Electrochemical sensing of nitrate ions at Cu-immobilized gold electrode in neutral medium

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Abstract

The Cu-immobilized Au surface was electro-catalytically employed for nitrate ions reduction in a neutral solution. According to cyclic voltammetric studies, the Cu/Au electrode has an improved electro-catalytic impact on converting nitrate ions into nitrite ions, governed by a two-electron transfer system. This modified electrode demonstrated good performance in real sample analysis along with good sensitivity ($3.2518\ \mu A \mu M^{-1} cm^{-2}$), long linear detection range (1.2 to 111.4 μM), a very lower limit of detection (0.85 μM), an excellent reproducibility. Thus, to determine nitrate ions in an aqueous media, an electrochemical sensor based on a Cu/Au electrode is suggested.

Keywords: Nitrate reduction, Environmental safety, Electrocatalyst, Sensor.

Highlights

- Improved electrocatalytic impact for nitrate to nitrite conversion.

- Sensitivity of 3.2518 $\mu A \mu M^{-1} cm^{-2}$ and long detection range.

- Lower detection limit of 0.85 μM with excellent reproducibility.

- Effective nitrate detection in real sample analysis.

Acknowledgement

1 Introduction

Nitrate contamination of groundwater has grown significantly in importance as a recent environmental problem. Due to the extensive use of fertilizers, significant amounts of nitrate ions are absorbed into the surface and subsurface waters [1]. Discharge of wastewater from aquaculture contains a good number of nitrogenous substances (ammonia, nitrate, and nitrite) dissolved in organic carbon and phosphorus, which severely affect the ecosystem [2]. Ammonia (NH_3) is created by the decomposition of too much organic material and fish respiration. Chemoautotrophic bacteria, Nitrosomonas, and Nitrobacter convert ammonium ions (NO_4^+) to nitrate (NO_3^-) and nitrite (NO_2^-) ions. Despite this, aquatic plants, algae, and bacteria remove them because they utilize these nitrogenous elements as a source of nitrogen, [3], but this removal is insufficient to lessen the impact of pollution. Eutrophication is brought on by these nitrogenous fertilizers and substances, substantially upsetting aquatic ecosystems [4], [5]. Agricultural and urban runoff, sewage effluents, industrial waste, and animal husbandry all raise the concentrations of nitrate, nitrite, and ammonia in aquatic ecosystems [3]. The easy transformation of nitrates to nitrites in food products by microorganisms, which then convert into carcinogenic nitrosamines in the man's digestive system, is another issue with nitrates [6]. Meanwhile, the transformation of nitrate to nitrite in human saliva can result in methemoglobinemia or blue baby syndrome, liver disorders, and cancer by reacting with amines to form dangerous and cancer-causing nitrosamines [7]–[9]. In fact, the nitrogen cycle includes nitrate, which is a common contaminant of soil and water [10].

A maximum of 50.0 mg/L NO_3^- (for newborns, 15.0 mg/L NO_3^-), 0.5 mg/L NO_2^-, and 0.5 mg/L NH_3 are permitted in drinking water [11], [12]. Interest in quantifying nitrate content is rapidly increasing, particularly for the treatment of wastewater. In order to prevent food that is produced using water as a raw material from becoming contaminated, checking the quality of the water is also essential. Because of their toxicity, nitrates are always being estimated in the food sector [13]. The removal of nitrate from water sources is therefore a serious issue.

Various analytical techniques are used today to detect and quantify nitrate, including polarography [6], colorimetry [14], [15], ion exchange chromatography [16], and direct UV spectroscopy [16]. However, these techniques require trained personnel and complicated equipment which has the disadvantage of making them time-consuming, and occasionally having poor selectivity and sensitivity, which makes them inappropriate for regular detection. A carbon source must be added, the pH must be adjusted, and the temperature must be controlled for biological denitrification to occur [17], [18]. Extractive technologies like ion exchange resins and reverse osmosis [4], [19] produce secondary pollution that has to be purified later, increasing the overall expenditure of the system. Therefore, because of its excellent treatment efficiency, lack of sludge formation, small footprint, and cheap instrumentation [20]–[22], electrochemical nitrate reduction has a great deal to study. In recent times, bimetallic or modified electrodes in the form of co-deposited films, alloys, or ad-atoms on the interface of a pure metal have been studied to control product selectivity and enhance reduction performance. When it comes to catalysis and determining product selectivity in the reduction of nitrate ions, electrode materials may play a crucial role. Different studies have demonstrated the potent electrocatalytic activity of Cu-based electrodes in the electrochemical reduction of nitrate process (NRR) [23], [24]. Several cathodes, including Cu, Fe, Pt/Ir, Zn, Pd, and Au have been used in electrochemical denitrification throughout the past few decades [25]–[28]. Some electrodes, such as those made of Cu and Fe [10], [29]–[31], were said to be good NRR promoters.

However, one approach for eliminating the NO_3^- ion from polluted waters is electrochemical nitrate reduction, which also produces a broad range of compounds, such as NH_2OH, N_2O, N_2, and NH_3 [29], [32], [33]. It has been noted that it is challenging to concurrently form nitrogen in electrochemical nitrate reduction when the electrolysis voltage is static [34]–[36]. During the cathodic cycle, the NO_3^- ions are primarily reduced to NO_2^- and NH_3 which are subsequently electrochemically inert. Voltammetric and chronoamperometric analysis techniques are more appropriate due to their excellent selectivity, sensitivity, stability, fast reaction times, and ability to detect on-site, even in turbid or colored samples [12].

To construct sensor materials for the electrochemical reduction of nitrates, we have reported a fundamental investigation in this paper. A bimetallic Cu/Au electrode has been presented as a nitrate sensor since it has been advanced as an electrocatalyst for the nitrate reduction reaction (NRR).

2 Methodology

2.1 Chemicals and reagents

The chemicals employed in this experiment were in analytical grade. Alumina powder, Sodium nitrate, and Copper (II) sulfate were purchased from Merck in Germany, and KCl was acquired from Aldrich Chemical Co. Inc. in Germany. Each solution was made with Millipore Milli-Q water (resistivity $< 18.2\,M\Omega\,cm^{-1}$).

2.2 Electrode modification and electrochemical investigation

The electrochemical investigations were observed using electrochemical workstations such as the Autolab 128N potentiostat and the CHI 660 potentiostat from Dutch. All the investigations were carried out in a three-electrode electrochemical cell with a nitrogen environment at 25°C. A glass cell of one compartment with three electrodes has been utilized as the reactor for voltammetric studies. The working electrode in this instance was an Au electrode treated with Cu NP. In the meantime, Pt wire is used as the counter electrode, and an Ag/AgCl (sat. KCl) is used as the reference electrode. An Au electrode with a geometrical surface area of 0.0314 cm^2 has been used for the electrochemical experiments as the working electrode for cyclic voltammetric measurements. Before use, the electrode was polished with alumina slurries (0.3 μm) to a mirror-like finish. The abrasive particles were then removed from the electrode by sonicating it for 15 minutes in a 0.1 M 10 mL sulfuric acid solution. Once the cyclic voltammetric characteristic peak for a clean gold (Au) electrode appeared, the surface was electrochemically cleaned by repeatedly performing CV scans at a scan rate of 0.1 Vs^{-1} in the potential ranges of -1.4 to +1.2 V and -0.2 to +1.5 V, respectively in 0.1 M NaOH and 0.1 M H_2SO_4 solution. The Cu nanoparticle was electrochemically deposited on an Au electrode surface by scanning the electrode at 0.01 M $CuSO_4$ solution from 0 to -1.0 V.

The freshly constructed Cu/Au electrode was properly cleansed with ultrapure water before being used for NRR, and the potential was repeatedly swept in a 0.1 M KCl solution between 0.0 and -1.4 V until stable CVs were achieved. The total amount of the electrolytic solution, which was used for the NRR tests, was 10.0 ml, and it contained nitrate ion and 0.1 M KCl solution. The employed potential range for CV tests was 0.0 to -1.4 V. A very potent hydrogen evolution reaction (HER) was seen at greater negative overpotentials. The chosen frequency range for electrochemical impedance spectroscopic (EIS) measurements was 0.1 MHz to 0.1 Hz with 50 measuring points. The DPVs were recorded from 0.1 to154.6 μM nitrate concentration. The data that were determined by EIS, CV, and DPV were all fitted using the data analysis program Sigma Plot v. 10.

3 Results and Discussion

3.1 Characterization of the fabricated Cu-immobilized Au-electrode by Electrochemical impedance spectroscopy

EIS, or electrochemical impedance spectroscopy, is a useful technique for examining the interface characteristics of electrodes with modified surfaces. The binding of the electroactive species that are undertaking electron transfer processes at the surface of the working electrode may also be learned through measurements of EIS spectra. In EIS, the charge transfer resistance, Rct, the double layer capacitance, C_{dl}, and the electrolyte resistance Rs, were used to estimate the total impedance. The sum of the real and imaginary Z components, which mostly come from the cell's resistance and capacitance, can represent the complex impedance.

The electrode/electrolyte interface's dielectric and insulating properties are essential to the function of the circuit's two components, Rct and C_{dl}. The semicircle diameter in EIS is equal to Rct, the electron transfer resistance [37]. The redox probe's kinetics of electron transport at the electrode contacts are controlled by this resistance. When various materials are adsorbed onto the electrode surface, their value changes. The comparative binding of the catalyst (Cu/Au) with a particular reactant (NO_3^-) in the presence of a supporting electrolyte has been investigated utilizing a three-electrode setup since NRR also happens because of heterogeneous electron transfer processes.
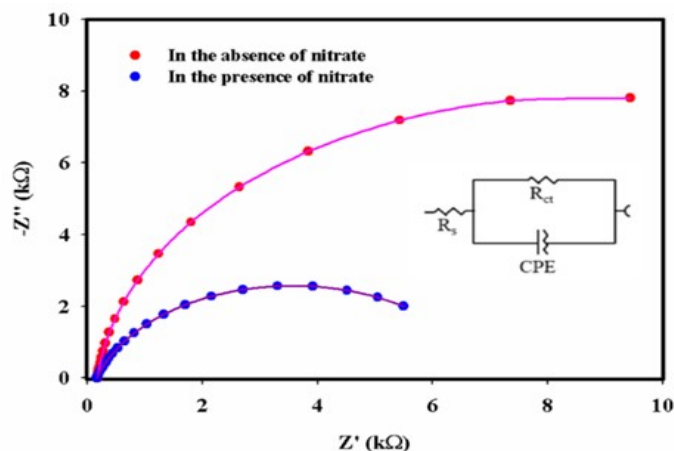

Fig 1. Nyquist plots of Cu/Au electrode in the presence (blue curve) of 3.0 mM NO_3^- and in the absence (red curve) of nitrate in 0.1 M KCl solution at -1.1V.

Fig. 1. shows the Nyquist plots obtained for the Cu/Au electrode in 0.1 M KCl solution in the presence and in the absence of 3.0 mM NO_3^- solution at -1.1V. The Rct value for the Cu/Au electrode without NO_3^- the solution was 17.05 kΩ around -1.1V potential. The Rct value has reduced significantly to 6.81 k Ω in the presence of NO_3^- solution, which proves the more capacitive behavior of the Cu/Au electrode to the NO_3^- reduction.

3.2 Influence of Cu particles on NRR

Electrode materials have an important role in the electro-chemical reduction of various species. Figure 2 shows CVs for NRR at a potential scan rate of 0.1 Vs^{-1} at different working electrodes e.g., bare Au, bare Cu, and Cu NPs electrodeposited Au electrodes in 0.1 M KCl. In Figure 2, the blue curve (bare Au electrode) shows no peak, which indicates that there was no reduction took place on the electrode. When we used the Cu/Au electrode (red curve in Fig. 2), we found four peaks around -0.1 V, -0.65 V, -0.86 V, and -1.26 V, which indicates that Cu deposited Au electrode is very effective for the nitrate reduction reaction. On the other hand, three peaks around -0.1 V, -0.65 V, and -1.26 V are observed at the bare Cu electrode. In the bare Au electrode (blue line), there is no peak appears but for Cu/Au (red line) electrode and bare Cu electrode (black line), peaks (E1) and (E2) are present. It can be said that these peaks are produced by the reduction of Cu(I) and Cu(II) species in the electrode surface represented by the reactions as follows [38], [39].

$$E1 : Cu(I) + 1e^- \rightarrow Cu \qquad (1)$$

$$E1 : Cu(II) + 2e^- \rightarrow Cu \qquad (2)$$
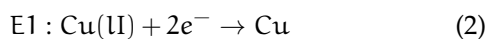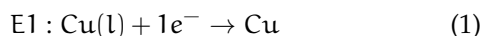
Peaks (E3) and (E4) are absent in the bare Au electrode surface whereas peaks (E3) and (E4) are present for Cu/Au surface. On the other hand, peak (E3) is absent on the bare Cu surface but (E4) is present. So, it can be said that these two peaks (E3 and E4) are related to NRR. From Figure 2, the NRR occurred at the bare Cu electrode in one step (E4) but at the Cu/Au electrode surface, the NRR occurred in two consecutive steps (E3 and E4).
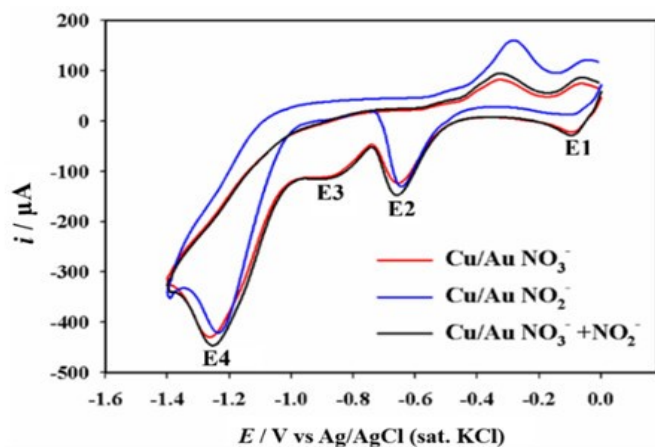

Fig 2. CVs were obtained for 83.2 μM NO_3^- ions in 0.1 M KCl using different electrodes (Cu/Au, bare Au, and bare Cu) at 0.1 Vs^{-1} scan rate.

The (E3) peak appeared at a relatively negative potential (-0.86 V) than the (E4) peak. For (E4), more current is observed at the Cu/Au electrode than bare Cu. Thus, the rest of the studies are done at the Cu/Au electrode surface for more detailed kinetic studies of NRR and effective nitrate ion sensing in a neutral condition.
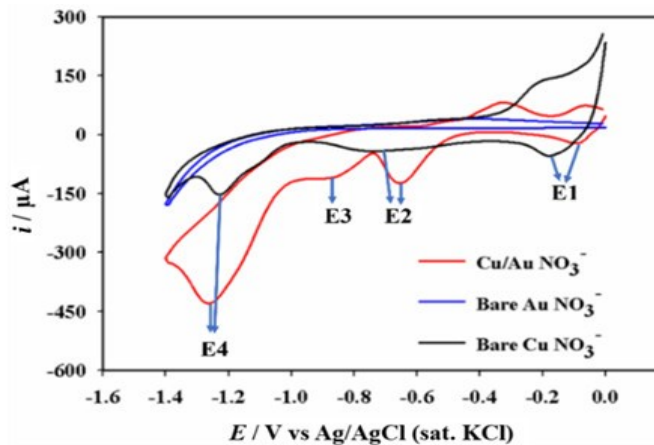

Fig 3. CVs obtained on Cu/Au electrode for 83.2 μM NO_2^-, 83.2 μM NO_3^- and a mixture of 47.0 μM NO_2^- and 47.0 μM NO_3^- solutions in 10.0 mL 0.1 M KCl at 0.1 Vs^{-1} scan rate.

3.3 Comparison of NO_3^- and NO_2^- reduction

To reveal the mechanism of NRR at the Cu/Au electrode surface, analyzing the CV peaks of nitrate and nitrite ions was essential. The peaks associated with the NRR, and nitrite reduction reaction (NiRR) are compared in Figure 3. Three peaks (E1, E2 and E4) were found for NiRR (blue curve) at potential -0.1 V, -0.65 and -1.22 V, while four peaks were obtained for NRR (red curve) at potential -0.1 V, -0.65, -0.86 V, and -1.26 V. The peak that occurred at potential -0.86 V was not seen for NiRR, so it can be suggested that this peak was produced during the formation of the nitrite ion from the nitrate ion by two-electron transfers, as per the following equation 3 [40].

Peak potential at about -0.86 V (for the nitrite formation as proposed) is not significantly changed from nitrate to nitrate-nitrite mixture. Peak current is slightly reduced at this potential as the concentration of the nitrate solution is reduced because nitrite is also added to the medium which contains nitrate. This also gives clear evidence that the peak at -0.86 V was due to nitrate-to-nitrite formation.
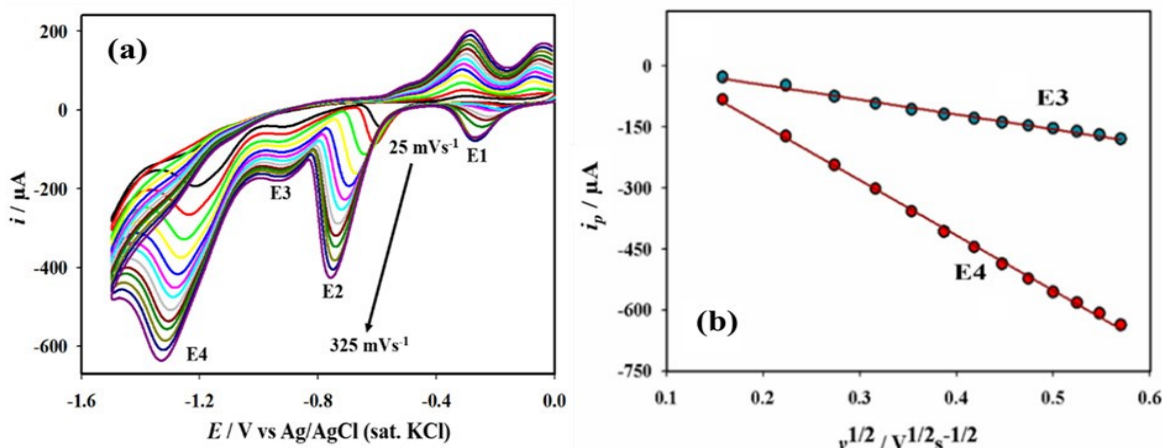
$$NO_{3ads}^- + H_2O_{ads} + 2e^- \rightarrow NO_{2ads}^- + 2OH_{ads}^- \qquad (3)$$
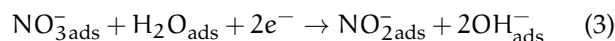
Fig 4. (a) CVs (forward) recorded at the Cu/Au electrode in 0.1 M KCl solution containing 56.6 μM NO_3^- at scan rates of 25 to 325 mV
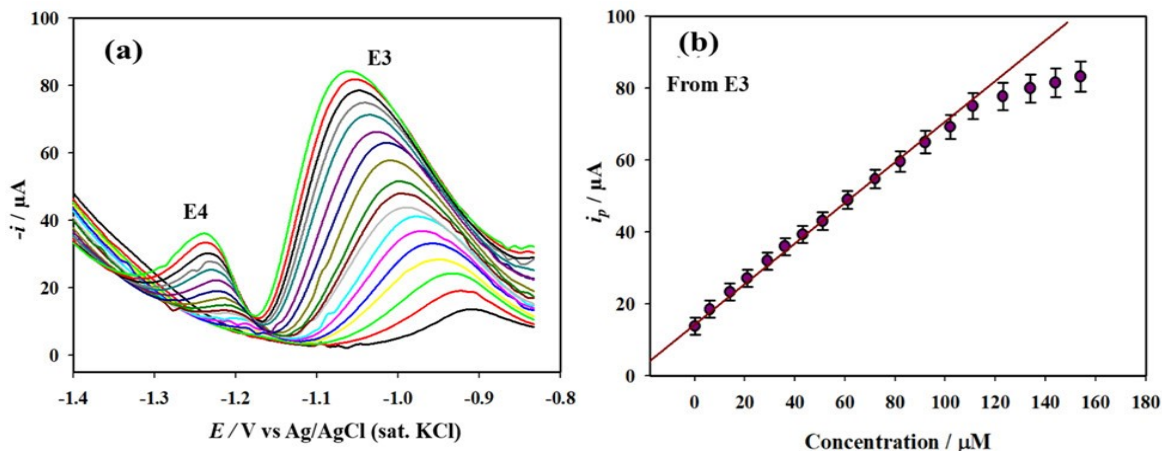

Fig 5. DPVs of nitrate ion detection in neutral medium using the Au/Cu electrode. (a) Current variation at different concentrations of NO_3^- ion (b) Peak current versus concentration plot.

3.4 NRR Kinetics

To study the electrochemical reduction process, the scan rate effect is an important factor. The dependency of peak current on scan rate is often used to estimate the number of electron transfers. The cathodic peak current, ip shows an increasing trend with increasing scan rate according to equation 4. As the scan rate is increased, the thickness of the diffusion layer is decreased. That's why peak current was increased with the increase in scan rate.

$$I_p = -2.99 \times 10^5 n \alpha_c^{1/2} A D_o^{1/2} \nu^{1/2} C \quad (4)$$

Where "C" is the concentration of nitrate in bulk (mol cm^{-3}), n is the number of electron transfers, α_c is the transfer coefficient, "A" is the geometric surface area of the electrode (0.0314 cm^2), Do is the diffusion coefficient (2.0 ×10-5 cm^2 s^{-1}) [27] and ν is the scan rate (0.1 Vs^{-1}).

Figure 4 shows the CVs of 56.6 μM NO_3^- solution in 0.1 M KCl supporting electrolytes at various scan rates (v) from 25 to 325 mVs^{-1}. Here two peaks are associated with nitrate reduction at different potential ranges denoted by E3 and E4.

In Figure 4, the cathodic peak currents were plotted as a function of $\nu^{1/2}$ for E3. According to equation 4, the peak currents neatly fall on a line that passes through the origin (R^2 = 0.9981 for E3), indicating that the NRR process was controlled by the mass transfer rate, i.e., this reaction is diffusion-controlled [44]. Cu/Au electrode is very much active for nitrate reduction reaction, so the reduction current does not depend anymore on the electrode characteristics, just depends on the number of nitrate ions or how fast those molecules are diffusing to the electrode surface. From the slope of the I_p versus $\nu^{1/2}$ for the E3 peak, the number of heterogeneous electron transfers (n) was

Table 1. Comparison of sensor effectiveness for nitrate ion detection at different electrodes

Electrode	Technique/Method	LDR (μM)	LOD (μM)	Ref.
(OD) Pt – Cu	DPV	120-990	0.159	[40]
PdNCs-PPy	DPV	0.453-1.511	0.453	[41]
Cu/Au	DPV	20-800	0.52	[42]
Cu BDD	LSV	10 - 100	1.5	[43]
Cu/Au	DPV	1.2 – 111.4	0.85	This work

determined as 2 means that the probable NRR followed by equation 4 (Figure 4). For the E4, the cathodic peak currents were plotted against $v^{1/2}$. In the case of E4, the peak currents neatly follow a straight line that passes through the origin (R^2 = 0.9949). The graph's estimated heterogeneous electron transfer (n) value of 5.9 indicated that the formerly produced nitrite (related to E3) was reduced to ammonia as per the following equation 5 [40].

$$NO_{2\,ads}^- + 5H_2O_{ads} + 6e^- \rightarrow NH_{3,ads} + 7OH^-_{ad} \quad (5)$$
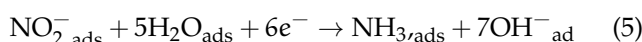
Meanwhile, the value of α_c for E3 was calculated from $E_p - E_{\frac{p}{2}}$, where $E_{\frac{p}{2}}$ is the potential when the current is half of its peak value and E_p is the peak potential through equation 6 [45].

$$\alpha = \frac{1.86\ RT}{F|E_p - E_{\frac{p}{2}}|} \quad (6)$$

From equation 6, the transfer coefficient (α_c) was calculated at 0.55. This result assumes that over the Cu/Au surface, electron transfer and N-O bond breaking at E3 took place consecutively.

4   Nitrate detection

4.1   Sensing performance determined by DPV

We employed the differential pulse voltammograms (DPV) of nitrate ions employing an Au/Cu electrode as shown in figure 5 to develop an effective sensor for the measurement of the nitrate ion (NO_3^-) in water. DPVs with varying nitrate contents between 1.2 and 154.6 μM were observed. For nitrate concentrations ranging from 1.2 to 111.4 μM, the Au/Cu electrode displayed a linear relationship (r2 = 0.9987). The sensitivity value, 3.2518 $\mu A\mu M^{-1} cm^{-2}$, was determined from Figure 5 and is superior to the previously published values, which are displayed in Table 1. The LOD of nitrate by the reduction of nitrate at the Au/Cu electrode was calculated as 0.1 nM using equation 7.

$$LOD = \frac{3 \times SD}{SR} \quad (7)$$

Where SR and SD represent the slope of the regression line and standard deviation, respectively.

The suggested sensor performs well in terms of LOD, sensitivity, and LDR. The Cu/Au sensor's overall performance is significantly better than a few of the prior articles about nitrate sensors, as shown in Table 1 [40]–[43].
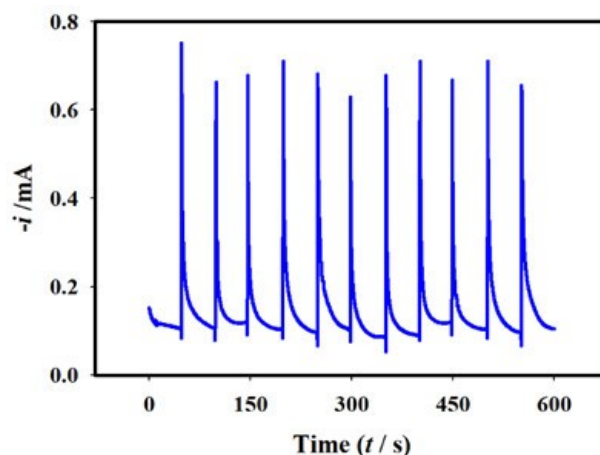

Fig 6. Reproducibility test of the modified Cu/Au electrode. The chronoamperogram was generated by repeatedly injecting 50 μL of 0.01 M $NaNO_3$ into the Cu/Au electrode surface at the operating potential of -0.86 V.

4.2   Stability of Cu/Au electrode

To evaluate the stability of the electrode surface, batch injection analysis (BIA) was utilized.

An electrolysis area arises when the sample is delivered on the electrode surface, this area readily disappears through repeated conveyance and carefully managed dispersion. The result of keeping the electrode's working potential constant throughout time is a momentary peak-shaped response that quickly returns to the baseline level as a result of the diffusing out process. As a result, a stable electrode will produce peaks with the neutral solution that have comparable spikes over time if any electroactive chemical is put onto the electrode's surface.

Table 2. . NO_3^- determination in actual samples utilizing the electrochemical method at the Cu/Au surface.

Samples	Added (μM)	Obtained[a] (μM)	RSD[b] (%)	Recovery[c] (%)
Firm-land water	74.20	75.10	3.05	101.2
Tap-water	76.20	76.40	2.84	100.3
Power plant water[d]	76.30	75.80	3.40	99.3

[a] *Average of the three repeated measurements*(S/N = 3) *at Cu/Au.*
[b] *RSD value represents the precision of three consecutive measurements.*
[c] *(Conc. of nitrate ion measured / Conc. of nitrate ion taken) × 100%.*
[d] *Power-plant water: Collected from the Energy Prima Limited (50 MW rental Power Plant), Kumargaon, Sylhet, Bangladesh.*

The chronoamperogram (i-t curve) in Fig. 6 was created by continuously infusing 50 μL of 0.01 M KCl onto the Cu/Au electrode surface for 600 s. The redesigned Cu/Au surface was stable in detecting nitrate ions in a neutral medium because the signals' heights were stable during the experiment. The same procedure was done with the same electrode the next day, and similar results were seen. The recommended electrode was therefore appropriate for a 10-minute NRR experiment in a neutral medium. It may be used as a nitrate ion sensor for routine detection, with the amplitude of the peaks equal to the nitrate concentration.

4.3 Interferences at Cu/Au electrode

The batch injection approach was used to assess the interference from the intended sensor using a homemade batch cell in chronoamperometric mode. The analysis took place for 600 s while the electrode's working potential was held at -0.86 V in 0.1 M KCl. An unflagging baseline current was ensured before the nitrate ion injection. Another 50 μL of 0.1 M nitrate was injected, and the current response for the Cu/Au electrode dramatically decreased from the baseline. Later, the same amounts of multiple analytes, such as urea, NO_2^-, NH_3, and PO_4^{3-} were injected over some time, with no significant current signal appearing (Fig. 7). Our results guarantee that this electrochemical sensor can be used to estimate nitrate in real samples.

4.4 Nitrate ion determination in real samples

To test the reliability of the proposed sensor for the analysis of real samples, nitrate ion concentration in real samples was measured using a Cu/Au electrode using the standard addition method. Water samples from the firm land, power plant and tap were gathered for the genuine sample analysis. The same method was used three times to analyze each sample.
The outcomes are listed in Table 2. The proposed Cu/Au electrochemical sensor's reliability and effectiveness are
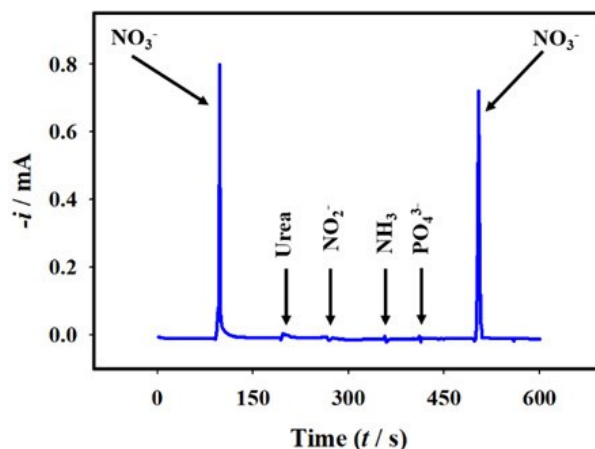

Fig 7. Investigation of species-specific interferences at the Cu/Au electrode at -0.86 V Working potential with injecting the analytes at 0.1 M KCl.

shown by the high nitrate ion recovery (99.3–101.2%), which highlights the sensor's efficiency.

5 Conclusion

The nitrate reduction was conducted using the simple, straightforward, and cost-effective method by using the Cu/Au electrode at room temperature. The electrokinetic analysis revealed that the NRR on the Cu/Au electrode includes a two-electron transfer process and occurs according to the standard NRR mechanism. This Cu/Au electrode was employed as a nitrate sensor for the first time in a neutral media. CV and DPV methods were used in the analysis in the neutral medium under an inert environment to avoid the influence from oxides or oxygen. The parameters of the sensor were studied carefully in terms of chronoamperogram, LOD, LDR, and sensitivity. This comprehensive approach provides a well-planned and reliable path to effective nitrate sensor development.

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