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Sorption of Cd(II) and Pb(II) ions by nanolimestone from underground water samples from Tehama region of Saudi Arabia

Ahmed H Ragab*, Inas A Ahmed & Dina D Bader
Department of Chemistry, Collage of Science, King Khalid University, Abha 61413, Saudi Arabia
Email: ahrejab@kku.edu.sa

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Powdered nano limestone (NLS) has been investigated as an in-expensive adsorbent for removal of heavy toxic metals such as cadmium and lead from aqueous solutions. Batch experiments has been carried out, the favorable pH for maximum metals adsorption is found to be 6.8 for both. The surface area has increased in case of NLS up to 6.2 m^2/g. The adsorption capacity calculated by Langmuir equation is found to be 75.1 mg/g for Cd (II) and 68.4 for Pb (II) ions at pH 6.8. The adsorption capacity has increased with temperature and the kinetics followed a First-order rate equation for both. The enthalpy change (ΔH^0) is 25.4 J mol^{-1} for Cd (II) and 20.8 J mol^{-1} for Pb (II), while entropy change (ΔS^0) is 41.6 J K^{-1} mol^{-1} for Cd (II) and 38.7 J K^{-1} mol^{-1} Pb (II), which indicate that adsorption process is endothermic and spontaneous in nature. About 25 collected samples of groundwater has been tested and found to be contaminated with cadmium and lead elements with different rates, with using NLS as adsorbent able to remove both metals from the samples. All of the results suggested that the NLS is excellent nano-adsorbents for cadmium and lead contaminated water samples.

Keywords: Cadmium, Lead, Underground water samples, Adsorption, Nanolimestone

The toxicity of heavy metals is a problem for ecological, evolutionary and environmental reasons[1]. Heavy metals such as lead and cadmium are highly toxic pollutants they affect vascular reactivity[2] in humans, germination and seedling growth of some plants[3-6] and affects aquatic life[7].

Due to the mobility and toxicity in natural water ecosystems, the presence of cadmium and lead ions in surface water and groundwater poses a major inorganic contamination problem. Up to now, there are various technologies for removing heavy metal ions from solution, including filtration, surface complexation, chemical precipitation, ion exchange, adsorption, electrode position and membrane processing.[8]

Adsorption is one of the most recommended physico-chemical treatment processes that is commonly used and applied for heavy metals removal from water samples and aqueous solutions. Adsorption was mainly based on the utilization of solid adsorbents from either organic, inorganic, biological or low cost materials.[9] Either naturally occurring materials, modified or unmodified organic adsorbents such as chitosan and cross-linked carboxymethyl-chitosan, polysaccharide-based materials and lignocellulosic fibres with their surface characteristic functional groups in the form of hydroxyl or carboxyl were also found great research interests. Biological adsorbents, referred as bio-sorbent are commonly derived from biological components that are characterized and capable of complex formation and/or ion-exchange reactions with metal ions via their functional groups in a process known as biosorption[10].

Removal and extraction of heavy metals based on applications of biosorption approach are commonly performed owing to high selectivity toward different metals[11]. Inorganic solid adsorbents as novel silica gel matrix alumina[12], with immobilized 1-nitroso-2-naphthol[13], nano-TiO_2[14] and bentonite adsorbent[15] are well characterized by their high mechanical properties and strong resistivity to thermal degradation as compared to other biosorbents or organic adsorbents.

In recent years, there has been interest in the development of new products with minimal environmental impact for restoration or remediation of natural resources[11]. Limestone (LS) which is produced in large quantities in many countries (among them is Egypt) is a low-cost reactive medium that can be used for the retaining of heavy metals and the subsequent clean-up of industrial effluents, leachates, and contaminated ground water.[16] Hence, the objective of the present work is to study the possibility of utilizing LS (which is naturally occurring or readily available and cheap) as a sorbent for removing cadmium and lead ions from aqueous solutions and natural waters. The different parameters influencing the adsorption of cadmium and lead ions onto powdered limestone were optimized and the results are presented in this paper.

Materials and Methods

Samples

The Limestone (LS), $CaCO_3$ samples used in this study was obtained from the Al-Mokattam area in Cairo (Egypt) where some private and governorate quarries are located. The samples were crushed and pulverized in the laboratory and those with a mean size of ca. 12.5 mm were used in the experiments.

The sample consists of about 92% calcite and 3% dolomite (as found by chemical analysis) along with some common minor constituents such as silica, clay, feldspar, pyrite and siderite as has been described[16,17]. The samples were dried for 2 h in an oven at 125 °C, packed into stoppered bottles and stored in a desiccator for future use. Functional groups of LS were characterized through infrared analysis.

The LS spectrum coincided with pure $CaCO_3$. The surface area and porosity of NLS was measured using Brunauer-Emmett-Teller (BET) method. NLS presented no BET porosity and its measured surface area was 6.2 $m^2\ g^{-1}$. The pH values of points of zero charge (pH_{PZC}) were 9.1 (not aged), 6.2 (aged 60 min) and 8.3 (aged several days) and this agree with the previously reported data[18].

Reagents

All the solutions were prepared from certified reagent grade chemicals. A cobalt chloride stock solution concentration of 1 M was prepared and the working solutions were made by diluting the former with doubly distilled water. Aqueous solutions of HNO_3 and NaOH were used for pH adjustments.

Nanolimestone was prepared by dissolving the powdered limestone in about 150 g of concentrated HCl. Obtained calcium Chloride solution was mixed with 1.5 g of chitosan, which was dissolved in 3% acetic acid and triphenyl phosphate with stirring for 1 h. This mixture was blended with 70 g Na_2CO_3 and slightly heated to complete the reaction. The mixture was kept overnight, then filtered and washed several times with water. Finally calcined in a muffle furnace at 650 °C for 2 h[19].

Procedure

All batch sorption experiments were conducted at room temperature (ca. 25 °C). Known volumes of metal ion solutions with concentrations ranging from 2 to 50 mg L^{-1} were pipette into quick-fit glass bottles containing 0.2 g of NLS sorbent in 100 mL aqueous solution. Since the pH of the resulting solutions was about 7.0, no further control was necessary since it was suitable for most adsorption experiments. The resulting solutions were then stirred with a magnetic stirrer at 250 rpm and the samples were taken at fixed periods (0.0, 0.3, 0.8, 1.0 5.0, 10, 20, 30, 60 and 90 min) in order to study the kinetics of the adsorption process. Preliminary experiments showed that this time length was sufficient for adsorption of Cd (II) ion and Pb (II) onto NLS. The samples were subsequently filtered off and the residual metal ions concentrations in the filtrate were analysed using atomic absorption spectroscope (AAS). The candidate can also be reused again in the industrial field[20].

Experimental data analysis

The percentage adsorption of Cd(II) and Pb(II) ion from the solution was calculated from the relationship

$$Adsorption = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{…(1)}$$

Where C_i corresponds to the initial concentration of metal ion and C_f is the residual concentration after equilibration. The metal uptake q (mg/g) was calculated as

$$q = \frac{(C_i - C_f)}{m} \times V \qquad \text{…(2)}$$

Where m is the quantity of sorbent (mg) and V is the volume of the suspension (mL).

Results and Discussion

FTIR & SEM analysis

FTIR spectral analysis is necessary for identifying different functional groups present on the surface of sorbent which are responsible for the binding of metal ions. The FTIR spectra of NLS sample after adsorption of Cd(II) and Pb(II) ions, respectively shows in Fig. 1(a & b). The spectral bands at 712, 874 and 1418 cm^{-1} can be assigned to cadmium and lead carbonates[21,22].

Scanning electron micrographs (SEM), recorded using software controlled digital scanning electron microscope are given in Fig. 2(a & b) for the Cd(II) and Pb(II) adsorbed NLS sample, respectively. The SEM images show presence of metal precipitates on the outer surface of the sorbent.

The sample composition and element contents were analysed by using the energy dispersive analysis system of X-ray (EDAX) (EDAX, Ltd., USA) as shown in Fig. 3(a & b). The EDAX spectra of NLS indicates the presence of Ca, Mg, O, and give the characteristic peak for Cd and Pb at 3.2 and 2.5 keV, respectively.[23] This confirms the binding of the cadmium and lead ions to NLS surface.

Effect of pH on adsorption behaviour of NLS

The pH value of the solution plays an important role in the sorption of Cd (II) and Pb (II) on NLS. The sorption of metal ions increases from ~20% to ~95% in the pH ranging from 4–7 and then maintains high level with increasing pH values as shown in Fig 4. Similar results were also reported for Cu(II) sorption on TiO_2.[24]

The pH values of the solution after sorption equilibrium changes a little to the acidic region, which indicates that H^+ was released during the sorption process. In aqueous systems, the surface groups of sorbent can be protonated in different extents. Therefore, the concentrations of surface species of the sorbent change under different pH values. With increasing pH, the negative charged groups or

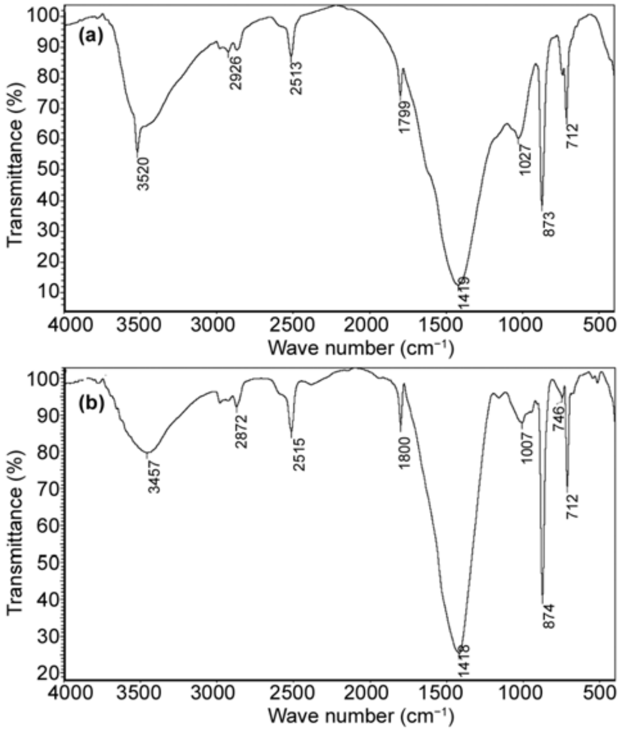

Fig. 1 — FTIR spectrum for NLS after (a) Cd(II) adsorption and (b) Pb(II) adsorption.

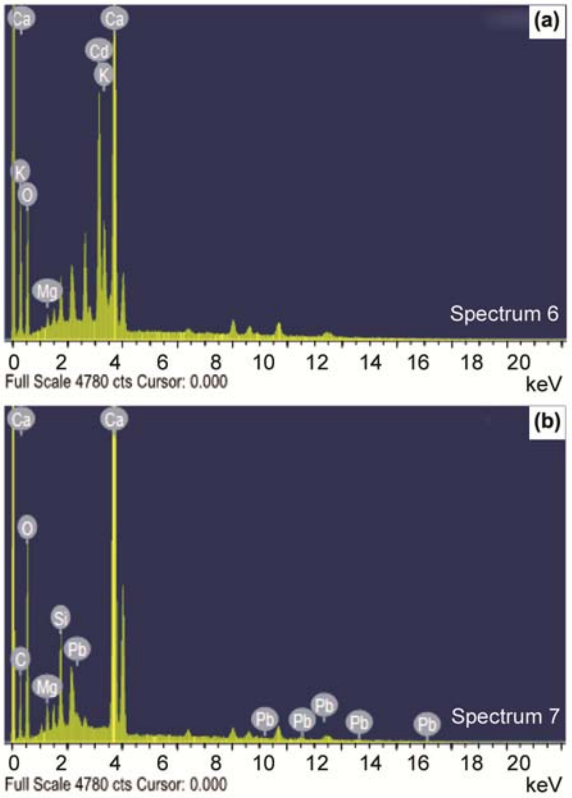

Fig. 3 — EDAX spectrum of NLS after (a) Cd(II) adsorption and (b) Pb(II) adsorption.

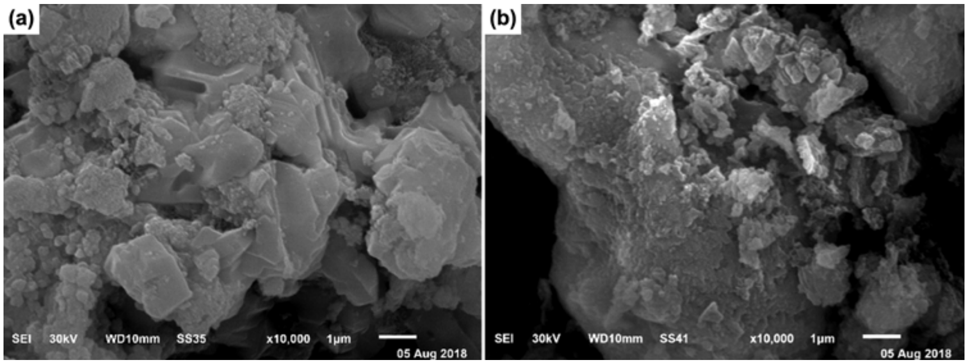

Fig. 2 — SEM image of NLS surface after (a) Cd(II) adsorption and (b) Pb(II) adsorption.

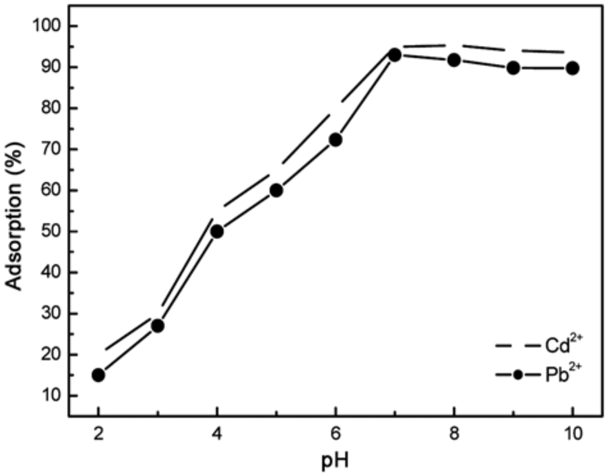

Fig. 4 — Adsorption (%) of Cd(II) and Pb(II) ions (5 mg L^{-1}) by NLS (0.2 g L^{-1}) vs pH.

deprotonated groups increase and the hydrolysis of Cd(II) and Pb(II) also increases. As can be seen, below pH 2, the removal of metal ions reaches zero which may be attributed to the complete solubility of NLS (consists mainly from $CaCO_3$ and $MgCO_3$), thereby hindering the sorption of metal ions. Above pH 2, the removal efficiency increases, reaching a maximum value (i.e., ~95%) over the pH range 6–7.

The removal of the metal ions at pH value 5 may be attributed to a possible ion-exchange mechanism between Cd(II) and Pb(II) ions with calcium of NLS in similar manner to that previously reported literature.[25] In addition, this was confirmed by measuring the concentration of calcium ion in the solution before and after adsorption where its value was increased. Adsorbed Cd(II) and Pb(II) ions generally occupy calcium sites within the calcite lattice.[26] The enhanced removal of metal ion as the solution pH was increased (more than 5) can be attributed to adsorption of hydrolytic product [$Cd(OH)^+$] and [$Pb(OH)^+$][27] and/or surface precipitation of the metal as the insoluble carbonates, MCO_3, forming successive layers on the sorbent surface which may be explained in the following equation[28]:

$$CaCO_3^o + M^{2+} + HCO_3^- \rightarrow MCO_3^o + H^+ \qquad \ldots(3)$$

$$MCO_3^o + M^{2+} + HCO_3^- \rightarrow MCO_3^o + H^+ \qquad \ldots(4)$$

The enhancement of the removal efficiency at higher pH i.e., pH 8 may be attributed to the precipitation of metals as metal oxides or carbonates as they tend to do so when pH of the solution increases above the solubility point.[16] Therefore, pH 7 was recommended throughout all the other experiments as it the pH of the neutral water.

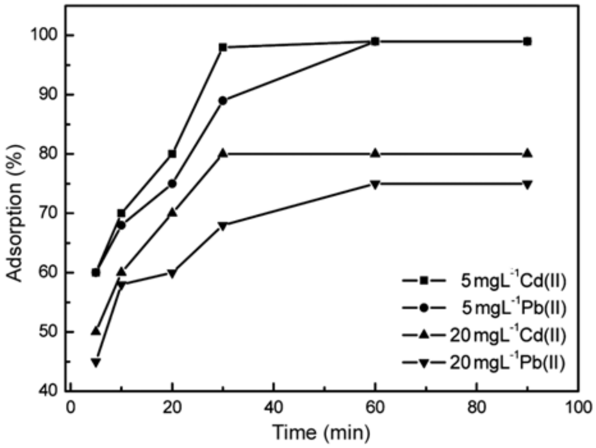

Fig. 5 — Influence of stirring time on the adsorption of various concentrations of Cd(II) and Pb(II) ions by NLS (0.2 g.L^{-1}) at pH 7.

Sorption model

Study of adsorption kinetics is important because the rate of adsorption (which is one of the criteria for rectifying the efficiency of the adsorbent) and the mechanism of adsorption can be concluded from kinetic studies. The variation of the amount of adsorbed (q_t) metal ion as a function of stirring time is shown in Fig. 5. Due to faster adsorption kinetics with smaller particles[29] the metal adsorption was initially rapid, after which it started decreasing.

The time required to reach equilibrium was 30 min for all Cd(II) and 60 min for Pb(II) ion concentrations. The initial rapid adsorption was presumably due to electrostatic attraction. The slow adsorption in the later stage may be either due to the decrease in the number of adsorption sites having affinity toward metal ions[30] or a gradual uptake of fluoride at the inner surface by complexation/ ion-ion exchange.

As a standard parameter for studying the behaviour of the metal adsorption at the adsorbent surface using Mories-Weber equation[31]:

$$q = K\mathrm{d}\sqrt{t} \qquad \ldots(5)$$

Where q is the amount of metal ions adsorbed (mg/g).

The Morris-Weber plot shows two linear portions in Fig. 6. The first linear portion may be due to the boundary layer effect and the second portion may be due to the intraparticle diffusion effect[32]. The value of the rate constant for the intrapore diffusion K_d was evaluated as 0.9 (g/g min^{-1}) for Cd(II) and 0.8 (g/g min^{-1}) for Pb(II) ions which give an indication about the mobility of the meal ions towards the NLS surface.

Lagergren equation examined the order of the adsorption, as cited by Gupta and Shukla[33]:

$$\log(q_e - q_t) = \ log q_e - \frac{K_{ads} \times t}{2.303} \qquad \ldots(6)$$

Where q_e and q_t are the amount of adsorbed metal ion on adsorbent (mg g^{-1}) at equilibrium and at time t (min), respectively, and K_{ads} is the first order rate constant for the metal ions adsorbed on the sorbent (min^{-1}).

The linear plot of log (q_e – q) vs t shows the appropriateness of the above equation and consequently the first-order nature of the process involved.

Bangham equation[34] investigate the amount of the metal which may introduce into the pores of the sorbent.

$$loglog\left(\frac{C_i}{C_i - q_t m}\right) = \log\left(\frac{K_0}{2.303V}\right) \alpha \ logt \qquad \ldots(7)$$

Where C_i is the intial concentration of the adsorbate in solution (mg L^{-1}), V is the volume of the solution (mL), m is the weight of the adsorbent (g L^{-1}), q_t (mg g^{-1}) is the amount of adsorbate retained at time t and α (less than 1) and K_o are the constant.

These results show that the diffusion of metal ions onto LS pores played a role in the adsorption process[35] (Table 1). The value of α is less than 1 in both cases suggesting the favourable sorption of Cd(II) and Pb(II) ions on NLS surface.

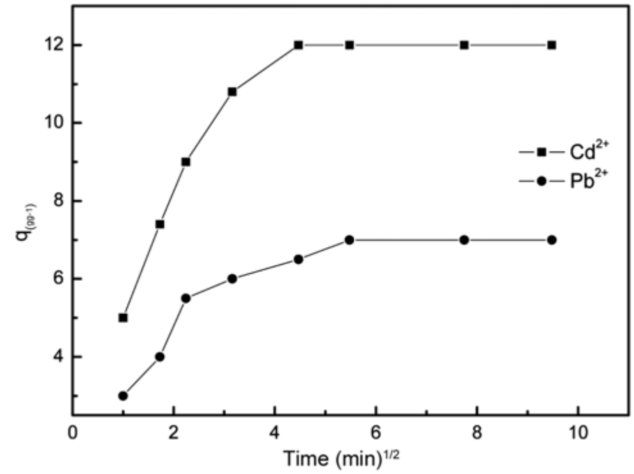

Fig. 6 — Plot of the adsorbed amount of Cd(II) and Pb(II) ions adsorbed onto NLS vs square root of time at pH 7.

Table 1 — Kinetics parameters calculated using different equation for sorption Cd(II) and Pb(II) on NLS

	Lagergren equation		
R^2	*q_e* (mg g^{-1})	*K_{ads}* (min^{-1})	
0.998	40.2	0.06	Cd^{2+}
0.988	36.4	0.04	Pb^{2+}
	Bangham equation		
R^2	*Ko*	*α*	
0.985	4.2	0.3	Cd^{2+}
0.987	3.8	0.2	Pb^{2+}

Isotherm model

Langmuir Isotherm

For modeling equilibrium data, the Langmuir model was widely used to indicate then monolayerity of the LS surface from the following equation[37]:

$$\frac{C_e}{q_e} = \frac{1}{b \times Q_{max}} + \frac{1}{Q_{max}} C_e \qquad \ldots(8)$$

Where b is the monolayer adsorption capacity and relates to the heat of sorption (L mg^{-1}), Q_{max} is the maximum adsorption capacity (mg g^{-1}).

Freundlich Isotherm

The Freundlich expression is an empirical equation describing sorption to heterogeneous surface[34]. The Freundlich equation is presented as:

$$lnq_e = \ lnK_f + \frac{1}{n} \ lnC_e \qquad \ldots(9)$$

Where K_f (mol^{1-n} L^n g^{-1}) represents the sorption capacity when metal ion equilibrium concentration equals to 1 and n represents the degree of dependence of sorption with equilibrium concentration. Favourable adsorption was demonstrated by the fact that the value of n is greater than unity.

Dubinin-Radusekevisch-Kanager Isotherm

The Dubinin–Radusckevisch (D-R) isotherm is more general than the Langmuir, because it does not assume a homogeneous surface or constant sorption potential. In general, the model is compatible between Gaussian energy distribution and adsorption processes on heterogeneous surface. The D–R equation is expressed as the following[38]:

$$lnq = lnq_{(D-R)} - ß\varepsilon^2 \qquad \ldots(10)$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad \ldots(11)$$

Where $q_{(D-R)}$ is the theoretical adsorption capacity (mg g^{-1}), ß is the activity coefficient related to mean sorption energy (mol^2 kJ^{-2}); ε is the Polanyi potential; R is the ideal gas constant (0.008314 KJ K^{-1} mol^{-1}) and T is the absolute temperature (K). E (kJ mol^{-1}) is defined as the free energy change required to transfer 1 mole of ions from solution to the solid surfaces, which equals to:

$$E = \frac{1}{\sqrt{2ß}} \qquad \ldots(12)$$

The magnitude of E is useful for estimating the type of sorption reaction. If E is in the range of

8–16 kJ mol^{-1}, the sorption is governed by chemical ion-exchange. In the case of E < 8 kJ mol^{-1}, physical forces may affect the sorption. On the other hand, sorption may be dominated by particle diffusion if E > 16 kJ mol^{-1}.[39]

From the results of D–R model simulation in Table 2, E value is 8.2 kJ mol^{-1} for Cd(II) and 8.1 kJ mol^{-1} for Pb(II) ions which in the range of 8–16 kJ mol^{-1}, indicating that sorption is governed by chemical ion-exchange according to the theory of D–R model or sorption may considered as physical-chemical adsorption[38].

Thermodynamic parameters

In order to investigate the effect of temperature on the adsorption of Cd(II) and Pb(II) ions onto NLS, the distribution coefficient, K_d (L g^{-1}), was calculated at the temperature 288, 298, 313 and 323 K by using the Eqn 13.

Thermodynamic parameters, the entropy change (ΔS^o) and the enthalpy change (ΔH^o) were calculated from the intercept and slope of the plot of lnK_d against 1/T, respectively[40].

$$lnK_d = \frac{\Delta S}{R} - \frac{\Delta H}{R} \times \frac{1}{T} \qquad \ldots(13)$$

The other thermodynamic parameter, Gibbs free energy(ΔG^o) was calculated by

$$\Delta G_0 = -RT\ lnK_d \qquad \ldots(14)$$

Where, R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature (K).

The K_d value increases with increasing the temperature which is reveals the adsorption of metals onto NLS to be endothermic.

Thermodynamic parameters, the enthalpy change (ΔH^o) and the entropy change (ΔS^o), were calculated from the data of the Eqn 13. The other thermodynamic parameter, Gibbs free energy (ΔG^o) was calculated by Eqn 14 the enthalpy change. The positive ΔH^o exhibited that the adsorption of Cd (II) and Pb (II) ions onto sorbents are endothermic. The positive sign for the entropy change (ΔS^o) as revealed from Table 3 indicates that the adsorption of metal ions onto NLS sorbents are random reactions. The negative sign of the (ΔG^o) indicates that the adsorption of metal ions onto NLS are feasible and spontaneous thermodynamically. In addition, the reaction proceeded physically, this results are in well agreement with D-R isotherm.

Table 2 — Isothermal parameters calculated using different models for sorption of Cd(II) and Pb(II) on NLS

	Langmuir model		
Metal ion	b (L mg^{-1})	Q_{max} (mg g^{-1})	R^2
Cd^{2+}	0.061	75.1	0.987
Pb^{2+}	0.055	68.4	0.978
	Freundlich model		
Metal ion	K_f(mol^{n-1} Ln g^{-1})	n	R^2
Cd^{2+}	4.4	6.7	0.980
Pb^{2+}	3.9	5.4	0.970
	D-R model		
Metal ion	E (kJ mol^{-1})	$q_{(D-R)}$ (mg.g^{-1})	R^2
Cd^{2+}	8.2	29.9	0.985
Pb^{2+}	8.1	26.5	0.978

Comparison of metal uptake capacity by NLS and other inorganic sorbents

Comparison of Cd(II) and Pb(II) ions uptake capacity by nanolimestone with other inorganic sorbents are summarized in Table 4. The Cd(II) and Pb(II) ions uptake by NLS was relatively high in comparison with those obtained by other sorbents. In conclusion, NLS may have a potential in treating the wastewater and underground water contained Cd(II) and Pb(II) ions.

Table 3 — Thermodynamic data for the adsorption of metal ions onto NLS

Cd^{2+}	288	6.2	−18.2	25.4	41.6
	298	6.5	−16.1		
	303	6.8	−17.1		
	313	7.3	−18.9		
	323	7.5	−20.1		
Pb^{2+}	288	5.9	−14.1	20.8	38.7
	298	6.3	−15.6		
	303	6.5	−16.3		
	313	6.9	−17.9		
	323	7.1	−19.0		

Table 4 — Adsorption performance for the adsorption of Cd(II) and Pb(II) ions onto different adsorbents

Metal ion	Adsorbent	q_e(mg/g)	Reference
Cd^{2+}	Chitosan biosorbent	95.2	[41]
	Modified Magnetic Iron-Oxide Nanoparticle	24.9	[42]
	Nanolimestone	75.1	This study
Pb^{2+}	Powdered marble	101.6	[43]
	waste	54.0	[44]
	Chitosan	80.6	[44]
	Chitosan-Grafted-Polyacrylic Acid Nanolimestone	68.4	This study.

Table 5 — Recovery of both Cd(II) and Pb(II) ions using 300 mg L^{-1} of NLS at pH~7

Sample	T.D.S. (ppm)	T.H. (ppm)	Cd^{2+} ion (ppm)	Pb^{2+} ion (ppm)	Recovery (%)
AL grean 1- mohayl	570	260	4.8	3.5	99.9
Al farsh 1 - mohayl	730	310	2.7	4.0	100.0
Mohayl city 1	2940	2950	0.9	2.4	99.8
Shamaran 1	2520	2800	0.7	1.2	99.9
AL grean 2- mohayl	345	160	3.9	1.2	99.7
AL grean 3- mohayl	384	168	5.0	1.9	99.9
AL garshoh 1 - mohayl	2040	2210	2.2	2.5	99.2
Al genah -mohayl	3012	1150	4.5	3.5	99.3
AL grean 4- mohayl	551	260	3.6	4.0	100.0
Thaloth 1- Bareq	421	240	3.7	2.6	100.0
AL garshoh 2 - mohayl	1956	2100	0.9	0.7	98.8
AL grean 4- mohayl	2052	2150	1.1	2.5	99.4
AL grean 6- mohayl	1422	230	1.5	2.1	100.0
Algahaf-Mohaul	381	150	3.5	1.5	100.0
AL grean 7- mohayl	79	190	0.9	0.9	100.0
Mohayl city 2	78	200	1.2	0.9	100.0
AL grean 8- mohayl	456	180	2.8	0.5	100.0
Thaloth 1- Bareq	3288	840	4.9	2.1	99.8
AL grean 9- mohayl	510	250	3.5	0.5	99.9
Mohayl city 3	138	220	0.013	0.02	99.8
Shamaran 2	1830	310	0.012	0.04	99.4
Shamaran 3	2460	2750	0.016	0.1	99.9
Shamaran 4	1980	1320	0.013	0	98.4
Shamaran 5	1860	2200	0.015	0.02	98.5
AL grean 10- mohayl	540	255	0.012	0.03	100.0

Application

To investigate the applicability of the recommended procedure a collection of 25 underground water samples were collected from the southern area of the Saudi Arabia Kingdom, Tahama region (Mohayl, Bareq and Shamran) to be polluted with the metals under studying with concentration 0.9 ~ 5 mg L^{-1} of Cd(II) and 0.7 ~ 4 mg L^{-1} of Pb(II) ions as shown in Table 5.

A series of primary chemical experiments was carried out to investigate the identity of the samples type as total dissolved salts (TDS), total hardness (TH), as the foreign ion may combine for the sorbent, as it clear some samples contain high salts concentration which may affect the recovery of the polluted metals. The adsorption experiments were carried out using 100 mL clear, filtered, uncontaminated sample solutions adjusted to pH ~7. The waters are found to be polluted with Cd(II) and Pb(II) of concentration 0.9–5 mg L^{-1}, respectively. All the results obtained are listed in Table 5 and it shows a satisfactory recovery rate.

Conclusions

The experimental results indicate that NLS can be successfully used for the adsorption of Cd(II) and Pb(II) ions from aqueous solutions. The equilibrium data well followed the Langmuir and Freundlich models. The value of mean sorption energy obtained from the D-R isotherm indicated that the adsorption of the metals on the LS was feasible and spontaneous. The negative ΔH^o value depicted that the adsorption of Cd(II) onto LS was an endothermic process, and the increase in K_d values with increasing temperature also supported this conception. The positive ΔS^o values revealed that the randomness of the adsorbed system. Based on all results, it can be calculated that nanolimestone can effectively be used for the removal of metal cations from wastewater and underground water using adsorption method. The nanolimestone presents a major advantage of giving low cost recovery processes making it useful for use in water purification.

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Author's Contributions: Ahmed H Ragab contributed to the methodology, analysed the data, and wrote the paper. Inas A Abdelsameh contributed to the methodology and reviewed the paper. Dina D Bader was involved in preparation of reagents and materials and was responsible for handing analysis tools.

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