

Green Synthesis of CdS Nanoparticles and their Potential Application towards Adsorption of Lead and Cadmium ions

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Abstract

Watermelon rind aqueous extract mediated synthesis of CdS nanoparticles was investigated for its efficiency towards removal of lead and cadmium ions from aqueous solutions. Batch adsorption investigations were performed to optimise the experimental conditions. The optimised conditions were found to be pH 6, 1 g L⁻¹, 30 min and 303 K respectively for the removal of lead and cadmium ions. The equilibrium data obtained was analysed with isotherm models and it was found that Langmuir and Freundlich isotherms explain better and the loading capacities were found to be 332.2 and 318.7 mg L⁻¹ respectively for Pb²⁺ and Cd²⁺ ions.

Kinetic investigations suggest that pseudo second order kinetic model fits well to the experimental data suggesting that chemical reactions govern the rate limiting step. The spontaneous and exothermic nature of the present process was successfully demonstrated by the thermodynamic investigations. Desorption and regeneration studies suggest that the CdS nanoparticles can be successfully regenerated 5 times and reused in the adsorption process.

Keywords: CdS, Nanoparticles, Adsorption, Kinetics.

Introduction

Heavy metals are used in various processes and finished industrial products and have become inevitable part of the industry²⁵. Use of these metals in majority of the process has resulted in environmental contamination leading to water and soil pollution¹. Water is basic and supports life on this earth and it is getting unfit for usage due to various factors and industrialization. Inorganic and organic contaminants are creating pollution since they are used in various industrial processes²². Heavy metal ions are carcinogenic in nature and significantly impact human health as well as aquatic life²⁷. Hence, it is desirable to eliminate these metal ions from industrial effluents before they are released into the water streams.

Various treatment techniques are available for the treatment and remediation of inorganic species from water streams and adsorption is reported as one of the most promising techniques for the treatment¹³. Adsorbents such as activated

carbon¹⁸, agro-wastes¹⁶, industrial by-products²⁸, zeolites¹⁰ and nanomaterials⁵ were explored for the removal of heavy metal ions from aqueous medium. Nanomaterials are promising as an adsorbent for the removal of heavy metal ions due to high efficiency, adsorption capacity and high regeneration ability⁶.

Nanomaterials were successfully synthesised via various routes and reported as adsorbents in literature. Ruba et al²⁶ reported the green synthesis of ZnO, CuO, MgO and MnO₂ nanomaterials as potential nanoadsorbents for the removal of textile dyes from textile effluents. Green synthesised iron nanoparticles were reported for the removal of Cu ions from aqueous solution². Ways towards cleaner production of water by nanoadsorbents have been well articulated in a review by Janani et al¹¹. Majority of reports showcase the synthesis of ZnO and Fe nanoparticles and nanomaterials as adsorbents for the removal of the organic and inorganic contaminants from wastewaters. CdS nanoparticles synthesised by watermelon rind aqueous extract reported earlier¹⁷ were investigated for the removal of lead and cadmium ions from aqueous solution.

Material and Methods

Batch adsorption studies: In general, adsorption experiments are performed in batch process to understand the process and various parameters are optimised to achieve the goals. In this study, batch studies were performed and parameters such as pH, adsorbent dose, contact time and initial concentrations were optimised. pH experiments were performed between 2 and 8 to understand the optimal pH of the solution for maximum removal. Adsorbent dose was varied from 0.5 to 2.5 g L⁻¹ for optimizing the dose. Contact time of adsorbent with metal ions was investigated by taking out the samples at pre-set time intervals between 10 and 120 mins. The initial concentrations of the metal ions were varied from 50 to 250 mg L⁻¹ to understand the equilibriums.

After each experiment, the adsorbent and solution were separated by a filtration process with Whatmann filters. The filtered supernatant solution was subjected to Atomic Absorption Spectroscopy to estimate the remaining metal ion concentration in the solution. The removal efficiency and adsorption capacity of CdS nanoparticles towards Pb²⁺ and Cd²⁺ ions were estimated by the following equations:

$$\% \text{ Removal} = \frac{(C_0 - C_1)}{C_0} \times 100 \quad (1)$$

$$q_e = (C_0 - C_1) \frac{V}{M} \quad (2)$$

where C_0 is the initial concentration of the adsorbate ions, C_1 is the residual concentration of the adsorbate ions, V is the volume of the solution, M is the mass of the CdS nanoparticles and Q_e is the loading capacity of the CdS nanoparticles synthesised by the aqueous extract of the watermelon rind.

Atomic absorption spectrophotometer analysis: Atomic absorption spectrophotometer (Varian AA240) with flame burner was employed in this study and acetylene and air were used as fuel and oxidant for the flame. Hollow cathode lamps of Pb and Cd were used in this study to provide the required wavelengths 283.3 nm and 326.1 nm for Pb and Cd respectively. Prior to the sample analysis, standard solutions of lead and cadmium were tested in the AAS to plot the calibration graphs and residual concentrations were auto calculated every time.

Results and Discussion

pH variation studies: pH or H^+ ions concentration of a solution can significantly influence the adsorption of adsorbate ions onto the surface of the adsorbent due to competitive adsorption. Hence, it is always essential to test and optimize the pH of the solution prior to any other parameter optimization in adsorption experiments. In this study, pH of the solution was optimised by changing the pH of the solution for the removal of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles and the results are presented in fig. 1. It is observed that with the incremental pH, the adsorption removal efficiency increased for both Pb^{2+} and Cd^{2+} ions by CdS nanoparticles and was found maximum at pH 5. Beyond pH 5, the removal efficiency was found to decrease with increase in pH to basic range for both the metal ions. Increase in removal efficiency observed for an increasing pH due to decline in the H^+ ion concentration.

Decrease in the competitive adsorption of H^+ ions with Pb^{2+} and Cd^{2+} ions for the active sites was observed. A maximum

of 91.4 and 88.2 % was obtained at pH 5 for the Pb^{2+} and Cd^{2+} ions respectively. The decrease in removal efficiency beyond pH 6 might be due to formation of metal hydroxides and CdS nanoparticles surface charge turning to positive which is explained by point zero charge study of the CdS nanoparticles¹². The pH of the metal ions solution is naturally found to be around 5.5 to 6 and the maximum removal efficiency is achieved at 5 with slight decrease in efficiency at pH 6. Hence the adsorption experiments were performed at their natural metal ions solution pH.

Effect of dosage of the CdS nanoparticles: Adsorbent dosage of an adsorption process determines the economic value of the adsorption process and hence it is highly essential to determine the optimal dose of the adsorbent. In view of the economic value, in this study CdS nanoparticles dose was optimised by varying the dose from 0.5 to 5 g L⁻¹. The results of the investigation for the removal of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles are represented in fig. 2. It is observed that with an incremental in CdS dosage, the removal efficiency improved and was found to be saturated very quickly. The obtained plot can be divided into two phases and the first phase is the immediate utilization of the active sites of the CdS nanoparticles since the active sites are free.

The second phase is slower adsorption phase of the Pb^{2+} and Cd^{2+} ions by CdS nanoparticles and with the increase in the adsorbent dose, the efficiency was found to be saturated due to agglomeration of CdS nanoparticles at lower liquid and higher solid ratio²³.

Thus the agglomeration of CdS nanoparticles reduces the surface areas and the nanoparticles resulting in saturation of the removal efficiency. Hence, lower dose of the nanoparticles is highly desirable due to higher surface area exhibition of the CdS nanoparticles. A dose of 1 g L⁻¹ is fixed as optimal dose for further experiments.

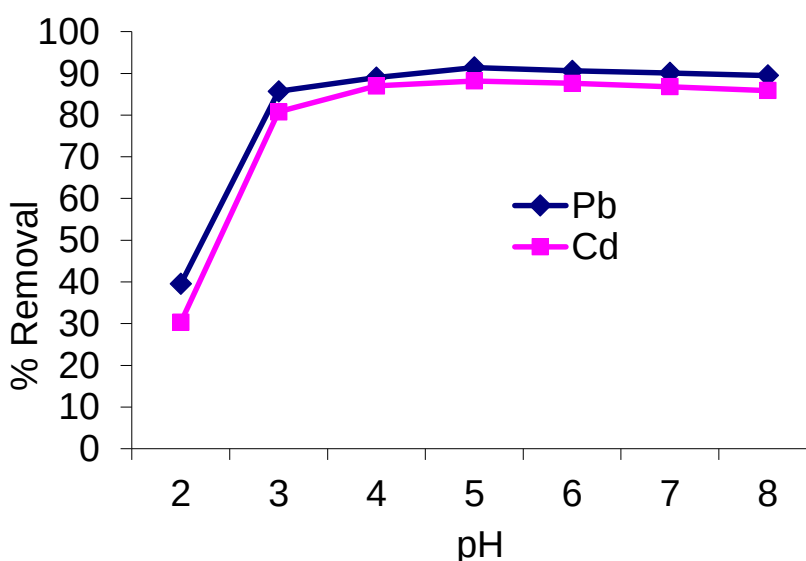


Fig. 1: Effect of pH for the removal of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles

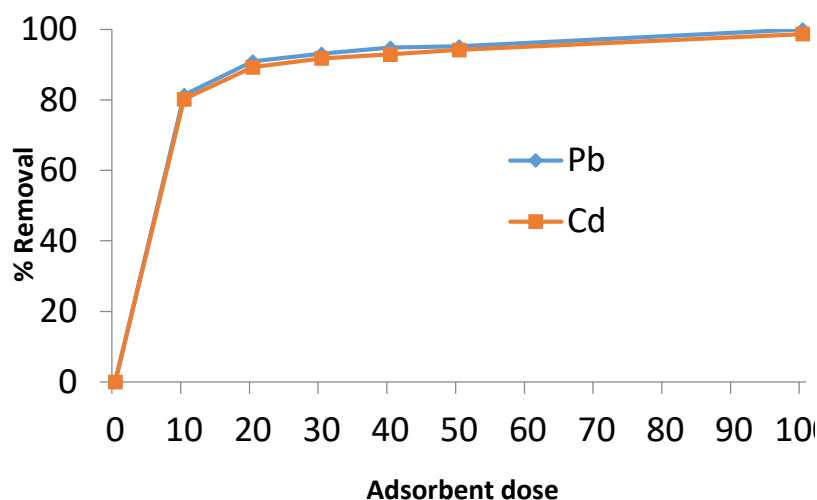


Fig. 2: Effect of adsorbent dose for the removal of Pb²⁺ and Cd²⁺ ions by CdS nanoparticles

Effect of liquid to solid contact time: The liquid to solid time of contact is highly essential for establishing the efficiency of the sorption process in terms of cost. If the time of contact increases, then the process would require additional cost due to delayed process and quick process will result in minimising the energy requirements. Hence, an experiment was carried out to understand the time of contact for the CdS nanoparticles and Pb²⁺ and Cd²⁺ ions. It is observed that the removal was found to be very spontaneous and 84 and 76 % of removal were achieved within 10 mins of contact time. With further increase in time, the removal percentage increased slightly and was found to be saturated beyond 60 min of contact time. The higher efficiency is due to immediate binding of the Pb²⁺ and Cd²⁺ ions onto the ample active sites of CdS nanoparticles¹⁴.

Initially the active sites on the CdS nanoparticles are free and when they come in contact with Pb²⁺ and Cd²⁺ ions, they immediately bind onto it and thus maximum is observed in initial phase of time. The later incremental efficiency is due to slow utilization of the active sites of the CdS nanoparticles. The CdS nanoparticles are around 30 nm in size and they exhibit higher surface areas for the binding of Pb²⁺ and Cd²⁺ ions. After 10 min of time, the efficiency was found to increase upto 30 min and beyond that it is found to be saturated. To have maximum uptake of the Pb²⁺ and Cd²⁺ ions, a minimum of 30 min was set as optimal contact time for the removal by CdS nanoparticles.

Effect of initial metal ion concentrations: The change in concentration of a process can alter the equilibrium and thus study of initial concentration variation is very essential. In view of the above, an investigation was performed to understand the change of initial concentration on the equilibrium.

It is observed that with the initial concentration change, the removal percentage decreased to lower values and this is due to the disappearance of the active sites on the CdS nanoparticles. At low concentrations, the active sites are

high and hence 100% removal efficiency is achieved while with the increase in concentration, the active sites decrease and metal ions have no active sites to bind. The equilibrium is significantly influenced by the change and concentration. However, the loading or adsorption capacity of CdS nanoparticles increased with the increase in initial concentration⁴. The loading capacity found in this study is high than several nanoadsorbents reported in literature.

Adsorption isotherms: Mathematical models are developed to understand and validate the experimental data and further help to understand the process. Several mathematical models are developed for the purpose of adsorption process prediction and two most commonly employed models of adsorption are Langmuir and Freundlich isotherms.

Langmuir isotherm: Langmuir is the one of the finest mathematical model that explains the monolayer adsorption of adsorbate onto adsorbent and further provides the theoretical loading capacity of the adsorbent that can be compared with the experimental values. The linear form the equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{bV_m} + \frac{C_e}{V_m} \quad (3)$$

where C_e is the equilibrium concentration of the adsorbate ions, q_e is the loading capacity of the adsorbent, V_m is the quantity of metal ions at the monolayer and b is the heat of adsorption constant.

A plot of C_e/q_e vs C_e was plotted with the experimental data and the slope and intercepts of the plots provide the constants V_m and b . The plots of Langmuir isotherm obtained for the removal of Pb²⁺ and Cd²⁺ ions by the CdS nanoparticles are shown in fig. 3 and the respective constants obtained are summarised in table 1. It is observed that the equilibrium data obtained for the Pb²⁺ and Cd²⁺ ions removal by CdS nanoparticles fit well with the model. The high correlation coefficients obtained for the Pb²⁺ and Cd²⁺ ions suggest that the process is well explained by the Langmuir model. The

correlation coefficients were found to be 0.998 and 0.999 respectively for Pb^{2+} and Cd^{2+} ions.

In addition to the correlation coefficients, the better fit is also supported by the loading capacities of Pb^{2+} and Cd^{2+} ions onto CdS nanoparticles. The theoretically calculated loading capacities were found to be 333.3 and 322.5 respectively for Pb^{2+} and Cd^{2+} ions while the experimental values were calculated as 332.2 and 318.7 mg L^{-1} . These observations strongly support the claims and conclude that the Langmuir isotherm is the best fit model for the adsorption of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles and the adsorption of Pb^{2+} and Cd^{2+} ions onto CdS nanoparticles is monolayer adsorption³¹.

An exclusive feature of Langmuir isotherm can be expressed in the dimensionless constant which suggests the favourable or unfavourable process of adsorption. The dimensionless constant is expressed as R_L , a separation factor. If R_L is greater than 1, then the adsorption of Pb^{2+} and Cd^{2+} ions by

CdS nanoparticles is considered to be unfavourable and if $R_L = 1$, then it is linear and irreversible. For adsorption of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles to be favourable, the condition is $0 < R_L < 1$. If the values are in between 0 and 1, then the process of adsorption is favourable. The separation factor R_L is expressed as follows:

$$R_L = \frac{1}{1 + bC_e} \quad (4)$$

where R_L is separation factor, b is heat of adsorption and C_e is the equilibrium concentration of the metal ions.

The separation factor R_L values obtained for the adsorption of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles is summarised in table 2. It is observed that the R_L values for both the metal ions at various initial concentration were found to be between 0 and 1 suggesting that the adsorption process is favourable.

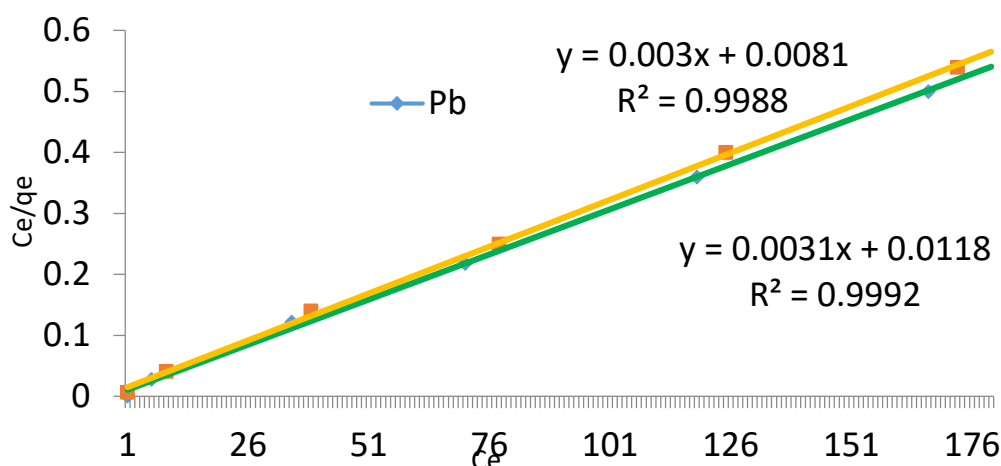


Fig. 3: Langmuir plots for the removal of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles

Table 1

Langmuir and Freundlich constants obtained for the removal of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles

Isotherms	Constants	Pb^{2+}	Cd^{2+}
Langmuir	b	0.0081	0.0118
	V_m	333.3	322.5
	R^2	0.998	0.999
Freundlich	K_f	2.09	1.91
	$1/n$	0.0135	0.0185
	R^2	0.992	0.962

Table 2

Separation factor calculated from Langmuir isotherm for the removal of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles

Initial concentration	Separation factor	
	Pb^{2+}	Cd^{2+}
50	0.999191	0.99007
100	0.949983	0.901112
150	0.777892	0.683181
200	0.636189	0.522008
250	0.508771	0.40308
300	0.424897	0.329051

Freundlich isotherm: One of the oldest isotherm models that is used in prediction of adsorption process is Freundlich isotherm model. This model states the multilayer adsorption of adsorbates onto the surface of the adsorbents. The linear equation of the model is expressed as follows:

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

where q_e is the loading capacity, C_e is the equilibrium concentration of metal ions, K_f is adsorption capacity and n is the intensity of the adsorption.

The equilibrium data obtained for the removal of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles was analysed with the Freundlich linear equation and a plot of $\log C_e$ vs $\log q_e$ will provide the Freundlich constants. The plots of Freundlich isotherm are represented in fig. 4 and the constants are summarised in table 1. It is noticed that the correlation coefficients obtained for the removal of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles is found to close to one suggesting that the Freundlich model is also well applicable to the system and the process is multilayer adsorption.

The applicability of Langmuir isotherm suggests that the process is multilayer and each layer obeys Langmuir isotherm. Hence the results suggest that the removal of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles is governed by Langmuir and Freundlich models.

Kinetics of adsorption: The sorption experiments conducted by varying the time of contact can provide valuable information such as the limiting step of the adsorption process and mechanism of adsorption such as physical or chemical adsorption. In view of the above, the kinetic experiments were conducted by varying the time of

contact of Pb^{2+} and Cd^{2+} ions onto CdS nanoparticles. The data obtained was verified and analysed with two frequent and most popular models such as pseudo first and second order kinetic models.

Further the Weber and Morris intraparticle diffusion model was also employed to understand the process of adsorption. The pseudo first order and pseudo second order kinetic model expressions are given as follows::

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where q_e is the loading capacity at equilibrium, q_t is the loading capacity at different time intervals, t is time and k_1 is the rate constant of pseudo first order.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where q_e is the loading capacity at equilibrium, q_t is the loading capacity at different time intervals, t is time and k_2 is the rate constant of pseudo second order.

The plots of pseudo second order are shown in fig. 5 and the respective constants are summarised in table 3. It is observed that the pseudo first order model fails to fit well to the kinetic equilibrium data. The correlation coefficients obtained were found to be low suggesting that the model is not suitable for explaining the data. Further, the loading capacity of Pb^{2+} and Cd^{2+} ions onto CdS nanoparticles calculated theoretically did not match with the experimental values which supports the failure of the model to explain the kinetic data. The kinetic equilibrium data was found to fit well to the pseudo second order kinetic model and the well fit was supported by the correlation coefficients being close to one for both the metal ions.

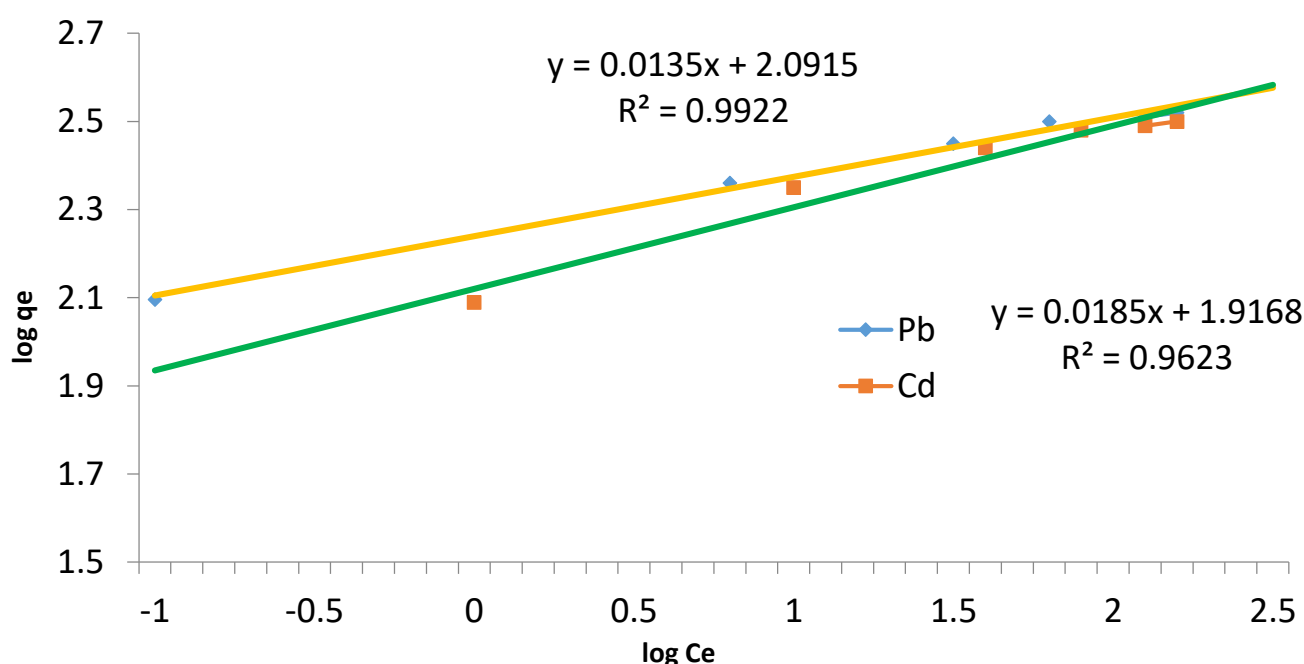
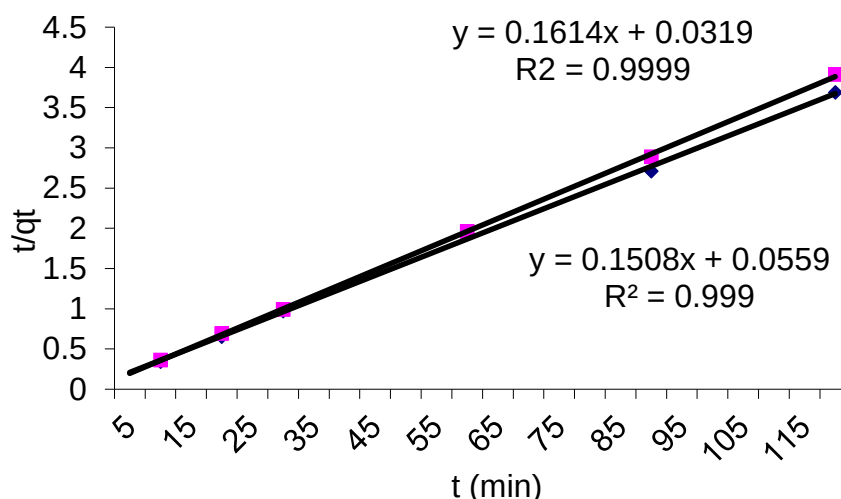


Fig. 4: Freundlich isotherm plots for the removal of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles

Table 3

Kinetic constants of pseudo first and second order for the removal of Pb²⁺ ions by CdS nanoparticles

Kinetic model	Parameters	Pb ²⁺ ions	Cd ²⁺ ions
Pseudo first order	k ₁	0.014	0.007
	q _e	7.90	9.65
	R ²	0.8707	0.967
Pseudo second order	k ₂	0.021	0.019
	q _e	120.9	117.5
	R ²	0.999	0.998

Fig. 5: Kinetic plots of pseudo second order kinetic model for the removal of Pb²⁺ and Cd²⁺ ions by CdS nanoparticles

The correlation coefficients were found to be 0.999 and 0.998 for the Pb²⁺ and Cd²⁺ ions respectively. Further, the theoretical loading capacities of the Pb²⁺ and Cd²⁺ ions onto CdS nanoparticles were closely matching with the experimental values suggesting that the pseudo second order kinetic model is the best suitable model for the present system. Applicability of pseudo second order suggests that the chemical reactions governed by the transfer of electrons are the rate limiting step. However, a number of conditions have to be met in order to conclude that chemical reactions at the surface are the rate limiting step. In majority of cases, the process tends to be physio-sorption in spite of being pseudo second order.²¹

Weber and Morris Intraparticle diffusion: Weber and Morris intraparticle diffusion model is very much helpful in studying the steps of diffusion of Pb²⁺ and Cd²⁺ ions onto CdS nanoparticles. The model equation is expressed as:

$$q_t = k_{int} t^{1/2} + C \quad (8)$$

where q_t is the loading capacity at varying time intervals, k_{int} is the intraparticle diffusion constant, C is the thickness of the layer of the boundary and $t^{1/2}$ is the half time.

The kinetic data obtained for the Pb²⁺ and Cd²⁺ ions adsorption onto CdS nanoparticles was analysed with the above equation by plotting the graph between q_t and $t^{1/2}$. It is observed that the plots for the removal of Pb²⁺ and Cd²⁺ ions by CdS nanoparticles were found to be linear suggesting that

the intraparticle diffusion is governing the adsorption process.

Thermodynamics of adsorption: The industrial effluents temperature will be moderate to high due to various processes and the temperature of the solution can impact the adsorption process. In view of the above, the temperature of the solution has to be optimised in order to gain maximum removal or adsorption efficiency. Hence, optimization of the temperature was performed by varying the temperature in this study for the removal of Pb²⁺ and Cd²⁺ ions by CdS nanoparticles between 303 and 323 K.

The thermodynamic studies can provide valuable information on the change in free energy (ΔG), entropy (ΔS) and enthalpy (ΔH) of the adsorption process. In order to derive the thermodynamic parameters, the following equations were employed.

$$K_D = \frac{q_e}{C_e} \quad (9)$$

$$\Delta G^\circ = -RT \ln K_D \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (11)$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

where K_D is the equilibrium constant, R is gas constant and T is temperature.

The thermodynamic constants obtained for the removal of Pb²⁺ and Cd²⁺ ions by CdS nanoparticles are summarised in

table 4. It is observed that the values of changes in free energy (ΔG) are found to be negative for both the metal ions at various temperatures. The negative indicates that the removal of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles is spontaneous in nature. It is also observed that with the increase in temperature, the negative value decreases suggesting that the spontaneity decreases with increase in temperature and further the adsorption capacity and removal efficiency also decrease.

The enthalpy (ΔH) values were found to be negative for both the Pb^{2+} and Cd^{2+} ions suggesting that the process is exothermic in nature and heat is released during the adsorption process and if heat is released, then the randomness among the Pb^{2+} and Cd^{2+} ions should increase. The entropy (ΔS) of the system was found to be positive for both the Pb^{2+} and Cd^{2+} ions and the positive values suggest that the randomness and disorderliness increase with increase in temperature and due to enthalpy being negative. The thermodynamic investigations suggest that the removal of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles is spontaneous in nature at low temperatures.

Desorption and regeneration studies: The sustainability of any process can be achieved only when the materials are reused or recycled and in order to make the current process sustainable, desorption and the regeneration of the CdS nanoparticles were investigated. Desorption studies were executed with different desorbing agents such as HCl,

CH_3COOH , NaOH and Na_2CO_3 for desorption of Pb^{2+} and Cd^{2+} ions from CdS nanoparticles. The results of the study are represented in fig. 6. It is observed that the desorbing agent HCl exhibited higher desorption efficiency compared to other acidic and basic desorbing agents for both the Pb^{2+} and Cd^{2+} ions.

The desorption efficiency was almost close to 100 % for of Pb^{2+} and Cd^{2+} ions and in case of other acidic and basic desorbing agents, the efficiency was low and not even 80 % was achieved. Weak base Na_2CO_3 exhibited very low desorption efficiency compared to other 3 desorbing agents. The higher efficiency exhibited by HCl is due to quick release of H^+ ions that can exchange the active sites occupied by the of Pb^{2+} and Cd^{2+} ions.

The regeneration of CdS nanoparticles was achieved successfully with the desorbing agent and its reusability has to be investigated in order to make it sustainable and economical process. The regenerated CdS nanoparticles were investigated for adsorption and desorption for 5 cycles towards Pb^{2+} and Cd^{2+} ions. It is observed that the CdS nanoparticle is highly regenerative and can be reused for several cycles without losing its efficiency. Even after 5 cycles, the desorption efficiency was found to be 96 % and 95 % towards Pb^{2+} and Cd^{2+} ions suggesting that CdS nanoparticles are superior in the adsorption of heavy metal ions.

Table 4
Thermodynamic parameters of adsorption of Pb^{2+} and Cd^{2+} ions by CdS nanoparticles

Metal ions	Temperature (K)	Free energy (ΔG)	Enthalpy (ΔH)	Entropy (ΔS)
Pb^{2+}	303	-6545.2	-1536.8	978.9
	313	-6023.5		
	323	-5736.9		
Cd^{2+}	303	-6348.2	-1452.2	919.6
	313	-5965.4		
	323	-5231.8		

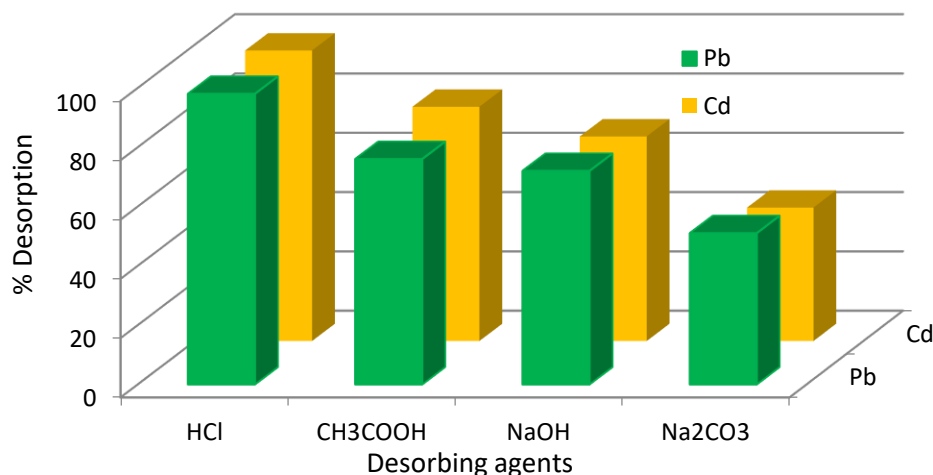


Fig. 6: Desorption efficiency of CdS nanoparticles towards Pb^{2+} and Cd^{2+} ions

Table 5
Loading capacity comparison of CdS nanoparticles with other adsorbents

S.N.	Nano adsorbent	Metal ion	Loading capacity (mg g ⁻¹)
1	Magnetic nanoparticles ¹⁵	Pb ²⁺	116.5
2	Fe ₃ O ₄ @SiO ₂ @PAA-SO ₃ H ³⁰	Pb ²⁺	182.5
3	Fe ₃ O ₄ /polyacrylic acid ²⁹	Pb ²⁺	195.3
4	Thiolbifunctionalized magnetic ¹²	Pb ²⁺	110.1
		Cd ²⁺	40.2
5	Fe ₃ O ₄ @SiO ₂ -cyclen ¹⁴	Pb ²⁺	127.9
		Cd ²⁺	105.2
6	Fe ₃ O ₄ -SO ₃ H MNP ⁴	Pb ²⁺	108.9
		Cd ²⁺	80.9
7	Ash/GO/Fe ₃ O ₄ ²³	Pb ²⁺	47.1
		Cd ²⁺	43.6
8	PVA/PAA nanofibers ³¹	Pb ²⁺	159
		Cd ²⁺	102
9	Nano chitosan ⁹	Pb ²⁺	123.6
		Cd ²⁺	84.6
10	MWCNT-Fe ₃ O ₄ @Zeo ⁸	Pb ²⁺	37.8
11	Ca doped Ni-Zn nanoferrites ²⁴	Cd ²⁺	128.2
12	Citric acid-silane modified Zirconia nanoparticles ¹⁹	Pb ²⁺	172.4
		Cd ²⁺	90.9
13	1,2,3-triazole functionalized magnetic nanoparticles ²⁰	Pb ²⁺	167.8
14	Cerium oxide nanorods ⁷	Cd ²⁺	59.9
15	NC@Co ₃ O ₄ nanocomposites ²¹	Pb ²⁺	55.2
		Cd ²⁺	52.9
16	Fe ₃ O ₄ /cyclodextrin polymer nanocomposites ³	Pb ²⁺	64.5
		Cd ²⁺	27.7
17	CdS nanoparticles*	Pb ²⁺	332.2
		Cd ²⁺	318.7

* Present study

The regeneration was achieved with desorbing agent HCl since it has exhibited highest desorption efficiency among the selected desorbing agents. These results conclude that the employment of CdS nanoparticles in adsorption process for the removal of heavy metal ions can be sustainable and can bring down the cost of the process in industries.

Comparison of loading capacities: The loading capacities of the adsorbents determine the efficiency of the adsorbents and that would be the primary choice of selection during an industrial treatment process. In this study, the loading capacities of the CdS nanoparticles were found to 332.2 and 318.7 mg g⁻¹ respectively for Pb²⁺ and Cd²⁺ ions. The loading capacities of CdS nanoparticles achieved in this study were compared with the other similar adsorbents reported in the literature. A comparison of loading capacities is summarised in table 5. It is observed that the loading capacities of CdS nanoparticles towards Pb²⁺ and Cd²⁺ ions were found to be higher than several similar adsorbents reported in literature.

Interestingly the nano adsorbents reported in literature as adsorbents are predominantly from chemical synthesis

method and in this study, the CdS nanoparticles were synthesised via green approach. The biomolecules on the surface of the CdS nanoparticles enhanced the adsorption capacities.

Conclusion

This study investigated the effectiveness of CdS nanoparticles in the removal of Pb²⁺ and Cd²⁺ ions from aqueous solution. Batch adsorption was adopted to maximise the adsorption and loading capacity of the CdS nanoparticles by varying the imperative parameters. The equilibrium data was verified with mathematical models to understand the mechanism and it was found that the process is multilayer adsorption and each layer obeys Langmuir isotherm. The kinetic data suggests that the process obeys pseudo second order kinetic model and chemical reactions are the rate limiting step.

Thermodynamic investigations reveal that the entire process is spontaneous and exothermic in nature at low temperatures. Desorption investigations proved that the CdS nanoparticles have tremendous reusable ability for successive cycles.

Thus, CdS nanoparticles prepared from green synthesis method are superior adsorbents.

References

1. Arora N.K., Chauhan R., Heavy metal toxicity and sustainable interventions for their decontamination, *Environmental Sustainability*, **4**, 1–3 (2021)
2. Amin R.M., Mahmoud R.K., Gadelhak Y. and Abo El-Ela F.I., Gamma irradiated green synthesized zero valent iron nanoparticles as promising antibacterial agents and heavy metal nano-adsorbents, *Environmental Nanotechnology, Monitoring & Management*, **16**, 100461 (2021)
3. Badruddoza A.Z.M., Shawon Z.B.Z., Tay W.J.D., Hidajat K. and Uddin M.S., Fe₃O₄/cyclodextrin polymer nanocomposites for selective heavy metals removal from industrial wastewater, *Carbohydrate Polymers*, **91**(1), 322-332 (2013)
4. Chen K., He J., Li Y., Cai X., Zhang K., Liu T., Hu Y., Lin D., Kong L. and Liu J., Removal of cadmium and lead ions from water by sulfonated magnetic nanoparticle adsorbents, *Journal of Colloid and Interface Science*, **494**, 307-316 (2017)
5. Di Natale F., Gargiulo V. and Alfè M., Adsorption of heavy metals on silica-supported hydrophilic carbonaceous nanoparticles (SHNPs), *Journal of Hazardous Materials*, **393**, 122374 (2020)
6. Ekrami E., Pouresmaeli M., Hashemiyooun E.S., Noorbakhsh N. and Mahmoudifard M., Nanotechnology: a sustainable solution for heavy metals remediation, *Environmental Nanotechnology, Monitoring & Management*, **18**, 100718 (2022)
7. Fouda-Mbanga B.G., Prabakaran E. and Pillay K., Cd²⁺ ion adsorption and re-use of spent adsorbent with N-doped carbon nanoparticles coated on cerium oxide nanorods nanocomposite for fingerprint detection, *Chemical Physics Impact*, **5**, 100083 (2022)
8. Gugushe A.S., Mpupa A. and Nomngongo P.N., Ultrasound-assisted magnetic solid phase extraction of lead and thallium in complex environmental samples using magnetic multiwalled carbon nanotubes/zeolite nanocomposite, *Microchemical Journal*, **149**, 103960 (2019)
9. Hussain M.S., Musharraf S. G., Bhangar M.I. and Malik M.I., Salicylaldehyde derivative of nano-chitosan as an efficient adsorbent for lead(II), copper(II) and cadmium(II) ions, *International Journal of Biological Macromolecules*, **147**, 643-652 (2020)
10. Isaac P.J., Amaravadi S., Msm K., Kk C., Cheralathan K.K. and Lakshmiapathy R., Synthesis of zeolite/activated carbon composite material for the removal of lead (II) and cadmium (II) ions, *Environmental Progress and Sustainable Energy*, **38**(6), e13246 (2019)
11. Janani R. et al, Advancements in heavy metals removal from effluents employing nano-adsorbents: Way towards cleaner production, *Environmental Research*, **203**, 111815 (2022)
12. Ji J., Chen G. and Zhao J., Preparation and characterization of amino/thiol bifunctionalized magnetic nanoadsorbent and its application in rapid removal of Pb (II) from aqueous system, *Journal of Hazardous Materials*, **368**, 255-263 (2019)
13. Khulbe K.C. and Matsuura T., Removal of heavy metals and pollutants by membrane adsorption techniques, *Applied Water Science*, **8**, 19 (2018)
14. Kulpa-Koterwa A., Ryl J., Górnicka K. and Niedziałkowski P., New nanoadsorbent based on magnetic iron oxide containing 1,4,7,10-tetraazacyclododecane in outer chain (Fe₃O₄@SiO₂-cyclen) for adsorption and removal of selected heavy metal ions Cd²⁺, Pb²⁺, Cu²⁺ *Journal of Molecular Liquids*, **368 Part B**, 120710 (2022)
15. Kothavale V.P., Sharma A., Dhavale R.P., Chavan V.D., Shingte S.R., Selyshchev O., Dongale T.D., Park H.H., Zahn D.R.T., Salvan G. and Patil P.B., Carboxyl and thiol-functionalized magnetic nanoadsorbents for efficient and simultaneous removal of Pb(II), Cd(II) and Ni(II) heavy metal ions from aqueous solutions: Studies of adsorption, kinetics and isotherms, *Journal of Physics and Chemistry of Solids*, **172**, 111089 (2023)
16. Lakshmiapathy R., Sarada N.C. and Jayaprakash N., Agricultural wastes as low cost adsorbents for sequestration of heavy metal ions and synthetic dyes from aqueous solution: A mini review, *International Journal of ChemTech Research*, **8**(5), 25-31 (2015)
17. Lakshmiapathy R., Sarada N.C., Chidambaram K. and Basha S., One-step, low-temperature fabrication of CdS quantum dots by watermelon rind: a green approach, *International Journal of Nanomedicine*, **10**(Sup 1), 183-188 (2015)
18. Mariana M., Abdul Khalil H.P.S., Mistar E.M. and Esam Yahya, Recent advances in activated carbon modification techniques for enhanced heavy metal adsorption, *Journal of Water Process Engineering*, **43**(4), 102221 (2021)
19. Majedi A., Davar F. and Abbasi A., Citric acid-silane modified zirconia nanoparticles: preparation, characterization and adsorbent efficiency, *Journal of Environmental Chemical Engineering*, **6**(1), 701-709 (2018)
20. Mokadem Z., Mekki S., Saïdi-Besbes S., Agusti G., Elaissari A. and Derdour A., Triazole containing magnetic core-silica shell nanoparticles for Pb²⁺, Cu²⁺ and Zn²⁺ removal, *Arabian Journal of Chemistry*, **10**(8), 1039-1051 (2017)
21. Mouden A. EI., Messaoudi N. EI., Guerraf A.E., Bouich A., Mehmeti V., Lacherai A., Jada A. and Sher F., Multifunctional cobalt oxide nanocomposites for efficient removal of heavy metals from aqueous solutions, *Chemosphere*, **317**, 137922 (2023)
22. Pant Manu, Choudhary Srashti, Mishra Anchal and Pant Kumud, Plant bioactives delaying aging and senescence through sirtuin activation: A review, *Res. J. Biotech.*, **17**(11), 155-163 (2022)
23. Pelalak R. et al, Oak wood ash/GO/Fe₃O₄ adsorption efficiencies for cadmium and lead removal from aqueous solution: Kinetics, equilibrium and thermodynamic evaluation, *Arabian Journal of Chemistry*, **14**(3), 102991 (2021)
24. Punia P., Aggarwal R.K., Kumar R., Dhar R., Thakur P. and Thakur A., Adsorption of Cd and Cr ions from industrial wastewater using Ca doped Ni–Zn nanoferrites: Synthesis, characterization and isotherm analysis, *Ceramics International*, **48**(13), 18048-18056 (2022)

25. Rai P.K., An eco-sustainable green approach for heavy metals management: two case studies of developing industrial region, *Environmental Monitoring and Assessment*, **184**, 421–448 (2012)
26. Ruba M., Ali K., Naqvi S.A.Z., Maqsood M.A., Bashir M.Z. and Noreen S., Biosynthesis of *Leucaena Leucocephala* leaf mediated ZnO, CuO, MnO₂ and MgO based nano-adsorbents for Reactive Golden Yellow-145 (RY-145) and Direct Red-31 (DR-31) dye removal from textile wastewater to reuse in agricultural purpose, *Separation and Purification Technology*, **306 Part A**, 122527 (2023)
27. Sahmoune M.N., Evaluation of thermodynamic parameters for adsorption of heavy metals by green adsorbents, *Environmental Chemistry Letters*, **17**(2), 697–704 (2019)
28. Soliman N.K. and Moustafa A.F., Industrial solid waste for heavy metals adsorption features and challenges; a review, *Journal of Materials Research and Technology*, **9**(5), 10235-10253 (2020)
29. Sadak O., Hackney R., Sundramoorthy A.K., Yilmaz G. and Gunasekaran S., Azo dye-functionalized magnetic Fe₃O₄/polyacrylic acid nanoadsorbent for removal of lead (II) ions, *Environmental Nanotechnology, Monitoring & Management*, **14**, 100380 (2020)
30. Shi X., Wang Y., Deng X., Wu W., Hua W., Zhou Z., Xin K., Tang L. and Ning Z., Excellent capture of Pb(II) and Cu(II) by hierarchical nanoadsorbent Fe₃O₄@SiO₂@PAA-SO₃H: A combined experimental and theoretical study, *Chemosphere*, **309**, Part 2, 136791 (2022)
31. Zhang S., Shi Q., Christodoulatos C. and Meng X., Lead and cadmium adsorption by electrospun PVA/PAA nanofibers: Batch, spectroscopic and modeling study, *Chemosphere*, **233**, 405-413 (2019).

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