فحص وإزالة المستويات الندرة لأيون النحاس الاحادي في العينات المائية بواسطة مادة ماصة نانوية

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الملخص

في هذا البحث نخلص إلى مقدار كمية التتبع وإزالة أيونات النحاس (I) في عينات مائية بواسطة أكسيد النيكل من خلال تعديل هيكل النانويوذلك من أجل تحسين أداء الاستخراج والتركيز المسبق بايستخدم. إجراء زيادة كثافة الأيونات في المحلول بطريقة مطياف الامتصاص الذري للهب. تم تحسين المعلمات الفعالة في الاستخراج مثل: تأثير الأس الهيدروجيني ، وكمية المذيب ، ووقت الاستخراج وتأثير الكاتيونات الآخرى. تم العثور على عامل التركيز 36 وتم العثور على طريقة للحد من الكشف إلى 1.77 ملغم إل-1. الانحراف المعياري النسبي هو 0.75٪ (rsd٪). كانت بيانات تساوي درجة حرارة توازن الامتزاز لكل من أيونات0(Cu^{1+}) أيونات متسقة مع فرونديلش متساوي الحرارة. تتميز الطريقة المقترحة بميزات مثل الدقة العالية ، وحد الكشف المنخفض ، والاسترداد الجيد ، والفصل السريع ، وعملية اقتصادية وفعالة من حيث التكلفة ، وقد تم استخدامها بنجاح لقياس كميات ضئيلة من ثاني أكسيد الكربون أيونات (Cu^{1+}) في عينات المياه الحقيقية.

كلمات مفتاحية : أكسيد النيكل تعديل هيكل نانو ، لهب امتصاص الذري مطياف(فاس) ، النحاس (1).

Examination and removal of trace levels of copper II ion in aqueous samples by a nanosorbent Abstract method

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Summary

In this research to amounting of the trace amount and removal of Cu (I) ions in aqueos Samples by nickel Oxide modified nano structure which in order to improve the performance of extraction and preconcentration was used. Amounting of the ions density in solution was performed by the method of flame atomic absorption spectrometry. The effective parameters on extraction such as: effect of pH, the amount and eluent solvent, time of extraction and effect of other cation were optimized. Concentrate factor was found 36 and LOD method of limit of detection was found to 1.77µg.L^{-1}. the relative standard deviation is 0.75% (RSD%).The adsorption equilibrium isotherm data for both Cu^{1+} ions were consistent with Freundlich isotherm. The proposed method has features such as high accuracy, low detection limit, good recovery, fast separation, an economical and cost-effective process, and has been successfully used to measure trace amounts of Cu^{1+} ions in real water samples.

Keywords: nickel Oxide modified nano structure, Flame atomic absorption

spectrometry (FAAS), Cu(I).

Chapter one

1-1-the introduction

Due to the rapid development of various industries (including mining and smelting of metals , energy and fuel production, fertilizer and pesticide industry, metallurgy, iron and steel industries, electrical electrolysis, leathering, photography, production of electrical household appliances, aerospace and Atomic Energy Industries), alarming amounts of toxic heavy metals along with waste from these industries have been released directly into the environment, which has endangered natural ecosystems and human health, especially in developing countries. Despite more stringent and strict rules in this regard, today heavy metals, as environmentally priority pollutants, are becoming one of the most serious environmental problems. [2[

Detecting and cleaning up toxic pollutants, especially heavy metal ions, which are highly dangerous to living organisms and the environment, is key to protecting the environment.

Biological samples or samples taken from natural resources often contain highly complex compounds that interfere with the decomposition process as disruptors, or the amounts of pollutant compounds are so small that they may not be measurable with the most powerful detection systems or incompatible with decomposition processes .

As it turns out, some dangerous pollutants have harmful biological effects in the same small amounts .It is therefore necessary to examine and develop highly sensitive and proprietary methods to measure such amounts of pollutants in the sample accurately and with high accuracy. Over the past few decades, there has been a significant growth in the use of sample measurement techniques .Analytical devices such as chromatography, spectroscopy, microscopy, as well as sensors and micro tools have also been affected by these improvements .But despite advances in the construction of analytical tools, highly accurate and non-destructive measurements are still not possible in most cases .So to help improve existing methods, in most cases one or more steps of sample preparation are necessary [3 .[

Some common steps along with analysis processes that also include the sample preparation step are shown in the figure below

1-2-steps of the measurement process

Sample preparation in a decomposition process mainly involves the extraction phase, which leads to the thickening and separation of the desired species from the sample tissue .The choice of extraction method depends on the working conditions, sample type and extractor phase type .The recent attention of chemists to sample preparation methods has led to new reforms .Determining solutions to reduce solvent consumption, automating and measuring very small amounts and finding environmentally friendly methods are among the important goals of these corrective methods.

Despite extensive advances in measurement techniques, sample preparation and separation operations are often based on nineteenth-century technology such as socket and solvent extraction. The old methods are often costly and time-consuming and involve several steps that waste samples. In addition, these methods use large amounts of organic solvents that are harmful to the environment and are prohibited from being consumed under international contracts. It's also difficult to shrink and automate these methods, so it takes a long time from each analysis to prepare the sample.

Due to the very low concentration of pollutants and the complexity of the tissue of natural samples, the importance of the sample preparation stage is greater. Today, a variety of techniques have replaced classic methods that are either solvent-free or the volume of solvent consumed is so small that they can be considered part of solvent-free methods. Sample preparation methods can be classified into different categories based on the type of extractor phase. The evolutionary and gradual process in decomposition chemistry is towards simplifying and miniaturizing sample preparation as well as reducing organic solvent consumption. Therefore, several micro-extraction methods have been introduced to reduce the analysis stages, pre-concentrate the sample and improve the quality and sensitivity of the analysis methods [1.[

1-2-1-miniature mining goals

The benefits of miniaturization:

-Using smaller prototypes to break down very small amounts.

-Special or more selective in mining.

-Increased potential to automate the method.

Finding environmentally friendly methods that used less polluting chemicals and organic solvents.

1-3-separation and pre-condensation

Atomic absorption spectroscopy of graffiti furnace and induced plasma mass spectroscopy is one of the most sensitive techniques for determining a large number of elements with very low detection limits. Separation and pre-condensation methods are widely used to determine the effect of precious metal ions, these include solid phase extraction method [6-4] decay method [8-7] column extraction [10-9] electrode ion method [12-11] liquid-liquid extraction method [15-13] and cloud point extraction method [20-16 .[

1-4-the importance of measuring chemicals

Today, the role of decomposition chemistry in the identification and measurement of various materials obtained by industrial or natural methods is not hidden from anyone. The science of decomposition chemistry is defined as the art of determining the composition of the percentage of materials by the elements or compounds in which they are present. Also, the role of decomposition chemistry in measuring substances in living systems, especially in the bodies of organisms, plants and humans, is so clear that it does not seem necessary to mention its importance. Today, there are various methods and devices for quantitative measurement and analysis of materials. Separation, identification and measurement of various materials is the ultimate goal of the science of decomposition chemistry, which has long been considered. Now, with the advances and developments in this field of Analytical Science, various, fast and accurate methods have been proposed to identify, measure and separate materials. These efforts continue to reform existing methods and devices and to invent new methods and devices. Traditional and old methods of chemical decomposition are mostly time-consuming, high-cost, or low-precision. To the extent that many of them are obsolete today and have given way to modern methods and mainly a device that not only saves time and money, but is very accurate. The decomposition of a particular species in a specimen that has complex tissue has always posed problems for materials decomposition experts in various disciplines. So in recent decades, a lot of work has been done to develop methods and devices that can make it possible to decompose a particular species with small amounts in the presence of other components in the sample, with great precision and sensitivity. Among these are the invention of methods and devices such as gas chromatography, high-performance liquid chromatography, absorption and diffusion and atomic fluorescence, spectrum and mass scoping and Ion electrodes. Each of these methods and devices has advantages and disadvantages that can lead to the selection of one of them in the analysis of a particular sample.

1-5-importance of sample preparation

Decomposition chemistry laboratories are under pressure to provide faster and more cost-effective decomposition methods. This responsibility in the laboratory is more about the sample preparation part. The sample preparation method should have the following characteristics such as: high repeatability, less technical skills, reduced consumption of organic solvents and the possibility of cleaner extractions to measure the device at higher speed and lower cost. The bulk of the sample decomposition time is spent preparing it, so the need to improve the sample preparation techniques is felt more than ever. A study shows that more than 60 percent of the analysis time is spent on sample preparation, while only 7 percent of this time is spent on sample collection and data collection. The popularity and application of solid-phase extraction (SPE) is increasing at a rapid pace. Solid-phase extraction is easily automated and generally more efficient. The particles used in SPE are not pollutants, and the amount of liquid solvents used is significantly less than the extraction of liquid - liquid.

1-6-solid phase extraction

Solid-phase extraction (SPE) is a sample preparation method used to thicken and purify the sample. In solid-phase extraction, analytes are transferred from a liquid phase to a solid phase containing small, porous particles from silica that are bound to an organic phase or an organic polymer. This is a non - continuous method in which the extracting solid is well mixed with a liquid sample solution and in many cases is used as a suitable substitute for liquid-liquid extraction. Materials extracted by solid particles can be separated by washing by a suitable solvent, usually the volume of solvent required for thorough washing of the analytes is much less than the volume of the original sample. This is how a condensed sample of the analytics is obtained. Initially, solid-phase extraction was based on the use of gravity such as xad resins used to analyze drugs. The current solid phase columns are a type of polypropylene or polyethylene that is filled by fillers with different operating groups. The weight of the filler of these columns varies between 50 milligrams and 10 milligrams. In these systems, a liquid sample passes through the column and its analysis is condensed and purified. Usually, the sample solution can be passed through using positive pressure or vacuum creation. Then the analysis is slightly absorbed, and then the column is washed with the appropriate solvent and the sample is removed. So solid phase extraction is a form of numerical chromatography in which the dissolved substance is transferred into the solid phase by various mechanisms (the numerical term relates to the off/on mechanism in absorption and absorption). the purpose of solid phase extraction is to quantitatively transfer analyte from the solution to the solid phase and recycle it completely with a suitable solvent. [21] An image of the solid-phase extraction device is shown in the figure below.

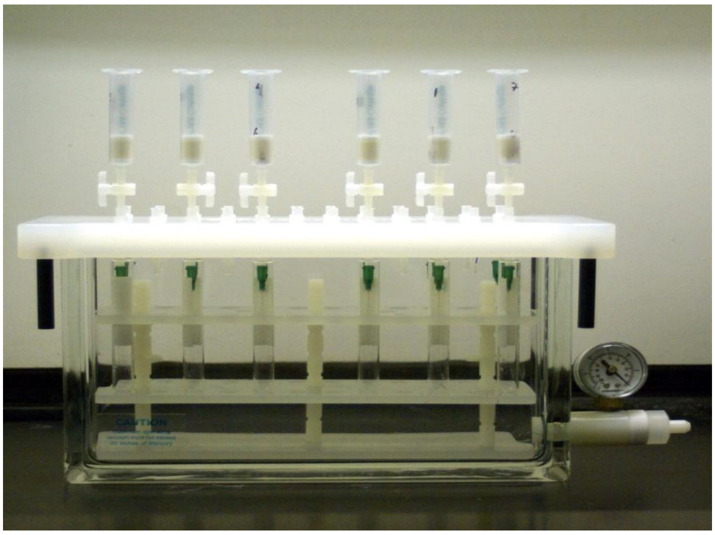


Figure 1-1 image of the solid phase extraction device

1-6-1-history of solid phase extraction

Solid-phase extraction is derived from conventional chromatography in which an absorbent medium is used to separate samples based on differences in balance with the absorbent medium.

The historical history of solid-phase extraction dates back to at least the early 1970s, when columns accumulated with xad resin particles were used to concentrate very small concentrations of organic pollutants in water. But-alumina and SDS were used several years before 1970 to thicken dissolved organic matter before the analysis was done.

In 1980, solid-phase manufacturing companies marketed a variety of filling materials with columns of various shapes. After this date, a combined attraction was introduced for drug analysis. New research is on solid-phase extraction towards the use of disks, microfibers and automation and many other products. This process continues to produce new solid-phase extraction products.

In 1950, Howard and Martin first published an article on what is now known as reverse-phase chromatography. They used a non-polar solvent instead of using a polar resident phase such as silica or calcium carbonate to absorb polar compounds and a polar solvent instead of using a non-polar resident phase to absorb non-polar compounds. They reacted the silica with diclero dimethyl Ceylon in order to correct the silica surface to create a nonpolar phase. They isolated high molecular mass fatty acids by aqueous solution of methanol as a moving phase and transition to a nonpolar resident phase that is N - octane saturated with methanol [22.[

In 1978, Waters introduced a cartridge called SEP-PAC to condense very small amounts of analyte by the reverse phase absorber C18.

Waters also developed a silica cartridge for normal solid-phase extraction. In 1979, analytics, now Varian, produced tubes called Jets - tubes from diatomaceous soil fillers of different purity. In addition, in the same year, the existing C18 gravity was produced in the form of a syringe, and this form of solid-phase extraction was widely used today. [23[

1-6-2-comparison of solid phase extraction with other methods

1-6-2-1-comparison of solid phase extraction with liquid-liquid extraction

The purpose of liquid-liquid extraction is to transfer the dissolved material from another liquid phase that is incompatible, and the dissolved material is mainly extracted from a more voluminous aqueous solution into an organic solvent with less volume. Usually, the extraction of the liquid - the decomposition liquid is carried out in a separating funnel, so that after the extraction is carried out, the separation of the two liquids is possible and the extracting liquid is heavier or lighter than water. The transfer process is balanced in the extraction of liquid.

One of the main problems with liquid extraction is the emulsion solution, which disappears very slowly or does not disappear at all. Although SPE, or solid-phase extraction, can also be done in a non-continuous equilibrium similar to what is used in liquid-liquid extraction. But the more common method is to use a small tube (column) or cartridge that is made up of accumulated solid particles; the liquid sample is completely in contact with solid particles during the passage of the column, which promptly balances and enables analyte condensation on the solid phase. Unlike non-continuous extraction, where dissolved materials have a single equilibrium between two phases, when solid phase extraction is done with a small column of solid particles, there will be several effective equilibrium. This is because the solved material is constantly encountering new particles as it passes through the column. Therefore, it is expected that the percentage of extraction in SPE columns is higher compared to the non-continuous liquid-liquid extraction. Usually, for final measurement, the transfer of analytes from solid particles to liquid phase is necessary. The chemistry of this stage will depend on the type of analytes and extractor solids used. [24[

1-6-2-1-1 comparison between SPE and HPLC

In liquid chromatography, the purpose of separating the different components of the sample from each other is based on the different velocities of their movement in the column, but in solid phase extraction, the purpose of condensing and collecting the species analyzed on the column and then washing by a suitable solvent is [25.[

1-6-3-types of solid phase

It is used in methods of separation and extraction of various compounds such as porous polymers, alumina, zirconia, diatomaceous soil, activated carbon, cellulose and various types of silicates as a solid phase. Alumina and activated carbon are most commonly used due to their potential and silicates due to their low cost and adequate physical and chemical strength.

1-6-3-1-activated carbon

There are many forms of carbon, one of which is activated carbon. It has privileges such as high thermal stability and high resistance to light, porous and strong building, high mechanical stability, high surface to volume ratio and achieving high purity, and has a high capacity to attract different species, making it suitable for separating ions and organic species from the aquatic environment. On the other hand, due to the oxygenated groups on the activated carbon surface, it is also possible to absorb metal ions. Activated carbon can be produced from various materials such as lycanite, coal and polymers, and any other carbonate material. Activated Carbon is also made from rice bran, shaftalo kernels, apricots, almond shells and vegetables.

The surface characteristics, the operating groups present in the surface, the size of the surface, the size and distribution of cavities in the active carbon vary depending on the type of raw material. The properties of activated carbon largely depend on the methods and conditions of activation [26.[

1-6-3-2-active aluminum

Alumina exists in two forms-alumina and-alumina. - Alumina has a positive charge on the surface and effectively absorbs negative charge species such as sodium dodecyl (SDS)2 at 6-1=pH. It means that about 250 milligrams of SDS is absorbed completely on 5/1 grams of alumina, while alumina has very little desire to absorb SDS because of its chemical nature, which means that its surface is neutral or ineffective. Alumina is activated chemically using mineral acids [27.[

1-6-4-applications of solid phase extraction

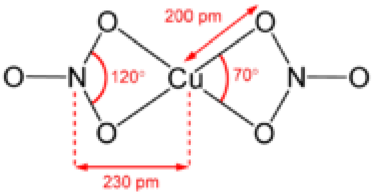
Bangsten and his colleagues are examples of this, published in 1995. They extracted pesticides from the water of a river containing 62 pesticides of different polarity; the average yield was about 72 to 81 percent. Also mentioned is the work of kaspafer and his colleagues, published in 1993. They extracted tin triphenyl in solid-phase environmental samples and then measured it with spectroscopy. In the above work, the volume was more than one liter and the detection limit was 0.7 milligrams per liter. This method can also achieve a density factor above 100 [28].

Chapter Two

Materials and methods

2-**Consumable**

in this study, the following materials for the tests has been used, which nickel nitrate, copper, ethanol and Tri ethylene Tetra ‹oxide-include: nano .Amine and nitric acid



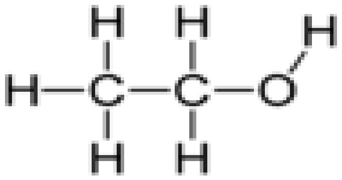
Copper nitrate

physical and chemical characteristics of nitrate, copper 1-Table 3

place the of production of	**boiling temperature of**	**melting temperature**	**‘ ‘density**	**mass, molar**	**Molecular formula**

merck	C°256	C°170	g/cm^3 3/05	g/mol 187/56	$Cu(NO_3)_2$

ethanol



physical and chemical characteristics of ethanol 2-Table 3

the place of production of	**boiling temperature of**	**melting temperature**	**‘ ‘density**	**mass, molar**	**Molecular formula**
merck	C°78/37	C°114	g/cm^3 0/789	g/mol 46/07	C_2H_6O

s physical and chemical 3-Table 3

‘ Location, Production	**shape, ‘ appearance**	**melting temperature**	**‘ ‘density**	**mass, molar**	**Molecular formula**
mer, c,k	liquid, ‘transparent	C°-35	g/cm^3 0/97	g/mol 146/23	$_2]_2NH_2CH_2CH$ NH_2 [CH

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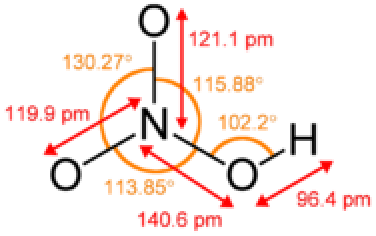


Table 3-3 physical and chemical characteristics of triethylene tetraamine

location, ، production of	**shape, ، appearance**	**melting temperature**	**، ،density**	**mass, molar**	**Molecular formula**
merck	colorless liquid	C°42	g/cm^3 1/51	g/mol 63/01	HNO_3

Fixed formation of complex copper ligands, organic

fixed formation of complex copper ligands, organic CHART(1-5)

ligand organic the ،	**Log K_1**	**Log K_2**
Ammonia(NH_3)	4/31	7/98
Ethylenediamine ($C_2H_8N_2$)	10/67	20/00
1,2-Diaminocyclohexane-N,N,N',N'-tetraacetic acid ($C_{18}H_{21}N_3O_8S$)	21/95	-
Ethylenediamine-N,N,N',N'-tetraacetic acid ($C_{18}H_{21}N_3O_8S$)	18/7	-
N'-(2-Hydroxyethyl) ethylen diamine - N,N,N' -triacetic acid ($C_6H_{16}O_2$, N_2)	17/40	-
Triethylenetetramine ($C_6H_{18}N_4$)	20/4	-
1-(2-Pyridylazo)-2-naphtol(PAN) ($C_{15}H_{11}N_3O$)	16	-
Propylene-1,2-diamine ($C_3H_{10}N_2$)	6/41	20/06
Pyridine (C_5H_5N)	2/59	4/33
Pyridine-2,6-dicarboxylic acid($C_7H_5NO_4$	9/14	16/52
EDTA($C_{10}H_{16}N_2O_8$)	18/80	-
Acetate (CH_3COO^-)	2/22	1/41

The stability constant is usually denoted by the β sign and is obtained by multiplying the constant values of the stage equilibrium (table 3-5). Internal factors affecting the stability constant depend on the nature of the central atom and the nature of the ligand. The nature of the central atom depends on the oxidation number of the central atom, the baralectricity of the central atom, and the effective charge of the nucleus, and the nature of the ligand depends on its play and volumetric properties. External factors affecting the stability of complexes can be called temperature, pressure, Ionic and solvent power. As can be seen, amino groups with Cu1+ form ideal complexes and have an acceptable stability [104]

2-1- devices and equipment needed

Table 3-6 devices used in testing**t**

model	**Device**
HR20V E. Baloon	shakers
, Mi 180 Bench meter	pH,km
PB990	samples
M. T. electronic Balance	Libra
VEGA/TE scan-XMU VEGA/TE scan-LMU	, SEM,
Bomem MB-series	FT-IR
BSEN 1392 5-1:2008	, XRD,

Table 3-7 conditions of copper ion measurement, flame atomic absorption spectroscopy device

analysis, linear	**bandwidth**	**the coefficient of the filter**	**flow ‹lamp**	**the limit of detection**	**Sensitivity**
nm324/7	nm0/4	1/0	ma5/0	mg/L 0/004	mg/L0/03

2-3- working methods

1-4-3preparation of solutions and standards

Cu1 + solution with ppm1000 concentration: 33/0 grams of copper nitrate dissolved and 100 TAML volume. The required solutions were prepared by diluting the mother solution. Sequential dilution of ppm1000 solution produced solutions with concentrations (ppm100, 50, 10, 2) and ppm10 solutions with concentrations (ppm 10 ،5 ،3 ،1 ،5/0) it was prepared as standard.

2-3-1- How to make nickel nanoxide

For this purpose, it has prepared the following 3 solutions.

Human a: dissolve 0.46 grams of nickel chloride in 20 ml of distilled water.

Human B: dissolve 2 grams of CTAB in 200 cc of distilled water.

Human C: dissolve 3 grams of NaHCO3 in 20 ml of distilled water.

Then mankind beat a Together for 30 minutes, and then mankind added B drops to it. After an hour of stirring, the human C was added drip by drop, after an hour of stirring, the sediment was separated on the funnel, and then washed with distilled water and ethanol. It was then dried in a 100 degree Avon for 3 hours, after which it was placed in the oven at 600 degrees for 3-5/2 hours to obtain the deposition of nickel nanoxide [105]. The CTAB here plays a molecular role and is used to stabilize the structure of nickel oxide and shrink the dimensions of nickel oxide particles, and because it is an organic substance, it burns and disappears during the reaction.

The mechanism of formation of nickel nanoxide by deposition method is as follows:

$$NiCl2 + NaHCO3 \rightarrow NiCO3 + NaCl + HCl$$

(After the furnace) $NiCO3 \rightarrow NiO + CO2$

The initial testing, the extraction and recovery of Cu^{1+} to determine the ligand fit

as nickel oxide - extraction and recovery of ions of copper by means of nano :befollows: mL 50 of solution ppm that in 2 pH compared to 2/5 Cu^{1+}set have been prepared and the amount of g) and nickel oxide Nano 0/05ppm (100mLprinciple for 20 -the ligand to which it was added. Mixed H ، 2 ature of percussionoflocation logging, and with the speed of 150 and a temper degrees Celsius 25 within the shakers do , and then the mixture can the concentration of centrifuged, andCu^{1+}in it by means of atomic absorption Once this experiment without adding a .spectrometry, flame, determine the We .weligand do

Parameters affecting the extraction and recovery ofCu^{1+}

to find the optimal conditions to achieve the highest efficiency of extraction and recovery of the effect of various factors including, the effect ofthe pH of thesolution, etc. solution , bathroom suits, the volume of a solution of .washing, extraction time, and..... were investigated

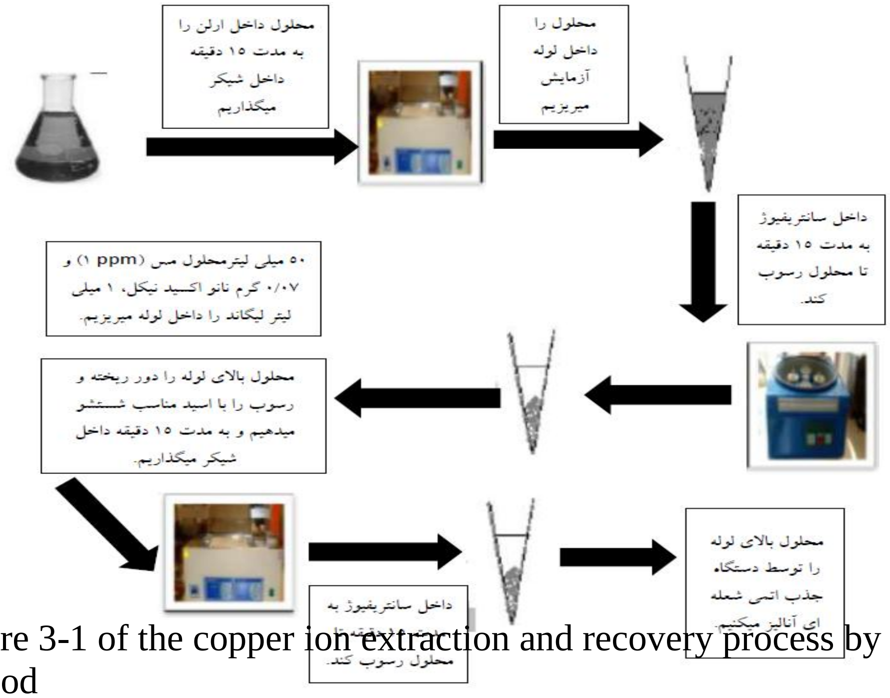


Figure 3-1 of the copper ion extraction and recovery process by the proposed method

2-3-3- effect of PH on Cu1 extraction and recovery

To examine the effect of pH on Cu^1 + ion absorption, a number of ppm0/2 solutions with a volume of 50 ml were first prepared compared to Cu^1+, which is the effect of aqueous solution on Cu^1+ ion recovery in pH. 2 ،5/2 ،3 ،4 ،5 ،6 ، 10 it was investigated. Buffer was used to set the PH. The method used to regulate the pH of the solution was to pour ppm 2 solutions into humans and float the pH meter electrode in it and add a very suitable volume of buffer to the pH at the desired value (2 ،5/2 ،3 ،4 ،5 ،6 ،10) we adjust. After adjusting the pH of the solution, g05/0 of nanoxide nickel absorbent was added to each solution and placed in the shaker for 20 minutes, then centrifuged the above mixture and removed the solution above the test tube and determined the concentration of Cu1+ in it by atomic absorption spectrometry of the flame.

2-3-4- effect of absorbent value for $Cu+^1$ recovery

First, he made 7 ppm 0/1 solutions with a volume of 50 ml compared to Cu+ and poured them into 7 arlens and adjusted the solutions at PH, 5 (optimal pH) and a different amount of nickel nanoxide (g 01/0 ،05/0 ،07/0 ،09/0 ،11/0 ، 15/0 ،2/0) we added it and put it in the shaker for 20 minutes, and then centrifuged the above mixtures and determined the top solution of the test tube by atomic absorption spectrometry of the flame .

7-4-3effect of stirring time on Cu^1 ion extraction and recovery +

To do this, first 5 balloons were removed and inside each 5/0 ml of PPM solution 100 copper nitrates along with mL 1 buffer 5 were poured and brought to volume, then 0.07 grams of absorbent were added to them and at times (25 ،15 ،10 ،6 ،2) the minute was inserted into the shaker, then centrifuged, and the absorption of the zinc solution was determined by the atomic absorption spectrometry of the flame.

8-4-3effect of different types of detergents for Cu^{1} ion recovery +

First, 6 ppm0/1 Solutions were made to the volume of mL50 relative to Cu^{1}+ and poured into 6 arlens and adjusted the solutions at PH, 5 (optimal pH) and added the value of g 07/0 of nickel nanoxide and placed in the shaker for 15 minutes and then centrifuged the above mixtures. We put aside the top solution and pour the resulting sediment into the erlenes and add mL7 from the following detergents (M1/0) 3HNO, (M 1) 3HNO, (M 3) 3hno, (M 1/0) NaOH, (M 1/0) 4SO2H, (M1)4SO2H and then we put it in the shaker machine for 20 minutes, then we centrifuge the mixture and concentrate the Cu^{1}+ we determined the top solution of the test tube by the atomic absorption spectrometry of the flame.

2-3-5- optimizing the volume of detergent solvent to recover Cu^{1} ions

In order to select the appropriate solvent volume for Ion recovery Cu^{1}+ was first poured into 5 small arlens 50 ml of ppm1 solution compared to Cu^{1}+, which was set at PH, 5, and added to each g 07/0 of nickel nanoxide, put into the shaker for 15 minutes, then centrifuged the mixture, emptied the zinc solution, poured the sediments into 5 arlens and into each of the arlens volumes (mL 5, 7 9, 11 and 13) add nitric acid M1 (optimal detergent) and put it in the shaker for 20 minutes, then centrifuge the mixture, and finally determine the concentration of Cu^{1}+ ion in the top solution of the centrifuge tube by the atomic absorption spectrometry of the flame We did.

10-4-3effect of sample solution volume (limit volume determination (

After finding the best pH value of the sample solution and the appropriate detergent solvent for thoroughly washing the copper ion (II) from the absorbent, the maximum volume of the aqueous solution including the copper ion (II) must be specified. To examine the effect of the sample solution Volume, 6 ppm 1 copper nitrate solutions were prepared under optimal conditions other than PH adjustment, nothing was added to the first solution, but to subsequent solutions 350, 200, 150, 100, 50 ml of distilled water was added and the PH was adjusted respectively, then stirred into the shaker for 20 minutes (optimal time), then centrifuged the mixture and finally washed with 7 ml of nitric acid M1 and re-adjusted for 20 minutes it was placed inside the shaker.we then centrifuged the resulting mixture and then determined the concentration of copper ions in the solution above the centrifugal tube by atomic absorption spectrometry of the flame.

11-4-3determination of the standard deviation of the witness (Sb(

First, 4 solutions were made with optimal conditions, then the buffer added 5 and 07/0 grams of absorbent to it was brought to volume by PH meter, set the pH at a limit of 5-9/4 and stirred into the shaker and centrifuged. the top solution was discarded and added to the CC absorbent 7 nitric acid M1 and put back into the shaker. we centrifuge the mixture and measure the absorption flame by atomic absorption spectrometry.

12-4-3determination of accuracy and repeatability of the method (%RSD(

To determine the accuracy, first 4 solutions were made with optimal conditions, then the buffer added 5 and 07/0 grams of absorbent and the mother solution to it was brought to volume by pH meter, set the pH at a limit of 5-9/4 and stirred into the shaker and centrifuged. the top solution was discarded and added to the absorbent cc 7 nitric acid M1 and put back into the shaker.we will

.

1-2-6- linear range and calibration chart

To determine the linear range, first into 8 balloons, 50 milliliters of ppb solutions .800 ،500 ،200 ،100 ،80 ،40 ،20 ،10) adjusted to Cu^1+ in , pH5-9/4, poured and added to each g 07/0 of nickel nanoxide and stirred into the shaker for 20 minutes, then centrifuged the mixture and finally washed with ML 7 nitric acid M 1 and put back into the shaker for 20 minutes.finally, centrifuged the mixture and absorbed the Cu^1+ ion in the solution above the centrifugal tube by the atomic absorption spectrometry of the flame was determined .

1-2-7- disturbances on Cu^1 ion extraction

To examine the effect of interference of other ions on Cu^1+ ion extraction, a number of ppm1 solutions were prepared compared to Cu^1+ in PH, 5 adjusted to volume (limit volume), and a certain amount of various intrusive factors and ions were added to the initial solution, and then G 07/0 of nickel nanoxide was added to each solution, and in 15 minutes it was stirred into the shaker and centrifuged, and finally with nitric acid M 1 washed and put back in the shaker for 20 minutes then we determined the concentration of Cu^1+ions in the solution above the centrifugal Tube by the atomic absorption spectrometry of the flame.

1-2-8- application to real samples

After the extraction method was completed with nanoxide and optimal conditions were found for it, several real water samples were analyzed. Real examples studied include: drinking water, well water and fish farming water. First, 6 100 ml balloons were prepared for sampling for each of the samples. Inside the bottles were washed with ordinary water and distilled water, after the balloons had completely dried, they were adequately labeled. It was used to remove water samples from previously washed dry and clean human beings. To start the analysis of samples, colloidal and suspended particles must be taken, so the samples must be passed through a 45/0 µm strainer, then poured into 3 bottles of drinking water, well water and fish farming water, respectively, along with 2 ml of 5 and 07/0 grams of absorbent buffer, and another 3 bottles of 5/0 ml of PPB 50 mother solution are added. The mixture was centrifuged for 15 minutes and finally washed with nitric acid M1 and put back in the shaker for 20 minutes. finally, after centrifuging the mixture, the absorption of copper ions in a sub-smooth solution was determined by the atomic absorption spectrometry of the flame .

1-2-8-determination of the equilibrium isotherm for copper ions

Absorption isotherms for copper ions were studied in the concentration range of 200-00/2 mg / L and at 9/4= pH and with 07/0 g of absorbent and the volume of the solution equal to 300 ml and a time of 25 minutes.

-determination of the kinetics of the copper ion reaction

In order to study surface absorption Kinetics, when the concentration of copper ion was equal to 2 mg / l, 9/4=pH and the absorbent value was 070/0 G and the volume of the solution was 300 ml, the remaining concentration of copper ion in the solution was measured in a time frame of 25-1 minutes.

-determination of reaction thermodynamics for copper ions

Thermodynamic absorption studies, where the concentration of copper ion was equal to 0.2 mg / l, 9/4=pH and the absorbent value was 0.070 G and the volume of the solution was 300 ml, were carried out at temperatures(318,308,298,288) Kelvin degrees to investigate the effect of temperature on the efficiency of copper ion removal.

Chapter Three

Data review And Results

3-Data review And Results

This section is dedicated to the analysis of research experiments. Results obtained in the experimental chapter, calibration curve and parameters affecting extraction (such as pH, time,temperature effect and... Copper ion (II) is discussed by nickel nanoxide and, while providing scientific explanation, a general conclusion has been drawn from this research .

2-4tests performed to confirm copper absorption by nickel nanoxide

-1 FT-IR

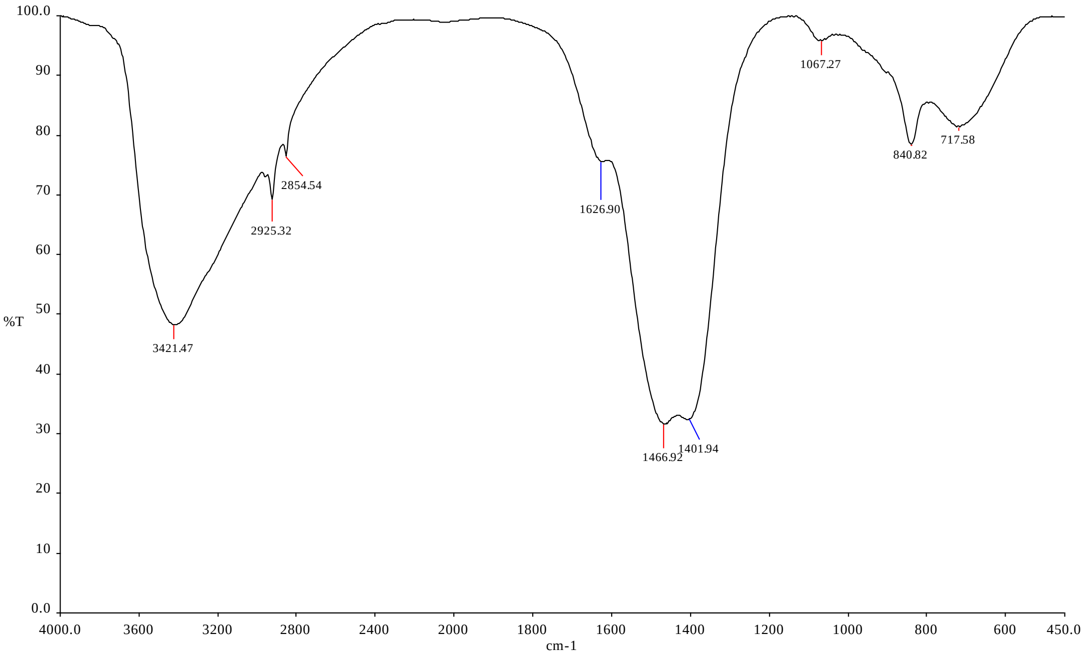
-2 XRD

-3 SEM

-4 TGA

1-2-4review of the results of the FT-IR spectrum

Figure 4-1 shows the Fourier transform infrared spectrum of nickel nanoxide.



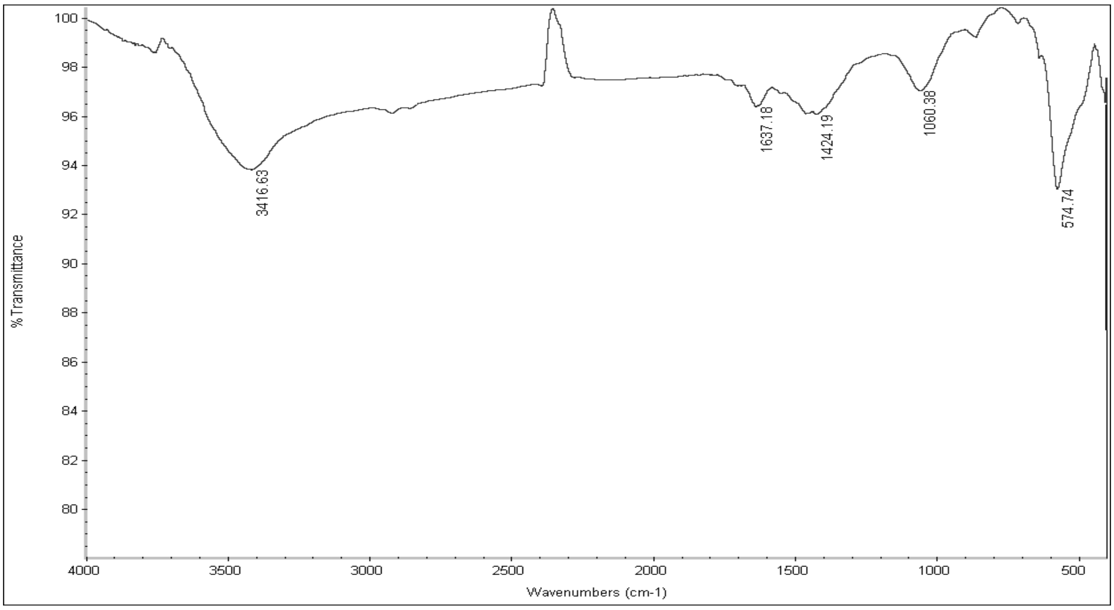


Figure 4-1 infrared spectrum Fourier conversion of nickel nanoxide before absorption

In the IR spectrum, nickel nanoxide is observed before peak absorption in the cm-1 1620 region, indicating that the OH molecule is trapped between Ni and O. And the peak observed in the cm-1 3421 and cm-1 2925 regions is related to the OH Factor Group, which can be attributed to the water molecules absorbed by the NiO .

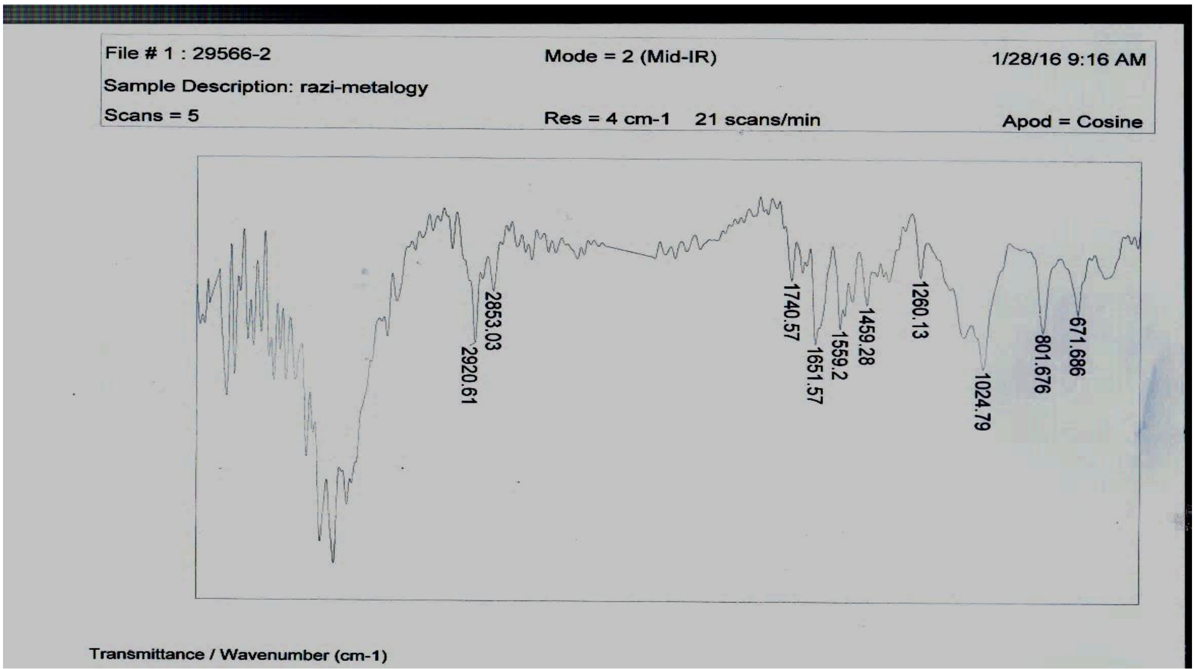

File # 1 : 29566-2
Mode = 2 (Mid-IR)
1/28/16 9:16 AM
Sample Description: razi-metalogy
Scans = 5
Res = 4 cm-1 21 scans/min
Apod = Cosine

Figure 4-2 infrared spectrum Fourier conversion of nickel nanoxide after absorption

Figure 4-2 also shows a new peak in the cm-1 1620 area, representing copper metal, and the cm-1 1424 area showing nitrates.

Examination of the results of the XRD spectrum

Here the Scherer equation was used to determine the size of the nickel :nanoxide. This equation is as follows

(1-4($\tau=K\lambda/(\beta \cos\theta)$

κ: average size of crystallite (in nanometers), K : coefficient of crystal shape (usually considered 9/0), λ : wavelength of the X-ray-producing tube (in .nanometers), β : peak width, θ : diffraction angle

The following figure shows the nanoxide nickel diffraction pattern, which can be seen as a peak diffraction of 5/26 = iodine.

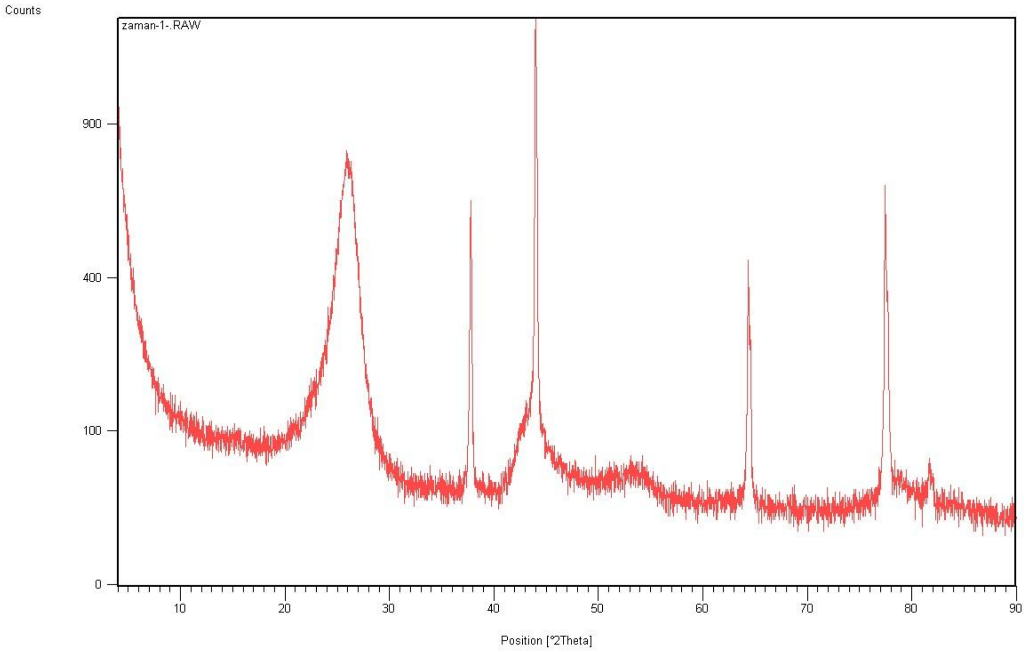


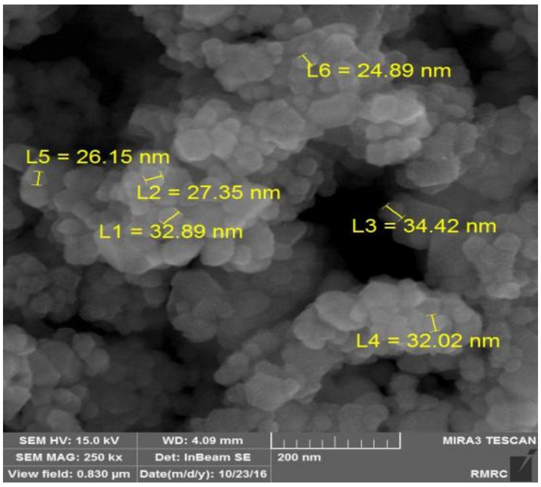
Figure 4-7 images of the XRD spectrum of nickel nanoxide before absorption

The XRD spectrum of this combination of three very high intensity peaks is related to nickel nanoxide, which represents the strongest peak in the area of 34/43 = ϴ and a very weak peak in the area of 43/79 degrees, which respectively has a very sharp and small peak.

Figure 4-8 images of the XRD spectrum of nickel nanoxide after absorption

review of the results of the SEM images 3-2-4

The figure below shows the SEM of nickel nanoxide.



Total 4-9 SEM images related to nickel nanoxide before absorption

And also the figure after absorbing the SEM image shows the metal on the nickel nanoxide, which can be concluded from the above images that the thickness of the plates has increased.

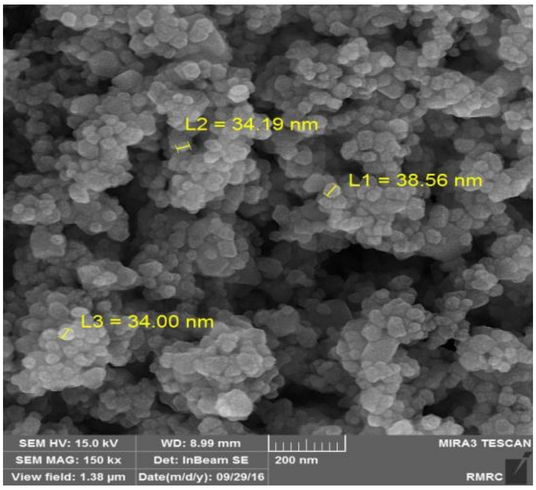
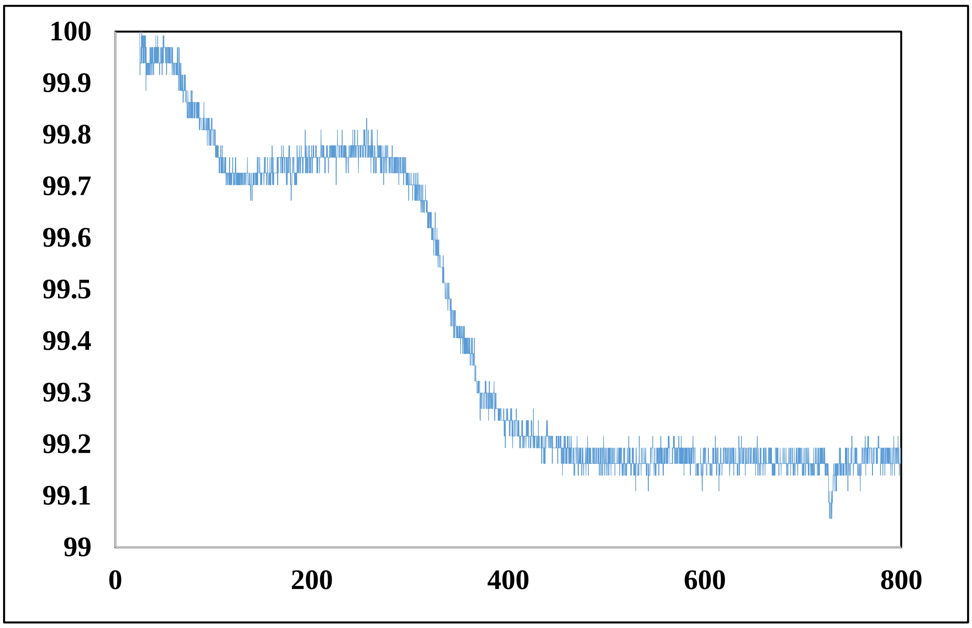


Figure 4-10 SEM images related to nickel nanoxide after absorption

results of the TGA spectrum 4-2-4

The results of the TGA spectrum are as follows in two stages before and after copper absorption.



Nickel nanoxide

before absorption

As can be seen in this spectrum at a temperature of 25 to 210 degrees Celsius, half of the crystallized water (8/8 percent) and in the second staircase at a temperature of 210 to 400 degrees Celsius, the removal of water from Ni(OH)2 and conversion to nanoparticle NO and weight loss of 7/17 percent is seen.

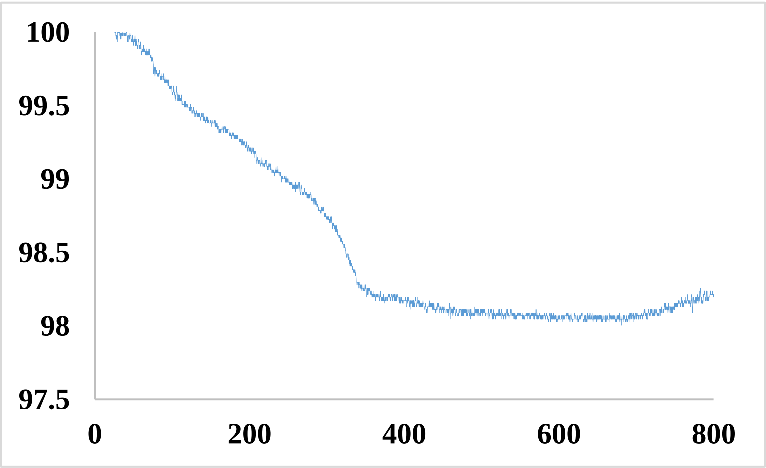


Figure 4-11 TGA spectrum of nickel nanoxide after absorption

In the post-absorption TGA spectrum, only a change in a staircase is seen, .indicating the absorption of copper by the nanosorbent

+examination of parameters affecting Cu^{1} ion extraction and recovery 3-4

review of extraction and recovery of Cu^{1}+ to determine the appropriate 1-3-4 ligand

The results of this study have shown that, according to the results, the percentage of absorption of a ligand-free solution is higher than that of a .ligand-free solution

+examination of the effect of PHS on Cu^{1} ion extraction and recovery 2-3-4

The results of this study were shown in (Table 4-1) and (chart 4-1), as the results of the table show that at 5pH= the percentage of copper ion absorption and recovery is maximized and at lower and higher pH the absorption rate is reduced, which indicates that extraction in values of 5< pH can be reduced by .nickel nanoxide and at 5>ph the inhibition of ions cannot be fully performed

Table 4-1 changes in recovery percentage by pH of sample solution relative to copper ion (II)

pH	**The percentage recovery of**
2	25(0/9)^{Z}
2/5	25/5 (0/6)
3	99/5(0/7)

4	97/7(0/3)
5	93/85(0/9)
6	93/85(0/6)
10	77/7(0/5)

A) RSD measurement after 3 repetitions

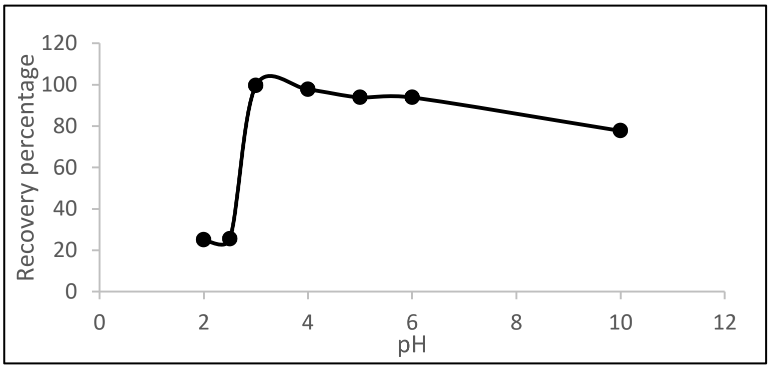


Chart 4-1 curve, the changes in the percent recovery of copper compared to the pH

4-2-1 The effect of the amount of nano-nickel oxide direction of the recovery of Cu^{1}+

The results of this review (Table 4-2) and (Chart 4-2) queries, as the results of the table show the amount of 07/0 g of nano nickel oxide absorption percentage and recovery, ion copper, to the maximum reached.

Table 4-2 changes in the percentage recovery of the warm absorber relative to the ions Copper(II)

e amount of Th (adsorbent (mg	**Percent Recovery**
10	34/8(1/2) ^{elves}
50	77/1(0/9)

70	89/6(1/6)
90	89/3(0/8)
110	83/6(1/2)
150	87/9(1/6)
200	92(1/5)

measured after 3 times repeatsize RSD (ElFe

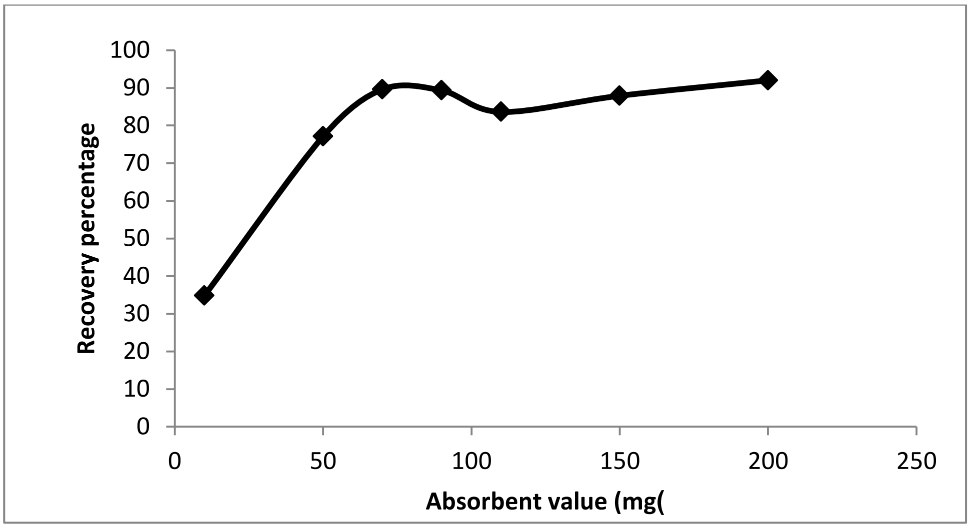


Chart 4-2 curve, the changes in the percent recovery of copper relative to the absorber

4-2-2 The effects of duration of time the direction of the recovery of Cu^{1}+

The results of this review (Table 4-3) and (Chart 4-3) queries, as the results of the table show the time duration of 15 minutes, mixing the greatest amount of absorption and recovery of copper ions by Nano-nickel oxide can¬be used.

Table 4-3 changes, the percentage recovery time, the proportion of the ions Copper(II)

(Time bash (minutes	percent recovery
2	83/98(2/9)^{Z}
6	87/52(1/9)
10	94/05(1/3)
15	95/51(0/5)
25	91/18(1/8)

Z) RSD size¬measured after 3 times repeat

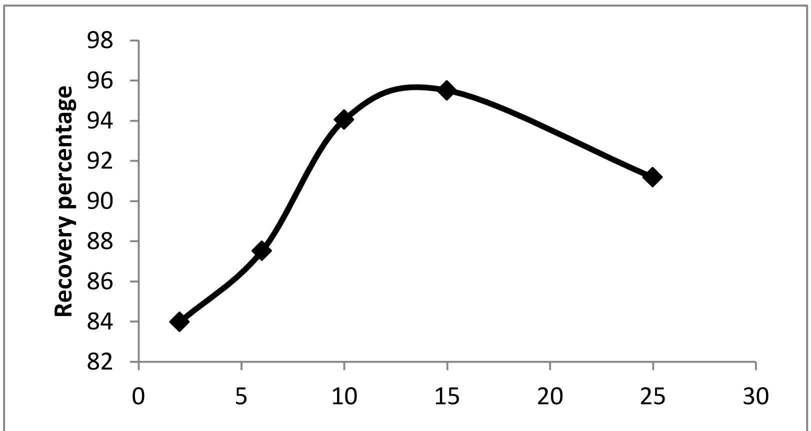


Chart 4-3 curve, the changes in the percent recovery of copper in proportion to the duration of time the

4-2-3 The effect of the type of detergent to recover ion Cu^{1}+

According to the results (Table4-4) cannot¬be made from sodium hydroxide BE as the right detergent used and the bases of power شویندگی complete them. so from mineral acids with غلظت¬determined that you are of 4SO2H and 3HNO was used. According to the results), Table 4-4) results in this table indicate is that all acids the power شویش well for ions of copper, have, etc. , but the rate of recovery of acid nitric compared to acids, other far more. The acidic environment causes the solution to become the deposition potential and increase the recovery of these ions¬can¬be used, but results in about 3HNO were achieved compared to the acid, 4SO2H better be like this, so that the solution M1 it 47/102 % of the ions copper from the absorbent wash داد. For the same reason, to continue studies, acid nitric, M, 1 , B,E , as a detergent solution was used.

solvent	Percent detachment

	FA
H_2SO_4 1M	79/21(0/5)^Z
H_2SO_4 0/1M	101/47(0/2)
HNO_3 3M	92/17(0/3)
HNO_3 1M	102/47(0/3)
HNO_3 0/1M	66/89(0/4)
L NaOH, 0/1M	78/22(0/8)

Table 4-4choosing the right detergent to restore ion Copper(II)

Z) RSD size¬measured after 3 times repeat

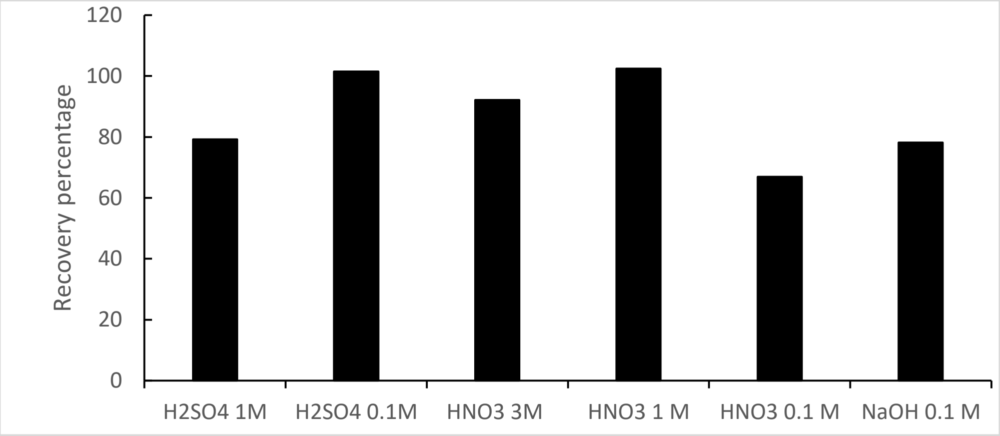


chart 4-4 curve, the changes in the percent recovery of copper compared to solvents, detergent, different

4-2-4 Check optimize the effect of the volume of solvent detergent to restore ion Cu^1+

After review and choose the type of detergent toofnot. the volume of the solvent was investigated and the results in (Table 4-5) and (Chart4-5) is collected, etc. , volume,mL 7 , acid nitric , as the volume is optimal for washing was selected.

Table4-5 , determine the volume of the optimal solvent detergent

e volume of the Th solvent	the percentage ‘ detachment FA
5 ml	94/19(1/5)[Z]
7ml	98/31(1/9)
9 ml	99/8(2/4)
11 ml	99/7(0/9)
13 ml	99/8(1/3)

(Z) RSD size¬measurement after three times

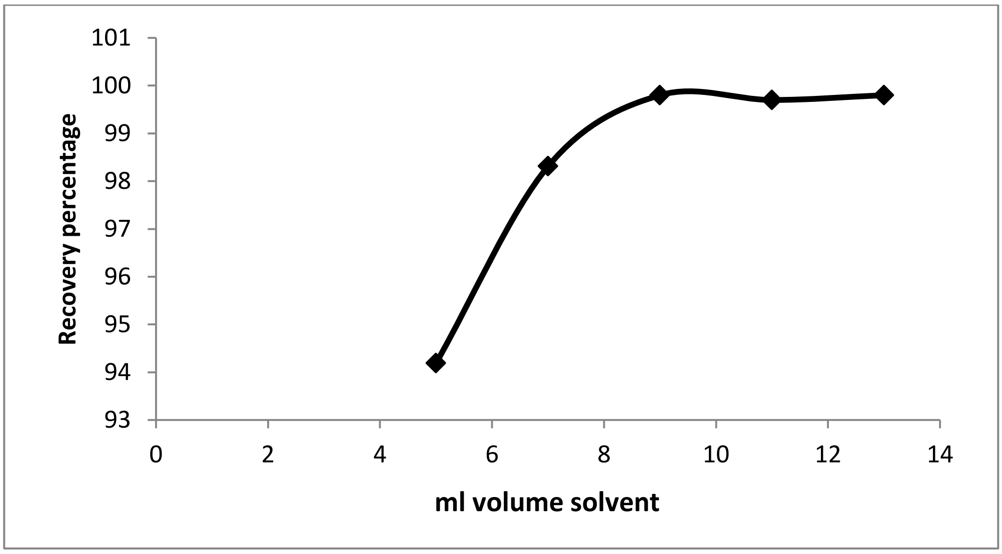


Chart 4-5 changes, the percent recovery based on changes in the volume of solvent detergent

comparison¬between the proposed method and the method of¬the other

According to the results of table (4-15) the superiority of the proposed method in comparison with the methods of¬the other in this case can¬be that the adsorbent used in this method: 1) has the special levels are very high¬, which is the main factor in choosing this material for application as an adsorbent ion¬, the metal is. 2) the adsorbent used in this method provided the ability reclamation is, i.e. is capable of many times experiments will also be responsive. 3) the superiority of the other proposed method in comparison with the methods of¬the other, which in the following table can see¬is that the method provided more quickly from reference 106, and the limit of detection of less than often the method-provided and the invoice condensed-right¬, in which more than often the method¬is easy method and the accuracy is high.

Table 4-15 comparison¬between the proposed method and the method of¬the other

‘ techniq‘ue	**percent repeat, flexibility**	**factor condensing**	**limit of detection** (mg/L)	**correlation coefficient**	**quation of the e calibration**	**References**
FAAS	3	100	0/3	0/9987	X+0/00005 Y=0/0076	[106]
FI-FAAS	2/1	220	1/2	0/9993	X+0/0022 Y=0/0017	[107]
GFAAS	2/77	100	0/26	0/9981	X+0/0025 Y=0/0067	[108]
ICP-AES	2/7	140	0/2	0/993		[109]
FAAS	0/75	36	1/77	0/9975	/0075X+0/4469 Y=0	method proposed

4-Result and ¬measurement

The proposed method compared to the method¬that used for the isolation and the size of the¬formation of copper (II) was reported has significant advantages that these advantages include being: this method is simple and inexpensive and has the speed to sample the¬environment includes the natural juice is used as-expected.In addition, the use of organic solvent, etc., toxic, and expensive, to minimize¬them. Also, the design and development of this method for the preconcentration of. isolation and size¬measurement of ion Copper (II) due to its importance in different industries and the low concentration of this ion in most examples¬, a basic requirement is. Therefore, the aim of this study was to present a method of efficient, choose now. cheap and simple to assess the amount of copper (II) in the sample¬, various can¬be. (In this study, the amount of the volume of the limit, the detection limit and RSD is obtained). Research the most recent showed that the size of the¬measurement of ion Copper (II) acceptable without the involvement of any pesky other can¬be used, and so the proposed method can¬be used to ease in the size of the¬measurement of the amount of copper (II) in a sample of¬water used.

4-1-suggestions

The proposed method has been one of the best methods¬for size,¬measurements and the removal of very small quantities ion¬metal copper (II) in a sample of-water and wastewater¬, industrial, can¬be. Also, Nano-adsorbent, zinc oxide, nickel can¬be as solid phase separator for the ion¬two-valence Copper (II), for cadmium, lead and... with ligands other code used to when compared to one or a few ion selection vulnerable act.

Suggestions else that can¬be done in this area to be considered include:

A) the use of nano-adsorbent¬for preconcentration and removal, and separation of insignificant amounts of ion¬metal copper (II) in a sample of¬different.

B) extraction and separation of ions¬, the other is nano-structures of nickel oxide

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