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Novel Ion Selective Coated Electrode for the Determination of Cadmium Ions by Using Green Chemistry Method

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Abstract:

In this study, cadmium ions were estimated in a new and simple way using green chemistry method, including the construction of an ion-selective electrode of nano-coated cadmium oxide (R-CdONPs) using Leucaena Leaves extract as a nanomaterial, Several techniques (SEM, XRD) were used to characterize the characteristics their. Through the XRD technique, the size of the nanoelectrode particles was observed to be 9.57 nm, Through the SEM technique, observed good crystallinity of prepared cadmium oxides nanoparticles (CdO NPs), The particles were seen by SEM to be spherical or semi-spherical in form. The results of the observation were pH (4-6), temperature range between (15-30) C˚, and response time (2-37). Secondly,the concentration calibration curve was a linear response of 1×10-1 - 1×10-11 M with a slope of-27.336 mV/decade, correlation coefficient (0.9975), detection limit (11.67 ×10-11) M, and electrode lifespan of 61 days, and recovery percentage 99.5- 100 %. This method was applied to determine the cadmium ions in industrial water.

Keywords: *Cadmium ions, industrial water, ion selective electrode, green synthesis.*

1-Introduction: Green nanotechnology is the science that is concerned with the study and characterization of nanomaterials and the study of their physical, chemical and mechanical properties with the study of phenomena resulting from their small size, and nanotechnology includes the synthesis of materials with nanometer sizes from 1 to 100 nanometers and nanotechnology is a multidisciplinary field that includes nanoelectronics, nanomaterials and nanobiotechnology, as three areas that overlap on a large scale. Green nanotechnology is the ideal approach to reduce the negative effects of the production and application of nanomaterials while reducing the risk of problems associated with other methods, as the green construction of nanoparticles is the preferred method because it is safe and environmentally friendly (1). Anastas

was the first scientist to use the term green chemistry in 1991 (2). To avoid the use or discharge of hazardous chemicals to a large extent during the synthesis of chemical compounds. Green chemistry programs were proposed by the United States Environmental Protection Agency (EPA) in 1990.

Then in 1998, Anastas and Warner published "The Twelve Principles of Green Chemistry", which summarizes the concept of green chemistry (3). Green nanotechnology plays an important role in the design of environmentally friendly and sustainable synthesis technologies to provide safer products for human health and environments (4). Green nanotechnology using plant extracts opens up new possibilities for the formation of new nanoparticles with the desired properties for the development of biosensors, biomedicine, cosmetics, electrochemical nanotechnology, antibacterial, and electronics (5). The application of metal nanoparticles (MNPs) has attracted a lot of attention due to its introduction of significant advances, particularly in the field of medicine through the increase in the therapeutic index of drugs and through the specificity of the site that prevents resistance to multiple drugs and the efficient delivery of therapeutic agents (6). Metal nanoparticles with a high specific surface area and a large part of surface atoms have been widely studied due to their unique chemical and physical properties such as optical properties, magnetic properties, electronic properties, catalytic activity and antimicrobial activity. Recent studies have shown that specially designed nanoparticles exhibit good antibacterial activity and form antimicrobial formulations (7-9). Cadmium oxide has unique photoelectric and optical properties as well as catalytic selective properties that can be used to analyze many environmental pollutants, dyes and certain organic compounds (10-12). Cadmium oxide is used in cadmium salts and cadmium coating baths, electrodes in storage batteries, and catalytic ceramic glass. The main uses of cadmium oxide are as an ingredient for electroplating baths and dyes (13-15).

2. Apparatus and Material:

2.1. Apparatus used:

1. Oven, KAROL, Korea.
2. Balance, KERN ABS, Germany.
3. Centrifuge, PLC-03, USA.
4. UV spectrophotometer, SHIMADZU, Japan.
5. pH meter, Jenway 3310, England.
6. Calomel Electrode, Me-SC900, England.
7. Magnatic stirrer and Hote plate, FTHPM-10, Korea.
8. FTIR Instrument (Shimadzu), Japan.

2.2. Chemical Substance and Solutions:

1-Cadmium Nitrate tetrahydrate Solution 0.1 M

prepare by dissolved 3.0848 gm from material in volumetric flask 100 ml and complete the volume to the mark by deionized water.

2-Sodium Hydroxide Solution 0.1 M

prepare by dissolved 0.400 gm from material in volumetric flask 100 ml and complete the volume to the mark by deionized water.

3- Hydrochloric Acid Solution 0.1 M

prepare by transfer (0.82) ml of hydrochloric Acid solution (12.06) M to volumetric flask100 ml and complete the volume to the mark by deionized water.

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

To prepare the solution, 0.3344 grams of 1,3-oxazepin-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.

2.2.1. preparation of Leucaena Leaves extract solution and CdO nanoparticles.

Leucaena leaves were collected from the gardens of Tikrit University, and thoroughly washed and cleaned with deionized water. Leucaena leaves were left for 5 days in the laboratory room to dry, then placed in an electric oven for about 3 hours at a temperature of 50 °C until completely dried. The dry leaves of Leucaena were ground by an electric grinder until they turned into a fine powder and the fine powder was sifted with a 300 micrometer sieve to get rid of the coarse fibers. (2)grams of dried ground powder was weighed and dissolved in (200) ml of deionized water in a capacity of (500) ml and placed on a thermal heater with a magnetic stirrer and then heated the solution to 80-90 º for about 30 minutes ,then 100 ml deionized hot water was added at the same temperature to reduce the thick texture of the prepared extract. Leucaena leaves extract was placed in the burnet and a solution of aqueous cadmium nitrate tetrahydrate $Cd(NO_3)_2.4H_2O$ at a concentration of (0.1) molar in a conical flask of (100) ml on a thermal heater at a temperature of approximately 60-70 °C and was slowly added from the burnet until the solution turned reddish-brown (evidence of the formation of cadmium oxide nanoparticles (CdONPs).

2.2.2. Preparation of R-CdONPs precipitate.

The R-CdONPs precipitate was prepared by placing (30) ml of cadmium nanoparticles in a suitable baker, and (30) ml of 1,3-oxazepin-3(2H, 4H, (7H)- yl) solution was added to it at an approximate concentration of (0.01) molar and stir the mixture well, and after a while a light brown precipitate is formed in the solution and the amount of precipitate increases over time, the precipitate is left to settle and filtered using filter paper and then dried in the oven at a temperature of 90 ° C for about two hours and packed in a dry tube for characterization and use purpose.

2.2.3. Construction Ion Selective Coated Electrode:

1. dissolve (0.19) gm of PVC Powder in a mixture consists of (5) ml Tetra hydrofurane and (5) ml acetone with mixing to complete dissolving.
2. Add to the mixture (0.1) g of R-CdONPs powder with mixing.
3. Add to the mixture (0.45) ml of Di-butyl phthalate with stirrer.
4. Take the graphite Electrode from Battery Type (Battery Mercury Free 777) and clean it by immersion in Sulfuric Acid Solution some periodic time then immersion with some acetone for three hours.
5. Coating Process include immersion of graphite Electrode in Coated Solution to several times in one minute until become membrane layer homogeneous coated on graphite electrode surface and allow to be drying in in laboratory for over a night.
6. After drying coated electrode, immersion it in Cadmium Nitrate tetrahydrate Solution (10^{-3}) M for 4 hours to complete ion exchange process.Figure (1)

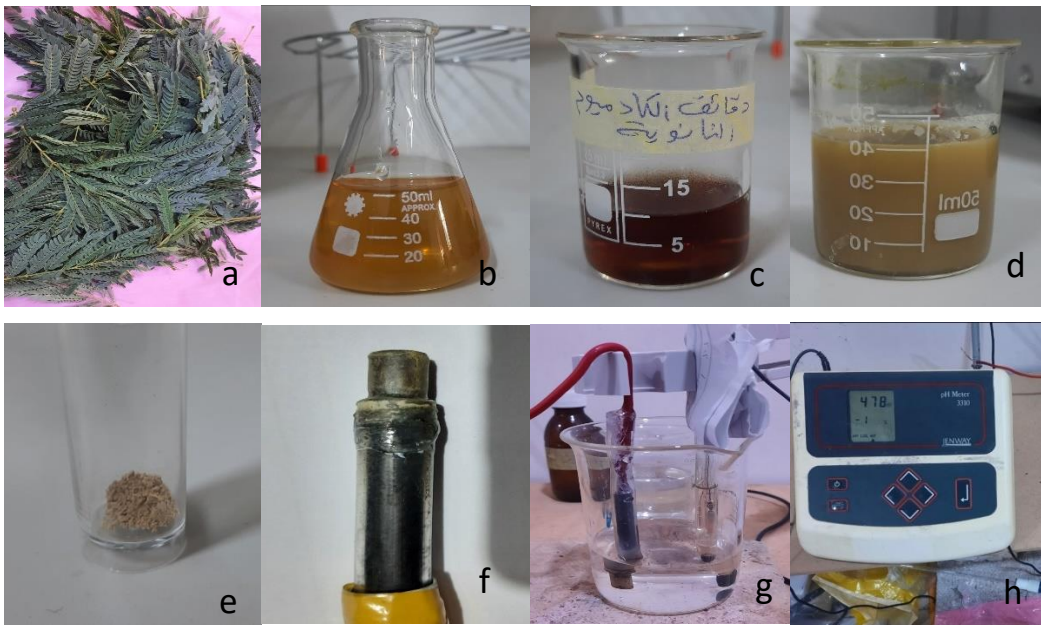


Figure: 1 The construction of R-CdONPs electrode

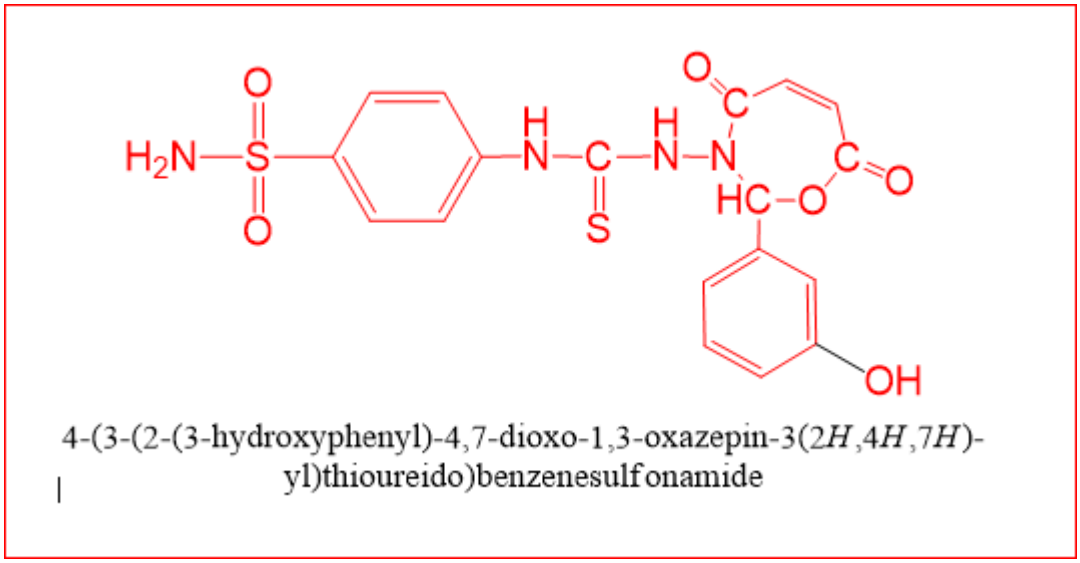
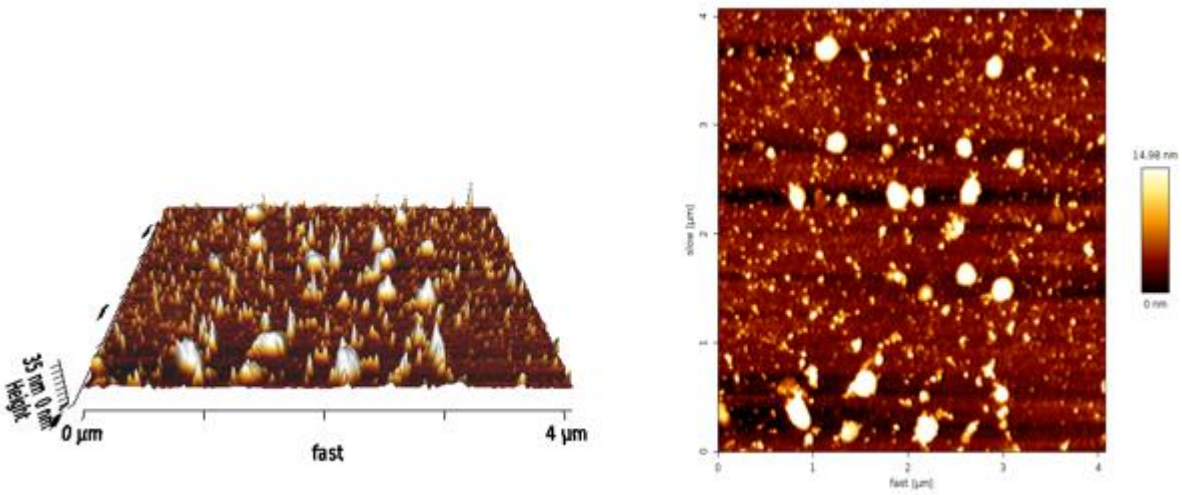


Figure: 2 The reagent used in the electrode construction

2.3. Characterization of R-CdONPs precipitate:

2.3.1. AFM spectroscopy for nanoprecipitate (R-CdONPs)

Figure (3) (A-B) shows the linear, two-dimensional and three-dimensional surveys extracted from (AFM) images of the nanoprecipitate (R-CdONPs), through these images the shape of the surface topography is illustrated where nanostructures appear in the form of prominent protrusions with the presence of scattered low areas and the total height of the surface that was recorded by (AFM) is (35nm) and the average diameter (14.98nm) and surface roughness (Ra = 1.953 nm) through this technique is close to the results of SEM and XRD technology.



(A) **(B)**

Figure 3: (A, B): AFM spectroscopy for nanoprecipitate (R-CdONPs)

2.3.2. X-ray diffraction measurements (XRD) for nanoprecipitate (R-CdONPs)

The crystal structures of the nanoprecipitate (R-CdONPs) prepared using Leucaena leaf extract were confirmed by XRD analysis as shown in Figure (2). X-ray diffraction analysis revealed characteristic beams of peaks at 2θ starting from (44.288-82.43). Table (2) shows the results of XRD for nanoprecipitate (R-CdONPs) using Leucaena leaf extract, which illustrated many parameters and structural properties of the materials such as particle size, the width of the beams at the average height and location of the peaks and distances between the crystal layers, and that D represents the particle size, and the average size of the crystals was (9.57 nm) according to the Scherrer equation (16) to calculate the size of the crystals.Figure(4).

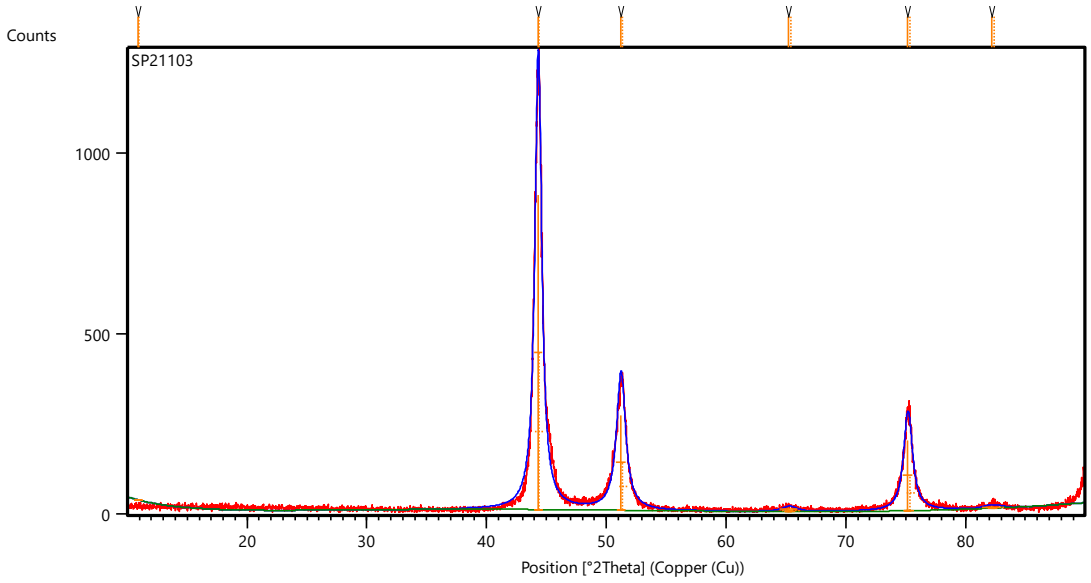


Figure 4: X-ray diffraction measurements for (R-CdONPs) precipitate

Table (1) explain XRD data for R-CdONPs precipitate

Pos. [°2Th.]	FWHM Left [°2Th.]	d-spacing	Height [cts]	Rel. Int. [%]	D nm	Average D nm
44.288	0.66	2.04360	873.29	100.00	13.58	
44.404	0.66	2.04360	437.29	50.00	13.58	
51.19	0.87	1.78300	263.23	30.13	10.58	
51.33	0.87	1.78300	132.23	15.07	10.59	
65.24	1.5	1.42889	11.1	1.21	6.57	**10.001**
65.43	1.5	1.42889	5.1	0.61	6.58	
75.14	0.82	1.26336	195.5	22.39	12.77	
75.36	0.82	1.26336	98.5	11.19	12.79	
82.18	1.7	1.17204	6.1	0.66	6.48	
82.43	1.7	1.17204	3.1	0.33	6.49	

2.3.3. SEM Microscopy of R-CdONPS prepared by plant extracts;

SEM analysis is used to determine the surface structure of reaction products during the biosynthesis of metallic NPs and shows morphological variation, Figure (5) shows SEM images of the R-CdONPs where the distribution of particles is evident during the surface area examined with an approximate force of (200 nm) where the particles appeared in a spherical or almost spherical form in the form of compact clusters with average sizes of (106.1nm), (61.41nm), (78.16nm), (50.24nm) and (44.66nm).

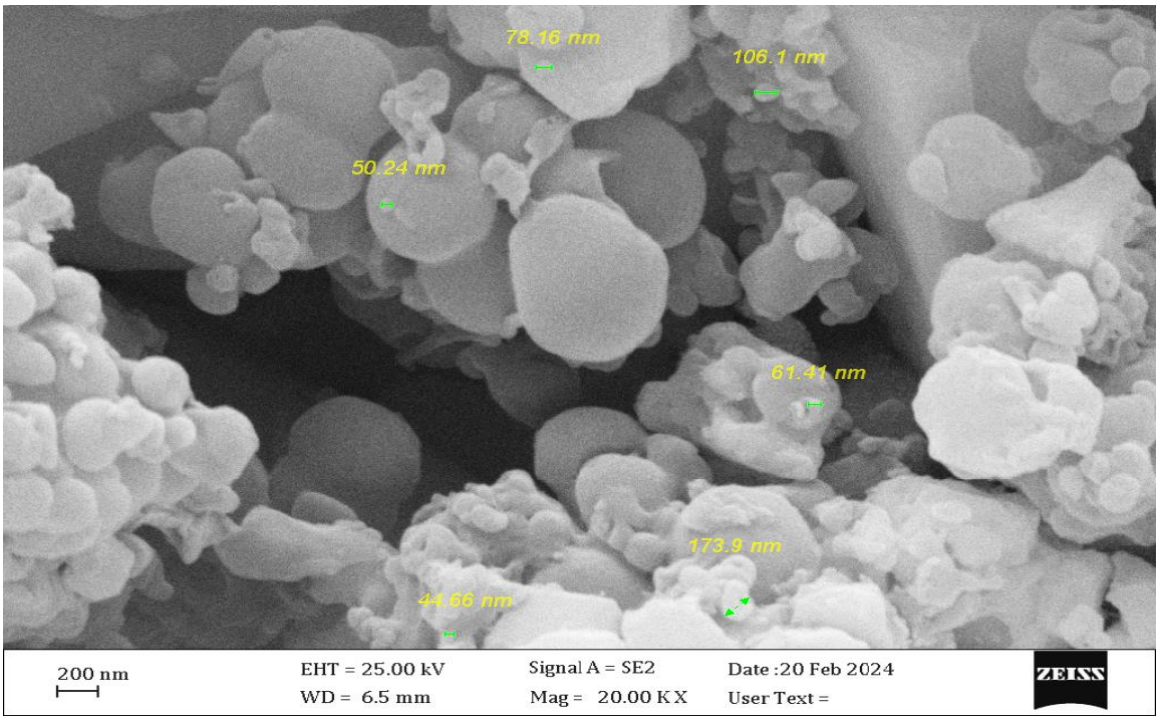


Figure: 5 SEM images of R-CdONPs used in electrode construction.

3. Result and Discussion:

3.1. Studying the ideal conditions for the manufactured electrode.

After the manufacture of R-AgONPS electrode, the properties and specifications of the manufactured nanoelectrode were studied by studying PH effect and the temperature effect as well as the determination of each of the electrode response time, range of linear concentrations, detection limit, correlation coefficient, slope value, , electrode age, accuracy and precision, selectivity and applications.

3.2. Effect of pH

The best pH range in which the coated electrode operates without affecting the voltage significantly was between (4-6), where the pH value was changed using a dilute solution of(0.1)M hydrochloric acid and(0.1)M sodium hydroxide,. Figure (6).

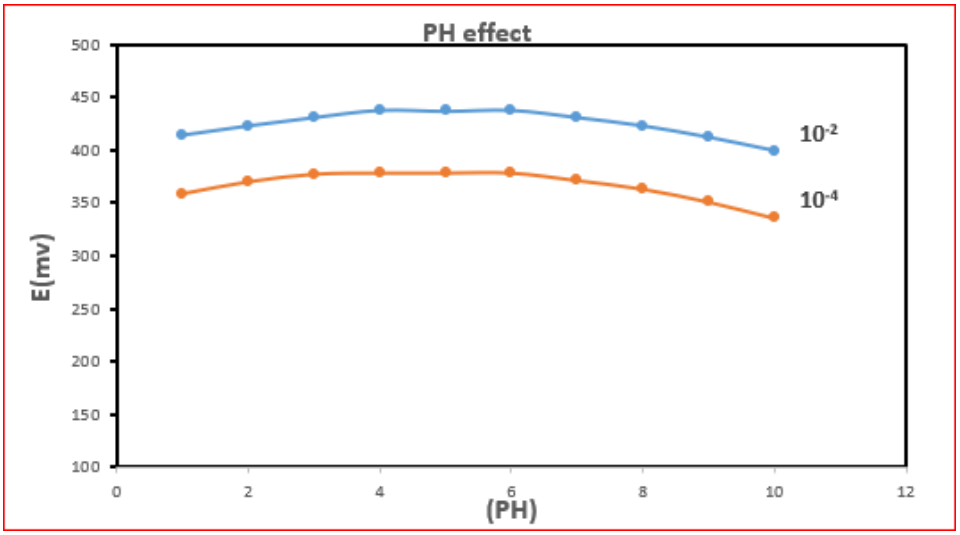


Figure: 6 pH Effect on R-CdONPs electrode

3.3. Effect of Temperature

The best range of temperature in which the coated electrode operates without significantly affecting the voltage was between (15-30) Ċ and it turns out that there is a significant reduce in the voltage difference values at higher temperatures from (30) Ċ, as shown in figure (5).

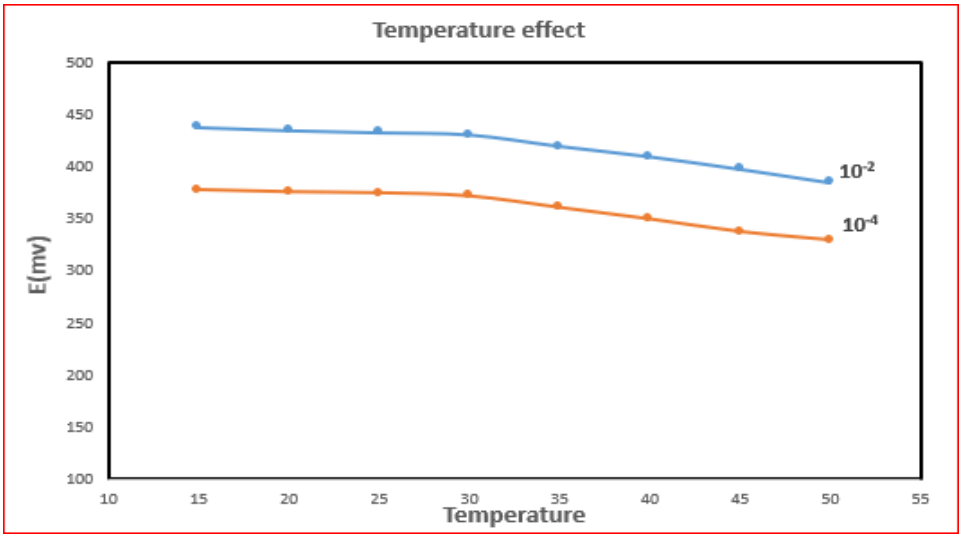


Figure: 7 Effect of Temperature on R-CdONPs electrode

3.4. Response Time

The response time of the coated electrode was studied by immersing R-CdONPs electrode with the calomel electrode in a series of standard solutions of cadmium nitrate tetrahydrate at descending concentrations starting from ($1x10^{-1}$)M and ending at ($1x10^{-10}$) M, the response time for the coated electrode ranged between (2-37) seconds, and It is noted that the response time is inversely proportional to the concentration of ions in the solution, where the high concentration of ions in the solution led to reduce the response time of the electrode, and vice versa, the low concentration of ions in the solution led to increase response time of the electrode, due to the small number of ions in the solution, so it will need a longer time to reach the equilibrium state at the electrode .as shown in figure(6).

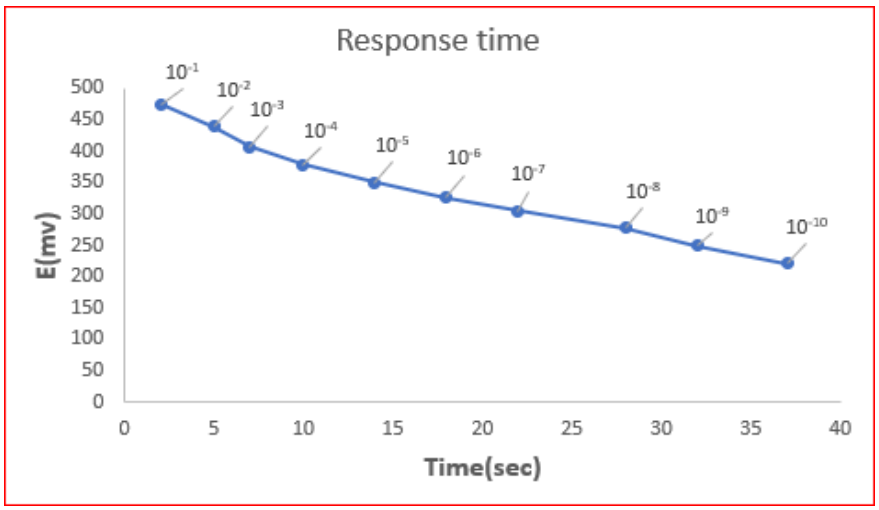


Figure: 8 Response Time for R-CdONPs electrode

Table (2) The ideal conditions for R-CdONPs electrode

Parameter	R-CdONPs electrode values
pH Effect	4-6
Temperature (C˚)	15-30
Response Time (sec)	2-37
Life Time (day)	61

3.5. Calibration Curve

After establishing the ideal conditions for the R-CdONPs from a temperature and PH effect, it was immersed with the calomel electrode in standard solutions of cadmium nitrate tetrahydrate in Baker capacity of (50) ml and descending concentrations from (1×10^{-1}) to (1×10^{-11}) molar and the potential difference was recorded six times for each concentration at temperature (25°C) and drawing the calibration curve, as shown in figure (7). The linear range of the Nernstian response was between 1×10^{-1}-$1\times10^{--11}$ molar, and the value of the correlation coefficient was 0.9975, and the slope given by the electrode was (-27.336 mv/decade), which close to the true value of the slope (29 mv/decade).

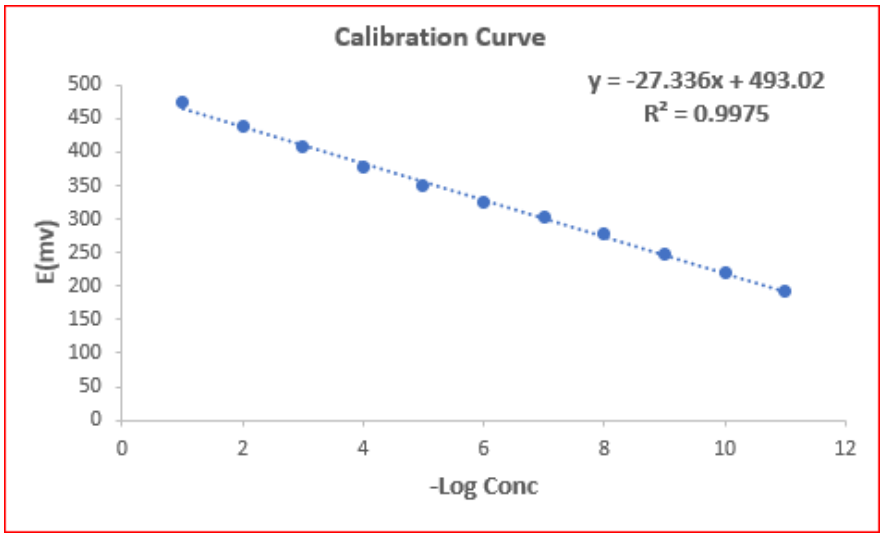


Figure: 9 Calibration Curve for R-CdONPs Electrode

Table (3) The potentiometric properties for R-CdONPs electrode

Properties	R-CdONPs electrode values
Linear range (M)	$1\times10^{-1} - 1\times10^{-11}$
Slope	-27.336
Intercept	493.02
Detection limit	11.67×10^{-11}
correlation coefficient (R^2)	0.9975

3.6. Accuracy and Precision

Accuracy and precision were studied by taking a different concentrations within standard calibration curve range for R-CdONPs electrode, and the voltage was measured six consecutive times for each concentration separately after installing the ideal conditions and the results shown in the table (3)

Table (4) Accuracy and Precision Values

Conc. Taken(mole\L)	Conc. Found(mole\L)	Rec%	RSD%
$1x10^{-2}$	**$0.988x10^{-2}$**	**98.8**	**0.32**
$1x10^{-4}$	**$1.05X10^{-4}$**	**105**	**0.37**
$1x10^{-8}$	**$0.983x10^{-8}$**	**98.3**	**0.50**

3.7. Selectivity

The effect of interferences ions on the response time of the electrode was studied by mixed solutions method by adding different concentrations of different salts to the cadmium nitrate tetrahydrate solution (10^{-2}) M and the selectivity coefficient was calculated by using the equation (1). Where the ability of a manufactured electrode to distinguish a particular ion without other ions is determined by the selectivity coefficient (17).

$$\log K_{A,B}^{pot} = \frac{E_2 - E_1}{S} \dots\dots\dots\dots (1)$$

Table (4) Selectivity coefficient values

$\log K^{pot}_{A,B}$ Selectivity Coefficient	Interferrence Ion Concentration	Type of interference ion
0.2195470752	10^{-2}M	Cl^-
0.3075068846	10^{-4}M	
0.4685585078	10^{-2}M	K^+
0.5545330329	10^{-4}M	
0.5097363734	10^{-2}M	Pb^{+2}
0.5540660801	10^{-4}M	
0.3639304858	10^{-2}M	Al^{+3}
0.3963157803	10^{-4}M	
0.7139582435	10^{-2}M	SO_4^{-2}
0.8449604982	10^{-4}M	

3.8. Life Time of the Electrode

The life time of the electrode was estimated by recording the potential between one day and another for a period of (61) days for the standard $Cd(NO_3)_2.4H_2O$ solution at a concentration of (1×10^{-3}) molar, and it was noted that the measured voltage is stable during this period, and thus the life time of the electrode was estimated at (61) days, where it was noted that after this period the voltage reading began to decrease, and the reason may be due to damage to the coated layer of the electrode. Figure (10)

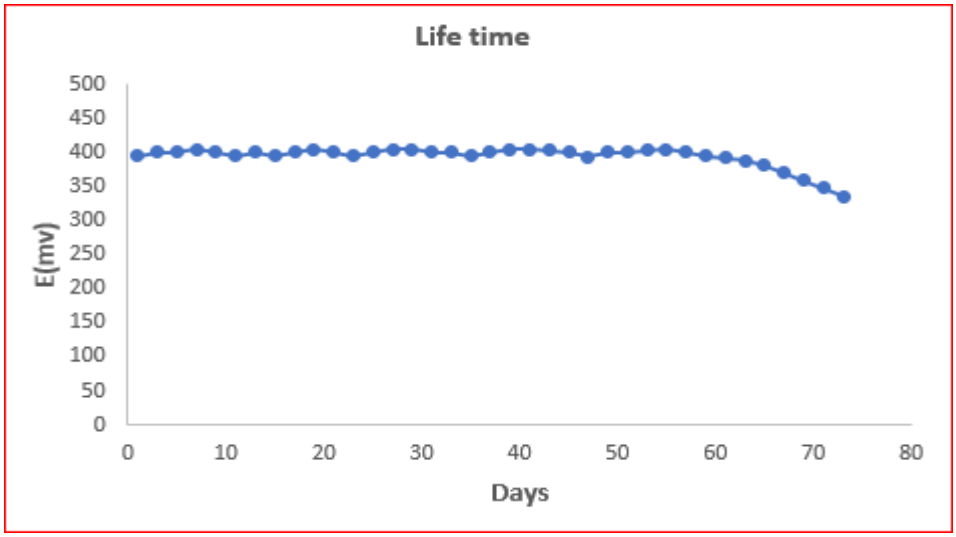


Figure: 10 Life Time for R-CdONPs Electrode

3.9. Applications

A different sample of water from different areas such as (Al-Qaim Cement Factory, Baiji refinery) were taken and were measured directly after fixing the ideal conditions of temperature and PH, the measured voltages were compensated in the slope equation of R-CdONPs electrode calibration curve, and the concentration was measured practically and theoretically for each sample as shown in the table (5)

Table 5: Direct Method Results

Sample	Taken Conc	Found Conc	Rec %	RSD %
Al-Qaim Cement Factory	$1x10^{-4}$	$0.995x10^{-4}$	99.5	0.42
Baiji refinery	$1x10^{-3}$	$1.001x10^{-3}$	100.6	0.38

4. Conclusions

In this study, Cadmium oxide nanoparticles were prepared from leucaena leaf extract using the green chemistry method without the use of chemical precipitators, and this is a new development in nanotechnology. Cadmium oxide nanoparticles were mixed with 1,3-Oxazepine-4,7-dione derivatives Solution in which prepared for the first time and the mixing process led to an increase in the precipitation process and the formation of the Cadmium oxide complex with the reagent (R-AgONPs), The SEM images show that the particles appeared in a spHerical or almost spHerical form in the form of compact clusters with average sizes from (106.1nm) to (44.66nm). Also, the XRD pattern demonstrated that the reagent led to decrease the intensity of CdO nanoparticles peaks with and the average size of the crystals was (9.57 nm). The complex (R-AgONPs) was used in the manufacture of a selective electrode for Cadmium ions. The manufactured selective R-CdONPs electrode has a unique properties, such as, low detection limit ($11.67x10^{-11}$)) molar, rapid response time (2-37) seconds, wide linear range ($1x10^{-1}$ _ $1x10^{-11}$) molar, high retrieval values (99.5- 100) %, long electrode life time (61) days. The electrode was successfully applied to different samples of contaminated water and the results were satisfactory.

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