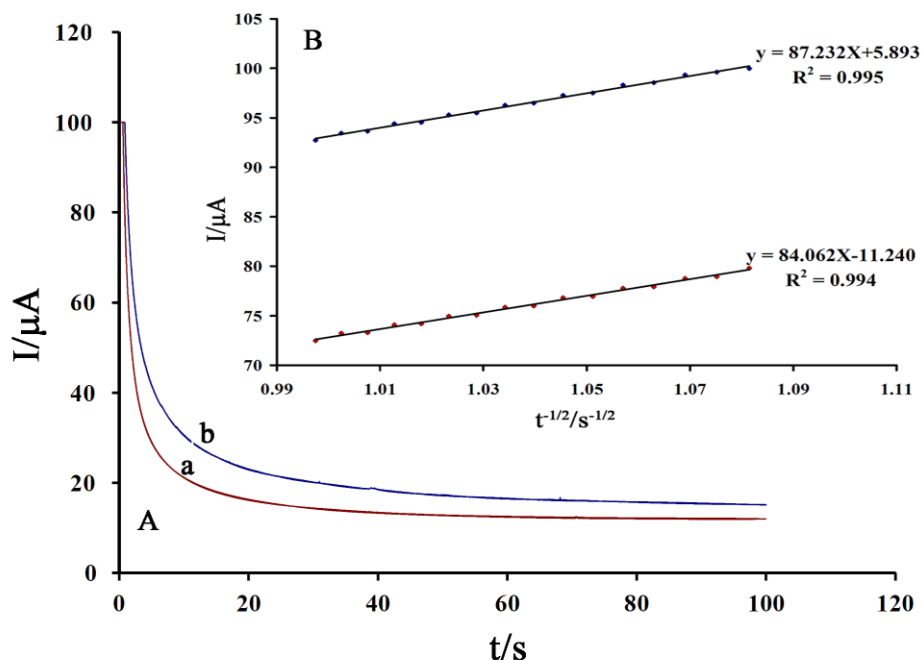


Figure 7. A) Chronoamperograms obtained at IL/CdO/NPs/CPE in the presence of a) 400 and b) 500 μM sudan I in the buffer solution (pH 8.0). B) Cottrell's plot for the data from the chronoamperograms.

Chronoamperometric measurements of sudan I at IL/CdO/NPs/CPE were carried out by setting the working electrode potential at 0.75 V vs. Ag/AgCl/KCl_{sat} for different concentration of sudan I in the buffer solutions, pH 8.0 (Fig. 7A). For an electroactive material (Sudan I in this case) with a diffusion coefficient of D , the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation. Experimental plots of I vs. $t^{-1/2}$ were employed, with the best fits for different concentrations of sudan I (Fig. 7B). The slopes of the resulting straight lines were then plotted vs. Sudan I concentration. From the resulting slope and Cottrell equation the mean value of the D was found to be $2.0 \times 10^{-4} \text{ cm}^2/\text{s}$.

Square wave voltammetry (SWV) was used to determine sudan I concentrations at a surface of modified electrode. The SW voltammograms clearly show that the plot of peak current vs. sudan I concentration is linear for 0.08–550 μM of sudan I, the regression equation being $I_p(\mu\text{A}) = (0.0142 \pm 0.0021)C_{\text{sudan I}} + (0.4230 \pm 0.043)$ ($r^2 = 0.9944$, $n = 9$), where C is μM concentration of sudan I and I_p is the peak current. The detection limit was determined at 0.05 μM sudan I according to the definition of $Y_{\text{LOD}} = Y_B + 3\sigma$. This value is comparable with values reported by other research groups for voltammetric oxidation of sudan I at the surface of chemically modified electrodes (Table 1).

In order to evaluate the selectivity of the proposed method in the determination of sudan I, the influence of various foreign species on the determination of 10.0 μM sudan I was investigated. Tolerance limit was taken as the maximum concentration of foreign substances that caused an approximate relative error of $\pm 5\%$. The results are shown in Table 2. These results demonstrate that the modified electrode has a good selectivity for sudan I analysis in the presence of other foreign species.

Table 1. Comparison of the efficiency of modified electrodes used in the determination of sudan I

Electrode	Method	pH	Linear dynamic range (μM)	Limit of detection (μM)	Ref.
Glassy carbon	SWV	7.0	0.05-2.01	0.01	[119]
Glassy carbon	Cyclic voltammetry	8.0-9.0	2.4-18.0	0.71	[120]
CPE	SWV	7.0	0.2-4.03	0.08	[121]
CPE	SWV	8.0	0.008-600	0.003	[55]
CPE	SWV	8.0	0.08-550	0.05	This work

Table 2. Interference study for the determination of 10.0 μM sudan I under the optimized conditions.

Selected compounds for interference study	Tolerance limits ($W_{\text{Substance}}/W_{\text{Sudan I}}$)
Glucose, Fructose, Lactose, Sucrose, Methanol, Ethanol	1000
Li^+ , Na^+ , K^+ , SCN^- , Cl^- , CO_3^{2-} , ClO_4^- , SO_4^{2-} , Mg^{2+} , Ca^{2+} ,	750
Glycine, Lucine, Histidine, Alanine, Tryptophan, Valine, Methionine, Phenylalanine, Cysteine	500
Ascorbic acid	50
Starch	Saturation

Finally to evaluate the analytical applicability of the proposed modified electrode, also it was applied to the determination of sudan I in food samples. Standard addition method was used for measuring sudan I concentration in the samples. The results are given in Table 3, confirm that the modified electrode retained its efficiency for the determination of sudan I in real samples.

Table 3. Determination of Sudan I in food samples.

Sample	Added (μM)	Expected (μM)	Founded (μM)	Recovery%
Chilli sauce	—	—	<Limit of detection	<Limit of detection
	0.5	0.5	0.48 \pm 0.06	96.0
	5.0	5.0	5.21 \pm 0.38	104.2
Chilli powder	—	—	< Limit of detection	< Limit of detection
	10.0	10.0	9.81 \pm 0.41	98.1
	15.0	15.0	15.12 \pm 0.22	101.33
Tomato sauce	—	—	< Limit of detection	< Limit of detection
	30.0	30.0	29.68 \pm 0.75	98.93
Strawberry sauce	—	—	< Limit of detection	< Limit of detection
	50.0	50.0	50.78 \pm 0.85	101.56

4. CONCLUSION

The new electrochemical sensor was developed for the rapid determination of sudan I. The IL/CdO/NPs/CPE showed great improvement to the electrode process of sudan I compare to the traditional carbon paste electrode. Compared with traditional CPE, a decrease of overpotential of oxidation of sudan I was about 40 mV with 3.7-fold increment in the oxidation peak current when using IL/CdO/NPs/CPE. Under the optimum conditions, the oxidation peak current was proportional to the sudan I concentration in the range of 0.08–550 μM with the detection limit of 0.05 μM . Finally, the propose sensor was successfully used for the determination of sudan I in real samples.

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