Electrochemical detection and degradation of textile dye Congo red at graphene oxide modified electrode

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ABSTRACT

The extensive treatment of most of the pollutants to make the water reusable involves many complex techniques. In the current work, an azo dye Congo red (CR), electrochemical degradation of it was performed via graphene oxide (GO) nanoparticles fabricated on glassy carbon electrode (GCE). The current technique has grabbed some attention due to its applicability for the analysis of CR dye in the soil as well as in water samples. Voltammetric techniques were adopted to study dye electrochemical performance and a linear relationship in $0.01\,\mu M$ to $0.2\,\mu M$ range with a LOD value of $2.4 \times 10^{-7}\,M$ was observed. The lower detection limit value makes the modified sensor valuable for the entire analysis of CR.

1. Introduction

Water pollution refers to the degradation of water quality because of human beings and the anthropogenic activities. Identifying the presence of undesirable destructive and toxic materials in water and their removal is a great promising challenge to the society in the current instance. As more and more methods of water treatment are employed which discovered the pollutants also galloped with greater pace making it a race that never can be completed. Effluents, especially from textile industries and from other industries like paper, paint, plastic, cosmetics, leather, and foodstuffs, etc., contain pollutants dyes, responsible for various environmental and biological problems [1–4].

Congo red (CR), an azo dye [1-napthalenesulfonic acid, 3,3′-(4,4′-biphenylene bis(azo)) bis (4-amino-) disodium salt], is asymmetric, sulfonated azo dye and belongs to the class of protein-binding dyes. Congo red solution color is pH-dependent. It is unsafe, toxic and also has the power to cause anaphylactic shocks and cancer. The cycle life belonging to plants and aquatic animals gets disturbed due to the discharge of untreated dye containing water by preventing the penetration of light.
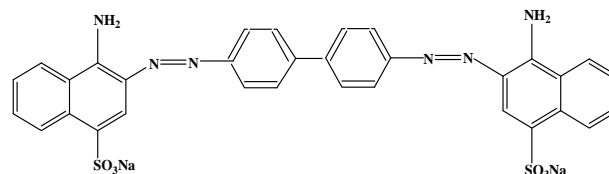
Structure of Congo Red Dye

There is generous confirmation of detrimental possessions. In textile and paper industries commonly used dyes are azo dyes because of low cost, easy usage. Such industries discard the expenditure without treatment to water sources. In human beings without being cleaved as aromatic amines, these may cause cancers involving kidney, liver and bladder. Still knowing their chemical, biological side effects they are paramount in utilizing. The contact with eyes origins allergies, nuisance to skin, respiratory tract and mucous membrane. Since these dyes can form covalent link with cellulose and woolen fibers, in the same way these are assumed to form bonding with −NH₂ and −SH group of proteins of living species. Side effects of dyes were reported on respiratory diseases in workers using reactive dyes. The complex structure

and size do not allocate for easy oxidation of azo dyes by simple treatments. A number of techniques such as electrochemical coagulation, photocatalytic decolorisation, electrochemical oxidation, adsorption and microbiological decomposition have been proposed from time to time for the exclusion of diverse types of dyes from effluents [5–24]. The deletion of dyes from effluents in an economic fashion remains a most important crisis. The electrochemical technique has found wide acceptance for wastewater remediation because these offers promising approaches for the prevention of pollution, versatility, environmental compatibility and cost-effectiveness.

Analysis and degradation of toxic molecules using various modifiers at lower quantity helps the industries for production, variation, and determination of structures. The adsorption practice of nanoparticles on solid electrodes is the easiest way to work with due to easy usage, less expenditure, and excellent efficiency. The toxicity of dyes and destiny of environment are required for selecting and designing the sensor for the treatment of contaminated water. This present proficient electrochemical oxidation of CR provides a direct and economically cheap route for the efficient elimination of dye from aqueous solution, as a process-integrated environmental protection and maximum energy management method. The present work throws light on the usage of voltammetric sensor for the examination of soil and water samples, the degradation needed for samples treatment, and also its detection at lower quantity which can contribute its applications in the present and future scenario.

2. Experimental

2.1. Chemicals and instrumentation

The voltammetric behavior of CR dye was studied by CHI company electrochemical analyzer connected with electrodes in a 10 mL cell with graphene oxide casted glassy carbon electrode 'GO-GCE' as working electrode, platinum wire as counter electrode, and 3.0 M KCl filled Ag/AgCl as reference electrode. Previous to every determination, working electrode was regenerated by polishing it using alumina powder and rinsed ultrasonically with deionized water. The pH of the prepared solutions was tested with Elico pH meter.

Congo red dye was procured from Sigma Aldrich and other reagents of analytical reagent grade was used. The desired concentration of CR solution was prepared by dissolving suitable quantity in 25 mL millipore water. Using different pH phosphate buffer solution (PBS), outcome of supporting electrolyte was deliberated ranging from 3.0 to 11.2 [25]. The samples subjected for analyzing CR include Red soil, clay, and black cotton soils which were collected from various sources and used in the investigation. The results verification by graphene oxide-coated glassy carbon electrode (GO-GCE) is highly sensitive to parameters like temperature and concentration of analyte solution among others. The current work records the detection of CR and also the samples containing it.

2.2. Preparation of modified electrode

The unmodified GCE prepared by polishing with alumina powder, and rinsing properly with deionized water before every use. GO suspension was prepared by dispersing 1 mg of GO into 10 mL of the ethanol solution. For voltammetric measurement, the working sensor was organized by casting around 10 μL of the GO suspension on the dried exterior of GCE. Sensing electrode was made active by taking CVs between 0.0 V to 1.2 V in pH = 8.0 PBS. For reuse of GCE, GO nanoparticles were removed from the sensing area of the working electrode by washing with water repetitively [26–31]. Bare GCE was prepared without casting nanoparticle suspension.

2.3. Preparation of sample solutions

The application part of the current work involves analysis of soil and water samples by utilizing voltammetric techniques. The soil samples (Red, Clay, and Black) of each 1 g dispersed in water, centrifuged for 15 mins and filtered through a filter paper. These soil samples as well as water samples were spiked with known amount of CR (0.1 mM) and subjected to analysis by SWV.

3. Results and discussion

3.1. Determination of surface area of the working electrode

The exposed area of unmodified and modified GCE was determined using Randles - Sevcik equation recording CVs of $K_3[Fe(CN)]_6$ (1.0 mM) in presence of KCl (0.1 M) as sustaining electrolyte, at varying sweep rates [32].

$$I_p = (2.69 \times 10^5) n^{3/2} A \, D_0^{1/2} \nu^{1/2} C_0^* \tag{1}$$

From Eq. (1), the exterior area of bare GCE was estimated to be 0.04 cm^2 and modification of GCE with GO suspension enhances it by 2–3 times.

3.2. Electrochemical behavior of CR

The electrochemical behavior of CR was studied by recording the cyclic voltammograms at unmodified and GO modified GCE using 1.0 mM Congo red in 0.2 M PBS of pH 8.0. The CV of 1.0 mM CR display an anodic peak at about 0.669 V at GCE and 0.632 V at GO-GCE as shown in Fig. 1. This effect in increasing in peak current was due to the interaction of CR dye with the electrode material. The CR electrode process is confirmed as irreversible due to the absence of the reduction peak in the reverse sweep. The modification using GO at GCE is beneficial over the results obtained at unmodified GCE [33,34]. The improvement in anodic peak current at GO-GCE exposes that nanoparticles GO acts as catalysts which helps for fast transfer of electrons and also shift in the potentials towards lower value at GO-GCE (Fig. 2). At successive CV sweeps, the first voltammogram showed considerable anodic oxidation current, later decreasing nature was observed due to the CR or its reaction products adsorption lying on the active electrode surface. Hence, the first cycle was considered.
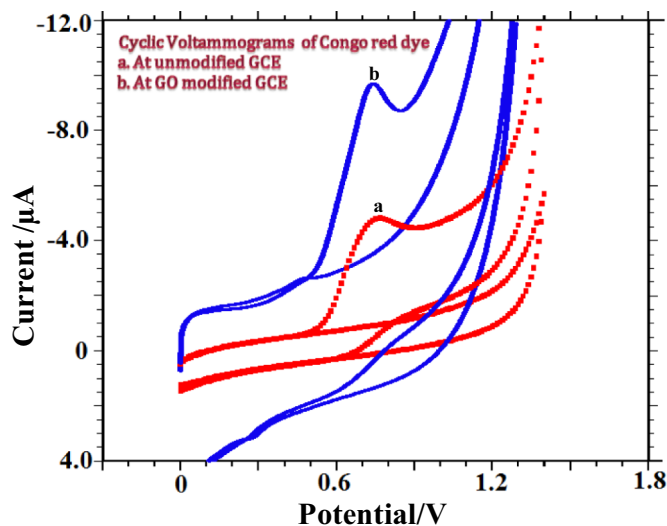

Fig. 1. Voltammetric behavior of 1.0 mM Congo red dye at unmodified and GO modified GCE in pH 8.0 PBS of I = 0.2 M; scan rate = 0.05 Vs^{-1}; accumulation time = 0 s.
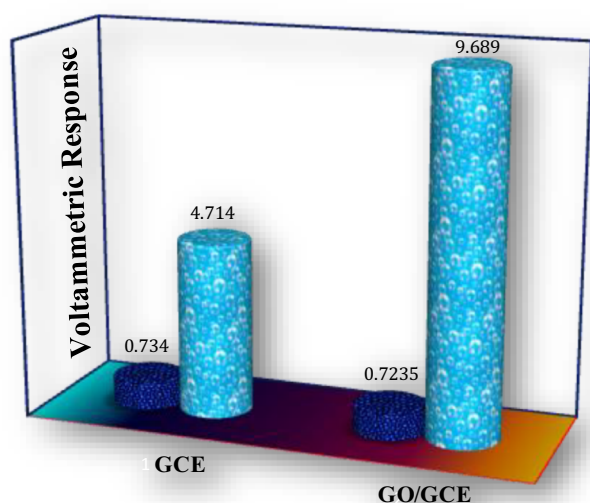
Fig. 2. Enhancement effect of GO for the electro-analysis of 1.0 mM CR at unmodified and GO-GCE in pH 8.0 PBS.

3.3. Effect of pre-concentration time

The movement of analyte molecules towards the sensing electrode surface for electro-oxidation reaction would depend on time. The effect of pre-concentration time was studied by taking CVs of 1.0 mM CR in a range of 0–100 s (Fig. 3). The peak currents decreased after 0 s accumulation time. Hence, further voltammogram were recorded without setting pre-concentration time.

3.4. Effect of pH

The voltammetric reply of CR was premeditated over pH range of 3.0–11.2 in 0.2 M PBS by CV method to know the result of supporting electrolyte pH on the electrochemical activities at GO-GCE. From pH 3.0 to pH 5.0, diminished peaks current was observed, whereas from pH 6.0 to pH 11.2, a linear region was observed with a slope value of about 48 mV/pH. The value was close to 59 mV/pH i.e. the Nernstian value, which implies, the electrochemical reaction involves identical
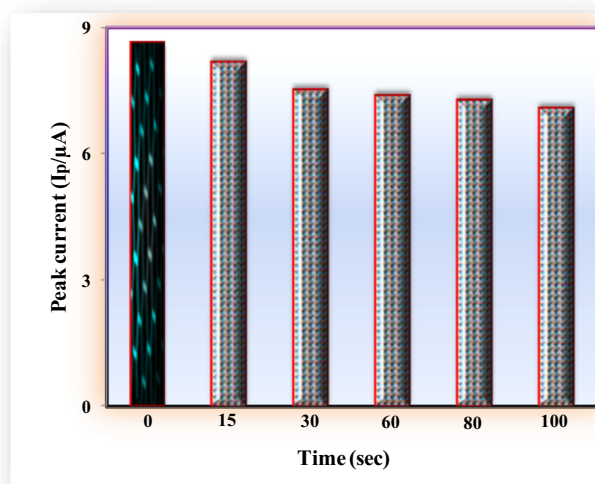

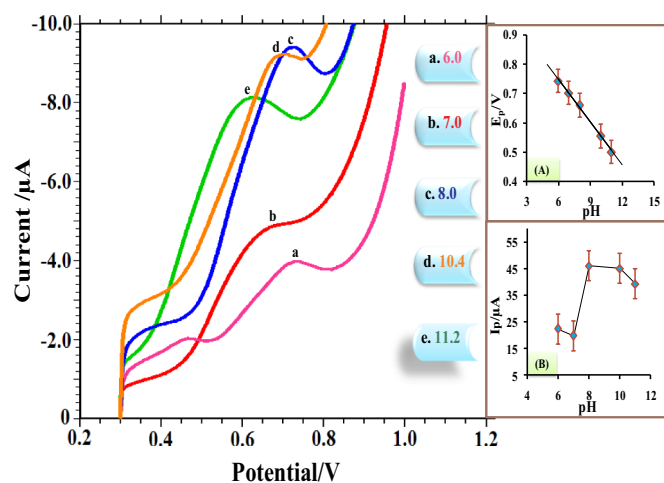**Fig. 3.** Influence of pre-concentration time on the anodic peak current of 1.0 mM CR.

Fig. 4. Linear sweep voltammograms of 1.0 mM CR in different pH PBS at GO-GCE; $\upsilon = 0.05\,\mathrm{Vs^{-1}}$. Plots: (A) Variation of peak potentials and (B) Variation of peak currents with pH.

quantity of protons and electrons [25,35]. Shift in the potential values observed with increasing pH of PBS. The peak current was highest at pH 8.0, as seen in Fig. 4, hence, pH 8.0 PBS used for the determination of CR and for further experiments. The correlation between E_p and pH is expressed as follows:

E_p (V) = 1.040–0.048 pH (mV); R^2 = 0.996 (between pH 6.0 and 11.2).

The oxidation peak enlarged gradually from 3.0 to 8.0 pH, due to involvement of few numbers of protons, which facilitates the electro-oxidation process at higher pH. For higher pH diminish in the intensity of peaks observed.

3.5. Influence of sweep rate

The scan rate influence assist to comprehend the reaction mechanism and the process involved either adsorption or diffusion controlled. The CVs of CR were recorded at unmodified and GO modified GCE by differing sweep rates in pH 8.0 without pre-concentration time.

It was evidenced that with increase in the sweep rates (υ), an improvement in voltammograms anodic peak current (I_p) was observed
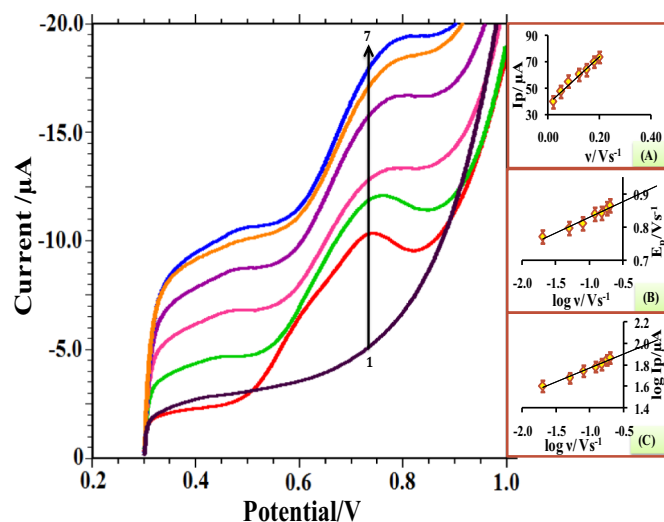

Fig. 5. Linear sweep voltammograms of 1.0 mM CR with increasing scan rates at GO-GCE, (1) Buffer to (7) 0.2 (υ in Vs^{-1}). Plots: (A) Variation of peak current and (B) Variation of peak potential with scan rates.

(Fig. 5). The linear regression equation can be given as; I_p (μA) = 177. 4υ − 38.58; R^2 = 0.985. According to: log I_p (μA) = 0.260 log υ + 2.032; R^2 = 0.982 equation, 0.260 the slope value, is nearer to the theoretical value of 0.5 for diffusion-controlled process [36–39]. Hence, the CR electro-oxidation process is controlled by diffusion rather than adsorption. Further, a linear relation between E_p and log υ with the regression equation: E_p (V) = 0.092 log υ + 0.873; R^2 = 0.971, was observed. Relationship between υ and E_p for a process was stated by Laviron's theory [40].

$$E_p = E^0 + \left(\frac{2.303RT}{\alpha nF}\right)\log\left(\frac{RTk^0}{\alpha nF}\right) + \left(\frac{2.303RT}{\alpha nF}\right)\log\upsilon \tag{2}$$

In Eq. (2), the signs have their usual implication. According to Bard and Faulkner [25], α was estimated as,

$$\Delta E_p = E_p - E_{p/2} = \frac{47.7}{\alpha n}mV \tag{3}$$

where, '$E_{p/2}$' is the potential in which the current is half of the peak value. From eq. (3), the 'α' was calculated as 0.55 and heterogeneous rate constant 'k^0' to be $2.60 \times 10^{-3}\,s^{-1}$, from the intercept of E_p versus log υ. The CR oxidation involves one electron transfer.

4. Analytical applications

4.1. Concentration variation

Differential pulse voltammetry (DPV) technique was utilized for the quantitative resolving of CR due to its defined peaks at lower concentrations of CR. The peak current of oxidation of CR showed an amplification in the current with the concentration (Fig. 6). The linearity in the plots for increasing concentration of CR in the range of 0.01×10^{-6} M to 0.2×10^{-6}M can be seen as follows:

Ip (μA) = 19.35 + 12.84C (R^2 = 0.985, C is in μM).

Limit of detection and quantification values (LOD, LOQ) were intended using standard equations, LOD = 3S/m, and LOQ = 10S/m, where 'S' is standard deviation of slope (6.797×10^{-6}) and 'm' is the slope of calibration curve (8.462). It was also noticed that at higher concentrations of CR, the peak potentials greatly deviated suggests that there is larger amount of adsorption of products as well as analyte at the active sensing base electrode. The LOD, LOQ values were calculated as
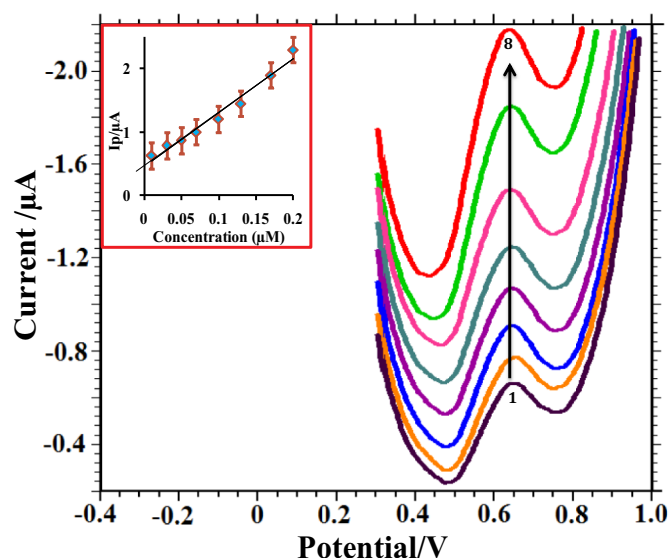

Fig. 6. Differential pulse voltammograms for increasing CR concentrations in pH 8.0 at GO-GCE: (1) 0.01; (2) 0.03; (3) 0.05; (4) 0.07; (5) 0.1; (6) 0.13; (7) 0.17; (8) 0.2 μM. Inset: Variation of concentration/μM versus peak current I_p/μA.

Table 1
Comparison of detection limits of CR by other techniques.

Sl. no.	Methods	LOD values	Reference
1	Electro-oxidation at GCE	0.1×10^{-6} M	[17]
2	Spectrophotometric methods	0.6×10^{-3} M	[41]
3	Voltammetric behavior of CR at GO-GCE	2.4×10^{-7} M	Present work

Table 2
Determination of CR in spiked soil samples by DPV technique.

Soil Sample	Spiked (10^{-4} M)	Detected[a] (10^{-4} M)	Recovery (%)
Red soil sample			
1	0.1	0.082	82.0
2	0.5	0.434	86.8
3	1.0	0.754	75.4
Black soil sample			
1	0.1	0.074	74.0
2	0.5	0.413	82.6
3	1.0	0.825	82.5
Clay soil sample			
1	0.1	0.085	85.0
2	0.5	0.486	97.2
3	1.0	0.920	92.0

[a] Average of five readings

Table 3
Determination of CR in spiked water samples by DPV technique.

Water Sample	Spiked (10^{-4} M)	Detected[a] (10^{-4} M)	Recovery (%)
Water Sample 1			
1	0.2	0.17	85.0
2	0.4	0.39	97.5
3	0.8	0.76	95.0
Water Sample 2			
1	0.2	0.18	90.0
2	0.4	0.37	83.2
3	0.8	0.77	96.2

[a] Average of five readings

Table 4
Effect of metal ions on the voltammetric behavior of CR at GO-GCE.

Sl. no.	Metal salts	Potential values		Signal change
		Sample	Standard	
1	$(NH_4)_2SO_4$	0.618	0.653	−5.35
2	NH_4Cl	0.626	0.653	−4.14
3	NaCl	0.626	0.653	−4.11
4	KCl	0.637	0.653	−2.46
5	$CuSO_4$	0.627	0.653	−3.96
6	$BaCl_2$	0.612	0.653	−6.24
7	KNO_3	0.616	0.653	−5.73
8	$(CH3COO)_2Cu$	0.617	0.653	−5.50

2.4×10^{-7} M and 8.1×10^{-7} M, respectively. In Table 1, limit of detection values are given obtained from other techniques. According to the current results with good sensitivity and lower detection limit, suggests that the method is better compared to other methods reported.

4.2. Repeatability and reproducibility of GO-GCE

The repeatability of GO-GCE was studied using 1.0 mM of CR. The developed working sensor was stored in a bottle containing no air for 7 days. The sensor exhibits retention value of 96.3% compared to
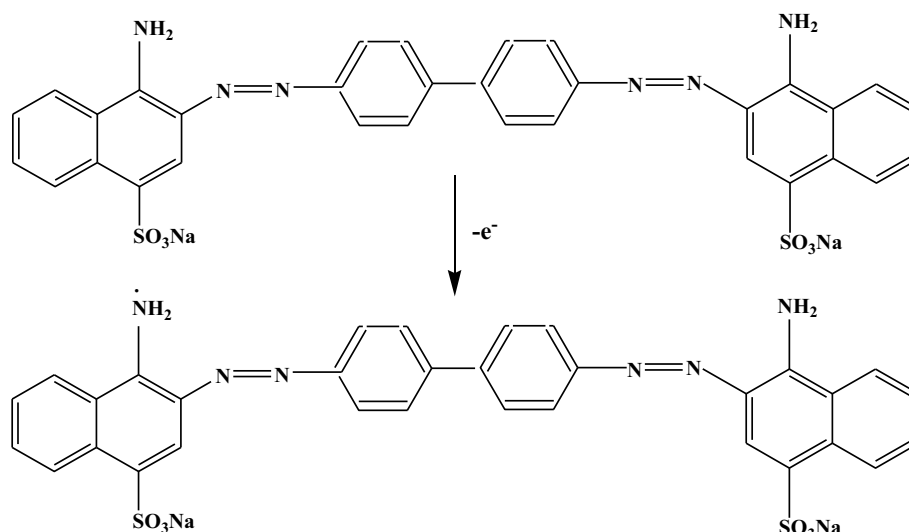
Scheme 1. Electro-oxidation mechanism of CR at GO-GCE.

original peak current reply for 1.0 mM CR. Hence, we conclude about long stability of modified GCE. We also checked the reproducibility of the sensing base by measuring five continuous voltammograms at constant concentration of CR (1.0 mM). Good reproducible values for CR at GO-GCE with RSD % of 2.10% were obtained. Hence, the method considered to be unique with great stability and reproducible values.

4.3. Detection of Congo red in water and soil sample

DPV technique was applied to detect CR in water and soil samples at constant temperature. To know the recovery reading, water and soil samples were spiked with an identified quantity of CR. From the calibration plot, designed for the estimation of CR in the samples, the finding results acquired are listed in Tables 2 and 3.

4.4. Effect of metal ions

The impact of metal ions on the peak potential and current of CR was studied using GO-GCE. The results exhibited that there is interference from metal ions such as ammonium sulphate, barium chloride, potassium nitrate, copper acetate and no interference from ammonium chloride, sodium chloride, potassium chloride, copper sulphate on CR voltammetric response shown in Table 4. Therefore, the proposed modified sensor can be used for the detection of CR.

4.5. Electro-oxidation mechanism of CR

An involvement of protons and electrons in the voltammetry of CR dye was detected from CV data at different sweep rates study. The results observed helped to write down a probable electrochemical response of CR (Scheme 1) which is similar to the oxidation of hydroxyl –substituted azo dye [10].

5. Conclusions

Electrochemical study of Congo red dye based on graphene oxide nanoparticles sensor demonstrated its potential to deal with the mentioned challenge. In the current work, GO-GCE showed an exceptional and progressively more significance to fulfill the preferred analytical necessities. Involvement of one electron and one proton was noticed in CR voltammetry study. This throws some light on the electrochemical properties of the toxic molecule such as CR dye, which is actively involved in polluting environment. The method was applied to water and soil analysis at ambient temperature. Thus, the analytical overlap with electrochemical applications provides a comprehensive overview of the fabrication, properties, and electrochemical applications of graphene nanoparticles. The output of this study helps in safety and development of healthy environment.

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