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Copper Oxide Nanoparticles: Effective Tool for The Removal of Heavy Metals

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Nanoparticles, heavymetals ,adsorption, nanosorbent, adsorption efficiency.

ABSTRACT:
Copper oxide nanoparticles were prepared by co precipitation technique and characterized well considering their chemical structure, morphology and adsorption behavior. In this research work, we study the copper oxide nanoparticle's absorb heavy metals from the surroundings by performing as a sorbent. Heavy metals like cadmium (Cd), and lead (Pb) eradicating from contaminated water during the treatment process. CuO NPs function as an inorganic adsorbent source for the removal of heavy metals. Different variables like varying contact time (t), and different doses of adsorbent (CuO) were studied to find its effect on removal efficiency. Two isotherm models (Langmuir, Freundlich) were tested to determine which adsorption procedure will be followed. In order to determine how time affected the removal process, kinetic tests were looked at. Adsorption of metals Pb and Cd has reached equilibrium after 20 minutes and at a concentration of 0.3g/L. Pseudo second order kinetic reaction has given a realistic description of the removal of Cd and Pb metal ions with the closer value of qe (calculated) and qe (exp). for both metal ions. Cd and Pb metal adsorption on CuO NPs follow Langmuir adsorption isotherm model.

1. Introduction

In the 21st nanotechnology is expected to bring revolution on the global level. The product of nanosized particles (below 100nm) is the main outcome of research in nanotechnology. Researchers have shown keen interest in nanosized particles due to their unique optical, electric, and catalytic properties [1]. It is important to note that metal nanoparticles have special detoxification properties for the removal of environmental pollutants [2]. Heavy metal contamination going to be the most serious environmental pollution these days due to its recalcitrance and persistent nature. In developing countries, there is the rapid development of industrialization like metal plating factories, fertilizer forming industries, and many more factories. Heavy metals from these industries and the pesticide-used area contained water directly or indirectly discharged into the environment. Wastewater that is discharged from refineries contained a high amount of heavy metal (Pb, Hg, Cd, Ni, etc.) percolating into the groundwater making it poisonous and drained into water bodies causing pollution to the aquatic life that becomes life-threatening for aquatic organisms. By the irrigation of agricultural land with sewage water (which contained heavy metals), these poisonous metals enter the food chain which causes danger to human health. Heavy metal contamination, when entered into the food chain, poses a great risk to human health including cancer, organ and nervous system damage, and even death [3]. In living beings, heavy metal ions get bound with the nucleic acid and with the protein binding sites of cells, making the cells lose their biological activities [4]. The abnormal biological activities of cells prove life-threatening including cancer and may lead to death. Heavy metal contamination is increasing in the

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ecosystem due to its non-biodegradable and persistent nature. Their poisonous level can be estimated if a child under the age of six years is exposed to a very low level of heavy metals contamination, it reduces his IQ, and hearing ability, stunts growth, and also causes behavioral problems [5]. At a high level of exposure, the child may fall into a coma and may die due to poison in the blood because of Pb poison [6]. So, it becomes necessary to eliminate or reduce their values up to certain limits from our ecosystem to save lives. Metal nanoparticles have emerged as a powerful tool worldwide to clean the harmful pollutant from the ecosystem. Copper oxide nanoparticles the unique member of the metal NPs family become the most precious tool of nano remediation technology to remove harmful heavy metals from the ecosystem. Copper oxide NPs remediation required less infrastructure, low power consumption, and inexpensive techniques to remove Pb, Cd, Hg, and Ni effectively from contaminated medium up to a greater extent. Several methods are available for the detoxifying the ions of heavy metals like 1.Method of ion exchange 2. Membrane filtration method 3. Electrolyte recovery method 4. Liquid-liquid extraction method 5. Adsorption [7]. Every method has its drawbacks and advantages in applications. These methods have disadvantages like incomplete removal, high energy requirement, and toxic sludge production which is hard to dispose of. Scientists were highly fascinated with the adsorption process of carbon because of the effective eradication of heavy metal ions [8]. But the high cost of this method becomes its major drawback. Therefore, low- cost adsorbent material becomes the focus point. Due to their size and absorption effectiveness, CuO NPs may provide a more affordable remediation technology. Copper oxide NPs found to be effective adsorbents because of their high surface-volume ratio, and more area available for the adsorption of metal. In this research work, we study the copper oxide nanoparticle's absorb heavy metals from the surroundings by performing as a sorbent. Heavy metals like cadmium (Cd), and lead (Pb) eradicating from contaminated water during the treatment process. CuO NPs function as an inorganic adsorbent source for the removal of heavy metals. Different variables like varying contact time (t), and different doses of adsorbent (CuO) were studied to find its effect on removal efficiency. Two isotherm models (Langmuir, Freundlich) were tested to determine which adsorption procedure will be followed. In order to determine how time affected the removal process, kinetic tests were looked at. Finally, under the predetermined conditions, the removal % of Pb and Cd metal ions from polluted water was estimated.

2. Material and method

Cu (No3)2.3H2O, 1M NaOH solution, Absolute C2H5OH, Cadmium Nitrate Hydrate, Lead Nitrate, Distilled Water. All the materials being used here are of A.R grade during the experiment. Some of the above chemicals required to synthesize CuO NPs and some are required to formstock solution of 1000ppm containing metals lead and cadmium metal ions**.**

2.1 Apparatus

- MagneticBeads
- MagneticStirrer
- BufferSolution
- BathShaker
- ConicalFlask
- DigitalWeighingmachine

2.2 Preparation of Cuo Nanoparticles

The following procedure had been followed in order to conduct the experiment [9]]. CuO nanoparticles were synthesized by the co precipitation method using Cu (No3)2.3H2O as a precursor. 50 ml distilled water was used to dissolve 0.5 M cupric nitrate and the solution was stirred on a magnetic stirrer for 15 minutes. 1M of NaOH solution was added to the above solution drop wise until the pH reached 10. The above solution was then stirred magnetically for 2:30hr till the blackish-brown precipitate of Cu(II) O nanoparticles have been obtained. The precipitate was then washed with the help of deionized water and ethanol so that excess impurities drained out. The precipitate was left to be dried in order to get its powdered form. The black powdered CuO nanoparticles were annealed at 450oC for an hour in order to achieve "stabilized CuO nanoparticles". The same set experiment was repeated for pH 8 and pH 12 also. The above process was repeated for different concentrations of precursor (1M, 1.5M).

3. Detection and characterization of CuO NPs.

Firstly, we confirm the formation of copper oxide nanoparticles with our naked eye observation by changing the color of the precursor from blue to black. The use of "XRD has been done to analyze the structural configuration and crystal size of CuO nanoparticles. The measurements obtained with the help of XRD have been used for crystal analysis of CuO nanoparticles.

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XRD measurements were taken with a Rigaku mini flex II diffractometer in the 2θ range of 20˚ - 60˚ using Kα radiation of the wavelength λ = 1.5406 A◦. The particle size, its distribution, and its morphology has been investigated with the help of "Scanning electron microscopy" SEM. The JEOLJSM-6510 (Japan) SEM has been used in the experiment. The information about optical studies has been gained with the help of "diffuse reflectance spectrum" which was recorded with Shimadzu UV-visible 3600 plus spectrophotometer. This has been furnished with a sphere accessory in the 200-500 nm range. FTIR- spectroscopic technique is used to find out the functional group attached to the CuO NPs surface by identifying their stretching and bending frequencies. The spectra were captured with ABB MB 3000 IR spectrophotometer (Japan) within the range of 600-4000 cm-1. The concentration of heavy metal ions after absorption was analysed by atomic absorption spectroscopy (AAS 301 thermo-scientific, wavelength range 190-900 nm).

4. Formation of Lead & Cadmium solutions

A contaminated mixture of 200 ml is prepared by adding 4 ml stock solution of metal (Cd and Pb) added into 200ml volumetric flask and make up the final volume up to mark with distilled water to prepare 20 ppm working solution. Industrial distilled water used that contained no bacterial contamination and negligible number of contaminants about 1ppm.

4.1 Metalion treatment experiment

We prepared artificial wastewater containing Pb (20ppm), and Cd (20ppm) as impurities. Several factors were studied. For example, 0.1, 0.2, 0.3, 0.4, and 0.5 g/L doses of CuO NPs were added to the 200ml contaminated solution each in a stoppered conical flask keeping contact time fixed for 60 minutes. All the conical flasks containing solution (I, II, III, IV, V) were put on the bath shaker at 150 rpm. The rate of adsorption on every concentration of CuO NPs after a given interval of time (60 min) was calculated by measuring absorbance using AAS (atomic absorption spectroscopy). The influence of the time variable on adsorption can be studied by varying contact times 5,10,15,20,30 minutes for every solution keeping the concentration of nano sorbent (CuO NPs) optimized i.e. 0.3 g/L. The rate of adsorption for each metal ion after every contact time was calculated by studying absorbance in AAS.

The adsorption efficiency of CuO NPs as an adsorbent can be estimated from the given equation:[10]

qe= CO- Ce/ W× V

(1)

qe= Capacity of adsorption at equilibrium (mg g-1)

C0= Initial concentration of metal ions (mg/L-1)

Ce= Metal ion concentration at equilibrium (mg/L-1)

V= Volume of the mixture (ml)

W= Weight of the nanosorbent

4.2. Isotherms methodology

Adsorbate species and adsorbent materials interact with one another in an adsorption system, and the adsorption isotherm is a key metric that explains this interaction and forecasts the theoretical maximum adsorption capacity. The importance of the adsorption process in calculating the solvent absorption rate & the necessary duration of time so as to absorb. Adsorption isotherms are also required to illustrate how pollutants interact with adsorbent surfaces and how adsorbents are employed to enhance pollutant removal from aqueous solutions. Illustrating the "best-fit" isotherm is crucial for adsorption research as new applications are developed. There are a variety of isotherm models, including the "linear isotherm model, Langmuir, Temkin, Dubinin-Astakhov". The two earliest models, Freundlich and Langmuir, are still widely used and favoured because of their simplicity and accuracy. Langmuir adsorption is used to show monolayer molecule deposition on adsorbent where as Freundlich adsorption is required to interpret heterogenous various affinities of surface adsorption (shown in figure 1)

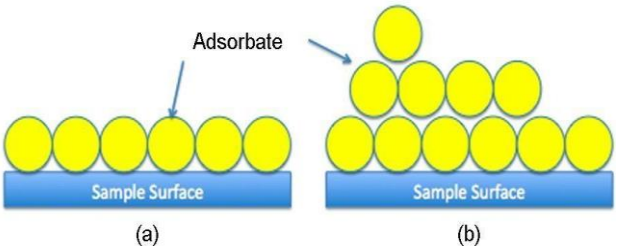

Fig1. (a)Monolayered adsorption (b) Multi-layered adsorption [Internet]

An empirical model called the Langmuir isotherm, it makes the following fundamental assumptions:

- Only one molecule can be engaged directly by each active site of an adsorbed layer.

- All adsorbent molecule sites in this unified, or energetically similar, process have a same affinity for the adsorbate.

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To identify the ideal parameters for the batch absorption process, isotherm and kinetic models were examined. Because they are the most popular isotherm model and can be estimated using formulae from the literature, Langmuir and Freundlich's adsorption isotherm models were utilised and can be calculated from literature-based equations 2 and 3[11].

Ce/ q e = 1/ K L q max + Ce /q max
(2)

Log (q e) = log (K f) + n log (Ce)
(3)

In equation (2) the binding capacity between metal ions and CuO nano sorbents is represented by the Langmuir equilibrium constant KL. In equation (3) K f constant (mg g-1) (L mg-1) n is regarding the adsorption efficiency of nanosorbent to adsorb.

4.3 Kinetic Methodology

Kinetics investigation is a crucial component of the adsorption system because it helps identify the adsorption technique and pinpoint probable adsorption rate-related processes such chemical reaction and mass movement. Adsorption kinetics research is crucial because it can estimate the amount of time needed to attain equilibrium in an adsorption process and show how an adsorption system can be designed to optimize the reaction pathway. The kinetics determines how quickly the adsorption takes place. Various kinetic models exist, including PFO and PSO. The linear regression coefficient value (R2) shows that the model's error level and the values are compared to determine which model fits the data the best.

Pseudo first order (PFO) kinetics

The PFO model, first put forth in 1898 by eminent scientist Lagergren, says that the rate of solute uptake change is a function of the difference between the saturation concentration and the present concentration[12]. This model is primarily utilised during the sorption process' earlier stages can be explained by given table 1

Log (q e- qt) = log q e- (K1/ 2.303) t
(4)

Here; qt = adsorption efficiency at contact time t K1 = rate constant (min-1) of PFO kinetics Pseudo Second Order Kinetics (PSO)

Ho and Mckay in 1999 popularised the PSO rate equation, which is a common model used to describe adsorption kinetics. The best part is that this model can evaluate equilibrium capacitywithout needing to calculate it from experiment. Mathematical equation is given by the following [12].

t/qt= 1/ K q 2+ (1/qe) t
(5)

where,

qt = adsorption efficiency at contact time t

K2 = rate constant (g mg-1 min-1).

5. Results and Analysis

5.1 Characterisation Analysis of Adsorbent

SEM images shown in figure (2) reveal the morphology and shape of nanosized particles of CuO synthesized by the coprecipitation method. Investigation through 1μm magnification shows the nano- rod-shaped structure of CuO NPs. The XRD pattern of as-synthesized CuO NPs is shown in figure 3. By using Debye- Scherer- formula i.e. D = (0.89λ/β cos θ) particle size can be calculated. By using the above formula average size of the nanocrystal was found 8.6 nm. By graphical representation and particle size, it has been observed that the sample does not contain any impurities and is highly stable. FTIR spectroscopy was analysed by scanning in the range of 600-4000 cm-1. Figure (4) reveals the FTIR spectra of powdered CuO nanoparticles. Peaks at 640 cm-1 confirmed the monoclinic phase of pure copper oxide [13]. Band obtained at 1643 cm-1 shows a C=O stretching bond. A strong broad band observed at 3556- 3310 cm-1 indicates the bending and stretching vibration of absorbed water molecules [14].

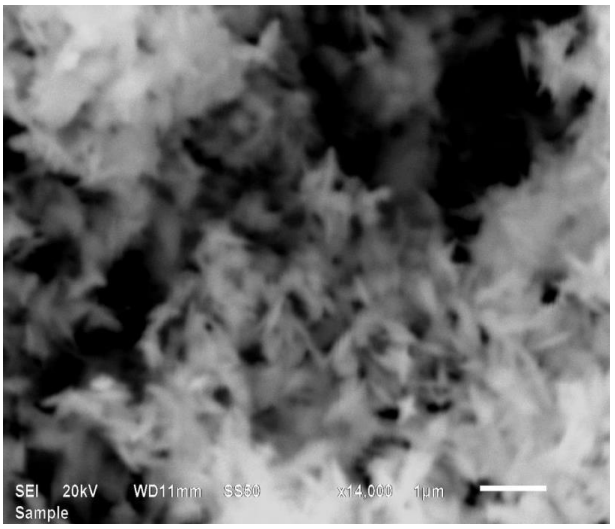

Fig2. SEM images of CuO nanocrystals

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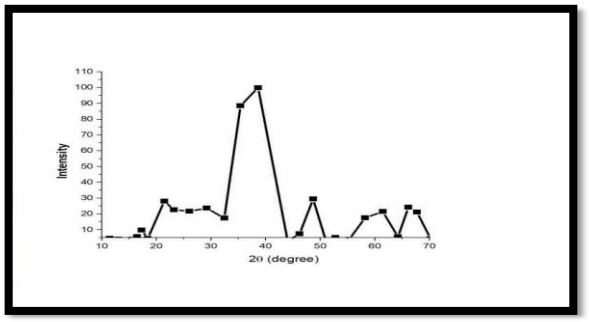

Fig3. XRD pattern of CuO nanocrystals

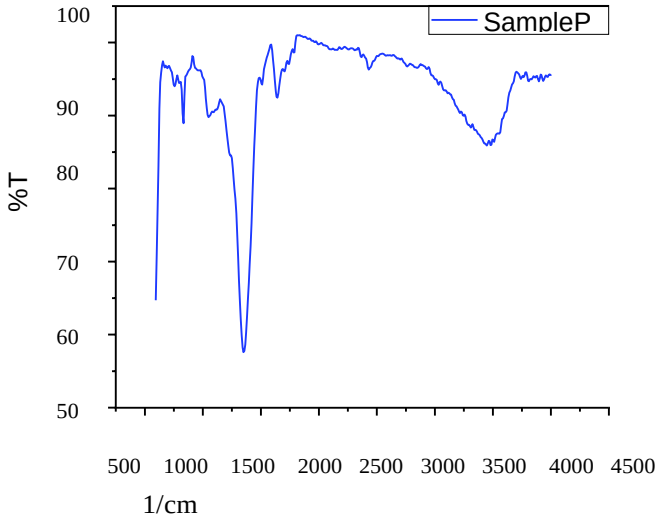

Fig4. FTIR spectra of copper oxide

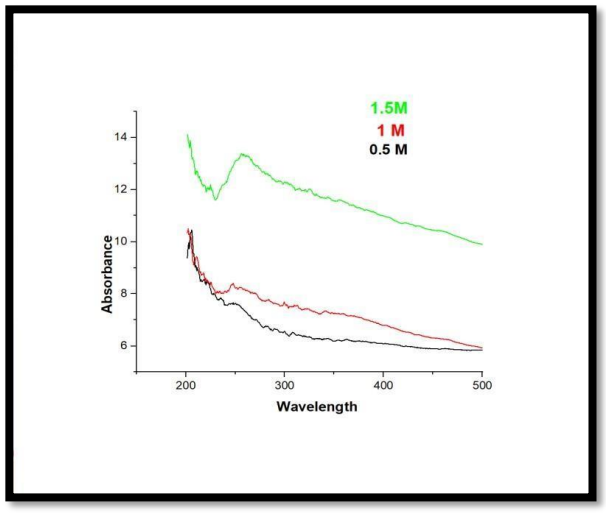

Fig6. UV-vis spectra Of CuO nanoparticles at different concentration of precursors.

The optical characterization of the CuO nanoparticles has been done by absorption spectra at different pH and concentrations (fig. 5,6). The above figure,5 graphically

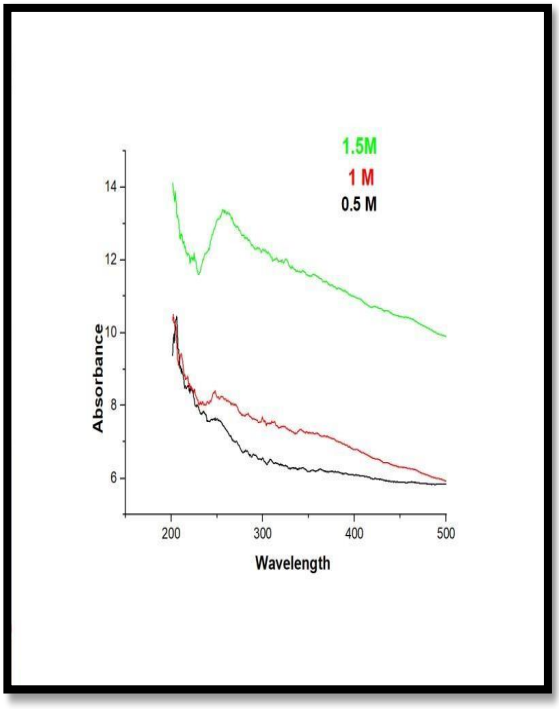

Fig5. Absorbance spectra of CuO nanoparticles at different pH value.

represents
the absorption spectra of the CuO nanoparticles in distinct pH. As the pH increased particle
size decreased, and the surface-to-volume ratio increased with a decrease in particle size. The absorption spectra study of CuO nanoparticles shows a sharp peak at 220 nm for 1.5 M due to the direct transition of electrons. The absorption band was at 230 for 1M and 240 nm for 0.5M, shown in figure(6).

5.2 a. Metal Ions Treatment Experiments

CuO NPs work as a nano sorbent, their exposed surface area and their amount play an effective role in the adsorption phenomenon. Different doses of CuO NPs (0.1, 0.2, 0.3, 0.4, 0.5 g L-1) NPs were utilized to analyze the capacity of eradicating the given metal ions. Figure (7). Predicted that the removal efficiency of Cd(II) and Pb (II) increased with increasing concentration of nano sorbent. The reason for this is due to more surface interacting sites available on the

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adsorbent surface that will make complexity with the metal ions. Figure have shown that Pb metal ions removal percentage is more than Cd metal ions because Pb metal have more electronegative properties than Cd and also have smaller atomic radius than Cd. Our findings concluded that 0.3 g L-1 dose of CuO NPs is best to use for further experiments. This concentration shows maximum percentage of removal, equilibrium attained at this concentration so this can be used as key parameter.

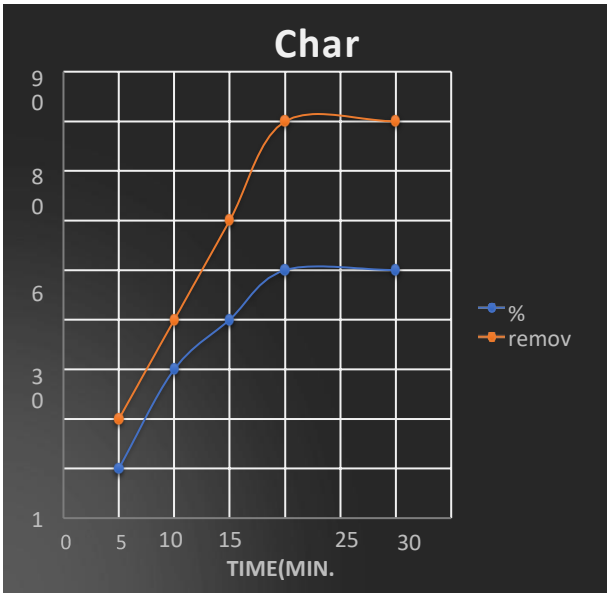

Fig7. Effect of nano sorbent doses on the % removal of Pb(II) and Cd(II) metal

5.2b. Effect of contact time:

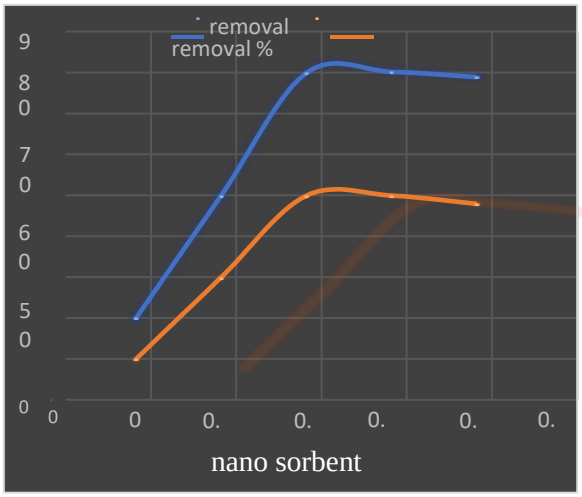

Fig 8. Effect of contact time on the removal of metal ions Pb(II) and Cd(II) keeping the concentration of CuO NPs (0.3 g L-1) constant.

The equilibrium time for maximum uptake and the kinetics of the absorption process were established by studying the adsorption of Cd and Pb metal ions on micro CuO sorbent as a function of contact time. The results are presented in fig(8). To assure that the equilibrium was indeed attained, the contact time was maintained for over 30 minutes. As seen in the graphic, concentration affects how long it takes to attain equilibrium. Because of abundance active binding sites on the nano sorbent, the removal effectiveness of metal ions by micro CuO sorbent grew quickly in the early stages. However, when these sites were gradually occupied, the adsorption efficiency decreased in the latter stages. That indicates that after 20 minutes of calculating the value of q e, equilibrium can be reached. The removal percentage of Cd and Pb is 50% and 80% respectively by using CuO nano-particles as an adsorbent.

5.3 Adsorption kinetics

The efficiency of adsorption is largely dependent on the adsorption kinetics, which is one of its most significant properties. Adsorbate i.e. Metal ions can be transported from the solution phase to adsorbent surface active sites in a number of processes, any one of which can act as a rate-controlling mechanism: (i) rapid mass transfer through the liquid film that forms the external boundary layer around the particles (ii) diffusion on solid surfaces (iii) various physical or chemical adsorption at surface level location.

5.3a. Pseudo- first order (PFO) kinetics

The adsorption data for the pseudo-first-order kinetic reaction is given by the following equation:(4)

Log (q e- qt) = log q e- (K1/ 2.303) t (4)

Fig (9,10) is plotted between values of log (q e- qt) with time (t) to give linear relation from that value of k1 and q e cal. Can be estimated from the slope and intercept of the graph respectively. Their respective values are given in table (1) for both metals (Pb and Cd) ions.

Fig(9), and (10) predicted the pseudo-first-order for Pb and Cd metal ions. It should be noted that values of q e exp does not match with the calculated ones which is obtained from pseudo first order [given in table 1]. So, this PFO model is not valid for the adsorption process.

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Table1. Kinetic parameter and correlation coefficients for pseudo-first-order kinetics for heavy metal removal ions.

Kinetics models Pseudo-first order kinetics	Cd	Pb
K1((min^{-1})	0.95055	-1.17695
R^2	0.99965	0.99395
qe.cal.(mgg^{-1})	1.052	-0.84822
qeexp.(mgg^{-1})	6.666	10.656

Table.2 kinetic aspects for the pseudo-second-order kinetic model for heavy metal removal.

Kinetic model: pseudo-second order	**Cd**	**Pb**
K2(gmg^{-1}min^{-1})		
R^2	0.99974	0.99665
qecal.(mgg^{-1})	7.3	11.3
qeexp.(mg g^{-1})	6.55	10.66

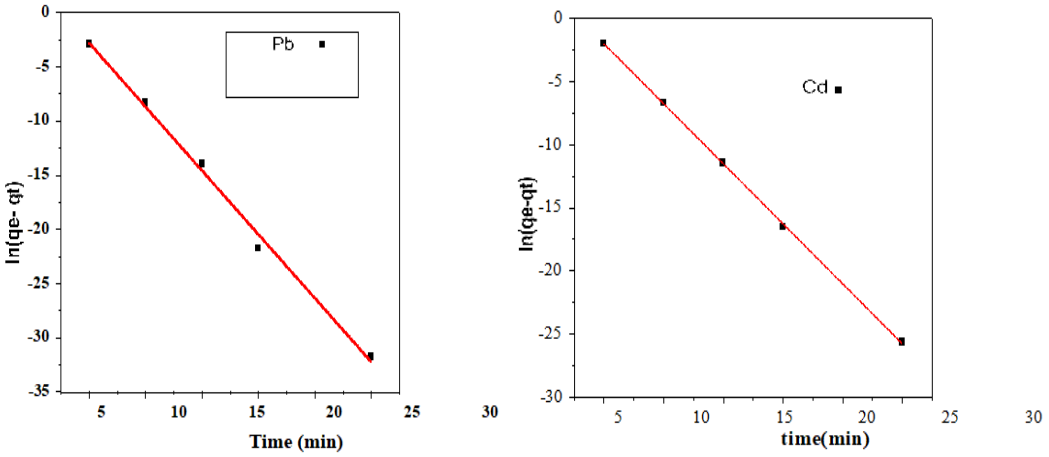

Fig 9. Pseudo-first order for Pb metal ions.

Fig 10. Pseudo-first order for Cd metal ions

5.3 b Pseudo-second-order (PSO) kinetics:

This kinetics model can be studied with the help of the following equation:

t/qt = 1/K2× 1/q 2 + 1/q e. t (Given above 5)

It will give a linear plot between t/qt versus time (t) if pseudo second order is applicable. The (equilibrium adsorption capacity) q e calculated from the slope of the graph and K2 from intercept of the graph.

Figure 11,12. explain the (PSO) pseudo-second-order kinetics for Pb & Cd ions. The figure shows the plot of (t/qt) verses (t) which predict reasonable agreement between q e exp. and q e calculated (table 2). The graph gives a linear plot of slope (t/q e) and intercepts 1/k2 q 2.

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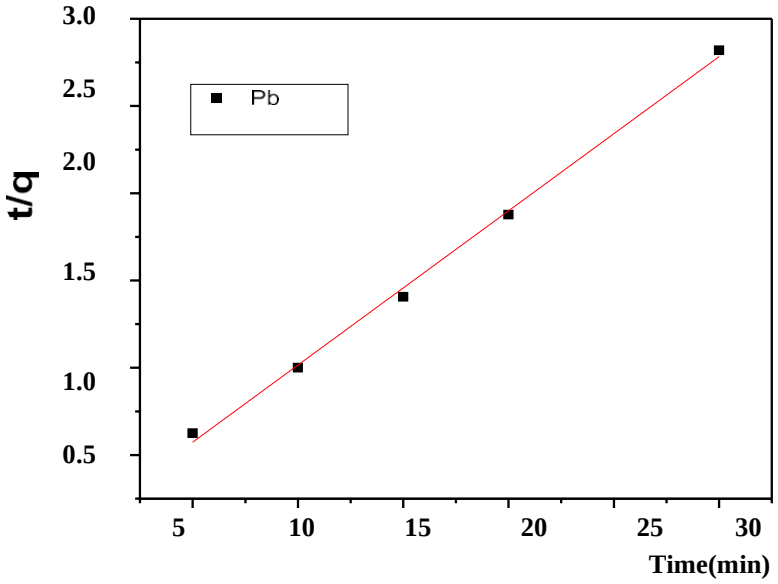

Fig 11. Pseudo- second order for Pb ions.

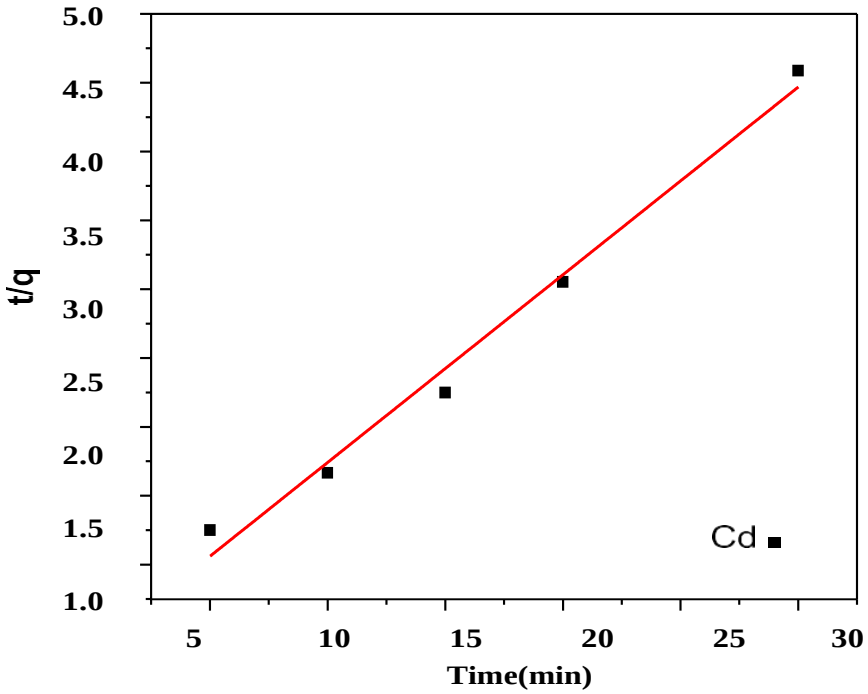

Fig 12. Pseudo-second-order for Cd metal ions.

5.3 Model of Adsorption Isotherm

In order to investigate the adsorption isotherm, the adsorption information is analysed using a number of relationships that describe the distribution of heavy metal molecules between the aqueous and solid phases. The adsorption data can be analysed to look into the adsorption isotherm of Langmuir and Freundlich adsorption isotherm equations 2 and 3. This modelling helps us to predict the maximum capacity of removal.

5.4(a) Langmuir Isotherm

This model explained that adsorption occurs homogenously and no further adsorption takes place after monolayered deposition. Fig (13) and (14) explain the Langmuir adsorption isotherm graph for Pb and Cd metals respectively.

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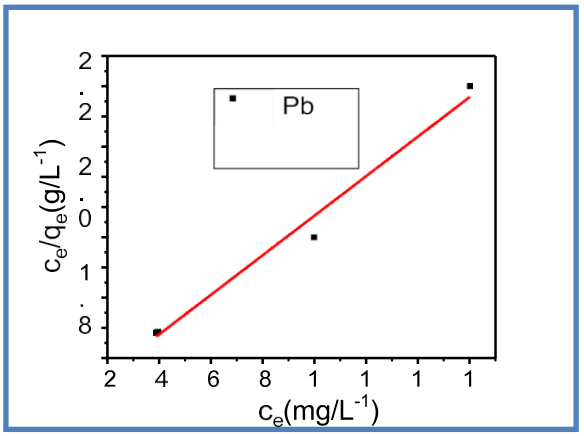

Fig 13. Langmuir plot for Pb metal ions.

Langmuir adsorption isotherm model is given by equation (2)`

Ce/ q e = 1/ K L q max + Ce /q max (2)

Where, q max is the maximum capacity of adsorption of metal ions per unit mass of adsorbent (mg g-1). Langmuir's plot is drawn between Ce/ q e and Ce giving linear plot of slope 1/q max and intercept 1/ K L q max. Their values for Pb and Cd is given in table (3). The validity of the models (Freundlich or Langmuir) was confirmed by the given set of experimental data.

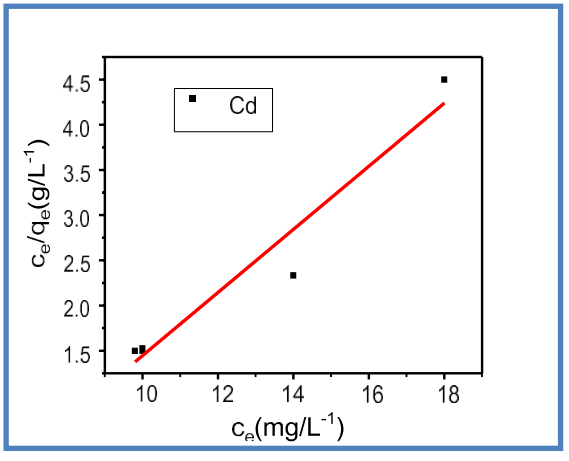

Fig14. Langmuir plot for Cd metal ions.

Table. Langmuir Isotherm Parameter and correlation coefficient for investigating heavy metal removal by CuO as nano sorbent.

Langmuir parameter	Pb	Cd
R^2	0.98246	0.93018
K_L(Lmg^{-1})	0.7656	0.1708

5.4(b) Freundlich isotherm

This isotherm describes the heterogenous, non-ideal adsorption process. This model suggests the multi-layered adhesion of metal ions occurred on the adsorbent. This isotherm model is expressed by the given equation (3).

Log (q e) = log (K f) + n log (Ce) (3)

Value of K f and R2 values given in table (4) govern the following of a particular model by given heavy metals. Freundlich plot for Cd is shown in figure 15 and 16 shown for Pb.

Table.4 Freundlich Isotherm parameter and correlation coefficient for investigating heavy metal removal by CuO as nano sorbent.

Freundlich parameters	Pb	Cd
Kf	9.1108	18.987
R^2	0.82285	0.85165

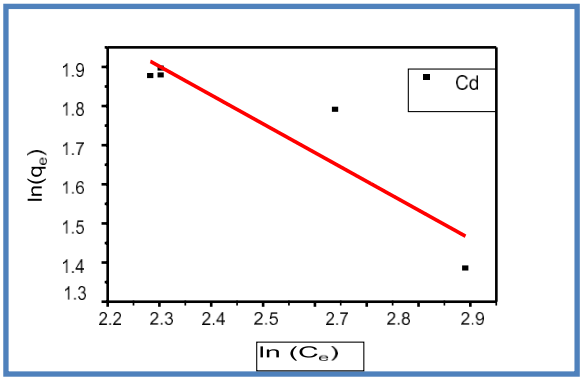

Fig15. Freundlich plot for Cd metal ions.

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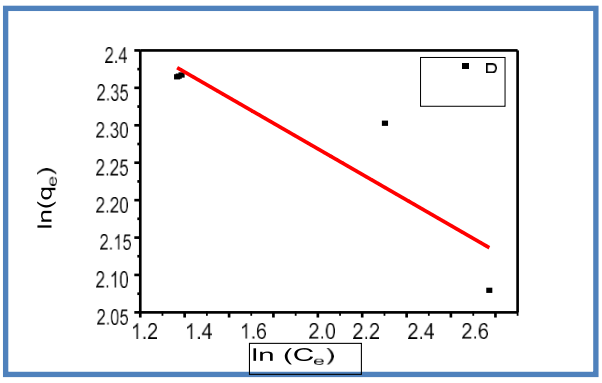

Fig16. **Freundlich plot for Pb metal ions.**

The isotherm data is represented in Tables (3) and (4). These tables represented the correlation coefficient values for Langmuir and Freundlich isotherm of both metals (Pb, Cd) which gives strong evidence that R2 values for Pb and Cd is higher in the Langmuir adsorption model than for Freundlich isotherm. Figure (13)and (14) shown a clear straight- line plot for Cd and Pb respectively. So, these evidences concluded the strong positive confirmation that Cd and Pb follow Langmuir adsorption isotherm model.

6. Conclusion

Nanoparticles of CuO work as an effective adsorbent to detoxify the heavy metals Pb and Cd from wastewater by the process of adsorption. The optimum condition of removal was obtained from the batch experiment. The experiment was analyzed with Langmuir and Freundlich isotherms. Adsorption of metals Pb and Cd has reached equilibrium after 20 minutes and at a concentration of 0.3gL-1. Pseudo second order kinetic reaction has given a realistic description of the removal of Cd and Pb metal ions with the closer value of qe (calculated) and qe (exp). for both metal ions. Cd and Pb metal adsorption on CuO NPs follow Langmuir adsorption isotherm model.

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