Preparation and Characterization of Copper Oxide Nanoparticles Used to Remove Nickel Ions from Aqueous Solution

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Abstract

In this study, copper oxide nanoparticles (CuO) was prepared by simple precipitation method and then it characterize by XRD, SEM, and AFM techniques. XRD spectrum revealed that particle size obtained was around (7.43 nm) for it, which agreed fairly well with XRD data. Surface morphology as a main nanoparticles phenomenon was studied in terms of SEM and AFM. The prepared oxide nanoparticles was used to remove nickel ions from aqueous solution and determining the best removal percentage at different contact time (30, 60, 90, and 120 min) and different initial concentration of aqueous solutions (100, 200, and 300 mg/L) with other constant condition such as pH of 3.5, adsorbent dosage (0.1g), and room temperature .

The result showed the percentage removal of nickel ions increase with increase in the contact time, and the maximum adsorption was recorded with 100 mg/L for the prepared oxide nanoparticles, Also the percentage removal seem to decrease with increase in the initial concentration of adsorbate. The correlation coefficient for the linear Freundlich isotherm regression fits are larger than that for the Langmuir one for (CuO), nanoparticles, so the Freundlich model could describe the adsorption isotherm for the uptake of nickel ions from aqueous solution on(CuO), nanoparticles surfaces.

Key Words : Copper oxide nanoparticles , Adsorption , Nickel ions , Preparation, Characterization , Removals .

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تحضير وتشخيص اوكسيد النحاس النانوي واستخدامه لازالة ايونات النيكل من المحاليل المائية

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الخلاصة

في هذه الدراسة، تم تحضير اوكسيد النحاس النانوي (CuO) باستخدام طريقة الترسيب البسيط ، و تم تشخيص خصائصه وصفاته باستخدام عدة تقنيات مثل حيود الأشعة السينية (XRD) ، ومجهر المسح الالكتروني (SEM)، ومجهر القوة الذرية (AFM). حيث اظهرت النتائج لقياس (XRD) ان حجم الجسيمات كانت (7,43) نانومتر للاوكسيد النانوي المحضر ، وهذا ما اكدته نتائج قياسات (SEM و AFM) التي تم اجرائها.استخدم اوكسيد النحاس النانوي (CuO) المحضر تطبيقيا لإزالة ايونات النيكل من محلولها المائي وتحديد أفضل نسبة مئوية لازالة لهذه الايونات في ازمنة مختلف (30، 60، 90، و 120 دقيقة) وكذلك تراكيز محاليل مائية ابتدائية مختلفة (100، 200، و 300 ملغم / لتر) مع تثبيت الظروف الاخرى كالرقم الهيدروجيني عند 3.5، وكمية المادة المازة (الاوكسيد النانوي) كانت 0,1 غرام ، وعند درجة حرارة الغرفة (25 مْ).أظهرت النتائج ان نسبة إزالة ايونات النيكل تزداد مع زيادة الزمن ، وكما سجلت النتائج ان اعلى امتزاز كان عند تركيز 100 ملغم / لتر بالنسبة للاوكسيد النانوي المستخدم وهذا يدل ان نسبة الازالة تنخفض مع زيادة التركيز الابتدائي للمادة الممتزة .معامل الارتباط اظهر قيمة اكبر لايزوثرم Freundlich عند امتزاز ايونات النيكل على سطح (CuO) النانوي مقارنة بمعامل الارتباط لايزوثرم Langmuir وهذا يدل ان معادلة Freundlich تصف سلوك (CuO) النانوي عند امتصاص ايونات النيكل .

الكلمات المفتاحية : اوكسيد النحاس النانوي ، الامتزاز ، ايونات النيكل ، تحضير ، تشخيص ، ازالة

Introduction

Copper oxide is one of the important metal oxide which has attracted recent research because of its low cost, abundant availably as well as its particular properties [1]. It is one of semiconductors material and gains considerable attentions due to its excellent optical, electrical, physical, and magnetic properties, and it is non-toxic and easily obtained by the oxidation of Cu [1,2]. CuO crystal structures possess a narrowband gap, giving useful photocatalytic and photovoltaic properties [3].

Copper oxide nanoparticles has a monoclinic structure and semiconductor behavior with an indirect band gap of 1.21 – 1.51 eV. It have the advantage of a lower surface potential barrier than that of metals, which affects electron field emission properties, and is considered as a potential field emitter, an efficient catalytic agent, as well as a good gas sensing material [4].Copper oxide has gained the most interest because of its wide applications, such as in solar energy conversion, field emission , magnetic storage media, lithium ion batteries, gas sensor, drug delivery, magnetic resonance imaging, and field emission device. It is extensively used in the many of fields like catalysis, heat transfer fluids, superconductors, batteries, ceramics as a kind of important inorganic materials etc. [1,2,3].It treatment is known to induce a disruption of the blood–brain barrier in vivo in mice and rats. [1].

Lately, application of nanoparticles for the removal of pollutants has come up as an important area of research. The unrivaled properties of nanosorbents are providing unmatched occasion for the uptake of metals in highly efficacious and cost-effective approximation, and different nanoparticles show good adsorption efficiency mostly because higher surface area and larger active sites for interaction with metallic species. Furthermore, adsorbents with specific functional groups have been advanced to ameliorate the adsorption capacity [5].

Copper oxide nanoparticles have been prepared with different sizes and shapes via several methods such as sonochemical, alcohothermal synthesis, vapor deposition, electrochemical methods, combustion ,colloid-thermal synthesis process, and microwave irradiation ,thermal oxidation ,pulsed wire explosion methods [1,2,6]. There are some techniques for the synthesis of copper oxide nanoparticles that have been reported recently such as the sol-gel technique, thermal decomposition of precursors one-step solid state reaction method at room temperature, and co-implantation of metal and oxygen ions [7]. Most of these techniques are intricate and have drawbacks like use of hazardous organic solvents, toxic by product, expensive reagent, drastic reaction condition, difficult to isolate nanoparticles and longer time required etc.[6]. Among these processes, precipitation method is a facile way which attracts considerable interest in industries because of low energy and temperature, inexpensive and cost-effective approach for large scale production and good yield. However, these CuO novel properties can be

improved by synthesis in CuO nanostructures that shown excellent performance comparing to bulk counterpart. Different nanostructures of CuO are synthesized in form of nanowire, nanorod, nanoneedle, nano-flower and nanoparticle [2].

Materials and Methods

Materials used : Analytical grade materials was used without any further purification in addition to deionized water and as shown in tables (1,2) :

Table (1): Materials used in copper oxide nanoparticles, CuO preparation

No.	Chemical	Formula	Phase	purity	Source
1	Copper(II) acetate	$Cu(CH_3COO)_2.H_2O$	Solid	99%	Bean Town
2	Glacial acetic acid	CH_3COOH	Liquid	99.5%	BDH
3	Sodium hydroxide	NaOH	Solid	99%	Alpha chemical
4	Absolute ethanol	C_2H_5OH	Liquid	99%	GCC

Table (2): Materials used in separation of nickel ion

No.	Chemical	Formula	Phase	purity	Source
1	Nickel (II) Chloride	$NiCl_2.6H_2O$	Solid	99%	Strem chemical
2	Sulfuric acid	H_2SO_4	Liquid	98%	Fluka
3	sodium hydroxide	NaOH	Solid	99%	Alpha chemical

Copper oxide nanoparticle, CuO preparation

Copper oxide nanoparticle ,CuO were synthesized by precipitation method , In which 600 ml of copper (II) acetate and 5 ml glacial acetic acid were mixed in beaker, and the mixture heated to boiling . Then 30 ml of sodium hydroxide solution was added to the mixture to notice the solution color turned from the blue color to black one directly and the black precipitate start forming, where the reaction performed at boiling temperature with a continuous stirring for 3 hours. The mixture thus obtained cooled to room temperature and separated by centrifuge and (CuO)

nanoparticle, that obtained is filtered off and washed with deionized water and absolute ethanol for several times, and the precipitate was dried at 60 °C for 8 hours to produce (CuO) nanoparticles.

Characterization of Copper Oxide Nanoparticles, CuO :

The X-ray diffraction pattern of the prepared oxide were recorded using XRD-6000 with Cukα (λ=1.5406A°) that have an accelerating voltage of 220/50 HZ which is produce by SHIMADZU company. The scanning electron microscope (SEM) used in imaging the nanoparticles was a scanning electron microscope AIS2300C . Atomic force microscopy (AFM) used to study surface morphology of the samples was AFM model AA 3000 SPM 220 V- angstrum Advanced INC , USA, and finally elemental concentration analysis was measure by atomic absorption spectrometer type AURORA TRACE AI 1200.

Separation of Nickel Ion by Adsorption Technique:

A stock solution containing nickel ion was prepared by dissolving a known quantity of Nickel (II) Chloride in deionized water. Batch adsorption studies were performed by mixing 0.1gm of copper oxide nanoparticle with 50 ml of solutions with different nickel ions concentrations (100, 200, 300 mg/L) in 100 ml volumetric flask and the pH value was adjusted to 3.5 using 0.5M H_2SO_4 and 0.5M NaOH. All the experiments were performed at room temperature of 25±1°C in a shaker water bath at a contact time of (30, 60, 90 and 120 min) and after that the samples were filtered off and the concentration of nickel ions measured.

Result and Discussion

Characterization of Copper Oxide Nanoparticles:

X-ray diffraction

Structural Characterization:

X-ray diffractometer has been used to investigate the structure of copper oxide nanoparticles. XRD patterns of copper oxide nanoparticles are shown in Figure (1), also the data of strongest three peak are shown in Table (3). The positions and intensities of peaks are in a good agreement with those reported in JCPDS file NO. 48-1548 for copper oxide nanoparticles.

Table (3): Strongest three peaks in XRD of copper oxide nanoparticles, CuO

No.	Peak No.	2θ (deg)	d (Å)	FWHM (deg)	Intensity(Counts)
1	4	38.6249	2.32916	1.13200	499
2	3	35.4796	2.52810	1.17570	387
3	9	48.7088	1.86794	1.38000	94

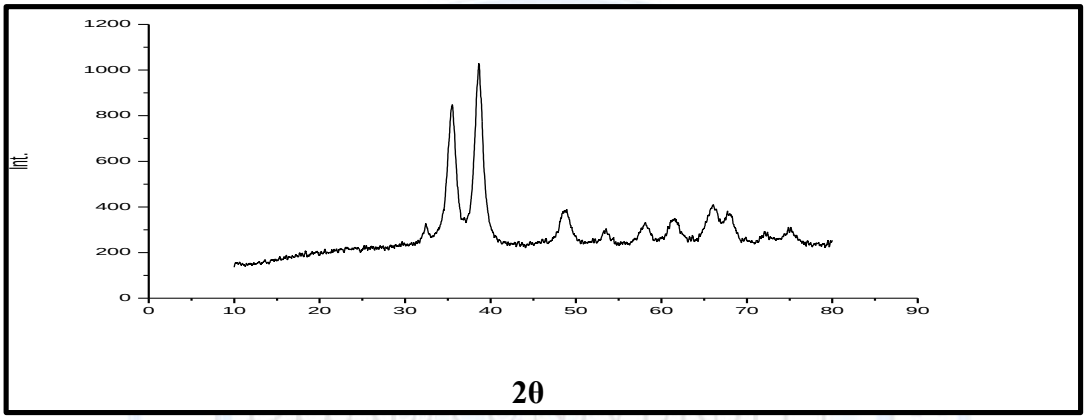


Figure (1) : XRD pattern of copper oxides nanoparticles, CuO

Particle Size Calculation of Copper Oxide Nanoparticles:

The particle size were calculated from Deby – Scherrer formula [8] in equation (1)

$$D = 0.9\,\lambda / \beta \cos\theta \quad \ldots\ldots\ldots\ldots\ldots (1)$$

Where **D** is the crystallite size , λ is the wave length of radiation , **θ** is the Bragg's angle and **β** is the full width at half maximum (FWHM) [8]

For copper oxide nanoparticles and it was 7.43 nm, The presence of sharp peaks in XRD patterns and crystallite size of less than 100 nm suggest the nano crystalline nature of all oxides.

Scanning Electron Microscope

The surface morphology of the prepared copper oxide nanoparticles (CuO) were revealed through the SEM image shown in Figure (2) , it show a homogeneous distribution of spherical shape like nanoparticles with irregular distribution. From SEM images it is confirmed that the

particles having size in between 50 -70 nanometers by simple counting and calculations of number of particles and their sizes and this confirm the nanostructure nature of the oxide.

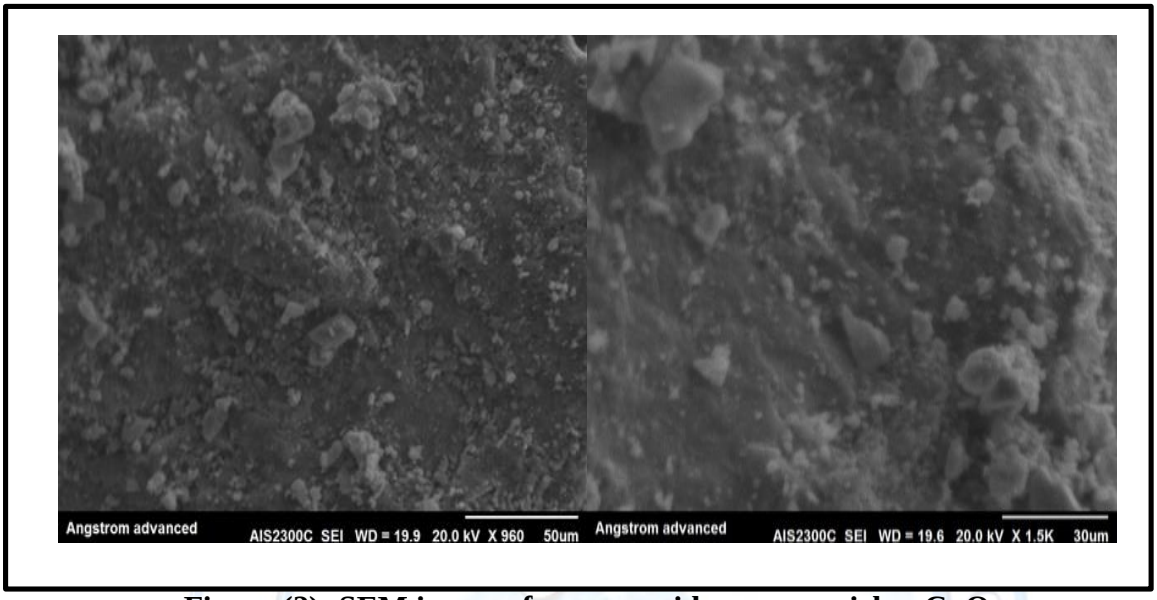
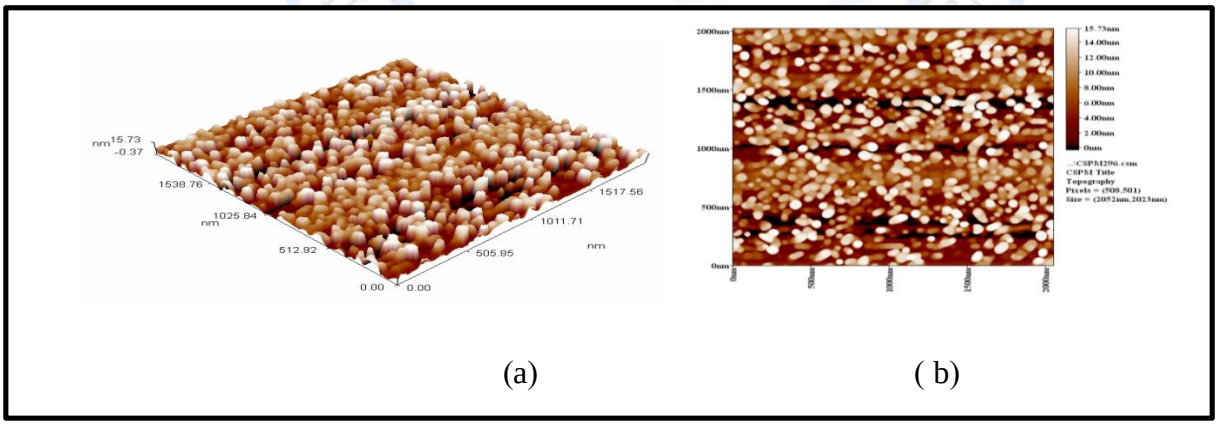


Figure (2): SEM image of copper oxide nanoparticles, CuO

Atomic Force Microscope

The AFM analysis provides a measure of average of grain size [10]. Figure (3) show a typical AFM images of copper oxide nanoparticles



(a) (b)

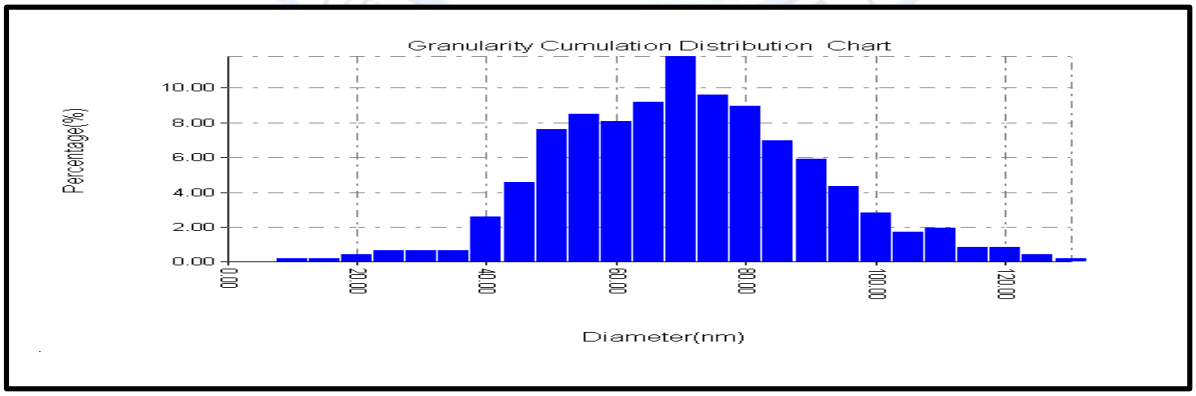
Figure (3): AFM for copper oxide nanoparticles, CuO

Figure (3) explains images of AFM for (CuO) nanoparticles, with area (size=2052nm X 2023nm) and ability analytical (pixels=508,501). Where Figure (3-a) is AFM picture in three

dimensions (3D), it explains structural shape for grains, and Figure (3-b) is AFM picture in two dimensions (2D) it is found that average roughness is 4.04 nm and RMS is 4.67 nm, and average diameter is 68.42 nm.Table (4), and Figure (4) show the granularity cumulating distribution and average diameter data of (CuO) nanoparticles.

Table (4): Granularity cumulating distribution and average diameter of copper oxide nanoparticles, CuO.

Avg. Diameter:68.42 nm								
Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)
10.00	0.22	0.22	55.00	8.52	26.20	100.00	2.84	93.89
15.00	0.22	0.44	60.00	8.08	34.28	105.00	1.75	95.63
20.00	0.44	0.87	65.00	9.17	43.45	110.00	1.97	97.60
25.00	0.66	1.53	70.00	11.79	55.24	115.00	0.87	98.47
30.00	0.66	2.18	75.00	9.61	64.85	120.00	0.87	99.34
35.00	0.66	2.84	80.00	8.95	73.80	125.00	0.44	99.78
40.00	2.62	5.46	85.00	6.99	80.79	130.00	0.22	100.00
45.00	4.59	10.04	90.00	5.90	86.68			
50.00	7.64	17.69	95.00	4.37	91.05			



Figure(4): Granularity cumulating distribution of copper oxide nanoparticles, CuO

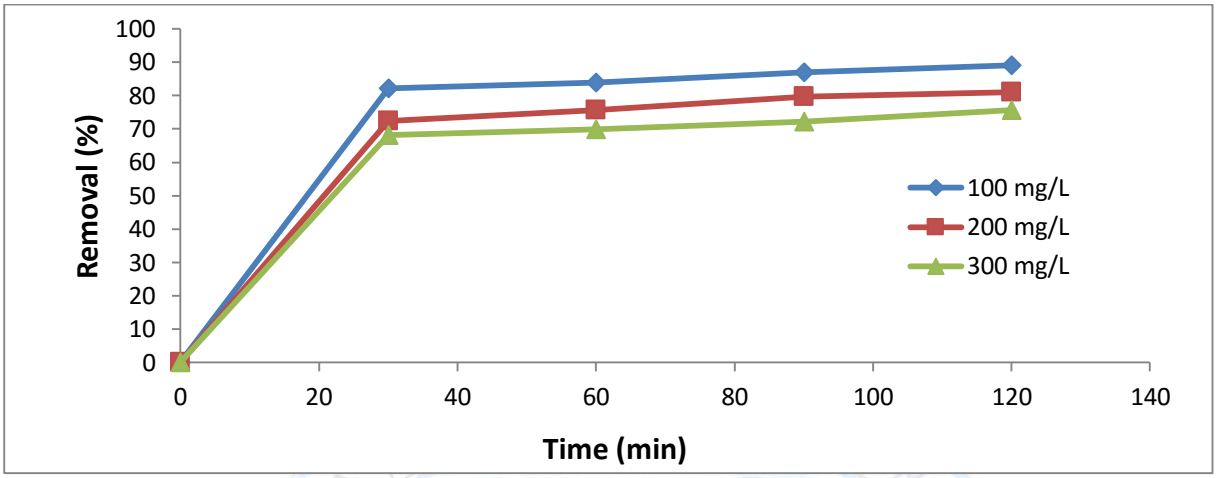
Batch Adsorption Separation Method of Nickel Ions

Contact Time of Adsorption of Nickel Ions on Copper Oxide Nanoparticles

The contact time between copper oxide nanoparticle oxide nanoparticles (Adsorbent) and nickel ions (adsorbate) that is sufficient for the adsorption process to reach equilibrium at room temperature of 25±1°C using a fixed concentration (C_o = 100 mg/L) and adsorbent dosage (0.1g) .and pH of 3.5 were studied at different times (0 , 30 , 60 , 90 and 120) minute. Table (5), show the changes of nickel ion removal and percentage removal at contact time of (0 , 30 , 60 , 90 , and 120) minutes using copper oxide nanoparticles, (CuO) , and the results are presented in Figure (5) also . It was observed that the increasing in contact time lead to increase in percentage nickel removal and this is due to the larger available surface area of the nanoparticles. Nickel adsorption percentage in the initial stage depends on increase Abundance in active binding site numbers on the surface of adsorbent. Finite mass transfer of the adsorbate molecules from the bulk to the adsorbent surface cause to gradual increase in adsorption subsequently realization of the equilibrium adsorption [11-14].

Table (5): Effect of contact time on the removal of nickel ions using copper oxide nanoparticles, CuO at initial concentration of (100,200, and 300 mg/L).

Initial concentration	100 mg/L				
Time, min	0	30	60	90	120
Residual concentration (C_t), mg/ L	100	17.848	16.154	13.056	10.948
Removed concentration (R), mg/ L	0	82.152	83.846	86.944	89.052
Residual (C_t)%	100	17.848	16.154	13.056	10.948
Removed (R) %	0	82.152	83.846	86.944	89.052
Initial concentration	200 mg/L				
Time, min	0	30	60	90	120
Residual concentration (C_t), mg/ L	200	55.256	48.614	40.552	37.910
Removed concentration (R), mg/ L	0	144.744	151.386	59.4481	162.090
Residual (C_t)%	100	27.628	24.307	20.276	18.955
Removed (R) %	0	72.372	75.693	79.724	81.045
Initial concentration	300 mg/L				
Time, min	0	30	60	90	120
Residual concentration (C_t), mg/ L	300	95.247	90.327	83.604	72.978
Removed concentration (R), mg/ L	0	204.753	209.673	216.396	227.022
Residual (C_t)%	100	31.749	30.109	27.868	24.326
Removed (R) %	0	68.251	69.891	72.132	75.674



Figure(5): Effect of contact time on percentage removal of nickel ions using copper oxide Nanoparticles, CuO at different initial concentration.

Effect of The Initial Concentration of Nickel Ions on Its Adsorption

The adsorption experiment was carried out at room temperature of 25±1 ºC with different initial concentration C_o (100 , 200 , 300 mg/L) and keeping the adsorbent dosage (0.1g) and pH of 3.5 at contact time of (0 , 30 , 60 , 90 , and 120) minutes. Table (6) show the variation of percentage of nickel ion removal and residual and initial concentration of nickel ions using copper oxide nanoparticles, (CuO), and also represented diagrammatically in Figure (6). The results indicated that the percentage of nickel ions removal decreases with the increase of initial metal ion concentration increasing the initial concentration of Ni(II) in a batch study, a saturation point appears which resulted in decreased percentage of Ni(II) removal and this is due to the fact that after the formation of mono ionic layer at low concentration over the adsorbent surface, further formation of the layer is highly hindered at higher concentration due to interaction between nickel ions on the surface and in these solution [11,13,14].

Table (6): Effect of initial concentration of nickel ion on its removal using copper oxide nanoparticles, CuO at contact time of 30 ,60 , 90 and 120 minutes.

Contact time	30 minutes		
Initial Concentration (C_o), mg/ L	100	200	300
Residual concentration (C_t), mg/ L	17.848	55.256	95.247
Removed concentration (R), mg/ L	82.152	144.744	204.753
Residual (C_t)%	17.848	27.628	31.749
Removed (R) %	82.152	72.372	68.251
Contact time	60 minutes		
Initial Concentration (C_o), mg/ L	100	200	300
Residual concentration (C_t), mg/ L	16.154	48.614	90.327
Removed concentration (R), mg/ L	83.846	151.386	209.673
Residual (C_t)%	16.154	24.307	30.109
Removed (R) %	83.846	75.693	69.891
Contact time	90 minutes		
Initial Concentration (Co), mg/ L	100	200	300
Residual concentration (Ct), mg/ L	13.056	40.552	83.604
Removed concentration (R), mg/ L	86.944	59.4481	216.396
Residual (Ct)%	13.056	20.276	27.868
Removed (R) %	86.944	79.724	72.132
Contact time	120 minutes		
Initial Concentration (C_o), mg/ L	100	200	300
Residual concentration (C_t), mg/ L	10.948	37.910	72.978
Removed concentration (R), mg/ L	89.052	162.090	227.022
Residual (C_t)%	10.948	18.955	24.326
Removed (R) %	89.052	81.045	75.674

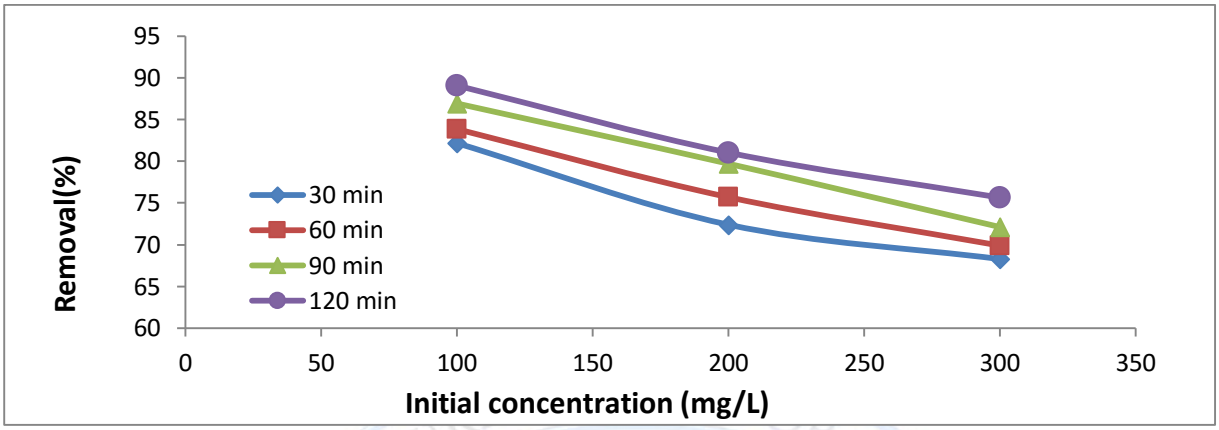


Figure (6): Relationship between initial concentration of nickel ion(100, 200, and 300 mg/L) on the percentage removal of it by adsorption on copper oxide nanoparticles, (CuO) at different contact times .

The Adsorption Isotherm

Adsorption of nickel ions from an aqueous solutions by using copper oxide nanoparticles, (CuO), was studied at room temperature 25±1˚C and keeping the pH of solution at 3.5 using a different concentration (C_o =100 , 200 , and 300 mg/L) and adsorbent dosage (0.1g) and different times (30 , 60 , 90 and 120) minutes. The results are represented by initial concentration of nickel ions C_o, the equilibrium concentration C_e measured at equilibrium time and quantity adsorbed Q_e , Q_e values were calculated from experimental data by using equation (2) [15,16] .

$$Q_e = (C_o - C_e)V/ m \ldots\ldots\ldots\ldots \quad (2).$$

Where **Q_e :** Adsorption capacity of adsorbent at equilibrium time t_e (mg adsorbate / g adsorbent) , **C_o :** Initial concentrations of adsorbate (mg/L), **C_e :** Equilibrium concentrations of adsorbate after adsorption (mg/L), **V :** Volume of solution (L), and **m :** Weight of adsorbent (g). The quantities adsorbed Q_e were plotted versus equilibrium concentration C_e to obtain general adsorption isotherms of nickel ions removal which are shown in Figure (7).

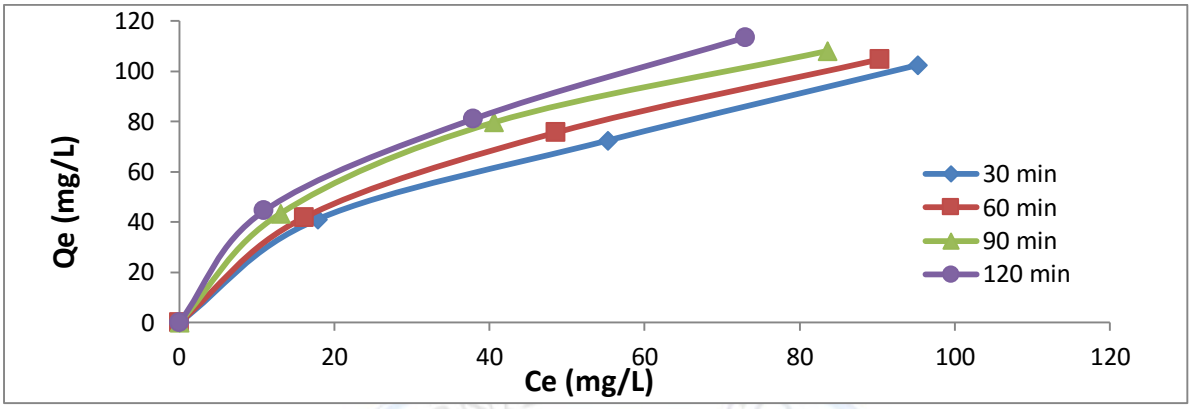


Figure (7): Adsorption isotherm of nickel ions removal on copper oxide nanoparticle, CuO surface at different contact times

The results showed increased in adsorption capacities copper oxide nanoparticles, (CuO), with the equilibrium concentration of solutions , and reached to high values. The general shape of the adsorption isotherms of nickel ions removal on the copper oxide nanoparticles, (CuO), is consistent with L-Type of Giles classification**.** The isotherm of the mentioned system obeyed to the assumption of high adsorption of nickel on adsorbent surfaces at the beginning . This strongly adsorbed on the adsorbent because there is no competition from solvent for adsorbent sites [17,18].

Langmuir equation (3) and Freundlich equation (5) were applied for adsorption equilibrium for the copper oxide nanoparticles, (CuO), at different times in order to see the best model that describe the adsorption phenomena.

$$\frac{Ce}{Qe} = \frac{1}{ab} + \frac{Ce}{a} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Where Q_e : the quantity adsorbed at equilibrium in (mg/g), C_e : the equilibrium concentration of adsorbate in (mg/L), a : the Langmuir constant which is a measure of adsorption capacity in (mg/g), b : also the Langmuir constant which is a measure of energy of adsorption in (mg/L) . This form can be used as a linearization of expermental data by plotting C_e/Q_e against

C_e the Langmuir constants (a) and (b) can be evaluated from the slope (1/a) and intercept (1/ab) of the linear equation [19].

$$Q_e = K_f C_e^{1/n} \quad \cdots\cdots\cdots \quad (4)$$

Where Q_e : the quatity adsorbed at equilibrium in (mg/g), C_e : the equilibrium concentration of the adsorbate in (mg/L), K_f and n: the freundlich constants, being indicators of the adsorption capacity and adsorption intensity, respectively.Take logarithms of equation (4) give :

$$\log Q_e = \log Kf + 1/n (\log C_e) \quad \cdots\cdots\cdots\cdots \quad (5)$$

If log Q_e is plotted against log C_e a straight line should be obtained with the slope of the line will give the value of 1/n and the intercept on the Y-axis gives the value of log K_f [19-23] Adsorption isotherm data for nickel ions removal were plotted and presented in Figures (8,9).The values of the Langmuir isotherm constants, *a* , which is the monolayer adsorption capacity , *b*, which is a constant related to the energy of adsorption were calculated from the slope and intercept of plots of (C_e/Q_e) versus C_e , and the Freundlich isotherm constants , K_f, which is the adsorption capacity of the adsorbent , and *n* , which is the adsorption intensity being calculated from the slope and intercept of plots of (log Q_e) versus (log C_e) .

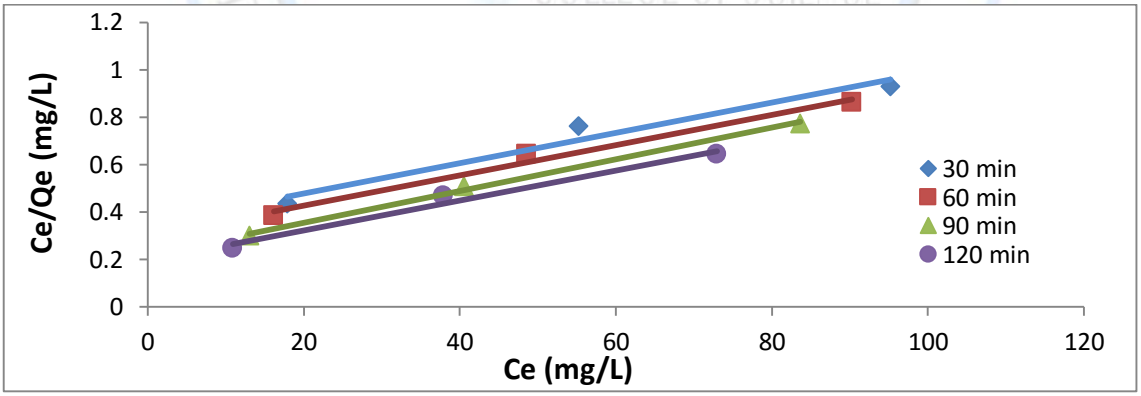


Figure (8) : Linear Langmuir isotherm of nickel ions adsorption copper oxide nanoparticle, CuO surface at different contact times

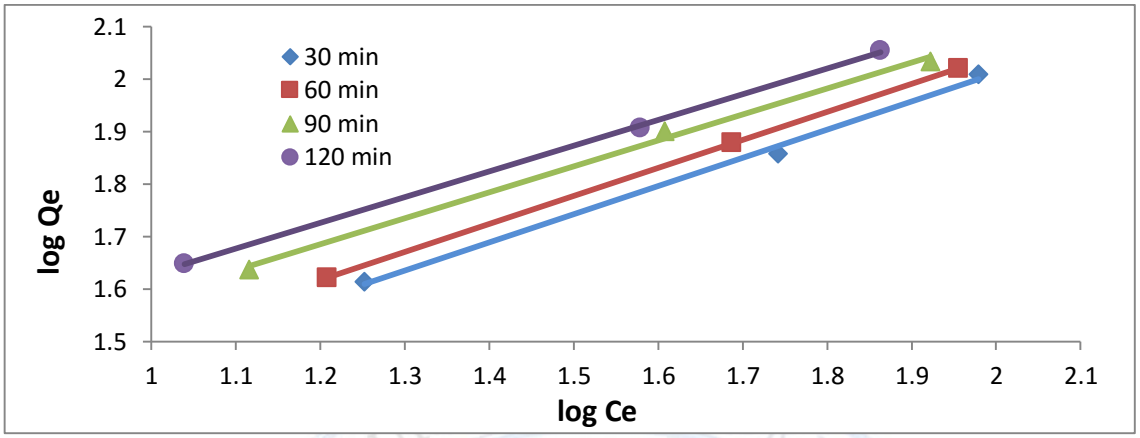


Figure (9): Linear Freundlich isotherm of nickel ions adsortion on copper oxide nanoparticle, (CuO) surface at different contact times.

Table (9): Langmuir and Freundlich constants and the correlation coefficients for the adsorption of nickel ions by copper oxide nanoparticle ,(CuO) , surface at different contact times .

Time (min)	Langmuir model					Freundlich model				
	1/a	a	1/ab	b	R^2	1/n	n	$\log K_f$	K_f	R^2
30	0.0064	156.250	0.3519	0.0182	0.9586	0.5380	1.8587	0.9359	8.627	0.996
60	0.0064	156.250	0.3004	0.0213	0.9859	0.5338	1.8734	0.9775	9.495	1
90	0.0067	149.253	0.2230	0.0300	0.9965	0.4953	2.0189	1.0909	12.328	0.996
120	0.0063	158.730	0.1952	0.0323	0.9795	0.4910	2.0367	1.1373	13.718	0.999

From Table (9) , the results show based on the correlation coefficient data for adsorption of nickel ions from aqueous solution on copper oxide nanoparticles ,which fit better to Freundlich isotherm model than the Langmuir one. So the adsorption of nickel ions was best described by the Freundlich isotherm model [12] .The results indicated that the mono layer adsorption

capacity ***a*** , energy of adsorption ***b***, adsorption capacities K_f , and adsorption intensity ***n*** of nickel ions removal copper oxide nanoparticles are increase with an increase of contact time.

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