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Research Article

Copper Oxide Nano Particles as Efficient Nano Adsorbent for the Removal of Pb^{+2} and Cd^{+2} ions From Aqueous Solution: Equilibrium and Kinetic Study

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Submitted: 26 June 2024

Accepted: 31 July 2024

Published: 02 August 2024

ISSN: 2333-6633

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Keywords

- Batch adsorption Copper oxide nanoparticles
- Isotherm studies
- Kinetics

Abstract

The present study has been initiated to investigate the adsorption potential of CuO nanoparticles for the removal of Pb^{+2} and Cd^{+2} ions from aqueous solution. Reported precipitation method has been used for the synthesis of CuO nanoparticles and characterisation has been done using XRD, UV spectroscopy and TEM. The average crystalline size has been found to be 19.96 nm using XRD which is well agreed with TEM. In order to obtain optimum set of conditions for maximum removal, batch adsorption experiments have been conducted at varying metal ion concentration (30-300 mg/L), contact time (15-180), adsorbent dosage and pH 3-12 for lead and 3-9 for cadmium. The equilibrium adsorption data obtained for maximum removal has been subjected to various isotherm models. A study of isotherm error analysis has been performed to evaluate the errors in applied isotherm curves, which shows that Freundlich and Langmuir isotherm models fitted well to experimental data as compared to Temkin isotherm model. Study of adsorption kinetic models suggests that adsorption process follows pseudo second order kinetics for both the metal ions. A study of intraparticle diffusion shows that the intraparticle diffusion occurs but is not the rate determining step.

INTRODUCTION

With increase in industrialisation, different contaminants including heavy metal ions and organic pollutants are released to wastewater, which cause serious threat to environment and human health [1]. Among these contaminants, heavy metal ions such as lead and cadmium are of major concern due to their toxicity and non biodegradable properties [2]. The presence of lead and cadmium ions in drinking water greater that permissible limit (i.e 0.05mg/L for Pb^{+2} and 2 mg/L for Cd^{+2}) [3,4] may cause adverse health effects such as chronic disorder, hypertension, anaemia, renal damage and nephritic syndrome etc [5,6]. There are various methods for the removal of heavy metal ions from contaminated effluent such as chemical precipitation, ion exchange, membrane filtration, Coagulation [7,8] and adsorption [5,9]. However, adsorption is considered to be the most efficient conventional method to remove heavy metal ions from aqueous media because of its low cost, high removal efficiency, selectivity and ease of operation [2,6]. Recently, development of cost effective and highly efficient nano metal oxides such as zinc oxide [10], iron oxide [11], titanium oxide [12], nickel oxide [8] and cobalt oxide [13] have been attracted a considerable attention for the removal of heavy metal ions from waste water for environmental remediation [5,6]. Nano metal oxides exhibit new or improved properties based on specific characteristics and offers high remedial capacity due to their small size, higher surface area, large number of surface sites for interaction with pollutants [5,13]. Therefore, the present study is an attempt to examine the adsorption potential of copper oxide nanoparticles for the removal of lead and cadmium ions from aqueous medium.

MATERIALS AND METHODS

Preparation of CuO nanoparticles

300mL of 0.02 M cupric acetate $(CH_3COO)_2Cu.H_2O$ solution was mixed with 1mL glacial acetic acid in round bottom flask equipped with refluxing device. The solution was heated to 100 °C with vigorous stirring, about 0.8 gm. of NaOH pellets were rapidly added to the above boiling solution until pH value of the mixture reached 6-7, a large amount of black precipitate were formed simultaneously. After being cooled to the room temperature, precipitates were centrifuged, washed with distilled water and dried in air at room temperature [14]. The sample of CuO was characterised by X-ray Diffractometer (Powder Method), Panalytical.s X.Pert Pro and TEM, Hitachi (7500).

Preparation of Adsorbate solution

0.403gm $PbCl_2$ and 0.461gm $CdCl_2$ (Merck, Pure) were separately dissolved in 1 litre of distilled water to get stock

Cite this article: *Dhiman N (2024) Copper Oxide Nano Particles as Efficient Nano Adsorbent for the Removal of Pb^{+2} and Cd^{+2} ions From Aqueous Solution: Equilibrium and Kinetic Study. Chem Eng Process Tech 9(1): 1089.*

solutions of lead chloride and cadmium chloride corresponding to 300 mg/L concentration of Pb^{2+}/Cd^{2+} ions. Working solutions for further experiments were obtained by dilution of varying concentrations (i.e ranges from 270 mg/L to 30 mg/L) [15].

Batch adsorption studies

A known weight of adsorbent (100mg) was separately placed in contact with 10 mL of lead and cadmium chloride solutions of varying concentrations (30-300 mg/L) at varying pH i.e 3-12 for lead and 3-9 for cadmium, adjusted by addition of 0.1 M HCl/NaOH, as required, for regular time interval (15-180 min., until equilibrium attained). Then samples were subjected to shaking using mechanical shaker at constant speed and the resultant solutions were centrifuged for the determination of metal ion concentration titrimetrically, using standard method [16], with the help of EDTA, xylenol orange as indicator and hexamine as buffer.

RESULTS AND DISCUSSION

Characterisation of CuO nanoparticles

XRD: The XRD pattern obtained at scattering angle(2θ) of 32.5265, 35.5022, 38.6928, 53.5068, 58.1202, 61.0685, 68.0489 correspond to the reflection from (111), (111), (202), (020), (202), (113), (311) planes respectively [Figure 1a], which indicates a single-phase CuO with a monoclinic structure. This XRD pattern points towards the purity of CuO nanoparticles. The peaks are broad due to nano-size effect [14]. The average diameter of synthesized CuO nanoparticle was calculated using Debye-Scherrer formula and was found to be 19.96nm.,

$$D = 0.89\,{}^{\lambda}\!/_{b}\,\cos\theta \tag{1}$$

where 0.89 is the Scherrer's constant, λ is the plane located at 36.24°.

TEM: Transmission electron microscopy was performed in order to evaluate the particle size of CuO nanoparticles [14]. The TEM image [Figure 1b] of CuO nanoparticles shows that average particle size was estimate to be 20 nm.

Effect of pH

The effect of pH on the removal of lead and cadmium was studied within the pH range of 3-12 for lead and 3-9 for cadmium (precipitation occur after pH 12 for lead and pH 9 for cadmium). The adsorption capacity was maximum at pH 6 for lead and pH 8 for cadmium. At pH below or above than maxima, there is a decrease in adsorption capacity for both the metal ions. At lower pH, metal equilibrium uptake was less due to the presence of H^+ ion in acidic condition, which competes with Pb^{+2} and Cd^{+2} ions for adsorption sites. While at higher pH, metal ions start precipitated in the form of hydroxide and adsorption decreases [5,9]. This can also be explained on the basis of Point zero charge (pH_{pzc}) of CuO nanoparticles, which is found to be 4.1 [17], i.e. surface of adsorbent is positively charged below that and negative when above pH 4. On the other hand, at pH where maxima obtained for both the metal ions (i.e pH 6-8), both the adsorbates have net positive charge and adsorbent have net negative charge, therefore adsorption is maximum[17][Figure 2].

Effect of initial metal ion concentration and contact time

In order to determine the equilibrium concentration and contact time for maximum uptake of both the metal ions, experiments have been performed in the concentration range of 30-300mg/L for regular time interval (15-180 min., until equilibrium attained). With increase in concentration and time [Figure 3a,b], amount adsorbed by CuO nanoparticles also increases and equilibrium is attained within 150 minutes. At initial stages and higher dilution, percentage removal increases rapidly due to the larger availability of active binding sites on the surface of adsorbent. While at later stage, available sites get occupied and adsorption become less efficient [4,15].

Effect of adsorbent dosage

In order to study the effect of adsorbent dosage on removal of metal ions, experiments have been conducted with the adsorbent dose in the range of 20-130mg per 10mL of adsorbate solution. With increase in adsorbent dose, percentage removal of metal ions increases and 100 % removal was achieved at 120mg dose for lead and 125mg for cadmium, after that no significant change was observed [7,9].

Adsorption isotherm

The adsorption data obtained at optimum conditions of initial concentration (300mg/L), contact time (150mins.) at pH 6 for lead and pH 8 for cadmium for adsorption of Pb^{+2} and Cd^{+2} on copper oxide nanoparticles were subjected to isotherm analyses.

Freundlich isotherm

The Freundlich equation is given as:

$$\log q_e = \log K_f + {}^{1}\!/_{n} \log C_e \tag{2}$$

where C_e is the equilibrium concentration (mgL^{-1}) and q_e is the amount adsorbed (mgg^{-1}). The values of n are 1.283 and 1.428 and K_f are 1.142 and 1.444 mgg^{-1} respectively for Pb^{+2} and Cd^{+2}, as determined from slope and intercept of the linear plot of log q_e vs. log C_e [Figure 4a,b]. The value of 1<n<10 suggests favourable and monolayer adsorption and high R^2 value (0.999) indicates the effectiveness of the adsorbent [5,8].

Langmuir adsorption isotherm

Langmuir equation is given by

$$C_e/q_e = 1/K_L + a_L/K_L\; C_e \tag{3}$$

where C_e is the solute phase concentration(mg/L), q_e is the

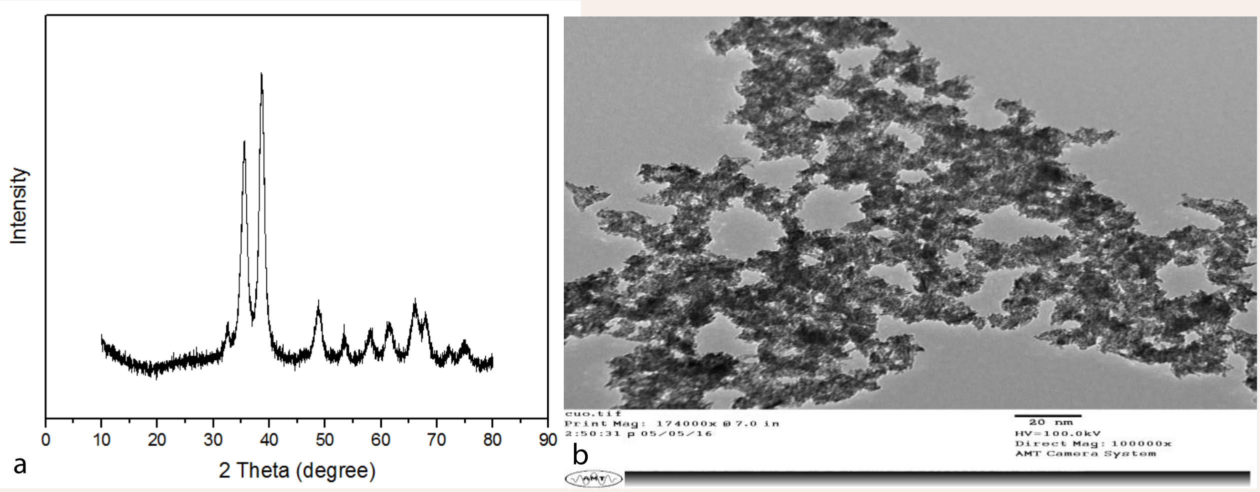

Figure 1 a) XRD pattern of prepared CuO nanoparticles. b) TEM images of CuO nanoparticles

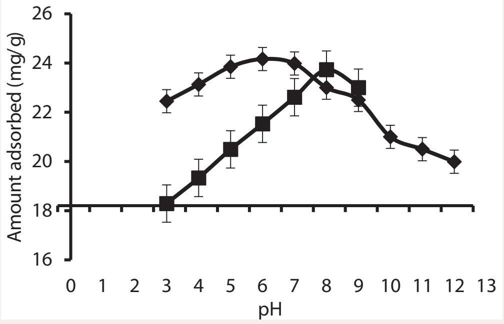

Figure 2 Effect of pH on amount adsorbed of Pb+2 and Cd+2 for the contact time of 150 min. and metal ion concentration 300 mg/L

amount of solute adsorbed per unit weight of adsorbent(mg/g), K_L related to affinity of the binding sites(Lmg^{-1}), a_L the Langmuir isotherm constant. Values of constants a_L and K_L can be determined from a plot of C_e/q_e against C_e and are given in Table 1. A straight line plot of C_e/q_e vs C_e and high R^2 value indicates that the adsorption of both the metal ions obeys Langmuir isotherm [7,10].

In order to know the feasibility of the isotherm, the essential features of Langmuir model can be expressed in terms of separation factor or equilibrium parameter R_L,

$$R_L = 1/(1 + a_L C_e) \tag{4}$$

The value of R_L lies between 0 and 1 for a favorable adsorption, while $R_L > 1$ represents an unfavorable adsorption, and $R_L = 1$ represents the linear adsorption, while the adsorption operation is irreversible if $R_L = 0$. The values of R_L [Table 1], indicating that favorable adsorption occurs in each case [9,10].

Temkin isotherm

The linearised form of Temkin equation is:

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{5}$$

Where, q_e is the amount of solute adsorbed per unit weight of adsorbent(mg/g), $B_T = (RT)/b_T$, is constant related to heat of adsorption ($Jmol^{-1}$), A_T is the equilibrium binding constant (Lg^{-1}) corresponding to maximum binding energy, T is absolute temperature (K) and R is universal gas constant, 8.314 J mol^{-1} K^{-1}[18]. The constant b_T is temkin isotherm constant and has been found to be 3.14 x 10^2 for Pb^{+2} and 1.26 x 10^2 for Cd^{+2}.The values of the isotherm constant A_T and B_T have been calculated using slope and intercept of the plot of q_e vs. ln C_e which is a straight line [Table 1] indicating that temkin isotherm is followed [18].

Error analysis of isotherm studies

In order to evaluate the error in isotherm models, five error functions of non-linear regression have been used.

Sum of squared errors (SSE): It is based on the assumption that the model which gives lesser SSE value is considered as best model for adsorption of metal ion.

$$SSE = \sum_{i=1}^{n} (q_{e,cal} - q_{e,exp})^2 \tag{6}$$

Sum of absolute errors (SAE): In Sum of absolute error (SAE), assumptions are similar to the SSE error function, which is given as:

$$SAE = \sum_{i=1}^{n} |q_{e,cal} - q_{e,exp}|_i \tag{7}$$

Average relative errors (ARE): This error function approaches to minimise the fractional error distribution across the concentration range studied.

$$ARE = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{q_{e,\,cal} - q_{e,\,exp}}{q_{e,\,exp}} \right| \tag{8}$$

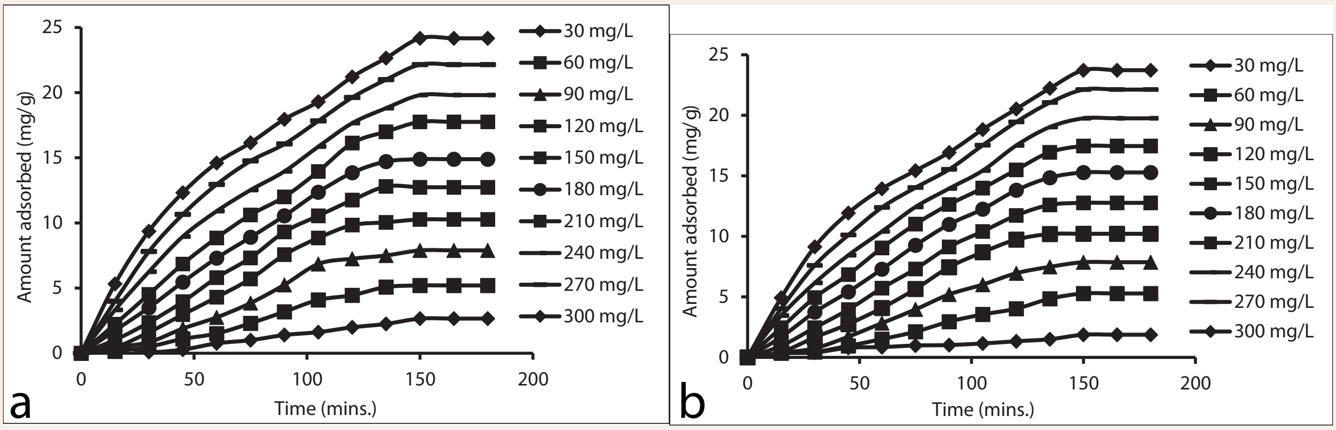

Figure 3 **a)** Amount of Pb^{+2} adsorbed *vs* time at different metal ion concentrations at pH 6, **b)** Amount of Cd^{+2} adsorbed *vs* time at different metal ion concentrations at pH 8

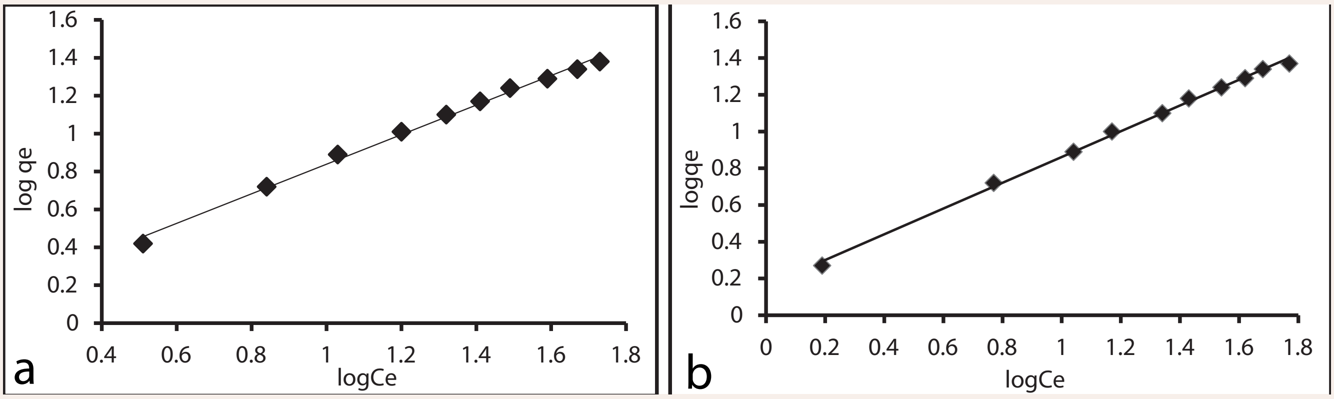

Figure 4 **a)** Freundlich isotherm for adsorption of Pb^{2+} on CuO nanoparticles at contact time 150 min. and pH 6. **b)** Freundlich isotherm for adsorption of Cd^{2+} on CuO nanoparticles at contact time 150 min. and pH 8

Table 1. Adsorption isotherm constants for adsorption of Pb(II) at pH 6 and Cd(II) at pH 8 on CuO nanoparticles

Metal ion	Freundlich			Langmuir			Temkin			
	n	K_f (mg/g)	R^2	a_L (mg/g)	K_L (L/mg)	R^2	A_T (L/g)	B_T (J/mol)	b_T	R^2
Pb(II)	1.283	1.142	0.994	0.015	0.836	0.990	0.062	7.88	3.14 X 10^2	0.947
Cd(II)	1.428	1.444	0.997	0.039	1.26	0.954	0.191	6.252	3.96 X 10^2	0.905

Table 2 Error analysis for adsorption of Pb(II) at pH 6 and pH 8 for Cd(II) on CuO nanoparticles

Pb(II)	Freundlich	Langmuir	Temkin
$q_{e, exp}$	24.16 mg/g	24.16 mg/g	24.16 mg/g
$q_{e, cal}$	25.44 mg/g	25.67 mg/g	26.12 mg/g
SSE	2.6 x 10^{-3}	1.2 x 10^{-3}	0.916
SAE	0.41 x 10^{-2}	0.41 x 10^{-2}	0.425
ARE	1.52 x 10^{-2}	0.12 x 10^{-3}	0.645
HYBRID	3.05 x 10^{-3}	0.56 x 10^{-3}	1.26 x 10^{-1}
MPSD	4.79 x 10^{-5}	0.13 x 10^{-5}	2.30 x 10^{-2}
Cd(II)			
$q_{e, exp}$	23.73 mg/g	23.73mg/g	23.73 mg/g
$q_{e, cal}$	24.13 mg/g	25.98 mg/g	27.1 mg/g
SSE	3.2 x 10^{-3}	0.9851	1.284
SAE	0.71 x 10^{-2}	0.546	1.67
ARE	1.85 x 10^{-2}	0.741	1.98
HYBRID	2.67 x 10^{-3}	1.39 x 10^{-1}	2.71
MPSD	3.81 x 10^{-5}	2.54 x 10^{-2}	2.94 x 10^{-1}

Hybrid fractional error function (HYBRID): This error function is a composite fractional error function, which is an attempt to improve the fit of SAE method by dividing SAE value with $q_{e,exp}$.

$$HYBRID = \sum_{i=1}^{n} \left[\frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \right]_i \tag{9}$$

Marquardt's percent standard deviation (MPDS): This is similar to geometric mean error distribution which is modified according to the degree of freedom of system.

$$MPSD = \sum_{i=1}^{n} \left[\frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right]^2 \tag{10}$$

The value of $q_{e,cal}$ has been calculated for all isotherm models and the values of the five error functions are shown in Table 2. The comparison of error function values for all the isotherm models suggests that Freundlich and Langmuir isotherm models have high correlation coefficient values and low error function values for the adsorption of both the metal ion on copper oxide nanoparticles [19].

Kinetic Studies

The equilibrium adsorption data was further studied using various adsorption kinetic models. The possibility of intraparticle diffusion has been studied using Morris Weber model.

Pseudo first order equation

$$log\ (q_e - q) = log\, q_e\ -\ k_{ad}\ \ X t\ /2.303 \tag{11}$$

where q_e and q (mg g^{-1}) are the amounts of metal ion adsorbed at equilibrium and at any time taken for study respectively, t (min) is the time of contact and k_{ad} is the adsorption rate constant (min^{-1}). The plot obtained from log(q_e-q) vs. t found to be linear [5,6]. The rate constant k_{ad} (min^{-1}) has been found to be 0.0161 and 0.0.0138 and q_e (mgg^{-1}) 25.06 and 24.43 for Pb^{+2} and Cd^{+2} respectively.

Pseudo second order equation: The adsorption kinetics was further studied using pseudo second order equation,

$$t/_{q_t} = 1/_{K_2}\ X\ 1/_{q_e{}^2} + t/_{q_e} \tag{12}$$

where K_2 is equilibrium rate constant of pseudo second order adsorption (gmg^{-1} min^{-1}), q_e and q_t (mg g^{-1}) is the amount of Metal ion adsorbed at equilibrium and at any time and t (min) is the time of contact [10,12]. The values of rate constants are K_2 = 2.6 $x10^{-4}$ and 2.3$x10^{-4}$ and q_e = 38.46 and 40.0 mg/g for Pb^{+2} and Cd^{+2} respectively. The comparison of both the models suggests that adsorption process follows pseudo second order kinetics.

Intraparticle Diffusion Study" The Morris Weber equation is given:

$$q = K_p\ x\ t^{1/2} \tag{7}$$

where q is the amount of metal ion adsorbed in mg for 1g of adsorbent at different time intervals (mgg^{-1}), K_p is the intraparticle diffusion constant (mgg^{-1} min^{-1}) and t is contact time (min.). K_p as calculated from the slope of the linear plot of q vs $t^{1/2}$ and has been found to be 6.234 and 6.309 mgg^{-1} min^{-1} for Pb^{+2} and Cd^{+2}. A straight line plot has been obtained, but does not pass through origin, thus it can be concluded that intraparticle diffusion occurs but is not the rate determining step [4,7].

CONCLUSIONS

The results of this study suggest that copper oxide nanoparticles can be effectively used as adsorbent for removal of Pb(II) and Cd(II) ions from aqueous solutions. The removal is found to be dependent upon concentration of metal ions, time of contact as well as pH. Maximum removal was found to be 80% for Pb(II) at pH 6 and 80.08% for Cd(II) at pH 8 for initial metal ion concentration of 300 mg/L and contact time 150 min. Study of error analysis for all the isotherm models suggest that the experimental data shows best fit to Freundlich and Langmuir isotherm models indicating favourable and monolayer adsorption. Kinetic studies suggest that the process follows pseudo second order kinetics and intraparticle diffusion also occurs but is not the rate determining step.

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