

Removal of Pb(II) and Cu(II) Ions from Aqueous Solutions by Cadmium Sulfide Nanoparticles

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Abstract

In this study, cadmium sulfide nanoparticles (CdS NPs) were prepared, characterized and used as a new adsorbent for simultaneous removal of Pb(II) and Cu(II) ions from aqueous solutions. Using a batch adsorption method, the effects of solution pH, contact time, adsorbent dose, and temperature were studied and optimized. Removal efficiencies, higher than 98% were obtained for both the metal ions at the optimum conditions. The adsorption process was rapid, as equilibrium was achieved within 15 min. The kinetic and isotherm experiment data could be well described with the pseudo-second order kinetic model and the Freundlich isotherm model. The maximum adsorption capacities for Pb(II) and Cu(II) ions were 200 mg/g and 166.7 mg/g, respectively. The thermodynamics of adsorption process such as changes in standard free energy, enthalpy and entropy were also discussed. This study revealed that CdS NPs are effective adsorbent for rapid removal of Pb(II) and Cu(II) ions from aqueous solutions.

Keywords: Cadmium sulfide nanoparticles, Fast adsorption, Heavy metals, Isotherm, Kinetic, Thermodynamic.

1. INTRODUCTION

Contamination of water by toxic heavy metals through the discharge of industrial wastewater is a worldwide environmental problem. Rapid industrialization has seriously contributed to the release of toxic heavy metals to water streams. Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders; therefore they must be removed before discharge [1-3]. Lead is found in various industrial activities like manufacturing of alloys, electrical goods, chemical catalysis, metal surface finishing and batteries. Lead heads the list of environmental threats because, even at extremely low concentration, it has been shown to cause brain damage in children. Inhibiting the synthesis of hemoglobin, disorders in the kidneys and

cardiovascular system, acute and chronic damage to the central nervous system are some of the other dangers of lead [4, 5]. Copper, as one of extensively used materials in the mechanical manufacturing industry, electroplating, light industry and architecture has caused many actual or potential sources of pollution. Excessive copper ions cause serious lesions in the central nervous system and even permanent damage especially for children [6-8]. World Health Organization (WHO) has set provisional guideline limits of 0.01 mg/L and 2 mg/L for lead and copper, respectively, in drinking water [9].

Many physical and chemical processes have been investigated for the removal of heavy metal ions from aquatic environments, including chemical precipitation, ion exchange, chemical

oxidation/reduction, reverse osmosis, membrane technologies and adsorption. Among these techniques, adsorption is regarded as the most promising one due to its clean and fast operation, high efficiency, ease of handling, low cost and availability of different adsorbents [10-12]. Several types of materials have been studied to determine their ability for adsorption of heavy metal ions from effluents, such as agricultural and industrial solids wastes [9, 13-15], montmorillonite and kaolinite [16], chitosan [17], polymeric materials [3, 18], and so on.

Currently, great interest is devoted to the development of new adsorbents with superior properties such as high adsorption capacity, fast adsorption rate and higher chemical and mechanical strength for water and wastewater treatment. With development of nanotechnology at the end of the 20th century, new techniques based on nanomaterials for the removal of heavy metal ions have been presented [19, 20]. Nanoadsorbents are quite efficient for the fast adsorption of heavy metal ions from aqueous solutions due to their high specific surface areas, high specificity, high reactivity, simple operation and the absence of internal diffusion resistance [21, 22]. Up to now, various nanomaterials have been investigated for the adsorption of heavy metal ions from effluents, such as nanoalumina [21], nanozeolite composites [23], carbon nanotubes [24, 25], nano-sized metal oxides [26, 27], magnetic nanoadsorbents [28-30], nano hydroxyl apatite [31, 32], and nano-scale diboron trioxide/titanium dioxide [33].

Cadmium sulfide nanoparticles (CdS NPs) as one of the most important semiconductor materials have many optoelectronic applications because of the availability of discrete energy levels, well developed synthetic protocols, good chemical stability and easy preparation techniques. In last decades, efforts have been devoted to the preparation of high-quality cadmium sulfide nanoparticles and

the investigation of their properties and applications [34, 35]. There are many reports about CdS NPs obtained by different methods and from various precursors [36-38]. The properties of these nanoparticles depend on their size. Some applications of CdS NPs include field-effect transistors, solar cells, detectors for laser and infrared, light emitting diodes, photocatalytic and biological sensors, gas sensors, optoelectronic devices and so on [34, 39].

The main purpose of the present study is to investigate the adsorption ability of CdS NPs for simultaneous removal of Pb(II) and Cu(II) ions from aqueous solutions. Using a batch adsorption mode, different experimental conditions, such as *pH*, adsorbent dose, contact time, and temperature for the maximum removal of both metal ions were investigated and optimized. Meanwhile, behaviors and mechanisms of both metal ions adsorption are comprehensively explored by kinetic and isotherm models as well as thermodynamic parameters.

2. MATERIALS AND METHODS

2.1. Apparatus and Characterization Methods

Heavy metals analysis was carried out using atomic absorption spectrophotometer (Shimadzu, AA-680/G, Japan) under the conditions given by the manufacturer with air-acetylene flame. The *pH* values were measured by a digital *pH*-meter (Metrohm, E-632, Herisau, Switzerland), supplied with a glass-combined electrode. A temperature-controlled orbital shaker (Technal, TE 4200, Brazil) and a centrifuge (Hettich, EBA 20, Germany) were also used throughout this study. X-ray diffraction (XRD) pattern of CdS NPs was recorded by X-ray diffractometer (Phillips, PW 1840, Netherland) with Cu-K α radiation source. A transmission electron microscopy (TEM, Philips, CM30, Netherland) was used to take a view of the adsorbent.

2.2. Chemical Reagents and Materials

Metal nitrates, sodium hydroxide, nitric acid, sodium sulfide, and all of the other reagents and chemical compounds used for experiments and analysis were of analytical grade and purchased from Merck (Darmstadt, Germany). Deionized water (DI-water) obtained from a Millipore Continental Water System (Bedford, MA, USA) was used throughout this study.

Stock solutions were prepared by dissolving appropriate amount of the nitrate salts of Pb(II) and Cu(II) as 1000 mg L⁻¹ solutions in DI-water. The working standard and experimental solutions were prepared daily by dilution of the stock solutions with DI-water prior to use.

2.3. Preparation of Cadmium Sulfide Nanoparticles

CdS NPs were synthesized in aqueous medium through the chemical precipitation technique by using glucose as capping agent [38, 40]. In detail, 10 mL of sodium sulfide aqueous solution (0.1 M) was added dropwise to 10 mL of cadmium nitrate aqueous solution (0.1 M). Yellow precipitate formed and the mixture was vigorously stirred by a magnetic stirrer for 15 h at room temperature. Then, 10 mL of glucose aqueous solution (0.2 M) was added dropwise to the mixture. The resulting precipitate was oven-dried at 100 °C for 6 h. Finally, the dried sample was washed several times by DI-water and dried again at 50 °C for 4 h.

2.4. Adsorption Procedure

Adsorption experiments were performed using batch technique to identify the effect of important variables such solution pH (2-6), contact time (1-20 min), adsorbent dosage (0.2-2.5 g/L), and temperature (278-348 K) on the adsorption of Pb(II) and Cu(II) ions from aqueous solution.

Batch adsorption experiments were carried out in a series of 100 mL Erlenmeyer flasks containing 50 mL aqueous solutions of Pb(II) and Cu(II) ions (100 mg/L, from each one). Desired pH

values in solution were adjusted by adding negligible volumes of NaOH or HNO₃ solutions. Appropriate amounts of CdS NPs were then added to each solution. The mixtures were agitated on shaker at a constant temperature. The samples were withdrawn at regular time intervals. Solid/liquid phases were separated by centrifuging at 600 rpm for 5 min, and then filtered through a 0.22 μm filter membrane (GSWP 47, Millipore, Billerica, MA). The residual concentrations of metal ions in the filtrate were then determined using flame atomic absorption spectrophotometer (F-AAS). The adsorption tests were continued until the equilibrium concentration was reached. Removal percentage and the solid phase heavy metal concentration, q_e (mg/g), were calculated as:

$$\text{Removal\%} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

Where C_0 and C_e are the initial and final concentrations (mg/L) of metal ions in solution phase, respectively; V is the volume of the treated solution (L); and m is the mass of adsorbent (g). All the experimental data were the averages of triplicate determinations.

Adsorption isotherms at various dosages of CdS NPs (0.2, 0.4, 1, 1.4, 1.8, and 2 g/L) were studied using the same above procedure. The solution pH, contact time and temperature were adjusted in the optimum amounts obtained from batch optimization procedure, i.e., 6, 15 min, and 298 K, respectively.

Kinetics of Pb(II) and Cu(II) ions adsorption on CdS NPs were also investigated by the same above procedure using different contact times (1, 3, 5, 9, 12, 15 min) at optimum amounts of pH, adsorbent dosage and temperature.

Thermodynamic studies at different temperatures (278, 288, 298, 308, and 318 K) were carried out by adding 0.05 g of CdS NPs into 50 mL of sample solution (100 mg/L of Pb and Cu). The solution pH

and contact time were adjusted in 6 and 5 min, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of Adsorbent

In the present study, CdS NPs were synthesized in aqueous medium through chemical precipitation technique by using glucose as capping agent [37]. Transmission electron microscopy was used to investigate the morphology and particles size of CdS NPs. Figure 1 shows a representative TEM image of CdS NPs, which clearly presents that the diameters of most particles are less than 100 nm. Obviously, CdS is formed by crystalline aggregates, resulted from fine and spherical nanoparticles. Thus, the offered method for preparation of CdS NPs was successful.

The XRD pattern of CdS NPs is displayed in Figure 2. The three peaks with 2θ values of 26.82, 43.53, 52.20, and 70.51 correspond to the (1 1 1), (2 2 0), (3 1 1), and (3 3 1) planes of the cubic phase CdS. The absence of peaks at 28.4, 36.62, and 47.84 which are associated only with hexagonal phase eliminates the possibility of incorporation of hexagonal phase of CdS in the sample [41]. This is in agreement with the results already reported by Prabhu et al. [39]. They synthesized CdS NPs through the chemical precipitation by using triethanolamine as capping agent.

Broadening of the peaks indicates the nanocrystalline nature of the material. The crystallite size (D) of CdS NPs was estimated from line broadening of the (111) diffraction peak, according to the Debye-Scherrer equation [34, 41]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (3)$$

Where λ is the wavelength of Cu-K α radiation ($\lambda = 1.542 \text{ \AA}$), β is the full-width at half maximum intensity and θ is the diffraction angle (in radian) of the considered diffraction peak. The crystallite size calculated by this method was 47.82 nm.

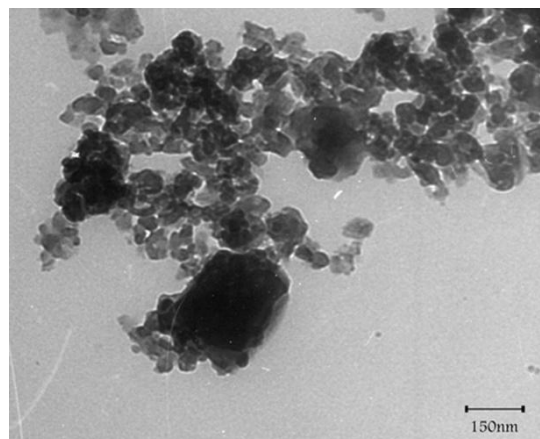


Figure 1. TEM image of CdS NPs.

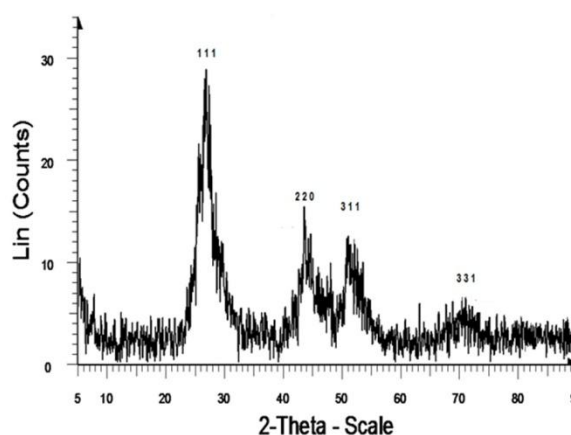


Figure 2. XRD pattern of CdS NPs.

3.2. Effect of pH

The pH of the solution has a significant impact on the uptake of heavy metal ions, since it determines the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate [17]. The effect of pH on the adsorption of Pb(II) and Cu(II) ions by 0.05 g of CdS NPs was studied over the pH range of 2–7, with known concentration of metal ions (100 mg/L), and contact time of 15 min at 298 K. As illustrated in Figure 3, removal percentages of both metal ions increased from pH 2 to 6. The maximum removal of metal ions was observed at $pH=6$. This may be attributed to the surface charge development of the sorbent and the concentration distribution of metal ions since both of them are pH -dependent. At low pH values, solution is strongly acidic and the surface of the sorbent is

surrounded by hydrogen ions. So due to the competition of hydrogen ions with metal ions, removal percentage is low. At pH values higher than 6, Pb(II) and Cu(II) ions begin to precipitate as $Pb(OH)_2$ and $Cu(OH)_2$, and therefore the separation may not be due to adsorption. So, in order to avoid any precipitation effect at higher pH values, pH of 6 was considered as the optimum pH for all further studies. Previous studies have also reported that the maximum adsorption efficiency for Pb(II) and Cu(II) ions was obtained at pH of 6 [42-45].

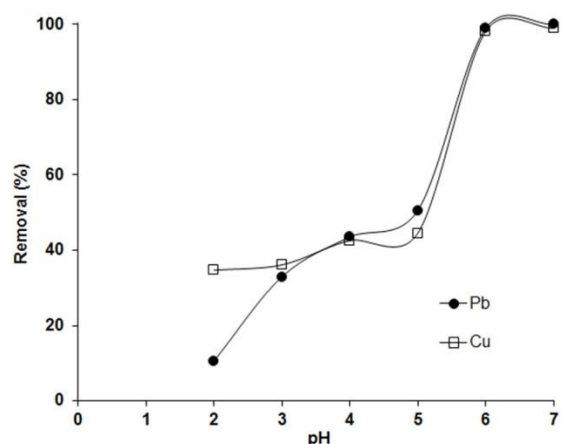


Figure 3. Effect of sample pH on the adsorption of Pb(II) and Cu(II) onto CdS NPs (Conditions: initial adsorbate concentration 100 mg/L; $C_{adsorbent}$ =2 g/L; agitation speed 200 rpm; t =15 min; T =298 K).

3.3. Effect of Contact Time

Equilibrium time is another important parameter to heavy metals wastewater treatment process. The effect of contact time on the removal of Pb(II) and Cu(II) ions by CdS NPs was studied using different stirring times from 1 to 20 min with 50 mL of 100 mg/L metal ions solution (pH =6), and 2 g/L of CdS NPs at temperature of 298 K. The removal percentage of metal ions as a function of contact time was illustrated in Figure 4. Obviously, the adsorption rate of metal ions onto the adsorbent was very rapid initially, which indicates that there were enough adsorption sites for the ions to be

accommodated. Subsequently, the adsorption rate slowly decreased as the adsorption sites became gradually saturated, and finally it reached equilibrium in 15 min and remained constant up to 20 min. Therefore, 15 min was selected as optimum contact time for subsequent isotherm studies. In comparison with the previous studies [43, 46-50], the adsorption process of both metal ions onto CdS NPs was fast.

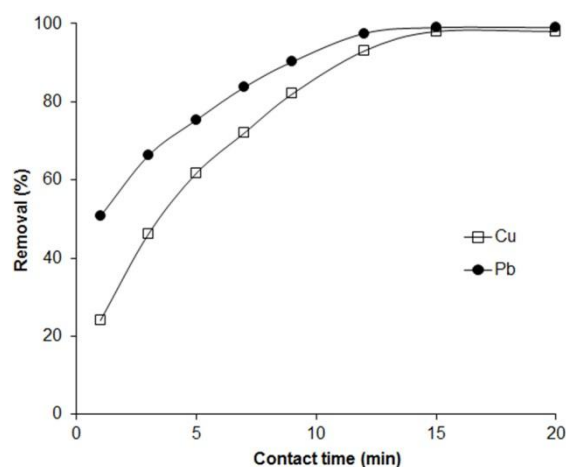


Figure 4. Effect of contact time on the adsorption of Pb(II) and Cu(II) onto CdS NPs (Conditions: initial adsorbate concentration 100 mg/L; pH =6; $C_{adsorbent}$ =2 g/L; agitation speed 200 rpm; T =298 K).

3.4. Effect of Adsorbent Dosage

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate [51]. Adsorption of metal ions at constant pH and contact time was studied by varying the adsorbent dosage from 0.2 to 2.5 g/L. As shown in Figure 5, increase in adsorbent dosage enhanced significantly the percent removal of metal ions. The maximum removal of heavy metal ions was obtained with 2 g/L of adsorbent; this was therefore selected as optimum amount for further experiments. At low adsorbent dosages, the adsorbent surface became saturated with the metal ions and the residual metal ion concentration in the solution was large. As the adsorbent dosage increases, the adsorbent sites

available for heavy metal ions are also increased and consequently better adsorption takes place [52]. However, higher dosages (>2 g/L) had no significant effect on the metal ions uptake as the surface metal ions concentration and the solution metal ions concentration came to equilibrium with each other.

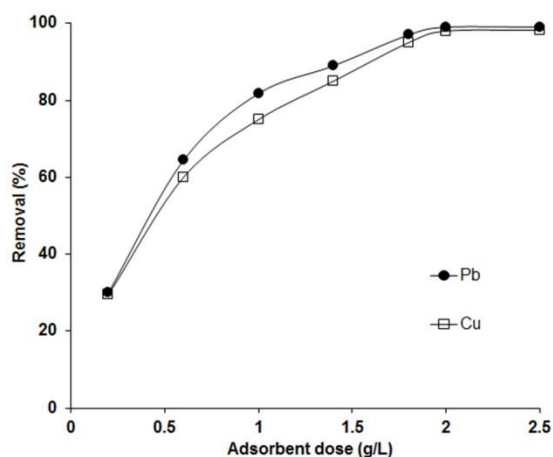


Figure 5. Effect of adsorbent dosage on the adsorption of Pb(II) and Cu(II) onto CdS NPs (Conditions: initial adsorbate concentration 100 mg L^{-1} ; $pH=6$; agitation speed 200 rpm ; $t=15 \text{ min}$; $T=298 \text{ K}$).

3.5. Effect of Temperature

The adsorption experiments of metal ions were performed at eight different temperatures in the range of 278-348 K with 50 mL of 100 mg/L aqueous metal ions solution and 0.05 g/L of CdS NPs at pH of 6, and contact time of 5 min. From Figure 6, the removal percentages of Pb(II) and Cu(II) ions by CdS NPs increase with the rise in solution temperature from 298 K to 318 K, suggesting that the adsorption process is endothermic. This increase can be due to the increased mobility of metal ions and to their tendency to adsorb from the solution to the surface of the adsorbent as well as due to a greater activity of binding sites as the temperature increases. This observation is in agreement with those reported by the other studies [43, 46, 47, 53-55]. However, at temperatures higher than 318 K, the adsorption of metal ions decreases. This may be due to the damaging of adsorbent surface and

decomposing of crystal structure of CdS NPs which can be lead to desorption.

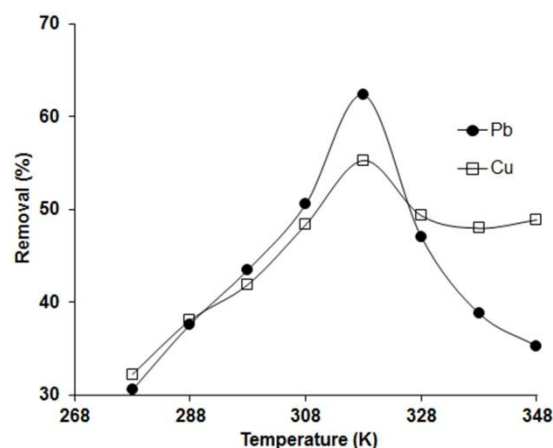


Figure 6. Effect of temperature on the adsorption of Pb(II) and Cu(II) onto CdS NPs (Conditions: initial adsorbate concentration 100 mg/L ; $pH=6$; $C_{\text{adsorbent}}=0.05 \text{ g/L}$; $t=5 \text{ min}$; agitation speed 200 rpm).

3.6. Adsorption Isotherms

Adsorption isotherms are used for describing adsorption equilibrium for wastewater treatments. In the present work, the sorption data have been subjected to different sorption isotherms, namely, Langmuir, Freundlich and Temkin models. Langmuir adsorption isotherm is valid in the case of monolayer adsorption onto the surface with a finite number of identical sites [56]. Freundlich isotherm is used for the description of multilayer adsorption with interaction between adsorbed molecules [57]. The Temkin isotherm model assumes that the adsorption energy decreases linearly with the surface coverage due to some indirect adsorbate/adsorbate interactions [58]. The linear forms of isotherm models are defined as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (4)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (6)$$

The experimental equilibrium adsorption data were fitted above equations using plot

of C_e/q_e versus C_e , $\ln q_e$ versus $\ln C_e$ (Figure 7), and q_e versus $\ln C_e$, respectively. Isotherm constants were determined from the slopes and intercepts of the corresponding linear plots. In Langmuir model, q_e is the amount of heavy metal ion adsorbed at equilibrium (mg/g), q_{\max} is maximum adsorption capacity (mg/g) on unit mass of adsorbent, and K_L is the Langmuir constant (L/mg), related to the free energy of adsorption. Furthermore, the essential characteristic of the Langmuir isotherm, i.e., dimensionless separation factor (R_L) was calculated using Equation (7). The R_L values between 0 and 1 indicate favorable adsorption [59]. In Freundlich isotherm K_F and n are the isotherm constants related to adsorption capacity [(mg/g) (L/mg)^{1/n}] and adsorption intensity, respectively. If $1 < n < 10$, the adsorption is favorable. In Temkin model, K_T is the equilibrium binding constant (L/mg), and B_T is a constant related to adsorption heat (kJ/mol).

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

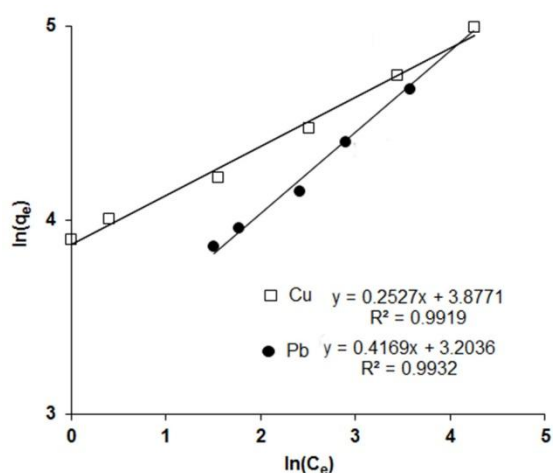


Figure 7. Freundlich plots for Pb(II) and Cu(II) adsorption onto CdS NPs (Conditions: initial adsorbate concentration 100 mg/L; pH=6; $t=15$ min; $T=298$ K).

The results obtained by fitting the experimental equilibrium adsorption data to the isotherm models as well as the correlation coefficients (R^2) for all models

were presented in Table 1. Examination of linear isotherm plots suggested that, for the adsorption of metal ions onto CdS NPs, the Freundlich isotherm yielded a much better fit with higher correlation coefficient ($R^2 > 99$) than other models. The values of Freundlich constant (n) were found to be greater than 1, which indicated that the adsorption process of Pb(II) and Cu(II) ions was favorable. According to this isotherm model, multilayer adsorption takes place on a heterogeneous surface of CdS NPs. Similar results have also been reported by other researchers for the adsorption of Pb(II) and Cu(II) ions onto nanoadsorbents [43, 46]. Moreover, maximum adsorption capacities for Pb(II) and Cu(II) ions were determined as 200 mg/g and 166.7 mg/g, respectively.

Table 1. Isotherm parameters for the adsorption of metal ions onto CdS NPs.

Isotherm model	Constants	Metal ions	
		Pb(II)	Cu(II)
Langmuir	q_{\max} (mg/g)	200	166.7
	K_L (L/mg)	0.05	0.17
	R^2	0.963	0.981
	R_L	0.17	0.06
Freundlich	K_F (mg/g)(L/mg) ^{1/n}	24.62	48.28
	n	2.40	3.96
	R^2	0.993	0.992
Temkin	K_T (L/mg)	1.51	8.02
	B_T (kJ/mol)	36.07	21.34
	R^2	0.947	0.938

3.7. Comparison of CdS NPs-Based Batch Adsorption Method with Other Published Methods

A comparison of the maximum uptake of Pb(II) and Cu(II) ions onto different nanoadsorbents together with the optimum contact time were given in Table 2. The variation in q_{\max} values between the adsorbents can be related to the type and density of active sites responsible for adsorption of metal ions from the solution. It is clear that the adsorption capacity of CdS NPs used in the present study is

significant. This may be attributed to the effect of particle size and distribution, morphology, and surface structure of the adsorbent. Moreover, the adsorption

process using CdS NPs is rapid. Therefore, CdS NPs are considered to be excellent and potential adsorbent for heavy metal ions removal from aqueous solutions.

Table 2. Comparison of maximum adsorption capacity and optimum contact time of different nanoadsorbents for the removal of Pb(II) and Cu(II) ions.

Adsorbent	q _{max} (mg/g)		t (min)		Ref.
	Pb(II)	Cu(II)	Pb(II)	Cu(II)	
Maghemite nanotube	71.42	111.11	240	240	[60]
INIS ^a	2.08	1.26	1440	1440	[61]
Nanocrystalline TiO ₂	80.64	100	420	420	[43]
Fe ₃ O ₄ nanoadsorbents	36.0	-----	-----	30	[46]
Nanostructure alumina	125	-----	180	-----	[21]
NSSCAC ^b	23.81	-----	240	-----	[62]
Graphene oxide	36.00	-----	1440	-----	[48]
TiO ₂ /Graphene oxide	65.60	-----	1440	-----	[48]
Graphene oxide	-----	117.50	-----	120	[63]
Fe ₃ O ₄ -MWCNT ^c	-----	38.91	-----	360	[49]
GA ^d modified MNPs	-----	38.50	-----	2.0	[53]
MCNPs ^e	-----	35.50	-----	240	[64]
Pectin-coated MNPs	-----	48.99	-----	120	[47]
CdS NPs	200	166.7	15	15	This work

^a Iron-oxide nanoparticles immobilized sand, ^b Nano-silversol-coated activated carbon, ^c Multiple walled carbon nanotube, ^d Gum Arabic, ^e Magnetic chitosan nanoparticles.

3.8. Adsorption Kinetics

Adsorption kinetics has been proposed to elucidate the adsorption mechanism. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transport process. In order to investigate the mechanism of metal ions adsorption on the adsorbents and examine the potential rate-controlling step, i.e., mass transfer or chemical reaction, different kinetic models were studied. The capability of Lagergren's pseudo-first-order, pseudo-second-order, and intraparticle diffusion models was examined in this study. The correlation coefficient (R², close or equal to 1) was introduced to evaluate the suitability of different models. The linearized-integral forms of studied kinetic models are expressed as [65-67]:

$$\ln(q_1 - q_t) = \ln q_1 - k_1 t \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \quad (9)$$

$$q_t = k_i t^{1/2} + C \quad (10)$$

Where q₁ (or q₂) and q_t (mg/g) are the values of amount adsorbed per unit mass of sorbent at equilibrium and at any time, k₁ (1/min) is the pseudo-first-order adsorption rate coefficient and k₂ (g/mg min) is the pseudo-second-order constant. In intraparticle diffusion model k_i (mg/g min^{1/2}) is the diffusion rate coefficient and C_i is the intercept and relate to the thickness of the boundary layer. The parameter values for each model were obtained from the respective linear plots of ln (q₁-q₂) vs. t, t/q_t vs. t (Figure 8), and q_t vs. t^{1/2}, respectively.

The results together with the correlation coefficient (R²) were listed in Table 3. Comparing the correlation coefficients of kinetic models revealed that the pseudo-second-order kinetic model with R² values

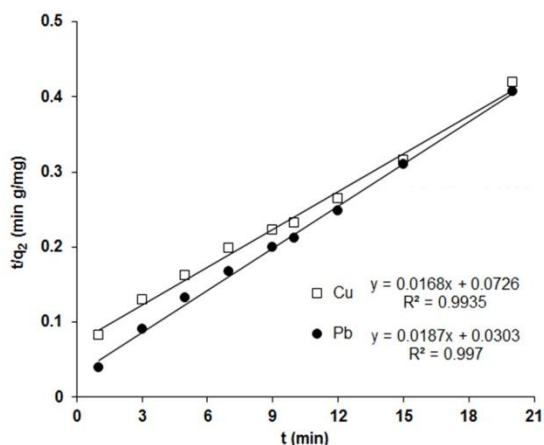


Figure 8. Pseudo-second-order kinetic plots for Pb(II) and Cu(II) adsorption onto CdS NPs (Conditions: initial adsorbate concentration 100 mg/L; pH=6; $C_{adsorbent}=2$ g/L; $T=298K$).

close to 1 matched better the experimental data than the other models. This model is based on the assumption that the rate limiting step may be a chemical sorption involving valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate [68]. Similar results have also been reported for heavy metal ions removal by other adsorbents [43, 47, 49, 60].

Table 3. Kinetics parameters for the adsorption of metal ions onto CdS NPs.

Kinetic model	Constant	Metal ion	
		Pb(II)	Cu(II)
Pseudo-first order	q_1 (mg/g)	38.63	77.32
	k_1 (1/min)	0.208	0.313
	R^2	0.954	0.908
Pseudo-second order	q_2 (mg/g)	55.56	62.5
	k_2 (g/mg min)	0.011	0.004
	R^2	0.997	0.993
Intra-particle diffusion	C_i	21.07	4.96
	k_i (mg/min ^{1/2} g ¹)	7.285	10.960
	R^2	0.906	0.930

3.9. Adsorption Thermodynamics

Thermodynamic studies are used to decipher any reaction in a better way. In the present study, the variation in the extent of adsorption with respect to

temperature has been explained based on thermodynamic parameters viz. changes in standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0). Thermodynamic parameters were evaluated in the temperature range of 278-318 K (to avoid thermal decomposition of adsorbent). The values of the thermodynamic parameters were calculated using the thermodynamic equations described below [21, 69]:

$$\ln C_e = \frac{\Delta H^0}{RT} + D \quad (11)$$

$$\Delta G^0 = -RT \ln K_c \quad (12)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (13)$$

Where R is the ideal gas constant (8.314 J/mol.K), T is the absolute temperature (K), and K_c is the thermodynamic equilibrium constant defined by q_e/C_e .

The values of thermodynamic parameters thus calculated were recorded in Table 4. Positive ΔH^0 values at different temperatures for both the metal ions suggested the endothermic nature of adsorption process, which was in good agreement with the results that the adsorption of metal ions increased with the increasing temperature. Positive ΔS^0 values show an increased randomness during metal ions adsorption. Positive ΔG^0 values at temperatures 288-308 K indicates that the adsorption reactions were non-spontaneous over the temperature range considered. However, as the temperature increased ΔG^0 values became negative. This suggests that the simultaneous adsorption of Pb(II) and Cu(II) ions on CdS NPs is favored at temperatures >308 K. Generally, ΔG^0 values lower than -20 kJ/mol are consistent with physisorption, while those around -40 kJ/mol or higher correspond to chemisorption [46, 70]. The ΔG^0 values obtained in this study indicate the physical adsorption of Pb(II) and Cu(II) ions onto CdS NPs. This is also supported by the fact that $\Delta H^0 < 40$ kJ/mol indicates the physical adsorption process [46].

Table 4. Thermodynamic parameters for the adsorption of metal ions onto CdS NPs.

Metal ion	Parameter	T (K)				
		278	288	298	308	318
Pb(II)	ΔH^0 (KJ/mol)	11.34	11.34	11.34	11.34	11.34
	ΔG^0 (KJ/mol)	1.89	1.21	0.12	-0.50	-1.33
	ΔS^0 (KJ/mol)	0.033	0.035	0.038	0.039	0.040
Cu(II)	ΔH^0 (KJ/mol)	6.88	6.88	6.88	6.88	6.88
	ΔG^0 (KJ/mol)	1.72	1.16	0.60	-0.16	-0.38
	ΔS^0 (KJ/mol K)	0.018	0.020	0.021	0.022	0.023

4. CONCLUSION

Cadmium sulfide nanoparticles with average particles size less than 100 nm were successfully synthesized and used for simultaneous removal of Pb(II) and Cu(II) ions from aqueous solutions. The batch adsorption parameters including the solution *pH*, contact time, adsorbent dosage and temperature were found to be effective on the adsorption efficiency of both the metal ions. The isotherm adsorption data were well fitted by the Freundlich model. The maximum adsorption capacities of 200 mg/g and 166.7 mg/g were obtained for Pb(II) and Cu(II) ions, respectively, at initial adsorbate concentration of 100 mg/L, *pH* of 6, temperature 298 K, and contact time

of 15 min. The adsorption process was fast and pseudo-second-order rate model accurately described the kinetics of adsorption, which suggested chemisorption as the rate-limiting step in the adsorption process. Thermodynamic studies confirmed the endothermic nature of the adsorption process, and its spontaneity for temperatures 308-318 K. In conclusion, CdS NPs can be recommended for wastewater treatments and control of environmental pollution.

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