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Use of Nano-Magnetic Material for Removal of Heavy Metals from Wastewater

Abstract: The reason of this study is to consider the removal of heavy metal lead (Pb) and cadmium (Cd) in wastewater by magnetic material using ferrite. It has been use batch experiments and operating condition are, ph(10,7and5) and time (20, 40, 60.80.100, 120) min and temperature (30) ^{0}C after that we find the optimum condition to remove heavy metal. heavy metal in water detected by using Atomic Absorption (AA) before and after adding Cu-ferrites powder while the Cu-ferrites was characteristic by XRD and SEM 'result indicate that Cu-ferrites powder spinel structure and the particle size in range (30-40)nm ,and explain antimicrobial effectiveness of ferrites material from effect on gram positive and negative bacteria and the results appeared ability of copper ferrites to inhibition growth of both E. coli as example of gram negative bacteria and S. aureus as example of gram positive bacteria while was the E. coli survival rate of all ferrite nanoparticles concentration is more than the S. aureus survival rate , the percentage survival of bacteria was (35 , 20 , 12 , 5 %) in (0.625 , 1.25 , 2.5 , 5 mg/ml) concentration of microorganisms E.coli and (28 , 15 , 8 , 3 %) in (0.625 , 1.25 , 2.5 , 5 mg/ml) concentration for bacteria Staph. Aureus

Keywords *Cu-ferrites, west water, Atomic Absorption (AA), XRD, SEM, antimicrobial, E. coli, S. aureus, batch experiments.*

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1. Introduction

One of the modern issues is Contamination water by dangerous metal particles like Cd(II), Pb(II) and pollution by a microorganism that causes danger satisfaction in water and turning into a serious natural and general medical problem. Many materials are used to remove heavy metals especially if they are able to sorbet the ions but depends on which is your interest in the efficiency and performance of the process. So that established many approaches to channel the west water such precipitation, particle trade, buoyancy, oxidation electrochemical medications, adsorption, invert osmosis, dissipation, film filtration, and biosorption procedures are broadly utilized [1-2]Improvement of the novel and financially savvy nanomaterials for natural remediation, contamination discovery and different applications has pulled in extensive consideration. Late advances propose that a number of problems including quality of water can be settled or significantly enhanced utilizing nanoparticles, nanofiltration or different items coming about because of the improvement of nanotechnology [3-4]. Ferrite is a term of a class of attractive iron oxide intensifies that have the property of unconstrained charge and is crystalline materials dissolvable just in solid corrosive [5]. Press particles in iron ferrite (FeO•Fe2O3) can be supplanted by numerous other metal particles without genuinely changing its spinel structure [6]. Ferrites were utilized as a part of the group for actinide and substantial metal expulsion from wastewater [7]. Other late reviews have exhibited the attractively improved remove of arsenic, chromium, cobalt, iron, and uranium from recreated groundwater and wastewater [8]. In most customary wastewater treatment forms metals are evacuated as metal hydroxides since they have low solubility. Ferric hydroxide is regularly added to search a wide assortment of overwhelming metal con taminants [9]. Therefore, direct help should in some cases be added to encourage the filtration procedure Ferrite works as an adsorption medium to drive out tainting species from the arrangement. In situ ferrite likewise, works in this way [10]. The adsorption component of ferrite happens through metal hydroxide species. In the basic arrangement, most metal particles frame insoluble species which might be complexed [11].
Impressive consideration has been paid to attractive nanoparticles because of their planned applications in the field of biomedicine, biotechnology, material science and building.

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These nanoparticles display great attractive properties and also different sub-atomic and cell level associations in a few natural procedures [12]. Attractive nanoparticles are very ideal; being biocompatible, they are moderately less harmful and have attractive properties [13, 14]. Free radicals are particles or iotas with an unpaired electron. These are exceedingly receptive species that destabilize different atoms and create numerous all the more free radicals. Inorganic frameworks, free radicals are shaped as a piece of the body's ordinary metabolic procedures when biomolecules connect with oxygen. In any case, expanded levels of free radicals are hindering to human wellbeing as they cause a few issue, including malignancy. Myocardial localized necrosis, atherosclerosis, and neurodegenerative issue [15]. Concoction substances, known as cancer prevention agents, can search these free radicals and, in this manner, diminish the event of oxidative anxiety initiated cell demise or harm. Analysts have demonstrated that nanoparticles can go about as engineered cancer prevention agents in the body and have great cell reinforcement properties contrasted with their mass material partners, which is ascribed to the expanded surface to volume proportion of the nanostructures [16, 17]. Correspondingly, the expanded surface range of nanoparticles can be appropriately functionalized to tie particularly to destructive cells and, therefore, offer an approach for tumor treatment. Also, it has been expressed that medication conveyance frameworks utilizing nanoparticles are extremely effective in the treatment of growth as a result of their unrivaled bio-appropriation profile and pharmacokinetics [18]. Nonetheless, potential utilizations of nanoparticles can be considered for all intents and purposes just when their poisonous impact is caught on. In spite of the fact that different ferrite nanoparticles are incorporated and described, their natural exercises including cytotoxicity are not all around investigated yet. To date, almost no data is accessible on the lethality of attractive nanoparticles [19].the aim of research was to study the effect of ferrites powder as heavy metal removable and antimicrobial effectiveness of ferrites.

2. Experimental

I. Preparation of ferrites powder

Cu ferrites with a generic formula $CuFe_2O_4$ prepared were synthesized by auto combustion method; all of the chemicals were analytical grade with purity ≥99% and were used. In a typical procedure, cupric nitrate hydrate Cu $(NO_3)_2$•$6H_2O$, ferric nitrate nonahydrate Fe $(NO_3)3$•$9H_2O$ were used as initial materials. Mixed solutions of these materials were prepared in deionized water with vigorous stirring at room temperature. A specific volume of ammonia NH_3OH was added to the above mixed solution. After, the solution of NH3OH was added until pH values reached 11. The pH of solution is one of the main factors on which the final composition of the product depends, which can be varied to get the desired final product. The final powder samples obtained were calcinations at 500°C for 2h.

II. West water treatment Procedure

Heavy metals (cadmium and lead) were adopted to synthesize the simulated laboratory waste liquid. Batch adsorption were studied , Ferrite which prepared separately using the situ procedures, With the in situ method, ferrous iron is added to the waste solution (heated to 30°C); with initial concentrations of Pb and Cd 25 ppm were mixed and placed in the stirrer with continued stirring then after (20, 40, 60, 100,120) min, take sample of water filtered through filter paper to remove ferrites powder and the heavy metal in water detected by using Atomic Absorption (AA) before and after adding ferrites powder The percentage of metal ions removed was obtained from equation (1)

$$R\,\% = \frac{C_o - C_t}{C_o} \quad * 100\% \qquad (1)$$

Where (R%) is the ratio of removal metal concentration , Where Co and Ct are the initial and final concentrations(ppm) of the heavy metals present in wastewater before and after adsorption, for a period of time(min) respectively where the ferries powder characterized by the ferrites was characteristic by XRD and SEM. Cu –ferrites which is The sorbent can be recovered by keeping it plugged in HCl arrangement with pH=3 for a couple of hours. It is then washed more than once with refined water and is reused.

III. Antimicrobial activity Procedure

The antimicrobial activity Cu-ferrite Nano particles powder is tested against *Escherichia coli* (*E. coli*), as Gram-negative bacteria, and *Staphylococcus aureus (S. aureus).* As gram-positive bacteria, all tests were performed on solid agar plates with different concentrations of Cu-ferrite Nano particles powder. E. coli and S. aureus are grown aerobically at 37 °C overnight (OVN culture), the reduction in viable cell

number after interaction was determined by the standard agar dilution method as follows:
One milliliter of bacterial solution was added to desired $CuFe_2O_4$ solutions at the concentrations of (0.625, 1.25, 2.5, 5) mg/ml. The equal mixture of saline and bacteria was as a control. The mixtures were cultivated at 37 ^{0}C and shacked at 160 rpm and incubated for 24 h. The suspension was serially diluted serially (1:10) with normal saline and 100 µl of these mixtures were spread on an agar plate using an L-shaped spreader ,the plates are incubated at 37 °C, and number of colonies on the petri dish was counted after 24 h. The colony forming units (CFUs) are calculated by multiplying the number of colonies bacteria by the dilution factor. The survival rate of bacteria was used to estimate the antimicrobial effectiveness of particles against bacteria which defined by the following formula:

$$\text{Survival}= \frac{\text{Colony number of tested bacteria}}{\text{Colony number of control bacteria}} \% \times 100 \quad (2)$$

4. Results and Discussions

I. XRD of powder Pattern

The XRD model of $CuFe_2O_4$ (pH=11) test appeared in. Figure. (1) With sharp and well-characterized peak, XRD patterns demonstrate that all peak ordered to cubic phase, where (111), (220), (311), (400), (511), and (440) be a symbol for the main crystal phase in $CuFe_2O_4$ spinel ferrite. Formation of single phase spinel ferrites structure clearly denotes, by X-beam diffract grams. Where utilized the Eq. (3) for a cubic framework for most intense peak (311) to collected the lattice parameter (a);

$$a^2= (h^2+k^2 +l^2).\ d^2 \quad (3)$$

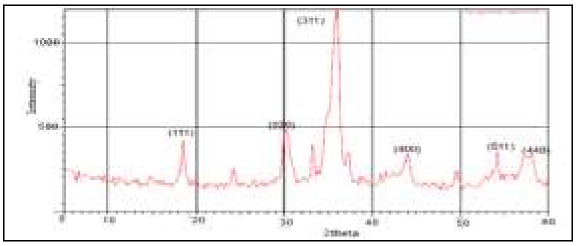
h,k,l= miler index, d= the entomb planer dividing. Crystallite size was calculated from the broadening of the (311) XRD peak, the normal grain size is **(11.7-12) nm** (D_x), normal molecule measure (D_X) was figured by utilizing Debye-Scherer Formula, from Eq. (4)

$$D_x=0.9\ \lambda/ (\beta \cos \theta) \quad (4)$$

The λ=wave length of X-ray1.54 ^{0}A, β=broadening of the diffraction peak, θ= diffraction angle.
X-ray density (ρ_x) is equal to (5.499g/cm^3), used Eq. (3) to calculate X-ray density (ρ_x):

$$\rho_x= (8\ M_w / N_a.a^3) \quad (5)$$

M_W=molecule Wight, N_a= Avogadro's number, a=lattice constant.



Figuer1: X-ray diffraction, (XRD) pattern of nanoparticle CuFe2O4 in powder form IV. Equations

II. Microstructure

SEM image indicated uniformity and homogeneity of the prepared $CuFe_2O_4$ particles, the present powder as ash and clear that powder has high porosity is compare with XRD density where the density is abatement when porosity is expanded. The scanning electron Micrograph for $CuFe_2O_4$ indicates they are dense and distributed regularly with-in the entire range as show in Figure 2.

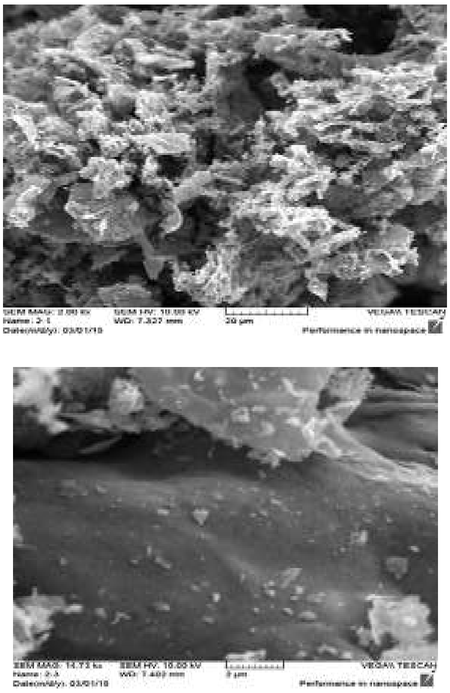


Figure 2: SEM images of Cu-ferrites powder in different magnification

III .Removal of Pb (II) and Cadmium

In this study of west water treatment, in situ ferrites, preformed ferrite, and magnetite were added at (0.125,0.25,0.5)wt% to synthetic 100 mg/L of Lead and Cadmium solutions adjusted to ph (5,7,10) and mixed for two hour. Results showed that each experiment removed over 99% of the Lead and Cadmium by adsorption process between heavy metals and the magnetite ferrite. The magnetite showed the best removal for both Lead and Cadmium.

IV. Effect of Ph

pH was the mainly essential parameters affecting Pb and Cd removal by ferrite. The pH effect on the removal efficiency of Pb and Cd using ferrite at different concentration (0.125, 0.25, and 0.5) ppm are shown in Figure. 2 and 3. It can be seen that for Cd is complete removal at different pH the removal efficiency of lead onto ferrite at detention time of 20 min and pH range of 5-10 and different concentration (0.125, 0.25, and 0.5) are 99.369 %-100%.and the best pH was 7 we see that from the sediments magnetic performance, the results indicate the removal is rise before 7 (pH) and gave the effective removal at ph 7 the sediments are composed by Cu-ferrites after 7.5 (pH). When the numerical value of pH reached 10, the decomposition rates are little dropped but still well.

V. effect of contact time

Effect of contact time was studied at (20,40,60,80,100,120)min to crrelated with the removal efficiency of Pb and Cd using ferrite at different concentration (0.125,0.25,0.5) ppm are shown in Figures. 4 and 5.we can see that removal efficiency when time 20 min the and pH range of 5-10 and different concentration (0.125, 0.25, and 0.5) are 99.369 %-100%. When increase time the removal efficiency was 100% that's for lead and for cadmium a few minute gave excellent removal its 100%.

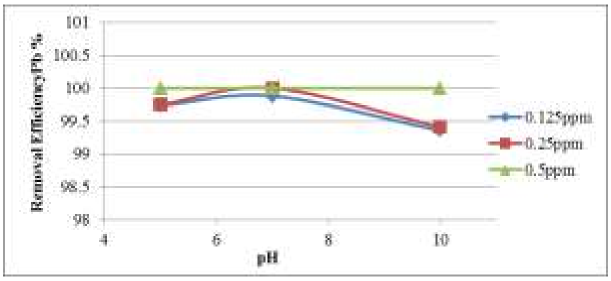


Figure 3: Removal Efficiency of lead vs with Ph

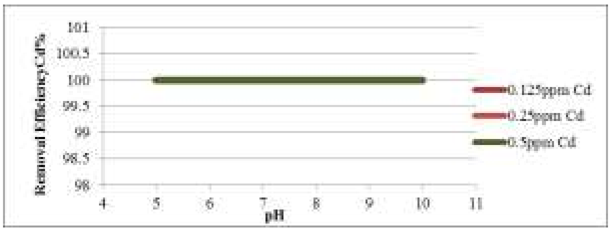


Figure 4: Removal Efficiency of Cadmium vs with pH

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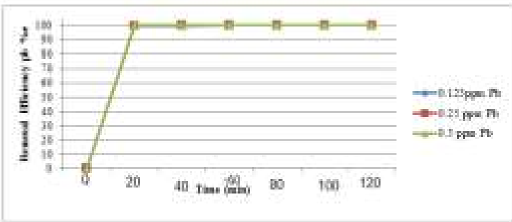

Figure 5: Removal efficiency lead VS time (min)

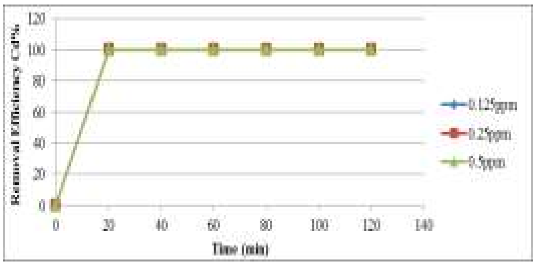

Figure 6: Removal efficiency cadmium VS time (Min)

VI Ferrite dose

Effect of Ferrite dose was studied at (0.125, 0.25, 0.5) ppm to removal efficiency of Pb and Cd. The effect of Ferrite dosages on the percentage removal of Pb and Cd has been shown in Figure 6 and 7. The removal of the Pb and Cd increased when the dosage was changed from 0.125 to 0.5 ppm and increase from 99.369 at 0.125ppm at 20 min to 100 removals at 0.5 ppm at 20 min this for the lead but for cadmium, at all dosage concentration the removal was 100% and that's effective for removal.

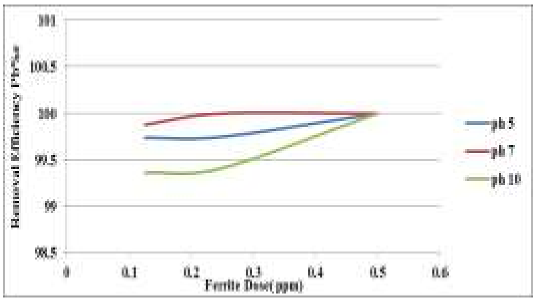

Figure 7: Removal efficiency lead VS ferrite dose (ppm) at time 20 (min)

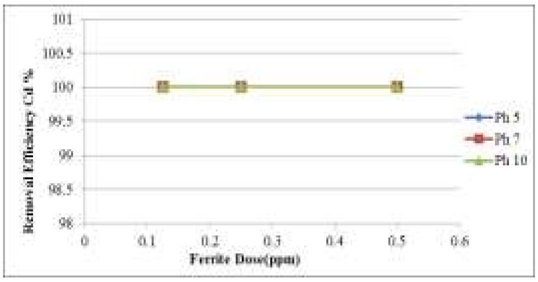

Figure 8: .Removal efficiency cadmium VS ferrite dose (ppm) at time20 (min)

VII. Antibacterial activities resulted and discussion

The antibacterial effectiveness of copper ferrite Nano particles against *E. coli* and *S. aureus* are shown in Figure. (9-10). Five concentration of copper ferrite nanoparticles was prepared at different concentration compared to sample of bacteria solution a lone, copper ferrite nanoparticles inhibit the growth of both *E. coli* and *S. aureus*, and the *E. coli* survival rate of all ferrite nanoparticles concentration is more than the *S. aureus* survival rate ,the percentage survival of bacteria was (35 , 20 , 12 , 5 %) in (0.625 , 1.25 , 2.5 , 5 mg/ml) concentration for bacteria E.coli and (28 , 15 , 8 , 3 %) in (0.625 , 1.25 , 2.5 , 5 mg/ml) concentration for bacteria Staph.aureus Figure.11. However, antibacterial effectiveness increase with the concentration of coper ferrite nanoparticles increased [19]. There are a lot of mechanisms of antibacterial effectivness of copper ferrite nano particles. Some researcher suggested when *E. coli* was treated with copper ferrite nanoparticles, a lot of variable in the morphology of cell membrane take place in. Nanomaterials act on adhesion to bacterial cell walls and then penetrate them as mentioned Lu Z, Li CM, *et al* [20]. Copper ions break down the cellular wall of the bacteria and this leads to the breakdown and degradation of cytoplasm and thus the death of the bacterial cell. Furthermore, copper nanoparticles show high cytotoxicity against *E. coli* when used in high concentrations [21]. Large surface area of nanoparticles enhances antimicrobial effectiveness compared to large-scale particles, where nanoparticles are thought to have the ability to transfer toxicity within bacterial cells. Copper nanoparticles appear a large surface to volume ratio, Which enhances the biological activity of these particles and makes them effective agents against microbes [22].

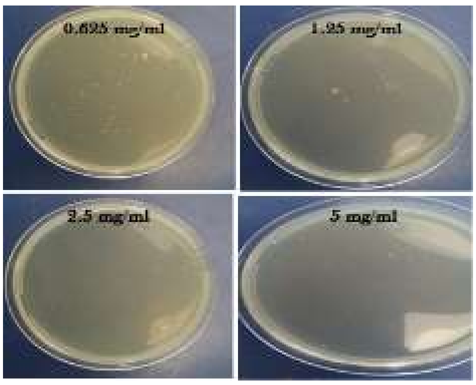

Figure 9: Photograph of the colonies number (CFU) of E.coli in different concentration of copper ferrite nano particles

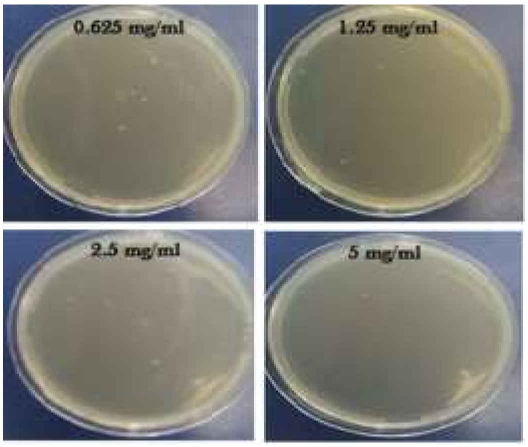

Figure 10: Photograph of the colonies number (CFU) of Staphaureus in different concentration of copper ferrite nanoparticles

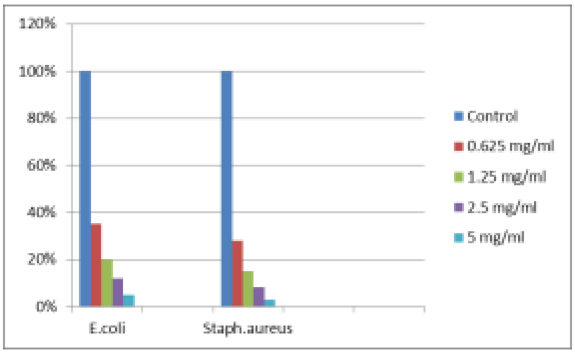

Figure11: percentage survival of E.coli and Staph.aureus in different concentration of copper ferrite nano particles

5-Conclusions

Uses of Cu-ferrites powder for remove of heavy metals has good results Cu-ferrites was characteristic, Found that powder spinel structure and the particle size in range 30nm, the adsorption of cadmium and lead by Cu- Ferrite was effective, especially for cadmium. The best pH used for removal between more than (7 -8) because when increasing to 10 the removal decreases little. The good removal reaches at the time 20 min for lead and a few minute for cadmium. When increasing dosage the removal efficiency increase. Copper ferrite nanoparticles boss antibacterial effectiveness it inhibit the growth of both *E. coli* and *S. aureus*, and the *E. coli* survival percentage of all ferrite composite nanoparticles is more than the *S. aureus* survival percentage.

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