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Comparative Study between Zn and Cu Nano Ferrite in Removal of Heavy Metals and Microorganisms from Water

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Abstract

The effect of Nano composite materials (CuFe2O4 and ZnFe2O4) was studied for removal of heavy metals (Cd (II) and Pb (II)) from wastewater by batch adsorption method and explain their effect on the antimicrobial effectiveness on gram positive and negative bacteria. Nano composite materials were characterized by XRD where the result indicates that the average crystallite sizes were around 36.19 nm for ZnFe2O4 and 12.22 nm for CuFe2O4.The effect of contact time, adsorbent dose, pH and type of adsorbents was used to find the optimum condition for removal of Cd(II) and Pb(II) ions .The equilibrium adsorption data was good fitted to the Langmuir and Freundlich isotherm models, and the pseudo first-order kinetic model showed the excellent fit in adsorption equilibrium capacity.

The best pH used for removal was 7. The good removal reaches at the time 45 min for cadmium and need more time for lead. When increasing dosage of adsorbents, the removal efficiency increases. Freundlich and Langmuir isotherm gave the best fit experimental data. Also, antibacterial effects of this nano particles demonstrated the effect of CuFe2O4 NPs on bacteria more than used ZnFe2O4 NPs, and the percentage of bacterial death was increased according to increase the concentration of this materials.

Keywords: Nano composites, batch adsorption, heavy metals, antimicrobial, isotherm.

دراسة مقارنة بين أكسيد الزنك والنحاس النانوي المغناطيسي في إزالة المعادن الثقيلة والاحياء المجهرية من الماء

ازهار جبار بوحان[1] ، غيد خلف سلمان[1] و غيداء مجيد جيد[2]

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الخلاصة

تمت دراسة تأثير المواد النانوية المتراكبة ($CuFe_2O_4$ and ZnFe2O4) في ازالة المعادن الثقيلة (Cd(II) and Pb(II) (من مياه الصرف الصحي بطريقة (Batch adsorption Method) و توضيح فعاليتهما على البكتريا الموجبة و السالبة لصبغة غرام . تم دراسة اهم خصائص تلك المواد النانوية باستخدام جهاز حيود الاشعة السينية XRD و كانت نتائج حجم البلرة 19.36 nm بالنسبة لأوكسيد الزنك المغناطيسي النانوي و 22.12 nm بالنسبة لأوكسيد النحاس المغناطيسي النانوي. و تم دراسة تأثير الوقت و درجة الحامضية و نوع و تركيز المادة المستخدمة لأيجاد الظروف المثالية لأزالة ايونات الرصاص و الكادميوم. و كانت بيانات الامتصاص جيدة بشكل عام عند استخدام (Freundlich and Langmuir isotherm models) اما عند استخدام(The pseudo- first- order kinetic model) فكانت نتائج الأزالة ممتازة في قابلية الامتصاص المتوازن، أفضل درجة حموضة مستخدمة للإزالة كانت 7. الإزالة الجيدة تصل في الوقت المحدد إلى 45 دقيقة للكادميوم وتحتاج إلى مزيد من الوقت للرصاص, عند زيادة جرعة الممتزات تزداد كفاءة الإزالة. اعطت (Freundlich and Langmuir isotherm) أفضل البيانات التجريبية الملائمة . كذلك التأثير المضاد للبكتريا لهذه المواد النانوية ,اظهر أن CuFe2O4 NPs المستخدمة اكثرتأثير من استخدام ZnFe2O4 NPs, وزادت نسبة الموت البكتيري حسب زيادة تركيز هذه المواد.

الكلمات المفتاحية : متراكبات نانوية، الأمتزاز، المعادن الثقيلة، الخاصية المضادة للبكتريا.

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Introduction

Water pollution is a considerable environmental problem confronted the world that leads to ecological deterioration and health hazards. As stated by world health organization (WHO) 80% diseases are waterborne [1-2].

There are great attentions in using magnetic materials in water treatment by removing water contaminants, including heavy metals, pathogenic bacteria, viruses, harmful chemicals, and pesticides etc. Magnetic ferrite-based adsorbents can be used to remove heavy metals from wastewater due to higher adsorption capacities, large surface area, excellent magnetic properties and easy recovery from aqueous solution [3-4].

Heavy metals enter aquatic systems through streams of the various industrial activities such as fertilizers, batteries, pesticides, and mining operations, etc. Heavy metals take a significant attention since they are non-biodegradable and toxic [5]. To reach safe and clean aquatic systems several techniques are used like adsorption, reverse osmosis, precipitation, electrochemical treatments, ion exchange, membrane filtration, and oxidation processes. Among these methods, adsorption method is considered quite attractive because of its effective, simple, low cost, and ease in equipment handling. Since the adsorption efficiency mostly depends on the adsorbent characteristic, the choice of suitable adsorbent is necessary [6-7].

The particular properties of attractive nanoparticles required for biomedical applications require exact control of molecule scattering, shape, size and any outside elements that impact these properties. On a basic level, it is important to balance out the attractive nanoparticle scattering in the watery condition. In this way, covering the attractive nanoparticles with a polymer envelope, including natural (e.g., phospholipids, polyethylene glycol, poly ethylene amine, and dextran, chitosan) or inorganic (e.g., silica) substances, prompts exceptionally scattered and top notch nanoparticles with great biocompatibility [8].

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As of late, Sanpo et al. [9] recommended another way to improve the biomedical applications of ferrite nano particles and their antibacterial properties. They found that replacement of spinel ferrite with a change metal can enhance the antibacterial capacity of nanoparticles. Nonetheless, the biomedical utilization of these recently integrated nanoparticles requires further examination concerning their antibacterial properties and biocompatibility.

In the present study, nano powder were synthesized copper and zinc ferrite ($CuFe_2O_4$ and $ZnFe_2O_4$) were used for removing the heavy metals (Pb) and (Cd) from synthetic waste water. Ferrite powder work in solution as an adsorption medium, for remove contaminating species from, waste water by batch reactors method. Then, study the effect of nano composites of ferrites powder synthesized of copper and zinc ferrite against *staphylococcus aureus* as gram positive bacteria and *E. coli*, *Pseudomous aeruginosa* as gram negative. Besides, silver nanoparticles stacked into copper ferrite (CuFe2O4) magnetic empty strands indicated magnificent antimicrobial adequacy against four microscopic organisms: V. parahaemolyticus, S. Typhi, E. coli, and S. aureus [10]. Also [11] explain the antimicrobial effectiveness results that a (Cu0.9Zn0.1Fe2O4) have the most antibacterial properties against two types of bacteria compared with another Nano ferrite that used in this research and the proportion of killing of the S. aureus killing was smaller than that of killing of E. coli all ferrite composite nanoparticles.

Experimental

1. Preparation of Ferrites Powder

Pure powder of $CuFe_2O_4$ and $ZnFe_2O_4$nano-ferrite (NF) with particle size 12.22 nm for $CuFe_2O_4$.and 36.19nm for $ZnFe_2O_4$was prepared using citrate-gel method in laboratory, that chemical method was used to prepare Cu and Zn ferrites powders. High purity cupric nitrate hydrate Cu $(NO_3)2.6H_2O$, ferric nitrate monohydrate Fe $(NO_3)3.9H_2O$ and Zn $(NO_3)_2$ are used as raw materials, 2M of citric acid ($C_6H_8O_7{\times}H_2O$) added to the mixture, in molar ratio 3:1 (acid: nitrates). Mixed solution of these materials was prepared in deionized water with vigorous stirring until the solution being a gel, and the produced powder Calcinate in about 500^0C for 2houer.

2. Batch Adsorption Experiments

The adsorption of lead and cadmium on copper and zinc ferrite ($CuFe_2O_4$ and $ZnFe_2O_4$) was investigated by batch technique. Various amounts of adsorbents were added to a number of conical flasks containing 100 (ml) aqueous solutions at room temperature with 10(mg/L) initial concentrations of cadmium and lead at different values of pH were mixed at 150 rpm then after, were taken a sample from aqueous solution at several time (15, 30 and 45,) min then filtered by Whatman filter paper before analysis to remove ferrite powder and the remaining lead and cadmium in water was detected by using Atomic Absorption spectrometer (AAs). The effect of pH, adsorbent dose concentrations, and contact time and the type of adsorbent was studied. The removal efficiency percentage (R %) and the adsorption capacities of lead and cadmium ions were calculated from the equations (1) and (2) [12-13]:

$$R\,\% = \frac{C_0 - C_e}{C_0} * 100\% \qquad 1$$

$$q = \frac{C_0 - C_e}{M} V \qquad 2$$

Where C_o Ce are the initial and equilibrium concentrations(mg/l) of lead and cadmium before and after adsorption, V is the volume of solution (l), and M is the amount of adsorbent (g).

Adsorption Isotherm

It gives a picture of how the adsorption process occurs and the relationship between adsorbate and adsorbent. In this work, two isotherm Models Langmuir and Freundlich, were chosen and studied for illustrate the relationship between the amount of adsorbate on the adsorbent and the equilibrium concentration in wastewater solution at ambient temperature at pH 7.

1.The Langmuir model assumption to monolayer adsorption takes place homogeneously on active sites on the surface expressed in equation (3) and the affinity between the adsorbate and adsorbent of Langmuir isotherm was checked by a dimensionless separation factor R_L which can be calculated from equation (4), [14-15].

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (3)$$

$$R_L = \frac{1}{(1+ b\,C_0)} \quad (4)$$

Where qe is the amount of heavy metals adsorbed (mg/ g), C_0 and C_e are the initial and equilibrium concentration of heavy metals in solution (mg/ l) , b is the constant of Langmuir (l/mg) , q_m is the maximum quantity of monolayer adsorption (mg/ g) and R_L indicates the type of isotherm to be irreversible ($R_L = 0$), linear ($R_L = 1$) (or) unfavorable ($R_L > 1$) and favorable ($0 < R_L < 1$).

2. Freundlich model is an empirical equation that describes the properties of multilayer isotherm adsorption and is based on heterogeneous surface energies [16-17].

$$\log q_e = \log k_m + \frac{1}{n}\log C_e \quad (5)$$

The linear form of Freundlich model is presented in equation (5). K_m (l/g) is the capacity of the adsorbent and n (g/l) is the adsorption intensity. The appropriate adsorption happens when the values of n is between ($1 < n < 10$).

Adsorption Kinetics:

The rate constant for adsorption of lead and cadmium ions on copper and zinc ferrite is also studied under the light of the pseudo first and second-order kinetic rate used for this adsorption system. The pseudofirst-order rate expression of Lagergren model is given by the following formula [18-20]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (6)$$

Where q_t, K_1 and q_e are the adsorption capacity at time t and equilibrium (mg/g), k_1 is the rate constant of pseudo first-order adsorption (l/min).

Pseudo second order model is utilize to inspect the adsorption kinetic rate which K_2 is expressed as [18-20]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad 7$$

Where k2 (g/mg min) is the rate constant for pseudo second order.

TEST OF ANTIBACTERIAL ACTIVITY

Pure cultures of *E.Coli and Staph. aureus* were culture on nutrient agar for 24 h at 37° C, full lopes of each culture was diluted to obtain concentration (10^5 cell/ml) that added to concentration (1.25, 2.5, 5) mg/ml of $CuFe_2O_4$ and $ZnFe_2O_4$alone, This mixture was cultured over night at 37° C in shaker incubation and after diluted in normal saline by serial dilution, 100µl of dilution was spread on Molar-Hinton Agar by L shape and incubated at 37° C for 24 h, and after the number of bacteria colony on plate was counted, and colony forming units (CFUs) were determined by multiplying the number of bacterial colonies by the dilution factor [21]. The percentage of bacteria survival, which is defined by flowing formula was utilized to assess the antimicrobial impact of particles and this method according to [22].

$$Survival\ \% = \frac{number\ of\ Colony\ bacterial\ treated}{number\ of\ Colony\ control\ bacteria} \times 100 \qquad (8)$$

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Results and Discussions:

1. XRD analyzes:

The phase Identification of the calcined powder at 500^0C, of $ZnFe_2O_4$ and $CuFe_2O_4$ samples, carried out by (XRD) diffraction of X-ray.

The XRD patterns of samples are shown in figure 1 both samples indicate a spinel structure with single phase and a well crystallinity. XRD patterns comparable with the standard JCPDS cards, where JCPDS (01-1108) for ZnFe2O4 and JCPDS (34-0425) for CuFe2O4, find that the two samples were be indexed perfectly to the spinel with cubic structure shown as seen in the reflecting planes (111), (220), (311), (222), (400), (422), (511), and (440) in the patterns. By used of Scherrer's [23] equation (9) the average particle sizes were is around 36.19nm for $ZnFe_2O_4$ and 12.22 nm for $CuFe_2O_4$.

$$D = 0.9\,\lambda / \beta \cos\theta \quad (9)$$

Where D was the crystalline size average, λ was the wavelength of Cu Kα, β was the full width at half maximum (FWHM) of the intense diffraction peak (311), and θ was the Bragg's angle,

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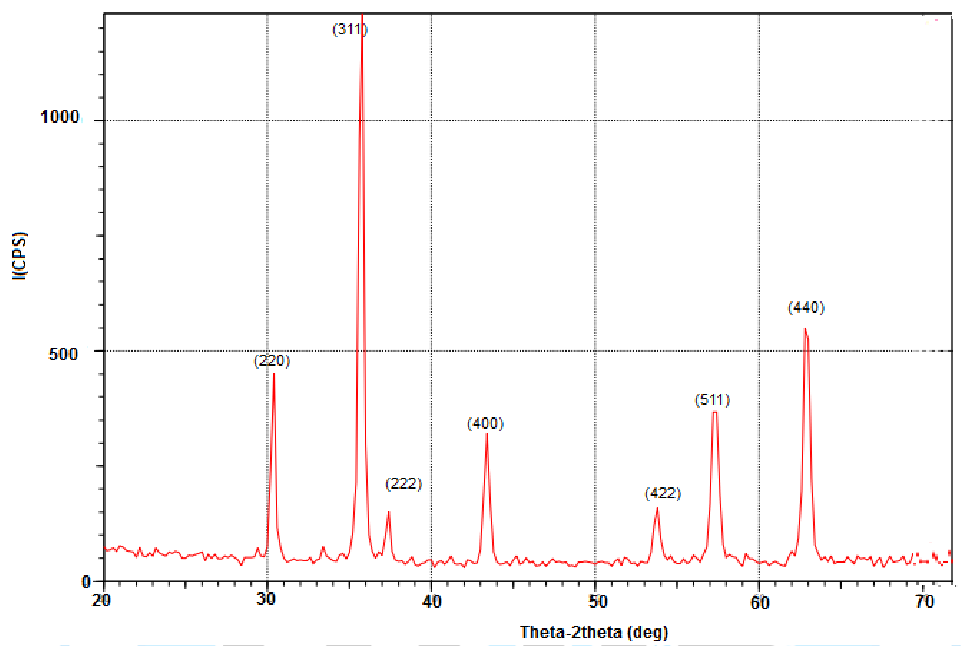
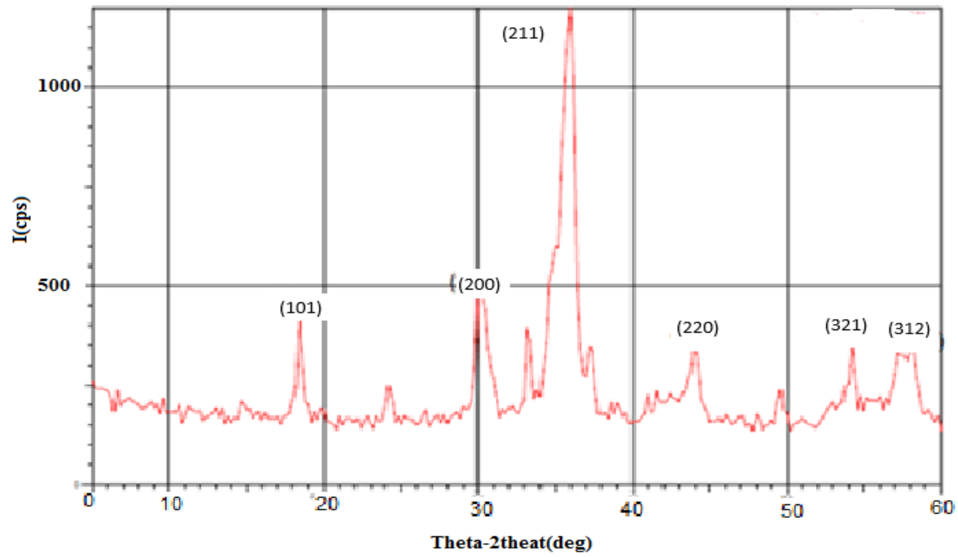


(a)



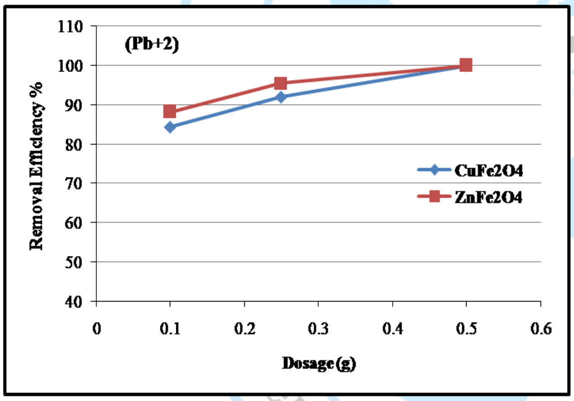
(b)

Figure 1: XRD present of (a) $ZnFe_2O_4$, (b) $CuFe_2O_4$ powder

2. Adsorption of heavy metals of Pb (II) and Cadmium (II):

2.1. Effect of Nano composites dosage:

The effect of nano composites dosage varied from 0.1 to 0.5 g on removal lead and cadmium are presented in figure 2. The impact of varying doses of copper and zinc ferrite was investigated using 100 mg/L initial concentration of metals, at initial pH 7 and contact time 45 min. It can be seen from figure 2 that the nano composites dose increase the removal efficiency of lead and cadmium due to providing more surface area and the availability of more adsorption sites [24]. .The figure shows that zinc ferrite reached to complete removal for cadmium and lead, copper ferrite removal were 100% for cadmium and lead at dosage 0.5 gm.



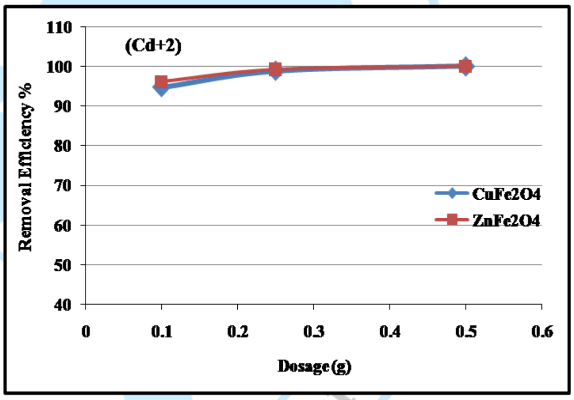


Figure 2: Removal efficiency of lead and cadmium adsorption onto $CuFe_2O_4$ and $ZnFe_2O_4$ VS dosage (gm), (at 45 min and pH 7)

2.2. Effect of pH on adsorption process:

One of the most dominant parameters that impact the adsorption process of removing metal is the pH of the solution. To find the optimum pH for removal Cd(II) and Pb(II) three pH values of 3, 7, and 9 are investigated at 0.1 g dosage of copper and zinc ferrite and 100 mg/L initial concentration of metals, at 45 min of contact time. Results are graphed in figure 3, for both two metals on two adsorbents with an increase of pH from 3 to 7 the removal efficiency was increased and when using pH 9 in the process the removal efficiency decreased, that making the optimum pH was 7. At pH 3 low adsorption happened because of the competition between the hydrogen and cadmium and lead ions of on the adsorption sites. At pH 9 and higher values insoluble ions hydroxide starts precipitating from the solutions [25]. Maximum removal efficiency of lead on copper ferrite and zinc ferrite was (84.4 & 88) % respectively, whereas maximum removal efficiency of cadmium on copper ferrite and zinc ferrite was (94.7& 96) % respectively.

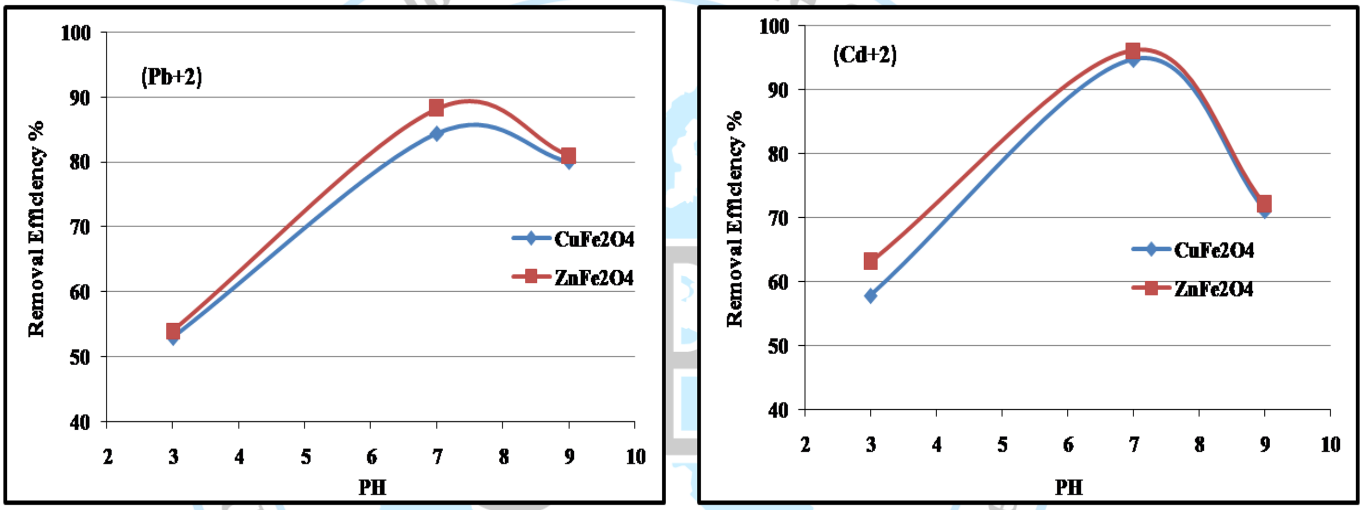


Figure 3: Removal efficiency of lead and cadmium adsorption onto $CuFe_2O_4$ and $ZnFe_2O_4$ VS pH dosage (gm) at 45 min and dosage=0.1 gm

2.3. Effect of contact time on adsorption process

The relation between contact time and the removal efficiency of cadmium and lead was studied at (15, 30 and 45) min under specific condition: 100 mg/L initial concentration of metals at 7pH and 0.1 g of nano composites adsorbents is shown in figure 4. There was a gradual increase in adsorption of Cd (II) and Pb (II) and reach maximum at 45 min. Removal efficiency for cadmium on copper ferrite was 94.7% and on zinc ferrite was 96.1% denoted that 45 min contact time was sufficient to reach equilibrium in cadmium, and the maximum removal efficiency for lead on copper ferrite was 84.4% and on zinc ferrite was 88% which indicated that need for more time to reach complete removal

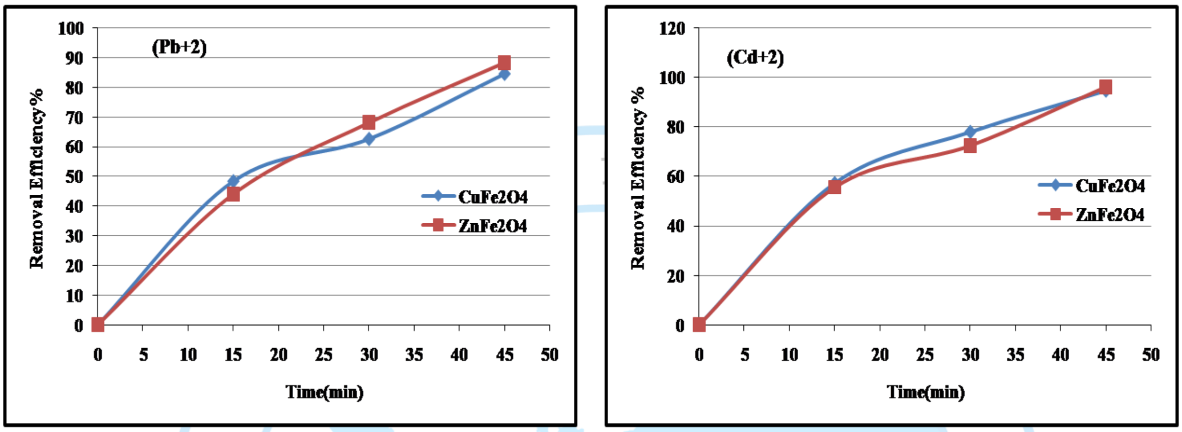


Figure 4: Removal efficiency of lead and cadmium adsorption onto $CuFe_2O_4$ and $ZnFe_2O_4$ VS pH Time (min) (pH=7 min and dosage=0.1 gm)

3. Adsorption isotherm:

Table 1: Isotherm parameters for Cd (II) and Pb(II) adsorption onto $CuFe_2O_4$ and $ZnFe_2O_4$.

Adsorption isotherm	Parameter	Adsorbent CuFe2O4		Adsorbent ZnFe2O4	
		Cd(II)	Pb(II)	Cd(II)	Pb(II)
Langmuir	qm	10.75	9.6	10.87	8.55
	b	11.62	3.85	15.33	4.03
	RL	0.00852	0.0253	0.0065	0.0244
	R2	0.881	0.774	0.872	0.726
Freundlich	Km	8.61	5.573	9.53	6.278
	n	4.5	6.54	4.22	5.81
	R2	0.871	0.744	0.876	0.793

The values of the highest adsorption capacity, qm (mg/g), calculated based on the Langmuir isotherm, and Freundlich parameter, Km, are given in Table 1which denotes that the adsorption of cadmium and lead studied followed the order Cd (II) > Pb (II) and this could be attributed to the interpreted dependence on the ionic radius of Cd (II) and Pb (II) ions. The ionic radii of Cd

(II) (0.97Å) and Pb (II) (1.20Å).This means that the lesser the ionic radius of a metal ion, the greater the adsorption rate [26].

The values of the determination coefficient, R^2, for both Freundlich and Langmuir models were close to unity, thereby indicating that excellent agreement between the experimental data and models of isotherms. This could be the result of preparation and structure of the magnetic materials [3].

4. Adsorption kinetics for Cd (II) and Pb(II) adsorption onto $CuFe_2O_4$ and $ZnFe_2O_4$:

The kinetics study for the cadmium and lead adsorption were conducted at optimum pH 7.0 and completed in 45 and (10 mg/l) concentrations for each ion onto 0.1g doses of both adsorbents in 100 ml solution.

Table 2: Adsorption kinetics model for Cd (II) and Pb (II) adsorption onto $CuFe_2O_4$ and $ZnFe_2O_4$.

Model	Parameter	Adsorbent CuFe2O4		Adsorbent ZnFe2O4	
		Cd(II)	Pb(II)	Cd(II)	Pb(II)
Pseudo first-order	qe	9.27	7.96	9.12	8.95
	K1	0.0576	0.0438	0.046	0.0484
	R2	0.998	0.978	0.983	0.998
Pseudo second-order	qe	14.085	13.5135	15.1515	17.857
	K2	0.00314	0.0025	0.00466	0.00314
	R2	0.992	0.916	0.935	0.998
experimental	qe	9.47	8.44	9.61	8.82

The kinetic model parameters like rate constant and adsorption equilibrium capacity were calculated and presented in table 2. From the results it is shown that pseudo-first -order model yield excellent in comparison with pseudo-second -order reaction model in adsorption equilibrium capacity, the theoretical value of adsorption equilibrium capacity of pseudo-first-order model are nearby to the experimented value of qe ,indicating that pseudo -first-order model is closer to describing the kinetic behavior of cadmium and lead adsorption onto $CuFe_2O_4$ and $ZnFe_2O_4$.

5. Antibacterial activities results and discussion

The results appeared ability of $CuFe_2O_4$ NPs to effect on bacteria more than used $ZnFe_2O_4$ NPs, the percentage of bacterial death was increased according to increase the concentration of this materials so the percentage death of *E.coli* bacteria was (99 , 99.4 ,100)% when using $CuFe_2O_4$ NPs and (70, 78,85)% when using $ZnFe_2O_4$ NPs while (84, 90 , 95)% when using $CuFe_2O_4$ NPs and (44, 58,69)% when using $ZnFe_2O_4$ NPs against *Staph. aureus* as shown in Fig (5), and this results agreed with [11] that explained ability of magnatic nano ferrite to effect on gram positive and negative bacteria.

A lot of studies accepting with our results that explain the ability of copper and zinc to effect on several types of bacteria [10-11]. The effect of copper appeared on cell membrane of bacteria and change in its morphology when attached on cell wall and penetrated cell membrane that leads to destruction of cell wall and lysis of cytoplasm and finally death of bacteria cell especially with increased concentration of copper nano particles [27]. Also when using of zinc nano particles its act to prolong the lag phase of growth cycle after bind to membrane of bacteria and each organism take more time to complete cell division because its lead to increase the generation time [28], also antibacterial activity maybe appearing by main chemical species were assumed to be active oxides; like super-oxide (O^{2-}), and hydrogen peroxide (H_2O_2) that are generated from surface of the zinc nano particles [29]. Readily the active oxides cause cell destruction by break through the cell wall of bacteria and this penetration of active oxides that have an important role in increased the killing rate of zinc Nanoparticles, also chemical and structure ingredients of the cell walls are different between *S. aureus* and *E. coli*. The cell wall of *S. aureus* consists of peptidoglycan, whereas *E. coli* cell wall consists of peptidoglycan, lipopolysaccharide and lipid A [30, 31].

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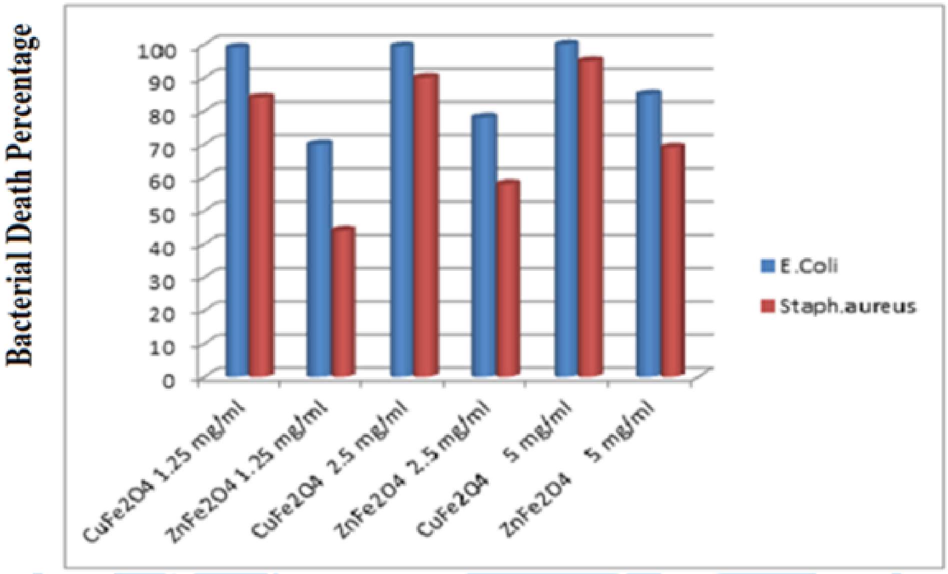

Figure 5: The percentage of bacterial death in deferent concentrations of ($CuFe_2O_4$ and $ZnFe_2O_4$) NPs

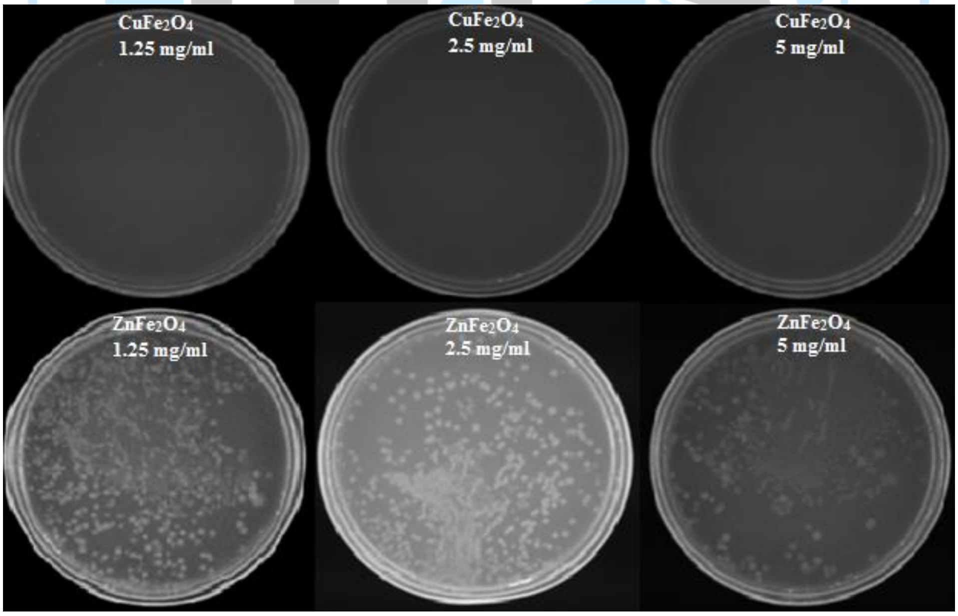

Figure 6: Antibacterial activity of different percentage of $CuFe_2O_4$ and $ZnFe_2O_4$ on *E.coli* bacteria

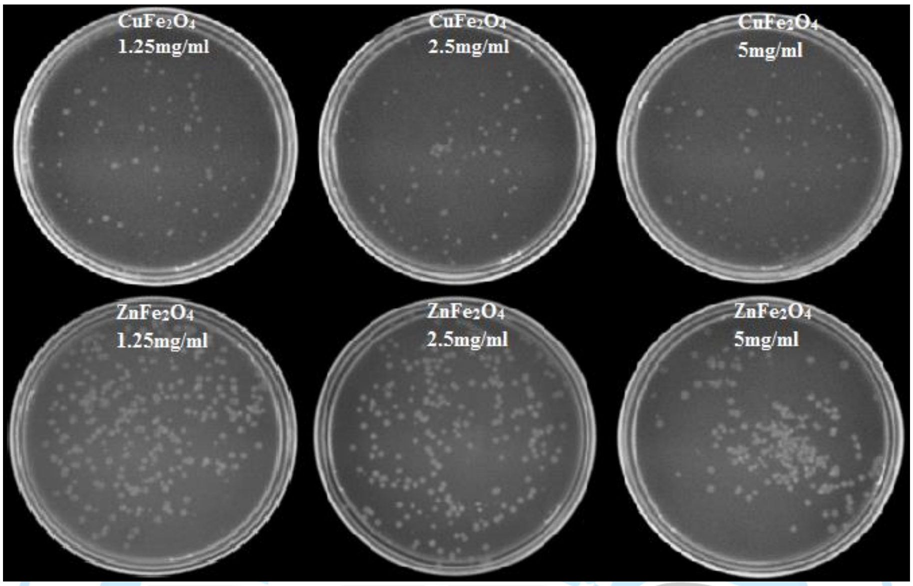

Figure7: Antibacterial activity of different percentage of $CuFe_2O_4$ and $ZnFe_2O_4$ on *Staph.aureus* bacteria

Conclusions

Preparing of nano composites synthesized copper ferrite and zinc ferrite is suitable for removal of heavy metals with very good results, the average particle sizes were around 36.19 nm for $ZnFe_2O_4$ and 12.22 nm for $CuFe_2O_4$, the adsorption of cadmium and lead by Cu- Ferrite was effective, especially for cadmium. The best pH used for removal was 7. The good removal reaches at the time 45 min for cadmium and need more time for lead. When increasing dosage of adsorbents the removal efficiency increases. Freundlich and Langmuir isotherm gave the best fit experimental data. The pseudo first-order model is closer in describing the kinetic behavior of cadmium and lead adsorption onto $CuFe_2O_4$ and $ZnFe_2O_4$. Also these nano materials were practically applied when using of copper nano ferrite against *E.coli* and *Staph. aureus* bacteria gave effect more than using zinc nano ferrite and the percentage of bacterial killing was differs according to the change in of ferrite materials concentrations.

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