Article

A nano-sensor for copper oxide was manufactured and developed using a new organic precipitant via green chemistry methods

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Abstract: Green chemistry methods were applied to fabricate a nanoelectrode to capture copper ions for the first time using the new organic reagent (4-(3-(2-(3-nitrophenyl)-4,7-dioxo-1,3-oxazepin-3(2H, 4H, (7H)- yl) thioureido. The ionic double was prepared to manufacture the new copper oxide nanoelectrode from the reaction of the new organic reagent and used as an organic precipitant with CuO-NP nanoparticles prepared from cinnamon extract using the simple green aqueous method. Several techniques were used (XRD, FTIR, SEM) to characterize these particles. This electrode shows excellent selectivity and sensitivity with a linear range of 10^{-3} -10^{-13} M, correlation coefficient of 0.9998, electrode life of 77 days, ideal temperatures of 30 °C and range Optimum pH 3-9, a slope of 11.082 mV/decade, limit of detection 9.79×10^{-13} M. The average crystal size measured by the XRD device was 25nm. The particles were seen by SEM as spherical. Or almost spherical. UV-visible spectroscopy, the peak was at a wavelength of 798 nm. This confirms that nanoparticles have been obtained for Copper material. Functional aggregates were determined by FTIR measurement. Recovery value of 101.1 %. This method was successfully applied to estimate copper ions in polluted water.

Keywords: Copper oxide nanoparticles; Ion-selective; Green synthesis; cinnamon extract.

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1. Introduction

Nanotechnology involves manufacturing materials with nanometer sizes from 1 to 100 nanometers, as their small size, chemical composition, and surface structure are what give nanoparticles their unique features. In recent years, there has become a connection between nanoscience and green chemistry, which is the ideal way to reduce the negative effects of the production and application of nanomaterials while reducing the risks of problems associated with other methods, as the green construction of nanomaterials is considered the preferred approach because it is safe and environmentally friendly [1]. The application of green chemistry in the field of nanotechnology has included plant extracts and biomolecular products such as nucleic acids or proteins, carbohydrates, lipids, and peptides as well. Green chemistry is defined as methods of preventing pollution with the help of chemicals used in specific fields such as environmentally friendly analytical chemistry, and clean and green analytical methodologies. Therefore, green synthesis is considered a viable method for preparing nanoparticles because it is biocompatible and environmentally safe [2,3]. Green chemistry has been applied to produce nanoscale elemental copper. Since copper is considered one of the most abundant elements in nature, it conducts electricity and heat well and has a high corrosion resistance. It is also flexible, so it is used in the manufacture of jewelry, coins, and weapons [4,5]. Metal nanoparticles are a new type of material that has wide applications in medicine, pharmacy, agriculture, and using biological, chemical, and physical methods (6). Copper oxide is considered a semiconductor and has received great interest due to its unique and distinctive electrical, optical, physical, and magnetic properties. Thus, it has been widely used for various purposes such as catalysis and sensors. Thus, these properties can be developed through the synthesis of nano-sized CuO particles to obtain better performance when used. Comparing them to their bulk counterparts. The physicochemical and multifunctional features, large surface area, strong binding properties, and great photoelectric stability of copper oxide nanoparticles (CuONPs) have been used in several analytical techniques, such as electrochemical sensors, medical and pharmaceutical applications, and drug delivery systems. The diverse structure and size of CuONPs provide great efficiency for constructing diverse catalytic sensing systems. These systems offer features of selectivity and sensitivity such as low detection limits, wide concentration ranges, high recovery ratio, and high speed [7,8] Ion-selective electrodes can be described as electroanalytical sensors that can respond selectively to the patterns to be analyzed through chemical reactions [9] if they are characterized by high sensitivity, simplicity and speed. The study aimed to manufacture a copper oxide nano electrode using cinnamon extract with a new organic reagent used as an organic precipitant.

2. Materials and Methods

2.1. Instrumentations

The following instruments were used: pH/mV meter (3310 Jenway); reference calomel electrode (ORION, model 90-01); PVC tubing; Graphite electrode taken from (Battery Mercury Free 777); balance (Balance kern ABS 120-4N); magnetic stirrer with hotplate (HPM-10); drying oven (BINDER); test sieve analysensieb (Hanna Germany)

2.2. Reagents and solutions

Copper (II) sulfate pentahydrate ($CuSO_4$. $5H_2O$), Sodium hydroxide (NaOH), Hydrochloric acid (HCl), Dibutyl phthalate (DBP), polyvinyl chloride (PVC), tetrahydrofuran (THF), Acetone, Dimethyl Sulfoxide, 4-(3-(2-(3-nitrophenyl)-4,7-dioxo-1,3-oxazepin-3(2H, 4H,7H)- yl) thioureido) benzenesulfonamide (We referred to it in this research as a reagent).

2.2.1. Preparation of cinnamon sticks Extract

Weigh 3 grams of the cinnamon sticks into a fine powder, wash and dry them in a convection oven at a temperature of 60 place them in a glass beaker. Add 200 ml of deionized water while continuously stirring using a magnetic stirrer. Heat the mixture to boiling at a temperature of 60 degrees Celsius for 45 minutes. Allow it to cool to room temperature. Filter the cooled mixture through a 0.22-micron filter to obtain a clear cinnamon stick extract.

2.2.2. Sodium Hydroxide Solution 0.1M

To prepare the solution, 0.4 grams of sodium hydroxide were dissolved in a suitable volume of distilled water. The volume was then completed to the mark in a volumetric vial with a capacity of 100 ml.

2.2.3. 1,3-Oxazepine-4,7-dione derivatives Solution 0.01M

To prepare the solution, 0.3794 grams of 1,3-oxazepam-3 (2H, 4H, (7H)- yl) were dissolved in a suitable volume of dimethyl sulfoxide. The volume was then completed to the mark in a volumetric vial with a capacity of 100 ml.

2.2.4. Preparation of copper oxide Nanoparticle CuO-NPS

Take 20 ml of pentahydrate copper sulfate salt, of which 0.1 molar was prepared in deionized water, and place it on the convector while stirring until the temperature of 60 degrees Celsius is reached. After that, we add 20 ml of the plant extract in droplets with continuous stirring, and then we add drops of 0.1 molar sodium hydroxide until the pH = 12 is reached, where we notice the color of the solution changing from blue to green, indicating the formation of copper oxide particles, which were later identified, and the solution is kept. After filtration by a Millipore filter with a diameter of 0.22 micrometers, it is used to form a copper oxide nanocomplex with the reagent.

2.2.5. Preparation of Precipitate Nano complex R_CuONPS Used in Electrode Manufacturing

mix 10 ml of copper oxide nanoparticles solution with 10 ml of reagent which was with continuous stirring for an hour, after which we begin the precipitate that forms are filtered, dried, and the required measurements are made. We use this precipitate to manufacture a copper oxide nanoelectrode.

2.2.6. Manufacturing the Nanoparticle R- CuO-NPS Electrode

1- We weigh 0.19 grams of PVC and dissolve it in a mixture of 5 ml of THF and 5 ml of acetone.

2- Add 0.05 grams of the precipitate that formed between the nano-copper oxide and the detector (the nano-copper oxide complex) with continuous stirring until complete dissolution.

3- Add 0.45 ml of dibutyl phthalate to the mixture and stir until the electrode membrane solution is ready.

4- We paint the prepared graphite electrode by immersing it several times in the above membrane solution until the membrane layer is on the electrode and leaving it until it dries.

5- After the membrane dries, we immerse the electrode in a 0.001 molar solution of aqueous copper sulfate for a full day so that the electrode is ready for study and application. Figure 1 shows a picture of the manufactured electrode.

a_Cinnamon powder

b_Cinnamon extract

c_Cu $(SO_4)_2.5H_2O$

d_CuO-NPS

d_R-CuO-NPS (solution)

e- R-CuO-NPS (powder)

f- R-CuO-NPS electrode

g- Measurement

Figure 1. Preparation of the nano substance and electrode construction.

2.3. Characterization of CuONPs and R-CuONPs

2.3.1. X-ray diffraction (XRD) of CuONPs and R-CuONPs nanoparticles

The XRD exam was carried out to determine the structure type of prepared copper oxide nanoparticles (CuO NPs) using the green synthesis method [10]. Figure 2(a, b) shows the XRD patterns of prepared copper oxide nanoparticles (CuO NPs). From figure 2(a), the characteristic peaks of prepared CuO nanoparticles without reagent (marked with black stars) observed at (2Ɵ = 32.69°) of plane (110) with d-spacing (2.7371 A°), (2Ɵ = 35.73°) of plane (002) with d-spacing (2.5108 A°), (2Ɵ = 38.92°) of plane (111) with d-spacing (2.3117A°), (2Ɵ = 49.06°) of plane (-202) with d-spacing (1.8553 A°), (2Ɵ = 53.71°) of plane (020) with d-spacing (1.7050 A°), (2Ɵ = 58.66 °) of plane (202) with d-spacing (1.5723 A°), (2Ɵ = 61.86 °)

of plane (-113) with d-spacing (1.4985 A°), (2Ө = 66.12 °) of plane (022) with d-spacing (1.4119 A°), (2Ө = 68.5 °) of plane (220) with d-spacing (1.3685 A°), these observed peaks corresponded to the monoclinic CuO NPs structure with space group (C12/C1 no.15), lattice parameters (a = 4.6530 A°, b = 3.4100 A°, c = 5.1080 A°) and (α = γ = 90^{o}, β = 90.48^{o}) which well matched with the standard data (JCPDS 96-110-0026). Other characteristic peaks (marked with blue stars) at (2Ө = 43.31 °) of a plane (111) with d-spacing (2.0871 A°), (2Ө = 50.44 °) of plane (002) with d-spacing (1.8075 A°) and (2Ө = 74.12 °) of plane (022) with d-spacing (1.2781 A°), which attributed to the cubic Cu NPs with space group (Fm-3m no.225), lattice parameters (a = b = c = 3.6150 A°) and (α = β = γ = 90^{o}) which well agreed with the standard data (JCPDS 98-004-3493).

The results referred to good crystallinity of prepared copper oxides (CuO NPs) and copper (Cu NPs). The XRD results revealed that the addition of reagent led to a decrease in the intensity of CuO NPs and Cu NPs peaks as shown in figure 1(b), and remained in the same crystal structures, which indicates the different degrees of crystallinity of CuO NPs and Cu NPs, where obtained less crystallinity degree of CuO NPs and Cu NPs in the presence of reagent. On the other hand, observed that other undefined diffraction peaks cannot be attributed to any copper-based compound and were considered as impurities.

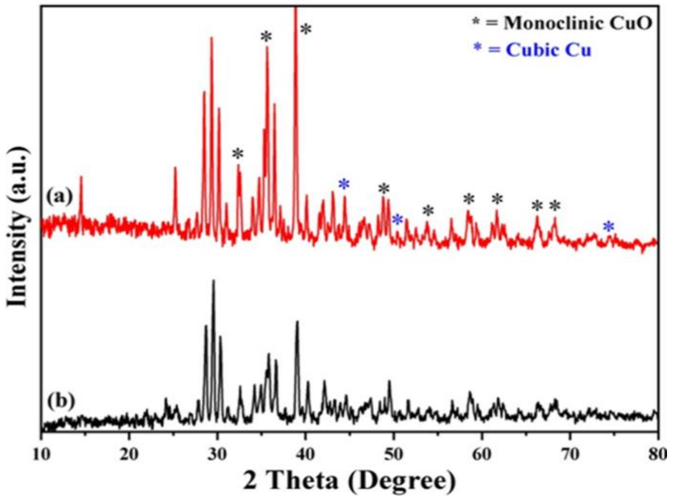

Figure 2. XRD patterns of prepared copper nanoparticles (a) without reagent and (b) with reagent.

2.3.2. Scanning Electron Microscopy (SEM) Measurements of Nanoparticles.

Scanning electron microscopy (SEM) has been done to study the surface morphology of prepared samples using scanning electron microscopy type (Thermoscientific Quattro S). Figure 3 (a, b) shows the captured SEM images at two different scales 1 μm, and 200 nm of prepared copper oxide nanoparticles with and without reagent. Figure 3(a) observed that the obtained CuO nanoparticles have a rock-like shape with different dimensions and an average particle size of 200 nm, and each nanoparticle consists of an agglomeration of ultra-fine nanoparticles with an average particle size of 15 nm. The synthesized CuO NPs with reagent exhibited a semi-spherical-like shape of nanoparticles with an average particle size of 235 nm, which consists of gathered ultra-fine nanoparticles with an average size of 25 nm, as shown in Figure 3(b). The SEM results proved that the synthesis method with reagent affects the shape and dimensions of the copper oxide nanoparticles CuO NPs, where each of them is distinguished by different shapes, widths, and lengths [11].

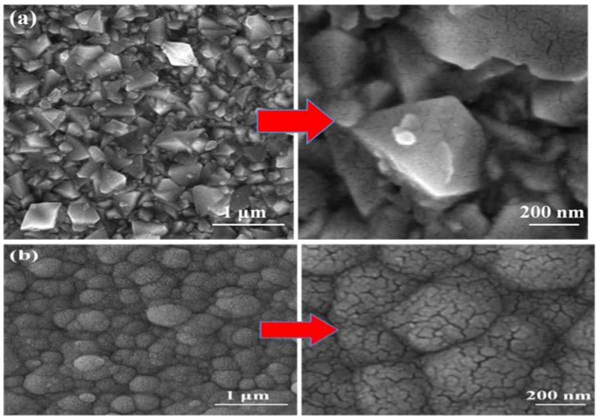

Figure 3. SEM images of prepared copper oxide nanoparticles (a) without reagent and (b) with reagent.

by using UV-visible spectroscopy, the peak was at a wavelength of 798 nm. This confirms that nanoparticles have been obtained for Copper material. As shown in figure (4).

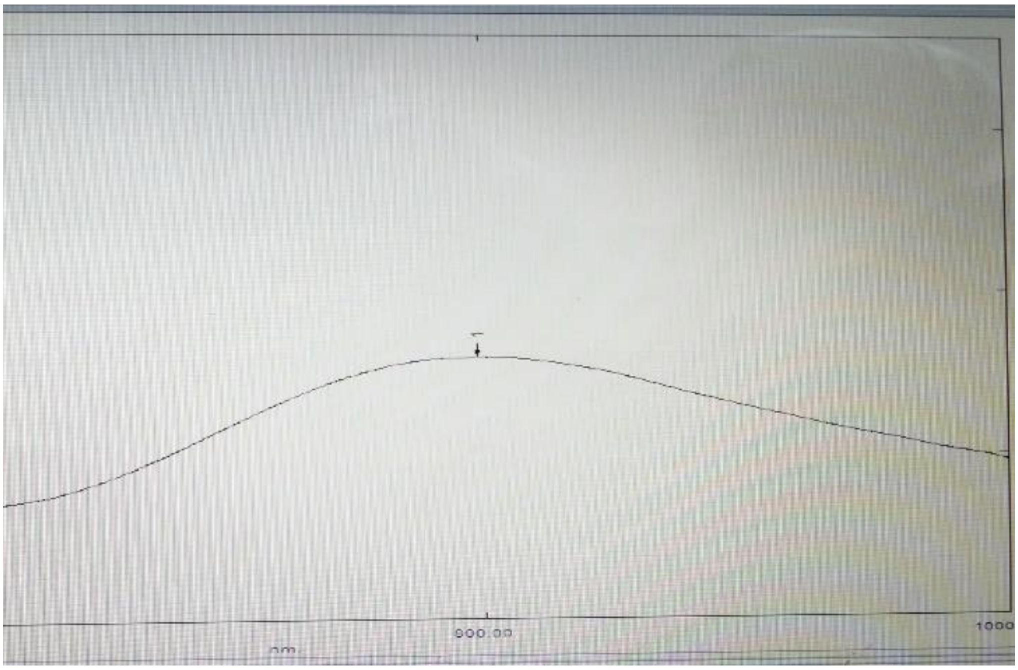

Figure 4. UV-Visible spectroscopy.

3. Results

3.1. Studying the Properties of the Manufactured Nano (R- CuONPs) Electrode

After selecting the optimal conditions for Nanosensor fabrication, the minimum sensitivity and the minimum non-Nernstian response were calculated using the stress method. This was achieved by measuring the voltage rate for each concentration three times compared to the reference electrode at pH 6 and a temperature of 30 degrees Celsius. Additionally, the response time of the manufactured Nano sensor was studied for the samples.

3.2 Effect of pH

The effect of the acid function on the electrode voltage was studied using solutions of sodium hydroxide and hydrochloric acid at a concentration of 0.1 molar and within the ranges 1-12. The voltage was measured for two salt concentrations, namely $10^{-3}$and $10^{-5}$the results were as in Table 1.

Table 1. Effect of pH.

pH	E(mv) for (10^{-3})	E(mv) for (10^{-5})
1	4	-10
2	-1	-12
3	-4	-20
4	-5	-21
5	-6	-23
6	-7	-25
7	-8	-26
8	-9	-28
9	-11	-30
10	-16	-37
11	-23	-42
12	-30	-50

The best stability of the voltage was at the values of the acid function (3-9).

3.3 Temperature effect

After studying the effect of the acid function, the effect of temperature was studied within the ranges 15-60 $\overset{o}{C}$, where two different concentrations of salt were taken 10^{-3} and 10^{-5}, and the results were as shown in Table 2.

Table 2. Effect of temperature.

Temperature (^{o}C)	E(mv) for (10^{-3})	E(mv) for (10^{-5})
15	-2	-10
20	-6	-15
25	-7	-17
30	-8	-18
35	-9	-19
40	-11	-21
45	-13	-22
50	-14	-23
55	-22	-30
60	-30	-40

The results showed that the best stability of the voltage is from 20 to 45 degrees, and at temperatures higher than 50, the electrode voltage He is greatly affected.

3.4 Response Time

After the ideal acid function and temperature conditions were established, a study was conducted on the electrode's response time. Standard concentrations of salt were taken, ranging from 10^{-2} to 10^{-13}, and the voltage was measured for each concentration, and the response time was determined in seconds, as shown in Table 3.

Table 3. Electrode response time.

Concentration(M)	E(mv)	Response Time(S)
10^{-1}	28	1
10^{-2}	12	2
10^{-3}	-1	3
10^{-4}	-`12	5
10^{-5}	-23	7
10^{-6}	-35	8
10^{-7}	-49	9
10^{-8}	-58	11
10^{-9}	-68	14
10^{-10}	-80	17
10^{-11}	-91	20
10^{-12}	-103	29
10^{-13}	-114	37

noted that the response time is inversely proportional to the concentration, as the response time ranged between 2 and 37 seconds, Table 4.

Table 4. Summary of ideal electrode conditions.

Effect of PH	3-9
Temperature effect ^{o}C	20-45
Electrode response time(second)	2-37

3.5. Calibration Curve

After testing the manufactured Nano electrode, a series of different concentrations of copper ion solution was prepared and measured under the selected optimal conditions. A calibration curve was plotted, representing the relationship between voltage change (mv) and concentration change (expressed –log [ion]), as shown in Figure (5).

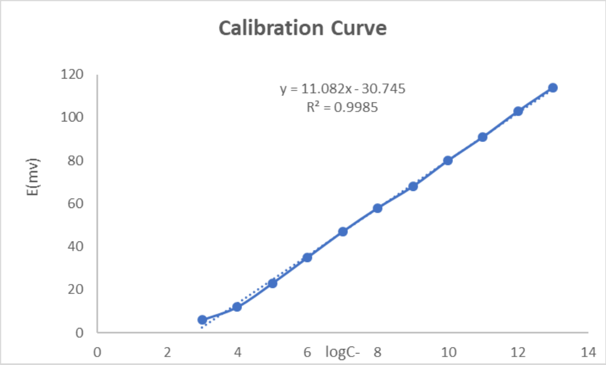

Figure 5. Standard calibration curve for the electrode.

3.6. Accuracy and Precision

The accuracy and precision of the method were calculated by taking the concentrations of the calibration curve 10^{-3}-10^{-13} and the voltage of each of these concentrations was recorded six times. This was after setting the optimum conditions for the electrode, and the results were as in Table 5.

Table 5. Accuracy and precision.

Conc. Taken (mole/L)	Conc. Found (mole/L)	Rec%	RSD%
1×10^{-4}	0.964×10^{-4}	96.42	0.26
1×10^{-6}	0.988×10^{-6}	98.8	0.46
1×10^{-8}	1.001×10^{-8}	100.1	0.65

3.7. The life of the electrode

The life of the electrode was estimated by recording the voltage of the salt with a 1×10^{-5} molar concentration. The voltage was recorded every two days and through measurement, it was found that the voltage was stable and consistent for 77 days as shown in Figure 6.

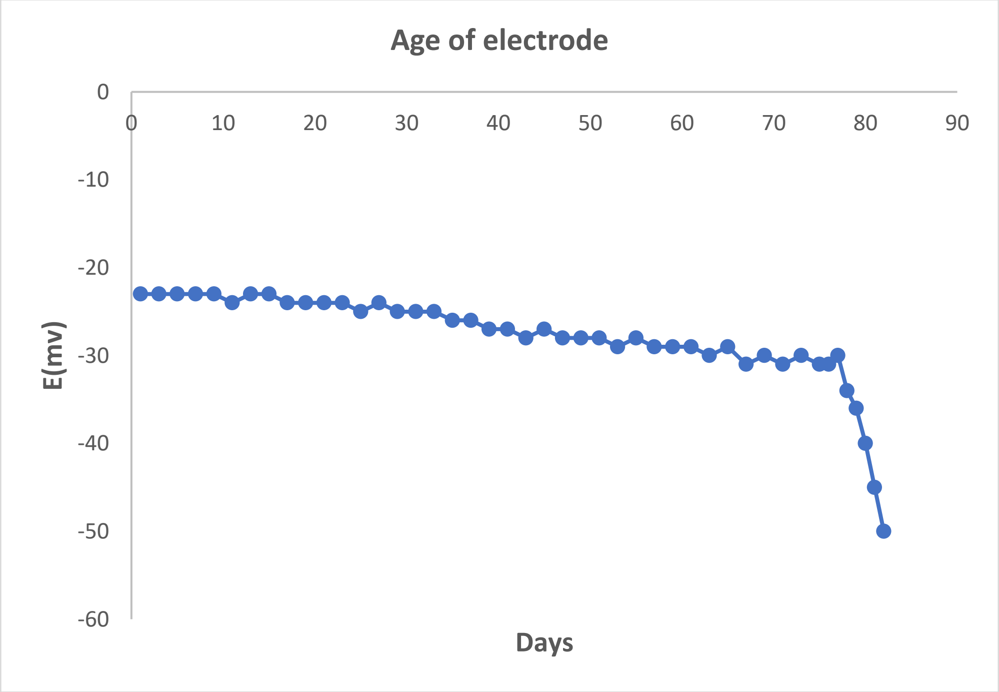

Figure 6. The life of the electrode.

3.8. Selectivity

The selectivity of the electrode means its ability to distinguish the ion itself from other ions. The effect of the interfering ions was studied using a mixed solution method by adding different concentrations of the interfering ion to the aqueous copper sulfate salt at a concentration (1×10^{-5}), and the selectivity coefficient was found according to the equation 12 below:

$$\log K_{A,B}^{pot} = \frac{E2-E1}{S} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where $K_{A,B}^{pot}$ is the selectivity coefficient (Table 6), E1 is an Ion potential alone, and E2 is an Ion potential with the interfering ion.

Table 6. Selectivity coefficient values.

K_{AB}^{pot} Selectivity coefficient values	Interference ion concentration	Type of interference ion
0.671	1×10^{-3}	Pb^{+2}
0.81	1×10^{-5}	

0.55	1×10^{-3}	Cl^{-1}
0.817	1×10^{-5}	
0.627	1×10^{-3}	Fe^{+2}
0.781	1×10^{-5}	
0.55	1×10^{-3}	Cd^{+2}
0.871	1×10^{-5}	
0.761	1×10^{-3}	Al^{+3}
0.8832	1×10^{-5}	

3.9 Limit of detection.

The limit of detection (LOD) was calculated by theoretical calculations from the straight-line equation, and the limit of detection value was 9.79×10^{-13} molar.

3.10 Applications.

The direct method was applied to the pole, where water samples were collected from different areas distributed between (Baiji Refinery, Al-Qaim Cement Factory, and the water of the Degla River in Tikrit). Where 10 ml of each sample was taken, and the copper oxide nanoelectrode was immersed directly in it, the voltage for each sample was calculated and from there according to the concentration theoretically and practically, as was done in the calibration curve as in Table 7. The summary of the method is shown in Table 8.

Table 7. Taken and found concentrations.

Sample region	Taken	Found concentration(M)	Rec%	RSD%
Baiji Refinery	1×10^{-2}	1.015×10^{-2}	101.5	0.28
Al-Qaim Cement Factory	1×10^{-3}	1.001×10^{-3}	100.1	0.22
Degla River in Tikrit	1×10^{-6}	0.998×10^{-6}	99.8	0.43

Table 8. Summary of method.

Parameter	Values for electrode R-CUO-NPS
Linear range of concentration (molar)	1×10^{-3} - 1×10^{-13}
slope	11.082
Intercept	-30.745
Correlation Coefficient	0.9985
limit of detection (LOD)	(9.79×10^{-13}) molar
Rec%	101.1 – 96.42
RSD%	0.26 - 0.65
Selectivity coefficient	0.55 – 0.8832
life of the electrode	(77) day

4. Conclusions

This study highlights the successful application of green chemistry methods in the synthesis and utilization of nanosized copper oxide for the development of a highly sensitive and selective electrode.

1- Green chemistry methods have been applied in the production of nanosized copper oxide with crystal sizes of 25nm, as these methods are environmentally friendly and inexpensive and use available plant extracts.

2- The nanoparticles were mixed with the reagent, which increased the deposition process and formed a complex with the nanoparticles of copper oxide, and thus this complex was used in the manufacture of the electrode.

3-The method gave excellent detection limits up to 9.79×10^{-13} M.

4-A quick response method, as the response time was good and ranged between 2-37 seconds.

5- A method with high selectivity for copper ions, where the selectivity coefficient values ranged between 0.55 - 0.8832.

6- This electrode shows excellent selectivity and sensitivity with a linear range of 10^{-3} -10^{-13} M, correlation coefficient of 0.9985, electrode life of 77 days, ideal temperatures of 30 °C and range Optimum pH 3-9, slope 11.082 mV/decade.

Future research should explore the application of this green synthesis method to other metal oxides, conduct long-term stability tests under varying environmental conditions, and investigate the scalability of industrial applications. Additionally, developing similar electrodes for detecting other metal ions and integrating these electrodes into portable and real-time monitoring devices for environmental and clinical applications could further enhance the impact and utility of this technology.

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