Asian Journal of Applied Sciences (ISSN: 2321 – 089)
Volume 04 – Issue 03, June 2016

Synthesis and Characterization of Copper,Iron Oxide Nanoparticles used to Remove Lead from Aquous Solution

Karim H. Hassan* and Eman R. Mahdi

University of Diyala, College of Science, Department of Chemistry
Diyala, Iraq

**Corresponding author's email : drkarim1953 [AT] yahoo.com*

ABSTRACT--- ***Copper oxide, CuO and Iron oxide, Fe_3O_4 nanoparticles were synthesized by simple and practically available methods from their corresponding salts, structural characterization using X-ray diffraction indicated that the particle size of CuO and Fe_3O_4nanopartices were 7.43 nm and 12.04 nm respectively, this is being confirmed by scannning electron and atomic force. microscopy techniques, finally these oxides were used to separate lead ion from its aqueous solution via adsorption batch method in which removal efficiency of 84.162 % was achieved using copper oxide and 88.028 % using iron oxide.***

Keywords---Copper oxide, iron oxide, nanoparticles, synthesis, leadion, characterization.

---

1. INTRODUCTION

It is well known that the problems of the ecosystem are increasing with developing technology. Heavy metal pollution is one of the main problems [1]. Consequently, removal of heavy metals from wastewater and industrial waste has become a very important environmental issue [2].

Lead is a toxic element released to the environment by various sources, If ingested or inhaled, lead and its compounds are poisonous to animals and humans.The permissible level for lead in drinking water is 0.005 mg/LCommonly used methods for the removal of lead from aqueous solutions are chemical precipitation, co-precipitation, adsorption, flocculation, reverse osmosis, ion exchange, electro deposition and filtration [3]. Most of these methods have several disadvantages such as chemical requirements, time consuming procedure, production of large amount of sludge, low efficiency and less cost effective [4]. However, adsorption method is considered to be more efficient, cost effective and free from sludge formation.

Recently, there has been a considerable interest shown in using iron, copper oxides for the removal of lead ions and other heavy metals from wastewater [5-7]. In addition, metal oxide nanoparticles are ideal adsorbents for heavy metal ions due to the larger surface area accomplished by the smaller particle size in comparison to bulk materials [8-10]. Iron and copper oxides treatment for the removal of trace metal ions from wastewater is more advantageous because the adsorbent can easily be separated from the solution by magnetic and other means. Some of the reports of iron oxides as adsorbents include adsorption of lead [11], removal of selenite [12], removal of arsenite [13], removal of mercury [14] and removal of neutral red dye [15]. Most of works focoused on studuing the preparation route and the effect of pH, materials used, effect of temperature of calcination etc…on structure and particle size of prepared nanooxides.As far as separation of heavy metals, studies focoused on the relation between efficency of separation or percent metal removal and temperature, pH, adsorbent and adsorbate dose in addition of analysis the adsorption models and kinetic and thermodynamic studies.

The present investigation aims to prepare and characterize some iron and copper oxide nanoparticles and using them to remove lead ion from aqueous solutions.

2. EXPERIMENTAL DETAILS

2-1 Materials used : Analytical grade materials was used with out any further purification in addition to deionized water and as follow :

2-1-1Materials used in copper oxide nanoparticles, CuOpreparation are copper (II) acetate, $Cu(CH_3COO)_2.H_2O$, glacial acetic acid, (CH_3COOH), sodium hydroxide, (NaOH) and absolute ethanol (C_2H_5OH).

2-1-2Materials used in iron oxide nanoparticles, Fe_3O_4 preparation are iron(II) sulphate, ($FeSO_4.5H_2O$), iron(III) Chloride, ($FeCl_3$), and sodium hydroxide. (NaOH).

2-1-3Materials used in separation of lead ion arelead (II) acetate, $Pb(CH_3COO)_2.H_2O$, sulfuric acid,(H_2SO_4) and sodium hydroxide (NaOH).

2-2 Preparation of metal oxides nanoparticles :

2-2-1 Preparation of copper oxide nanoparticles:

Copper Oxide Nanoparticles (CuO) were synthesized by mixing the required amount of copper(II) acetateand glacial acetic acid in beaker and the mixture was heated to the boiling temperature with a continuous stirring, then sodium hydroxide solution was added to the mixture until the mixture solution color turned from blue color to the black one directly and the black precipitate formed. Finally the mixture cooled to the room temperature and separated by centrifuge and copper oxide nanoparticles that obtained is filtered off and washed with deionized water and absolute ethanol for several times and then dried at 60^oC for 8 hours to obtain dry product of copper oxide nanoparticles[16-17].

2-2-2 Preparation of iron oxide, Fe_3O_4nanoparticles:
Iron oxide nanoparticle (magnetite) was prepared by precipitationmethod [6] wherestoichiometric amount of Iron(II) sulphateand Iron(III) chloride solutions mixed together ,then sodium hydroxide solution was added into the mixture with stirring for 1 hour at room temperature so as to obtain pH value between (10-11), it is noted thata dark precipitate was formed, this is filtered, washed several times withdeionized water and finally it was dried at 150^oC for 3 hours in oven andgrinded to fine powder[18].

2-3 Characterization of metal oxide nanoparticles :

The X-ray diffraction pattern of the prepared oxides 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 byatomic absorption spectrometertype AURORA TRACE AI 1200.

2-4 Separation of lead ion by adsorption technique:

A stock solution containing lead ion was prepared by dissolving a known quantity of lead (II) acetate in deionized water . Batch adsorption [19] studies were performed by mixing 0.1 of metal oxide nanoparticle with 50 ml of solutions with different lead ions concentrations (100 , 200 , 300 ppm) 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^oC in a shaker water bath at a contact time of (30 , 60 , 90 and 120 min) and after that the samples were filtered of and the concentration of lead ions measured.

3. RESULTS AND DISCUSSION

3-1 X-ray diffraction and particle size calculationof metal oxides nanoparticles:

XRD patterns and data of metals oxides nanoparticles are shown in Fig.1 and table 1andFig.2 and table 2 for CuO and Fe_3O_4 respectively, The positions and intensities of peaks are in a good agreement with those reported in JCPDS file NO. 48-1548 for copper oxide nanoparticle and NO. 19-0629 for iron oxide nanoparticles.

Table1: Strongest three peaks in XRD of copper oxide nanoparticles

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

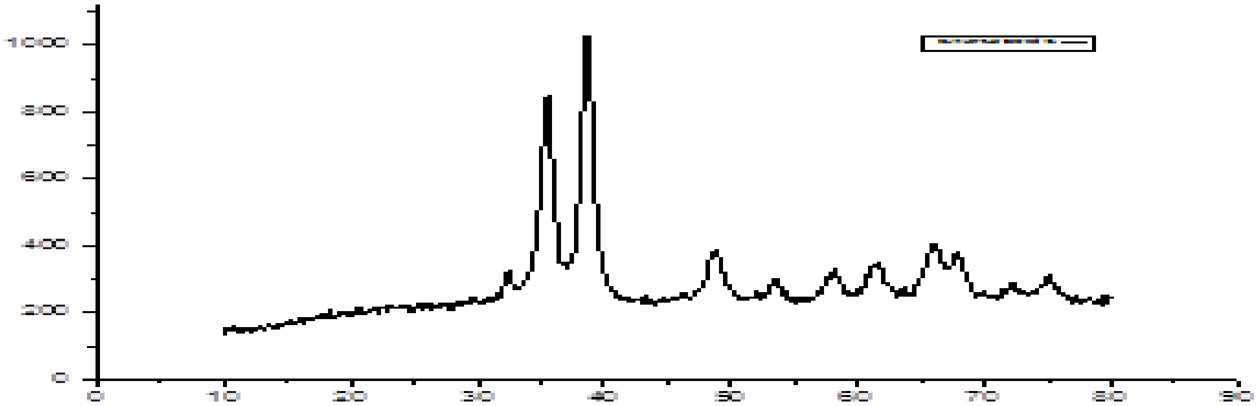


Figure 1:XRD pattern of copper oxides nanoparticles.

Table 2: Strongest three peaks in XRD of iron oxide nanoparticles Fe_3O_4

No.	Peak No.	2θ(deg)	d(Å)	FWHM (deg)	Intensity (Counts)
1	21	35.6106	2.51910	0.69330	68
2	38	62.8434	1.47756	0.76000	30
3	18	30.2031	2.95666	0.68000	20

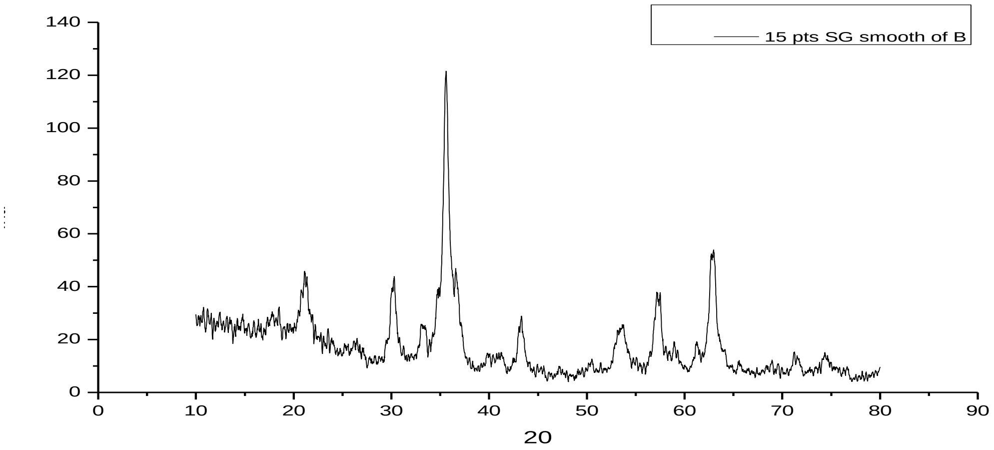


Figure 2 :XRD pattern of iron oxides nanoparticles

The crystal size has been calculated from the XRD pattern by use of Debye Scherer equation [20-21].

$$D = 0.9\,\lambda / \beta \cos\theta$$

Where D is the crystallite size , λ is the wavelength of radiation , θ is the Braggs angle and β is the full width at half maximum (FWHM) .The crystallite size corresponding to the highest peak [22-23] in XRD pattern was found is 7.43 nm for copper oxide nanoparticles (CuO) , and 12.04 nm for iron oxide nanoparticles (Fe_3O_4).The presence of sharp peaks in XRD patterns and crystallite size less than 100 nm suggest the nano crystalline nature of both oxides.

3-2 Scannning electron microscope and atomic force microscope:

The surface morphology of the prepared CuO and Fe_3O_4nanopartices were revealed through the SEM image and shown in Figs.3 and 4. Both show a homogeneous distribution of spherical shape like nanoparticles with ieeigulardistribution.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,thiswill confirm the nanostructure nature of both oxides.

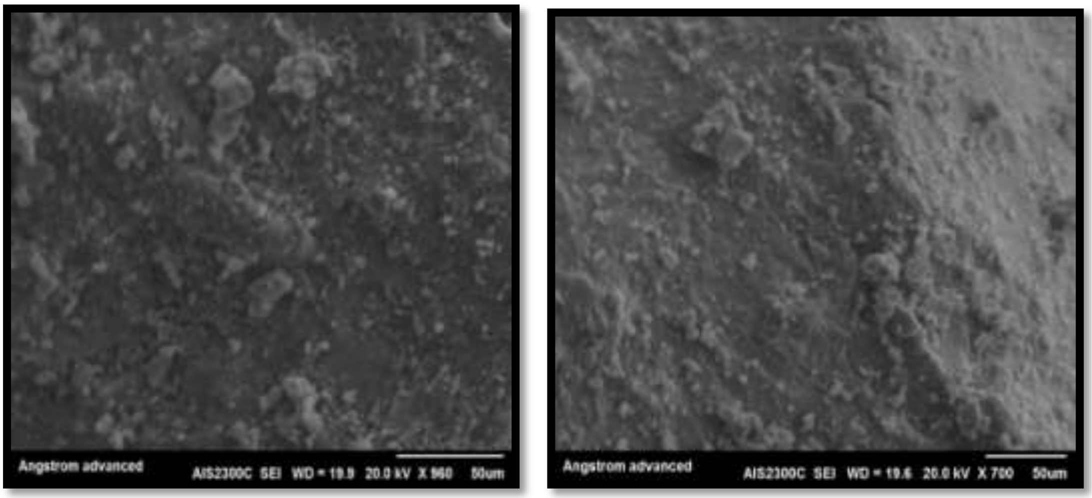


Figure 3 :SEM image of copper oxide nanoparticles.

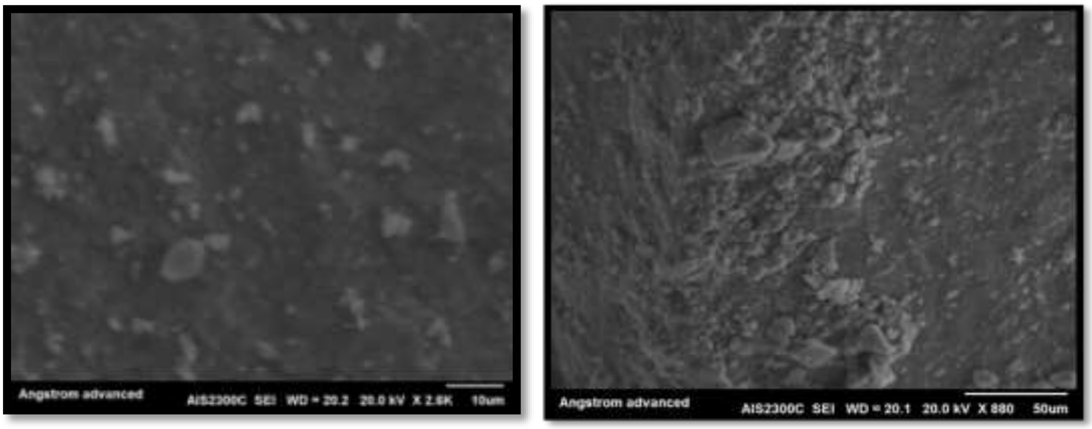
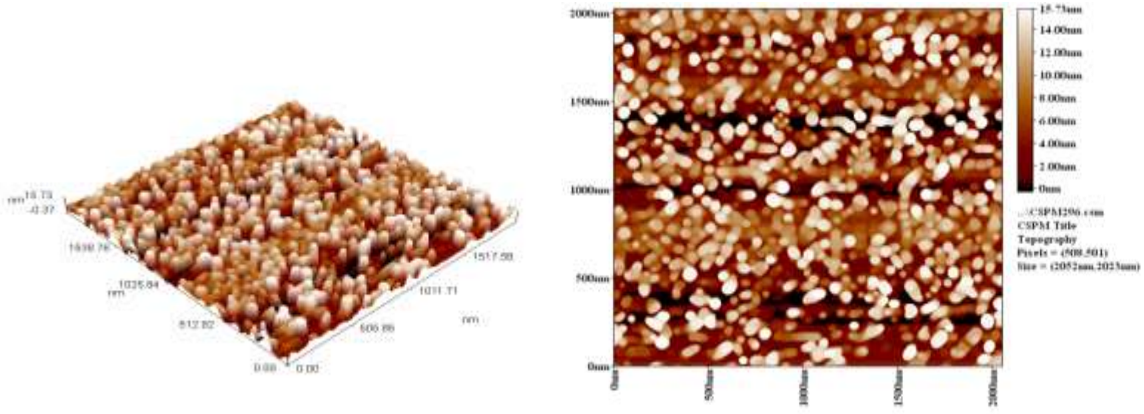
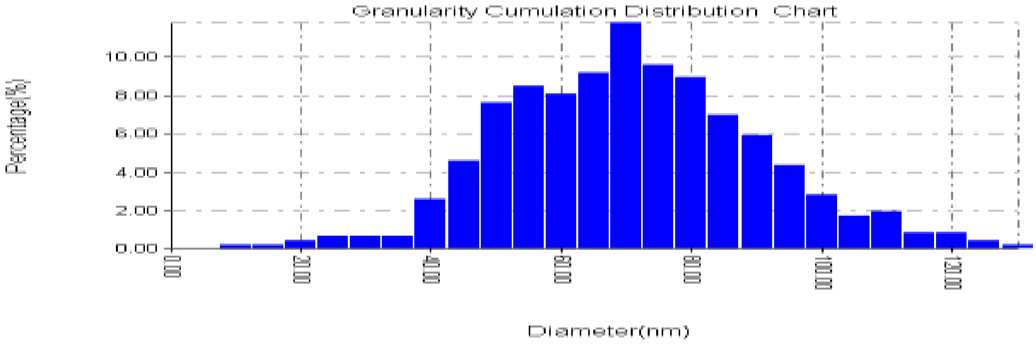


Figure 4 : SEM images of iron oxide nanoparticles.

The surface morphology of CuO nanoparticles examined by AFM shown in Fig.5 and Table.3, images of AFM for copper oxide nanoparticles with area (size= 2052nmX2023nm) and ability analytical(pixels=508,501).Fig.(5-a) is AFM picture in three dimensions (3D) , it explains structural shape for grains ,Fig.(5-b) is AFM picture in two dimensions (2D) it is found that the average roughness is 4.04 nm and RMS (Root mean square) is 4.67 nm, also Fig. (5-c) represents particle size distribution, which is also explained numerically in table 3, where average diameter is 68.42 nm ,and the particle size of less than 10 % of the total particles is 40 nm, less than 50 % is 65 nm and less than 90% is 90 nm and these are agree also with those obtained from SEM .



(5-a) (5-b)



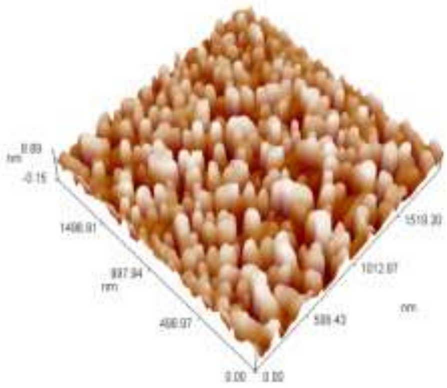
(5-c)

Figure 5 :AFM for copper oxide nanoparticles

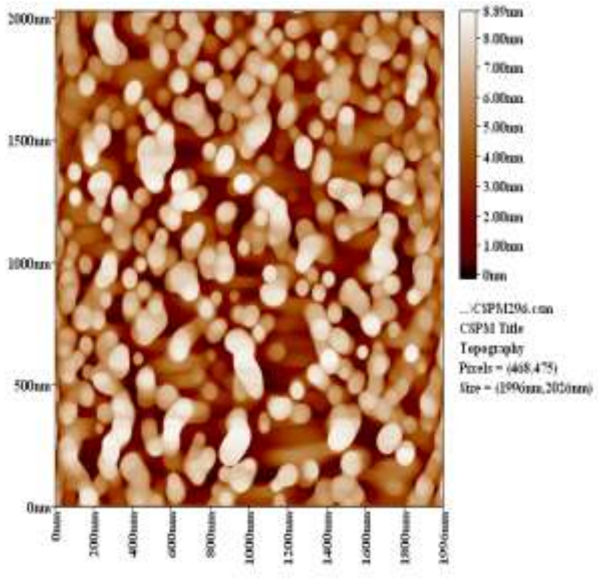
Table 3 : Granularity cumulating distribution and average diameter of nanoparticles

Diamter (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			

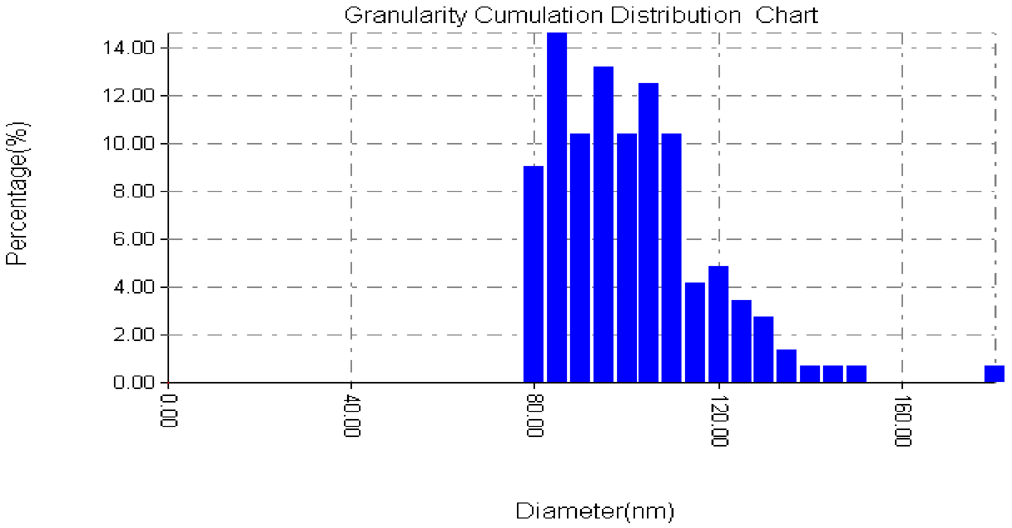
Fig.6 and Table 4 explain images and data of AFM for iron oxide nanoparticles (Fe_3O_4)with area (size= 1996nmX2026nm) and ability analytical(pixels= 468,475.Fig. (6-a) is AFM picture in three dimensions (3D) , it explains structural shape for grains ,Fig. (6-b) is AFM picture in two dimensions (2D) it found average roughness is 1.96 nm and RMS (Root mean square) is 2.3 nm also Fig. (6-c) represents particle size distribution, which is also explained numerically in table 4 where average diameter is 64.70 nm ,and the particle size of less than 10 % of the total particles is 40 nm, less than 60 % is 65 nm and less than 90% is 85 nm and these are agree also with thoseobtained from SEM.



(6-a)



(6-b)



(6-c)

Figure 6 :AFM for iron oxide nanoparticles

Table 4: Granularity cumulating distribution and average diameter of nanoparticles

Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume(%)	Cumulation (%)	Diameter(nm)<	Volume (%)	Cumulation (%)
80.00	9.03	9.03	110.00	10.42	80.56	140.00	0.69	97.92
85.00	14.58	23.61	115.00	4.17	84.72	145.00	0.69	98.61
90.00	10.42	34.03	120.00	4.86	89.58	150.00	0.69	99.31
95.00	13.19	47.22	125.00	3.47	93.06	180.00	0.69	100.00
100.00	10.42	57.64	130.00	2.78	95.83			
105.00	12.50	70.14	135.00	1.39	97.22			

3-3 Separation of lead ions using CuO and Fe_3O_4 nanoparticles.

The batchwiseremoval of lead was performed at room temperature using lead ion concentration of 100, 200 and 300 ppm and a contact time of 20, 60, 90 and 120 minutes while all other experimental parameters being the same. Figs7 and 8 show the relation between percent lead removal and contact time using copper oxide and iron oxide nanoparticles respectively. In both cases there isincrease in percent removal of lead as contact time increase as was expected and shown in other work[5,8,24],

It seem that, lead ion, Pb^{2+} ions were adsorbed onto CuO and Fe_3O_4nanoparticles rapidly, and equilibrium was established within 30 minutes.This could be due to the small size of both oxides nanoparticles, which was favorable for the diffusion of Pb^{2+} ions from bulk solution onto the active sites of the solid surface.The short equilibrium time was in agreement with that reported by other researchers for the adsorption of other metal ions onto iron oxide nanoparticles [25-27]. This is in contrast to other conventional porous adsorbents [28] in which adsorption occurs through pore diffusion steps, This result is promising as equilibrium time plays a major role in economic viability for wastewater treatment plant.

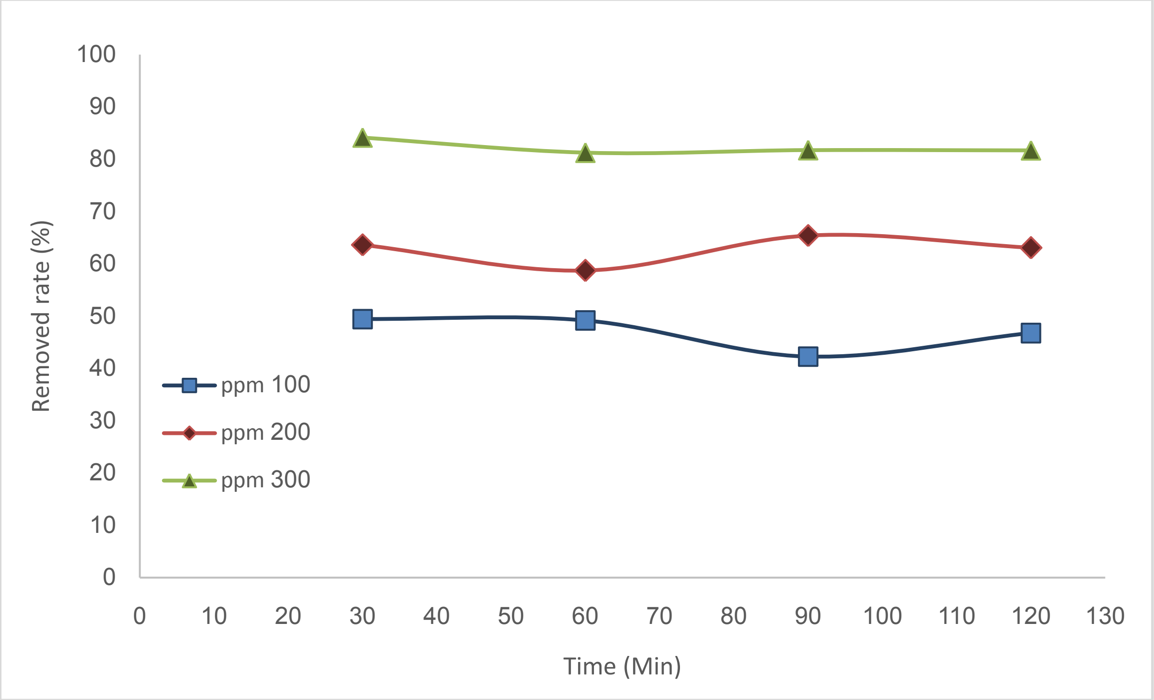


Figure 7 : Percent removal of lead ion using copper oxide nanoparticles.

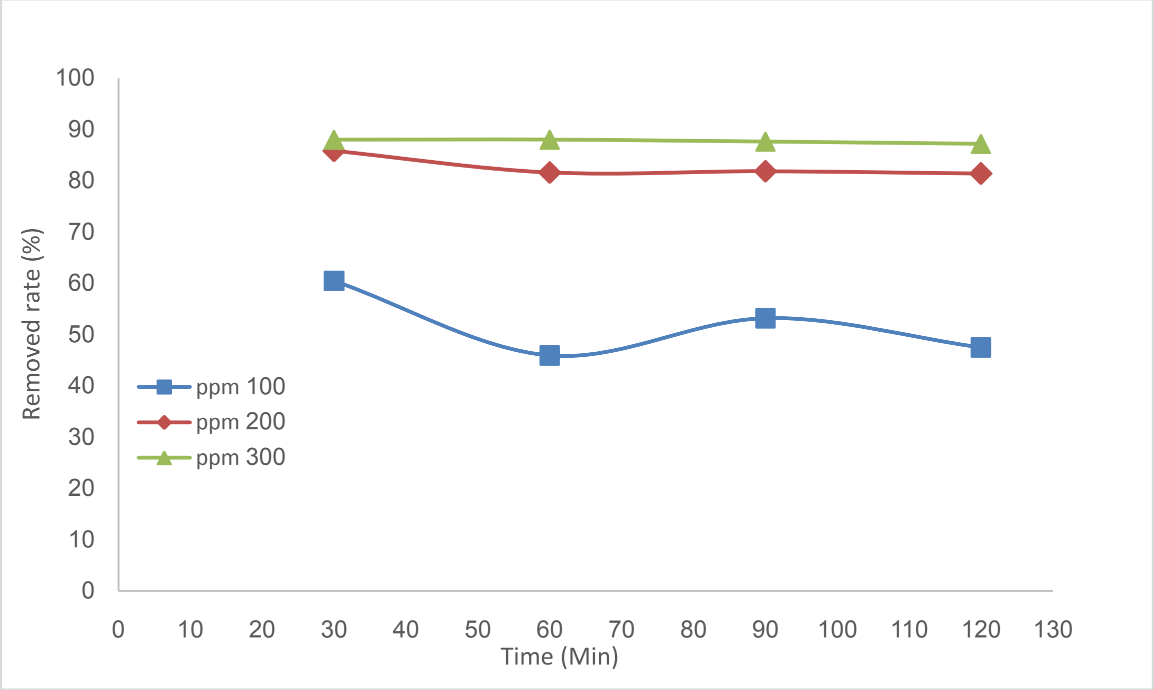


Figure 8 : Percent removal of lead ion using iron oxide nanoparticles .

4. CONCLUSIONS

It was concluded from the present work that both CuO and Fe_3O_4 nanoparticles can be prepared by a simple precipitation method. XRD spectrum revealed that particle size obtained was around 7.43 nm and 12.04 nm respectively which agreed fairly well with XRD data.surface morphology as a main nanoparticles phenomenon was studied in terms of SEM and AFM spectroscopic techniues which prove XRD data.

These nanoparticles were successfully tested for the removal of toxic lead metal from synthetic aqueous solutions,The adsorption process was conducted into acidic and basic environment with lead ion concentration of 100, 200 and 300ppm and a contact time of 30, 60, 90 , 120 minutes.
The obtained adsorption data indicated a higher adsorption tendency for lead ion.The adsorption study showed that the electrostatic attraction was responsible for the metal removal in case of both oxides.The obtained data represents only the preliminary result obtained for achieving a systematic study regarding the removal of heavy metals from wastewaters using adsorbents nanoparticles with high capacity of adsorption due theirs high surface area.

5. ACKNOWLEDGMENTS

The authors wish to acknowledge the technical analysis staff in chemistry department of college of science in Diyala university for facilitating the use of atomic absorption spectrophotometer and for providing laboratory facilities and also the central service laboratory ,Collage of Education Ibn Al-Haitham ,Baghdad University ,Iraq,for use of SEM and XRD and other analysis.

6. REFERENCES

[1] Uzun I., andGuzel F., ‘‘ Adsorption of some heavy metal ions from aqueous solution by activated carbon with those of some other adsorbent ’’, Turk. J. Chem., 24, 291-297, 2000.

[2] Awan M. A., Qazi I. A., and Khalid I.,‘‘Removal of Heavy Metals through Adsorption Using Sand ’’, Environ. Sci., 15(3), 413-416, 2003.

[3] N. Li, and R. Bai,‘‘Highly Enhanced Adsorption of Lead Ions on Chitosan Granules Functionalized with Poly(acrylic acid) ’’, Ind. Eng. Chem. Res., 45, 7897-7904, 2006.

[4] V.K.Gupta, S.Agarwal, and T.A.Saleh,‘‘ Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal’’, J.Hazard.Mater, 185, 17-23, 2011.

[5]Z.Cheng, A.L.K.Tan, Y.Tao, D.Shan,K.E.Ting, andX.J.Yin,‘‘Synthesis and Characterization of Iron Oxide Nanoparticles and Applications in the Removal of Heavy Metals from Industrial Wastewater’’,International J Photoenergy, 2012 ,1-5, 2012.

[6] K.L.Palanisamy, V.Devabharathi, andN.M.Sundaram,‘‘ The utility of magnetic iron oxide nanoparticles stabilized by carrier oils in removal of heavy metals from waste water’’, International Journal of Research in Applied, Natural and Social Sciences, 1, 4, 15-22, 2013.

[7] A.A..Farghali, M.Bahgat, and M.H.Ghedr,‘‘Adsorption of Pb(II) ions from aqueous solutions using copper oxide nanostructures ’’, BeniSuef university Journal of Basic ans Applied Sciences, 2, 61-71, 2013.

[8]A. Imtiaz and U.Rafique, ‘‘Synthesis of Metal Oxides and its Application as Adsorbent for the Treatment of Wastewater Effluent’’, International Journal of Chemical and Enviromental Engineering, 2, 6, 399-405, 2011.

[9] U.Rafique, A. Imtiaz, and A.K.Khan, ‘‘Synthesis, Characterization and Application of Nanomaterials for the Removal of Emerging Pollutants from Industrial WasteWater, Kinetics and Equilibrium Model’’, Journal of Water Sustainability, 2,4 , 233-344, 2012.

[10] X.Wang, Y.Guo, L.Yang, M.Han, J.Zhao and X.Cheng, ‘‘Nanomaterials as sorbent to removeheavy metal ions in wastewater treatment’’, Environmental and Analytical Toxicology, 2, 7, 2-7, 2012.

[11] N. Savage, and M. S. Diallo,‘‘Nanomaterials and Water Purification: Opportunities and Challenges’’, J. Nanopart. Res., 7, 331-342, 2005.

[12] N.N. Mallikarjuna, and A.Venkataraman, ‘‘Adsorption of Pb 2+ ions on nanosized γ-Fe$_2$O$_3$: formation of surface ternary complexes on ligand complexation’’,Talanta., 60,1, 139-147, 2003.

[13] C.M. Gonzalez, J. Hernandez , J. R. Peralta-Videa, C. E. Botez, J. G. Parsons, and J. L. Gardea-Torresdey,‘‘Sorption kinetic study of selenite and selenate onto a high and low pressure aged iron oxide nanomaterial’’, J. Hazard. Mater, 211,138-145, 2012.

[14] B. Prasad, C. Ghosh, A.Chakraborty, N. Bandyopadhyay, and R.K. Ray,‘‘Adsorption of arsenite (As 3+) on nano-sized Fe $_2O_3$ waste powder from the steel industry’’, Desalination. 274,1 ,105-112, 2011.

[15] P.I. Girginova P. I., A. L. Daniel-da-Silva, C. B. Lopes, P. Figueira, M. Otero, V. S. Amaral, E. Pereira, and T. Trindade,‘‘ Silica coated magnetite particles for magnetic removal of Hg^{2+} from water.’’, J. Colloid Interface Sci.,345, 234-240, 2010.

[16]MaqusoodAhamed, Hisham A. Alhadlaq, M. A. Majeed Khan,PonmuruganKaruppiah,andNaif A. Al-Dhabi, ‘‘Synthesis, Characterization, and Antimicrobial Activity ofCopper Oxide Nanoparticles’’,Hindawi Publishing Corportion,Journal of Nanomaterials, 2014, 4, 2014.

[17]Amrut. S. Lanje, Satish J. Sharma, Ramchandara B. Pode, Raghumani S. Ningthoujam,‘‘Synthesis and optical characterization of copper oxide nanoparticles.’’,Pelagia Research Library, Advances in Applied Science Research, 1, 2, 36-40, 2010.

[18] K. L. Palanisamy, V. Devabhrathi, and N. Meenakshisundaram, ‘‘ The Utility of Magnetic Iron Oxide Nanoparticles Stabilized by Carrier Oils in Removal of Heavy Metals from Waste Water.’’,International Journal of Research in Applied, Natural and Social Sciences ,IJRANSS, 1 , 4, 15-22, 2013.

[19]Areej. A. JarullahKarim. H. Hassan and Mahasin. F. Alias,‘‘Removal of Nickel (II) from Aqueous Solution Using Activated Charcoal Derived from the Leaves of Bitter Orange Tree (Citrus aurantium)’’, J. Chem. Chem. Eng. 6,1003-1009, 2012.

[20] S.Nath S., D.Chakdar, and G.Gope, ‘‘Preparation of Silver Nanoparticles and Their Characterization’’, A journal of nanotechnology and its application, 02, 03, 2007.

[21] B. D. Hall, D. Zanchet and D. Ugarte, ‘‘Estimating nanoparticle size from diffraction measurements’’,Journal of Applied Crystallography", 33, 6 , 1335-1341 ,2000.

[22] Karim H Hassan, Tahseen H Mubarak Al-Bayati, and Zena M Ali Abbas,‘‘Study and Characterization of Copper Oxide Nanoparticles Prepared by Chemical Method using X-Ray Diffraction and Scanning Electron Microscope’’,American Journal for Scientific Research. ,77, 49-53,2012

[23] A. AshaRadhakrishnan*, and B. BaskaranBeena,‘‘ Structural and Optical Absorption Analysis of CuO Nanoparticles’’,Indian Journal of Advances in Chemical Science, 2, 12, 158-161, 2014.

[24] Areej. A. Jarullah, Mahasin. F. Alias and Karim H Hassan,‘‘Purification of aquous solution from Ni(II) ions using commercial and Bitter Orange leaves activated charcoal’’,,Journal of Al-NahrainUniversity Science, 17, 1, 32-40, 2014.

[25] A. Uheida, M. Iglesias, and C. Fontas et al.,‘‘Sorption of palladium(II), rhodium(III), and platinum(IV) on Fe_3O_4 nanoparticles’’, Journal of Colloid and Interface Science, 301, 2, 402–408, 2006.

[26] A. Uheida, G. Salazar-Alvarez, E. Bjorkman, Z. Yu, and M. Muhammed,‘‘Fe_3O_4 and [gamma]-Fe_2O_3 nanoparticles for the adsorption of Co^{2+} from aqueous solution’’, Journal of Colloid and Interface Science, 298, 2, 501–507, 2006.

[27] H. Sun, X. Zhang, Q. Niu, Y. Chen, and J. C. Crittenden, , ‘‘Enhanced accumulation of arsenate in carp in the presence of titanium dioxide nanoparticles’’,Water, Air, and Soil Pollution, 178, 1–4, 245–254, 2007.

[28] M. Hussain , Synthesis, characterization and application of metal oxides nanostructures, Division of Physics and Electronics Department of Science and Technology (ITN), Linkoping University, Sweden, 2014