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The use of zinc oxide nanoparticles in the manufacture of redox sensors to measure metal ions from contaminated water

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Abstract
In this study, zinc oxide nanoparticles were first used. The synthesized nanoparticles were evaluated, and their particle size and crystallinity were determined by FTIR and XRD spectroscopy. The FT-IR results indicate that the main functional groups, such as hydroxyls, have been synthesized. The results of XRD showed proper crystallinity of the nanoparticles. After the synthesis of the nanoparticles, carbon powder was added along with silicone oil, and the initial paste was prepared. A copper wire was placed inside it as a conductor wire. A solution containing cadmium ions was used to evaluate the performance of the electrode. For this purpose, the cyclic voltammetry method was used. It was also found that modifying the carbon electrode with zinc oxide nanoparticles significantly increased the oxidation and reduction capability of the electrode.
Key word: zinc oxide nanoparticles, Spectroscopic analysis, carbon electrode.

استخدام جزيئات أكسيد الزنك النانوية في تصنيع مستشعرات الأكسدة والاختزال لقياس أيونات المعادن من المياه الملوثة

حبيب عبد الحسين شاهر ال شاهر

خلاصة

في تم استخدام جزيئات أكسيد الزنك النانوية لأول مرة. تم تقييم الجسيمات النانوية المصنعة، وتم تحديد حجم الجسيمات وبلورتها بواسطة التحليل الطيفي FTIR وXRD. وتشير نتائج FT-IR إلى أن المجموعات الوظيفية الرئيسية، مثل الهيدروكسيلات، قد تم تصنيعها. أظهرت نتائج XRD التبلور المناسب للجسيمات النانوية. بعد تركيب الجسيمات النانوية، تمت إضافة مسحوق الكربون مع زيت السيليكون، وتم تحضير المعجون الأولي. تم وضع سلك نحاسي بداخله كسلك موصل. تم استخدام محلول يحتوي على أيونات الكادميوم لتقييم أداء القطب. ولهذا الغرض تم استخدام طريقة قياس الجهد الدوري. وقد وجد أيضًا أن تعديل قطب الكربون باستخدام جزيئات أكسيد الزنك النانوية أدى إلى زيادة كبيرة في قدرة القطب على الأكسدة والاختزال.

كلمات مفتاحية: أكسيد الزنك النانوية، التحليل الطيفي ، قطب الكربون..

Chapter One

General research

1-1-the introduction

The rapid growth of industries and the frequent use of chemicals in the textile, pharmaceutical, food and automotive industries have contributed to a major threat to the survival of organisms on Earth. Emissions of harmful toxins from car exhaust and plant exits have become a major source of environmental pollution. Therefore, a valid tool for the effective detection of harmful chemicals using chemical and biological sensors has an urgent need for the present. Of the available types of semiconductor sensors for different types of chemicals and

biological toxins, zinc oxide-based sensors (Znos) have received widespread attention around the world. The presence of a good response rate to chemical toxins with its extraordinary selectivity and sensitivity makes it one of the most important materials for the preparation of low-cost sensors. The presence of a diverse range of morphologies such as nanomiles, wires, needles, ovals, hedgehogs, spirals, shoulders, flowers and disc shapes from ZnO materials provided good control over the surface-to-volume ratio for the nanomaterials prepared and increased their application. The safety of water resources around the world has been compromised by various human activities and climate change over the past decades. As a result, the world is now facing severe water supply shortages and a water safety crisis among the growing population. With poor environmental regulation, indiscriminate germination of urban slums, poverty, and a lack of basic sanitation knowledge, Africa's water supply has been severely threatened by various organic and mineral pollutants leading to numerous health issues. Inorganic pollutants such as heavy metals are especially noted, as they are mostly stable and non-biodegradable. So they don't get out of the water easily. In different regions of the continent, the concentration of heavy metals in drinking water is far exceeded. Worse, the problem is expected to increase as the population grows, industrialization, urbanisation and, of course, corruption of state and local authorities. Most of Africa's population is unaware of healthy water standards. In addition, people do not have access to affordable and reliable technologies and tools that can be used to quantify these pollutants. This problem can be used not only for domestic water sources, but also for commercial, shared and industrial water sources. Hence, a global campaign has been launched to ensure an ongoing assessment of the presence of these metals in the environment and to promote awareness of the risks associated with unsafe exposure to them. (1(

One of the important functions provided by nanoparticles is the construction of electrochemical sensors surrounded by selective membranes. These electrodes separate the internal reference ion solution organization around the electrode from the external analyte solution. It creates an electrical potential between two ion solutions that can be measured.

1-2-electrochemical methods of measuring chemical species

One of the newest techniques of decomposition chemistry in measuring different species is the use of chemical sensors. Chemical sensors provide direct information about the chemical environment around them. These sensors include a physical transducer and a chemical selective layer, which are divided into different types based on the type of transducer. The physical transducer converts the interaction between the chemical layer and the analyte into an electrical signal. Chemical sensors consist of a symptom-transmitting element covered by a chemical or biological identification layer, and as a result of the interaction of the target experimental species with this layer, chemical changes are converted

into electrical symbols. Electrochemical sensors are an important sub-branch of chemical sensors in which an electro-D is used as a sign-transmitting element that represents a breakdown sign in the form of electrical potential or current intensity . For the successful development of electrochemical sensors, it is very important to strengthen the decomposition mark and reduce the novelty to determine and measure the target experimental species in biochemical decomposition. Since the synthetic electron exchange of some important biological and pharmacological experimental species is very slow at the level of conventional electrodes, these processes are required to apply a lot of overvoltage. Therefore, improving the surface properties of conventional electrodes as a result of fixing or importing appropriate modifiers, as a suitable solution to reduce overvoltage and overcome slow synthesis of many electrode processes (2). In fact, modifiers or intermediaries facilitate the transfer of electrons between the electrode surface and the test species in question, increasing sensitivity and reducing the degree of detection in their electrochemical measurements .

1-3-electrochemical sensors

These sensors are mainly used to display oxidation – reduction reactions. In other words, these sensors show the interaction between chemistry and electricity. Electrochemical sensors measure three different types of parameters which are divided into three categories based on the type of measurement

1-amp sensors: measuring the current

2-Potentiometric sensors : measuring the potential

3-conduction sensors : measuring the conductivity

.Electrochemical sensors have wide applications due to their high sensitivity low cost and fast response

1-3-1-amp Sensors

Amperometric sensors show a rapid response to analytics and have good repeatability, high sensitivity and long-term stability]21[. The signal generated in these types of sensors is the current intensity, which is proportional to the analyte concentration. The signal generated in amperometric sensors is useful when its value is independent of the potential of the working electrode. Selecting the action potential for the working electrode is a method of selecting these types of sensors, but this method provides little selectivity in these sensors. Additional chemical layers should be used to modify the sensors to increase selectivity .

1-3-2-conduction sensors

In this type of sensor, the measure of action is electrical conductivity. Conduction sensors act based on changes in the conduction of the sensor layer due to interaction with the sample]15[. In fact the performance of conduction sensors is based on the changes in the electrical conductivity of a film or a mass

of a particular sex which is affected by the presence of analytics in the sensor environment and the sensor directly measures the conductivity of analytics

1-3-3-Potentiometric sensors

These types of electrochemical sensors are based on the relationship between the electromotor force of the electrochemical cell and the concentration of chemical species in the sample. Potentiometric measurements are usually made in zero flow. Potentiometric sensors are generally divided into two categories :

The first category is symmetric Potentiometric sensors, which include traditional ion electrodes, and the second category includes asymmetric devices. In this category of Potentiometric sensors, one side of the species-sensitive membrane is exposed to a solid phase and the other side is exposed to a measured solution containing the species. Solid state gas sensors fall into this category because they are always asymmetrical (3). Asymmetric potentiometer sensors are smaller and have a smaller volume than symmetric potentiometer sensors .

1-3-4-mass sensors

Mass change measurements, like reaction heat measurements, are useful criteria for use in chemical sensors. Based on this feature, a new class of chemical sensors called mass sensors have been developed that can measure mass changes, so that these types of sensors convert the mass changes created on the surface of a converter into an electrical signal (4)[. In theory, any change in mass in the receiver oscillator causes a certain change in frequency .

1-3-5-heat sensors

Heat sensors have the ability to detect temperature. In many reactions, due to the absorption of the beam, during the reaction, changes in temperature cause the sensor temperature to rise, and certain parameters of sensor materials such as special electrical resistance, contact voltage, and polarization change spontaneously. These changes are proportional to the desired analytic concentration (5(

When a bolometer detector is used in the manufacture of heat sensors, as a result of increasing temperature, the resistance of the bolometer has changed, which changes the resistance to voltage or current .

1-3-6-optical sensors

Optical sensors emerged from two decades as an important branch of research. Optical chemical sensors are compact, suitable for miniature and resistant to electrical interference. Optical chemical sensors are used at various levels such as environmental, clinical, industrial and analytical. In this type of sensor, optical converters are used. In this type of sensor, a color detector and polymer membrane are usually used. Optical sensors are similar to electrodes, but differ from electrodes in terms of working principles and have advantages such as no electrical disturbance, no need for reference electrodes, cheapness and ease of

preparation over electrodes. At the same time these sensors also have disadvantages compared to electrodes which include longer response times and interference of ambient light in their operation

Optical sensors are made for various purposes, including ION optical sensors, optical biosensors, PH optical sensors, optical gas sensors, and optical humidity sensors. (6(

1-4-**voltametric methods**

Voltmeter is an electrochemical method in which three electrodes are used: work, auxiliary and reference. The electrode is reactivated. The reference electrode is usually a calumel electrode with a large surface that acts as an ideal non-polarized electrode.the potential applied to the working electrode is assessed relative to this electrode .

The auxiliary electrode is usually made of platinum rod or graffiti.any reaction that takes place on the surface of the working electrode is the opposite reaction on the surface of this electrode, resulting in the current between this electrode and the working electrode .

At the voltmeter, a potential is applied by the potentiostat between the working electrode and the reference, and the current is measured, and at the end of the current curve is plotted by stability according to the potential. To draw a polarogram, the electrode potential of mercury drops is usually gradually reduced relative to the electrode of the witness .In this case, the droplet electrode acts as a cathode, and many ions are resuscitated on its surface .

In some cases, the voltmeter wave may cause a compound to oxidize at the surface of the mercury drop electrode, in which case the potential of the mercury drop electrode is gradually increased relative to the witness electrode, which are the same Andic waves at the voltmeter. (7)

Potentio acetate applies a potential program to the working electrode so that the potential starts from zero, and goes towards positive potentials. In the initial potentials of the current is not zero and we have a value of current this current is called the residual current which is caused by the presence of impurities of heavy elements and oxygen or capacitive current as the potential increases we get to the point where the analyte on the mercury electrode surface is revived by increasing the potential the amount of current increases to the point where the current becomes independent of the potential this current is called the current limit in this current the concentration is completed so the speed of the material reaching the electrode surface is not enough to create the desired current. This is the limit flow that is proportional to the concentration and is used for small tasks. There are several ways to get the material to the electrode surface .

1-convection: caused by thermal and mechanical transfers between the surface of the electrode and the solution .

2-migration: the reason is the presence of electrostatic forces between the electrode and the solution, so that the electrode has a negative charge and the analyte has a positive charge .

3-diffusion: caused by a difference in the concentration of analyte at the level of the electrode and solution .

In fact, the current measured at the voltmeter is the result of this emission current, and this is the emission current, which is proportional to the concentration, so the convection and migration current must be removed, the migration current is removed by increasing the inert electrolyte and the convection using mechanical and vibrational insulation systems in the voltmeter path.

Research shows that the emission flow is not dependent on temperature and depends only on the concentration and height of the mercury column and the emission coefficients although the temperature does not directly affect the equation, it indirectly affects the emission coefficients so that as each temperature increases, the emission coefficients change by 9/2 percent, which is equivalent to 9/1 percent in the current limit, so temperature control is very important at the voltmeter. (8)

The types of voltametric methods are divided into the following categories .

Polarography Andy nudity voltameter cathode nudity voltameter and gravitational nudity voltameter measurement techniques in voltameter methods also vary greatly and include DC direct current sampling technique normal Lacey foot polarography differential wave Technicolor alternating current voltameter square wave technique and they're cyclic voltametric techniques .

Today, the use of the voltmeter method of wheels is very high .This method is generally used for synthetic studies and is used for reversible systems. in this method, the potential is returned once or several times at a constant speed from the point of application of the potential to the final potential of application and again at the same speed to the starting potential. In this technique, the electrode is platinum or gold. (9)

1-4-2-voltmeter with linear potential rubbing

In this method, the sloping potential is applied to the static electrode floating in the static solution and records the resulting current changes relative to the electrode potential. The resulting curve, which has an asymmetrical nose shape, is called the voltamogram .

A linear rubber voltmeter is a potentiostat method that uses three working, auxiliary, and identifying electrodes, and depending on the direction of the rubber, the electrode process and its dependent current may be Andean or cathodic in nature.

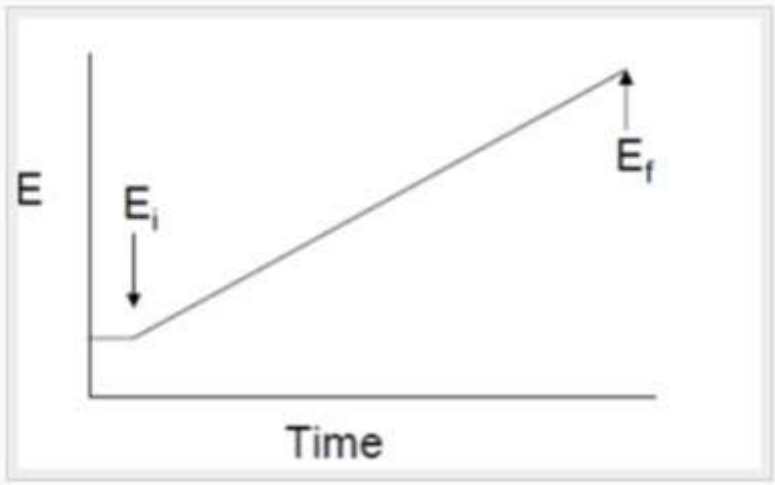


Figure 1-1 - potential applied in the voltametric method between initial potential 1E and final potential 2E

First, species in the vicinity of the working electrode participate in the electrode reaction and create a concentration gradient that transmits matter by emission around the electrode within the emission layer.

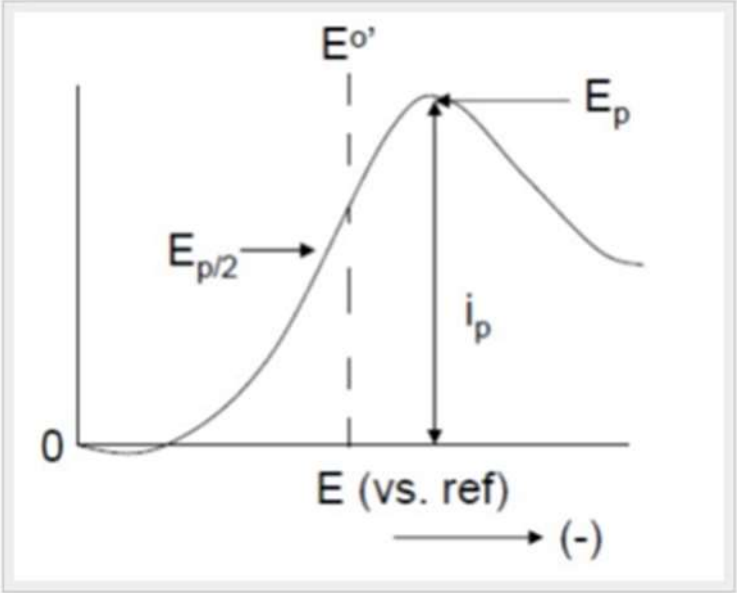


Figure 1-2-changes that have increased the flow of changes to the business model and to the linear

As the electrode potential gradually changes, more and more electroactive species enter the electrode process, and the current intensity increases to the point where the concentration of adjacent species of the electrode surface reaches zero, and the current reaches its highest level.

From this moment on, the effects of expansion appear in the emission layer, and the flux of the material reaching the electrode surface gradually decreases due to the expansion of the emission layer, resulting in a gradual decrease in current.

The intensity of the brain flow is proportional to the concentration of the experimental species. In addition, the flow of the nose increases in proportion to the root of the ribbon, so the sensitivity of the method can be increased by increasing the speed of the ribbon. On the other hand, the capacitance current increases in proportion to the increase in the speed of the potential. (10)

1-4-2-Rosh Hashanah calendar

The technology and the measurement of the device are linear, where the voltage of the device varies depending on the type of device in which the device is installed. Where Roche Technologie has been able to study the electrochemistry studies using the jarop process and make changes in the flow, inform the company about the course of the electrochemistry friendship, the system will be approved and the syntectical parameters will be set according to midhed's opinions. It has the title of an example paper on reftar khordagi metals, properties of exaishi-kahshi materials, assignment of a diffusion tax and .... Visit <url> for more information .In addition, it is necessary to specify the parameters of the device, i.e., the mechanical, chemical and chemical systems of the device. They are two powerful technical technologies, including mechanical and mechanical design, electron density counting, synthetic and thermodynamic parameter designations,and electrochemical pair designations.

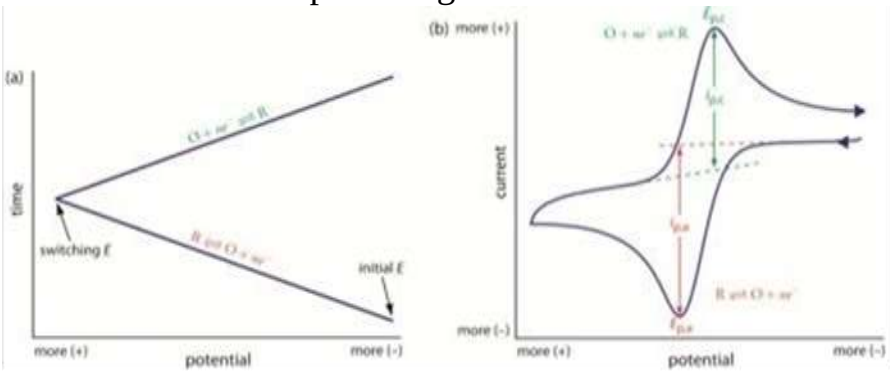


Figure 1-3-a: ground flow changes by Business Model / B: time changes by business model

In the staircase voltmeter method, the device travels the distance between the initial potential of the vans in a staircase. It means that it applies potential pulses at fixed times and fixed sizes, but in the linear scanning method, this scan is .linear, and the potential is increased by linear time

In Voltametry, like other methods of machine analysis, the concentration of elements is evaluated by methods such as calibration curve drawing and standard augmentation. (11(

In the calibration curve method, standard concentrations of the measured sample are produced in a certain range, and these standard concentrations are measured one by one with a voltmeter, and the waves from these standard combinations are drawn obviously, the surface below the peak or peak height is proportional

to the concentration, and at the end of the curve, the surface below the peak or peak height is drawn with the concentration.

After the calibration curve is drawn, the unknown sample is injected into the machine and the peak height is measured, and the concentration is determined by the calibration curve drawn .

1-5-use of the potentiostat device

A device for measuring polarization and changing the potential of a compound. This device uses potential changes based on current intensity to draw a graph .

By applying the Andy potential and another cathode to the working electrode, and measuring the potential difference of this electrode with the reference electrode, as well as measuring the intensity of the Andy net current and another cathode, the relationship between the potential and the current intensity and its graph is obtained.

1-5-1-use of the modifier on the electrode surface

Modifying the electrode surface to provide some controls on how the electrode interacts with its surroundings has been one of the most active areas of interest in electrochemistry.

While the efficiency of an electrode is limited to materials such as the type of electrode, the solution in which the electrode is located and the potential to apply to the electrode, today the ability of modified electrodes has provided a powerful path to improve their efficiency. It was very important for the Analytical Electrochemistry that the modification of electrode surfaces provided paths to increase selectivity, rust resistance, species thickening, improving electrocatalysis properties, and limiting the access of intrusive species to the electrode surface in a complex sample, such as a biological fluid . It has also played an important role in research in the field of energy conversion and storage, corrosion protection, molecular electronics, electrochromic tools and fundamental research in the field of phenomena affecting electrochemical processes .(12)

In electrocatalysis purposes, chemically modified electrodes are used to accelerate the electron transfer rate of the compound in question at the potential that this transfer is slow at the surface of the bare electrode. Electrode reactions of many important decompositions, on the surface of the bare electrode, require potentials much higher than their formalistic potential to be performed at the expected high speed. The acceleration of such kinetically slow electrode reactions is done by load transfer mediators and a process called electrocatalysis .The electrocatalytic advantages of electrodes modified with metal particles or semiconductors stabilized in an ion or polymer layer include the following.

These systems are easily developed .

Catalysis and charge transfer are separate between the base surface of the electrode and the particle particles of the catalyst .

Like oxidation-reduction sites within a redox polymer, there is a three-dimensional splash for the catalytic particles inside the polymer body. In addition to electrocatalysis, these electrodes can be used in the field of simultaneous measurement of several substances and to increase sensitivity in biochemical measurements .(12)

1-5-2-chemically modified electrodes

Chemically modified electrodes are a new approach to electrode systems. These electrodes are created by placing a representative on the surface of an electrode, with the aim of using electrotechnical or electrochemical behavior of the representative stabilized on the electrode surface. So, this deliberate change in electrode surfaces can eliminate many of the problems of decomposition electrochemistry and provide the basis for new decomposition applications and various sensory devices .. To produce a modified electrode, the modifying group must be fully stabilized on the electrode surface. For this purpose, depending on the purpose of modifying the electrode surface, various modifiers are used, some of which are mentioned below .

1-5-3-electrodes modified with polymer films

Today, electroactive polymer films with Multi-Molecular layers are more common compared to single-layer species for electrode modification, as it is easier to apply polymers to electrode surfaces compared to layers stabilized by covalent bonding. In addition, these types of electrodes have more electrochemical locations than single layers, which makes it easier to study their electrochemicals . Also, in some situations, their electrocatalysis properties can be improved. In general, polymer films are more durable than single-layer films .

When using conductive polymers, molecular detection or their electrocatalysis activity is possible by inserting an agent duplex such as complexing agents with an electron transfer intermediator. Conductive polymers can therefore act as the efficient molecular distance between the identifying elements and the electron transporters. The unique physical and chemical properties of conductive polymers, especially their intense and controllable electrical conductivity and the rapid exchange of doping ions, create various electrochemical applications for them, including batteries, fuel cells, corrosion protection, or chemical sensors . Recent cases include detection of amperometry of non-electroactive ions in current solutions, solid-state gas sensor, trapping / coupling and stabilization of biological components, direct examination of biological interactions, electrochemical control of membrane permeability, array of sensors based on multiple films, new identification of ions by potentiometry, pre-condensation and nudity of metal traces and control they're chemicals . The growth of polymer films at the electrode level can lead to the creation of conductive or non-conductive films. These films are often used as selective or protective permeability layers or are used to physically trap biomolecules. In principle, polymer films can be stabilized on the surface of electrodes using a

polymer or Monomer solution. Methods such as molding, fast-rotating coating, drip evaporation, and electrochemical coating are used when using a polymer solution. Whereas electrochemical polymerization is polymerization with radiofrequency plasma discharge and polymerization in the vacuum of methods based on the application of monomer-based solutions .(13)

1-5-4-electrodes modified with molecular mold polymers

Recently, there have been many attempts to replace biological receptors with synthetic counterparts as a detection element in biochemical sensors .Molecular molding technique is a powerful tool for the production of polymers that have the ability to connect specifically with the chemical species in question. Molecular molding polymer production generally involves the pre-assembly of molding molecules and agent monomers and subsequent copolymerization with transverse binding monomers . The exit of the pattern molecule from the polymer structure creates holes that are in the shape, size and operating groups, the pattern molecule, and are actually the locations of the target molecule. Molecular molding polymers have been widely used as sensitive components in biochemical sensors to detect various materials due to their mechanical and chemical stability, low cost and convenient production . For Molecular mold polymer-based sensors, molecular mold layers can be produced in place by electroplymerization at the electrode level. It is clear that the sensitivity of the sensor is determined by the extent of the effective detection sites at the sensor level. Although the rate of detection sites increases with increasing molecular mold membrane thickness thick membranes can lead to slow penetration of the desired experimental species into detection sites and inefficient communication between Link sites

And the surface is electroded. The easiest way to increase the number of effective detection sites at the sensor level is to use an electrode with a larger surface area .(14(

1-5-5-electrodes modified with nanoparticles

In recent years, the use of nanoparticles has always been considered due to its important and unique optical, magnetic, electronic and chemical properties . The properties of nanoparticles generally depend on their size, shape and how they are stabilized, which are controlled by the conditions of their production. The use of intermediate metal nanoparticles in electrochemistry and the use of these materials as modifiers has attracted a lot of attention.

The wide effective surface, high electrical conductivity and high electron transfer speed are reasons for the use of nanoparticles in electrochemistry. Catalytic properties using intermediate element nanoparticles are among the most important chemical applications of metal nanoparticles. [. These substances exhibit many catalytic properties in many organic reactions as homogeneous and heterogeneous catalysts. The catalytic process occurs at the level of the active sites of metal particles.

This mechanism is similar to the heterogeneous catalytic reaction. The applications and electrochemical behavior of nanoparticles have attracted a lot of attention. A large proportion of atoms on the surface with the capacity layer increase the catalytic activity used in electrocatalysis reactions. In general, there are four main advantages to using a modified electrode with nanoparticles over conventional electrodes, which include improved mass transfer, catalytic properties, wide effective surface area and the possibility of control over small environments of the electrode. The use of electrodes modified with nanoparticles significantly increases the accuracy and sensitivity of measurement to other types of common electrodes .

1-5-6-electrodes modified with enzymes

Enzymes are among the materials used to make modified electrodes. Enzymes are proteins that catalyze chemical reactions in vital systems. Enzymes are often very effective catalysts and catalyze the oxidation or reduction of their substrates with an additional voltage close to zero. To make an enzyme-modified electrode, a layer of the enzyme can be fixed to the electrode surface. Although enzymes also work very selectively for their substrates, since the stability of isolated enzymes is limited and some enzymes are expensive or even unavailable, cellular substances such as plant tissues containing the enzyme in question can be used to modify the electrode surface. For example banana tissue rich in polyphenol oxidase can be inserted into the carbon paste by mixing it to create a sensitive and rapid response sensor for dopamine

1-5-6-electrocatalysis at the level of modified electrodes

Most of the reactions of the redox in question are performed at the level of the bare electrode to the slowness and at potentials above their thermodynamic potential. Such reactions can be catalyzed by the electron transfer mediator present on the electrode surface]52-53[. That is, the intermediary accelerates and complements the transfer of charge between the electrode and the test species in question. So the electron transfer is done between the electrode and the intermediator instead of directly between the electrode and the experimental method. As a result, the electrode process is performed at a potential closer to the thermodynamic potential, meaning that the use of the catalyst at the electrode level reduces the excess potential and increases the current density. Accordingly, many modified electrodes have been used to electrocatalyze the electron transfer of various materials, the most important of which is the modified polymer electrodes with noble metals distributed in them . The catalytic activity of infelates depends on the diffusion rate and properties of their surfaces. The larger the diffusion rate of the metal particles, the greater their catalytic activity. Polymer films can provide a very suitable platform for stabilizing metal particles due to their porous structure and very large cross sectional area

One of the most important applications of metal catalysts is the oxidation of important fuels such as methanol, which are used as a liquid fuel with relatively high activity in the fuel cell system .It is also important to note that although formaldehyde can also be used as a liquid fuel in fuel cells it has been less noticed due to its lower energy density higher toxicity and higher cost than methanol

1-5-7-use of modifiers in carbon yeast tissue

Among the different electrodes, the increasing growth of modified carbon paste electrodes can be attributed to their interesting properties. The carbon paste electrode has been widely used in decomposition electrochemistry due to its low cost, easy preparation, surface renewability, low ground flow and high sensitivity .In general, organic liquid is a carbon paste adhesive agent, a non-conductive mineral oil such as adolescent oil, liquid paraffin, or the like. Due to its high chemical stability and adequate adhesion ability, this non-conductive viscose liquid has always been considered for the manufacture of conventional carbon dough electrodes. Nevertheless, the mineral oil adhesive agent still has two basic forms . First, mineral oil does not have fixed components, because when it is produced from crude oil, it is involved in various refineries and processes, and some unknown components may have unpredictable effects on the detection and analysis of materials, and the second fundamental drawback is that it is an insufficient adhesive agent that causes the electrochemical response of the electrode to be reduced to the extent that it is especially important to detect small amounts of the species.the chemicals in question are a fundamental defect. It has been shown that replacing adolescence and paraffin with Ion fluids as adhesive agents increases the electrical conductivity of the electrode, the speed of electron transfer, and also increases its sensitivity. So it can be a good and efficient modifier for the production of carbon dough electrodes. That's why over the last few years, a lot of these electrodes have been made and used for various decomposition purposes.

When these polluting metallic elements and / or their ions are dispersed in the environment, they accumulate in soil, surface, or groundwater, potentially entering the food chain through drinking water or biological accumulation in animals and plants. The type of metal determines the degree of toxicity, its biological role and, most importantly, its concentration. Increased concentrations of iron, cadmium, lead, copper, chromium, arsenic or nickel in drinking water are the most common causes of human poisoning.

Voltametry offers an ideal solution to these challenges and offers a quick, simple and inexpensive replacement for many other techniques. Voltametry can be done even for untrained personnel, which can provide a detection limit within the ng/L range. In addition, it can turn heavy metal surfaces into an interesting and valuable way for mobile applications.Ideally, new sensors are made from inexpensive, non-toxic materials. However, the properties of these substances

can lead to some limitations. A problem is a limited number of elements that can be detected on a particular electrode material, such as carbon.Successfully determining the number of elements simultaneously in a sensor can be problematic, but it can be addressed through the careful selection of the most suitable electrode material along with the optimal sensor design.

1-5-8-Cadmium metal

Research on the accumulation of cadmium shows that environmental contamination with the element cadmium in areas close to industrial cities and metal melting furnaces is a serious issue , and there is now evidence that cadmium is considered a carcinogen and a factor in the development of defective embryos .It also has detrimental effects on the lives of birds and aquatic animals. It enters the environment in two ways: anthropomorphic and natural, which in the past produced much higher than its natural type .

Metallic cadmium is relatively rare, soft, with a bluish-white and venomous color . It is dual capacity metal, soft, hammer-eating, and flexible the most common oxidation state is cadmium 2+, although rare examples of 1+ have also been observed .Cadmium is used in plating coatings, paint making , plastic strengthening, and Ni-Cd batteries

Cadmium dust inhalation quickly causes problems in the respiratory tract and kidneys that can be fatal. Eating a significant amount of cadmium causes rapid liver and kidney poisoning. Compounds that contain cadmium cause deformation and softness of the bone

Method of Investigation

2-necessary materials and equipment

Zinc acetate salt
Twice distilled water
Sodium hydroxide
Cadmium salt
Ethanol
Potassium nitrate
Powdergraphite
Silicone oil
Acid –neutral and alkaline buffer solutions
Xrd device
PH meter
Flat paper
Avon
Voltmeter

2-1-synthesis of nanoparticles on oxide:

2 grams of powder was poured on two-water acetate, weighed and poured into a 500 ml balloon, then 50 ml of dionized water was added to it and placed on a magnetic mixer to obtain a homogeneous solution. The pH regulation of the resulting mixture was carried out using the addition of 2/0 molar sodium hydroxide drops. The balloon of the desired compounds was severely stirred on the magnetic mixer for 2 hours. At the end, the mixture was passed through a flat paper, and the resulting sediment was rinsed several times with water twice distilled and ethanol. The resulting sediment was placed in the Avon at a temperature of 60 ° C for 2 hours, and finally the nanoparticles were obtained on the oxide. The resulting nanoparticles were stored in a closed container for the next steps .

2-2-construction of the modified carbon electrode

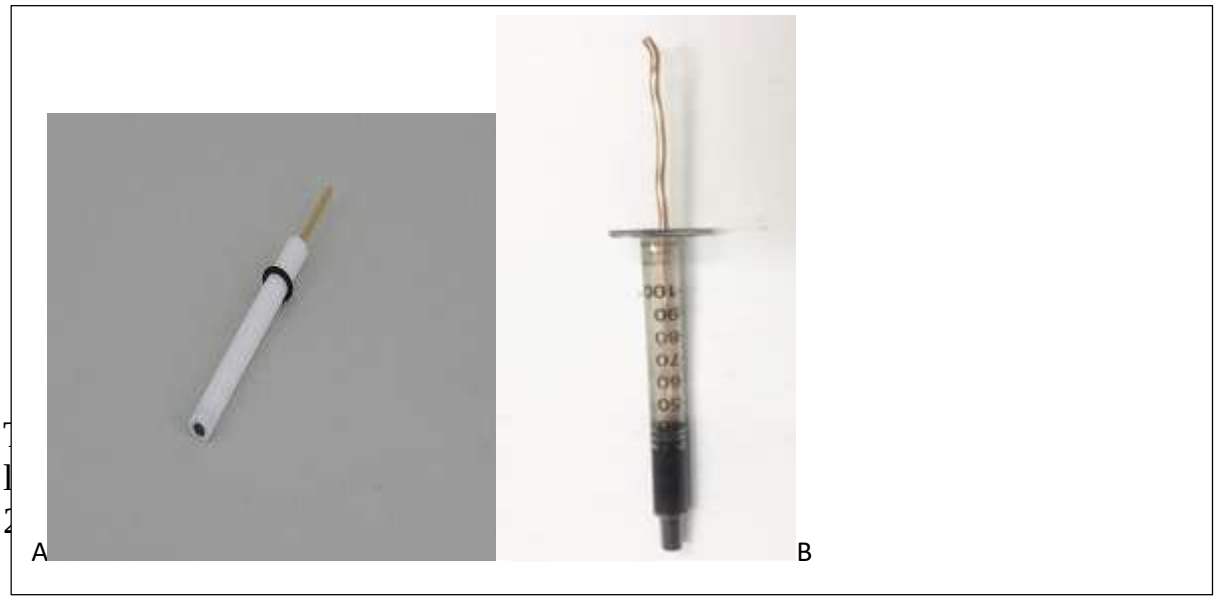
In the second stage, the modified carbon paste electrode was prepared . To do this, a mixture of silicone oil and various amounts of graphite powder was well mixed in a hand-held mortar. Then part of the resulting dough was poured into the syringe and a copper wire was placed inside the syringe as an electrical current conductor .The addition of silicone creates a good adhesion and the yeast-shaped mixture does not leak out of the syringe.

In the next step, graphite powder, zinc nanoparticles and silicone oil were mixed with ratios of 20%, 50% and 30%, respectively, and in the next step with ratios of 60%, 20% and 20% respectively.

After the electrode was made, the electrode was investigated for responding to oxidation - reduction reactions .

Voltametry is a chemical analysis method used to measure the concentration of ions in aqueous solutions .

Figure 3-1 shows the standard carbon electrode and the modified electrode with zinc oxide nanoparticles prepared in the laboratory



To prepare standard solutions, first the mother solution was prepared at a concentration of 5/0 molars and then by diluting the mother solution , less concentrations were prepared .

2-4-preparation of buffer solutions

Buffer solution 3: Mix a certain volume of acetic acid 1 molar and sodium acetate 1 molar and a solution with an approximate pH of 1 is obtained. Then a drop of acetic acid is added to 3PH .=

Buffer 7: a certain volume of dipotassium hydrogen phosphate 1 molar and potassium hydrogen phosphate mixed together with a concentration of 1 molar and then added a drop of potassium hydrogen phosphate, which plays an acidic role, became PH=7

Buffer 9: a certain volume of ammonium salt is mixed with 1 molar and ammonia with a concentration of 1 molar and then obtained by adding an additional ammonia drop, 9 =pH.

After preparing the necessary solutions, a three-voltmeter electrode system was used to measure the sensitivity of the electrode . In a three-electrode system, platinum wire acts as an auxiliary electrode, silver-silver chloride electrode acts as a witness electrode, and modified carbon paste electrode acts as a working electrode. Potassium nitrate solution was used as an auxiliary electrolyte.

To this end, 15 ml of a sample containing cadmium with 10 ml of potassium nitrate solution was poured into a special voltameter sample container as an auxiliary electrolyte. The witness electrode, silver/silver chloride and the electrode made as the working electrode were connected. The starting potential was set to zero and the Switch potential was set to 1.5 volts .The speed of the Rob was adjusted by 50 mV / s and the intensity of the current generated was measured.

Figure 3-5-voltmeter and sample container

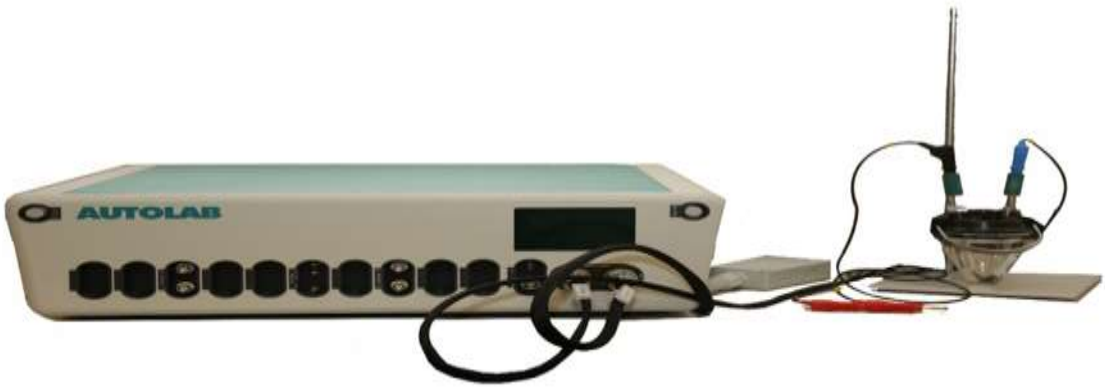


Figure 3-5-voltmeter and sample container

Figure 3-6-interface cables between electrodes and the device

The standard deviation was calculated after 3 repetitions , 065/0, which indicates a small dispersion of the obtained answers relative to the mean value and is an acceptable result.

SD= [∑(yi-ȳ)2/N-1]1/2

SD= standard deviation

ȳ= mean data

yi= data

N= Test times

3-Analysis of the data

1-examination of zinc oxide nanoparticles

2-preparation of a sample for the analysis of infrared spectroscopy of the Fourier transform

To examine the Fourier Transform Infrared Spectroscopy, the nanoparticle mixture was centrifuged for 30 minutes at a circumference of 18,000. Then the zinc solution was discarded and the nanoparticles were washed with water twice distilled and the resulting samples dried at 60 degrees Celsius. Then, with the aim of analyzing FT-IR, it was mixed with potassium bromide and Spectra related to synthesized nanoparticles were prepared.

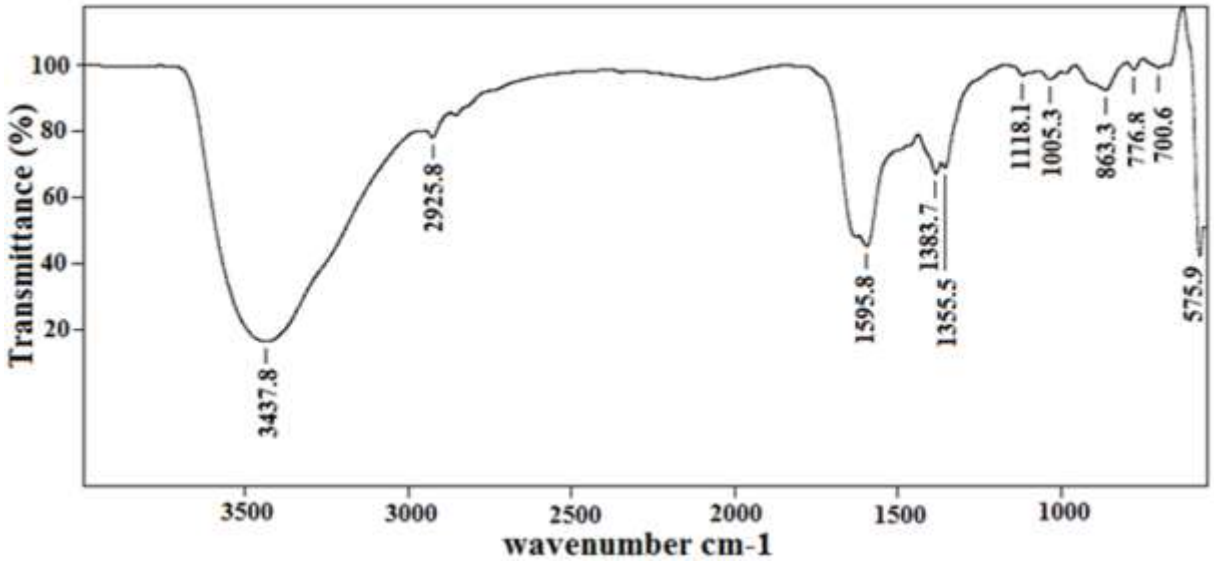


Figure 4-1-infrared spectrum of the Fourier Transform of nanoparticles on oxide

The spectrum of nanoparticles on the prepared oxide is shown in Figure 4-1. The peaks observed in the range of 800-500 indicate the formation of ZnO nanoparticles.

3-1-preparation of sample for analysis with X-ray diffraction device

The resulting nanoparticle solution was centrifuged for 20 minutes in order to concentrate with the centrifugal device. Then the zinc solution was discarded and the nanoparticles were washed with water twice distilled. Dried ZnO nanoparticles at 500 ° C were displayed on a special plate and subjected to XRD analysis.

The scatterpieces are observed in 2θ respectively corresponding to the pages (100) ،(002) ،(101) ،(102)،(110)،(103) ،(200) and (112) are. All of these diffraction patterns were correctly attributed to the hexagonal structure of zinc nanoxide. The presence of plates (100), (002) and (101) in the XRD pattern indicates the formation of high-purity ZnO nanoparticles.

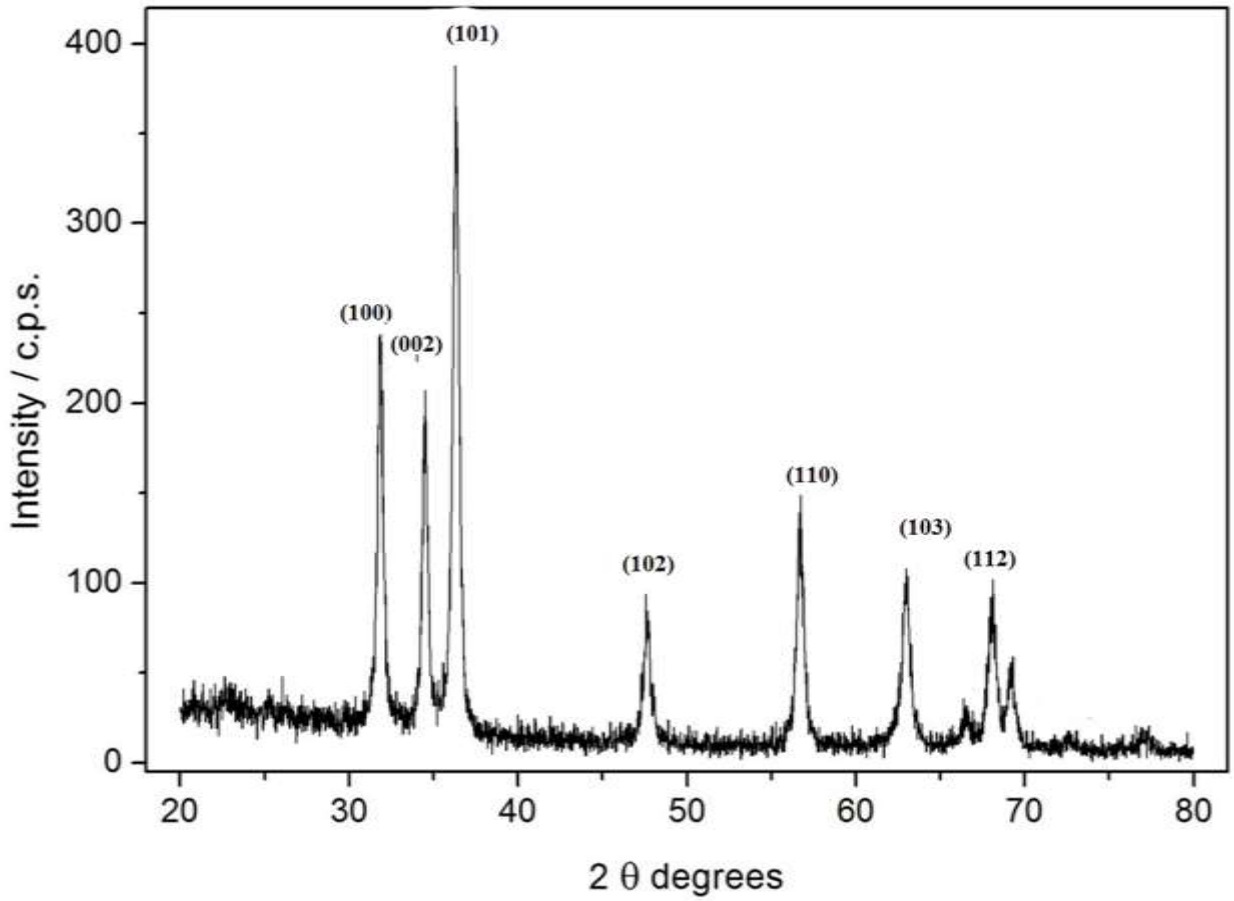


Figure 4-2-X-ray diffraction spectrum diagram of zinc oxide nanoparticles

After ensuring the synthesis of zinc oxide nanoparticles and the preparation of carbon electrodes modified by nanoparticles , oxidation –reduction reactions were examined by the voltmeter . To this end the optimal test conditions were first determined

3-2-examination of the effect of PH on the reactions carried out

To check the cyclic voltameter, 15 ml of cadmium nitrate solution, 10 ml of potassium nitrate was poured into the tuberculosis as an auxiliary electrolyte to increase the conductivity of the solution and a few drops of buffer solution. The reference electrode, working electrode and auxiliary electrode were used, and then in the range from zero to 2 volts, the rubber was started. It should be noted

that the cyclic voltmeter was astronomed at PH 4 to 10. As shown in Figure 4-3, at pH=8, the highest current intensity was created by oxidation and cadmium reduction, and was used as an excuse to continue. Figure 4-3 shows the effect of pH on the intensity of the current produced.

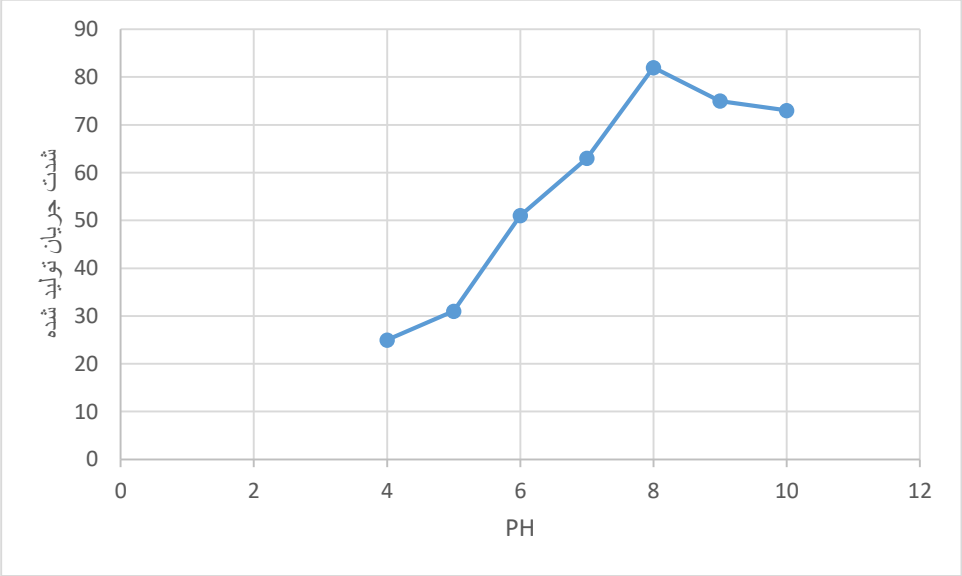


Figure 4-3 - effect of the pH of the environment on the intensity of the current produced

3-3-check the amount of nanoparticles added to the carbon paste

After the calculations were made , three times and each time with a weight percentage of 20-50 and 70 percent of the nanoparticles were added to the carbon paste and silicon oil respectively. The adhesion of the dough was acceptable and placed inside the corresponding sorghum. Reference and auxiliary electrodes and all test conditions were carried out equally. The results are visible in Figure 4-4.

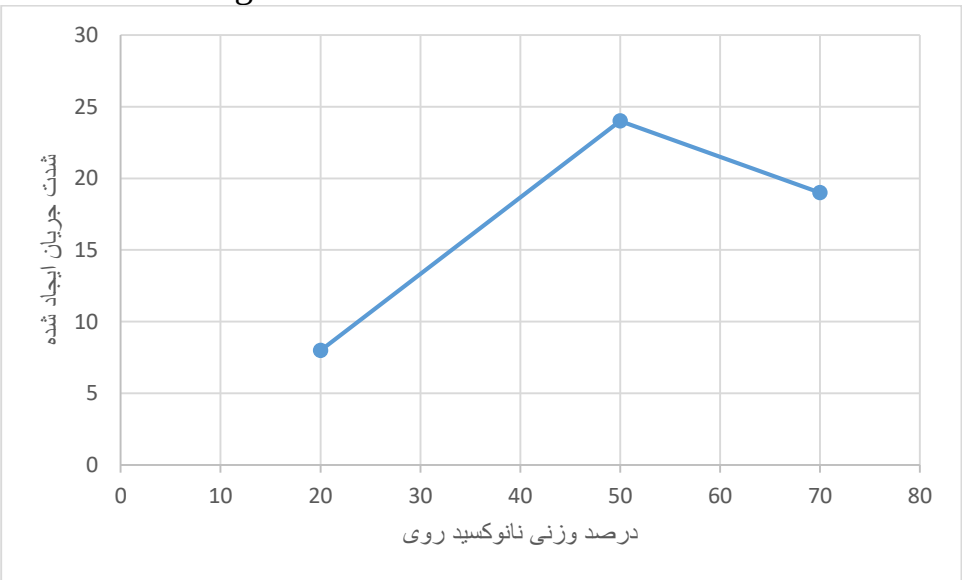


Figure 4-4-effect of the amount of nanoparticles added on the intensity of the current produced

As deduced from figure 4-4, the excess addition of the nanoparticle reduces efficiency and reduces flow intensity .

After determining the optimal test conditions, the electrode made in the laboratory was compared to the standard carbon electrode. The results show that the electrode modified by zinc nanoxide intensifies the oxidation and reduction reactions and the amount of current it produces in cyclic voltmeters exceeds the standard electrode of the device.

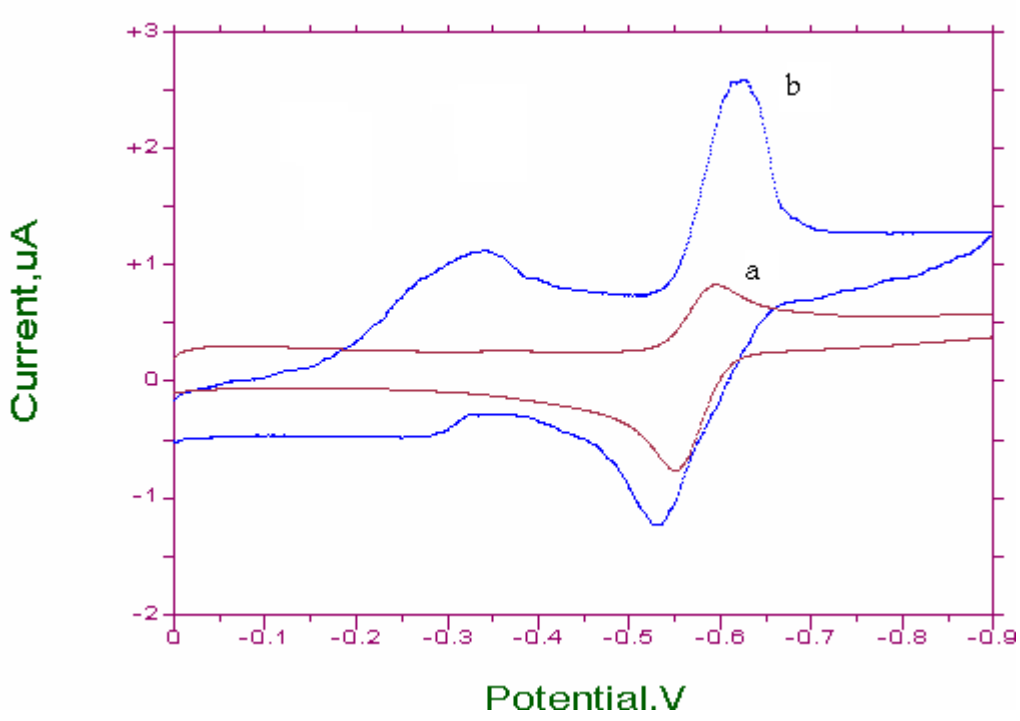


Figure 4-5 cyclic voltamogram of the working electrode in a solution of cadmium ions

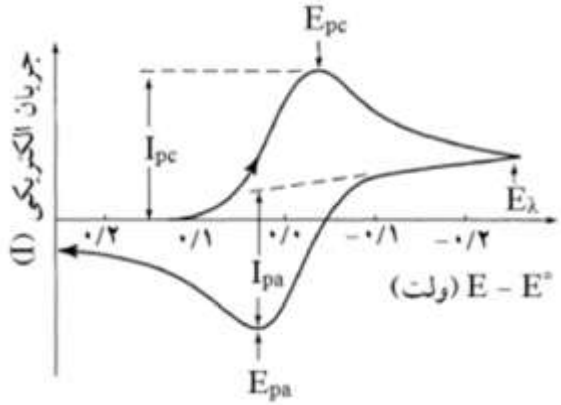
As shown in Figure 4-5, graph a is the current intensity generated during the oxidation reaction-the reduction of cadmium ions by the standard carbon electrode, and graph b is the current intensity generated by the electrode modified by zinc oxide nanoparticles (19). The half-wave is related to the half-reactions of cadmium oxidation and the half-wave is related to the reduction of cadmium ions.

During a cyclic voltmeter (CV), the potential is programmed from the initial value (Ei), but at the end of its linear rob, the direction of the potential dynamics is reversed and stopped at the initial value (Ei), or it may start at another potential. The potential in which the direction of the rubber is reversed is known as the Switch potential (Eλ). Almost generally, the dynamic velocity between Ei and Eλ is the same value between Eλ and Ei. The values of the speed of scanningرفت ν Andبرگشت ν always with positive numbers can be written. In the figure, the voltamogram for a simple redox couple is shown in the soluble phase. Such a diagram is known as a cyclic voltamogram (CV.(

Like other voltametric methods, the amount of electric current is proportional to the concentration. Therefore, being equal

IP back and forth implies the quantitative recovery of the substance participating in the electrochemical reaction, which follows the rules of Faraday. At the end of the cyclic voltamogram, when the potential reaches Ei, there is still a small amount of electric current, indicating that a small amount of matter has not yet been reduced and remains next to the electrode. If the applied potential to the electrode is much more negative than Ei, this partial residual current will also reach zero. In cyclic voltamograms, peak potential is called Ep. So the peak cathode potential is Epc and the peak Andy potential is Epa. (20)

$$E^{\circ} = 2/(E_{pa} + E_{pc})$$



In the study, the starting potential is zero and the Switch potential is 1 Volt, and the maximum current intensity is 5/2 microamps , which is significantly higher than the current intensity created by the standard electrode(approximately 5/0 microamps). Spikes (brain) caused by oxidation and reduction of cadmium

4-Conclusion

Simple and quick analysis of cadmium ions in environmental and biological samples , due to the extreme toxicity of this heavy metal is of great importance.

Cyclic voltmetry can be used to provide appropriate qualitative information about electrochemical processes under various conditions, such as the presence of intermediates in oxidation-reduction reactions and the reversibility of a reaction. In the electrochemical results of the cyclic voltametric method, it was found that the oxidation reactions were performed and the cadmium ions became the most oxidized number .

And then in the return cycle, the action of reduction happened . If the cycles are completely symmetrical, the analysis does not change in nature during the voltmetry, and this is another advantage of this method. The results of the cyclic voltametric technology showed that zinc oxide nanoparticles used in the electrode had a significant impact on improving electrochemical results of the electrode in the study of the electrochemical behavior of cadmium ions. The

addition of the nanoparticle in question increases the Andy current and cathode current relative to the carbon paste electrode without surface modification, and the density of the current obtained on the surface of this electrode with the sample of the electrode without surface modification, indicates the very good efficiency of this electrode to examine the oxidation - reduction of metal ions , and in particular , cadmium ions in the aquatic environment .

Cadmium is widely used in various industrial work environments such as electroplating, metallurgy and procurement of nickel-cadmium batteries. The use of cadmium can cause significant damage to living organisms . Therefore, it is necessary to track the level of cadmium concentration using fast, simple, sensitive, selective and efficient analytical methods . Carbon paste electrodes belong to a certain group of heterogeneous carbon electrodes. These electrodes are mainly used for voltametric measurements. However, carbon paste-based sensors can also be used in coulometry. The study concluded that adding a small amount of zinc oxide nanoparticles increases the sensitivity and efficiency of the carbon paste electrode and will be easier to measure metal elements. This modified electrode can be used as a sensor to measure cadmium in water.

Suggestions

Chemical electrode modification by other nanoparticles
Determining the sensitivity of the electrode made in this study to other ions
Determination of the concentration of elements using the intensity of the obtained current

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